INTERNATIONAL CONFERENCE
CONTAMINATED SITES
ZNEČISTENÉ ÚZEMIA
MEDZINÁRODNÁ KONFERENCIA

INTERNATIONAL CONFERENCE
CONTAMINATED SITES 2018
BANSKÁ BYSTRICA | SLOVAKIA, 08 – 10 OCTOBER 2018

CONFERENCE PROCEEDINGS

OP KŽP
European Union
Cohesion Fund
MINISTRY
OF ENVIRONMENT
OF THE SLOVAK REPUBLIC
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09 OKTOBER 2018	**7.30 – 8.45**		**REGISTRATION, POSTERS ARRANGEMENT**
	8.45 – 10.40		**SESSION 1**
	CHAIR: Vlasta Jánová Slovak Republic + **Richard Přibyl** Czech Republic		
Nr.	**TIME**	**Presenter** Country	**PRESENTATION TITLE**
	8.45 – 9.00	**WELCOME SPEECH** **RNDr. Vlasta Jánová, PhD.,** Ministry of Environment of the Slovak Republic **RNDr. Richard Müller, PhD.,** Slovak Environment Agency	
1	9.00 – 9.20	**Vlasta Jánová** Slovak Republic	CONTAMINATED SITES IN SLOVAKIA – CURRENT RESEARCH AND REMEDIATION PROJECTS
2	9.20 – 9.40	**Richard Přibyl** Czech Republic	CONTAMINATED SITES IN THE CZECH REPUBLIC – PRESENT STATE AND PERSPECTIVE
3	9.40 – 10.00	**Gábor Hasznos** Hungary	CONTAMINATED SITES IN HUNGARY – PRESENT STATE AND PERSPECTIVE
4	10.00 – 10.20	**Grzegorz Siebielec** Poland	CONTAMINATED SITES IN POLAND – PRESENT STATE AND PERSPECTIVE
5	10.20 – 10.40	**Soline Mourmant** Belgium	DEVELOPMENT OF DATABASE AND PROTOCOLS TO SELECT PHYSICAL, CHEMICAL AND TOXICOLOGICAL PARAMETERS FOR ALMOST 280 POLLUTANTS IN WALLONIA (BELGIUM)
	10.40 – 11.00		**COFFEE BREAK**
	11.00 – 13.00		**SESSION 2**
	CHAIR: Yuliya Vystavna Czech Republic + **Jakub Kostecki** Poland		
6	11.00 – 11.20	**Marco Falconi** Italy	ITALIAN SOIL GAS GUIDELINE 2018
7	11.20 – 11.40	**Yuliya Vystavna** Czech Republic	TRANSBOUNDARY LOADING OF PRIORITY SUBSTANCES AND EMERGING COMPOUNDS FROM CONTAMINATED WASTEWATERS: RISK FOR FULFILMENT THE REQUIREMENTS OF EU WATER DIRECTIVE
8	11.40 – 12.00	**Andrzej Greinert** Poland	HISTORICAL AND CONTEMPORARY SOIL POLLUTION IN THE CITY OF ZIELONA GÓRA (POLAND)
9	12.00 – 12.20	**Jozef Kobza** Slovak Republic	CURRENT STATE OF MAIN RISK ELEMENTS IN AGRICULTURAL SOILS OF SLOVAKIA
10	12.20 – 12.40	**Lilit Sahakyan** Armenia	CONTAMINATION ISSUES OF ARMENIAN’S MINING SITES
11	12.40 – 13.00	**Nosir Shukurov** Uzbekistan	DISTRIBUTION, MINERAL FORMS, AND BIOAVAILABILITY OF HEAVY METALS IN SOILS, THEIR IMPACTS ON SOIL BIOGEOCHEMICAL PROPERTIES (ANGREN-ALMALYK MINING-INDUSTRIAL AREA, UZBEKISTAN)
	13.00 – 14.20		**LUNCH**

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	14.20 – 16.20	**SESSION 3**	
	CHAIR: Claudia Neculau Belgium + **Karel Waska** Czech Republic		
12	14.20 – 14.40	**Meshari Almutairi** Kuwait	VERMIREMEDIATION STRATEGY FOR REMEDIATION OF KUWAITI OIL CONTAMINATED SOIL
13	14.40 – 15.00	**Karel Waska** Czech Republic	CHEMICAL AND BIOLOGICAL REMEDIATION OF KUWAIT GROUNDWATER AFTER THE GULF WAR: LABORATORY TESTING
14	15.00 – 15.20	**Giovanni Preda** Italy	CASE HISTORIES OF CONTAMINATED SITES REMEDIATION AND SEDIMENT MANAGEMENT IN ITALY: TECHNOLOGY AND RESULTS
15	15.20 – 15.40	**Marina Gakhutishvili** Georgia	ARSENIC MINING POLLUTION IN GEORGIA: REMEDIATION APPROACHES
16	15.40 – 16.00	**Claudia Neculau** Belgium	POSIDON – POLLUTED SITE DECONTAMINATION PCP
17	16.00 – 16.20	**Christoph Noller** Austria	REMEDIATION AND REVITALIZATION OF TRACE METAL CONTAMINATED GARDEN SOILS USING A SUSTAINABLE EDTA WASHING TECHNIQUE
	16.20 – 16.40	**COFFEE BREAK**	
	16.40 – 18.10	**SESSION 4**	
	CHAIR: Katarína Dercová Slovak Republic + **Gerhard Soja** Austria		
18	16.40 – 17.00	**Svetlana Sushkova** Russian Federation	MONITORING OF PAHs CONTAMINATION IN CONTAMINATED SITES OF ELECTRIC POWER STATION
19	17.00 – 17.20	**Zdeněk Suchánek** Czech Republic	SPECIFICATION OF THE METHODOLOGY FOR THE REVISION OF CLUES OF CONTAMINATED SITES OBTAINED WITH THE USE OF REMOTE SENSING METHODS, AND PRELIMINARY STATISTICAL DATA ON THE NUMBER AND SPACIAL DISTRIBUTION OF THESE CLUES IN THE CZECH REPUBLIC
20	17.20 – 17.40	**Boris Urbánek** Czech Republic	INDIRECT METHODS OF POPs CONTAMINATION SPREAD ESTIMATION ON DEPOSITORY SITE NUBARASHEN – ARMENIA
21	17.40 – 18.00	**Gerhard Soja** Austria	BIOCHAR APPLICATIONS TO SUPPORT SOIL REMEDIATION
22	18.00 – 18.10	**Edgars Dimitrijevs** Latvia	HIGH RESOLUTION SITE CHARACTERIZATION TOOLS (INCLUDING LIF (LASER-INDUCED FLUORESCENCE)) FOR ASSESSMENT AND REMEDIATION OF CONTAMINATED SITES
	18.10 – 18.30	**DISCUSSION**	
	20.00 – 22.00	**WELCOME DINNER**	

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10 OCTOBER 2018		**8.00 – 8.30**	**REGISTRATION**
		8.30 – 10.10	**SESSION 5**
		CHAIR: Marie Hechelski France + **Leonard Mgbeahuruike** United Kingdom	
Nr.	**TIME**	**Presenter** Country	**PRESENTATION TITLE**
22	8.30 – 8.50	**Leonid Perelomov** Russia	ADSORPTION OF HEAVY METALS BY NATURAL AND MODIFIED HUMIC SUBSTANCES
23	8.50 – 9.10	**Leonard Mgbeahuruike** United Kingdom	LEACHING PROFILE OF CONTAMINATED SOIL IN NIGERIA AND ITS POTENTIAL FOR EX SITU REMEDIATION USING DIFFERENT CHELATING AGENTS BY SOIL WASHING
24	9.10 – 9.30	**Elena Bocharnikova** Russia	SILICON-BASED APPROACH TO DETOXIFICATION AND PURIFICATION OF CONTAMINATED SITES
25	9.30 – 9.50	**Marie Hechelski** France	AN ORIGINAL APPROACH IN GREEN CHEMISTRY: FROM ASSISTED-PHYTOREMEDIATION OF CONTAMINATED SOIL TO UPCYCLING OF PLANT BIOMASS FOR BIOSOURCED CATALYST PRODUCTION
26	9.50 – 10.10	**Tatiana Minkina** Russia	COMBINING SELECTIVE SEQUENTIAL EXTRACTIONS AND X-RAY ADSORPTION SPECTROSCOPY FOR Zn SPECIATION IN SPOLIC TECHNOSOLS
		10.10 – 10.40	**COFFEE BREAK**
		10.40 – 12.20	**SESSION 6**
		CHAIR: Adeline Janus France + **Zdeněk Suchánek** Czech Republic	
27	10.40 – 11.00	**Davit Pipoyan** Armenia	RISK ASSESSMENT OF Cu AND Mo EXPOSURE THROUGH CONSUMPTION OF VEGETABLES GROWN UNDER THE IMPACT OF KAJARAN'S MINING COMPLEX
28	11.00 – 11.20	**Ivan Alekseev** Russia	TRACE ELEMENTS CONCENTRATION IN SELECTED URBAN SOILS OF THE RUSSIAN ARTIC
29	11.20 – 11.40	**Adeline Janus** France	INFLUENCE OF TWO AMENDMENTS ON PHYTO- AND SANITARY AVAILABILITY OF METALS IN HIGHLY CONTAMINATED SOILS: A GREENHOUSE STUDY
30	11.40 – 12.00	**Palaniswamy Thangavel** India	ROLE OF HYPERACCUMULATORS IN PHYTOMANAGEMENT OF METAL CONTAMINATED SITES
31	12.00 – 12.20	**Van Xuan Nguyen** France	IMPORTANCE OF ENVIRONMENTAL AND TOXICOLOGICAL AVAILABILITIES OF Cd AND Pb IN MANAGEMENT OF DREDGED SEDIMENTS
		12.20 – 12.40	**DISCUSSION/CONCLUSION**
		12.40 – 14.00	**LUNCH**

CONTAMINATED SITES IN THE CZECH REPUBLIC – PRESENT STATE AND PERSPECTIVE

Richard Přibyl

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At such a relatively small territory we have about 5 000 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. Principle documents governing remedial of contaminated sites in the privatisation process are the Government Regulation No. 51/2001 and Directive of MoE and Ministry of Finance No. 4/2017. These documents form the basic framework for the process of remediation works. Czech republic, however, as the former proprietor is responsible for remediation of contaminated sites, which contamination occurred before they were privatised. For this purpose, environmental contracts are concluded. The Czech Environmental Inspectorate, 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. In the period 1991 and 2017, Government of the CR approved 325 "remediation" contract guarantees. Remediation works were finished at 179 sites and payments were made in an amount of 61,6 bil. CZK (2,4 bil. EUR). Works on other sites continues, but the trend of slowing down is evident, as can be seen from the following table, which shows the annual cost of removing old environmental burden.

Financing trends in individual years (bil. CZK)

2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
4,7	3,6	5,4	3,5	3,4	3,4	2,3	1,2	0,8	0,7	0,7

In the period from 2008 to 2014, the Ministry of Finance slowed down the pace of new procurement, which was reflected in the following years, when the number of completed projects was gradually declining without adding new projects. Fortunately, the number of new orders is gradually increasing since 2014, but this will only affect the coming years.

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 198 million EUR, now in the period 2014-2020 it will be about half.

In order to provide additional resources from the year 2015 the MoE declared a National environmental program, which is designed, among other things, to clean up illegal landfills and old ecological burdens owned by individuals.

Another program that helps repair the damage from the past is the Revitalization and restoration of sites damaged by mining of minerals and oil. The program began in 2002 and the MoE here acts as specialized adviser. This program supports actions as revitalization of forest a agricultural sites and can be used to remediation of sites owned by municipalities, privatized minig companies and state-owned enterprises as DIAMO and Palivový kombinát Ústí.

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 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.

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.

CONTAMINATED SITES IN HUNGARY – PRESENT STATE AND PERSPECTIVE

Gábor Hasznos

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KEYWORDS
contaminated sites, groundwater, national program, legislation, priority

ABSTRACT

National Environmental Remediation Program (OKKP) was established by the Hungarian Government in 1996 for the identification, survey and remediation of environmental pollution. First legislative framework was adapted in 2000 by Government Decree No. 33/2000 and in the 10/2000 joint ministerial decree on the limit value system for groundwater and geological medium. Data on the identification, registration and technical classification of all contaminated sites is stored in the National Environmental Information System (OKIR) which also holds remediation information in its subsystem, the KÁRINFO. "Register System of Groundwater and Geological Media" is called FAVI database. It was ruled by Gov. dec. on Groundwater protection No. 219 in 2004 and the Ministerial Decree No. 18. in 2007. Part of the FAVI is so called KÁRINFO sub-system which collects basic information about the contaminated or potentialy contaminated sites in Hungary. A different sub-system of FAVI is the FAVI ENG which collects data on potentially contaminating activities requiring licensing. This register is used for controlling the plants where the stored and used hazardous substances can be dangerous to the groundwaters.

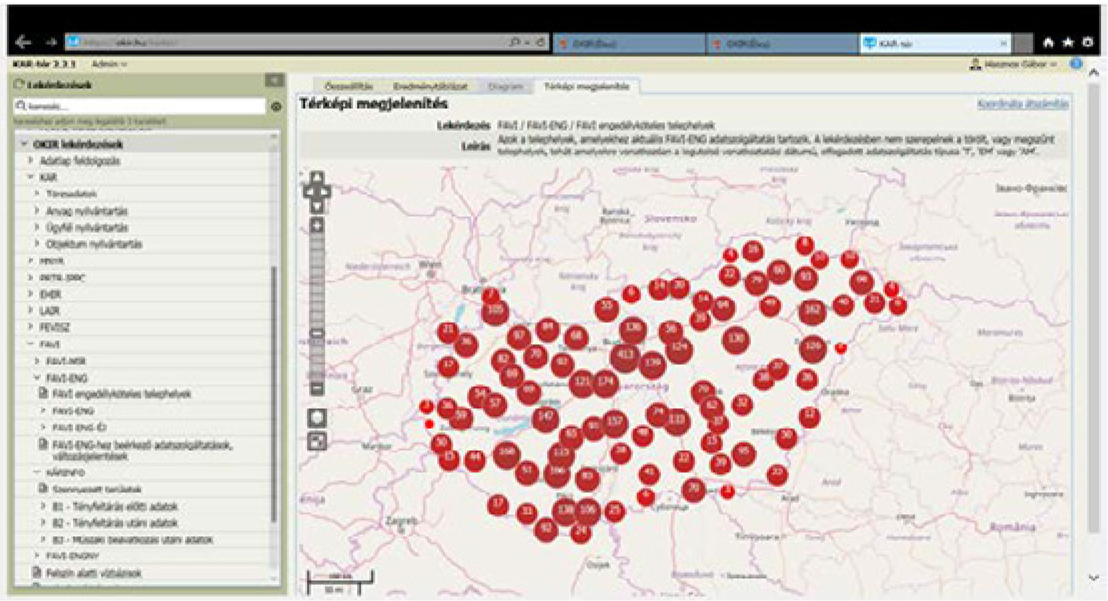
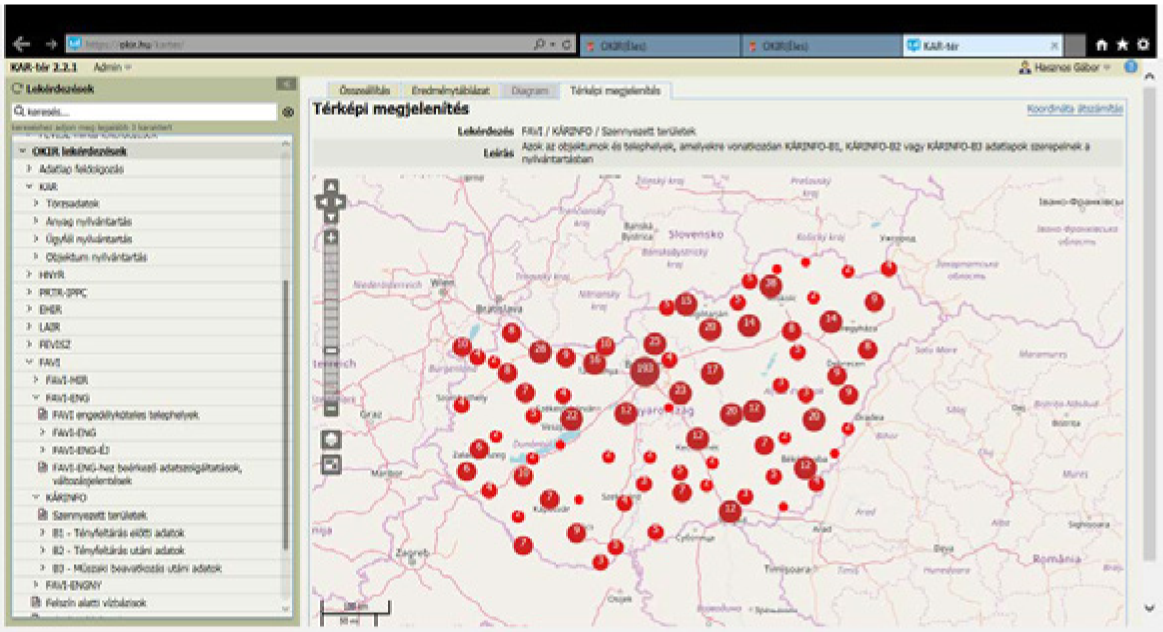


Fig. 1 Potentially polluting activities in Hungary

FAVI-KÁRINFO database include:
- B1 technical datasheets – sites before site investigation
- B2 technical datasheets – sites after site investigation, before remediation
- B3 technical datasheets – sites after remediation



Térképi megjelenítés

Lekérdezés: FAVI / KÁRINFO / Szennyezett területek

Leírás: Azok az objektumok és telephelyek, amelyekre vonatkozóan KÁRINFO-B1, KÁRINFO-B2 vagy KÁRINFO-B3 adatlapok szerepelnek a nyilvántartásban

Fig. 2 Registered contaminated sites in Hungary

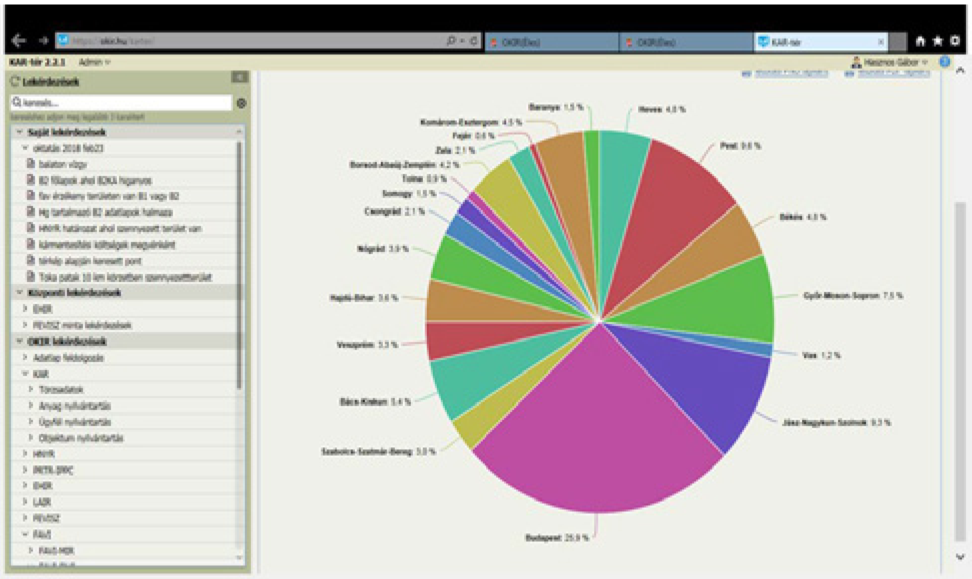


Fig. 3 Contaminated sites distribution of county breakdown.

Financing the clean-up of contaminated sites is generally guided by the “polluter pays principle”. In cases where this is not applicable, funds are allocated from the government budget or financed through the EU Cohesion Fund. Within the framework of the Environment and Energy Operational Programme (KEOP 2.4.0) 23 sites were remediated for a total of 39.3 billion HUF during the 2007 – 2013 period. In the 2014 – 2020 period, funds of a 22.8 billion HUF are available for environmental remediation tasks through the Environment and Energy efficiency Programme (KEHOP 3).

Fig. 4 Contaminated site Üröm-Csókavár limestone mine (near Budapest) – finenced by European Funds and Hungarian state budget

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DEVELOPMENT OF DATABASE AND PROTOCOL TO SELECT PHYSICAL, CHEMICAL AND TOXICOLOGICAL PARAMETERS FOR ALMOST 280 POLLUTANTS IN WALLONIA (BELGIUM)

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KEYWORDS
pollutants, protocol, physicochemical properties, toxicological properties, soil legislation, risk assessment, trigger values

ABSTRACT

In Wallonia, soil investigations are carried out for characterization studies required by the Walloon Soil Decree (2008) and baseline reports required by the Industrial Emissions Directive (European Directive 2010/75/EU, transposed in 2014). If the selection of relevant pollutants, depending on historical and industrial activities, is typically done by using an "activities/pollutants matrix", collecting and selecting their physicochemical and toxicological properties is more complex and needed a joint approach by two public institutes under the authority of The Walloon Government (SPAQuE and ISSeP). A common standardized protocol was designed to select physicochemical and toxicological data of pollutants from international reference databases for site-specific risk assessments and to calculate soil guideline values for human health and groundwater protection. All of this data has been brought together in a free access database[1], available online and soon will be translated into English by September 2018. It includes almost 280 pollutants' parameters, as well as human health limit values in soils according to different exposure scenarios.

INTRODUCTION: SOIL LEGISLATION IN WALLONIA

The Industrial Emissions Directive, adopted on 24 November 2010 and transposed in Wallonia on 16th January 2014, asks European Countries to establish a "baseline report" of new industrial activity in an area and after the update of reference documents for Best Available Techniques (BAT) by the European Commission. Further, Walloon Soil legislation was enforced through the Soil Decree passed in December 2008, modified in 2018 for which characterization studies are required to determine the pollutants in soil or groundwater media. Both pieces of legislation call for a knowledge of historical industrial activities to select relevant pollutants. The selection of the relevant chemicals likely to be present is done by, often, the judgment of environmental consultants or by using existent "activities/pollutants matrix", thereby linking pollutants and industrial activities together.

In this context, many pollutants may be analyzed in soils and groundwater. When these substances are quantified, an acceptable threshold (equal to the maximum acceptable concentration, also called "screening values") in soil and groundwater are required to determine pollutants limits above which a risk is expected. Because of these thresholds, in part, are dependent on pollutants characteristics, physicochemical and toxicological properties are needed.

These properties can be obtained in different international scientific databases that can recommend coherent or very different values for the same property. In the latter case, it is very difficult to choose one value over another. The Walloon Government has called out to two institutes, SPAQuE and ISSeP, to undertake the following:

- to establish a standardized approach for searching and selecting the physicochemical and toxicological properties of substances found in soil and groundwater media;
- to calculate the soil and groundwater screening values.

The aim of the approach is to define to environmental consultants a step by step selection process that allows them to select a single value from different international databases.

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[1] http://dps.environnement.wallonie.be/home/liens--documents/le-coin-des-specialistes-experts-laboratoires/polluants-non-normes-pnn.html

METHODOLOGY TO SELECT PHYSICAL, CHEMICAL AND TOXICOLOGICAL PROPERTIES

As a result of a feedback from almost six years of seleting properties of different types of pollutants (pesticides, phthalates, organic compounds, inorganic metallic compounds, etc.) and various quantities of data, protocols have been implemented by the collaboration between the two Institutes, SPAQuE and ISSeP. This work has allowed the selection of relevant databases and the implementation of a procedure that provides a balance between quality scientific data and time spent searching.

In this way, two protocols have been established (last version in March 2018):

- a protocol giving instructions for searching and selecting physicochemical properties;
- a protocol for searching and selecting toxicity reference values.

Regarding the protocol for searching and selecting toxicity reference values, not developed in this article, these values are collected from a priority list of international agencies who proposed toxicity values (WHO, JECFA, EFSA, US-EPA IRIS, ATSDR, OEHHA, Canada Health, RIVM)[2]. Then, the most relevant values – and not the most cautious – are selected on the basis of their date of elaboration, the sources of data, etc. If no toxicity data is available in this priority list, toxicology skills are needed.

Regarding the physicochemical properties selection, the first step is the selection of a CAS (Chemical Abstracts Service) number, specific to one substance, to make a distinction, for instance, between isomers and technical products. Different databases are filled in the protocol.

The protocol establishes a list of fourteen physical and chemical properties, describing the pollutants behavior in soil and groundwater media. These properties are needed for the risk assessment models to calculate screening values (human health and groundwater leaching). Table 1 detailed these properties.

Tab. 1 Physical and chemical properties selected into protocols

Properties	Symbols	Units
Molecular weight	M	g/mol
Vapor pressure at 10°C	P	Pa
Henry's law constant at 10°C	H	$Pa.m^3/mol$
Solubility in water at 10°C	S	mg/L
soil/water partition coefficient	Kd	L/kg
Octanol-water partition coefficient	Kow	–
Organic carbon-water partition coefficient	Koc	–
Acid dissociation constant	pKa	–
Permeation organic substance through PE drinking-water service pipe	Dpe	m^2/d
Bioconcentration factor for contaminants soil/plant	BCF	For inorganic contaminants: (mg/kg plant dm)/(mg/kg soil dm) for organic contaminants: (mg/kg plant dm)/(mg/m^3)
Biotransfer factor to meat, kidney, liver and milk	BTF	(mg/kg fw)/(mg/d)
Dermal permeability coefficient for water	Kp	cm/h
Dermal absorption factor for soil and dust	ABSdermal soil/dust	–
Fraction absorbed water	FA	–

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[2] Word Health Organization, FAO/WHO Expert Committee on Food Additives, European Food Safety Authority, United States Environmental Protection Agency Integrated Risk Information System, Agency for Toxic Substances and Disease Registry, Office of Environmental Health Hazard Assessment, Canada Health, Rijksinstituut voor Volksgezondheid en Milieu

To search for these properties, two lists of databases have been proposed. The first one, the priority list, contains the most referenced and complete international handbooks and databases, recommended by other agencies in other countries: HSDB (Hazardous Substances Data Bank), Mackay D. and al. (2006), Verschueren K. (1996; 2008) and Syracuse Research Center (SRC). If any value is not available for certain properties in this list, then a second list, not exhaustive, of twelve different sources could be consulted, not only international references: ATSDR, Lide D. (2009 – 2010), Lijzen et al. (February 2001), etc. Other sources or databases could be used, but this approach would need to be justified.

When several values are proposed, the final value is selected following three rules:

- experimental data is prefered to calculated, estimated or extrapolated data;
- the coherence of the selected value with another source or database, listed in the protocol, is checked;
- if available, the value of a property is selected at a temperature of 10°C (±2,5°C) which is the annual average temperature of soils in a temperate oceanic climate.

The protocol define an exemption if the search values are not coherent between different values, under justification.

APPLICATION: CALCULATION OF SCREENING VALUES IN SOIL AND GROUNDWATER

Since 2013, the Walloon Government has been implementing a reference guideline for risk assessment (GRER). This guideline has been updated 3 times, especially due to the change in methodology of assessment risk and equations from risk assessment model (application from RISC-HUMAN v3.3 model to S-RISK® model, developed by VITO, a Flanders Public Institution specialized in risk assessment) in order to harmonize the soil legislation in the 3 regions of Belgium (Flanders, Brussels, Wallonia).

In Wallonia, the risk assessment follows a tiered approach, with increasing complexity:

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

The selected physical, chemical and toxicological properties allow the calculation of two types of soil screening values:

- a human health screening value, calculated with S-RISK® model (VITO, 2017), called VL_H (VL for Limit Value);
- a groundwater leaching screening value, calculated using the Connor model (Connor, 1997), called VL_N.

Also, these parameters allow the calculation of two groundwater screening values:

- a human health screening value similar to drinking water criteria (for tap water), called VL_nappe;
- a human health screening value to take into account the volatilization of certain pollutants from groundwater; called VL_nappe_volatilisation.

As part of the Walloon Soil Decree, screening values for fifty usual pollutants (metals, BTEX, Polycyclic Aromatic Hydrocarbons, mineral oil, chlorinated solvents and cyanides) are already calculated for 5 land uses (natural / agricultural / residential / recreational & commercial activities / industrial). Screening values for more pollutants have been calculated since the application of the protocols.

PERSPECTIVES

To keep this information available to everyone, the Walloon Government has brought together the physicochemical and toxicological properties of almost 280 pollutants in a free online database. Different types of pollutants have been collected: inorganic compounds (metals, sulfates, phosphorus, etc.), chlorinated organic compounds, chlorobenzenes, phenol and compounds, phthalates, pesticides, dioxins and other compounds.

An update is scheduled every 6 months for taking into account continuous service provider's requests.
To promote this huge task, these protocols and the online database will be translated into English for September 2018.

These protocols as well as the online database are constantly improved through feedback and discussions of the working group gathering the Walloon Government, SPAQuE and ISSeP.

LITERATURE

SPAQuE, ISSeP, Mars 2018 : Protocole pour la démarche d'élaboration des Valeurs Limites (VLH, VLN et Vlnappe) – Cas des PNN (Polluants Non Normés), version 3, utilisation du modèle S-RISK®.
ISSeP, SPAQuE, Mai 2018 : Procédure pour la sélection des valeurs Toxicologiques de Référence et la Prise en Compte du Caractère Cancérogène d'un Polluant, version 1 provisoire.
Direction Générale Opérationnelle (DGO3), Février 2018 : Décret du 5 décembre 2008 relatif à la gestion des sols, Code Wallon de Bonnes Pratiques, Guide de référence pour l'Etude de Risques – Partie B : Evaluation des risques pour la santé humaine, version 03.
C.Cornelis, A. Standaert, H.Willems, February 2017: S-Risk version fort the Walloon region: Technical guidance document, final report, 2016/MRG/R/0771. VITO.

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ITALIAN GUIDELINE FOR MONITORING OF VAPOURS IN CONTAMINATED SITES 2018

MONITORING PLAN, ANALYTICAL METHODS, USE OF DATA IN RISK ASSESSMENT

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KEYWORDS

soil gas survey, vapoUr sampling, analytical methods, risk assessment, vapor inhalation, vial, canister, lines of evidence, conceptual site model

Italian guideline for monitoring of vapours in contaminated sites comes after 3 years of research and experiments that involved ISPRA and many Italian Regional EPA at various level.

The guideline is composed by three main parts:

1. Analytical methods for measurement of VOC in soil gas
2. Monitoring plan of vapours in contaminated sites
3. Operating procedure for the evaluation of data from soil gas measures in the risk assessment of contaminated sites

Any part could be helpful to clarify what is expected and how to use different techniques for soil vapour monitoring (active soil gas survey, flux measures, passive samples, etc.) for a better understanding of inhalation risk that is often the most critical pathway.

The first part, **Analytical methods for measurement of VOC**, illustrates the analytical methods to be used for all soil vapour monitoring techniques in contaminated sites on the various sampling supports available for active soil vapour sampling (solvent desorption vials, thermal desorption vials, canisters).

For the definition of analytical methods, also experimental comparison activities were carried out between regional EPA laboratories on standard samples of aromatic hydrocarbons and chlorinated compounds, prepared in matrix (chemical desorption vials and thermal desorption vials) to evaluate:

- the recovery of the analytes on the two different supports starting from a gaseous standard;
- comparison of the results between the analytical techniques and between the different laboratories that have participated;

The documents enter into details on the technical specifications (sample treatment, handling, storage, transport, reagents, selectivity, interferences) for VOCs, aromatic and aliphatic hydrocarbons C<12, PAH, Tetraethyl lead, Mercury.

Lastly, indicative LOQs (Limits Of Quantifications) have been defined for 70 pollutants (elements or compounds) according to the support chosen (Table 1). These LOQs (expressed in terms of total mass recovered from each support and in terms of concentration considering a typical volume sampled) could be subject to variations due, for example, to different performances and/or instrumental variability over time (for the acquisition of new instruments or for the inevitable obsolescence of the existing instruments by the various laboratories).

Table 1 – LOQ for BTEXS and soil gas $C_{threshold}$ for indoor exposure

Substance	$C_{threshold}$ soil gas [mg/m³] Indoor (α = 0,1)		Limits of quantification according the sample support					
	Residents	Workers	Chemical Desorption Vial		Termal Desorption Vial		EPA TO15 Canister Vacuum Bottle	
BTEXS			**LOQ [mg/m³] V=30 lt**	**LOQ [ug/camp.] VS=1ML**	**LOQ. [mg/m³] V=7 litres**	**LOQ [ng/camp.]**	**LOQ [mg/m³]**	**LOQ [ppbV]**
Benzene	3,31E-03	1,57E-02	3,33E-03	0,1	1,43E-03	10	3,20E-03	1
Toluene	5,59E+01	2,19E+02	3,33E-03	0,1	7,14E-04	5	3,80E-03	1

Ethylbenzene	1,03E-02	4,91E-02	3,33E-03	0,1	7,14E-04	5	4,30E-03	1
m-Xilene	1,12E+00	4,38E+00	6,66E-03	0,2	7,14E-04	5	8,60E-03	2
Stirene	5,16E-02	2,45E-01	1,67E-01	5	7,14E-04	5	6,40E-03	1,5

The second part, **Monitoring plan of vapours in contaminated sites**, includes technical indications agreed at national level for the sampling of vapours in the context of contaminated sites management procedures.

The document takes into consideration the sampling procedures aimed at assessing the extent of the volatile fraction of contamination and the emission of vapours from soil and/or groundwater (soil gas measurements, mass flux measurements). Although important also for the environmental assessment of the site, indoor and outdoor air sampling is not included in the document, because it concerns also health aspects of exposure of residents and/or safety of workers whose evaluation is not an exclusive responsibility of ISPRA and Regional EPAs.

A paragraph is dedicated to the evaluation of the influence on the survey of physical parameters, such as pressure, temperature, humidity, wind and precipitation in order to identify the best condition for a representative sampling and assess the uncertainty related to the time variability of the accumulation of gases and their emissions from soil. An indication of the number of campaigns and of the minimum number of monitoring points (Table 2) is also provided together with a minimum list of documents that should be delivered to the control authority to evaluate properly the monitoring plan for its approval.

Additionally, three appendices have been prepared: "*Appendix A - Sampling of pore gases (soil gas survey) in active mode*" and "*Appendix B - Flux measurements (flux chambers) in active mode*" and just for informative purposes, an overview of the techniques for monitoring of soil gases through passive samplers in "*Appendix C - Passive monitoring systems for soil gas*".

Table 2 – Monitoring points on the basis of building area

Building surface (m^2)	**Monitoring points** *(outdoor or subslab probes)*
up to 140	2
from 140 to 450	3
from 450 to 900	4
from 900 to 1.800	5
from 1.800 to 4.500	6
from 4.500 to 23.000	8
from 23.000 to 90.000	10
> 90.000	> 12

The third part, **Operating procedure for the evaluation and use of data resulting from soil gas measures in the risk analysis assessment of contaminated sites**, includes the following elements:

1. gradual approach for the evaluation of soil gas data in risk assessment
2. criteria underlying the definition of risk-based threshold values in soil gas matrix
3. criteria for site specific risk assessment based on soil gas data
4. site management criteria based on soil gas monitoring

The evaluation of soil gas data for risk assessment follows gradual approach: the first step is the comparison with threshold concentrations to verify if the inhalation pathway can be excluded from conceptual site model; if threshold values are exceeded a a site specific risk assessment has to be carried out from soil gas data in order to establish if inhalation pathway pose a significant risk to human health and therefore an intervention is needed.

The document has the purposes of reviewing the exposure parameters for the "vapour inhalation" route on the basis of most recent studies available, facilitating the management of field data, setting simplified criteria for the exclusion of the volatilization pathway and overcoming some critical application of current risk assessment software. The proposed procedure was tested on real cases proposed by Regional Agencies involved in the WG.

The minimum number of soil gas campaigns depends on the objectives and the level of the assessment:

- at least 4 campaigns (representative of the seasonality of one year) for the exclusion of the volatilization pathway (comparison with the threshold values) are required;
- from 4 to 6 campaigns (representative of the seasonality of one or two years) are required for the Verification of the acceptability of Risks associated to soil gas concentrations (VdR soil gas).

Compliance with threshold values must be verified in all campaigns carried out. If representative concentrations are lower than threshold values, but in some points non-compliances are recorded, on the basis of the observed concentrations and site-specific conditions (contaminants, receptors involved), the Control Authorities will be able to request:

- further monitoring;
- the application of site specific risk assessment to soil gas data or alternatively the verification of compliance with site-specific acceptable concentrations in soil gas only for areas where the threshold values were exceeded.

If threshold values are exceeded in one campaign then a site-specific risk assessment based on soil gas data has to be carried out in order to assess the level of inhalation human health risk associated to vapour migration. If acceptable risk values are exceeded, then site-specific acceptable concentrations in soil vapours may be determined in order to establish remediation needs.

The whole procedure for soil gas evaluation has been agreed with ISS (Italian National Health Institute) and INAIL (National Institute for Insurance against Accidents at Work), that are the main reference for health aspects of the general population and workers respectively.

TRANSBOUNDARY LOADING OF PRIORITY SUBSTANCES AND EMERGING COMPOUNDS FROM CONTAMINATED WASTEWATERS: RISK TO FULFIL THE REQUIREMENTS OF EU WATER DIRECTIVE

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KEYWORDS
Emerging compounds, contaminated wastewater, transboundary water basin, EU Water Framework Directive

ABSTRACT

The occurrence and fluxes of 18 priority substances and emerging pollutants listed in the European Union Water Framework Directive and a Watch List (trace metals (Cd, Pb and Ni), nonylphenols, octylphenols, 8 polyaromatic hydrocarbons, 4 dioxin-like polychlorinated biphenyls and diclofenac) were investigated in a Ukrainian city and the mass discharge loads of these compounds into EU-transboundary watersheds were estimated. Fluxes of chemicals were calculated per capita and per area of the Ukrainian urban territory and used to estimate mass loading of priority and emerging concern compounds from Lviv, Uzhorod and Chernivtsi (West Ukraine) to neighbouring EU-transboundary rivers. The highest loading was found for trace metals (1.15 t a^{-1}), diclofenac (0.7 t a^{-1}) and nonylphenols (0.4 t a^{-1}). Transboundary water contamination must be considered in order to successfully manage water resources in a manner that fulfils the requirements of EU environmental quality standards (Figure 1).

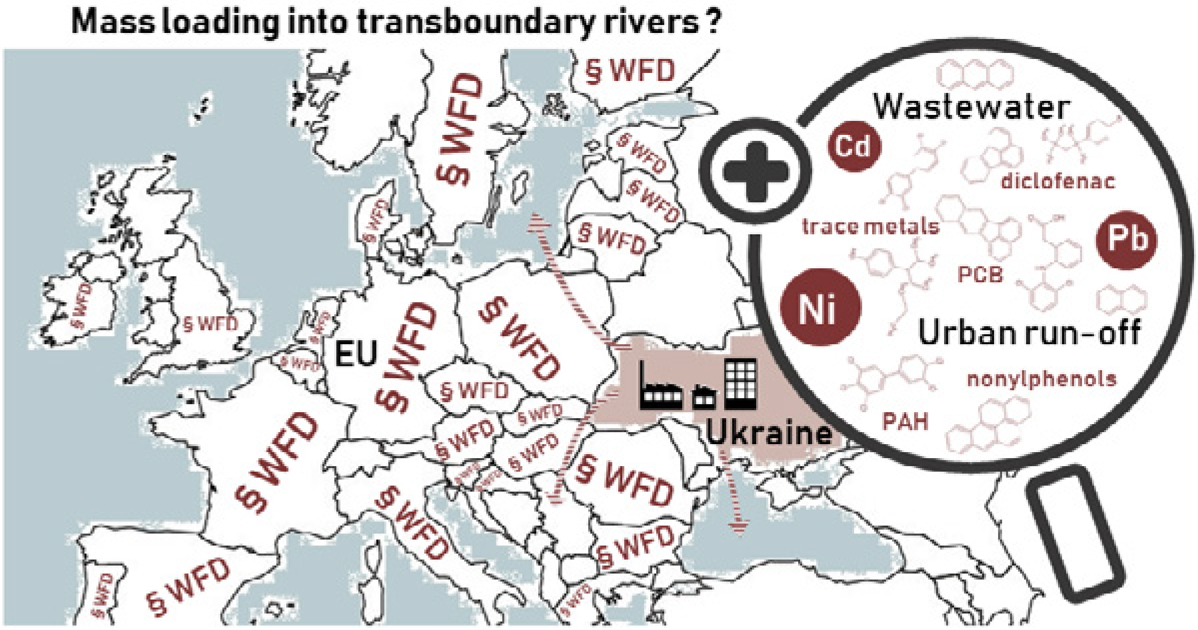

Fig. 1 Potential contribution of emerging contaminants with wastewaters into transboundary water basins (Vystavna et al. 2018)

Water sampling was performed in the urban river crossing large Ukrainian city (Kharkiv city; 1,439,039 inhabitants, 308 km^2 area). The concentration and fluxes of priority substances (EU WFD 2000) and a compound of emerging concern (diclofenac) (EU Watch List) were calculated per capita of urban area in Ukraine (Table 1). The detailed procedure of water sampling and chemical analysis is presented in Vystavna et al. (2012, 2017, 2018). Fluxes and loading of contaminants were estimated based on concentration and water flow rates and presented in details in the Vystavna et al. (2018). These fluxes were used to approximate the loading of studied compounds from other cities in Ukraine including Lviv, Uzhorod and Chernivtsi, all of which discharge treated wastewaters into EU-transboundary rivers (Figure 2). The employed approach is based on the assumption that Ukrainian cities have identical wastewater treatment (type of facilities, removal efficiency) and socio-economic (connection to sewerage, industrial profile, consumption patterns) conditions.

Tab. 1 Concentration and environmental quality standards of target compounds (average±standard deviation, exceeding environmental quality standards (EQS) is in bold), ng L^{-1}

Substance	Upstream	City centre	Downstream WWTP	European Union		Ukraine EQS	Specific fluxes with wastewater effluents, g ca^{-1} a^{-1}
				AA-EQS	MAC-EQS		
Pb	70±5	80±5	150±5	1,200	14,000	100,000	0.029
Ni	2,060±120	2,200±100	**5,620±200**	4,000	34,000	10,000	1.105
Cd	18±3	17±3	50±3	90	600	5,000	0.010
Naphthalene	<33	<33	67±0	2,000	130,000	n/a	0.013
Anthracene	9.4±0.4	12.1±0.5	11.3±0.4	100	100	n/a	0.002
Fluoranthene	<10	<10	<10	6.3	120	n/a	n/d
Benzo(a)pyrene	**4.5±0.1**	**4.1±0.1**	**2.9±0.1**	0.17	270	n/a	0.001
Benzo(b)fluoranthene	<1.3	2.6±0.1	<1.3	n/a	17	n/a	n/d
Benzo(k)fluoranthene	<8.9	<8.9	<8.9			n/a	n/d
Benzo(g,h,i)perylene	<0.4	1.5±0.0	<0.4	n/a	8.2	n/a	n/d
Indeno (1,2,3,-cd)pyrene	<0.9	<0.9	<0.9			n/a	n/d
Σ8 PAHs	13.9±0.3	20.3±0.3	81.2±1	n/a		n/a	0.016
Nonylphenols	50±1	220±8	**2,110±10**	300	2,000	n/a	0.436
Octylphenols	<10	10±0	**110±10**	100	n/a	n/a	0.023
Diclofenac	4±0.1	**98±2**	**3,560±10**	100[1]	n/a	n/a	0.738
PCB 77	77.6±1	76.9±0.3	77.7±2	n/a		n/a	0.014
PCB 126	79.4±1.9	78.4±0.5	81.2±5	n/a		n/a	0.014
PCB 169	48.8±3.4	46.5±2.1	51.7±10.1	n/a		n/a	0.009
Σ4 PCBs	205.8±6.4	201.8±2.9	210.6±17.1	n/a		n/a	0.037

n/a refers to that data are not available and n/d refers to not determined values; LOD–limit of detection;
[1] water quality limit

Results of the loading estimation revealed that over 2.4 t a^{-1} of target compounds, arising from urban runoff and wastewater effluent of three cities (Lviv, Uzhorod and Chernivtsi) in West Ukraine could enter the EU-transboundary waters. Highest loading was found for trace metals (1.15 t a^{-1}), particularly Ni (1.1 t a^{-1}), diclofenac (0.70 t a^{-1}) and nonylphenols (0.42 t a^{-1}). Mass loading of Σ4 PCBs and Σ8 PAHs was 0.04 t a^{-1} and 0.02 t a^{-1} respectively, and comprised of mostly naphthalene (80 % of the Σ8 PAHs). Persistent organic chemicals are highly mobile in aquatic environments and thus can potentially contribute to river contamination in Poland, the Slovak Republic and Romania, and should be considered in the management of transboundary water.

Fig.2 Location of study areas and sampling sites in Ukraine (Vystavna et al. 2018)

Our results indicate that aquatic concentration and fluxes of trace metals (Cd, Pb and Ni), nonylphenols, octylphenols, 8 PAHs, 4 PCBs and diclofenac from Kharkiv city, Ukraine are comparable to those in EU rivers. They show that studied priority and emerging concern compounds could enter the EU-transboundary waters from treated urban wastewater in West Ukraine. Given this contamination threat, improved transboundary water management is required and should include preventive measures. Without this it may be impossible to reach the established EU water quality standards.

LITERATURE

Vystavna, Y., Frkova, Z., Celle-Jeanton, H., Diadin, D., Huneau, F., Steinmann, M., Crini, N., Loup, C., 2018. Priority substances and emerging pollutants in urban rivers in Ukraine: Occurrence, fluxes and loading to transboundary European Union watersheds. Science of the Total Environment 637 – 638C, 1358 – 1362

Vystavna, Y., Frkova, Z., Marchand, L., Vergeles, Y., Stolberg, F. 2017. Removal efficiency of pharmaceuticals in a full scale constructed wetland in East Ukraine. Ecological Engineering 108, 50 – 58

Vystavna, Y., Huneau, F., Grynenko, V., Vergeles, Y., Celle – Jeanton, H., Tapie, N., Budzinski, H., Le Coustumer, P., 2012. Pharmaceuticals in rivers of two regions with contrasted socio-economic conditions: occurrence, accumulation and comparison for Ukraine and France. Water Air and Soil Pollution 223(5), 2111 – 2124.

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HISTORICAL AND CONTEMPORARY SOIL POLLUTION IN THE CITY OF ZIELONA GÓRA (POLAND)

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KEYWORDS
urban soils, Technosols, SUITMA's, heavy metals

ABSTRACT

The pollution of soils is particularly noted in industrial, urban and communication areas. In some cities the agricultural impacts are also observed, which are connected with intense agriculture. Zielona Góra city (western Poland) occupied in the past a small area surrounded initially by the agricultural land extensive used, next was heavy industrialised and partly intensive cultivated. Nowadays, the former land has been reconstructed and covered with housing estates and in part commercial ones. As an effect of the land use transformations soils covering the area have been changed to Anthrosols, Technosols and Regosols. In some parts of the city, the evaluated EC values, concentration of Cu and relatively less of Pb and Zn were noted. Many places with rised Cu content have been in close relationship to the former land cultivation. Contemporary construction works often "rejuvenate" materials creating urban soils, so a content of contaminants in a new formed soil horizons can be relatively low. Contemporary urban areas are very complicated. Incorrect are the simplifications indicating industry and communication as the only sources of pollutants in urban soils. The condition of soils in potentially contaminated areas must be subject to very careful research due to the risk to humans, other organisms, surface- and groundwaters.

INTRODUCTION

In the 21st century, it can be observed a constant growth of cities, both in terms of their total area and the number of inhabitants. At the end of 2014, approximately 54 % of the world's population and 73 % of the European population are urban dwellers. According to forecasts, in 2050 these indices will reach 66 % and 82 %, respectively (UN 2015). Today, urban areas cover ca. 6 % of the total area of the European continent, and this value increases every 5 years by 0.34 – 0.50 % (UN 2011). Therefore, it is of particular interest to recognize changes caused in urbanosphere by human impact.

An important part of discussion about the urban soils has been their chemical state. Many chemical changes have been indicated by scientists as a result of multi-factorial transformation, including the presence of different waste materials (Greinert et al. 2013, Hulisz et al. 2018). The results obtained from research on soils and land in the urban area of the town of Zielona Góra support this thesis (Pickett and Cadenasso 2009, Greinert et al. 2013, Greinert 2015). The most common anthropogenic materials in urban soils are: building debris, slags, dusts and ashes, translocated rock material, communal wastes, sludges, subgrades and mulches. The most commonly described artefacts in Technosols are widespread admixtures of building materials, wastes and waste building materials produced as a result of mass demolition of buildings (Wessolek et al. 2011, Nehls et al. 2013).

The recognition of the geochemism of urban soils is especially important due to the possibility of direct impact of pollutants on people and other organisms (Irvine and Perrelli 2009, Pfeiderer et al. 2012, Charzyński et al. 2013). A common phenomenon in the industrial and communication areas is accumulation of salt in the soil. Despite this, in the most of urban areas, a relative low EC (below 1 mS cm^{-1}) is a typical value (Linde et al. 2001, Madrid et al. 2002, Ruiz-Cortes et al. 2005). The local higher EC values (above 2 mS cm^{-1}) have been reported in soils occurring near the roads, chemical plants and in the waste disposals. The soils of urban areas can be characterised also by a high content of heavy metals, the main sources of which are industrial wastes, vehicle emissions and coal burning plants (Manta et al. 2003). Most of the research results show a relatively low bioavailability of heavy metals in the soils of urban areas (Madrid et al. 2002, Yang et al. 2006, Tack 2010).

SITE DESCRIPTION AND METHODS

Zielona Góra is a medium-size town inhabited by about 140 thousand residents, located in the western part of Poland (51°56'07"N, 15°30'13"E). Until the mid-nineteenth century, the small town was surrounded by cultivated fields, gardens and vineyards. Then the character and appearance of the town have changed. Intensive industrialization processes have taken place in the 19th century and early 20th. After the political transformation of Poland, Zielona Gora lost its industrial character, becoming a town with mainly tertiary economy.

Most of geological materials building superficial layers of the Zielona Góra locality are medium and coarse sands of glacial and water origin, gravels and in some areas silts and clays within glacitectonically disturbed moraine structures. In the close surroundings of Zielona Góra the presence of Podzols and Brunic Arenosols is a typical phenomenon. In smaller areas, the presence of Luvisols, Albeluvisols, Gleysols and Phaeozems has been noted. As a result of multilateral human pressure, in the area of Zielona Góra the presence of Anthrosols, Regosols and Technosols is noted (IUSS WG WRB 2015).

Weather conditions are typical of the transition area, influenced by the oceanic and continental climate, with average values for: monthly temperatures – 9.0°C, min. -22°C (I), max. +35.3°C (VII); annual precipitation – 572 mm (high annual volatility – 505 – 757 mm from 2000 to 2011); number of rainy days per year – 175.1.

The researches were carried out in the town of Zielona Góra. In total 200 soil profiles at the depth of 150 cm (samples from each of the morphological layers or genetic horizons) + 60 collective surface samples (an area of approximately 20 m^2 each, samples from humus horizons).

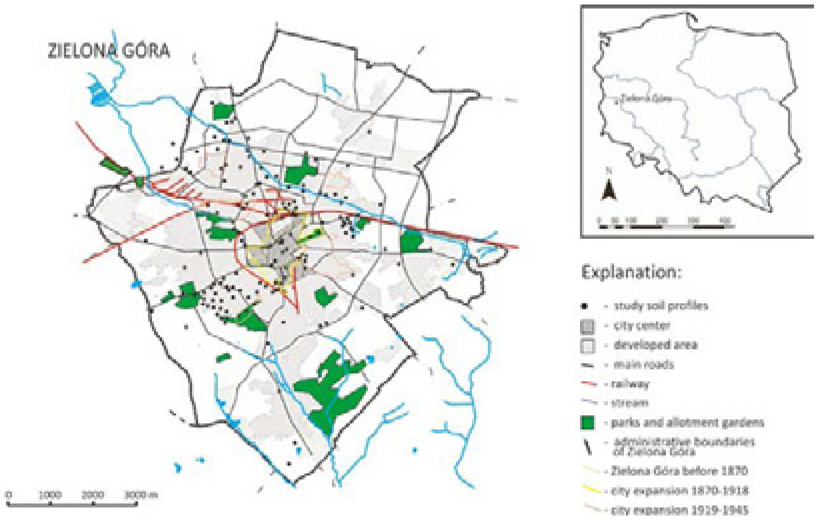


Fig. 1 Location of soil profiles in the urban area of Zielona Góra

Particle size distribution was determined for the parts above 2 mm and the sand particles by sieving and for silt and clay particles using the hydrometer method and described following the PSSS classsification (2009). pH was determined in 0.01 M $CaCl_2$ potentiometrically with a glass electrode WTW SenTix 41 in the 1:2.5 soil:supernatant suspension. The content of heavy metals in the soil samples from the beginning of 21st C. was determined by means of atomic absorption FAAS (Varian analyser) and the newer ones using ICP-OES technique (Perkin Elmer analyser). Extracts in aqua regia ($3HCl:HNO_3$) were made acc. to ISO 11466, extracts in 0.1M HCl – the fraction potentially available to plants acc. to Baker and Amacher (1982).

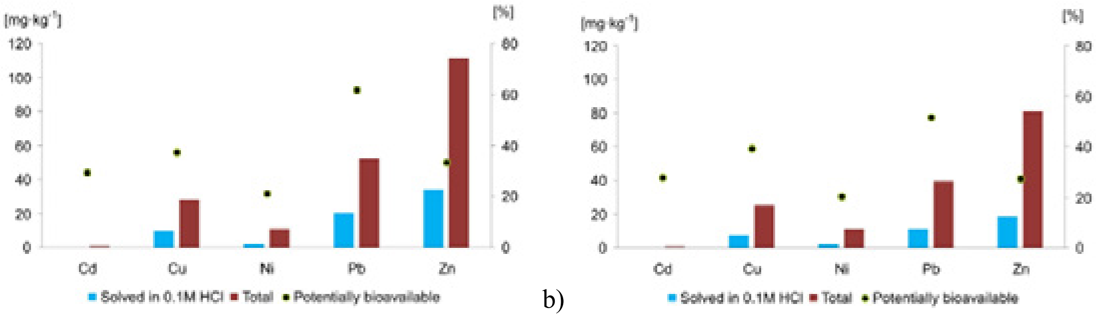
RESULTS AND DISCUSSION

The most frequently noted urban soils transformation is the raise of skeleton content. Particle-size composition of Zielona Góra soils clearly shows the domination of the sand fraction. An average content of separated fractions from all of the investigated profiles should be shown as follows: skeleton 23.5 %, particles < 2 mm 76.5 %, incl.: 2 mm – 50 μm 81.2 %, 50 – 2 μm 17.8 % and < 2 μm 1.0 %. The most frequently noted were the admixtures connected with different construction activities (60 % of soil samples). This is a typical feature described in literature, among others by Pouyat et al. (2007), Pickett and Cadenasso (2009). In 4.5 % of soil samples different communal wastes were found. Park et al. (2010) noted variation in particle size distribution with urban age. Observations from the Zielona Góra area do not confirm this dependence.

Determining the amount and quality of anthropogenic admixtures is an important factor influencing the chemical state of Technosols. In building materials isolated from the tested soil samples, the heavy metals were found – in ceramic materials (extracted with 0.1M HCl, $mg \cdot kg^{-1}$): Cd 0.2, Cu 1–3, Ni 2 – 6, Pb below the detection limit, Zn 34 – 41, and in concrete rubble (extracted with 0.1M HCl, $mg \cdot kg^{-1}$): Cd 0.2, Cu 8 – 17, Ni 1 – 2, Pb 1 – 3, Zn 2 – 34. For the Zielona Góra area the slag presence in soils is common observed phenomena. This is due to the fact that in the past local depression was filled, and alleys and roads were hardened with that material. In slag of different origin it was detected the content extracted with 0.1M HCl ($mg \cdot kg^{-1}$): Cd 0.1, Cu 8 – 57, Ni 8 – 18, Pb 19 – 22, Zn 12 – 125.

The retention and mobility of heavy metals in soil, beside the grain-size composition, depend on the organic matter content and pH. The analysis of the surface horizons of the studied soils showed that merely 21.9 % of soil samples were characterized by a neutral reaction and 9.4 % – by alkaline. In case of deeper horizons, often enriched with alkaline materials (construction site wastes), it was 24.4 % and 50.7 %, respectively. The alkalization of urban soils causes the possibility of stabilising a number of pollutants (especially lead), which are, in this case, less mobile in the soil. A clear decrease in the solubility of the majority of heavy metals as well as an increase in pH is a broadly described phenomenon (Yang et al. 2006, Tack 2010).

Urban soils are typically enriched with heavy metals. Soils in Zielona Góra do not usually contain high concentrations of elements included in this group. Most of them are present in soils in the form of salts relatively easily dissolved in water, which migrate vertical, in a case of high soil permeability. The rebuilding of the internal structure of town results in the extraction of pattern materials and filling excavations with a new ones – from outside the town. This causes a significant change in distribution of heavy metals in the soils of Zielona Góra. The content of heavy metals was noted is as follows: Cd – 0.2 – 2.7 mg·kg^{-1} s.m. (av. 0.4), Cu – 4.6 – 192.0 mg·kg^{-1} s.m. (av. 24.8), Ni – 1.2 – 46.8 mg·kg^{-1} s.m. (av. 11.1), Pb – 3-241 mg·kg^{-1} s.m. (av. 39.5) and Zn – 9 – 510 mg·kg^{-1} s.m. (av. 80) in a subtotal form. In surface samples higher contents of lead and zinc were found, average values of which were respectively 52 and 111 mg·kg^{-1} s.m. According to the Polish Regulation of the Minister of Environment, only in a few samples the heavy metals concentration was higher than the threshold limits for soils covering the urban areas. All of the oversized Pb and Zn values were noted on the roadside areas. The very different situation was connected with the Cu spatial distribution. The highest values were found on the former vineyard areas, where copper compounds were used for the fungal disease control. The Bordeaux Mixture (a mixture of copper(II) sulfate ($CuSO_4$) and slaked lime ($Ca(OH)_2$) has been known in vineyards as a fungicide to control infestations of downy mildew, powdery mildew and other fungi since 1882.



a) b)

Fig. 2 The content of heavy metals – total and solved in 0.1M HCl in topsoil (a) and subsoil (b), dots combined with the right scale are illustrating the bioavailability of heavy metals (Greinert 2003, 2015, Hulisz et al. 2018)

The analysis of the properties of soils in Zielona Góra shows high solubility, which indicates high bioavailability of heavy metals. This phenomenon is interesting in the context of the high pH of the soils. At this point it is also necessary to remember the young age of transformed soils. Similar results were reported by Madrid et al. (2008), in soil samples taken in Torino and Sevilla. In the surface layers of soil profiles in Zielona Góra potential availability of heavy metals was found, indicated as the ratio HM-0.1M HCl/HM-Aqua Regia, on the level: 29.5 % Cd, 37.2 % Cu, 20.9 % Ni, 61.8 % Pb and 33.3 % Zn. In deeper layers and levels this ratio is as follows: 27.7 % Cd, 39.2 % Cu, 20.3 % Ni, 51.6 % Pb and 27.4 % Zn.

An important deviation from the tendencies described in literature, which is important in terms of urban soils monitoring, are indications localising so-called “hot points”. In the case of heavy metals they are always searched for in the emission routes of industrial plants and roads with heavy traffic. A different situation has been found in the case of roads with the heaviest traffic in Zielona Góra. The concentration of heavy metals in roadside soils is lower in comparison to other locations. This results from the short exposure time of the soils located near the newly built roads. During the construction, part of the material constituting the soils under discussion was brought from clean areas out of town. However, hot points in other areas are different in character, occurring close to one another with high density. It happens in industrial and post-industrial areas in the town. Due to intensive urbanization of Zielona Góra in second half of 20th century, industrial areas located in the suburbs or outside the town at the beginning of the 20th century have been included into the area of the town. Research done in the areas of metallurgical industry, textile industry, electrical industry plants, and different warehouses and transhipment bases indicates that there are large quantities of heavy metals and oil derivatives in their soils, down to a considerable depth (Fruzińska 2011, 2012; Greinert et al. 2012).

CONCLUSIONS

- In the majority of the Zielona Góra area there was no high concentration of heavy metals. Such a situation took place despite the historically high degree of industrialization, and contemporary a dense network of communication and urban development.

- The content of heavy metals in urban soils is the result of many factors affecting both the deposition of heavy metals and their retention. Week, mostly sandy grain-size composition and low carbon content in soils do not allow the retention of large amounts of cations, including heavy metals.
- The traditional approach to the problem of soil contamination with heavy metals oriented to industrial and communication areas does not reflect in all cases occurrence of real threats. This results from the difficulty to assess the places of direct deposition of communal, construction and industrial wastes, containing significant amounts of heavy metals.
- A specific source of heavy metals in soils can be pesticides used in agriculture. In Zielona Góra a high copper content was found in the areas of former vineyards protected with fungicides based on its compounds.
- An important indicator for assessing the condition of urban soils is the construction time of a given area. New areas are often constructed using clean materials from outside the city.

LITERATURE

Baker, D.E., Amacher, M.C., 1982. Nickel, copper, zinc, and cadmium. In: Page, A.L., Miller, R.H., Keeney, D.R. (Eds.), Methods of Soil Analysis. Part 2. Chemical and Microbiological Methods. American Society of Agronomy/Soil Science Society of America, Madison, WI, 323–336.

Charzyński P., Bednarek R., Hulisz P., Zawadzka A., 2013. Soils within Torun urban area. In: Charzyński P, Hulisz P, Bednarek R (eds) Technogenic soils of Poland, Polish Society of Soil Science, Toruń, pp 17–30.

Fruzińska R., 2011. Accumulation of iron in the soil-plant system in a metal industry area. Civil and Environmental Engineering Reports, No. 7, 59–68.

Fruzińska R., 2012. Aluminum, manganese and iron in the soils of metal industry area. In: Innowacyjne rozwiązania rewitalizacji terenów zdegradowanych 2011,. J. Skowronek (Ed.). Katowice: Instytut Ekologii Terenów Uprzemysłowionych, 167–175.

Greinert A., Kostecki J., Fruzińska R., Bednarz K., 2012. Mobility and phytoavailability of lead in urban soils. In: Proceedings of ECOpole, Vol. 6, no. 1, 105–111.

Greinert A., Fruzińska R., Kostecki J., 2013. Urban soils in Zielona Góra. In: Charzyński P, Hulisz P, Bednarek R (eds) Technogenic soils of Poland. Polish Society of Soil Science, Toruń, pp. 31–54.

Greinert A., 2015. The heterogeneity of urban soils in the light of their properties. J Soils Sediments 15: 1725–1737.

Hulisz P., Charzyński P., Greinert A., 2018. Urban soil resources of medium-sized cities in Poland: A review. J Soils Sediments, 18: 358–372.

Irvine K.N., Perrelli M.F., 2009. Metal levels in street sediment from an industrial city: spatial trends, chemical fractionation, and management implications. J. Soils Sediments, 9: 328–341.

ISO 11466:1995, Soil quality – Extraction of trace elements soluble in aqua regia. Technical Committee: ISO/TC 190/SC 3, Chemical and physical characterization ICS: 13.080.10 Chemical characteristics of soils.

IUSS WG WRB, 2015. World Reference Base for Soil Resources 2014, update 2015. International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports No. 106. FAO, Rome.

Linde M., Bengtsson H., Öborn I., 2001. Concentrations and pools of heavy metals in urban soils in Stockholm, Sweden. Water Air Soil Pollut 1(3): 83–101.

Madrid F., Biasioli M., Ajmone-Marsan F., 2008. Availability and bioaccessibility of metals in fine particles of some urban soils. Arch. Environ. Contam. Toxicol. 55: 21–32.

Madrid L., Diaz-Barrientos E., Madrid F., 2002. Distribution of heavy metal contents of urban soils in parks of Seville. Chemosphere 49(10): 1301–1308.

Nehls T, Rokia S, Mekiffer B, Schwartz C, Wessolek G, 2013. Contribution of bricks to urban soil properties. J Soils Sediments, 13: 575–584.

Park S.-J., Cheng Z., Yang H., Morris E.E., Sutherland M., McSpadden Gardener B.B., Grewal P.S., 2010. Differences in soil chemical properties with distance to roads and age of development in urban areas. Urban Ecosyst 13: 483–497.

Pfeiderer S., Englisch M., Reiter R., 2012. Current state of heavy metal contents in Vienna soils. Environ Geochem Health 34: 665–675.

Pickett S.T.A., Cadenasso M.L., 2009. Altered resources, disturbance, and heterogeneity: A framework for comparing urban and non-urban soils. Urban Ecosyst. 12: 23–44.

Pouyat R.V., Yesilonis I.D., Russell-Anelli J., Neerchal N.K., 2007. Soil chemical and physical properties that differentiate urban land-use and cover types. Soil Sci. Soc. Am. J. 71: 1010–1019.

PSSS, 2009. Particle size distribution and textural classes of soils and mineral materials – classification of Polish Society of Soil Science 2008, Soil Science Annuals, LX(2), 5–16.

Ruiz-Cortes E., Reinoso R., Diaz-Barrientos E., Madrid L., 2005. Concentrations of potentially toxic metals in urban soils of Seville: relationship with different land uses. Environ Geochem Health 27(5–6): 465–74.

Tack F.M.G., 2010. General soil chemistry, principles and processes. Mobilization of trace elements [In:] Trace elements in soils, ed. Hooda PS, 19–24.

UN, 2011. Population distribution, urbanization, internal migration and development: an international perspective. Department of Economic and Social Affairs, Population Division. United Nations Publication. ESA/P/WP/223.

UN, 2015. World Urbanization Prospects: The 2014 Revision, (ST/ESA/SER.A/366). United Nations, Department of Economic and Social Affairs, Population Division.

Wessolek G., Kluge B., Toland A., Nehls T., Klingelmann E., Rim Y.N., Mekiffer B., Trinks S., 2011. Urban soils in the Vadose zone – 4.3. Soils on WWII Rubble. In: Perspectives in urban ecology, W. Endlicher et al. (Eds.), Springer Verlag, Berlin-Heidelberg, 89–134.

Yang J.Y., Yang X.E., He Z.L., Li T.Q., Shentu J.L., Stofella P.J., 2006. Effects of pH, organic acids, and inorganic ions on lead desorption from soils. Environmental Pollution 143: 9–15.

CURRENT STATE OF MAIN RISK ELEMENTS IN AGRICULTURAL SOILS OF SLOVAKIA

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KEYWORDS: soil monitoring, soil contamination, risk elements, Slovakia

ABSTRACT

The main risk elements have been measured based on soil monitoring system which consists of 318 monitoring sites on agricultural land in Slovakia. Risk elements were analysed in extraction by aqua regia (Cd, Pb, Cu, Zn, Cr, Ni, As, Se, Co) and Hg (total content using AMA analyzer) in topsoil and subsoil, as well.

On the basis of measured values of risk elements the slightly increased values of some heavy metals (Cd, Pb, Cu, Zn) from among the evaluated soil types occur in Fluvisols which could be transported from the catchment and accumulated on the alluvial deposits especially along lower part of rivers. Increased values of some risk elements (As, Co, Cr, Cu, Zn) were determined in Cambisols – mostly in areas influenced by geochemical anomalies occurrence. Unlike soils with low to very low content of humus and clay fraction (Regosols) are characteristic with the lowest content of all measured risk elements.

Contaminated sites are mostly situated in the industrial areas (anthropogenic impact) and in the areas influenced by geogenic impact (occurrence of geochemical anomalies). Their unfavourable state persists often a long period and therefore it will be necessary to monitor them also in the future.

INTRODUCTION

Conception of european soil policy and soil protection strategy as well as its sustainable land use was established in Proposal of European Commission (EC) on the 6-th Environmental Action Programme, which was accepted by European Council as well as European Parliament on the 22-nd of July, 2002 where one of the basic strategies is just soil and monitoring of its next development. The main aim of soil monitoring system is to obtain the knowledge of the most current state and development of soil properties according to main threats to soil including soil contamination. There are permanently monitored important parameters in connection to recommendation of EC for evaluation of current state and development of soils (van Camp et al. 2004). Monitored parameters are the basis for modeling and assessment of soil functions as well as for assessment of ecosystem services of agricultural land.

Governmental soil policy of Slovakia declares that the soil is and will be the basics of environmental, ecological, economical and social potential of Slovakia and therefore it must be carefully protected against damage. The new regulation concerning agricultural soils is the Act n. 220/2004 Z. z. on protection of agricultural soils and land use (MPRV SR, 2013) in effort to increase protection against degradation. Background soils contain native heavy metals concentrations plus an anthropogenic addition by the ubiquitous deposition resulting from diffuse heavy metal sources. The objective of this study is the evaluation of current hygienic state of agricultural soils in Slovakia.

METHODOLOGY

The obtained results are evaluated on the basis of soil monitoring system in Slovakia, which has been running since 1993 year. Soil monitoring network in Slovakia is constructed on ecological principles and includes the important data of all main soil types and subtypes, soil substrates, climatic regions, emission regions, contaminated and non-contaminated regions as well as various land use. There are 318 monitoring sites on agricultural soils in Slovakia. All soil monitoring sites are located in WGS 84 coordinates. The monitoring site represents the circular shape, with a radius of 10 m and an area of 314 m^2. The most important risk elements concerning soil contamination are included (Cd, Cr, Pb, Ni, Zn, Cu, Se, Co extracted with aqua regia) and Hg (total content – using AMA analyzer).

RESULTS

The human influence on contamination of soils in Slovakia (former Czechoslovakia) was the most significant after the Second World War and especially during the industrial period in the second half of the 20-th century. The geochemical anomalies occur mostly on volcanic and crystalline rocks, mainly in mountainous regions, this process is manifested in agricultural land with less intensity. The most extended areas of geochemical anomalies appear in Štiavnické vrchy, Low Tatras and Slovenské Rudohorie mountains. These regions are often characterized by high to very high concentrations of some risk elements, especially in all soil profile (Cd, Pb, Cu, Zn, As).

The distribution of risk elements on agricultural soils of Slovakia is given in the following tables 1, 2 and 3 and Figure 1.

Table 1. Content of risk elements (mg.kg^{-1}) extracted with aqua regia in agricultural soils (0 – 10 cm) in Slovakia

Elements Statistics	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Se**	**Hg^1**
x	10.16	0.38	8.80	42.00	24.48	29.43	26.42	80.88	0.25	0.09
median	8.91	0.27	8.04	41.66	20.21	26.87	19.28	70.89	0.19	0.07
Xmin	1.00	0.07	1.00	0.99	0.39	0.24	3.45	19.80	0.04	0.01
Xmax	223.00	9.90	28.60	141.00	155.34	136.14	1238.00	1191.00	0.72	0.80
Sd	7.14	0.39	4.15	19.47	14.97	14.21	37.79	46.34	0.11	0.06
Vc (%)	61.35	83.36	49.08	48.91	59.36	48.67	100.46	48.48	50.08	66.50
n	318	318	318	318	318	318	318	318	318	318

Explanations: x – arithmetic mean, Xmin – minimum value, Xmax – maximum value, Sd – standard deviation, Vc – coefficient of variability, n – frequency, Hg^1 – total content (AMA analyzer)

Table 2. Content of risk elements (mg.kg^{-1}) extracted with aqua regia in agricultural soils (35 – 45 cm) of Slovakia

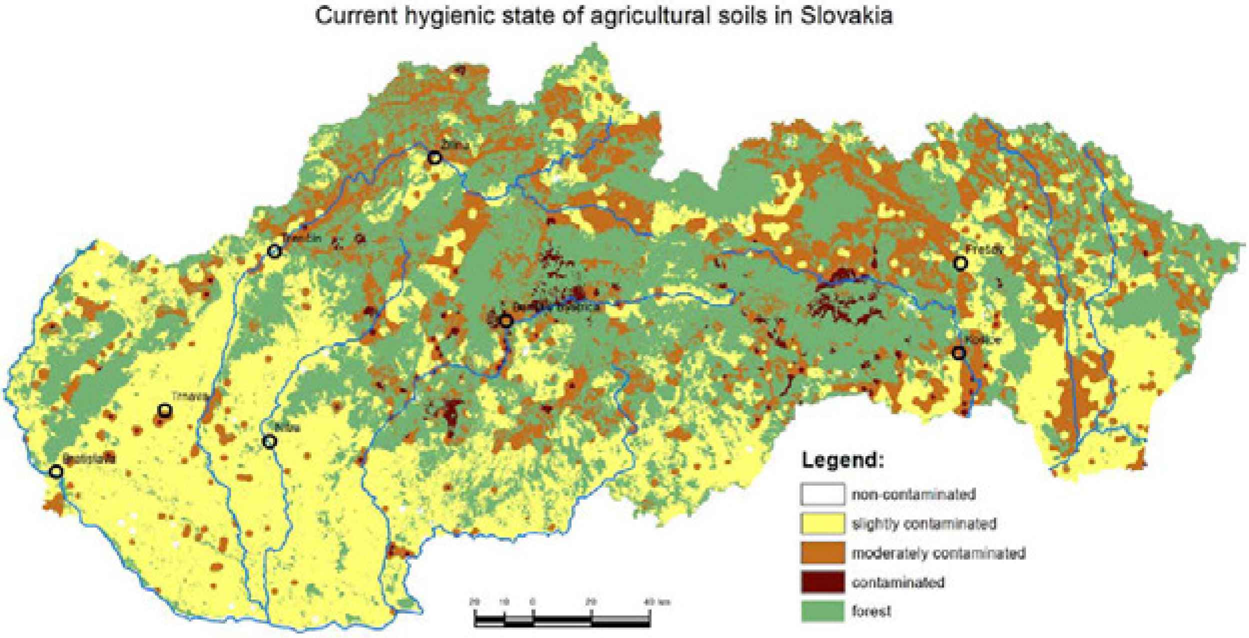
Elements Statistics	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Se**	**Hg^1**
x	9.55	0.41	10.02	42.87	23.09	32.10	22.70	71.22	0.21	0.05
median	8.60	0.21	8.85	40.34	19.05	29.00	14.73	62.91	0.13	0.04
Xmin	0.77	0.01	1.00	1.99	1.33	0.29	4.10	3.80	0.02	0.01
Xmax	100.00	89.00	215.70	135.00	137.00	141.00	1941.00	1340.00	0.62	0.55
Sd	6.40	1.57	7.36	21.50	14.93	16.64	45.41	44.24	0.10	0.04
Vc (%)	65.26	191.75	66,97	56.60	60.85	56.05	121.39	53.83	43.93	69.85
n	318	318	318	318	318	318	318	318	318	318

Explanations: see Table 1

Table 3. Average content of risk elements (mg.kg^{-1}) extracted with aqua regia in surface horizon (0 – 10 cm) of main soil types in Slovakia

Soils	As	Cd	Co	Cr	Cu	Ni	Pb	Zn	Se	Hg[1]
FM	10.8	0.7	8.8	39.1	34.0	37.0	54.3	122.8	-	0.2
ČA	10.0	0.4	7.8	42.9	22.7	29.6	21.1	75.6	0.2	0.06
ČM	10.0	0.4	7.8	42.9	22.7	29.6	21.1	75.6	0.3	0.1
HM	9.2	0.2	10.0	41.5	22.9	32.6	19.7	68.8	0.1	0.05
LM+PG	9.9	0.3	9.7	42.8	17.0	23.3	24.2	66.7	0.2	0.07
KM	14.8	0.3	12.6	52.2	28.9	29.2	27.0	93.5	-	-
RM	3.4	0.1	2.0	19.5	17.0	12.0	7.7	41.0	0.3	0.03
RA	13.1	0.5	11.8	55.2	30.6	42.0	36.3	103.1	-	0.13

Explanations: FM – Fluvisols, ČA – Phaeozems, ČM – Chernozems, HM – Luvisols, LM+PG – Albic Luvisols and Planosols, KM – Cambisols, RM – Regosols, RA – Rendzic Leptosols, Hg[1] – total content (AMA analyzer)



The highest values of arsenic content occur on Cambisols especially with existence of geochemical anomalies (mostly Cambisols on granitic, methamorphic and volcanic rocks).

Average values of cadmium are the highest on Fluvisols (Table 3) as the result of its transport along the rivers where anthropogenic and geogenic influence can be mixed.

The variability of cobalt in the subsoil is higher opposite the topsoil. Finally, it may be said that anthropogenic input of cobalt in soils of Slovakia is not significant.

Difference of chromium content between topsoil and subsoil is very low. It means the content of chromium in soil profiles is even-tempered and reflects mostly the natural distribution of chromium in soils of Slovakia.

The highest concentrations of copper were determined in some Cambisols and Fluvisols (the areas with geochemical anomalies occurrence and alluvial deposits with accumulated soil-sedimentary material from those areas).

The average content of nickel is the highest on Fluvisols and Rendzic Leptosols (Table 3), what is in harmony with previous work (Čurlík, 2011).

The highest values of lead were determined in Fluvisols where Pb was often accumulated on alluvial deposits in lower part of rivers.
Zinc in conditions of Slovakia is common especially in areas with geochemical anomalies occurrence as well as in some alluvial deposits. The highest content of zinc was determined on Fluvisols – especially on alluvial deposits in lower part of rivers similarly as cadmium.

Selenium is characteristic with irregular distribution (Wedepohl, 1995) and low to high content in soils of Slovakia. Its occurrence is often common in soils on volcanic rocks. In individual soil types exist evident differences in content of Se, while is indicated narrow relationship between soil forming substrates rich in Se and its content in soils (Čurlík, 2011).

Average content of Hg in agricultural soils of Slovakia is 0.09 mg.kg^{-1} what is the lower value than valid hygienic limit in Slovakia (MPRV SR, 2013). The high variability of Hg in evaluated soils of Slovakia is characteristic for this element (>60 %) (Table 1) caused by volatility of Hg.

DISCUSSION

Distribution and behaviour of risk elements in soils of Slovakia are often in harmony with other authors. Similar results were obtained also in soils of Czechia (Poláková et al., 2011). Arsenic is an important component of arsenopyrite (FeAsS), which is the most extended arsenic mineral in Slovakia. Its migration in soil is limited (sorption with clay, hydroxides, oxides and with soil organic matter) – Čurlík , 2011). The distribution of risk elements depends on parent material, land use, soil type and potential source of elements origin (geogenic, anthropogenic, resp. mixed influence) (Wilcke et al. 2005). Concerning the measured values of risk elements presented in the Table 3 the slightly increased values of some risk elements (Cd, Cu, Pb, Zn) from among the evaluated soil types occur on the Fluvisols which could be transported from the catchments and accumulated on the alluvial deposits especially along lower parts of rivers (Kobza et al. 2014). Mean value of some risk elements on Cambisols could be also increased (As, Co, Cr, Cu, Zn) in areas influenced by geochemical anomalies. Unlike the soils with low to very low content of humus and clay fraction (Regosols) are characteristic with the lowest content of all risk elements, what it was already confirmed also in previous work (Wilcke et al. 2005).

CONCLUSIONS

In general, on the basis of our results it may be said that the hygienic state of agricultural soils in Slovakia is good except of some contaminated sites which are mostly situated in the industrial areas (anthropogenic impact) and in the areas influenced by geogenic impact – occurrence of geochemical anomalies (mostly mountainous areas). The area of contaminated agricultural soils is less than 1 % of total area of soils in Slovakia. Their unfavourable state of these contaminated sites persists often a long period without significant change during soil monitoring period in Slovakia since 1993 year and therefore it will be necessary to monitor them also in the future.

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REFERENCES

Čurlík, J. 2011. Potenciálne toxické stopové prvky a ich distribúcia v pôdach Slovenska (Potentially toxic trace elements and their distribution in Slovakian soils). PFUK Bratislava 2011, 462 p. ISBN 978-80-967696-3-6.

Kobza, J., Barančíková, G., Dodok, R., Hrivňáková, K., Makovníková, J., Pálka, B., Pavlenda, P., Schlosserová, J., Styk, J., Širáň, M. 2014. Soil monitoring of Slovakia (in Slovak). NPPC – VUPOP Bratislava, 252 p. ISBN 978-80-8163-004-0.

MPRV SR - Ministry of Agriculture and Rural Development, 2013. Act No. 59 from 11.3.2013 (in Slovak).

Poláková, Š., Kubík, L., Malý, S., Němec, R. 2011. Monitoring zemědělských půd v ČR (Monitoring of agricultural soils in Czechia) 1992 – 2007, ÚKZUZ Brno, 2010, 118 p.

Van Camp, B., Bujarrabal, A. R., Gentile, R. J. A., Jones, L., Montanarella, L., Olazabal, O., Selvaradjou, S. K. 2004. Reports of the Technical Working Groups Established under the Thematic Strategy for Soil Protection. EUR 21319 EN/5 (2004) p. 872. Office for Official Publications of the European Communities, Luxembourg.

Wedepohl, K.H. 1995. The composition of continental crust. *Geochemica Cosmochemica Acta*, 59, pp. 1217 – 1232.

Wilcke, W., Krauss, M., Kobza, J. 2005. Concentrations and forms of heavy metals in Slovak soils. *Journal of Plant Nutrition and Soil Science*, 2005, 168, 676 – 686. doi: 10.1002/jpln.200521811.

CONTAMINATION ISSUES OF ARMENIA's MINING SITES

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KEYWORDS

Mining, contamination, heavy metals, environmental risk assessment, health risk assessment, soil contamination, water contamination, crop contamination

ABSTRACT

This abstract is aimed at the revealing of contamination issues in some of Armenia's mining regions through generalization of data on complex investigations implemented at the Center for Ecological-Noosphere Studies NAS RA between 2005 and 2017 and is focused on pollution of different environmental compartments: water, atmosphere, soil, agricultural produce, human bio-substrates.

Mining in Armenia (Fig. 1) has a very long history going back to IV BC. In XX century the historically shaped areas underlay development of industrial mining centers, operation of which entails a plenty of environmental issues. Today, a share of mining industry of Armenia is 17 %, 97 % of which belong to metal mining. According to official data, Armenia (with an area of 29,7 thousand sq.km) accommodates 670 solid mineral deposits including 30 metallic deposits with resources estimated by national inventory. 400 deposits are currently exploited, 22 of which are metallic. Armenia is rich in iron, copper, molybdenum, lead, zinc, gold, silver and rare elements.

Fig. 1 Armenia's position on the world map

Some 80 % of ore mining and particularly metal mining belong to Lori and Syunik marzes situated in the north and south of Armenia. These regions accommodate almost all huge mining complexes of the Republic. The cities (Kapan, Kajaran, Alaverdi) are specific as the mining centers with raw material sources, ore processing plants and agroecosystems lie within the bounds of natural biogeochemical provinces enriched with Cu, Mo, Zn and Pb (Kovalsky V.V. 1974; Saghatelyan A.K. 2004; G. Tepanosyan, L. Sahakyan et. al 2018). Besides mines and processing plants, significant sources of heavy metals in mining centers are active and abandoned tailing repositories and mine waters, which are used in irrigation without pretreatment or empty into irrigation waters (Saghatelyan A. K., Sahakyan L. V. et al. 2010).

Numerous environmental problems these regions are facing at present have a historical character, stem mainly from the Soviet past, but currently manifest themselves in quite new ways. The issues are diverse: tailing repositories (Fig. 2) both active and idle, runoffs, unmanaged industrial waste, degradation of natural landscapes, emissions and as a result – polluted territories.

Fig. 2 Tailing repositories in Kajaran

Investigations implemented in 2005 through 2017 (www.cens.am) allowed identifying heavy metal-polluted sites throughout the regions, evaluating pollution levels and assessing pollution-caused environmental and health risks. The territories of mining towns and adjoining sites used for agricultural purposes were assessed as well. The studied materials were soils, waters, atmosphere, agricultural produce and in some cases human bio-substrates. The tailing repositories were investigated separately.

The obtained data indicate that as a result of ore mining and processing contaminants move out onto the surface, travel into air and water migration streams and finally bring to pollution of all environmental compartments. In this respect a special emphasis should be placed on elements-admixtures, which are not economically valuable and are ignored when exploiting ore deposits, whereas some of these elements depending on individual toxic properties are classified under the first and second class of hazard.

Extremely hazardous are active and abandoned tailing repositories, which are involved in agricultural cycle in different ways.

The presence of polluted soils is a special concern to areas attached to the mining regions and used for agricultural purposes. It has been found out that industrial and mining waters enter the irrigation network and then are used in irrigation. Locally raised agricultural products, too, are polluted with heavy metals.

These results support a conclusion that environmental issues of these regions have changed into those associated with food safety that require researches of different character.

The implemented assessment of health risks helped reveal carcinogenic and non-carcinogenic risks to adults and children from the environment and locally raised agricultural products. So, the complex health risk assessment for the population in mining regions should consist of the sum of environmental pollution risk and food chain risk.

LITERATURE

Kovalsky V.V. (1974) Geochemical Ecology. Moscow, Nauka, 300 pp. (in Russian).

Saghatelyan A.K. (2004). The peculiarities of heavy metals distribution on Armenia's territory. Yerevan, CENS NAS RA, 2004, 157 pp. (in Russian).

Saghatelyan A.K., Sahakyan L.V., Menchinskaya O.V., Zangiyeva T.D., Kajtukov M.Z. & Uzdenova Z.H. (2010) Medical Geology in Connection to Mining. Ed. Olle Selinus, et. al. Springer, Heidlberg, London, New York, 2010, 242–247.

G. Tepanosyan, L. Sahakyan, O. Belyaeva, S. Asmaryan, A. Saghatelyan (2018) Science of the Total Environment, 2018, 639, pp. 900–909; DOI: https://doi.org/10.1016/j.scitotenv.2018.05.211

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DISTRIBUTION, MINERAL FORMS, AND BIOAVAILABILITY OF HEAVY METALS IN SOILS, THEIR IMPACTS ON SOIL BIOGEOCHEMICAL PROPERTIES (ANGREN-ALMALYK MINING-INDUSTRIAL AREA, UZBEKISTAN)

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KEYWORDS

Heavy metals in soil, distribution, mineral forms, bioavailability, soil microorganisms, bioindicators, soil microorganisms, Angren-Almalyk industrial area, Uzbekistan

ABSTRACT

The present study examined air pollution effects on soil health applying microbiological parameters. It was carried out near the Angren-Almalyk mining and industrial area in a semiarid region of Uzbekistan. This area was selected in order to establish a national monitoring program for assessing environmental condition of areas remote but downwind from greater emission sources. Moreover, little information exists about how air pollution affects microbiological functioning of soils in semiarid and arid regions of the world, and especially those of Central Asia. The soil samples, which are heavily impacted by aerial emissions from the coal burning and metal-processing industry of the Angren-Almalyk industrial area, were the main subject of our intensive investigation (Fig 1).

Knowledge of chemical mobility of heavy metals is fundamental to understanding their toxicity, bioavailability, and geochemical behavior. Mineralogical means and sequential extraction were employed to analyze the total contents, existing states, and chemical forms of heavy metals in soil. The aims of our studies were (i) to assess the relationship between distance from the emission sources and heavy metal concentrations in soil and to analyze the depth distribution of the metals as indication of their mobility along the downwind transect; (ii) to evaluate the mobile and immobile metal forms, and (iii) to analyze the composition of heavy metals mixtures by means of statistical methods to get hints of common sources of different metals. The second part of our intensive studies was focused to determine the influences of heavy metals (Cu, Pb, Zn, Cd and As) on soil microbial and nematode characteristics in Angren-Almalyk mining industrial area along the two deposition transect. Nematode population, community structure, ecological indices, pollution tolerance and other indicators including microbial biomass, metabolic quotient were studied in soil samples. Soil microbial biomass, nematode population and community ecological indices response to heavy metal pollution in Angren-Almalyk mining industrial area were evaluated. Metal pollution indicators and tolerance species are established and recommended for developing biomonitoring and bioremediation measures which planned in future for this region. Microbiological ecosystem properties were assessed by biological indicators such as basal respiration (R_B), microbial biomass related C and N contents, and microbial community functioning coefficients like the metabolic quotient qCO_2.

Soil samples were collected along the two 20-km down-wind transects in the Akhangaran river valley, nearby the industrial complexes. In the laboratory, all samples were sieved through a 2 mm mesh sieve and separated into two parts. The first part was stored in a refrigerator at 4ºC for the biological studies, the second part of the soil samples (n=176) were used for chemical and mineralogical studies. These samples were air-dried, grounded in an agate mortar, and homogenized for sequential chemical extraction (AAS, ICP-MS) and preparation of powder pellets for XRF and XRD analyses. QA/QC was performed on basis of certified reference materials (CRM). We have completed the analyses of the total metal concentrations (Cu, Pb, Zn, Cd, Ni, Cr and Mn) and metal forms (mineralogy and chemistry) in all soil samples. Were quantified the mineralogical characteristics, morphology, and chemistry of air-borne spheroids to characterize the mineralogical sources of the soil contamination by heavy metals using JEOL scanning electron microscope (SEM). Sub-samples for mineralogical studies were separated by gravity and size. Particle-size fractionation was carried out by sieving and by sedimentation in aqueous media. The fine-grained fraction was subjected to gravity separation and

fractionated into (A) the heavy mineral fraction (ore minerals and spherical airborne metal-rich particles) and (B) the light mineral fraction (parent rock minerals). The heavy mineral fraction separated from the fines were embedded in epoxy resin. Element mappings were performed with the polished and carbon-coated thin sections using a JEOL microprobe.

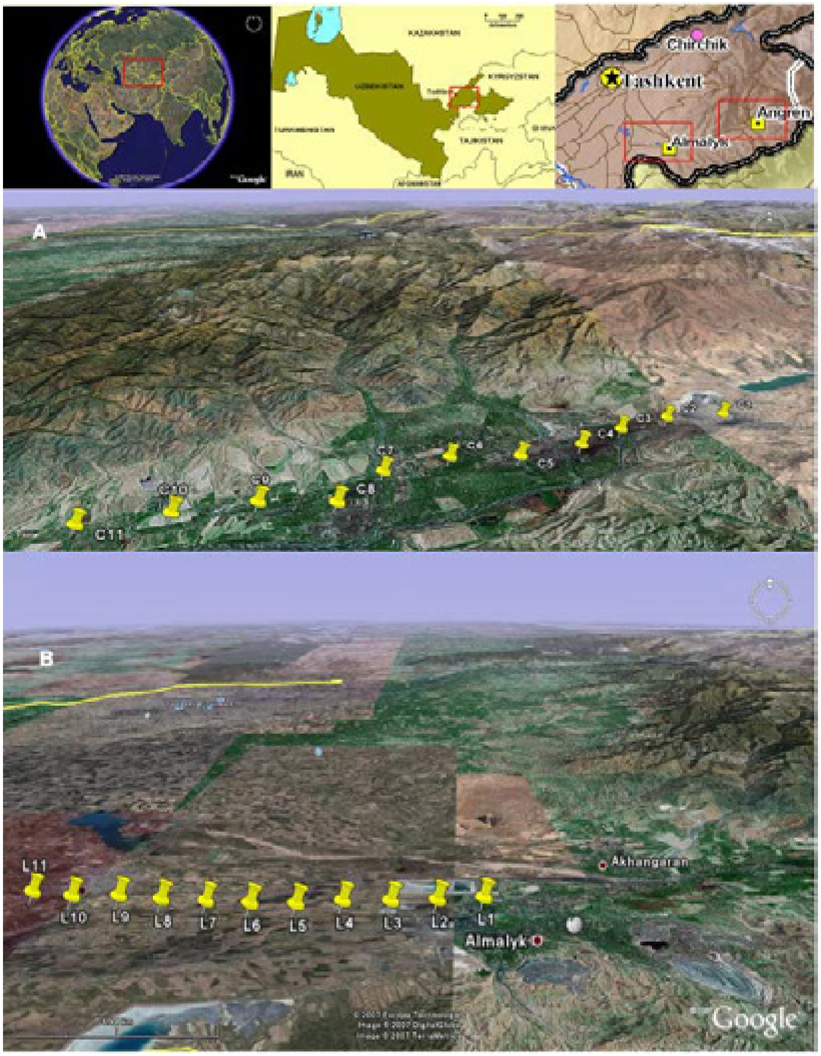
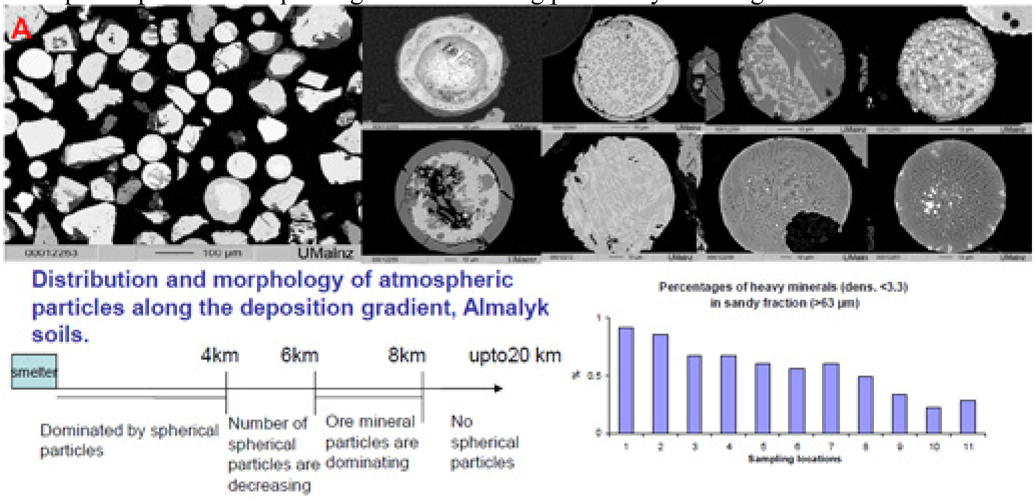


Fig. 1 Soil sampling locations in Angren-Almalyk mining industrial area (A – Angren; B – Almalyk).

Heavy metals were also fractionated by the sequential extraction procedure, in which the metal fractions were defined as exchangeable, carbonate-, Fe–Mn oxide-, organic matter-bound, and residual fractions. The sequential extraction scheme was developed from that of Tessier at al. (1979) and the same terminology is retained. Since this is the method that has given results about the possible bioavailability of the elements and their extractability or leachability, it is described in detail. Extraction was carried out progressively on an initial weight of 1.000 gram of soil sample. To measure the bioavailable heavy metal fraction were used diffusive gradients in thin films (DGT) at the maximum water holding capacity (MWHC) of the sub-samples. In particular, were separated the concentrations and effects of geogenic and smelter metals with the help of the stable isotopic signature.

The concentrations of a number of potentially toxic metals varied along the sampling transects, revealing a gradual decrease at increasing distance from the emission sources. The highest levels were found for the relatively volatile heavy metals (Cu: 457–871, Zn: 424–1695, and Pb: 163–441) in soils near the Almalyk metal smelter, and Zn (850–1051 ppm) and Pb (270–320 ppm) in soils near the Angren power plant suggesting that the metal pollutants probably derive from local stack emissions. Significant differences ($p<0.05$) were observed between the upper (0–10 cm) and deeper (10–20 cm) soil layers and among the particle size fractions for Cu, Zn, Pb, U, and Th, at most sampling locations of both study areas. The concentrations of a number of metals (Zn, Cu, Pb, Cd and As) were higher in the upper soil layer and in the clay fractions at all sampling sites. The distribution and concentrations of some other metals (Co, Cr, Ni, V, and Sc) showed an opposite trend, probably due to the native geochemical background. Furthermore, heavy metals were fractionated by a sequential extraction procedure, in which the metal fractions were defined as exchangeable, carbonate-, Fe-Mn oxide-, organic matter-bound, and residual fractions. Most of Cd was extracted with the exchangeable and carbonate-bound fractions. The highest concentrations of Ni and Cr were found in the residual fraction. The speciation of Cu, Pb, Zn, and Cd was related to distance from the emission source and soil depth. The mean contributions of Cu, Pb, Zn and Cd in the exchangeable fraction to the total concentrations were higher at the locations (nearest to the pollution sources) and decreased with increasing distance. Metals bound to carbonates and Fe–Mn oxides increased consistently with depth in first sampling location. There were almost no significant changes in the metal contents in all fractions after 12 km.

Several metal phases such as galena, chalcopyrite, sphalerite, pyromorphite, cerusite, hydrocerussite, leadhillite, and anglesite were identified by XRD. Of the crystalline metal phases, the presence of cerusite, malachite, azurite, hydrocerussite, and pyromorphite were identified as weathered forms of primary ore minerals at the first sampling location in Almalyk. A lot of grains and spherical particles with bright contrast appeared in the microprobe scans indicating a metal-rich composition. Spherical particles dominated in the soil samples collected near the metal smelters, whereas angular sulfide minerals (pyrite, galena, chalcopyrite, sphalerite) dominated in samples collected near the mine spoils and tailings depository (Fig 2). The morphology and internal microstructure of the spherical particles in a heavy mineral fraction of the soil samples from the Angren-Almalyk area indicate formation from a pre-existing molten phase, probably emitted by an inefficient air pollution control technique of the smelter in Almalyk and thermal power plant in Angren. Spherical particles can be divided in pure metal particles (Cu, Zn, Al), metal-rich cores with silicate rims, small spherical metal sulfide or oxide particles within larger heterogeneous glassy particles, well-organized particles with dendrite structure. Fine grains of sulfide ore minerals, covered with weathering rims of secondary ore minerals (sulfates or carbonates), can be related to contamination by mining activities. Fe was abundant in most particles from the Angren soils, associated with Ti, S or Pb, and Zn. A few bright grains showed a rim dominated by Si and K. Other associations found were Fe+S+Pb+Mn, or S+Pb+Zn+Mn+Fe, or pure Cu or Zn only. The absence of an O peak indicates that Cu, Zn, and Pb are largely associated with sulfides rather than sulfates. Numerous spherical particles showed distinct dendrite-like structures within a dark grey matrix. The matrix is composed largely of Si, Mn, Zn, Pb, Al and Fe or Fe alone, Ti, Cu, Si, and Ca, whereas the bright areas were formed mainly by Fe and Al, presumably in an oxide (spinel) form considering the strong O signal. Most of the spherical particles showed holes inside or had metalliferous rims around alumina cores, which indicates formation from a pre-existing molten phase. Occasionally, these technogenic spheres contained angular grains of primary ore minerals. Percentage of heavy minerals in Angren soils is more than in Almalyk's (1>4). Elemental composition of spherical particles very poor than Almalik's (almost all of them have elevated content of Fe oxide with less Si, Al, Mn, Ca content. In some particles fewer contents of Pb, Cu and S were observed. Spherical particles in Angren soils can be divided into 3 groups: a) well organized massive dendritic particles containing Fe oxide in light growing crystals and matrix containing Si, Al, Ca, Fe; b) homogenous spherical particles without any structures containing Fe oxide; c) small microscopic particles coated Fe oxide. Ore mineral particles mainly Hematite, titan-magnetite, magnetite and very fewer pyrite particles. Many of them covered with secondary ore minerals as Fe hydroxide and carbonates. The calcareous condition of soils in studied areas can stabilize atmospheric particles and prolong their weathering process by covering them with carbonate material (Fig 2).



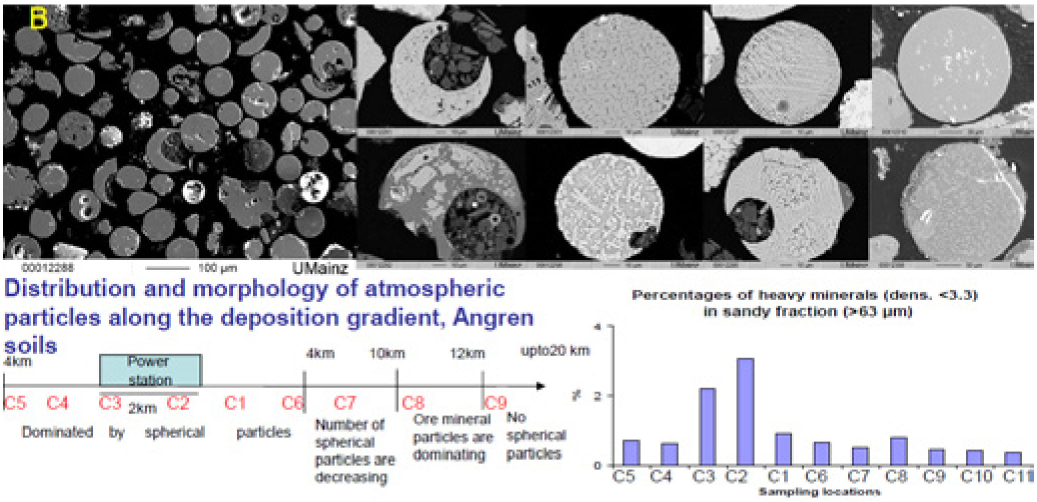


Fig. 2 The morphology and internal microstructure of the spherical particles in a heavy mineral fraction of the soil samples from the Angren-Almalyk area, and their distribution along the deposition gradient (A – Almalyk; B – Angren).

Twenty-nine nematode taxa were identified in the present investigation for Almalyk downwind transect: twelve taxa belonged to the bacterivore trophic group, 5 were fungivores, 7 were planted parasites and 5 were omnivores-predators. The mean density of the soil free-living nematodes increased with distance from the pollution source in both soil layers. Moreover, nematode density in the upper (0–10) cm soil layer showed a gradual increase in T_{NEM} population between sampling locations, yielding significantly high $R^2 = 0.98$ values, a value which decreased to a level of $R^2 = 0.69$ with the increase in distance (20 km). In the deeper (10–20 cm) soil layer, the R^2 values obtained for a similar distance were found to be similar ($R^2=0.8$). The nematode density was higher in the upper soil layer (from 1.2 to 2.0 times at the different sampling locations) than in the deeper soil layer ($p<0.02$). The percentage of each trophic group out of the whole population was found to be affected by the distance from the pollution sources. Trophic group density increased with distance; however, these increases were not always similar along the both transects. Bacterivores (BF) and plant-parasites (PP) in the deeper soil layer and omnivore- predators (OP) in both soil layers, increased consistently from the pollution source to the edge of the study area, whereas BF, PP and fungivores (FF) in the upper soil layer increased to first three locations and then decreased to other locations in Almalyk. Nematode data obtained from the Angren sampling site also show almost similar responses to pollution with small varieties because of the complicated nature of disturbance (coal ash, resin, and metalloorganic) and also the nonlinear distribution of pollutions sources along the transect. The effect of pollution on the density and biomass of soil free-living nematodes was found to be highest at the pollution source in Almalyk, with fungivores and plant parasites dominating at the upper and deeper soil layers next to the pollution source. These groups decreased along the transect, yielding domination to bacteria and fungi feeders. The females of the total soil free-living nematodes were found to be the most resistant to heavy metal pollution levels, while the juveniles were found to be sensitive to changes in heavy metals. The Maturity and modified maturity indices, that reflect the degree of disturbance of the soil ecosystem, were found to be the most sensitive indices.

Microbiological ecosystem properties were assessed by biological indicators such as basal respiration (R_B), microbial biomass related C and N contents, and microbial community functioning coefficients like the metabolic quotient qCO_2. There was a significant spatial dependence and differences for all soil chemical and microbiological parameters tested. The highest contents were found for the relatively volatile metals Zn (≤1,136 mg/kg) and Pb (≤373 mg/kg) in upper soil layers near the power station suggesting that the metal pollutants are derived from local stack emissions. Soil microflora was obviously affected by heavy metals. Significant positive correlations ($p \leq 0.001$) were found between the metal content, RB, and qCO_2, while a negative one was found for the mineralizable N and C_{mic}/C_{org} ratio. A high total number of nematodes was found only most distant from the industrial emission sources. The results disclosed remarkable spatial dependence not only of the heavy metal impact onto the soil but also of microbiological soil properties in the study area. The latter suggests bioavailability of the anthropogenic metals in the soil affecting the soil microbial community. This is suggested by less biomass formation and higher qCO_2 values in heavy metal-contaminated compared to less-polluted soil plots. Knowledge of these spatial ecosystem functioning patterns and dependence could be very useful in determining and delineating specific land use and management programs that would be suited and feasible for the highly polluted area. Results of this study can be utilized to develop a monitoring program that may quantify the harmful effects on the soil health and impact of any future remediation activities. Studies on the relationship between soil biota and pollution levels have raised the question regarding the status of natural soil microbial health, stressing the importance of background data of environmental conditions, and elucidating the importance of this environmental monitoring approach even in semiarid and arid regions. Soil microbiological parameters, in particular, the metabolic quotient qCO_2 as one of the most sensitive bioindicators identified for that region, should clearly become part of the national environmental monitoring program.

LITERATURE

Alloway, B.J., 1990. Heavy metals in soils. Blackie, London.

Anderson, G.L., Boyd, W.A., Williams, P.L., 2001. Assessment of sublethal endpoints for toxicity testing with the nematode Caenorhabditis elegans. Environmental Toxicology and Chemistry 20, 833–838.

Bakonyi, G., Nagy, P., Kadar, I., 2003. Long-term effects of heavy metals and microelements on nematode assemblage. Toxicology Letters 140, 391–401.

Bardgett, R.D., Speir, T.W., Ross, D.J., Yeates, G.W., Kettles, H.A.,1994. Impact of pasture contamination by copper, chromium, and arsenic timber preservative on soil microbial properties and nematodes. Biology and Fertility of Soils 18,71–79.

Bongers, T., Bongers, M., 1998. Functional diversity of nematodes. Applied Soil Ecology 10, 239–251.

Shukurov, N., Pen-Mouratov, S. and Steinberger Y. “The impact of the Almalyk industrial complex on soil chemical and biological properties”. Environmental Pollution, 2005, 136, 331–340.

Shukurov N., Pen-Mouratov S., Steinberger Y., Kersten M. “Soil biogeochemical properties of Angren industrial area, Uzbekistan”. J. Soils & Sediments, 2009, 9, 206–215

Tessier A., Campbel P.G.C., and Bisson M., 1979. Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. Analytical Chemistry, vol.51, No.7, 844–851.

Yeates, G.W., Percival, H.J., Parshotam, A., 2003. Soil nematode responses to the year-to-year variation of low levels of heavy metals. Australian Journal of Soil Research 41, 613–625.

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VERMIREMEDIATION STRATEGY FOR REMEDIATION OF KUWAITI OIL CONTAMINATED SOIL

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KEYWORDS

Vermiremediation, TPH, oil contaminated sand, *Eisenia fetida*, *Lumbricus terrestris,* organic wastes

ABSTRACT

The concept of using earthworms to degrade organic wastes (vermiremediation) has been accepted all over the world for many years. Currently many developed as well as underdeveloped countries are implementing it effectively on varying scales of operation. However, the technology of using earthworms to biodegrade petroleum organic wastes has not been addressed yet in the case of Kuwaiti oil contaminated sand or weathered contamination. This paper deals with earthworms their potential of decomposing petroleum hydrocarbons in terms of total petroleum hydrocarbon (TPH) present in Kuwaiti oil contaminated sand. Laboratory scale experiments were carried out to assess the efficiency of earthworms (*Eisenia fetida*) to degrade TPH ranging from 5000 – 25000 mg/kg. It was found that the TPH of < 5,000 mg/kg was not harmful for the survival of earthworms however, TPH of 10,000 mg/kg reduced their survival to 50 %. This paper indicates that vermiremediation can effectively reduce the TPH of about 5,000 mg/kg every 5 weeks. As the presence of crude oil was challenging for the survival of earthworms, the remediation process was enhanced to support the earthworm's activity.

1. INTRODUCTION

Vermiremediation is slowly becoming an inexpensive and suitably acceptable method to clean up chemically contaminated sites throughout the globe. Generally, earthworms (especially *E. fetida*) have good resistance against contaminants including heavy metals and organic pollutants within the soil. It has been described that they bio-accumulate the contaminants within their bodies and biodegrade or bio-transform them to safe products aided by enzymes Vermiremediation is slowly becoming a less expensive and more acceptable method of clean up for chemically contaminated sites around the world. This approach involves the use of earthworms to bio-accumulate the contaminants within their bodies and biodegrade or bio-transform them into safe products with the assistance of enzymes. Sinha (2010) reported that the worms host microbes that are able to biodegrade chemicals within their gut. 5 kg of earthworms (totalling some 10,000 individual creatures) are typically able to degrade 1,000 kg of waste within only 30 days, converting the waste into vermin-compost. A study by Martin-Gel et al., (2007) on the efficiency of composting and vermicomposting in degrading fuel oil in water emulsions from oil spills. Three trays for vermicompost processes of 0.40 × 0.50 × 0.12 m^3 in volume and 0.20 m^2 in surface area, the density of *Eisenia foetida* earthworms were 300 g-earthworms/m^2. The moisture was maintained between 60 % and 80 %, for a 6 months period. After short period, the asphaltens can be as a source of microorganisms to obtain carbon and energy. The addition of factors, like potato peelings and *cow bed*, allows the complex compound to breakdown into smaller compound, which leads to further degradations with earthworms are necessary.

The evaporation, dissolution and/or photo-oxidation of composting processes can be helpful to degrade or remove volatile hydrocarbons and asphaltens into CO_2 and H_2O. So that, high efficiency for removal, destroy or degrade complex organic matters such as 'asphaltens and resins' from oil contaminated soil is the composting techniques, followed by vermicomposting techniques. Safawat et al., (2002) carried out a laboratory study to determine the maximum concentration of crude oil in the soil that keeps the worms survive. The outcomes demonstrated that, the worms were able to tolerate 0.5 % crude oil and survived in this environment for 7 days. However, the survivals of worms were reduced to less than 40 % when exposed to soil containing 1.5 % oil. Verimremedition for soil with 1.2 % crude oil was not harmful to survival of earthworms for 10 days. Also, the result showed that earthworms degraded oil-contaminated soil contained 0.2 % TPH in worm's vermicast. A study was performed by Ma et al. (1995), focussing on the influence of earthworm species L. rubellus on the disappearance of spiked PAHs phananthrene & fluoranthene (100 µg/kg of soil), It was revealed that both PAHs disappeared faster in soils containing worms as compared to the bare soils. 86 % of phenanthrene was eliminated after 56 days (8 weeks). A study by Contreras-Ramos et al., (2006) emphasising on the uptake of three PAHs namely phenanthrene, anthracene and benzo(a)pyrene at various concentrations by *Eisenia fetida*. The PAHs concentrations in the soil and in the earthworms tissues exposed to PAHs were measured and compared for 11 weeks. The anthracene concentration dropped by more than double from 51 % to only 23 % as compared against the soil without earthworms. On the average, the benzo(a)pyrene concentration was reduced by between 1 to 4 times with 47 %

average removal against only 13 % with the absence of earthworms. Total (100 %) removal of Phenanthrene was achieved by earthworms when the chemical content was less than 100 mg/kg of soil, whilst 77 % was removed by microbes in soil without earthworms. The study conducted by Schaefer (2005) showed that the presence of *Eisinia fetida* had caused the increased microbial catabolic activity, which resulted in the loss of 91 % (1,074 mg/kg of soil to 96 mg/kg) of crude oil contamination within treatment period of 56 days. Furthermore, Schaefer and Juliane (2007) were Investigated the degradation of an oil contaminated soil with three different earthworm species (*Eisenia fetida*, *Lumbricus terrestris* and *Allolobophora chlorotica*) for 28 days, the results had shown that the concentrations of TPH in samples decreased 30 – 42 %, 31 – 37 % and 17 – 18 % respectively. Nevertheless, the concentration of TPH in samples without earthworms was slightly decreased (9 – 17 %) compared to the initial concentration of TPH. When the concentration of TPH in the oil-contaminated soil is less than 4,000 mg/kg, earthworms can be used as useful tools in the in situ bioremediation. Generally, earthworms have high resistivity to a number of chemical pollutants present in the soil. The beauty of this economic and environmental importance is that polluted land is not only cleansed but also improved in terms of its physical, chemical and biological quality.

2. METHODOLOGY

A bench-scale investigation will be conducted to study the degradation rates of oil-contaminated soil under a combination of various remediation techniques over a period of time. The laboratory work was focused on vermiremediation. Four bench-scale experiments will be conducted, each of which will contain 5 kg of contaminated soil. Experimental control is required to confirm the test results and this will therefore be simulated in the first bench-scale, but without microbial activity. The second bench-scale will be designed to simulate the combination system of various remediation methods. The experiment will be sampled weekly. Environmental factors including microorganisms, water temperature, water/soil pH and moisture content will be observed for certain duration. Bench-sale testing will be determined to be feasible if the combination system is able to reduce the concentrations of hydrocarbon to acceptable levels (regulatory objective of 2,000 mg/kg TPH) within a short period, at a low cost and with lower environmental effects. It is recommended that the following scheme be established in order to deal with Kuwait environmental issue. All experiments will be run in the Kuwait University Glass house, as illustrated in Figure 13. This will allow for a controlled environment in which ambient temperature can be effectively maintained between 20 and 21 °C.

2.1 SAMPLE PREPARATION

A physical separation technique will decrease the volume of contaminated soil by reduction of the concentration of contaminated soil, according to the size of the particles. In this case, a sample will be dry-screened using a 2 mm screen to isolate material finer than coarse sand and a 20 mm screen to separate out the gravel material. The bioremediation process requires the soil to be homogeneous before the start of the treatment. Generally, the screening process is able to separate oversized fractions, as long as they are not contaminated, such as with debris, metals or rocks.

2.2 VERMIREMEDIATION

The vermiremediation method is not always successful in destroying or removing residual, heavy and hydrocarbons in contaminated soil. However, there is some evidence that this remediation is able to degrade such oil (Sinha, 2010). In this paper, the available compost reactor has been constructed from a plastic box, the length, width and height of which are 0.49 m, 0.30 m and 0.35 m, respectively. This gives the box a total surface area of 0.147 m^2, see Figure 1. The reactor was drilled with 1.5 mm ventilation and drainage holes around the base, upper edge and lid. 5 kg of oil-contaminated soil will then be transported from the sample tray to the compost reactor, after which 3 kg of *Esienia Fetida* will be added. As a result, the stocking density of the compost reactor should be 20.41 kg/m^2.

Fig 1: The compost reactor for vermiremediation process

The earthworm activity is dependent on a number of critical factors, including temperature, density, feeding, pH and moisture content, while distilled water will be used to maintain the moisture within content ranges of 50 – 80 %. These factors will be observed weekly.

2.3 DATA ANALYSIS

The treatment process will be replicated three times in each stage of the combining remediation system in order to confirm data obtained, while the “Statistical Package for Social Science” (SPSS Window) Version 12.0 will be used to analyse the collected data. The samples will be coded before being entered into the computer. Median, means, standard deviation and multivariate statistics will be used to detect differential expressions. Means will be selected for normal distribution graphs and medians for abnormal distribution graphs. Obtaining the same value in each replicate process will be supported data obtained.

2.4 EXTRACTION OF OIL FROM SAND

A number of researchers have developed and utilised methods for the extraction of oil from soil, sand or sediment (Saeedet al., 1997; Hu and Guo, 2001; Parra-Barrazaet al., 2003; Xingang Li et al., 2012). Almutairi, 2016 has suggested the following procedures to measure TPH for the extraction of Kuwaiti-residual oil from sand are 1 g of sample and an acetone:hexane (1:1 mix) for a period of 5 minutes.

3 DISCUSSION

Three experiments were conducted to determine the survivability of earthworms in the presence of crude-oil-contaminated soil. The experimental units were plastic containers, the length, width and height of which are 0.49 m, 0.30 m and 0.35 m, respectively. This gives the box a total surface area of 0.147 m^2, approximately 3 kg of soil was added to each container and the container was divided centrally across the width with a thin rigid plastic barrier. As a result, the stocking density of the compost reactor should be 20.41 kg/m^2. The soil on one half was treated with un-weathered oil to contain 0.0, 0.5, 1.0, 1.5 and 2.0 % oil on a soil dry weight basis. Water-content was adjusted to 25 % on a soil dry weight basis on both sides of the barrier. Water content was maintained during incubation by aking additions as determined from reweighing containers. The jars were kept in an incubator at 20 °C as recommended and the number of viable earthworms was determined after 5, 7, 10 and 15 days as shown in Table (1). Although the containers were quite large only 200 earthworms were added so that it would be easier to monitor movement. Once each day the earthworms were observed to determine if they were in contaminated or uncontaminated soil. Because of space requirements the containers were incubated in a room maintained between 20 and 22 °C.

Tab 1. Survival of earthworms in soil treated with different concentrations of weathered and unweathered crude oil

Day	*Eisenia fetida*				*Lumbricus terrestris*				
	Survival of earthworms				Survival of earthworms				
	0.5 %	1.0 %	1.5 %	2.0 %	0.5 %	1.0 %	1.5 %	2.0 %	2.5 %
5	100	100	100	80	100	100	100	80	40
7	100	90	40	40	100	100	20	20	20
10	100	80	20	0	100	60	0	0	0
15	90	70	10	0	40	40	0	0	0

The experimental design was randomized with three replicates of each treatment. Data were compared by analysis of variance. Twenty-four hours after the addition of the earthworms to the containers with soil treated with 0.5 % oil, samples of soil and earthworm casts were collected from the container. They were carefully picked from the surface of the soil of each replication with a spatula to minimize contamination with soil. The casts were collected to determine if the digestive systems of the earthworms were being exposed to oil. The casts were analyzed for TPH according to EPA method 418.1 using an infrared spectrophotometer (EPA, 1979). In the first experiment *E. fetida* was used in this investigation because it is recommended by Kula and Larink (1998) for laboratory toxicity tests. The experimental design was completely randomized, with a factorial arrangement of treatments and three replications. The second experiment was similar to the first except that only unweathered crude oil was used and the oil concentrations in the soil were 0.0, 0.5, 1.0 and 1.5 %. *L. terrestris* was used in this investigation because it is a deep burrowing earthworm and would be likely to have higher exposure to oil in soil than *E. fetida* which normally feeds on litter at the soil surface (Edwards and Bohlen, 1996) because these earthworms were much larger than *E. fetida*. The experimental design was completely randomized with three replicates of each oil concentration. Furthermore, a third experiment was designed to determine survival of earthworms when they had opportunity to move away from oil-contaminated soil into uncontaminated soil. It can be concluded that this paper is working with worms and utilising there potential in decomposing petroleum hydrocarbons in term of total petroleum hydrocarbon (TPH) in the Kuwaiti oil contaminated sand. Laboratory scale experiments were carried out to assess the efficiency of using earthworms (*Eisenia fetida)* to degrade TPH of 5.0 – 20.0. It was found that the TPH of < 5.0 % was not harmful to survival of earthworms however, TPH of 10.0 % reduced survival to 50 %. This paper indicated that the Vermiremediation was able to reduce the mean values of TPH 5,000 mg/kg after 5 weeks. Earthworms was in hard position in front of crude oils therefore, the remediation process was enhanced to support the earthworm's activity.

4 CONCLUSION

Vermiremediation considerably gives a total quality improvement of the soil and land inhabited by worms. They consume significant quantity of soil daily, blend them in their gizzard and absorb them in their intestine aided by enzymes. Most of the digested and indigested material is excreted out in the soil as fine mucus coated granular aggregates known as 'vermicastings' whilst only between 5 to 10% is absorbed into the body. These 'vermicastings' contains a lot of nutrients such as NKP (nitrates, phosphates and potash), micronutrients and beneficial soil microbes including the 'nitrogen fixers' and 'mycorrhizal fungus' (Sinha et al., 2010). The beauty of this economic and environmental importance is that the polluted land is not only cleansed but also 'improved in physical, chemical & biological quality'.

LITERATURE

Contreras-Ramos, Silvia M., Alvarez-Bernal D. & Dendooven L. 2006. *Eisenia fetida* increased removal of polycyclic aromatic hydrocarbons (PAHs) from soil; *Environmental Pollution;* Vol. 141: pp. 396 – 401; Elsevier Pub.

Ma, W. C., Imerzeel and Bodt, J. 1995. *Earthworm and food interactions on bioaccumulation and disappearance* *of PAHs:* studies on phenanthrene and flouranthene; *Ecotoxicology and Environmental Safety;* Vol. 32: 226 – 232.

Martin-Gil, J., Navas-Gracia, L. M., Gomez-Sobrino, E., Correa-Guimaraes, A., Hernandez-Navarro, S., and Sanchez-Bascones, M. 2007. Composting and vermicomposting experiences in the treatments and bioconversion of asphaltens from the Prestige oil spill; Bioresource Technology*;* Vol. 99: pp. 1821 – 1829.

Safawat, H., Hanna, S., Weaver, R.W. 2002. Earthworms survival in oil contaminated soil; Plant and Soil*;* Vol. 240: pp. 127 – 132.

Schaefer, M and Juliane, F. 2007. The influence of earthworms and organic additives on the biodegradation of oil contaminated soil. Applied soil ecology 36: pp. 53 – 62.

Sinha, R. K., Herat, S., and Valani, D. 2010. *Earthworms – The Environmental Engineers: Review of Vermiculture Technologies for Environmental Management & Resource Development*, *Int. J. of Environmental Engineering,* In Rajiv K Sinha, Sunil Herat & Sunita Agarwal (Eds.) Special Issue on Vermiculture *Technology for Environmental Management and Resource Development.*

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CHEMICAL AND BIOLOGICAL REMEDIATION OF KUWAIT GROUNDWATER AFTER THE GULF WAR: LABORATORY TESTING

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KEYWORDS

Crude oil, TPH, salinity, groundwater contamination, biostimulation, enhanced bioaugmentation, ISCO

ABSTRACT

The ecological consequences of the Gulf War (1990-91) are considered among the most disastrous throughout the history of war: The “scorched-earth” strategy applied by the retreating Iraqi forces included sabotaging of over 700 oil wells and other petroleum infrastructure and placing mines around their perimeter to prevent quick fire extinguishing. After the military operations termination, the firefighting took additional eight months, during which almost one million m^3 of crude oil burned daily[1]. In total, 240 million m^3 of crude oil was burnt, 3.5 million m^3 leaked into the terrestrial environment forming 300 crude oil lakes of up to 2 m depth and total area extent of 49 km^2 [2]. Another almost 2 million m^3 of crude oil were deliberately released into the waters of the Gulf of Persia[1] in order to prevent seaborne invasion of allied forces. Toxic combustion products (ash and soot) covered about 1722 km^2, representing roughly 10% of the area of Kuwait.

The EPS biotechnology company had the opportunity to take part in the biologic and physicochemical remediation technology testing for the purpose of groundwater remediation at the two main Kuwait fresh water aquifers impacted by the environmental contamination. The remediation concepts are further developed in EPS biotechnology.

INTRODUCTION

In 2017, the EPS biotechnology consortium had the opportunity to participate in the laboratory testing campaign of biologic and abiotic techniques for the remediation of Gulf War (1990–91) environmental consequences, implemented under the auspices of United Nations Environment Programme (UNEP). The core of the ecologic burden remains mainly in the chemical composition of the leaked crude oil consisting essentially of a complex mixture of multi-carbon chains and Volatile Organic Compounds (VOCs; e.g., saturated alkanes, or aromatic hydrocarbons), nitrous compounds (e.g., pyrrole, pyridine), or sulphuric compounds (e.g., thiophenol, benzo-thiophene). Further, the Kuwaiti crude-oil is specific by relatively high content of molecular sulphur (2.25 wt. %), whose uncontrolled combustion gives origin to acid rains. Another substantial environmental risk represent natural and/or combustion-derived polycyclic aromatic hydrocarbons (PAH; e.g., benzo[a]pyrene) released into the environment.

Given the desert conditions of the State of Kuwait, where majority of freshwater consumption is covered by desalination, the imperative protection of all and any natural freshwater resources is obvious[3]. The contamination potential may be summarized by four main exposure scenarios: 1) Direct infiltration from the crude-oil lakes (not very likely, because of the strong asphalting tendency of the crude-oil. According to numerical and empirical models, the crude-oil retardation is estimated to exceed 100 years within the vadose zone) [2]; 2) Combustion products deposited on ground surface, leached by atmospheric precipitation (recently, the most serious threat identified, with less than 20 days of contaminated water infiltration through the vadose zone) [2]; 3) Concealed underground crude-oil leakages from sabotaged oil wells and infrastructure; 4) seawater infiltration from the fire extinguishing efforts (risk of salinization of the already scarce Kuwait freshwater sources present at the Al Raudhatain and the Umm Al-Aish aquifer areas (figure1).

Environmental remediation in Kuwait targets soil and groundwater of the source as well as recipient areas. EPS biotechnology was invited to participate on the remedial technology testing within the project „Groundwater Remediation Pilot Project – Raudhatain & Umm Al-Aish Fresh Water Aquifers PTR & In situ (bio) Remediation (WBS: 265.0.003)“ (PTR stands for pump-treat-reinject). A sample of contaminated soil (sand) and groundwater from the Umm Al-Aish aquifer was delivered to EPS labs and the testing of environmental remediation techniques was performed thereon. Based on the experimental outcomes, decontamination technologies were suggested for the removal of TPH (total petroleum hydrocarbons) and salinity, with respect to the major remediation pilot project objectives summarized in Table 1.

METHODS

The experimental setup followed the desired combination of biotic and abiotic remediation techniques. The biotic experiments compared techniques of natural attenuation, biostimulation (i.e., enhanced natural attenuation with nutrient addition and/or TPH bioavailability enhancement through surfactant addition), bioaugmentation (using biodegrading strains isolated from the Kuwait soil sample or biodegrading strains from the EPS biotechnology microbial library), or the combination thereof.

The main abiotic technology was the *in situ* chemical oxidation (ISCO) using Modified Fenton's Reagent (MFR; based on H_2O_2) or sodium persulfate ($Na_2S_2O_8$), both with different activation/stabilisation formulae.

Fig. 1 Map of Kuwait with the target aquifer areas shown in red hatching.

Table 1. Pilot test parameters and target outcomes.

Parameter	*In situ* conditions	Remediation target values
TDS	**A:** 1 500 ppm	< 600 ppm
	B: > 3 000 ppm	
TPH	**A:** 0,01 ppm	< 0,01 ppm
	B: 0,35 ppm	
Odour	**B:** ≤ 3 TON[1]	≤ 2 TON[1]
Colour	**B:** ≤ 15 TCU[2]	≤ 10 TCU[2]
Discharge	Up to 20 $L \times s^{-1}$	
Remediation Unit Size	Small footprint, relocatable unit	
Design lifetime	Temporary (minimum 2 years)	

Note: A = prior to the War, B = after the War, [1] = Threshold Odour Number, [2] = True Colour Unit

Given the number and total volume of experimental batches, the acquired groundwater sample was utilized merely as the geochemical matrix for the biotic techniques' testing, while the ISCO experiments were performed in an artificially prepared model seawater[5]. Because of the high limit of quantitation (LOQ > 0.1 ppm) of the FTIR (Fourier Transformation Infrared) spectroscopy method used for the TPH concentration analyses, and because of the relatively low concentrations of the TPH in the acquired sample (see table 1), particular experimental batches were amended with an aliquot amount of crude oil, allowing for better distinguishing among their relative remedy efficiencies.

RESULTS

The bioremediation techniques' results initially indicated a good cultivation potential of autochthonous consortia under the agar plate conditions (Fig. 2a) and at the DAPI epifluorescent microscopy (Fig. 2b and 2c). However, after the six day incubation, the negative influence of the brackish matrix eventually suppressed the microbial proliferation, causing a decrease in the bioaugmented degrading consortia numbers and resulting in TPH reduction data only within the FTIR method uncertainty interval.

The ISCO results showed the best efficiency for MFR setups containing up to 5 % (v/v) H_2O_2 and various concentrations of the activation/stabilisation agents, showing 86 % – 90 % oxidation of TPH present, within six days of the model seawater batch trials (Fig. 3 and Fig. 4).

Since the amount of delivered groundwater sample did not allow for a true capacity membrane-desalination experiments, the desalination topic was only addressed by discussing the potential of the suggested electro-dialysis method with no actual results obtained.

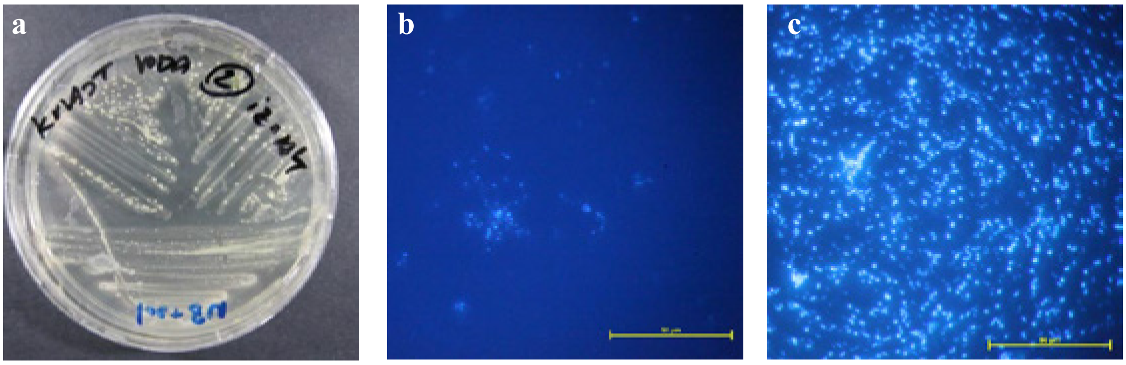

Fig. 2 Cultivation results: Agar-plate strains isolation (a), epifluorescent microscopy – prior to bioaugmentation (b) and after bioaugmentation (c); Scale bar = 50 µm.

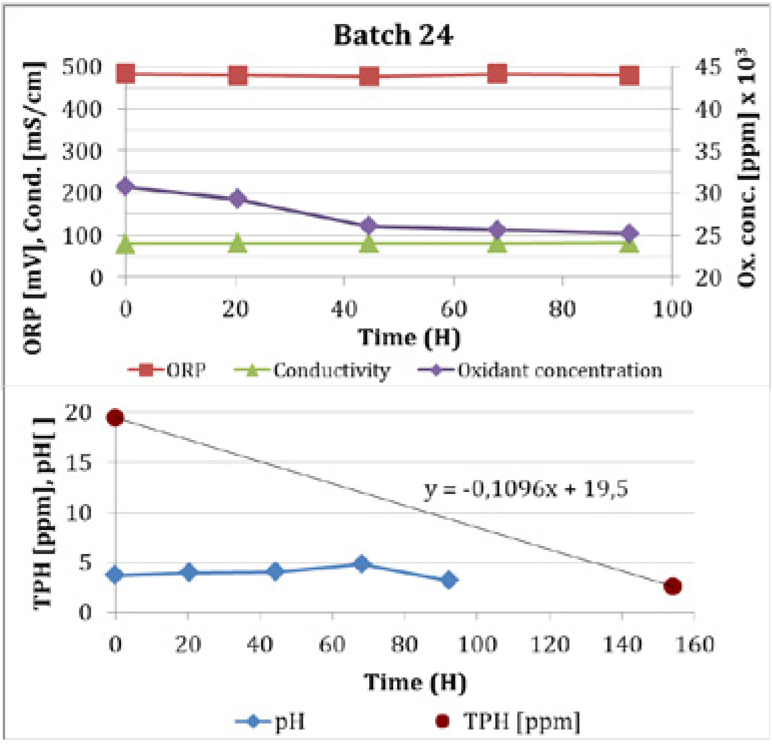

Fig. 3 Most effective ISCO batch monitoring: physico-chemical parameters, oxidant concentration, and TPH concentration development.

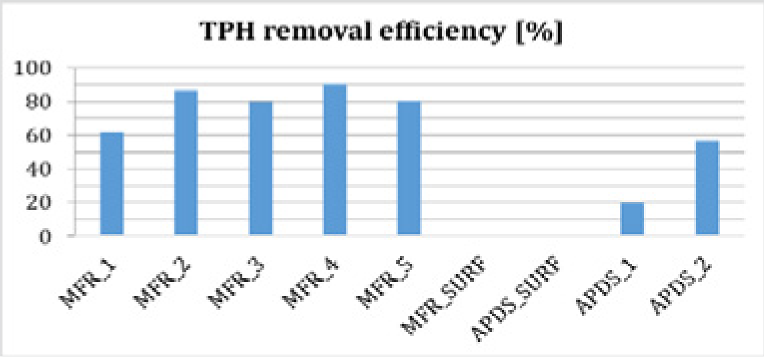

Fig. 4 Efficacy of tested oxidant configurations on the removal of TPH (MFR_4 = Batch 24).

DISCUSSION

The above described experiments showed that the provided soil (sand) and groundwater samples do not represent a media suitable for bioremediation, unless previously treated (desalination, nutrient addition). The critical factors are mainly the low water activity and the limited nutrient contents of the desert soil (C, N, P, S) hindering any substantial biomass development. Further, the relatively low concentrations of TPH in the groundwater, likely do not induce the production of relevant biodegrading enzymes, which usually is triggered by pollutant concentrations in the range of tens of ppm[6]). Although the laboratory trials showed the bioremediation techniques ineffective for the direct treatment of the obtained groundwater sample, it shall be mentioned that the received samples had the history of a prolonged shelf-period before the actual testing (sampled in April 2017, delivered to EPS facilities in mid-June 2017). This lag time may have caused substantial changes in the autochthonous microbial composition, rendering the samples inactive for most bioremediation attempts.

Despite the substantial mineralization of the model seawater (EC ≈ 3.4 mS/cm), no profound extinguishing of the oxidation reaction by present salt ions was observed. The most effective ISCO batches displayed quantitative pollutant oxidation within 171 – 178 hours. Given the lower mineralization of the acquired Umm Al-Aish groundwater sample (EC ≈ 2.99 mS/cm), even greater effectivity of ISCO in the field conditions could be inferred.

The target remediation values obviously aim at the drinking water quality levels, while the required discharge of the small-footprint mobile remediation unit is equivalent to the capacity of smaller to mid-sized municipality waste water treatment plant (Table 1) (based on 450 L × day^{-1} per capita of population equivalent). Yet, at the same time, there is a requirement for the remediation unit to be of a small footprint and relocatable. Simultaneous sustaining of both of these parameters does not provide a trivial task.

CONCLUSION

Despite the poor biodegradation potential shown in this study, a pilot-scale bioremediation test is advisable as a part of the eventual pilot field testing – using the autochthonous microbial populations (immediately after their withdrawal from the subsurface) and supplying them with necessary macronutrients (enhanced natural attenuation). The suggested treatment train line up – with the electro-dialysis desalination unit at the first stage, followed by ISCO remediation unit at the second stage, and ending with a bioremediation unit for clean-up finish at the third stage – offers a good potential for obtaining a sufficient amount of low-salinity water necessary for additional testing of bioaugmentation techniques (using the introduced biodegrading microorganisms).

Thus, the combination of above discussed remediation technologies was proposed for further pilot-scale field testing.

LITERATURE

[1] Akbar S.S.S.A.A. (2011) Remediation of Oil Polluted Groundwater Resources of Northern Kuwait: Challenges and Solutions. The 20th Joint GCC-Japan Environment Symposium. Abu Dhabi, UAE.

[2] Hamed M.M. (2004) Screening level modeling of long-term impact of petroleum hydrocarbon contamination on fresh groundwater lenses in the Arabian Gulf Region. Environmental Modeling and Assessment 9: 253–264.

[3] Al-Damkhi, Ali Mohamed, S. A. Abdul-Wahab, and A. S. Al-Nafisi. “On the Need to Reconsider Water Management in Kuwait.” *Clean Technologies and Environmental Policy* 11, no. 4 (December 2009): 379–84. Doi: 10.1007/s10098-009-0201-z.

[4] Al-Sulaimi J., Viswanathan M.N., Székely F. (1993) Effect of oil pollution on fresh groundwater in Kuwait. Environmental Geology 22: 246–256.

[5] Schlösser, U. G. (1982). Sammlung von Algenkulturen. Berichte Der Deutschen Botanischen Gesellschaft, 95(1), 181–276. Doi: 10.1111/j.1438-8677.1982.tb02862.x

[6] Tate, RL., III. (2000) Soil Microbiology, 2nd Edition. New York: Wiley, pp. 536. ISBN: 978-0-471-3179.

CASE HYSTORIES OF CONTAMINATED SITES REMEDIATION AND SEDIMENT MANAGEMENT IN ITALY: TECHNOLOGY AND RESULTS

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KEYWORDS

Contaminated sites, Directional Drilling, Plastic Cut-off Walls, Permeable Reactive Barriers, Sediment Washing, Reuse, Recycle

INTRODUCTION

Trevi Group has been working on natural heritage protection for more than 20 years, devoting its efforts to the study, research and application of many types of technology. Examples of dramatic events draw more and more attention to the issue of urban and industrial waste, which is the main cause of pollution affecting watercourses and surrounding lands. Trevi Group has been coping with may different problems for years and has been gaining wide experience in groundwater, waste, radiaoctive waste and sediment-related contamination assessment and management. This essay illustrates 4 different cases and the types of technology employed.

CASE 1 – GROUNDWATER REMEDIATION FROM CHLORINATED COMPOUNDS – NORTHERN ITALY

The landfill, authorized in 1991 as a disposal area for foundry slag, is located in the Dora Riparia Valley, about 10 km west of Torino. Water monitoring tests carried out by ARPA (regional environmental protection agency) on August 1999 detected contamination of the shallow groundwater, caused by the presence of chlorinated solvents, and specifically of trichloroethylene. A permeable reactive barrier (PRB) was installed in order to treat the chlorinated compounds without interfering with the groundwater flow down to the river.

The permeable reactive barrier, made up of zerovalent iron, was installed between the landfill and the river, with an alignment parallel to the riverbed, a few meters from the bank. It has a surface of 1520 m^2, a linear extension of 120 m, an average depth of 13 m and a thickness of 60 cm.

The trench was excavated within a sandy-gravelly soil, turning to silty-sand deep down, and embedded 1.0 m in the bottom clay. 1700 tons of zerovalent iron were cast into the trench; the iron was composed of grain-sized particles, measuring 0.2 - 3 mm, utterly free from oil or other impurities.

Inside the barrier, five piezometers were installed to monitor the chemical and physical groundwater parameters and to evaluate the evolution of the barrier performance through the years.

The principle of the Permeable Reactive Barriers is the interception of the contaminated water flow with a material capable of removing, through chemical reactions, precipitation or absorption procedures, the contaminants released into the water, to prevent them from further spreading. The continuous permeable reactive barrier intercepts the groundwater flow without significantly altering the local hydrological regime. This system is capable of avoiding contaminants‘ migration beyond the barrier and it also allows aquifer’s reclamation over time. The flow geometry, location and development were studied and defined by a numerical model, to define location and extension of the permeable barrier for the site reclamation (di Molfetta 2005).

The trench is excavated by means of a rope-suspended grab, operated by a suitable crawler crane. The reactive material is cast in panels with variable depth and length, depending on construction design. During casting activities, each panel is enclosed at both ends by TSP (Temporary Separation Pipes), characterized by a shape apt to separate the cast iron from the adjacent excavation. The upper part of the barrier is filled with sand, or other inert material, and capped at the top with clay.

Upon completion of casting works, degradation of the polymeric mud still present in the trench was accelerated by circulating specific enzymes through pipes purposely installed in said trench.

Upon completion of all the works, , three clay-strata were placed on top of the barrier and in the adjacent area by rolling, to create a protective capping.

The project, completed in November 2004, is the first case of permeable reactive barrier with zerovalent iron in Italy.

Fig. 1 PRB construction

Fig. 2 ZVI poured into the excavation

CASE 2 – REMEDITION OF FORMER LANDFILLS IN MANFREDONIA – SOUTHERN ITALY

The landfills are located in an area characterized by high biodiversity and by numerous gorges (small canyons) of erosive origin, creating a highly naturalistic rocky environment. The collected data show a 25 – 40m layer of soft rock in the form of calcarenite. The primary permeability (through interstitial porosity) of calcarenites is very low - k = 10 – 8 cm/sec. However, and most likely due to tectonic events or other geomechanical actions, the calcarenites have macro-fissures – whose the distribution can be hardly reconstructed – that create a high (local) increase in conductivity, depending on the quantity and type of fissures (detected during the test). Calcarenites lie over a formation of whitish or pink limestone (calcilutites), well-stratified and highly fissured; fissures are often widened by karst dissolution having higher mechanical features. The permeability degree of said limestone ranges from high to very high and and can be classified as secondary type permeability – only due to fissures and karst phenomena.

The screen was specially sized to match the contour of the landfill bottom and to be placed at a 2.5 – 3 m distance from the waste bottom, seamlessly joined end-to-end to the perimetral barrier. The rock was treated along a thickness of 3 m,

The construction of the screen through traditional techniques would have required thousands of vertical drillings crossing the waste to reach the rock layers to be injected. However, this solution was considered too expensive, time-consuming and environmentally risky. As a result, an innovative solution was put forward, inspired by the recent introduction in the geo-engineering sector of the Horizontal Directional Drilling (HDD) techniques, which are widely used in the oil industry and for the installation of underground utility services. The aforementioned techniques (renamed TDDT: Trevi Directional Drilling Technology), properly modified and integrated, make it possible to drill sub-horizontal curvilinear boreholes of increased length (in this case, up to 180m).

In this specific case, the horizontal directional drillings were performed from one of the sides of the landfill and under it as well, in order to fully cross it from underneath, while simultaneously intersecting the two sides of the vertical perimetral screen.

Project specifications required a drilling directional accuracy of 30 cm. Steel sleeve port pipes were placed inside the boreholes for cement and silicate mix grouting.

The same solution was adopted for the perimetral barrier. In this case, straight boreholes were drilled in two rows, tilted 15 degrees (in the opposite direction for each row) with respect to the vertical axis, in order to cross all the fissures when drilling and grouting the cement mix. A third central row of vertical boreholes, grouted with long-lasting silicate grouts, was drilled to complete the intervention. In the event of loss of circulation (which is very common in primary boreholes), a special technique named "down-stage" was implemented: drilling is interrupted, special expanding cement mixes are grouted, then drilling is resumed (after re-drilling the grouted portion). The use of expanding grouts allowed us to perform grouting in the specific area only, thus minimizing absorptions, times and costs. The preliminary grouting was performed as described above; for the following ones we used the so called "MPSP" (multiple-packer sleeved pipe system). With this technique, grouting is performed by using specific pipes fitted with ports and collars slipped around them. Once the collars are inflated, the hole is divided into sectors that can be grouted separately according to the pressures set by the project. To carry out the HDD, a specific technique was chosen; said technique allows to detect drilling progression by measuring the artificial magnetic fields previously created in the site, using special sensors assembled onto the drilling string. Data are real-time collected; they are processed by a software and compared with the pre-calculated ones concerning the theoretical drilling progression. If deviation tolerance is exceeded, special eccentric tools are used to correct drilling progression and bring it back to the envisaged deviation range.

Fig. 3 Remediation sketch

Fig. 4 automatic grouting plant

CASE 3 – INCAPSULATION OF CONTAMINATED SOIL UNDER LEAKING TANKS – NORTH ITALY

The plant is located inside a petrochemical multi-company site, in an industrial area of about 270 hectares, 4.5 kilometers away from the city center of Ravenna. The surrounding territory, in particular the coast and the first part of the outback, is characterized by the presence of many wetland areas and pine forests with natural peculiarities. The planned remediation and permanent securing works involved the southern zone, the so called Island 28.

The intervention mainly consisted in the construction of a diaphragm wall around the area occupied by the containment basin of 4 tanks filled with MtBE (metil-t-butil-etere, a chemical compound used as antiknock instead of other additives based on lead) and methanol. Works included removal of the residual contaminated soil through excavation up to a depth of 3 meters. This barrier – whose total length was 460 meters – was executed with a plastic diaphragm wall with a HDPE layer along 445 meters and, for the remaining 15 meters, through jet grouting column treatments.

The vertical barrier was rmbedded 3 meters down into the clayey layer located at about 30 meters from ground level.

The following techniques were used for the project:

- Continuous 80 cm thick slurry wall made by pre-mixed sel hardening grout and HDPE layer at a maximum depth of 32 meters. (Execution of 13.350 m^2)
- Plastic cut-off wall with secant jet grouting columns with a diameter of 1000 mm. The jet grouting section has a length of approximately 420 – 450 m with a minimum thickness of 4.6 m.
- Site covering through capping complying wih the D.L. 36/2003, made up of different layers (Regularization layer, thickness greater than 5 cm; HDPE layer, thickness 1 mm; Bentonite geocomposites; Protection geotextiles; Reinforced concrete layer, thickness 15 – 30 cm).

Fig. 5 Slurry wall excavation

Fig. 6 HFPE liner placing drum

CASE 4 – TREATMENT OF CONTAMINATED SEDIMENT AND SUCCESSFUL REUSE OF THE SANDY PART – SOUTHERN ITALY

At the end of the 80s Palermo Port Authority started works to construct the 150.000 DWT Dry Dock, within Palermo Industrial Port. Works were stopped due to a dispute arisen with the Subcontactor. Up to now, the following works – which are included in the original project – were carried out.

At the beginning of the 2000s Palermo Port Authority, after terminating the Contract, started to plan the completion works. In order to assess the state of works already carried out, it was necessary to perform consolidation and static safety works before emptying the dock basin.

Works specified in the Contract included dredging of approximately 76.000 m^3 of sediments and waste, for a total of about 117.000 tons of mainly sandy material, contaminated by hydrocarbons C>12, heavy metals and mixed waste, mostly conveyed by 2 sewage pipes (about 500.000 AE) which, until 2014, would discharge next to the Dock. Trevi Spa, after being awarded the Contract, drew up the executive design required to perform works, proposing a washing treatment of the waste to be dredged known as Sediment Washing.

Trevi Plant is made up of five technological units which were specifically devised to carry out the whole waste management process. The plant has a variable output, mainly according to the granulometric features of the waste to be treated, especially in terms of fine fraction percentages ($\Phi < 0.063$ mm). In fact, these fine fractions are separated from the turbid suspension, dehydrated by means of filter presses or centrifuges, which are devices whose productivity/costs ratio is very low. The largest granulometric sections are separated by means of screens and cyclones, which are highly productive. In this specific case, the features of sediments to be treated allow a maximum productivity equal to 60 tons/hour.

The objective of the Sediment Washing treatment is the recycling of materials and subsequent reduction of waste to be disposed of. This technology, if properly applied, always reduces the amount of waste to be recycled/disposed of in external plants; for that reason it can be considered environmentally sustainable and developed in compliance with waste management regulations (Art. 179 of D.Lgs. 152/2006). The plant is recovering material - R5 “Recycling/recovery of other inorganic substances” – from the waste’s sandy and gravelly fraction ($\Phi > 0.063$ mm), according to previously designed specific purposes.

After undergoing a compliance audit at the jobsite, the sand achieves CE certification as recycled aggregate satisfying the technical requirements for the specific purposes, regulations and existing standards applied to products. The separated and densified fine fraction and the other waste are recycled or disposed of in specifically authorized external plants, while waste slurry is cleaned up in a specific section of the Sediment Washing plant and is eventually discharged into surface waters (according to Tab.3 Part 3, Attachment 5 of D.Lgs. 152/2006).

Once the works were finished, approximately 111.000 tons of waste were treated, recovering 41.400 tons of sand, 15.200 tons of gravel, while 25.400 tons of contaminated fine fraction were disposed of in an external plant.

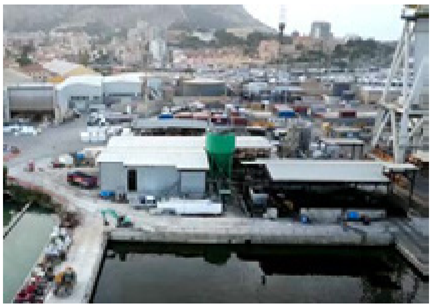

Fig. 7 Aerial view of the job site

Fig. 8 CE certified clean sand ready to be recycled

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ARSENIC MINING POLLUTION IN GEORGIA: REMEDIATION APPROACHES

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KEYWORDS
arsenic, pollutions, remediation, extraction.

ABOUT ARSENIC

Arsenic is the main constituent of more than 200 mineral species, of which about 60 % are arsenate, 20% sulfide and sulfosalts and the remaining 20 % include arsenides, arsenites, oxides and elemental arsenic. The most common of the arsenic minerals is arsenopyrite, FeAsS. Moreover arsenic is found associated with many types of mineral deposits, especially those including sulfide mineralization. The ability of arsenic to bind to sulfur ligands means that it tends to be found associated with sulfide-bearing mineral deposits, either as separate As minerals or as a trace of a minor constituent of the other sulfide minerals. This leads to elevated levels in soils in many mineralized areas where the concentrations of associated arsenic can range from a few milligrams to > 100 mg/kg. [1]

THE OCCURRENCE OF AS MINERAL DEPOSITS IN GEORGIA

Gold-arsenic, arsenic and gold-antimony deposits in Georgia are of significant economic importance.
ReaIgar As_4S_4-Orpiment As_4S_6(Lukhuni, Racha) and Arsenopyrite FeAsS (Tsana and Chorokhi, Svanety) ores of Georgia are unique in the world. The arsenic content in these ores is particularly high and reaches an average of 12%. Besides, it is very important that these arsenic ores (ReaIgar As_4S_4-Orpiment As_4S_6(Lukhuni, Racha)) do not contain impurity elements[2]. This gives the best chance to produce not only highly pure metal arsenic, but also other arsenic containing products.
Until the 1990's high purity arsenic for semiconductor systems and 16 other arsenic containing compounds were produced in the Racha (vil. Uravi) and Svaneti (vil.Tsana) regions of Georgia. The purification process involved the burning of arsenic concentrates in special furnaces, the emissions from which contained high concentrations of arsenic oxides, so called "white arsenic". These emissions impacted and area of more than 20 km around those furnaces causing significant environmental damage. These facilities have now ceased operation, however recent scientific studies found the content of arsenic in the soils around the factory were 20 to 30 times those of background levels (State of Environment report of Georgia Republic). For getting arsenic and its compounds from ores, first of all the concentrate was burned in special furnace which did not prevent pollution of environment with sulfur dioxide, and arsenic compounds. After pyrometallurgical processing , arsenic comes out of the technological scheme in the form of white arsenic and is present in industrial residuals. Elemental arsenic is produced by reduction of arsenic trioxide (As_2O_3). As_2O_3 is produced as a by-product of metal smelting operations.The content of arsenic in tailings varies between 8 % and 60 %. At the same time, they contain commercially important quantities of the precious metals gold, silver. (Gold extraction from pyrometallurgical residuals can by suggested later). During the Soviet era, when the industrial sector operated at full capacity, the mining industry and the production of metal arsenic were the most significant waste generating sectors. One of these sites located in Racha & Svaneti is of significant concern, as it contains more than hundred thousand tons of arsenic containing waste. It is estimated that more than 100 000 tons of this hazardous arsenic containing waste are stored in the Ambrolauri districts and also, some of tailings are in the open ground in the Lentekhi. (*In addition to latter we should mention that during Soviet period containments have been constructed in the villages of Uravi and Tsana, and directly at sites of the mines. There were buried not only residues of local Arsenic, but also some unknown materials were imported from Russia and buried. These containments are in a poor condition and are highly threaten to human health and the environment.)* The mining of arsenic deposits have temporarily ceased, though the license for arsenic extraction at the Lukhuni deposit was issued for 25 years and allows for the extraction of 9, 534 tons of arsenic. There are still quite large quantities of industrial wastes remaining at the sites.

POTENTIAL ENVIRONMENTAL POLLUTION BY ARSENIC IN GEORGIA

Mining, smelting of non-ferrous metals and burning of fossil fuels are the major industrial processes that contribute to anthropogenic arsenic contamination of air, water and soils in Racha and Svaneti (Georgia) high mountain mining region.
Arsenic enters the environment naturally through

- mineral ore
- ground water
- geothermal processes

In nature, arsenic-bearing minerals undergo oxidation and release arsenic into ground water. This could be one explanation for the problems of arsenic in the groundwater of Racha and Svaneti mining region in Georgia. Burial of the sediment, rich in ferric oxyhydroxide and organic matter, has led to the strongly reducing groundwater conditions.
Many thermal springs in the Racha and Svaneti high mountain mining regions are naturally rich with high levels of arsenic (not studied yet) .

DOES DRINKING WATER IN SVANETI AND RACHA REGIONS CONTAIN ARSENIC?

Arsenic contained in the groundwaters of Georgia high mountain region (Racha and Svaneti) is believed has been released during wreathing and is naturally absorbed onto new forming of iron oxyhydroxides. In Racha and Svaneti region arsenic is released into the atmosphere primarily as As_2O_3, As_2S_2, As_2S_3 or, less frequently, as one of several volatile organic compounds. Risk of fatal arsenic poisonings in this regions is quite real.
The drinking water in these areas, however, has not been tested for arsenic. Although detailed studies are not yet available for all regions, we can assume that risks related to arsenic comes primarily from the consumption of drinking water with elevated arsenic concentration. Arsenic in soil and dust may be a significant source of arsenic intake by children, particularly in locations near industrial and hazardous waste sites. The area in which waste from the mining process was stored (the tailing ponds) is heavily contaminated not only wastes including arsenic, but also with metal copper, zinc, iron sulphates. The risk of arsenic exposure to populations living in or near arsenic-contaminated environments is always high. In particular, contamination of home-grown vegetables and reared livestock, or wild collected foods must be considered. In the absence of substantial remediation measures this area cannot be used for agricultural or other purposes, and will remain a contaminated site.
Set of works conducted (research officers of Caucasian Alexander Tvalchrelidze Institute of Mineral Resources) during 2008-2010 clearly showed that content of toxic elements like Arsenic, Manganese and Cadmium in Rioni river waters and bottom sediments largely exceeds maximum permissible concentrations, which can be explained by existence of such polluting objects as Arsenic (Tsana, Lukhuni), Manganese (Chiatura), coal (Tkibuli) mines, Zestaponi Ferro Alloys Plant and other smaller industrial enterprises. For example, in several water samples in the Rioni River and its sediments, near the city of Poti, the total amount of Arsenic is about 25,6mg/kg, when permissible rate should be equal to 2,9mg/kg . On similar abnormal contents of arsenic in soils and sediments is confirmed by other researchers of the region
Polluting of Rioni River with residues of Tsana and Lukhuni Arsenic mines currently is one of the key environmental problems for Georgia.
Arsenic containing waste has already caused a serious ecological problem to the unique biodiversity of Caucasian flora and fauna as well as human health. Several illness and poisoning have been cause by tailings of residues from the mineral processing plants. Increased levels of cancers have been observed among people and domestic animals in the surrounding areas. Residents of Racha have expressed the opinion that this pollution of the river Madnis-Gele (river Lukhuni) valley has resulted in a dramatic decline in the number of bees and swallows in the region. Wastes are not properly fenced and protected, allowing farm animals such as cattle and sheep to have free access to the landfills. Animals grazing there are poisoned and may die. This Georgian ecological problem affects not only highly sensitive Caucasian regions. It poses also a serious pollution problem to the Black Sea. The major inputs to the marine environment are river runoff and atmospheric deposition. Biological uptake caused changes in arsenic speciation resulting in measurable concentrations of reduced and methylated arsenic species. The overall cycle is similar to the phosphate cycle, but the regeneration time for arsenic is much slower.

REMEDIATION TECHNOLOGIES

will be proposed aiming at minimization of risk at waste disposal sites. Several approaches will be considered:

1. Removal of Arsenic from water
2. Removal of Arsenic from soils
3. Processing of waste for recovery of Arsenic

Several approaches can be proposed:

- Treatment of soils and industrial wastes with aluminosilicate bacteria
- Oxidation using bacteria and lightening of the existing arsenic compounds in the waste
- planting can extract and accumulate arsenic in the contaminated territory around the cottage
- Planting plants that can extract and accumulate arsenic

- extraction and storage of arsenic compounds from lightening solutions and from planted green masses
- treatment of arsenic waste with iron salts and their burial in a concrete waste storage

There are in Georgia opportunities to remove arsenic from industrial waste. Mainly there is possibility of hydrochemical or microbiological extraction of arsenic compounds (Oxide, sulphide) from realgarr (As_4S_4)-or-piment(As_4S_6) and arsenopyrite FeAsS ores of Georgia and from the residuals of pyrometallurgical processing (1. M. Gakhutishvili The best is recycling efforts. IncoNet EECA FP7 Information and Brokerage Event, October 7 – 8, 2010, Yerevan, Armenia 2. R. Gigauri Investigation of Arsenic-contained Industrial Wsate of Mining Factory in Racha (Georgia) Georgian Chemical Journal, 6 (6), 599 – 604 2006). The utilization of arsenic containing waste materials and leftovers is very important from the economical and ecological point of view. To avoid environment pollution, residuals are buried in a special burial ground (sepulchers) that is associated with material and financial expenses. The best are efforts in recycling in order to produce relatively cheap but important materials with specific properties. In this purpose Research Team from Ivane Javakhishvili Tbilisi State University (Georgia) offers to industry the methods of possibilities of rational use of mineral resources and industrial waste productions[3]. Industrial wastes of arsenic containing ores and pyrometallurgical waste of non-ferrous and noble metals can be hydrochemically extracted by an sodium or potassium alkaline and alkaline sulfide solution; or isolated using highest alcohols ($R \geq Bu$) Or can be remediate by the method of microbiological extraction.[4-6] The heterotrophic *Thiobacillus ferrooxidans* strain has been used for the purpose[7]. The proposed method makes production lest costly and concurrently waste-free and safe. Its introduction will greatly contribute to the solving of environmental problems both domestically and globally. It is very important, that the residue remained after filtering does not contain the amount of arsenic which can be dangerous for the environment. Even it's keeping on the open ground is possible from the ecological point of view (M. Gakhutishvili and R. Gigauri Arsenic Removals. International Conference and Exhibition, Batumi-Spring-2010. Batumi, Georgia). The obtained extract is the best isolated substance to produce not only high purity arsenic for semiconductor systems, but also other products. Based on arsenic compounds obtained by transformation of arsenic industrial waste [arsenic(III) oxide, arsenic(III) chlorides, alkoxides] Our Research group from Ivane Javakhishvili Tbilisi State University have synthesized and studied new cationic-anionic complexes and chelates [8 – 11].

REFERENCES

1. S. C. Grund, K. Hanuscha, H U. Wolfe Arsenic and Arsenic Compounds, in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH, 2012. V.4 200 – 239.
2. Gakhutishvili , A. Khidesheli, R. Gigauri Realgar-Auripigment Mass Ratio in Lukhuni Mine and Racha Mountain Chemical Plant Waste.Georgia Chemical Journal, 2001, N 1. v.1. p. 94 – 96.
3. M. Gakhutishvili, R. Gigauri, E. Vachnadze, O. Chikovani Arsenic Eduction from Realgar- Auripigment Ores of Racha (Georgia). Georgian Engineering News, 2000. N 2. p. 174 – 176.
4. W. Brostow, M. Gahutishvili, R. Gigauri, H. E. Hagg Lobland, S. Japaridze, N. Lekishvili Separation of natural trivalent oxides of arsenic and antimony. Chemical Engineering Journal, 2010, N 159, p. 24 – 26. US.
5. M. Gakhutishvili Arsenic Utilizing ProductionWaste. Foundation For Development of Sciences and Society. Periodical scientific Journal Intelecti, 2000, N 17. p. 23 – 24.
6. M. Gakhutishvili, R. Gigauri Extraction of Arsenic from Mineral Resources and Industrial Waste. Georgia Chemical Journal, 2010, N 4, 10. p. 53 – 54.
7. R. Gigauri, M. Gakhutishvili, I. Chelidze, A. Chirkadze, L. Sakhvadze, Z. BuaCidze, R. Sakhvadze Bacterial-Chemical Leaching of Arsenic From Arsenic Containing Waster And A Novel Technology of High-Purity Metallic arsenic Production. St.Andrew the First-called Georgian University of the Patriarchate of Georgia.
Nano chemistry and Nanotechnologies, Proceedings of Papers of the First International Conference, March 23-24 2010, Tbilisi, Georgia. Publishing House "Universal", 2011.
8. M. Gakhutishvili, R. Gigauri, Z. Machaidze, G. Koranashvili, M. Kokhreidze Synthesis and Investigation of Ammine Complexes of d-Metal 's dithioarsenates. Bulletin of the Georgian Academy of Sciences, 2001, N 1. 164. p. 42 – 59.
9. M. Gakhutishvili, R. Gigauri Coordination Compounds of d- metals(III) dithioarsenates witth Acetilphenylhydrazine. Georgian Engineering News, 2001, N 1. p. 138 – 140.
10. R Gigauri, M Gakhutishvili, K. Giorgadze, Z. Machaidze A Method of Sodium Dithioarsenate(V) Production from Hydrometaiiurgical Industrial Wastes of Non-ferrous and Noble Metals. Proceeding of the Georgian Academy of Sciences, 2004, v.30. N 3-4. p. 205 – 206.
11. W. Brostow, S. Brumbley, M. Gahutishvilia, N. Hnatchuk Arsenic Antibacterial Polymer Composites Based on Poly(Vinyl Chloride). Macromolecular Symposia Volume 365, Issue 1, 2016 . p. 258 – 262.

POSIDON – POLLUTED SITE DECONTAMINATION – PRECOMMERCIAL PROCUREMENT

SOIL DECONTAMINATION: DEMAND SIDE POLICY OF THE EUROPEAN COMMISSION TO CREATE NEW MARKETS FOR INNOVATION

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KEYWORDS

Precommercial procurement, contaminant, contaminated sites, groundwater, remediation, soil decontamination, solution design, prototyping, developing and testing of prototypes

ABSTRACT

POSIDON gathers 5 European procurers facing similar problems in the sites they manage, affected by analogous pollutants (2 front-runners-Trieste, IT and Bilbao, ES – and 3 observers - Spaque, BE; Vitoria Gasteiz, ES; Baja do Tejo, PT), leveraging public demand to identify fit-for-purpose and cost-effective innovative and sustainable solutions to soil contamination. The common challenge faced by the buyers' group is identifying a new, life-cycle cost-effective technology for soil and groundwater remediation, capable of decontaminating heterogeneous anthropic soils in brownfields with a mixture of industrial waste, filling soils polluted by petroleum hydrocarbons) and soils consisting of clays and sands of marine origin, highly polluted by petroleum hydrocarbons (TPHs and PAHs) and heavy metals. Studies on the state of the art, patent analysis, foresight scanning and early market engagement meetings, show that no available technology can meet all identified needs, thus appropriate remediation technologies cannot be acquired through traditional off-the-shelf procurement.With PCP, procurers aim to achieve ambitious improvements in terms of quality and effectiveness, efficiency and sustainability of new technology to bring to the market. R&D will be split into three phases: solution design, prototyping, original development and testing of 2 prototypes. Evaluations after each phase progressively identify solutions offering the best value for money. This phased approach allows successful contractors to improve their offers for the next phase based on feedback from procurers. POSIDON intends to create a critical mass through the consolidation of a pan-European network of procurers who, sharing their needs and efforts, can enable the development – through PCP – and subsequent deployment – through a PPI – of novel technologies aimed to cover bigger market challenges in areas of common European interest.

PROJECT

"POSIDON PCP – POlluted SIte DecontaminatiON" is a pre-commercial public procurement action that has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement N. 776838.

Member states are making effort to establish national decontamination/remediation strategies, which are generally very costly. The POSIDON PCP project's aim is to address the lack of innovation driven public demand in the soil decontamination sector in Europe, investing in research and development.

The POSIDON project originates from and capitalizes upon the results of the EU funded CSA BRODISE, completed on 30 September 2016 and launched by Bilbao, with the participation of EZIT (later replaced by Regione Friuli Venezia Giulia) and Seixal.

The BRODISE project was characterized by pragmatism, having assessed and confirmed the effective commonality of the innovation needs of the three sites involved in three countries, and ambition, having promoted the widening of the buyers' group. Such widening was substantiated in a call for interest to report sites with very similar characteristics, in order to share a concrete R&D path. Several players participated and expressed interest in different subjects, even without naming their own sites. All soil owners having a site with similar characteristics to the three initial procurers and interested to benefit from the R&D results to eventually restructure and restate their investment plan for the decontamination of soils, have been involved in POSIDON, overcoming considerable resistance to PCP.

POSIDON PCP gathers 5 European procurers facing a common challenge in the sites they manage, affected by analogous pollutants – 2 front runners: Port Network Authority of the Eastern Adriatic Sea Port Of Trieste (IT) and Bilbao City Council (ES) and 3 observers: Spaque (BE), CEA – Vitoria Gasteiz City Council (ES), Baja do Tejo (PT) – leveraging public demand to identify fit-for-purpose and cost- effective innovative and sustainable solutions to soil decontamination.

The common need identified by the buyers' group concerns new, life-cycle, cost-effective technology solutions for soil and groundwater remediation, capable of decontaminating heterogeneous anthropic soils in brownfields with a mixture of industrial waste (like filling soils polluted by petroleum hydrocarbons) and soils consisting of clays and sands, highly polluted by petroleum hydrocarbons (TPHs and PAHs) and heavy metals

The POSIDON project ultimate goal is establishing an enlarged buyers group with critical mass able to trigger industry to scale up its production chain for bringing products on the market with desired quality / price ratio by a specific time.

After the end of the POSIDON project, results evaluation and preparation of the followup PPI will continue, in a demonstration of enduring, founded and concrete ambition of our procurers.

Studies on the state of the art, patent analysis, foresight scanning, will be complemented with additional open market consultations in the upcoming months (June-September 2018), to have a confirmation that no available technologies can meet all identified functional requirements, thus appropriate remediation technologies cannot be acquired through traditional off-the-shelf procurement.

The technologies that will be selected as remedial solutions, will be applicable on each specific brownfield (Trieste, Bilbao, Lisbon/Seixal, Vitoria-Gasteiz and Liege), for a similar performance range. High cost effectiveness, short time performance and green sustainable guidelines will be crucial for the technology selection. The application of such innovative solutions is expected to contribute significantly to leverage this case study on brownfields redevelopment, and, in addition, to be successfully applicable in similar brownfields across EU.

With PCP (pre-commercial public procurement which is a competitive multiple-sourcing procedure for procuring applied research and technological development services), procurers aim to achieve ambitious improvements in terms of quality and effectiveness, efficiency and sustainability of new technologies, creating new markets. It involves different suppliers competing in parallel through three different phases of development: solution design, prototyping and original development and testing of 2 prototypes. Each of the 2 solutions to be field-tested will be deployed in two diverse sites (Bilbao and Trieste), with different urbanistic provisions that foresee future land uses.

Evaluations following each phase progressively identify solutions offering the best value for money. This approach allows successful contractors to improve their solutions based on feedback from procurers.
Further info are available in the PIN (Prior Information Notice) published in the Official Journal of the European Union, document number 197574-2018.

POSIDON intends to create a critical mass through the consolidation of a pan-European network of procurers who, sharing their needs and efforts, can enable the development (through PCP) and subsequent deployment (through a Public Procurement of Innovation – PPI) of novel technologies aimed to cover bigger market challenges in areas of common European interest. POSIDON is working for inclusion, in order to prepare for the future cross-joint border PPI for soil decontamination of European brownfields.
Further info available at: http://www.posidonproject.eu/

POSIDON
POLLUTED SITE DECONTAMINATION PCP

EUROPEAN INDUSTRIAL CONTAMINATED BROWNFIELDS: THE PROBLEM

Member states are making effort to establish national decontamination/remediation strategies which are generally very costly. The POSIDON aim is to address the lack of innovation driven public demand in the soil decontamination sector in Europe.

THE CHALLENGE

POSIDON PCP project gathers 5 European procurers, two front-runners: Port Network Authority of the Eastern Adriatic Sea Port Of Trieste (IT) and Bilbao City Council (ES) and three observers: Spaque (BE), CEA - Vitoria Gasteiz City Council (ES), Baja do Tejo (PT), **all facing a common soil decontamination challenge in their managing sites and all leveraging public demand to identify fit-for-purpose and cost - effective innovative and sustainable soil decontamination solutions**.

THE COMMON NEED

identified by the buyers' group concerns a soil (and eventually groundwater) remediation new, life-cycle, cost-effective technology, preferred as in-situ (and eventually on-site), capable of decontaminating the heterogeneous anthropic soil in brownfields, composed of a mixture of various industrial wastes (like filling soils highly polluted by petroleum hydrocarbons and heavy metals) and soils consisting of clay and sand highly polluted by petroleum hydrocarbons (TPHs), PAHs and heavy metals.

PCP - PRE COMMERCIAL PUBLIC PROCUREMENT

is a competitive multiple-sourcing procedure for procuring applied research and technological development services. It involves different suppliers competing in parallel through different phases of development: solution design, prototype development, original development of (at least) 2 prototypes (per each bidder) to be field-tested in 2 diverse sites (Trieste and Bilbao), with different urbanistic provisions that foresee future land uses.

POSIDON PCP AT A GLANCE

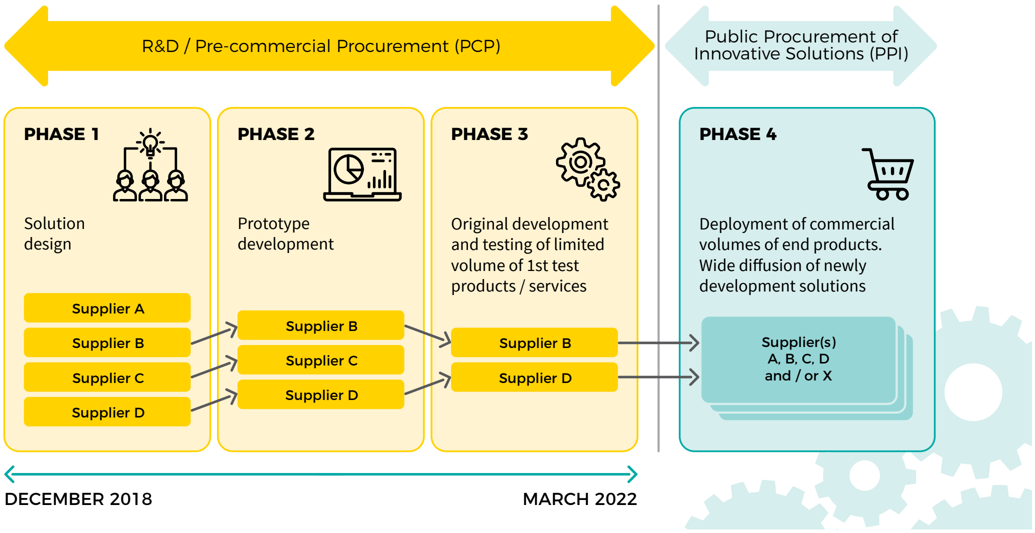

Fig. 1 POSIDON PCP

Fig. 2 POSIDON partners

JOIN POSIDON!

Are you an industry or a research institution operating in soil decontamination?

Preparing the PCP, POSIDON actively approaches the market in order to identify the state of the art and current development in the related sector.

Please fill in the POSIDON questionnaire to express your feedback on the innovation challenge and PCP setup.

The survey is open on the POSIDON website until 30th September 2018.

Are you a procurer interested in POSIDON PCP activities and results?

POSIDON intends to create a critical mass through the consolidation of a pan-European network of procurers who, sharing their needs and efforts, can enable the development (through PCP) and subsequent deployment (through a Public Procurement of Innovation - PPI) of novel technologies aimed to cover bigger market challenges in areas of common European interest. POSIDON is working for inclusion, in order to prepare for the future cross-joint border PPI for soil decontamination of European brownfields.

Please join POSIDON procurer network and take a look at POSIDON call for interest!

Fig. 3 Join POSIDON

LITERATURE

Application form of POSIDON project
Flyer of POSIDON project

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REMEDIATION AND REVITALIZATION OF TRACE METAL CONTAMINATED GARDEN SOILS USING A SUSTAINABLE EDTA WASHING TECHNIQUE

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KEYWORDS
soil washing, contaminated sites, bioavailability, trace metals, soil amendments

ABSTRACT

Soil washing techniques are an efficient and sustainable option to remediate trace metal contaminated soils. Amendments applied after the washing procedure may help to revitalize the treated soil. A pot trial using radish (*Raphanus sativus L.*) was performed under greenhouse conditions to investigate the effects of an EDTA soil washing procedure on plant growth and bioavailability of trace metals (Zn, Cd, Pb and Mn). A Cambisol obtained from Arnoldstein, a former lead mining and smelting region in Carinthia (Austria) was used in combination with organic and inorganic amendments as growth substrate. A water treatment sludge-amendment in combination with biochar significantly decreased the bioavailability of Zn and Mn ($p < 0.05$) in the variants using the natural, unwashed soil. No significant effects on trace metal plant availability were found for the different soil amendments on washed-soil treatments. Further indicators of soil health (biota, nutrient cycle, soil structure) will be investigated in a field trial to examine amendment-effects on the soil revitalization and plant growth.

INTRODUCTION

The increasing world population with its associated industrialization and urbanization are leading towards a shortage of arable land due to the degradation and loss of soil. The introduction of soil conservation agricultural practices to prevent further losses, and the remediation of polluted sites by extracting or stabilizing organic and inorganic pollutants has gathered increasing attention (Adriano et al., 2004; Sharma and Nagpal, 2018). Different in- and ex-situ remediation approaches have been intensively investigated, in combination with complimentary soil amendments (e.g. biosolids, biochar, liming etc.). Among this broad portfolio, the soil washing techniques have the advantage of combining high trace element extraction rates in multi-contaminated soils and short treatment cycles (Voglar and Lestan, 2014). However, the associated side effects of these rather invasive treatments are the destruction of the natural soil structure and the microbial community. The washing procedure may also remove essential plant nutrients (Jelusic et al., 2014).

The “Garden Soil” project seeks to investigate different aspects of a recently developed soil washing procedure, able to extract up to 80, 40 and 70 % of Pb, Cd and Zn respectively, while working in a closed circuit without appreciable losses of both, process water and the chelating agent in use (EDTA) (Voglar and Lestan, 2012). After several successful pot trials, the applicability of the remediated soil for re-use is currently tested in an outdoor experiment, consisting of 12 raised beds (100x50x30cm) containing two trace metal contaminated soils from Austria and Slovenia. The trace metal bioavailability and plant uptake will be monitored over a 2-year period to determine possible trace metal remobilization processes e.g. due to a shift in the concentration equilibrium between the soluble and mineral phase or due to the incomplete complexation of the remaining EDTA (Udovic and Lestan, 2010a). Finally, the processed soil will be treated with soil additives (compost, biochar and mineral additives) to immobilize trace metals and to support soil revitalization (Kaurin et al., 2018). The success of the procedure will be evaluated using microbiological- and molecular techniques and an in-depth investigation of the nutrient cycle using plant material labeled with stable isotopes (^{13}C, ^{15}N).

METHODS

Radish cultivars were selected as indicator species towards their ability to accumulate trace metals in shoots. In a preliminary pot trial, radish plants grown on contaminated soil from Arnoldstein, with expected trace metal concentrations of 913 mg kg^{-1} Pb, 5.6 mg kg^{-1} Cd and 545 mg kg^{-1} Zn (Friesl-Hanl et al., 2009). After 6 weeks the plants were harvested, dried, digested in aqua regia and analyzed using an GF-AAS. The “Topsi” radish cultivar showed the highest uptake of trace metals into the aerial plant tissue, while “F. Breakfast” plants had the lowest concentration (Figure 1). To monitor the effect of soil amendments on the metal bioavailability, the Topsi cultivar was used in the pot trial with the different substrate variants, assuming the higher up-take response of this cultivar. Furthermore, the F. Breakfast cultivar was implemented to investigate possible differences among radish varieties. This pot trial was set up using EDTA-washed and natural Cambisol from Arnoldstein. The experiment aimed to select appropriate soil amendments among several compost (5 and 10 % (w/w)) and biochar variants (3 % (w/w)), as well as iron and manganese-rich mineral amendments (1 % (w/w)); tested in combined and single treatments. The experiment was set up in a fully randomized block design (n=5) under greenhouse conditions. After six weeks, the aerial tissue was harvested, dried at 40 °C and subsequently weighted. The dried plant material was milled, digested and analyzed for trace element concentrations (Zn, Mn) using an ICP-OES, except for Cd and Pb which were analyzed by GF-AAS and are always given as concentration per dry mass (DM). Due to inhomogeneous variances a logarithmic data transformation was performed. Welch's t-test was used to examine differences between the variants using washed and unwashed soil and to identify differences between the amendments, the non-parametric Kruskal Wallis test and the Scheffe post-hoc test were applied. The statistical analysis was done using SPSS v.23.0 (IBM, Armonk, NY).

RESULTS & DISCUSSION

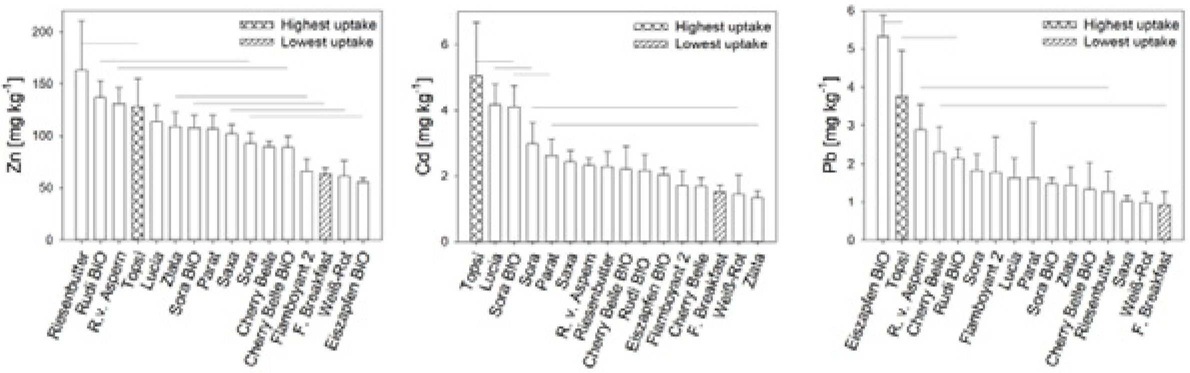


Fig. 1 The trace metal uptake of 16 radish cultivars (n = 5) were ranked with respect to the concentration their aerial tissue. The cultivar with the highest and lowest position in a cumulated ranking ("Topsi" and "F. Breakfast") were used for further investigation. The lines over the Boxplots indicate homogeneous subsets and are significantly different (p < 0.05). The arrow bars represent the standard deviation.

Figure 1 shows the result of the cultivar-selection trial and indicates the plants with the highest and lowest trace metal accumulation. To select these two, the cultivars were given ranks from 1 to 16, according to their mean concentration of Zn, Cd and Pb in their aerial tissue. The two cultivars selected for the pot trial, Topsi and F. Breakfast, had the highest and lowest accumulated rank.

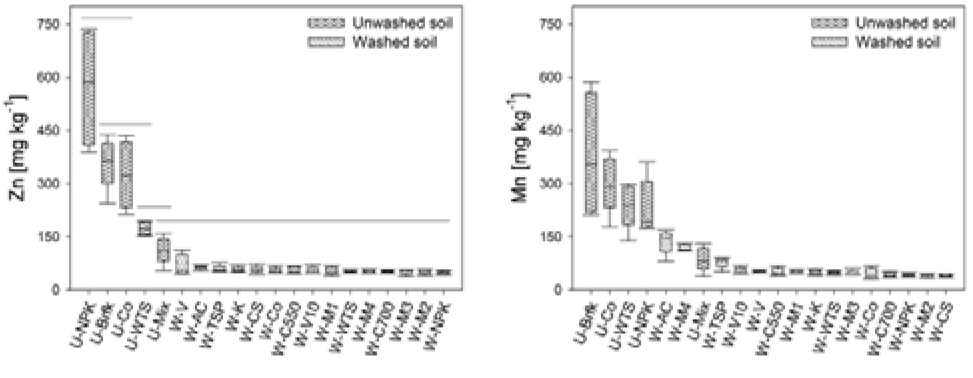
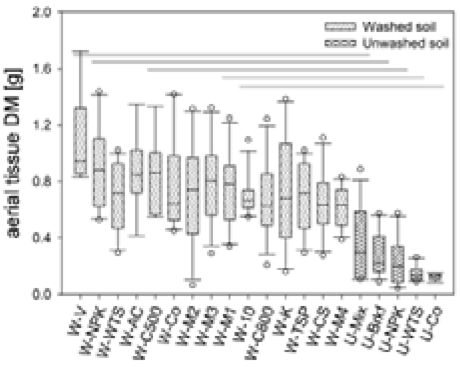


Fig. 2 Zn and Mn concentrations in the aerial tissue of "Topsi" radish plants (n = 5) were investigated on different soil treatments. *U* = unwashed; *W* = washed; *Co* = control; *NPK*= fertilized; *Brfk* = F. Breakfast cultivar; *WTS* = water treatment sludge; *V* = vermicompost; *V10* = 10 % (w/w) V; *K* = compost; *CS* = straw-biochar 600 °C; *C550* = miscanthus-biochar 550 °C; *C700* = miscanthus-biochar 700 °C; *Mix/M1* = V + CS; *M2* = V + CS + WTS; *M3* = V + WTS; *M4* = V + FeO + MnO. The lines over the Boxplots indicate homogeneous subsets and are significantly different (p < 0.05).

The measured trace metal concentration in plants grown on substrate using unwashed soil (U), ranged between 100 and 600 mg kg^{-1} (Figure 2), only the water treatment sludge-biochar-mix (U-Mix) showed a significant decrease in both, Zn and Mn ($p < 0.05$). The single use of water treatment sludge (U-WTS) only lead to a decrease in Zn ($p < 0.05$). While Zn and Mn are essential for human and plant nutrition, they can exert toxic effects on spinach at concentrations over 100 mg kg^{-1} DM in the aerial tissue and should not exceed 75 (Zn) or 50 (Mn) mg kg^{-1} DM in leaf vegetables if meant for human consumption (Adriano, 2001). In almost all replicates of the U-variants these values were exceeded, and the toxic effects most likely contributed to the significant reduction in plant DM ($p < 0.05$) (Figure 3). The EDTA-washing procedure significantly reduced the trace metal availability to the radish plants in the washed control (W-Co) by 269 mg kg^{-1} Zn and 253 mg kg^{-1} Mn compared to unwashed control (U-Co). The substrate mixture using activated carbon (W-AC) and the vermicompost-FeO/MnO variant (W-M4), showed a slight increase in Mn concentration compared to some of the other variants, but overall the soil amendments showed no significant effect on the Zn/Mn uptake by the radish plants. The concentrations in W-variants ranged from 30 to 80 mg kg^{-1} (Zn, Mn), values reported to be sufficient in supplying the plants demand and match the recommendations for human nutrition (Adriano, 2001). However, a replenishment of easily available trace metals could still be triggered by nutrient deficiency and potentially increased root exudation (Udovic and Lestan, 2010b). The soil amendments have the potential to stabilize the trace metals on a longer time scale and this effect will therefore be further investigated in a long-term trial.



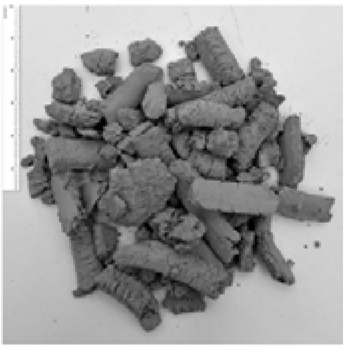


Fig. 3 (left) The DM of the harvested radish plants are presented as boxplots of the single variants. For abbreviations see figure 2. The lines over the boxplots indicate homogeneous subsets and are significantly different ($p < 0.05$). Fig. 4 (right) Resulting from the post treatment of the washing procedure, the soil gains the structure of small pellets up to 3 cm long.

The use of washed soil for the substrate mixtures lead to a significant increase in plant DM ($p < 0.05$), even though plants showed a high variance. Within the treatments which only used the washed and unwashed soil, no significant difference was found ($p \geq 0.05$). However, plants growing on the vermicompost variant (W-V) showed a significantly higher plant DM ($p < 0.05$) compared to most of the unwashed treatments (except U-Mix) and tended to have the highest yield among all W-variants. The almost non-detectable influence of the different soil mixtures on plant growth might have been caused by the physical properties of the washed soil. The favorable properties of the soil amendments could have been compounded by the structural changes caused by the post treatment after the washing procedure, were the soil sludge is pressed through a sieve and cut into small pellet-like pieces (Figure 4). This positive property was already observed during the germination stage, were radish plants grown in the variants including washed soil showed faster development. The positive effect of the physical properties and/or lower trace metal concentrations apparently exceeded the expected loss of plant nutrients due to the EDTA washing (Jelusic et al., 2014).

CONCLUSION

In two plant trials it was possible to show the reduction in trace metal accumulation, satisfying nutrition recommendations. The reduction was achieved by cultivar selection and EDTA soil washing. When all remaining contaminants (Cd, Pb) have been evaluated, two soil amendments will be selected for the field trial. Currently the vermicompost-variants show the most promising results and a promising potential to revitalize the washed soils. Furthermore, the structure of the washed soil and further soil quality indicators (e.g. soil bulk density, aggregate stability, macro nutrients) will be measured in the follow-up experiments. Effect of the soil amendments on the soil biota will be further investigated, since it is a fundamental indicator for soil health and will help to quantify the revitalization.

LITERATURE

Adriano, D.C., 2001. Trace elements in terrestrial environments: Biogeochemistry, bioaccessibility and the risk of metals, 2nd ed. Springer, New York, US.

Adriano, D.C., Wenzel, W.W., Vangronsveld, J., Bolan, N.S., 2004. Role of assisted natural remediation in environmental cleanup. Geoderma, Biogeochemical processes and the role of heavy metals in the soil environment 122, 121–142. https://doi.org/10.1016/j.geoderma.2004.01.003

Friesl-Hanl, W., Platzer, K., Horak, O., Gerzabek, M.H., 2009. Immobilising of Cd, Pb, and Zn contaminated arable soils close to a former Pb/Zn smelter: a field study in Austria over 5 years. Environ. Geochem. Health 31, 581–594.

Jelusic, M., Vodnik, D., Lestan, D., 2014. Revitalization of EDTA-remediated soil by fertilization and soil amendments. Ecol. Eng. 73, 429–438.

Kaurin, A., Cernilogar, Z., Lestan, D., 2018. Revitalisation of metal-contaminated, EDTA-washed soil by addition of unpolluted soil, compost and biochar: Effects on soil enzyme activity, microbial community composition and abundance. Chemosphere 193, 726–736.

Sharma, A., Nagpal, A.K., 2018. Soil amendments: a tool to reduce heavy metal uptake in crops for production of safe food. Rev. Environ. Sci. Biotechnol. 17, 187–203. https://doi.org/10.1007/s11157-017-9451-0

Udovic, M., Lestan, D., 2010a. Redistribution of residual Pb, Zn, and Cd in soil remediated with EDTA leaching and exposed to earthworms (Eisenia fetida). Environ. Technol. 31, 655–669.

Udovic, M., Lestan, D., 2010b. Fractionation and bioavailability of Cu in soil remediated by EDTA leaching and processed by earthworms (Lumbricus terrestris L.). Environ. Sci. Pollut. Res. 17, 561–570.

Voglar, D., Lestan, D., 2014. Chelant soil-washing technology for metal-contaminated soil. Environ. Technol. 35, 1389–1400.

Voglar, D., Lestan, D., 2012. Pilot-scale washing of metal contaminated garden soil using EDTA. J. Hazard. Mater. 215, 32–39.

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SPECIFICATION OF THE METHODOLOGY FOR THE REVIEW OF CLUES OF CONTAMINATED SITES OBTAINED WITH THE USE OF REMOTE SENSING

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KEYWORDS

Inventory of contaminated sites, methodology, remote sensing, clues of contamination, interpretation of clues

ABSTRACT

In the initial phase of the 2nd stage of the National Inventory of Contaminated Sites (NIKM), we are focusing on the collection of clues of contaminated sites using Remote Sensing methods. Looking over the first batch (about 38,7 % of the territory is evaluated) of data recorded in the ORPs ("small districts“), we set the details of the methodology for the 2nd degree of interpretation of the clues, i.e. for the review of the data from the 1st degree of interpretation. Four reviewers (review interpreters) are involved in the review of the clues interpreted by twelve 1st degree evaluators. A simulation of three kinds of approaches to the interpretation was done in one “average” ORP. A considerable part of the clues from the 1st stage of interpretation was eliminated via unification in the case of multiplied clues, or deleted in the case of misinterpretation and/or of their little importance or insignificant interpreted volume. In some cases, retyping was applied. Final selection of clues is considered to be the result of the standardized approach of the reviewers. Comments from the discussion forms a set of recommendations for the review process.

1. INTRODUCTION

The 2nd stage of the NIKM project is focused on the inventory and evaluation of information on contaminated sites throughout the Czech Republic. The partial project task "Support of the Inventory by Remote Sensing Methods and Map Services" is taking place from January 2018 to April 2019 and it is provided by CENIA. Inventory methodology includes analysis of raster data (aerial photomaps and satellite images). The supplier's mapping teams for the field inventory will obtain, among other data sources, a data layer containing information about the type of clue of the contaminated site.

2. TYPOLOGY AND KNOWLEDGE BASES OF OBJECTS OF INTEREST

Types of clues were already defined in the 1st stage of the NIKM project, being based on the published methodology [1] [2] [3]. In February 2018, at the beginning of the 2nd stage of the NIKM project, the types were slightly updated, i.e. - completed with three new types ***b, t*** and ***r*** [4] **–** see Table 1. The knowledge base of the expressions of clues and the specification of their typology were included in the methodical aid - the interpretative key (manual).

Tab. 1 Types of clues of contaminated sites used for interpretation within the NIKM 2nd stage project

Code	*Contamination type*	*Code*	*Contamination type*
a	industrial park with an impact on the environment	*p*	suspicion of illegal dump site
b	industrial brownfield	*s*	a new clue linked to the site already included in SEKM database
c	illegal dump / landfill	*v*	scrapyard
h	dunghill	*z*	abandoned agriculture object/farm / agricultural brownfield
j	silage pit	*n*	unrecognized, other type of clue
l	abandoned quarry	*t*	waste dumps within the industrial area
o	abandoned property	*r*	object identified only in DMR (Hill Shaded Digital Terrain Model)

2. SCHEDULE AND STATE OF THE INTERPRETATION WORK

Work started in early 2018. In January and February, a preparatory phase took place, including the updating and optimization of the methodology for the interpretation of the clues in raster documents and the training of the team for the use of the QGIS software and the development of methodological instructions (interpretation key). As a mapping unit we chose regional districts – ORP (Municipality with extended competence = “small districts”, there are 206 in Czechia). Their areas are very different in size (the smallest is 45 km^2, while the largest is 1242 km^2), but their number (206) allows for a fairly accurate division of tasks among team members. Working standards were set so that the entire task of interpreting the clues would be completed by a set deadline of April 30, 2019.

As to the basic statistical characteristics of the information already obtained, until 10. 9. 2018 the area of 38,7 % of the territory of Czechia where the inventory will occur (approx. 78 000 km^2) has been already covered with the 1st degree interpretations. On 10. 9. 2018, a few days after the beginning of the review works (2nd degree of interpretation) we have covered 1760,5 km^2 (i.e. 2 % of the territory subjected to NIKM inventory).

3. STANDARDIZATION OF PHOTOINTERPRETATION OF CLUES FOR USE IN THE REVIEW PROCESS

3.1 Simulation of inputs to interpretation and to the review process

Primary data on contaminated sites and potentially contaminated sites are collected by a team of 12 trained specialists. In spite of the fact that already during the design of the primary data collection process, the phenomenon of individual approach to interpretation has been foreseen, it is necessary repeatedly to consider the individual differences in the evaluation of clues. Therefore, it is necessary to find a way how to get the optimal set of clues for the field survey, to capture the clues of the most serious suspected contaminations and to suppress the less serious ones. For the review interpretation stage, we simulated possible different approaches to evaluations. For modelling of variation in primary interpretation, independent interpretations of clues were carried out on ORP Jaroměř by 4 leading reviewers. The goal was to homogenize and standardize the quality of the data acquired. Each reviewer took a different approach (simulation role) to acquiring primary data, close to his own evaluation method, so that we can obtain sets of clues in a given ORP of different density and different spectrum of types. Emphasis was placed on the consensus assessment of localization and on accuracy of the assigning to the type of clue. The following Figures 1 and 2 show the results of the interpretation achieved with these different approaches.

The comparison of reviewers' approaches took place on the predominantly industrial and agricultural ORP Jaroměř district. Its area is 139 km^2. Figure 1 shows a superposition of the data of each interpreter used to compare the results of the primary interpretation according to different approaches. The triangular signs of the clue differ in colour by four interpreters (see legend in Table 2). Blue and orange colours indicate clues from a very economical interpretation (interpreters A and B), red coloured clues are from the optimal access to interpretation (interpreter C), and green signs are for clues from a thorough evaluation (interpreter D).

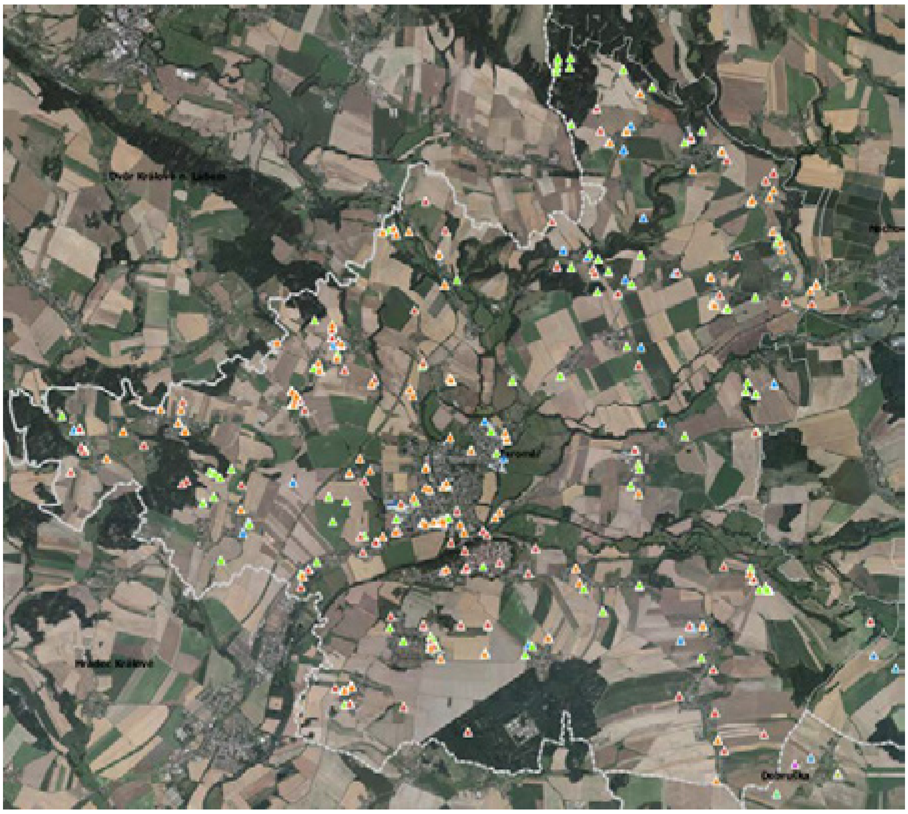

Fig. 1 Summary of the clues recorded in the ORP Jaroměř by four interpreters (the 1st degree of interpretation)

3.2 Comparison of different approaches to the interpretation

For economic reasons, it is necessary to select from the collected records only those clues that necessarily require a visit by field groups. Comparison of the reviewers outputs therefore took place in three steps: In the first step the results of the 1st degree evaluation were aggregated into one common file in which multiplicities were solved. In the second step we worked on the merged first step output and a review of all recorded clues was subsequently performed. Above each record, there was a discussion of the type of clue and its inclusion or exclusion from the final set of clues. Several findings were reassigned to a more appropriate type of clue. The final – third step was merging the result of primary interpretation and review. Removal of redundant and reassignment of misidentified clues were performed by operations within the attribute table in the QGIS software application. For the field survey, evaluators and reviewers' comments (limited to 50 characters) are also important.

In the case of simulation and standardization of the performance of the 4 reviewers in the ORP Jaroměř, out of the 385 clues (the sum of the interpretations of the 1st degree from 4 interpreters) 139 clues there remain for a mandatory, on-site visit and assessment within the future field survey – see Table 2. This is the result of a collective, standardized review.

Tab. 2 Data and comments from common interpretation and review of clues in ORP Jaroměř

Type of clue	Interpreters and the signs of their clues in photomaps				No. of clues	Comments and recommendations for reviews
	A ▲	*B* ▲	*C* ▲	*D* ▲		
a	0	0	0	4	*7*	The "a" type includes also agricultural areas, specify in comments (e.g. incudes "p", "t", "v").
b	2	2	1	5	*5*	Do not record individual houses / objects in destruction.
c	2	18	0	3	*3*	Mark only obviously operated landfill, which is not registered in the IPPC and SEKM
h	6	2	6	4	*8*	Mark only long-term and unsecured dunghill, from 100 m^2. Do not delete. Mark "d".
j	0	3	0	0	*1*	Rare, if possible keep it.
l	14	2	0	2	*16*	Visible in the image even without DMR.
n	0	4	0	3	*3*	If it cannot be assigned to other types, keep it.
o	0	0	4	3	*2*	Do not record individual houses / objects in destruction.
p	21	33	71	41	*63*	The key to include in "p" is the size, which should be at least 20 m^3. Already recorded clues do not delete, just mark "d". Do not record the earth from excavations and storages of bulk materials (gravel, sand, coal, peat, compost etc.).
r	0	0	5	23	*3*	From the DMR, to assess taking into account the neighbourhood, obvious old quarries mark directly "l".
s	0	0	1	1	*1*	Mark only new superimposed clues to older SEKM sites.
t	1	17	4	20	*4*	Mark only individual "technological" landfills suspected to risk management, otherwise to mark the whole site as "a".
v	1	3	1	16	*3*	An irrelevant scrapyard just mark ‚d‘. In case of a small number of up to 5 wrecks on private area do not record if manipulation is not apparent (e.g. dismantling).
z	13	3	2	18	*20*	Do not record individual houses / objects in destruction.
Sum	*60*	*87*	*95*	*143*	*385*	Total number of interpretations from interpreters and sum of all clues. The average number per interpreter is 96 clues.
Number of eliminated multiplicities					*120*	Fusion of the clues of the same type or of different but aggregatable type on one site or on one area.
Number of deleted clues ("d")					*126*	The clues misinterpreted or non-conforming to size requirement .
Total of discarded clues					*246*	They are not the basis for field survey.
Final number of clues (=385-246)					*139*	Total number of clues after review. In subsequent field survey, they will be required to be visited and assessed. 36% of the original number of clues from the 1st degree of interpretation.

In Figure 2 the result of the common review is presented in graphical form. The white crosses represent excluded clues and the clues prepared for subsequent field investigations are indicated by the red triangles.

Fig. 2 The result of the standardization of the interpretation of the clues by a common interpretation of the 2nd degree (review), ORP Jaroměř

3.3 Standardized output from discussion of interpretations of clues in the ORP Jaroměř district

It is quite rare to see the exact match of the assessment of the same location even with experienced specialists. However, a more detailed view shows important insights:

- Despite a different approach, many clues are placed relatively close to similar clues from another evaluator.
- The indices tend to concentrate on certain areas of which have favourable conditions for emergence.
- A too economic (“low-density”) approach leads to a lower number of indications from the 1st degree of the evaluation, but there is a risk of omission of significant clues.
- Review work with a higher number of clues is paradoxically faster, as the reviewer no longer has to deal with the risk of omitting a significant finding and evaluate the entire ORP again.
- It seems to be optimal to make a record of medium-density, and then to evaluate each of them in a detailed view, usually above the actual photomap.
- The reviewer should no longer go through the whole ORP, but only assess the clues already recorded.

3.4 Feedback to primary photointerpretation

In the case of a larger number of evaluators (12) their different individual approaches have to be taken into account. These differences are reflected in the collection of primary data, as there are not mathematically precisely defined requirements for data form, but rather the use of personal experiences and their projection into graphic and text recordings in a relatively free form. The task of the reviewer is to unify and optimize the records. The content of feedback from the reviewer to the primary evaluator is especially important and can help with the quality of input for review. The recommendations for evaluators are mainly:

1. Accurately record the observed phenomena, but avoid obviously unnecessary records.
2. Not try to play a role of a reviewer, an important finding could be omitted.
3. In case of doubt it is better to record the clue instead of omitting it. If the clue is irrelevant, it will be eliminated in the review process.

3.5 The procedure for 2nd degree interpretation (review) and the first data acquired from it

The process is paradoxically simpler in the case of a sufficient density of clues. It is enough to browse row by row through the attribute table in the QGIS software environment and display each clue in a scale of 1:1000. In the case when the reviewer decides to exclude an inappropriate clue, then fills the "d"(deprecated) character in the

REV column in the attribute table. If he finds that the finding is correct but differs from the type of clue, he will enter the correct type of clue in the REV column. If one of the primary evaluators applies a very restrictive approach with a small number of clues, it is necessary to go through the entire ORP at least briefly, or randomly, for example, on every 10th square (4x4km), and by a new interpretation to check that obvious clues are not systematically neglected. The first set of data from the review works is provided in Table 3.

Tab. 3 Summarization of the data from recently started reviews in 4 ORPs (1,8 % of the inventory area of Czechia)

ORP	*Area in km²*	*Number of clues*			
		1st interpretation	*2nd interpretation (review)*	*Difference*	*Reduction in %*
Jaroměř	138,6	143	139	-4	97
Kutná Hora	643,1	362	171	-191	47
Nepomuk	308,7	139	119	-20	86
Nové Město na M.	292,8	148	104	-44	70
Říčany	377,3	388	271	-117	70
Total	*1 760,5*	*1180*	*804*	*-376*	*67*

5. CONCLUSIONS

According to the first findings, we are achieving the goal of the optimal coverage of the territory subjected to inventory using the established review procedure.

The monitored parameters are the numbers, respectively density of clues and their importance. The standardization of interpreters' performance and the optimization of quantity and credibility of recorded clues is crucial to streamline financial and logistically demanding field surveys within the NIKM 2nd stage project.

LITERATURE

[1] Suchánek Z., Řeřicha J., Doubrava P., Roušarová Š, Petruchová J., 2010. Raster Platform within NIKM Project - State and Outlook. Proceedings of International Conference Contaminated Sites Bratislava 2010, Volume 1 Scientific Articles,, ISBN 978-80-969958-6-8, Ekotoxikologické centrum Bratislava s.r.o., pp. 116 – 123.

[2] Doubrava P., Jirásková L., Petruchová J., Roušarová Š., Řeřicha J., Suchánek Z., 2011: Methods for remote sensing of the National inventory of contaminated sites (in Czech). CENIA, Czech Environmental Information Agency, ISBN: 978-80-85087-91-8, Prague, pp. 1 – 94.

[3] Suchánek Z., Řeřicha J. (2016): Update of the methodology for raster data interpretation (remote sensing) for detecting clues of contamination within the contaminated sites inventory project. Proceedings of International Conference Contaminated Sites 2016, Bratislava, pp. 69 – 74.

[4] Suchánek Z., Řeřicha J., 2018: Running state of collection of clues of contaminated sites by Remote Sensing methods in the NIKM 2nd Stage project (in Czech). Proceedings from the Conference Remediation Technologies XXI, May 23 - 25, 2018, Tábor, ISBN 978-80-88238-07-2, Vodní zdroje Ekomonitor spol. s r.o., Chrudim, pp. 109 – 104.

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METHODS OF POPs CONTAMINATION SPREAD ESTIMATION ON DEPOSITORY SITE NUBARASHEN - ARMENIA

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KEYWORDS
Contaminated site, POPs, site investigation, contaminated soil volume estimation, landfill, Armenia

ABSTRACT

Contaminated soil volume estimation strategies has been a subject to dramatic sophistication since the digital era entered the contamination geology field. Hand in hand with development of the state-of-the-art software instruments goes the illusion of ever increasing accuracy of contaminated soil volume estimations dismissing the importance of correctness of software outcomes. It is still the immensely complex process of sampling, chemical analyses and interpretation of resulting data which make these aspects driving within the process of contaminated soil volume estimation. Moreover, entering the volume estimation process various supportive indirect investigation methods make the estimation even more fuzzy. Not surprisingly, there are still the same fundamental principles of contamination investigation in place that should be applied when assuming on contamination spread and its quantification. Simple judgement approach considering geomorphological, geological, hydrogeological and/or former operational patterns of the contaminated site should be respectable method that, in combination with direct investigation methods, may remarkably speed-up, ease and cheapen the contamination volume estimation process and the remediation process itself. This investigation approach has been applied on the POPs depository site in Nubarashen, Armenia, within the UNDP project funded by Global Environemtnal Facility and implemented by Dekonta a.s. – GEOtest, a.s. Standing question is whether such an approach is globally acceptable for public investors, international financial institutions and other decision making stakeholders.

INTRODUCTION

The depository site (DS) of the obsolete pesticides, founded in a landslide area of Nubarashen District - Yerevan, Armenia, has been the subject of increased interest particularly since the unprofessional operations and release of deposited material due the vandalism and illegal excavation of pesticides done into the landfill body before 2010. Due to the handling of the deposited pesticides, these have been spread beyond the landfill body. In compliance with the commitment of the country as a signatory party of Stockholm Convention, Armenia together with the international community has acceded to the systematic solution of the environmental load at the pesticides burial site. The quality, extent, degree, spreading of contamination as well as evaluation of the health risk assessment was the subject of several previous investigations and studies co-financed largely by the international donor community including OSCE, Global Environment Facility and UNDP.

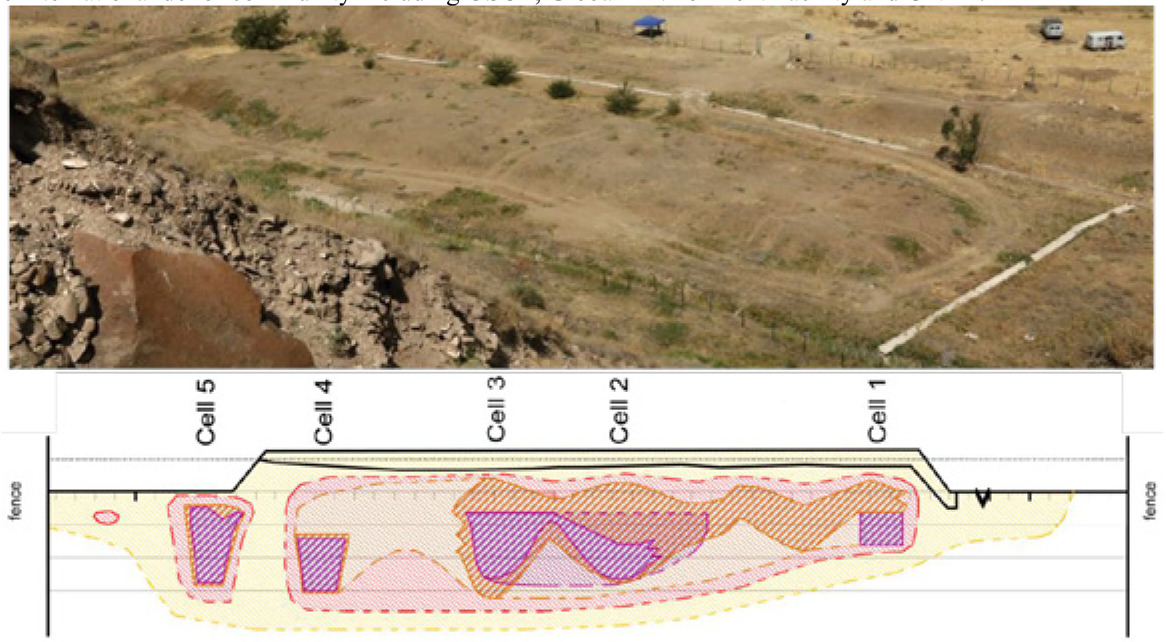

Fig. 1 Depository site with its schematized longitudinal crossection

The results of these surveys have directed the future activities towards the purposeful remediation of DS.
The landfill was constructed in 1976 as a depository site for obsolete pesticides and other chemicals (POPs). The closest non-permanent housing is located ca 300 m at the western and south-western side of NBS. The area of the landfill body is ca 0.15 ha (105 × 15 m), maximal expected thickness is 4 m. The contamination spread is limited to vadose zone, alternatively to creek sediments and surface water.

THE PURPOSE OF THE INVESTIGATION

Although a number of the site investigations has been done earlier, information on contamination spread were not complete to estimate the extent of pesticide contamination in vadose zone including on-site creek sediments. There was a shortage of data on especially surface; out-of-landfill subsurface contamination spread; and vertical extend of landfill cells. Therefore, the purpose of site investigation on stake (2017) was chiefly a detailed delineation of areas of contamination with particular emphasis on the identified landfill burial cells and their surroundings. The survey was to serve for obtaining, gathering and evaluating relevant information relating to the site and required for the subsequent evaluation of risks and for the design of remedial measures. However, not all parts of the site were fully accessible for direct investigation methods (core drilling, collection of samples, chemical analyses, etc.) and only a limited budget and time was available for investigation of 5 ha area. In reaction to this, and predominantly in landfill surroundings, innovative approaches were combined with conventional direct investigation approach to reach the investigation goal.

METHODS OF OUT-OF-LANDFILL CONTAMINATION SPREAD ESTIMATION

For calculation of the contaminated material volume surrounding the landfill, the simple "area × thickness" method (total area of contaminated soil in one depth level multiplied by the thickness of the layer) was applied on data collected within 3 sampling campaigns between 2013 and 2017. The thickness of each layer followed the depth interval of conventional sampling – typical sampling vertical range was 0.5 m for one sample – resulting in the following sampling intervals: 0 – 0.5; 0.5 – 1.0; 1.0 – 1.5; 1.5 – 2.0; 2.0 – 2.5 m below ground level. For each depth layer the delineation of the area with a different intensity of pesticide contamination was done, assuming that the contamination intensity is homogeneously spread within the whole depth interval.
In places with sufficient density of analytical data on contamination, the linear method of interpolation was applied. When estimating the extent of contamination, chemical data on each sampling point in each depth level was interpolated with the existing analytical data in typically 4 directions (approx. to N, S, W, E). In places with low density of analytical data (typically inaccessible parts of the site) from chemical analyses for interpolation (both vertical and horizontal) various supportive instruments had been applied for delineation of contamination. These included both survey supplementary methods and judgement methods. The following list presents the supportive instruments used:

- Results of field measurement by X-ray fluorescence analyzer
- Electrical conductivity measurement results
- Knowledge of the recent site contaminating operations
- Geomorphological patterns
- Geological patterns

These tools had been used either as a self-contained instrument or in combination with the other instrument(s) to speed up the process of investigation and to reduce costs significantly.

Field measurements by portable X-ray fluorescence analyzer were conducted on site during the sampling campaign in 2017 for verification of presence of contamination on surface, in probes and trenched pits done in the area surrounding the landfill body. The results of these measurements were recorded, correlated with results of natural background measurements and later used for the operational field contamination identification and its rough quantification. With knowledge of natural chemical composition of soil on site (quorum), trenched pits between the fence and the landfill body were examined with the portable X-ray fluorescence analyzer Delta Premium (Innov-X). Results from measurement by the analyzer were subsequently compared with results from chemical analyses and potential correlation between these two types of exploration was done.

Electrical conductivity (EC) is a geophysical method revealing materials with a different EC than the one of a natural soil. In a natural environment, the increased conductivity can be represented by materials with high content of water with dissolved ions, for instance. Clean water does not increase EC substantially. This method enables to distinguish between the natural geological background and anthropogenically affected geological environment (typically fill material). However, this method is an indirect method not capable of specific detection of pesticides location. Based on on-site measurement of the EC natural background, it can be identified which material differs from natural state. While EC of 100 – 150 mS/m can be assessed as natural, the values higher than 150 mS/m indicate anomalous situation. Values of EC were generated as an average value of conductivity in the given depth layer. When contouring the above-limit contamination, results of the EC were utilized in the following way. The value of EC detected on place with available analytical data was considered as indicating the contamination of analogical intensity in places where:

- the analytical data on contamination were not available, but contamination was indicated by chemical analyses in adjacent place (in vertical or horizontal manner) or
- the analytical data on contamination were not available, but contamination was indicated by X ray measurement in that particular place or in adjacent place,
- and the intensity of EC was comparable on both places.

Knowledge of recent site contaminating operations was the key enabler to judgement methods. The primary contamination is to be expected exclusively in the landfill cells. Most of the out-of-landfill secondary contamination spread is a result of unauthorized manipulation with pesticides in 2009 and its reclamation attempts. As a result of such activities, the out-of-the-landfill contamination is formed rather by a mixture of various types of pesticides and soil.

Geomorphological patterns contributed to decreased level of uncertainty especially places areas of steep slopes between the northern fence and the landfill body, it was presumed that no subsurface contamination (no deeper than ca 0.5 m below ground level) could be present (as a result of wind migration) because:

- no fractures and fissures were documented on the slope (i.e. spreading of contamination by infiltration of surface water is limited because of the quality of soil, also considering a limited solubility of typical pesticides in water),
- no subsurface contamination was detected on the above-laying plateaus and
- steep slopes are inaccessible for heavy machinery.

Another place where the geomorphological patterns were used is the area between the southern edge of the landfill body and trench running along the foot of the unstable slope. In this area it was assumed (judgement) that the > 50 ppm contamination did not spread behind the surface water drainage trench in depth deeper than 0.1 m. The depth of the trench differs in its length varying from 1.0 to ca 2.5 m. This presents geomorphological barrier for potential spreading of contamination either natural or anthropological. In case of surface water creek beds in the N-W edge of the site that are periodically run through during rain and snow-melting seasons the horizontal spread of contamination was assumed to be limited to the width of the creek bed. In the following picture areas where the above mentioned assumptions were applied are presented in green-hatched fields.

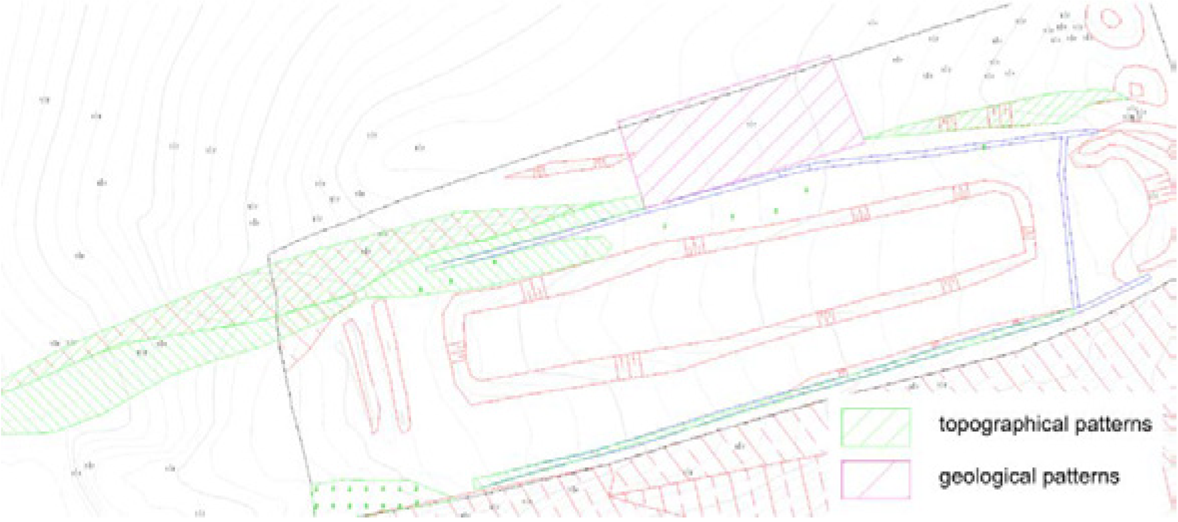

Fig. 2 Areas of the depository site where assumption methods on topographical and geological patterns were applied

Geomorphological patterns discussed above and shown in the picture were applied as a supportive instrument for contamination delineation for contamination layers ranging from the depth of 0.5 to 2.5 m bgl.

Geological patterns – the original geological material on site is formed by marine sediments of Oligocene age with abundant presence of natural gypsum. Clays in its natural state are hard with typical brownish coatings of Fe oxides and gypsum crystals (up to 3 mm). When doing the primary documentation of all survey probes, boreholes and trenched pits, the presence of these indicators were tracked in order to identify the original geological environment. This knowledge was later used for delineation of contamination on places with lower density of analytical data implying that the presence of original undisturbed geological profile excludes the possibility of contamination presence. Another typical geological feature on the site was a presence of vertical fractures formed from the surface of terrain to variable depth levels (2 – 4 m), where closed cracks prevent further potential spreading. In deeper horizons migration of contamination in natural environment is not expectable because of low solubility of pesticides and low permeability of clays-silts. Therefore, where the analytical data on contamination were missing and the presence of natural geological profile without vertical fractures was documented, the presence of contamination by pesticides was not included. Areas where the above mentioned assumptions on geological patterns were applied are presented in the picture as the red-hatched fields.

CONTAMINATION SPREAD EVALUATION

Contour lines of contamination developed in accordance to the methodology above were then transformed into the real coordinate system WGS-UTM maps of contamination for individual depth level in the Microstation software. With use of the Microstation software an areal spread of contamination in particular depth levels were computed. To obtain the volume of contamination in the individual depth level the area was multiplied by the thickness of each layer (typically 0.5 m).

CONCLUSION

Although modern contaminated land management generates ever increasing demand for sophisticated investigation methods contaminated sites deserve nature-based approaches. As site remediation costs play vital role in CS management the greatest pressure is, in paradox, put on reduction of site investigation costs. In this context “back-to-roots” contamination investigation approach may present a sustainable strategy. In this context back-to-roots approach refers to judgement methods used, in combination with primary data from direct investigation, as input data for interpretation and evaluation of contamination spread. Although careful considerations of geomorphological, geological, hydrogeological and operational patterns of each contaminated sites have always been considered as a part of a contamination site puzzle, these should be approached with even higher respect nowadays. Nubarashen burial site (Armenia) is a good example of a contaminated site where not only results of direct and quantitative investigation methods had been used but also a site where supplementary non-quantitative methods contributed to delineation of contamination.

LITERATURE

Barson P., Lacina P., Cerny M., Pazdirek O., Zapletal A., Polak M., Urbanek B., Musil V., 2017: Project title: Detailed Design, Technical Definition of Works, and Supporting Assessments/Studies required for the Removal of POPs Pesticides and Recovery of Associated Contaminated Soil along with Site Cleanup, Stabilization, Containment, and Monitoring applied to the Nubarashen Burial Site (Yerevan, Armenia) - Comprehensive Site Mapping and Analytical Assessment Report, DEKONTA. UNDP

Fokke B., Coterlet G., Pronk W., 2013: Site Assessment and Feasibility Study of the Nubarashen Burial Site of Obsolete and Banned Pesticides in Nubarashen, Armenia; TAUW. OSCE

Mkrtchian H., 2017: Engineering geological analysis. Assessing geological conditions of the areas investigated as possible site to be set-up as temporary storage facility for POPs and obsolete chemicals to be removed from Nubarashen burial site in Yerevan, Armenia. UNDP.

Basel Convention (1989): online 23. 10. 2017).:
http://www.basel.int/TheConvention/Overview/tabid/1271/Default.aspx

Urbanek B., Lacina P., Barton J., 2013: Strengthening National Capacities on Comprehensive Chemicals (Persistent Organic Pollutants) contaminated site assessment in Armenia, Analytical Report on Sampling on Nubarashen Site, Transfer of Czech Knowledge, GEOtest. UNDP

NAS RA (2010): Assessing a discharge of contaminants from the Nubarashen toxic chemicals repository site, Center of Ecological-Noosphere Studies.

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ADSORPTION OF HEAVY METALS BY NATURAL AND MODIFIED HUMIC SUBSTANCES

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New technologies for cleaning of the environment from chemical contamination require the development of efficient materials characterized by high absorption capacity, selectivity, eco-friendly etc. These requirements are fully satisfied humic substances. Humic substances are ubiquitous in the environment and comprise the most abundant pool of nonliving organics. Humic substances account for 50 to 80 % of the organic carbon of soil, natural water, and bottom sediments (Aiken et al, 1985; Orlov, 1990). Humic substances are usually derived on an industrial scale from peat, sapropel, and coal, where their reserves reach hundreds gigatons.

Because of its great complexity, the organic fraction has been classified operationally rather than chemically into 3 fractions: humin, which is insoluble in both acid and alkaline solutions; humic acid, which is soluble in alkaline solution but insoluble in strong acid; and fulvic acid, which is soluble in both strongly acid and alkaline solutions (Aiken et al., 1985). The structure of humic substances contains numerous functional groups and organic fragments. The main functional groups present in humic materials are carboxylic acids, alcohols, phenols, carbonyls, phosphates, sulfates, amides, and sulfides, and all of these groups are able to interact with metal species in solution (Senesi, 1992). Multiple interactions between humic substances and heavy metals include: binding interactions that impact chemical speciation and bioavailability of the pollutants; sorptive interactions affecting physical speciation or interphase partitioning of the metals; redox interactions that impact metabolic pathways of elements (Perminova and Hatfield, 2005).

Thus, the reactivity of humic substances depends on the presence of different functional groups and it reflects the content of aromatic conjugates and degree of condensation. Purposeful chemical modification of humic substances may change the composition and increase the content of the desired functional groups and thereby improve their sorption properties. Among the possible methods for modifying of humic substances are their reduction, oxidation (oxidative degradation, oxidation of phenolic groups, oxidative polymerization), the introduction of fragments of organic molecules into the structures of humic substances. The possibility of chemical modification of peat humic acids by reduction with tin(II) chloride and sodium borohydride and also by carboxylation using the Kolbe method was analyzed (Lebedeva et al., 2005).

Oxidative methods have been frequently and successfully used to degradation and modification of humic substances (Hayes and Swift, 1978). The most widely used methods of humic substances oxidation include reactions with permanganate-ion, hypochlorite, metal oxides, nitrobenzene, hydrogen peroxide, peracetic acid and nitric acid. Partial degradation with solutions of potassium permanganate of a large number of humic acids from soils, waters and sediments have yielded aliphatic, phenolic and benzenecarboxylic acids as major fragments (Gjessing, 1976). Alkaline solutions of cupric, mercuric and silver oxides have also been used to degrade humic substances, but only the first has been widely applied. It also yields aliphatic, phenolic and benzenecarboxylic acids but the relative amounts are not the same as for potassium permanganate oxidation (Schnitzer and Ortiz de Serra, 1973). These two degradation methods are usually employed in alkaline conditions and produce a drastic breakdown of the structure, with the possibility of secondary reactions accelerated by the presence of 02. The use of oxidants under acidic conditions has also been applied to humic substances. Meneghel et al. (1972) described the use of peracetic acid but the percentage of original polymer degraded, the total yield of fragments and the types of structures identified were similar to those obtained with the permanganate and cupric oxide methods. Modification of the humic acids by hydrogen peroxide increases sorption capacity to cations in comparison with unmodified acids (Zherebtsov et al., 2017). The methylation steps are introduced to protect easily oxidizable functional groups and to prevent polycondensation during oxidation.

It is necessary to investigate the use of other, less drastic reagents as oxidants. Martin et al. (1981) have suggested an oxidation method, which is carried out under acid conditions and employs a new reagent, potassium persulfate, which is used by the oceanographers to determine the carbon in seawater (Sharp, 1973) and which is a mild oxidant of humic substances. The type and relative quantities of the products or fragments released varied with the source of the polymers. Humic acid extracted from an Inceptisol yielded fatty, benzenecarboxylic and phenolic acids; humic acid from a Typic Chromoxerert produced largely dialkyl phthalates, and humic acid from an Humic Haplorthod gave only branched and straight-chain fatty acids.

Oxidizing agents capable of easily releasing oxygen: hydrogen peroxide or OH radical (Fenton's reagent), organic peroxides, iodic acid (HJO_4), persulfates, lead tetraacetate and potassium nitrosodisulfonate (Fremy's salt) oxidize phenols causing their hydroxylation, quinone formation and polymerization. The Elbs persulfate oxidation is the reaction of phenols with potassium persulfate under alkaline conditions to form *para*-diphenols:

In the present study we investigated an adsorption of heavy metals (Pb, Zn, Cu, Ni) by natural and chemically modified humic acids. Two different methods of chemical modification were used. The first is to enrich humic acids with phenolic hydroxyls by oxidizing these organics (Elbs persulfate oxidation). The second is the introduction of dibenzoylmethane into the structure of humic acids.

Mixed sample of mesotrophic sphagnum peat were collected from the small sphagnum bog situated in Tula region, Russia. Humic substances from the peats were isolated using alkaline extraction procedure as described by Stevenson (Stevenson, 1994). For the extraction, a portion of the peat was added to a 0.5 N NaOH solution in the ratio of substrate to alkali 1:10, and the mixture was refluxed for 3 h with constant stirring, and then stored for 24 h at room temperature (25±2 °C). Dark colored supernatant liquor with humic substances was decanted, filtered through a 0.45 μm membrane filter and dried for the preparation of the humic acids fractions. The yield of humic substances in the employed procedure was 12.4 %. For the preparation of the humic acid fraction, concentrated HCl was added to the solution of humic substances to adjust the pH to pH 1 following the alkaline extraction. The acid precipitated humic acids were filtered through a 0.45 μm membrane filter and thoroughly washed with distilled water until a neutral pH (pH = 7) was achieved. Samples of peat humus substances were oxidized by Elbs persulfate oxidation reaction (Sethna, 1951). The FTIR and NMR spectra of humic acids used were obtained.

Twenty milligrams of natural or oxidized humic acids were added to conical flasks containing 20 ml of 0.02 mol L^{-1} KNO_3 (adjusted previously to pH 5) and 5 ml of 0.02 mol L^{-1} $Pb(NO_3)_2$, $ZnCl_2$, $CuSO_4$, $NiSO_4$ with pH 5. The total volume of experimental solutions was 25 ml and final concentration was 4 mmol L^{-1}. The suspensions were shaken at 20◦C for 4 h. The supernatant of each sample was collected by filtering through acetate membranes syringe filter (pore size <0.2 μm) and the heavy metals concentrations were determined by ICP OES (spectrometer Perkin Elmer Optima 5300 DV) at wavelengths 222.778 nm for Cu, 217.000 nm for Pb, 213.857 nm for Zn and 221.648 nm for Ni. The amount of each heavy metal adsorbed was calculated by the difference between the amount of heavy metal added and that remaining in the supernatant.

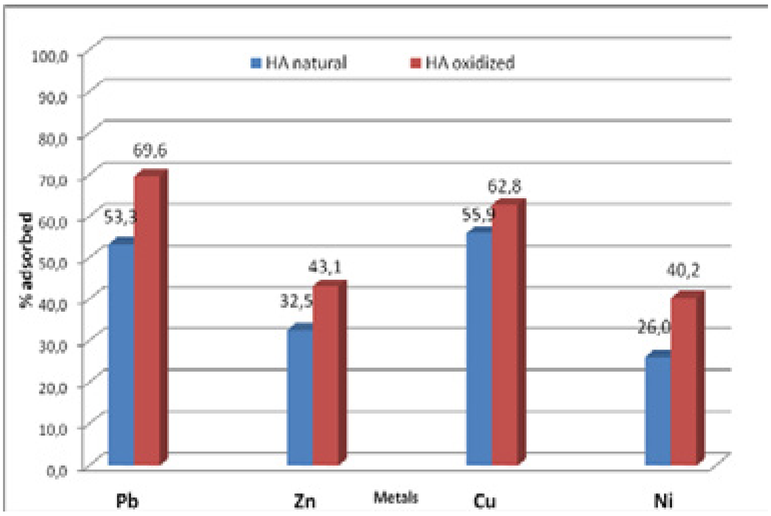


Fig. 1 Adsorption of heavy metals by natural and oxidized humic acids

Our data on the adsorption of four heavy metals by natural and modified humic acids are shown in Figure 1. The absorption of heavy metals by natural humic acids at pH 5 was 26 % for nickel, 32.5 % for zinc, 53.3 % for lead and 55.9 % for copper at an initial concentration 4 mmol. Our results demonstrate that persulfate oxidation of humic acids leads to an increase in adsorption of all heavy metals. The increase ranges from 6,8 % for Cu to 16,3 % for lead. For nickel and zinc, the absorption increases by 14,2 and 10,6 %, respectively. Thus, a simple procedure of chemical modification of humic acids by oxidation able significantly increase the absorption efficiency of these widely available and accessible substances in relation to heavy metals.

Humic acids are characterized by typical absorption bands of IR spectra of different intensities as reported elsewhere. A broad band with an absorption maximum of ~ 3400 cm^{-1} indicates the presence of hydroxyl groups bonded by a hydrogen bond. The bands at 2926 and 2850 cm^{-1} are attributed to aliphatic asymmetric and symmetric C-H stretching, respectively (Rodrigues et al., 2009; Perelomov et al., 2018). For the humic acids obtained, bands at ν 1700–1710 cm^{-1} are observed due to stretching vibrations of the C=O bond of carboxylic and ketonic groups. A peak at 1615 cm^{-1} are attributed to stretching vibrations of conjugated double bonds C=C and aromatic fragments, as well as C=O and COO^{-}groups. A couple of peaks at 1449 cm^{-1} and 1373 cm^{-1} are due to C-H stretching the aliphatic groups CH_3 and CH2. Spectral bands. Bands at 1240 and 1216 cm^{-1} are attributed to bonds of C-O carboxylic acids, esters, O-H phenols and at 1123–1028 cm^{-1} – C-O bonds of cyclic and aliphatic esters and alcohols. As a result of HA treatment by the oxidizer, the intensities of the bands at 1701 and 1624 cm^{-1} (C=O bond of carboxyl groups), at 1260 cm^{-1} (bonds of C-O carboxylic acids, esters, O-H phenols), at 1124 cm^{-1}, 1034 cm^{-1} (C-O bond of alcohols and ethers) and at 3343 cm^{-1} (hydrogen-bonded OH groups) increased (Figure 2).

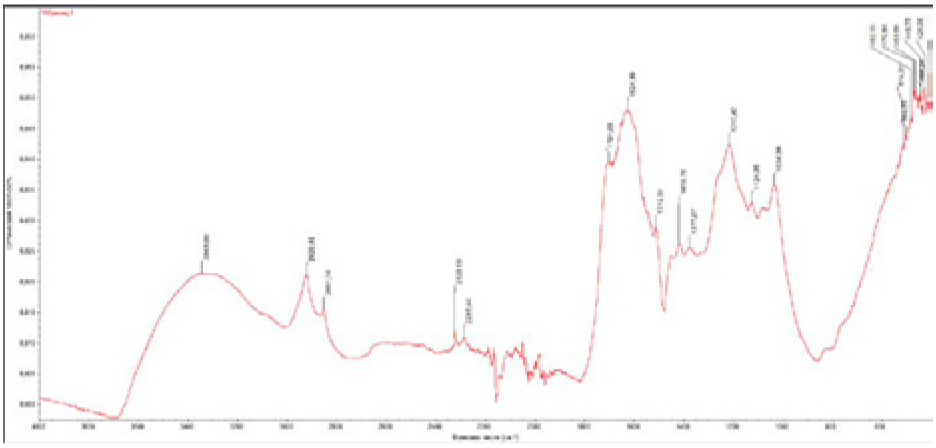
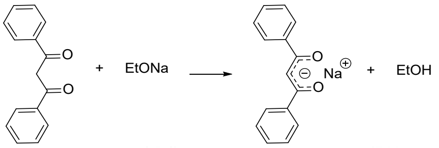
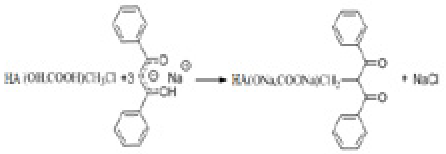


Fig. 2 Infrared spectra of oxidized humic acids

Chemical modification of the natural humic acids by dibenzoylmethane was carried out according to equations 1-3:



(1)



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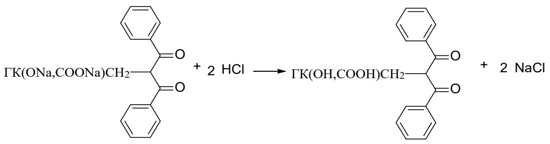

(3)

Ten milligrams of natural or modified humic acids were added to conical flasks containing 8 ml of 1 mmol L^{-1} solutions of $Pb(NO_3)_2$, $ZnCl_2$, $CuSO_4$, $CdCl_2$. The suspensions were shaken at 20°C for 4 h. The supernatant of each sample was collected by filtering through acetate membranes syringe filter (pore size <0.2 μm) and the heavy metals concentrations were determined by AAS.

The adsorption of heavy metals by chemically modified humic acid preparations increased by 13 % for Pb, 4 % for copper, 26 % for zinc and 21 % for cadmium, as compared to the initial natural preparations.

So, binding interactions of natural and chemically modified humic substances with heavy metals are of particular importance in remediation, as such interactions reduce concentrations of freely dissolved metals and as a result leave the offending contaminant less available to living organisms. Widespread of humic substances, easiness of their extraction and modification make these organic substances are very promising for the cleaning of contaminated sites.

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LITERATURE:

Aiken G.R., McKnight D.M., Wershaw R.L. (eds.) (1985) Humic substances in soil, sediment and water, Wiley, New York.

d'un acide humique apres oxydation peracetique. *Bulletin de la Societé Chimique de France 7,* 2997 – 3001.

Griffith S.M., Schnitzer M. (1989) Oxidative degradation of soil humic substances. In Humic Substances II. In Search of Structure. Eds. Hayes M.H.B., MacCarthy P., Malcolm R.L., Swift R.S. John Wiley & Sons, Chichester, New York, Brisbane, Toronto, Singapore, 69.

Hayes MHB, R.S. Swift RS (1978) The chemistry of soil organic colloids. In 'The Chemistry of Soil Constituents'. (Eds DJ Greenland, MHB Hayes) pp. 179-320, Wiley: Chichester, England,).

Lebedeva G.F., Yarkova T.Ya., Platonov V.V., and Proskuryakov V.A. (2005) Chemical Modification of Peat Humic Acids To Increase Their Bioactivity, Russian Journal of Applied Chemistry, Vol. 78, No. 8, 2005, pp. 1360 – 1363.

Martin F., Gonzalez-vila F.J. (1984) Persulfate oxidation of humic acids extracted from three different soils, Soil Biol. Biochem. Vol. 16, No. 3, pp. 207 – 210.

Meneghel R., Pelit-SarloUe C. and Bloch J. M. (1972) Surla caracterisation et I'isolemenl des produits de degradalion

Orlov D.S. (1990) *Soil humic acids and general theory of humification*, Moscow, Moscow State University Publisher, (In Russian).

Perelomov L., Sarkar B., Sizova O., Chilachavaa K., Shvikin A., Perelomova I., Atroshchenko Y. (2018) Zinc and lead detoxifying abilities of humic substances relevant to environmental bacterial species, Ecotoxicology and Environmental Safety, 151, 178–183

Perminova I.V., Hatfield K. (2005) Remediation chemistry of humic substances: theory and implications for technology. In: Perminova, I.V., Hatfield, K., Hertcorn, N. (Eds.), Use of Humic Substances to Remediate Polluted Environments: From Theory to Practice. Springer, Dordrecht, Netherlands, pp. 3–36.

Rodrigues A., Brito A., Janknecht P., Proenca M.F., Nogueira R. (2009) Quantification of humic acids in surface water: effects of divalent cations, pH, and filtration. J.Environ. Monit. 11, 377–382

Schnitzer M. and Ortiz de Serra M. l. (1973) The ehemical degradation of a humic acid. *Canadian Journal of Chemistry* SI, 1554 – 1566.

Senesi, N. (1992) Metal{humic substance complexes in the environment. Molecular and mechanistic aspects by multiple spectroscopic approach. *In* "Biogeochemistry of Trace Metals". (Ed. D. C. Adriano.) pp. 429–96, (CRC Press: Boca Raton, FL.).

Sethna S.M. (1951) The Elbs persulfate oxidation.Chem. Revs., 49, 91.

Sharp J. H. (1973) Total organic carbon in seawater. Comparison of measurements using persulfate oxidation and high temperature combuslion. *Marine Chemistry 1,* 211–229.

Stevenson F.J. (1982) Humus chemistry. John Wiley & Sons, New York.

Zherebtsov S., Malyshenko N, Bryukhovetskaya L, Ismagilov Z. (2017) Spectral Study of Modified Humic Acids from Lignite , E3S Web of Conferences 21, 02022 (2017), The Second International Innovative Mining Symposium.

LEACHING PROFILE OF CONTAMINATED SOIL FROM NIGERIA AND IT'S POTENTIAL FOR EX SITU REMEDIATION USING DIFFERENT CHELATING AGENTS BY SOIL WASHING

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KEYWORDS

Heavy metals; extraction; leaching; efficiency; extractants; contamination; decontamination.

ABSTRACT

The contamination of soils with toxic metals has become a major environmental concern, especially in rural communities where medium and low scale contaminants impact negatively on soil resources and exposes the local habitats to impaired living conditions. The study focussed on comparing the leaching potentials and metal solubilisation with ethylene diamine tetra acetic acid (EDTA), ethylene diamine disuccinic acid (EDDS), acetyl acetone (Hacac), and citric acid (CA) at molar ratio of extractants to metal (2:1), acidic conditions (pH 4.7) and extraction time (150 min) for sustainable metal leaching purposes. Results for the comparative study showed that an optimum breakthrough point was observed after 150 min extraction time. Overall, over 50 % leaching efficiency was achieved across the different extraction processes evaluated. The individual extractants performed differently by swapping positions in their extraction efficiency. For Cd (EDTA > CA > Hacac > EDDS), Pb (EDTA > CA > EDDS > Hacac), and Zn (CA > EDTA > EDDS > Hacac), with EDTA giving the best overall extraction (> 2 fold those of other washing ligands). The comparatively higher efficiency observed for EDTA could be attributed to its stronger complexation constants compared to the other extractants. Hacac and EDDS displayed similar leaching potentials for Cu (Hacac ≈ EDDS > EDTA > CA) and Ni (EDDS ~ Hacac > EDTA > CA), which were larger than those of the other extractants, including the EDTA. The leaching potentials of the different metals from the treated soil was studied to identify rate-determining steps that could influence the time-dependent metal leaching/desorption. Kinetic data was fitted to first-order, Elovich and power function models. Among the kinetic equations, the Elovich function exhibited the best fit to experimental leaching profile data with R^2 values ≥ 0.90, indicating a heterogeneous diffusion process.

In conclusion, the outcome of this study shows that concentrations of these metals could be reduced to safe levels, making the soil safe and available for agriculture, which enhances food security.

INTRODUCTION

Soil contaminated with potential toxic elements (PTEs) constitutes a serious environmental problem throughout the world (McLaughlin, 1999). This is most worrisome in developing countries where intervention values are much higher than in the developed world. Its impact is potentially both long-term and far reaching due to the mobility, toxicity and persistence of PTEs in the environment (Klavin et al. 2000; Yaun et al. 2004). Various anthropogenic activities such as industrial waste, mining and smelting operations, use of fertilizers, auto mechanic wastes, and fly ash from incineration and combustion processes (Mireles et al., 2012; Wei and Yang, 2010; Yaylali-Ababus, 2011) have all contributed to rendering the ecological soils contaminated as a result of deposition of heavy metals on top soils (Nwajei and Iwegbue, 2007).

Although many of these metals occur naturally in the soil, and are intrinsic elements of the earth's crust, excessive amounts introduced into the soil can present a potential environmental and health risk, depending on the chemical form of the metal, which, in turn, controls both its mobility and reactivity in the environment (McBride et al., 2000).

Imo State is one of the states in eastern Nigeria with its capital situated in the Owerri metropolis. The city houses myriads of mechanic workshops conducting automobile work such as mechanic and auto-electric repairs, spray-painting, panel beating, and welding. While this development is accommodated because of its economic value, the ecological impact thereof, considering its geological location and poor management, has now become an issue affecting land-use, water and public health management (Nwachukwu et al. 2012).

As observed by Nwachukwu et al. (2012), large quantities of pollutants have continuously been introduced into the soil because of these automotive services and repairs activities, which generated different types of wastes. Some of these wastes include waste from solvents used for cleaning metallic parts, asbestos from brake pads, and corrosion of scrap auto bodies, used oil and fluids. The chemical component of these solvents are tremendously toxic when in contact with agricultural products cultivated within and around the vicinity of any mechanic village. Several studies (Nwachukwu et al., 2012; Amadi et al., 2017, 2018) to assess the heavy metal concentrations and the ecological and health risk associated with automobile waste in Owerri metropolis Nigeria, have been conducted already. Yet, no data has been presented on a sustainable approach that could be adopted to potentially remediate or reduce the concentrations of these potentially toxic metals in the soil to a safe threshold level. Therefore, the purpose of this paper is to attempt a decontamination exercise that is aimed at reducing pollution or remediating the impacted site to a sustainable level by comparing the leaching potentials of selected extractants for metal extraction. Finally, the efficiency of the applied decontamination technique was assessed.

MATERIALS AND METHODS

Soil

The soil used in this study was collected from a polluted automobile site in Owerri, Imo state, Nigeria**.** Soil samples were randomly collected at drainage points along the natural flow direction from the site, within the auto-mechanic village environment at each location as shown in Figure 1. The samples were collected at selected depths of 0–15 cm, 15–30 cm, and 30–45 cm within a 10 m radius of each other using a soil auger. The three samples from each depth were homogenized to make a composite sample at each depth, resulting in four homogenised samples from the area. Sampled soils were dried at 40^{o} C, and sieved to > 2 mm. Soil properties are shown in Table 1.

Chelating agents

Four chelating agents (EDTA, EDDS, Hacac, and CA) were used for this study. EDTA and CA were purchased from Sigma Aldrich. EDDS was obtained from Innospec and Hacac and industrial methylated spirit (IMS) were bought from Alfa Aeser. Throughout the investigation, high purity deionized water (18.2 mΩcm) was used. All glassware and PTFE containers were previously soaked in 10 % (v/v) nitric acid for 12 h and then rinsed with high purity deionized water prior to use.

Metal extractions

Column tests were conducted to evaluate the leaching behaviour, as well as extraction of Cd, Cu, Ni, Pb, and Zn, from the contaminated soil under investigation. Metal extractions were carried out in a glass column (diagram not shown) at a solid: solution ratio of 1: 10. The packed soil was placed into the column (internal diameter 0.2cm and 30cm in height) between two layers of sand (0.5cm each). The slurry technique was adopted as packing technique, as this practically seems to be the most suitable approach for the type of soil been studied. The soil was seated at a height of 8cm by gently tapping the column with a rubber rod to achieve a uniform bulk density as well as minimize band broadening effects. The sand layer placed at the bottom of the leaching column prevented loss of sample during the leaching process. Before exposure of the slurry to leaching solutions, deionized water used in making the slurry was removed via the column outlet with small amount left to keep the column intact and hydrated. The volume and metal concentration of the water leachate were used as a control to assess the contribution of the solution extractants used. Each column was initially saturated with the leaching solution after which leaching experiment started immediately. The leaching agents used were acetylacetone (2,4-pentanedione, referred to as Hacac hereafter), EDDS, citric acid (referred to as CA hereafter) and EDTA. Factors influencing the choice of leaching agents were: (i) cost, (ii) environmental sustainability (iii) potential leaching efficiency, and (iv) potential to be used in a different phase or modified for selective recovery. In particular, EDTA was included in the study as a regularly used standard treatment. A range of concentrations was used for the extractants, based on previous studies reported in literature (Wasay et al., 1998a; b). EDTA was employed at 0.034 mol.dm^{-3}, EDDS at 0.034 mol.dm^{-3}, Hacac at 0.03 mol.dm^{-3}, and CA at 0.026 mol.dm^{-3}. All these concentrations ensured an excess of extractant for each metal concerned. The pH of the leaching solutions used in this experiment were 4.75 ± 0.1, 3.51 ± 0.1, 2.71 ± 0.2, and 4.2 ± 0.2 for EDTA, EDDS, CA, and ACAC respectively.

The solution level in the columns varied slightly according to outflow rate, and was maintained at approximately 10cm above the soil surface by the addition of the leaching solution, as it demands. A sand layer placed on the soil surface minimized sample disturbance from the addition of leaching solution. Leaching of Cd, Cu, Ni, Pb, and Zn from the soil samples was determined using different of chelating agents (EDTA, EDDS, CA and pure Hacac) over a leaching time intervals of 30, 60, 90, 120, and 150 min. Each extractant run was replicated in three columns each. Preliminary studies (not reported here) was conducted to optimize experimental conditions. The flow rate was set at 0.8 mL min^{-1} with a constant head of 10 cm. The pH measurements of the leachate samples was taken before metal analysis on the ICP-OES instrument.

Analytical Methods

The total organic content was estimated by Loss on Ignition (Goldin, 1987). The pH was measured at solid : liquid ratio 1: 10 after mechanically agitating at 120 revolution min^{-1} using a reciprocating shaker for a minimum of 60 min (Mettler Toledo, Gawlik et al., 2001). Specific surface area (SSA) and cation exchange capacity (CEC) were measured using standard methods by Cokca and Birand (1993) and Santamarina et al. (2002), respectively. Particle size fraction was determined with a Malvern mastersizer 2000; and the acid soluble metal contents of the soil was determined after dissolution in aqua regia. The dissolved Cd, Cu, Ni, Pb, and Zn concentrations were measured with ICP-OES.

RESULTS AND DISCUSSION

1.2 Soil characterisation

The soil parameters of colour (munsell), CEC, mineral profile, and pH were used to characterise the soil under investigation as summarized in Table 1.

The soil exhibited a reddish brown colour (munsell 5YR.5/1), attributed to the presence of red earths characteristic of oxidized ferric iron oxide. CEC gave a low value (7.3) suggesting a reduced surface area for metal exchange capacity, a phenomenon, likely to influence leaching dynamics. X-ray diffraction shows that the kandite clay, kaolinite, titanium oxide and anatase are known to contribute to the mineralogy of the investigated soil. Due to the presence of these highly weathered clay (kaolinite) minerals, the ability for the soil to retain cations will be solely influenced by surface area, which is a reflection of its CEC content. The pH (3.7) has an acidic character, anticipating that metals in soil will be readily leached. The soil bulk geochemistry suggests that the metals of interest were higher than the EU regulatory standards, but lower than that set for DPR Nigeria.

1.3 Column extraction

In situ column leaching experiments with a solid: liquid ratio of 1: 10 were used to investigate the leaching behaviour of Cd, Cu, Ni, Pb and Zn bound to different soil components. To illustrate the leaching trend over time, the leaching concentration of metal (mgkg^{-1}) extracted from the contaminated soil after 30, 60, 90, 120, and 150 minutes contact time with selected extractants (EDTA, EDDS, Hacac, and CA) were considered.

Comparative extraction performance of the selected extractants at chelant-to-metal molar ratios of 2:1 under acidic pH conditions are illustrated in Figure 2a. It can be deduced that considerable differences in the extraction efficiencies were observed across the four extractants examined. In the case of Cd, EDTA showed the best extraction efficiency when compared to the other extractants. The magnitude of extraction by EDTA was in the range of 4.3 to 0.7 times greater than the other three extractants (on the average 62 % compared to the 47.5 %, 33.5% and 14.5% for EDTA, CA, EDDS and Hacac respectively). For Cu, Hacac and EDDS displayed similar and maximum extraction efficiency when compared to EDTA and CA. Hacac and EDDS extracted between 1.6 and 1.2 times more than the rest of the other extractants. For Ni, EDDS displayed the highest extraction efficiency when compared to the other extractants. EDDS extracted between 1.7 and 1.1 times more than the rest of the other extractants (on the average 72.9 % compared to the 64.7 %, 57.2% and 42.3% for EDDS, Hacac, EDTA and CA respectively). For Pb, EDTA showed the maximum extraction efficiency when compared to the other extractants. EDTA outperformed the other extractants by a range of 8.7 to 2.7 times, with an average efficiency of 52 % compared to 19.6 %, 18 % and 6 % for EDTA, CA, EDDS and Hacac respectively. In the case of Zn, CA showed the highest extraction efficiency when compared to the rest of the extractants. The magnitude of extraction by CA was in the range of 1.7 to 1.1 times greater than the other three extractants (on the average 51.6 % compared to the 46.2 %, 44.9 % and 29.6 % for CA, EDTA, EDDS and Hacac respectively).

Overall, the better extraction efficiency of EDTA for Cd, Pb and Zn when compared to the other chelants can be explained by considering the high stability constants of Cd, Pb and Zn complexes (log K=16.5, log K=18.8 and log K=17.5) respectively. The extractions of Cd and Pb were lower for both EDDS and Hacac (Tandy et al., 2004; Pettit and Powell, 2001). The poor extraction performance of EDDS could be attributed to the formation of FeEDDS complexes over other metal – EDDS species at lower pH conditions (Begum et al., 2013). Pb/Cd complexes for both EDDS and Hacac have low stabilities and likely result in metal exchange and re-adsorption that could liberate Pb/Cd for binding with Fe-(hydro) oxides (Koopmans 2008). The extraction study was investigated under acidic condition (~3.7) with soil predominated by ferric iron oxide. Hacac and EDDS performed better than EDTA and CA for Cu and Ni extraction, irrespective of the pH condition. This phenomenon could be attributed to kinetic hindrances that is often experienced by reacting species (metals and the multidentate ligands) during coordination interactions, which may take priority over the general extraction preferences (Nowack, 2002). Previous results suggest that EDDS could be a better metal extractant for Cu and Ni than EDTA at pH values above 6, because it forms a weak metal alkali complex. Figure 2b shows a decontamination efficiency graph before and after soil treatment using the selected chelating agents. The average efficiency of the various extractants was found to be > 50 %, suggesting that the extractants are potentially efficient for a clean-up exercise.

1.4 Leaching profiles

The results presented in Table 2 shows the data for the kinetics of Cd, Cu, Ni, and Pb and Zn extraction from contaminated soil using selected extractants at pH 3.7 for a reaction time of up to 3h. Three models (Elovich, power function and 1st order function) were fitted to the data to describe the extraction dynamics. These models are commonly used in literature (Sparks et al., 1980; Havlin et al., 1985). For reasons of brevity, we only presented the discussion of the Elovich model as it best describes the extraction kinetic behaviour when compared to the other models (Jang et al., 2005; Li et al., 2001). The Elovich model was chosen as the best fit to the experimental data as judged by its R^2 and low standard error values. The values of the α and β^{-1} variables (Table 2) were typical of fast desorption processes for Cd, Cu, and Ni using EDTA, EDDS and Hacac respectively. This is an indication that diffused extraction may have occurred spontaneously within exchangeable and carbonate fractions.

Table 1. Physicochemical properties and elemental concentrations of contaminated soil with reference to regulatory limits of various heavy metals investigated as per EU and Nigerian DPR values

		Characterization				Elemental concentration (mgkg^{-1})				
Soil	Mineral Type	Texture	pH	SOM (%)	CEC (meq/ 100g)	Cd	Cu	Ni	Pb	Zn
Nig-S	Kaolinite, Anatase and Quartz	Sandy loam	3.7	0.3	7.3	26.3	155.0	75.0	210.0	350.0
The European Union Standard (MEF, 2007)						1.0	100.0	50.0	60.0	200.0
Nigerian Intervention value (DPR, 2002)						17.0	190.0	210.0	530.0	720.0

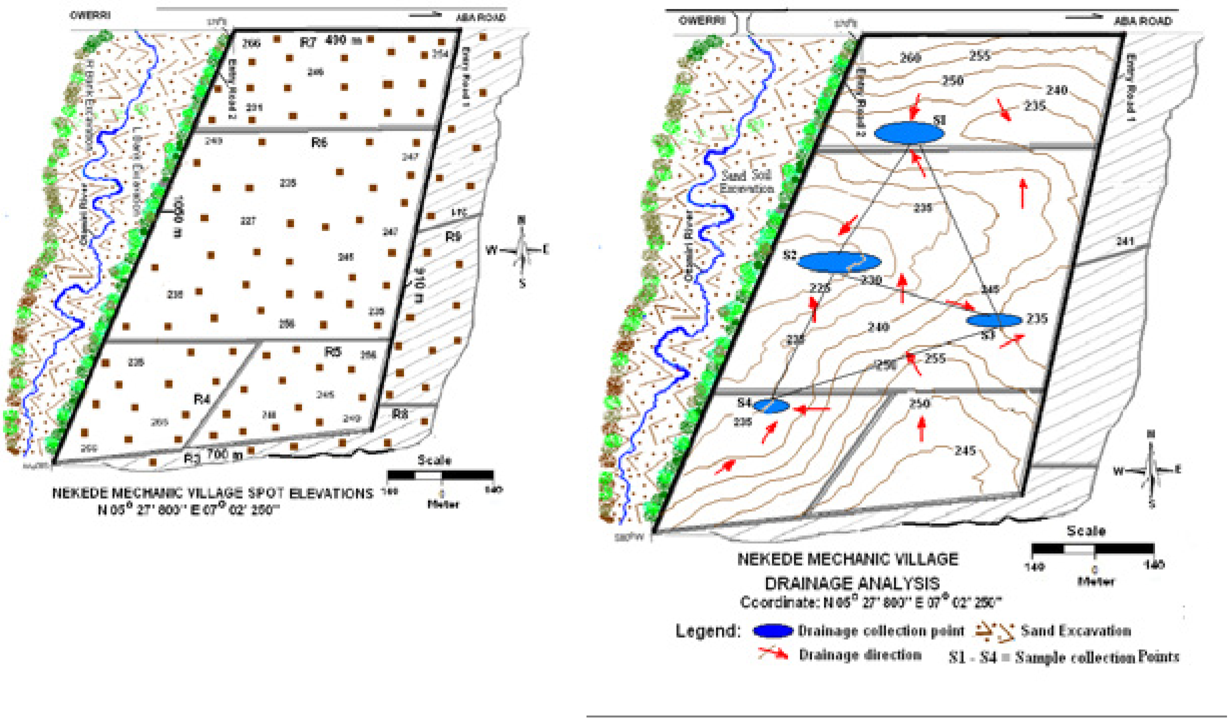
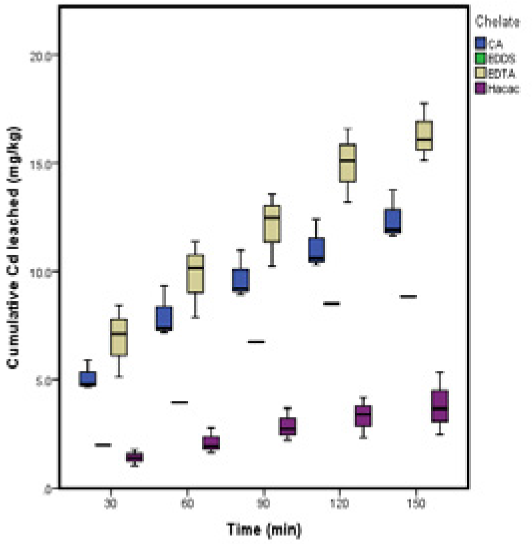
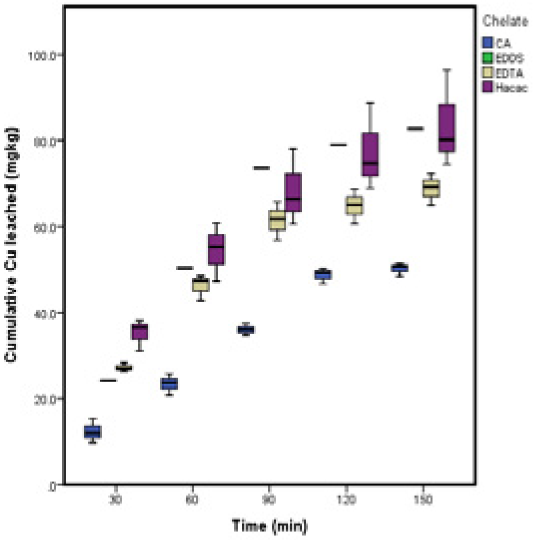


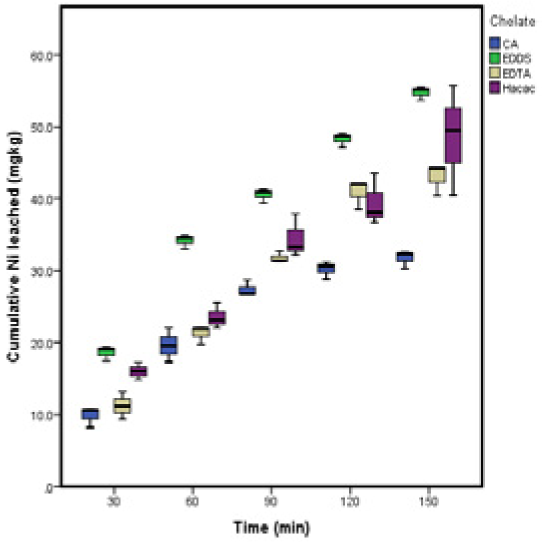
Figure 1 a), b) showing spot elevation, and sample collection points used for analysis.

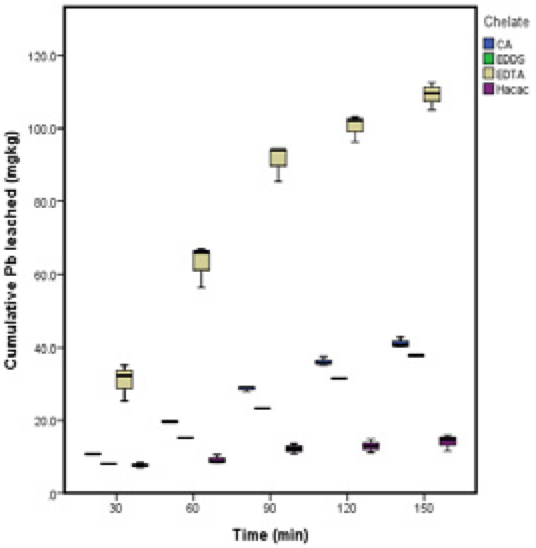
Table 2: Parameters of kinetic models calculated for the extraction of base metals of interest from extractants as a function of time and soil in a column leaching process at pH (3.7).

Soil	Metals	Extractant	Elovich			Power function			First order		
			$q_t = \left(\frac{1}{\beta}\right)\ln(\propto \beta) + \left(\frac{1}{\beta}\right)\ln(t)$			$\ln q_t = \ln a + b \ln t$			$\ln(q_e - q_t) = a - k_1 t$		
			α	β^{-1}	r^2	a	b	r^2	a	k_1	r^2
EDTA	Cd	EDTA	1.390	1.450	0.963	2.410	1.330	0.949	2.324	0.0005	0.598
		EDDS	1.900	0.370	0.993	1.760	0.630	0.972	1.808	0.0006	0.485
		Hacac	1.110	7.780	0.979	0.351	0.500	0.955	0.715	0.0005	0.532
		CA	0.940	4.610	0.893	0.392	0.460	0.856	2.146	0.0005	0.329
	Cu	EDTA	1.640	6.380	0.930	2.399	1.090	0.843	3.704	0.0005	0.835
		EDDS	0.730	27.900	0.993	1.001	0.760	0.973	4.018	0.0005	0.407
		Hacac	0.690	22.990	0.986	0.713	0.520	0.962	4.018	0.0005	0.407
		CA	0.470	62.250	0.826	1.660	0.570	0.866	3.615	0.0005	0.238
	Ni	EDTA	2.740	1.590	0.981	2.331	1.090	0.881	3.377	0.0005	0.824
		EDDS	2.740	1.590	0.981	0.588	0.450	0.857	3.586	0.0005	0.688
		Hacac	2.740	1.590	0.981	2.514	1.340	0.974	3.534	0.0005	0.299
		CA	0.220	110.590	0.894	2.078	1.000	0.969	2.985	0.0050	0.882
	Pb	EDTA	1.940	3.960	0.969	2.311	1.040	0.890	4.267	0.0005	0.786
		EDDS	0.990	18.330	0.987	1.635	0.960	0.973	3.383	0.0006	0.286
		Hacac	0.080	292.060	0.982	0.867	0.480	0.957	2.030	0.0005	0.493
		CA	0.370	82.850	0.858	1.109	0.640	0.789	3.393	0.0050	0.948
	Zn	EDTA	1.300	39.150	0.836	2.694	1.410	0.985	4.703	0.0005	0.945
		EDDS	0.160	61.530	0.992	0.599	0.740	0.980	4.776	0.0006	0.158
		Hacac	0.190	416.310	0.987	1.273	0.780	0.968	8.030	0.0050	0.927
		CA	0.170	160.820	0.896	0.593	0.490	0.858	7.470	0.0500	0.690









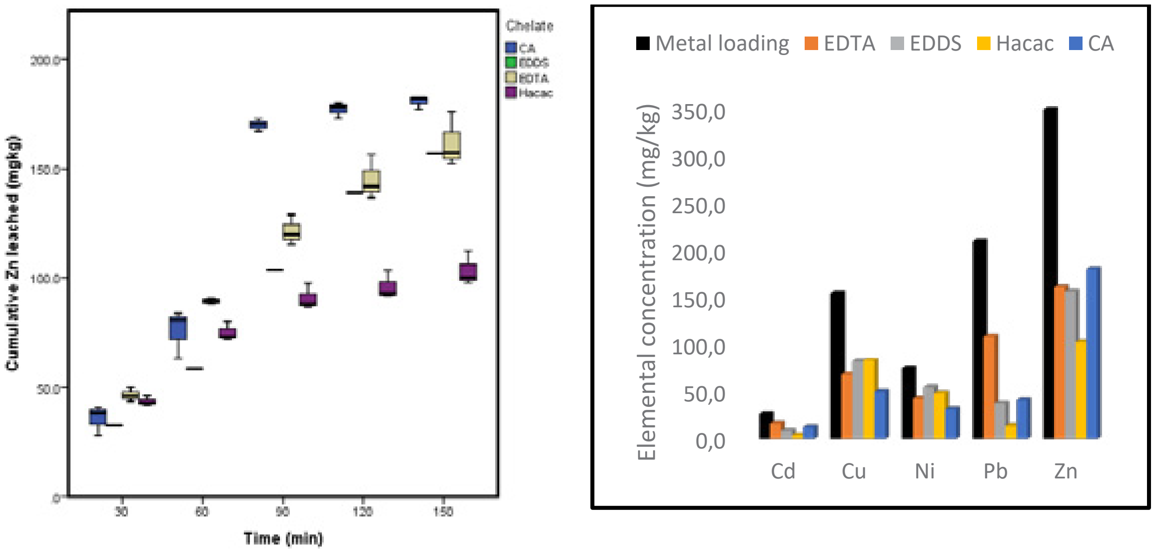


Figure 2. Box plots comparing the extraction potentials of selected chelants used for metals (Cd, Cu, Ni, Pb & Zn) extracted from contaminated soil. The middle line in box represent the median values, the lower and upper boundaries indicate 25 and 75 percentiles and sample size (n = 5). (b) Graph showing decontamination efficiency of the soil before and after treatment

CONCLUSIONS

The decontamination technique used in our study could be further optimized by using a combination of extractants (that is, mixture of EDTA + EDDS or Hacac or CA) to achieve a higher metal extraction compared to an individual application. In addition, the kinetic extraction model derived could be utilised for design of a reactor to optimally facilitate contaminant extraction process. In most cases at least half (> 50 %) of the initial metal loading of the contaminated soil could be removed, which would render the soil mostly complying with EU contamination levels and probably very suitable for agricultural purposes. A useful follow up study would be to carryout techno economic study to ascertain the viability for further studies.

REFERENCES

Amadi, P. U. and Agomuo, E.N (2018). Oral ingestion risks of heavy metal accumulation at top soils of automobile workshops in Owerri capital city of Imo State, Nigeria ACTA Chemica /AS/ 26–1, 21–44

Begum, A; Ramaiah, M; Harikrihna, K. I.; Veena, K (2009). Analysis of heavy metals concentration in soil and litchens from various locations of Hosur Road, Bangalore, India. Orbital: Electron. J. Chem; 6 (1), 13 – 22

Cokca, E. and Birand, A. A. (1993). 'Determination of cation exchange capacity of clayey soils by the methylene blue test.' *Geotechnical Testing Journal,*, 16(4), pp. 518–524.

Gawlik, B. M., Lamberty, A., Pauwels, J. and Muntau, H. (2001b). 'Certification of soil-pH (suspension of water and $CaCl_2$) and adsorption coefficient for atrazine, 2,4-D and lindane in six different reference soils (Euro Soil).' *IRMM*, p. 442

Goldin, A. (1987) 'Reassessing the use of loss-on-ignition for estimating organic matter in non-calcareous soils.' *Comm. Soil Sci. Plant Anal.*, 18, pp. 1111–1116.

Havlin, J. L., Westfall, D. G. and Olsen, S. R. (1985) 'Mathematical models for potassium release kinetics in calcareous soils.' *Soil Science Society of America Journal*, 49, pp. 371–376.

Mclaughlin, M.J; Parker, D.R; Clarke, J.M (1999). Metals and micronutrients food safety issues. Field Crop Research, 60, 143–163.

McBride, M. B., Martinez, C. E., Topp, E. and Evans, L. (2000). 'Trace metal solubility and speciation in calcareous soil 18 years after no-till sludge application.' *Soil Science*, 165 pp. 646–656.

Nwajei, G.E and Iwegbue, C. (2007). Trace metal concentrations in soil in the vicinity of Uwelu motor spare. Journal Chemistry SC. Nigeria 32, 282–286

Nwachukwu, M.A; Huan F; Alinnor, J; Nwachukwu, M (2012). A comparative analysis of trace metal pollution parity between sandy and shaly soils: evidence from two mechanic villages in the Imo river basin. J. Environ Earth Sci. 65: 765 – 774

Nowack, B. (2002). 'Critical review: environmental chemistry of aminopolycarboxylate chelating agents.' *Environment Science Technology*, 36 pp. 4009–4016.

Koopmans, G.F, Schenkeveld, W.D.C, Song, J. (2008). Influence of EDDS on metal speciation in soil extracts: measurement and mechanistic multicomponent modelling. Environ Sci Technol 42: 1123–1130

Pettit, L. D. and Powell, H. K. J. (2001). 'IUPAC stability constants database.' *Academic Software, Otley*, (Version 5.3)

Santamarina, J. C., Klein, K. A., Wang, Y. H. and Prencke, E. (2002). 'Specific surface determination and relevance.' *Canadian Geotechnical Journal,*, 39, pp. 233–241.

Wei-Yang, L. (2010). 'A review of heavy metal contaminations in urban soils road dusts and agricultural soils from China.' *Microchemical Journal*, 94, p. 99.

Sparks, D., L., Zelanzy, L. W. and Martens, D. C. (1980). 'Kinetics of potassium desorption in soil using miscible displacement.' *Soil Science Society of America Journal*, 44, pp. 1205–1208.

Yaylali-Abanuz, G. (2011). Heavy metal contamination of surface soil around Gebze industial area, Turkey. Microchem. J. 99, 82–92.

SILICON-BASED APPROACH TO DETOXIFICATION AND PURIFICATION OF CONTAMINATED SITES

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KEYWORDS
Antimony mine, monosilicic acid, remediation, silicon substances, waste water

ABSTRACT

Over the last decade numerous studies related to interaction of silicon (Si) substances and inorganic pollutants in water, soil and plant have been reported. Monosilicic acid, the product of dissolving Si-rich minerals, reacts with heavy metals forming insoluble silicates. Many Si substances possess high adsorption capacity. Improved Si nutrition was shown to benefit growth and development of plants exposed to any type of contamination. In laboratory and greenhouse tests, calcium silicate slag from iron smelting, zeolite, concentrated monosilicic acid and silicic acid-treated slag and zeolite were used for detoxification of contaminated ground and purification of waste-water collected in the antimony mine area (Hunan Province, China). Waste water filtration through materials resulted in decreases in inorganic pollutants (As, Cd, Cu, Hg, Sb and Pb) by 70 to 98 %. Silicon substances provided increase in the biomass of barley plants by 50 to 130 % and in the leaf content of chlorophyll by 40 to 70 %. The pollutant mobility in the ground was reduced as well. Higher effect being demonstrated by silicic acid-treated slag is ascribed to greater release of monosilicic acid.

Mining is one of the most serious sources of pollutants in the environment. The Xikuangshan mine in the Hunan Province, China has the largest antimony (Sb) deposit in the world. It is located between 27.7^0 N and 111.4^0E in the northern part of the Xiangzhong Basin of Hunan Province near Lengshuijiang City. The annual production capacity of the Xikuangshan mine is 40 000 metric tons of Sb products (He, 2007). The heavy contaminated area around this mine operation occupies more than 1.8 km^2 (Figure 1). Waste waters from the mine are highly polluted with As, Cd, Cu, Hg, Sb, and Pb.

Fig. 1 Contaminated site in Xikuangshan mine area

Fig. 2 Contaminated waste water stream in Xikuangshan mine area

By now a lot of environment remediation techniques have been developed. Most of them are costly, environmentally destructive and time and labor consuming. So, new cost-effective, eco-friendly and feasible technologies are necessary. One of possible ways to reduce cost is using local by-products for soil and water purification and restoration.

Over the last decade, numerous investigations have shown that soluble forms of Si or solid Si-rich materials can be effective for detoxification of contaminated areas and controlling the migration and translocation of heavy metals and other pollutants in the soil-plant system (Ji et al., 2016; Liang et al., 2007; Meharg and Merhag, 2015). The main underlying mechanisms include precipitation of inorganic pollutants via the formation of insoluble silicates, sorption on Si-rich surface, activation of soil microorganisms promoting the decomposition of organic pollutants. Soluble Si compounds enable to impact directly the inorganic pollutant uptake by and transport inside plant (Ji et al., 2016).

The aim of this investigation was to demonstrate the effect of local metallurgical slag and zeolite treated with active Si on the heavy metal immobilization at contaminated sites.

Waste-water and soil samples were collected from a contaminated area near the Xikuangshan mine (south mine). This place was selected for sampling due to high level of contamination (He, 2007). Soil had the following characteristics: clay loam texture, pH_{H2O} 5.5±0.1; organic matter 3.2±0.5%, cation exchange capacity (CEC) 8.4±0.4 cmol 100 g^{-1}. Waste-water was filtered through a Whatman paper filter Grade 4 and stored in a plastic bottle at a temperature of +4°C.
The following Si-rich minerals were used:

1) a zeolite - brand DSP, ZeoTradeResource Ltd. Orlov region, Russia, consisted of dense light gray granules, contained SiO_2 – 69.0 – 74.0 %, TiO – 0.08 – 0.16 %, Al_2O_3 – 11.4–14.0 %, Fe_2O_3 – 0.60 – 1.8 %, MnO – 0.02–0.05, CaO – 1.7 – 3.3 %, MgO – 0.4 – 1.7 %, K_2O – 0.5 – 5 %, Na_2O – 0.4 – 0.9 %, P_2O_5 – 0.4; pH 6.5; particle size < 40 µm; average surface area 60 $m^2 g^{-1}$, porosity 54 %;

2) calcium silicate slag – blast furnace slag from the Valin metallurgical enterprise (Loudi, Hunan Province, China), with 4.6 ± 1.5 mg kg^{-1} of water-soluble Si; pH of 8.5; particle size 1-2 mm, contained Si – 19.3 %, Fe – 2.6 %, Ca – 20.5 %; Mg – 4.1 %, Pb – 0.2 mg kg^{-1}, As, Cd, Hg and Se were undetectable.

Zeolite and slag were activated by the treatment with concentrated monosilicic acid (18% of Si as monosilicic acid; Bei Jing Plum Agrochemical Trading Co., Ltd., Beijing, China). The solid materials were treated by liquid Si at a proportion of 50:1, dried at 65°C and ground. Activated zeolite (A-Zeolite) and activated slag (A-Slag) were used in all tests.

Greenhouse test was conducted in a climatic chamber at 30°C and day/night regime 12/12 hours. Plastic pots were filled with 250 g of pure quartz sand. Contaminated soil from the Xikuangshan mine site was added at a rate of 250 g pot^{-1}(a proportion of 1:1). Silicon materials were added at a rate of 5 g pot^{-1}, which is equal to 10 t ha^{-1}. All treatments were conducted in 4 replications. Rice (*Oryza sativa* L.) was grown for 3 weeks, then harvested and biomass and chlorophyll content was measured. The soil after the greenhouse test was dried at

65 °C, ground and analyzed for mobile (0.1 n HCl-extractable) and potentially mobile (2 n HNO_3-extractable) As, Cd, Cu, Hg, Sb and Pb with ICP OES spectrometer Perkin Elmer Optima 5300 DV.

Column experiment was conducted in plastic columns with a volume of 10 cm^3 and a diameter of 1 cm. Waste water from the Xikuangshan contaminated site was added to a column at 6-8 mL h^{-1} at the total volume of 100 mL using peristaltic pump. Percolated solutions were collected and analysed for As, Cd, Cu, Hg, Sb, and Pb by ICP OES spectrometer Perkin Elmer Optima 5300 DV. Each treatment had 3 replications.

The biomass of rice plants and the content of chlorophyll are presented in Table 1. The application of untreated and treated Si-rich materials significanly increased the underground and aboveground biomass of plants. The contents of chlorophyll a, chlorophyll b and carotenoids also were remarkably uncreased under the application of Si-rich substances. This data evidences that the pollutant-induced toxicity in the soil was reduced. In general, the application of Si-rich substances provided an increase in the biomass of barley plants by 50 to 130% and in the leaf content of chlorophyll by 40 to 70 %. Thus, Si materials tested, especially activated forms, would benefit the greenery of contaminated area.

The content of mobile and potentially mobile pollutants in the soil after greenhouse test is presented in Table 2. The use of Si-rich materials significantly reduced the moblity of hazardous elements. Untreated slag was less efficient. However, the activation of slag by concentrated monosilicic acid considerably inreased its efficacy. The 2- to 10-fold decreased pollutant mobility provides a reduction in the risk of underground water contamination.

Tab. 1 Biomass of rice and chlorophyll content

	Roots	**Stems and leaves**	**Chlorophyll a**	**Chlorophyll b**	**Carotenoids**
	--dry weight, g plant^{-1}--		**------------- mg kg^{-1}-on fresh weight---------------**		
Control	0.15	0.11	1.5	0.7	0.21
Zeolite	0.19	0.18	2.4	1.1	0.27
Slag	0.18	0.16	2.1	1.0	0.24
A-Zeolite	0.28	0.33	2.9	1.6	0.48
A-Slag	0.31	0.32	2.8	1.8	0.45
LSD$_{05}$	0.02	0.02	0.2	0.1	0.03

Tab. 2 Mobile and potetially mobile forms of pollutants, mg kg^{-1}

	As		**Cd**		**Cu**		**Hg**		**Sb**		**Pb**	
	0.1 n HCl	2 n HNO_3	0.1 n HCl	2 n HNO_3	0.1 n HCl	2 n HNO_3	0.1 n HCl	2 n HNO_3	0.1 n HCl	2 n HNO_3	0.1 n HCl	2 n HNO_3
Control	30.5	128	5.4	6.7	25.3	78	0.82	n/d	6.6	10.3	12.3	80
Zeolite	3.4	35	2.1	4.3	10.4	43	0.34	n/d	3.5	4.5	4.5	45
Slag	15.6	89	3.2	5.5	18.9	66	0.57	n/d	4.4	7.6	7.6	76
A-Zeolite	2.1	12	0.6	1.2	4.5	12	0.05	n/d	0.4	1.2	0.4	21
A-Slag	2.0	25	0.6	1.3	5.0	14	0.04	n/d	0.6	1.1	0.5	18
LSD$_{05}$	0.2	5	0.1	0.2	0.2	4	0.01		0.1	0.2	0.1	3

In the variant with non-activated zeolite, the concentration of pollutants in the percolated solution was reduced significantly, whereas non-activated slag as a filter demonstrated a low performance (Tab. 3). However, the application of both A-Zeolite and A-Slag remarkably reduced the concentration of contaminants in the percolated solution (by 70 to 98 %). It should be noted that slag is a local by-product having a very low price.

Tab. 3 Concentration of pollutants in percolated solution, ppm

	As	Cd	Cu	Hg	Sb	Pb
Control	7.9	0.25	0.54	0.14	14.5	1.40
Zeolite	5.4	0.12	0.33	0.09	5.6	0.93
Slag	7.5	0.20	0.50	0.10	10.2	1.21
A-Zeolite	1.2	0.03	0.12	0.03	2.5	0.34
A-Slag	0.4	0.04	0.08	0.03	2.1	0.32
LSD_{05}	0.1	0.01	0.02	0.01	0.3	0.03

As evident from our results, Si-rich materials such as natural Si-rich mineral zeolite and some types of industrial wastes (slag) can be used for detoxification of contaminated sites and as filters for purification of industrial or mine waste-waters. The efficiency of Si-rich materials can be enhanced by special treatment with concentrated monosilicic acid. The monosilicic acid treatment provides enlarging surface area of the materials.

Several mechanisms can be supposed of Si-rich substances action in the polluted soil-plant system or filter system.

1) Chemical interaction between monosilicic acid and heavy metal with the formation of slightly soluble or insoluble silicates.
2) Inorganic pollutants are chemically adsorbed on the surface of Si-rich materials.
3) Both metal and non-metal pollutants are physically adsorbed by Si-rich substances.
4) Improved plant Si nutrition provides enhancement of plant defense system against pollutant-induced toxicity.

To manage and use these mechanisms efficiently, the information about a type and level of pollution at contaminated site is required. The availability of local Si-rich by-products allows the cost for remediation of polluted area and purification of mine waste-waters to be reduced. To enhance the efficacy of local Si-containing sources, several ways are suggested such as activation and treatment with special substances. Considering a large scale of polluted areas and variability of pollutants, soil-climatic and hydrological conditions, special investigations for further developing and adaptation of the technologies are necessary.

The data obtained has demonstrated the potential of Si-rich substances to reduce the toxicity and mobility of pollutants at a contaminated site. Silicon-rich substances also can be used as filters for reducing the concentrations of metal and non-metal pollutants in mine or industrial waste-waters.

LITERATURE

He, M. 2007: Distribution and phytoavailability of antimony at an antimony mining and smelting area, hunan, China. Environ Geochem Health, 29:209 – 219.
Ji, X., Liu, S., Huang, J., Bocharnikova, E., Matichenkov, V. 2016: Monosilicic acid potential in phytoremediation of the contaminated areas. Chemosphere 157: 132 – 136.
Liang, Y., Sun, W., Zhu, Y.G., Christie, P. 2007: Mechanisms of silicon mediated alleviation of abiotic stresses in higher plants. Environ Pollut. 147: 422 – 428.
Meharg, C., Meharg, A.A. 2015: Silicon, the silver bullet for mitigating biotic and abiotic stress, and improving grain quality, in rice? Environ Exp Bot. 120: 8 – 17.

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AN ORIGINAL APPROACH IN GREEN CHEMISTRY: FROM ASSISTED-PHYTOREMEDIATION OF CONTAMINATED SOIL TO UPCYCLING OF PLANT BIOMASS FOR BIOSOURCED CATALYST PRODUCTION

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KEYWORDS

Assisted phytoremediation, phosphorous amendment, metal, upcycling, ecocatalyst

ABSTRACT

A kitchen garden soil was sampled in a contaminated urban area located in the north of France. Samples were air-dried and crushed to pass through a 10-mm stainless steel sieve. Due to the high heterogeneity of garden soils in the studied area, much attention have been paid on the homogeneity of soil samples. After this step, the mass of sampled soils (48 kg) was divided to obtain four subsamples. Each of them was divided in six replicates, unamended or amended using dicalcium phosphate (DCP) or monocalcium phosphate (MCP) or a mixture of these two compounds (MxP=75%DCP+25%MCP). The phosphorous amendments were added into the soil in small quantity (0.02 %) with the aim at reducing the environmental availability of carcinogenic metals and to increase the Zn availability (Figure 1). After the stabilisation period (2 months) in a greenhouse, 1.5 g of ryegrass seeds (*Lolium perenne* L.) were sown in the 24 containers. Eight weeks after sowing, ryegrass shoots were harvested, oven-dried at 40 °C and calcined at 500 °C in a muffle furnace (Nabertherm P330, Lilienthal, Germany).

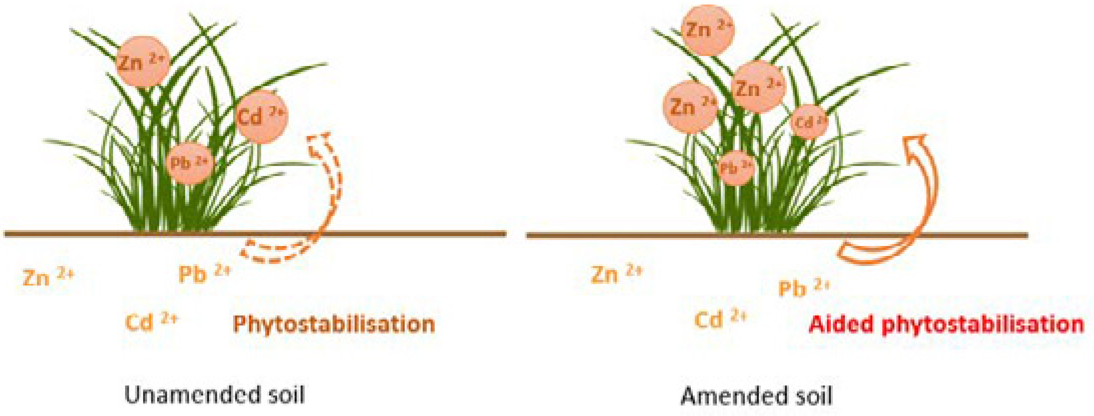


Fig. 1 General scheme of the current study

The shoots of ryegrass were digested by means of an hot block digester (HotBlock$^{\text{TM}}$ Environmental Express$^{\circledR}$SC100, Charleston, USA) according to the USEPA 3050 B method. The concentrations of metals (Cd, Pb and Zn) were determined using an absorption spectrometer (FAAS; Shimadzu, Tokyo, Japan) following the recommendation described in the literature (Savio et al., 2010; Waterlot and Douay, 2009; Waterlot et al., 2011). Note that INCT-OBTL-5 (Virginia tobacco leaves; *n*=3) was used as certified material to check the quality of the analytical procedures. The measured concentrations in the reference material corresponded well to the certified ones (< 10 %).

The concentrations of Cd, Pb and Zn in the shoots of ryegrass were summarized in Table 1. The results clearly showed a significant decrease of the Pb concentrations in the calcined shoots of the ryegrass grown on the amended soil whereas a significant reduction of Cd was only highlighted for DCP amendment. In contrast, a significant increase in the Cd phytoavailability was observed with MCP and MxP. The average concentrations of Zn significantly increased with MCP and MxP while a non-significant increase was observed with DCP.

Lolium perenne L. has been recently described as a suitable plant to restore metallurgical sites (Arienzo et al., 2004; Santibanez et al., 2008; Carvalho et al., 2013). The results of the current study showed that this plant species seems to be appropriate for the accumulation of Cd and Zn from soils and correlated well with few studies in which the authors showed that this ryegrass was a suitable plant to remove Cd and Zn from soils (Jia et al., 2010; Zalewska, 2012).

Tab. 1 Concentration (mean ± standard deviation; *n*=6) of Cd, Pb and Zn measured in the calcined shoots of ryegrass grown in unamended and amended soils

	Unamended soil	**Amended soil with DCP**	**Amended soil with MCP**	**Amended soil with MxP**
Cd (mg kg^{-1})	21.0 ± 0.30	19.5 ± 0.6	26.1 ± 0.6	24.2 ± 0.8
Pb (mg kg^{-1})	57.5 ± 5.5	34.8 ± 5.5	45.0 ± 3.8	47.3 ± 4.6
Zn (mg kg^{-1})	3135 ± 117	3363 ± 220	3870 ± 190	3475 ± 169

Applications of hyperaccumulating plants have been recently summarized in the literature with the aim of producing organic products under green conditions (Hechelski et al., 2018; Deyris and Grison, 2018; Deyris et al., 2018). In view of the above, it was highlighted that the conception of ecocatalyst from these plants appeared interesting when the concentration of metals capable to be transformed into Lewis acids were higher than 1000 mg kg^{-1} dry weight (Escande et al., 2014; Oustriere et al., 2017). It was not the case in the current study since the average concentration of Zn in the shoots of ryegrass from amended soils was 545±73 mg kg^{-1} DW. However, very good ratios Zn/Cd and Zn/Pb were highlighted. As shown in Figure 2, the best results were obtained from ryegrass grown on amended soils with DCP and were up to 172.8±5.3 and 98.4±13.7 for DCP, respectively instead of 149.2±5.3 and 55.0±6.7 for the unamended soils.

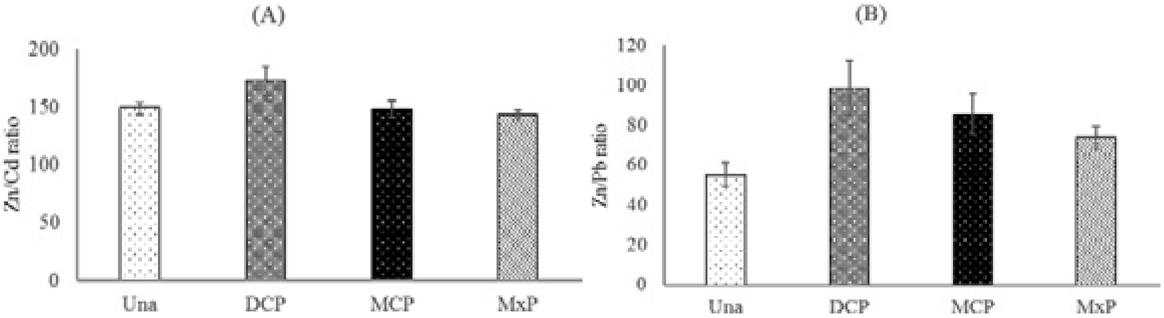
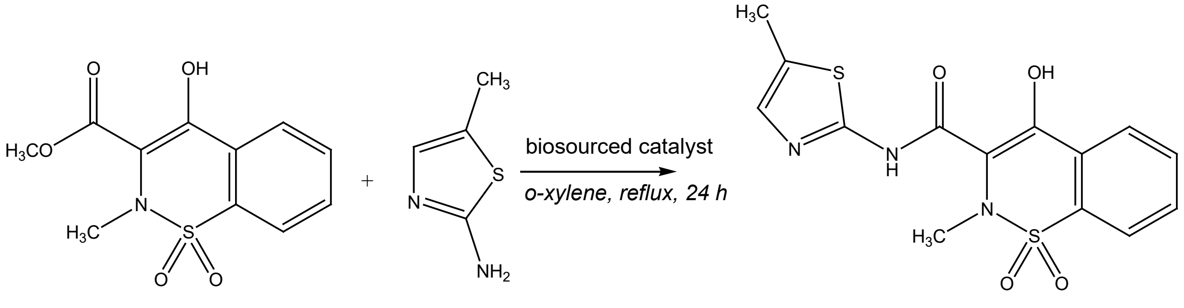


Fig. 2 Zn/Cd (A) and Zn/Pb (B) ratios calculated from the concentration of metals measured in the shoot of ryegrass grown on unamended soils (Una) and amended soils using DCP, MCP and MxP

In view of these results, we have attempted to produce a biosourced catalyst in order to use it in the synthesis of Meloxicam® (**3**), a common nonsteroidal anti-inflammatory agent. This well-known drug was obtained by condensation of methyl 2-methyl-4-hydroxy-2*H*-1,2-benzothiazine-3-carboxylate 1,1-dioxide (**1**) and 5-methyl-2-aminothiazole (**2**) in presence of the biosourced catalyst according to the general scheme described in Figure 3.



1 **2** **3**

Fig. 3 Condensation of substituted methyl carboxylate and 5-methyl-2-aminothiazole using the biosourced catalyst

In order to complete this approach, meloxicam was also produced using commercial zinc chloride following the procedure described in Dufrénoy et al. (2017). Although meloxicam (**3**) was obtained in very good yield using the commercial zinc chloride (82 %; Dufrénoy et al., submitted for publication), better yield was highlighted with the biosourced catalyst (94 %). An important result of this experiment is the limitation of risks related to the human exposition to the Lewis acids due to the volatization of HCl during the hydrolysis reaction of zinc chloride. By using the biosourced catalyst, no hydrolysis is needed and the catalyst may be recovered by simple filtration in order to be re-used in a different process (Dufrénoy et al., in preparation).

In conclusion, the utilization of ryegrass in combination with phosphorous amendments may be a convenient assisted phytoremediation technique to restore the contaminated gardens. On the other hand, dicalcium phosphate was found to be the best amendment to use the shoot biomass of ryegrass as green material to produce a biosourced catalyst. This one was successfully used in the synthesis of drugs like meloxicam (Figure 4), the first advantage being the limitation of waste production.

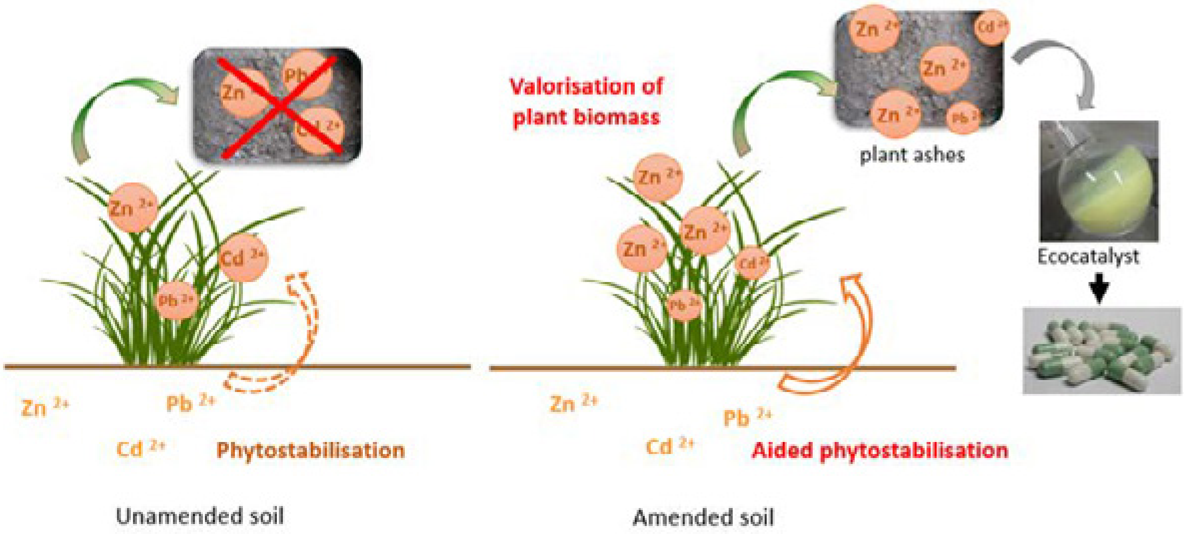


Fig. 4 Assisted remediation of contaminated soils and valorization of plant biomass

LITERATURE

Arienzo, M., Adamo, P., Cozzolino, V., 2004: The potential of *Lolium perenne* for revegetation of contaminated soil from a metallurgical site. Science of the Total Environment, 319, 13–25.

Carvalho, A., Nabis, C., Roiloa, S.R., Rodriguez-Echeverria, S., 2013: Revegetation of abandoned copper mines: the role of seed banks and soil amendments. Web Ecology, 13, 69–77.

Deyris, P.A., Grison, C., 2018: Nature, ecology and chemistry: An unusual combination for a new green catalysis, ecocatalysis. Current Opinion in Green and Sustainable Chemistry, 10, 6–10.

Deyris, P.A., Bert, V., Diliberto, S., Boulanger, C., Petit, E., Legrand, Y.M., Grison, C., 2018: Biosourced polymetallic catalysis: A surprising and efficient means to promote the Knoevenagel condensation. Original Research, 6, 1–9.

Dufrénoy, P., Ghinet, A., Hechelski, M., Daïch, A., Waterlot, C., 2019: An innovative and efficient method to synthesize meloxicam in one-step with respect to the green chemistry. Journal of the Iranian Chemical Society. Submitted for publication.

Escande, V., Olszewski, T.K., Grison, C., 2014: Preparation of ecological catalysts derived from Zn hyperaccumulating plants and their catalytic activity in Diels-Alder reaction. C.R. Chimie, 17, 731–737.

Hechelski, M., Ghinet, A., Louvel, B., Dufrénoy, P., Rigo, B., Daïch, A., Waterlot, C., 2018: From conventional Lewis acids to heterogeneous montmorillonite K10: eco-friendly plant-based catalysts used as green Lewis acids, Chemistry & Sustainability Energy & Materials, 11, 1249 – 1277.

Jia, Y., Tang, S., Wang, R., Ju, X., Ding, Y., Tu, S., Smith, D.L., 2010: Effects of elevated on growth, photosynthesis, elemental composition, antioxidant level, and phytochelatin concentration in *Lolium multiforum* and *Lolium perenne* under Cd stress. Journal of Hazardous Materials, 180, 384–394.

Oustrière, N., Marchand, L., Roulet, E., Mench, M., 2017: Rhizofiltration of a Bordeaux mixture effluent in pilot-scale constructed wetland using Arundo donax L. coupled with potential Cu-ecocatalyst production. Ecological Engineering, 105, 296–305.

Santibanez, C., Verdugo, C., Ginocchio, R., 2008: Phytostabilization of copper mine tailings with biosolids: implications for metal uptake and productivity of *Lolium perenne*. Science of the Total Environment, 995, 1–10.

Savio, M., Cerutti, S., Martinez, L.D., Smichowski, P., Gil, R.A., 2010: Study of matrix and spectral interferences in the determination of lead in sediments, sludges and soils by SR-ETAAS using slurry sampling. Talanta, 82, 523–527.

Waterlot, C., Bidar, G., Pruvot, C., Douay, F., 2011: Analysis of cadmium in water extracts from contaminated soils with high arsenic and iron concentration levels. Journal of Environmental Science and Engineering, 5, 271–280.

Waterlot, C., Douay, F., 2009: The problem of arsenic interference in the analysis of Cd to evaluate its extractability in soils contaminated by arsenic. Talanta, 80, 716–722.

Zalewska, M., 2018: Response of perennial ryegrass (*Lolium perenne* L.) to soil contamination with zinc. Journal of Elementology, 329–343.

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COMBINING SELECTIVE SEQUENTIAL EXTRACTIONS AND X-RAY ADSORPTION SPECTROSCOPY FOR ZN SPECIATION IN SPOLIC TECHNOSOLS

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KEYWORDS

Contaminated soil, zink, fractional composition, XANES, EXAFS

ABSTRACT

The input of heavy metals (HMs) into land and aquatic ecosystems is favored by large chemical enterprises, which put a great pressure on the environment by their waste (gaseous, liquid, and solid). Environmental risks especially increase for soils in river floodplains, which is related to their location in the lower part of cascade landscape-geochemical system (Glazovskaya, 1988). The composition of metal compounds significantly affects their mobility, bioavailability, and toxicity in contaminated soils and adjacent environments. Chemical methods of sequential extraction are widely used for assessing the forms of metal compounds in soils (Minkina et al., 2010).

Study of Zn accumulation and transformation in highly contaminated technogenically transformed soils near the sediment pond of chemical plant using a combination of chemical fractionation with direct nondestructive physical methods, including X-ray absorption spectroscopy (XANES and EXAFS).

X-ray diagnostic methods—X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) — have identified forms of many metals and metalloids in contaminated soils and sediments at the molecular level during the last 30 years (Jacquat et al., 2009; Manceau et al., 2000; Singh and Gräfe, 2010).

The area under study is located in the Severskii Donets River floodplain, Kamenskii district of Rostov region, southern Russia (48°20′42.15" N, 40°14′14.46" E). Lake Atamanskoe, which was used as a wastewater disposal basin of a chemical plant from the early 1950s to the 1990s, is a dried up oxbow (Fig. 1.).

In the present work, two monitoring plots with high levels of technogenic contamination were selected on the area adjacent to the lake. Monitoring plot D0, which is at 2 km from the contamination source, is occupied by a background soil: Fluvisol (IUSS, 2015) (Fig. 1). Technogenically transformed soils on plots D1 and D4 are classified as Spolic Technosols.

The main physical and chemical characteristics of the soil were determined according Vorob'eva (2006). The contents of total Mn, Cr, Ni, Cu, Zn, Pb, and Cd were determined by the X-ray fluorescence method on a MAKS-GV spectroscane. The composition of Zn compounds in soils was determined by the sequential fractionation method proposed by Tessier et al. (1979).

This method ensures the separation of five metal fractions: exchangeable (1 M $MgCl_2$), carbonate-bound (1 M CH_3COONa), Fe/Mn (hydr)oxide-bound (0.04 M NH_2OH•HCl in 25 % CH_3COOH), organic matter-bound (0.02 M HNO_3 + 30 % H_2O_2 (pH 2), then 3.2 M CH_3COONH_4 in 20 % HNO_3), and residual (HF + $HClO_4$, then HNO3conc.) fractions. The content of Zn in extracts was determined by atomic absorption spectrophotometry (AAS).

XANES and EXAFS spectra were collected at the Zn K-edge (9659 eV) on the beamline "Structural Materials Science" (Chernyshov et al., 2009) of the Kurchatov Synchrotron Radiation Source (National Research Center "Kurchatov Institute", Moscow, Russia) with the storage ring operating at 2.5-GeV beam energy and beam currents between 70 and 90 mA. EXAFS data were analyzed using the Viper and IFEFFIT 1.2.11 data analysis packages.

Characterization of some physical and chemical properties of the investigated soil are given in Table 1.

Chemical fractionation of Zn compounds on monitoring plot D0 taken as a background plot revealed the dominance of Zn in the residual fraction bound to silicates (64 % of the sum of all fractions). Fe–Mn (hydr)oxides also significantly contribute to the strong fixation of Zn: they contain 17 % of total metal (Fig. 2). The low mobility and dominance of Zn in the residual fraction confirm the absence of significant amounts of technogenic metal in the background soil. In the uncontaminated (background) soil, the following distribution of Zn among the compounds forms is revealed: residual fraction > Fe–Mn (hydro)oxide-bound fraction > organic matter-bound fraction > carbonate-bound fraction > exchangeable fraction.

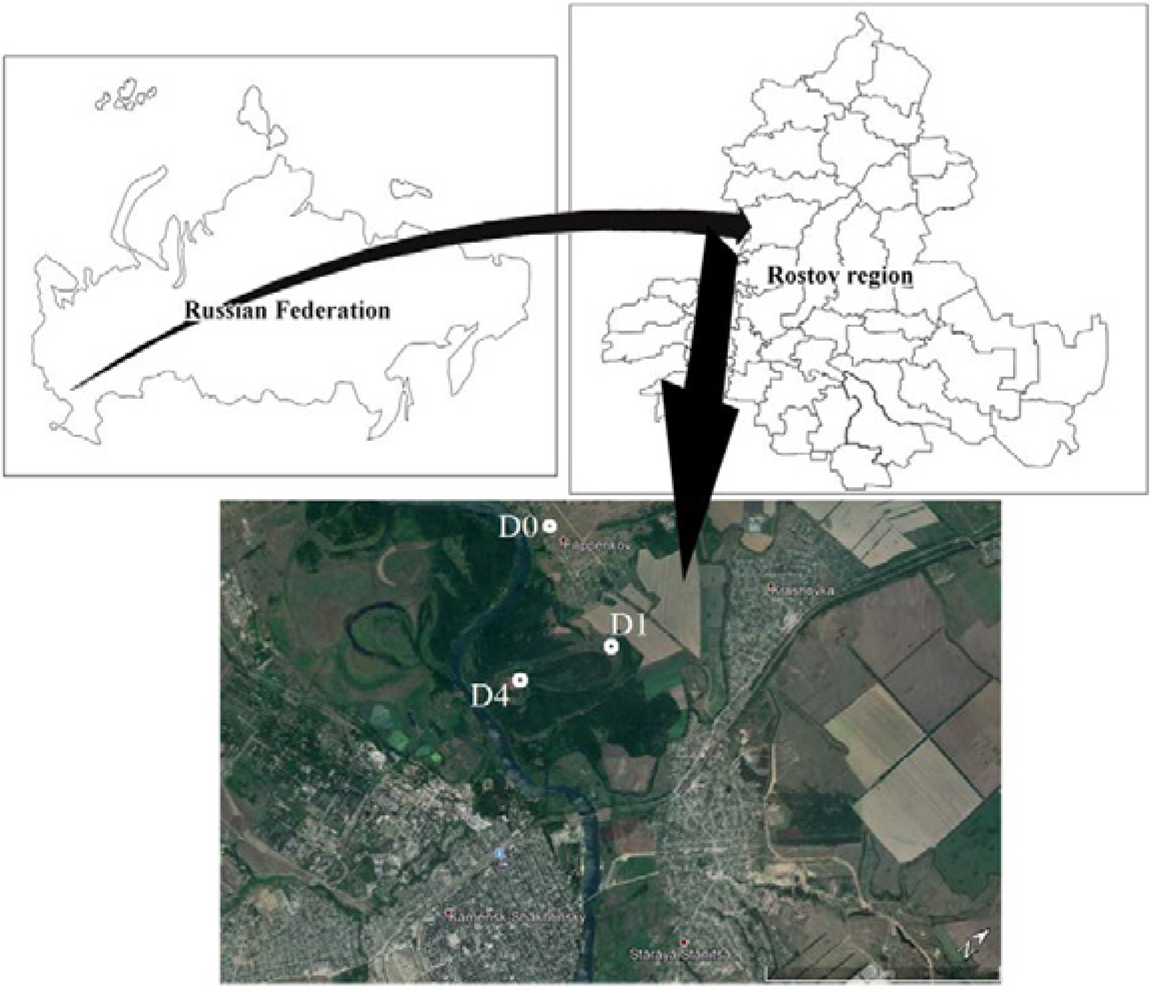

Fig. 1 General scheme of the Lake Atamanskoe region in the industrial zone of the city of Kamensk-Shakhtinskii, Rostov oblast, Russia. Monitoring plots are denoted with circles

Tab. 1 Physical and chemical properties Fluvisol (background soil D0) and Spolic Technosols of the investigated monitoring plots

Sample/Parameter		D0	D1	D4
C_{org},%		3.4±0.1	2.8±0.2	4.4±0.2
pH_{H2O}		7.3±0.2	7.7±0.1	7.7±0.3
$CaCO_3$, %		1.3±0.02	7.8±0.2	5.3±0.3
Exchangeable Ca^{2+}, cmol(+)/kg		31.0±2.4	29.2±2.0	35.2±1.7
Exchangeable Mg^{2+}, cmol(+)/kg		4.5±0.3	4.8±0.1	5.0±0.2
Material (chemical) composition, %	SiO_2	62.8±7.1	61.1±4.1	54.8±5.4
	Al_2O_3	14.7±0.6	15.0±0.8	11.8±0.7
	Fe_2O_3	7.5±0.3	7.9±0.1	6.0±0.1
	CaO	3.2±0.1	3.6±0.05	11.7±1.0
	MgO	1.5±0.09	1.3±0.03	2.0±0.1
	K_2O	2.1±0.08	1.9±0.03	1.4±0.2
	P_2O_5	0.2±0.02	0.2±0.003	0.2±0.001
	SO_3	0.03±0.003	4.3±0.03	7.3±0.1
	Na_2O	1.0±0.04	0.9±0.02	0.9±0.03
Total Zn content, mg/kg	Zn *(83*)*	90.0±7.6	**25973.0±1780.0**	**62032.0±5903.0**

(*) lithosphere clark (Vinogradov, 1957); excesses over the clarks are highlighted in bold.

In highly contaminated technogenic soils, an increase in the exchangeable fraction and the fractions bound to Fe and Mn oxides and carbonates, which increased their relative contents (Fig. 2). In soils on monitoring plots D1 and D4, the residual fraction is dominant; it makes up 46 % of total metal content (Fig. 2).

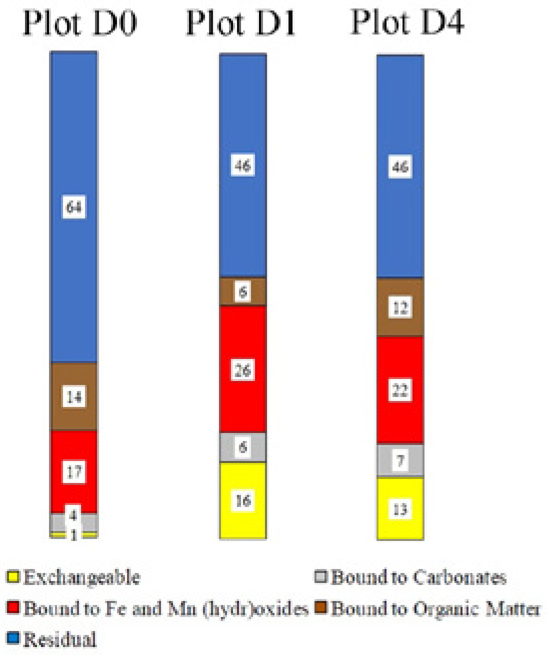

Fig. 2 Fractional composition of Zn in Fluvisol (D0) and Spolic Technosols, % of total content

The distribution of Zn among the fractions is changed compared to the background soil: residual fraction > Fe–Mn (hydro)oxide-bound fraction > exchangeable fraction ≥ organic matter-bound fraction > carbonate-bound fraction.

The sensitivity of the XANES spectra to the geometry of bonds can be used for the preliminary qualitative estimation of the molecular structural state of local Zn surrounding in soil samples. The XANES spectra of Zn for several standard compounds with the known structure of Zn–S (ZnS) and Zn–O (ZnO and $ZnSO_4$) bonds show a significant difference in the position of absorption edge, which makes it possible to discriminate these types of Zn surrounding in soil samples.

The XANES and Fourier transformed K-edge EXAFS spectra of Zn in two Spolic Technosols samples show obvious differences, which confirm the different speciations of Zn in these samples. The Fourier transformed EXAFS spectrum for soil sample D1 is more similar to the analogous spectrum of $ZnSO_4$, although it contains an additional intense peak at lower R. The absence of the peak corresponding to the second coordination sphere (Zn–Zn) indicates that ZnO is not the dominant component of the sample. In the Technosols of monitoring plot D4, the main peaks in the Fourier transformed EXAFS spectrum correspond to sphalerite, which is indicative of the dominance of Zn–S bonds (Minkina et al., 2018). However, an additional feature at lower R is indicative of presence of Zn–O bonding in the sample. It was shown (Voegelin et al., 2005), that when the soil is contaminated with zincite, ZnO is transformed and mainly enters into Zn-containing trioctahedral structures (up to 64% during the first year).

The Zn–O bond lengths for D1 samples are closer to those of $ZnSO_4$ (1.95–2.04 Å) than to ZnO. The estimations on the basis of the Zn–S and Zn–O coordination numbers for soil D4 show that it contains about 70 % Zn–S bonds and 30 % Zn–O bonds. According to the results obtained for the upper horizon of strongly contaminated soils in Palmerton (Scheinost et al., 2002), the dominant fixation of Zn was due to sulfide (sphalerite).

Representative soils from area with high level of Zn contamination have been selected. Zn distribution in the soil components was investigated using sequential chemical extraction and X-ray absorption spectroscopy. The occurrence forms of Zn have been identified in studied Spolic Technosols compared to the uncontaminated soil. Phyllosilicates and Fe and Mn (hydr)oxides were the main stabilizers of Zn mobility. The residual fraction of technogenically transformed soils contained the highest proportion of Zn (46%) indicating the most form of Zn is strongly retained in soil. The fitting results of EXAFS data on the metal state in Spolic Technosols revealed 70% of Zn–S bonds and 30% of Zn–O bonds. Dominant portion of authigenic minerals in mineral phase of Spolic Technosols was due to the composition of pollutants contaminating the floodplain landscapes for a long time.

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LITERATURE

Chernyshov, A.A., Veligzhanin, A.A., Zubavichus, Y.V., 2009: Structural materials science end-station at the Kurchatov Synchrotron radiation Source: recent instrumentation upgrades and experimental results. Nucl. Instr. Meth. Phys. Res. A. 603, 95–98.

Glazovskaya, M.A., 1988: Geochemistry of Natural and Industrial Landscapes of the USSR. Vysshaya Shkola, Moscow (in Russian).

IUSS Working Group WRB. World reference base for soil resources 2014, update 2015., 2015: International soil classification system for naming soils and creating legends for soil maps. World soil resources reports, FAO, Rome, issue 106.

Jacquat, O., Voegelin, A., Kretzschmar, R., 2009: Soil properties controlling Zn speciation and fractionation in contaminated soils. Geochim. Cosmochim. Acta. 73, 5256–5272.

Manceau, A., Lanson, B., Schlegel, M.L., Harge, J.C., Musso, M., Eybert-Berard, L., Hazemann, J.L., Chateigner, D., Lamble, G.M., 2000: Quantitative Zn speciation in smelter-contaminated soils by EXAFS spectroscopy. Am. J. Sci. 300, 289–343.

Minkina, T.M., Motusova, G.V., Nazarenko, O.G., Mandzhieva, S.S., 2010: Heavy metal compounds in soil: transformation upon soil pollution and ecological significance. Nova Science Publishers Inc.

Minkina, T., Nevidomskaya, D., Bauer, T., Shuvaeva V., Soldatov,, A., Mandzhieva , S., Zubavichus, Y., Trigub, A., 2018: Determining the speciation of Zn in soils around the sediment ponds of chemical plants by XRD and XAFS spectroscopy and sequential extraction. Science of the Total Environment. 634, 1165–1173.

Scheinost, A.C., Kretzchmar, R.S., Pfister, S., 2002: Combining selective sequential extractions, X-ray adsorption spectroscopy, and principal component analysis for quantitative zinc speciation in soil. Environ Sci. Technol. 36, 5021–5028.

Singh, B., Gräfe, M., 2010: Synchrotron-Based Techniques in Soils and Sediments, Elsevier.

Tessier, A., Campbell, P.G. C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem. 51, 844–850.

Vinogradov, A.P., 1957: Geochemistry of rare and dispersed chemical elements in soils, RAN, Moscow (in Russian).

Voegelin, A., Pfister, S., Scheinost, A.C., Marcus, M.A., Kretzshmar, R., 2005: Changes in zinc speciation in field soil after contamination with zinc oxide. Environ. Sci. Technol. 39 (17), 6616–6123.

Vorob'eva L.A., 2006: Theory and practice chemical analysis of soils, GEOS, Moskow, pp 1 – 400, (in Russian).

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RISK ASSESSMENT OF Cu AND Mo EXPOSURE THROUGH CONSUMPTION OF VEGETABLES GROWN UNDER THE IMPACT OF KAJARAN'S MINING COMPLEX

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KEYWORDS
Daily intake, exposure, health risk, mining, soil-to-plant transfer, trace elements.

ABSTRACT

Mining industry is one of the priority branches of Armenia's economy. The activities of mining complexes without treatment facilities have a grave impact on the environment. Transfer of trace elements from soil to plant cannot be underestimated as it is the major pathway of human exposure. For this purpose, firstly, trace element contents in soils and plant species were determined, afterwards, transfer factor (TF) and estimated daily intakes (EDI) were calculated. Topsoil sampling was done according to Standard Operation Procedures (SOPs). Locally grown and widely consumed plant samples were collected from the same soil sampling points according to WHO and FAO requirements (WHO/FAO 2008). 12 samples of soil and 32 samples of vegetables were collected. Concentrations of trace elements (Cu and Mo) in soil and plant samples were estimated using atomic absorption spectrophotometer. This study included the development of a food frequency questionnaire (FFQ). The obtained results indicated that TF values varied from element to element depending on vegetables types. The smallest value of TF was obtained for Cu (carrot) and the highest one for Mo (fennel). Soil-to-plant transfer factors were less than 1. Lower values indicate poor response of plants towards element uptake. It should be stressed, that EDIs of Mo for all investigated vegetables exceeded the reference value, while EDI of Cu exceeded only for potato and bean. Furthermore, detailed investigations need to be done for the overall assessment of health risks, taking into consideration also the adverse health effects posed by more than one toxic trace element.

INTRODUCTION

Mining industry is one of the key elements for economic development of a country, while at the same time it is an important source of environmental contamination by heavy metals (Ding et al., 2017). In Armenia the grave impact of mining industry on environment is linked with violations, particularly mining complexes without treatment facilities, discarding the waterways of miner waters, inappropriate management and failure of tailings dams (Pipoyan et al., 2018).

The previous studies carried out in Kajaran city, one of the largest mining centers of Armenia, reported the high concentrations of Mo and Cu in soils. Moreover, the results of continuous geochemical investigations in this province declare that mentioned elements are of primary environmental concern (Saghatelyan et al., 2010, Tepanosyan et al., 2018). It is also crucial to note, that intensive accumulation of trace elements in agricultural soils is a both environmental and food safety concern as several plants can accumulate toxic trace elements and pose adverse health effect (Pipoyan et al., 2018).

Plant origin products have a significant share in diet of Armenia's population. According to the data of Statistical Committee of the Republic of Armenia (Armstat, 2016) per capita consumption of potatoes, vegetables and fruits is equal to 1074.4 g from which potatoes are 189.9 g, vegetables are 617.2 g and fruits are 267.3. This indicates that exposure of trace elements through consumption of these food items is highly important as it is the major pathway to human exposure (Li et al., 2018). Therefore, this research aims to study the transfer of Mo and Cu from soil to plant and assess linked health risks to residents of Kajaran city. This is the first attempt to understand the health risk posed by consumption of local vegetables produced in small farmlands. Moreover, produced plant origin items are intended for self-consumption and are out of state control. Therefore, the obtained data would be important also for public awareness.

MATERIAL AND METHODS

Study site

The city of Kajaran (N 39°9′and E46°9′) is located on east slope of Zangezur Mountains (Syunik province), and partially covers northern spurs of the Meghri ridge, in headwaters of Voghji River. Kajaran is one of the largest mining centers of Armenia. The main activity of the city is related to exploitation of Zangezur Copper Molybdenium Combine (ZCMC). In formulation of geological structure of the study area take part volcanogenic sedimentary and intrusive rocks of Tertiary period - minzonits and porphyry granites. To the monozites, it is dated Kajaran's sulphidic copper-molybdenum (Cu-Mo) field located near Mount Gandzasar, there are two types metalizing: stringer-disseminated (the main type) and vein (subordinary type). The main minerals of the Kajaran field - molybdenite and chalcopyrite, with which associate pyrite, magnetite, hematite, blende and so forth and also tellurium (Te) and gold (Au). Besides ore and ore concentrates contain significant amounts of rhenium (Re), selenium (Se) and silver (Ag) (Saghatelyan et al., 2008, Tepanosyan et al., 2018).

Sampling

Topsoil sampling was done according to Standard Operation Procedures (SOPs) based on ISO and US EPA standards (Tepanosyan et al., 2018). Locally grown and widely consumed plant samples were collected from the same soil sampling points according to WHO and FAO requirements (WHO/FAO, 2008). Overall, 12 samples of soil and 32 samples of available cultivated vegetables (potato, carrot, bean, fennel and pumpkin) were collected in September of 2015.

Analyses

The total contents of heavy metals (Cu, Mo) in soils were determined by X-ray fluorescence spectrometry (EDXRF X-5000) (Innov-X Systems, 2003, USA). A PerkinElmer Analyst 800 AAS was used to quantify the total metal concentrations in vegetables. Standard stock solution of 1000 ppm for all the metals was obtained from SchelTec, authorized distributor of PerkinElmer.

The quality assurance and quality control (QA/QC) of soil and plant analyses include application of standard reference materials (NIST 2711a, NIST 2710a, SRM 1570a, SRM 1573a) purchased from the National Institute of Standards and Technology of the USA. Precision and accuracy of analyses were guaranteed by repeated analysis of samples.

Diet assessment

For diet study, individual based approach was used. A food frequency questionnaire (FFQ) was developed as a "list-based diet history" consisting of a structured listing of individual foods (WHO/FAO, 2008). 103 males and 97 females (18 – 70 years old) participated in this study. The data analyses were carried out from August to December, 2015 using SPSS software (SPSS Inc., version 11).

Data analysis

Transfer factor (TF)

Transfer of Cu and Mo from soil to edible part of the plant was calculated as follows:

$$\mathrm{TF} = C_{plant} / C_{soil} \qquad (1)$$

where C_{plant} and C_{soil} represent the concentration of element in plant and soil (Adamo et al., 2014).

Estimated daily intake (EDI)

The EDI of Cu and Mo was calculated using the equation recommended by the US EPA (US EPA, 1997).

$$\mathrm{EDI} = (C \times IR \times EF \times ED)/(B_W \times AT) \qquad (2)$$

where C is the trace element content in vegetable; EF is the exposure frequency (except potato (365 d/year), for all other investigated vegetables 183 d/year); ED is the exposure duration (63.6 year for males and 69.7 year for females, based on the average life expectancy, starting from 8 years of age); B_W is the body weight (kg) for males and females (70 and 60 kg, respectively); AT is the time period over which the dose is averaged (365 d multiplied number of exposure years). According to our diet survey (FFQ) in the studied region, the ingestion rate (IR) for potato, carrot, bean, fennel and pumpkin was 0.21, 0.09, 0.11, 0.01 and 0.03 kg/d, respectfully.

Cumulative daily intakes were calculated as the sum of individual EDI values for each trace element.

Target hazard quotient (THQ)

The human health risk through Cu and Mo exposure is defined by the THQ (US EPA, 1997) which is based on non-carcinogenic risk and is calculated by the ratio of the EDI to the oral reference dose (RfD) of element.

$$THQ = {}^{EDI}/_{RfD} \qquad (3)$$

Dietary reference intake (0.01 mg/kg/BW/d) was used as a RfD for Cu (ATSDR, 2004). The RfD of Mo was considered 0.005 mg/kg/BW/d (US EPA, 1992).

RESULTS AND DISCUSSION

Soil-to-plant transfer of Cu and Mo

The soil-to-plant transfer factors (TF) were evaluated by dividing the contents of trace elements in studied vegetables (Table 1) by average content of trace element in soil samples (Table 2).

Soil-to-plant TFs for Cu and Mo are given in Table 3. Obtained results indicate that TF values varied from element to element depending on type of vegetables. The smallest value of TF was obtained for Cu (carrot) and the highest one for Mo (fennel). For all studied vegetables soil-to-plant TFs were less than 1, which indicate poor response of plants towards element uptake.

Table 1. The contents of trace elements in vegetables from investigated areas

Plant species	**Contents (mg/kg, fresh matter)**			
	Cu		**Mo**	
	Mean	**SD**	**Mean**	**SD**
Potato	12. 01	3.38	26.59	9.13
Carrot	5.77	1.75	6.95	9.13
Bean	12.0	2.79	47.93	8.77
Fennel	27.62	6.28	46.42	17.55
Pumpkin	13.17	7.18	28.86	10.64

Table 2. The contents of trace elements in soil samples from investigated areas

Metals	**Contents (mg/kg fresh matter) in soil samples**												**Average (mg/kg)**
	K1	**K2**	**K3**	**K4**	**K5**	**K6**	**K7**	**K8**	**K9**	**K10**	**K11**	**K12**	
Cu	540	580	480	440	340	420	380	320	280	330	220	260	**383**
Mo	140	220	240	260	180	130	220	240	140	300	180	320	**214**

Table 3. Soil-to-plant transfer factor of Cu and Mo

Plant species	**Transfer factor of Cu**	**Transfer factor of Mo**
	Range	**Range**
Potato	0.03	0.084 – 0.112
Carrot	0.014 – 0.018	0.026 – 0.047
Bean	0.027 – 0.034	0.16 – 0.2
Fennel	0.067 – 0.079	0.17 – 0.44
Pumpkin	0.034 – 0.040	0.083 – 0.134

Non-carcinogenic risk assessment of Cu and Mo

The health risk assessment of Cu and Mo includes also the diet study for residents of Kajaran city. The corresponding estimates for daily intake of Cu and Mo through consumption of fife species of vegetables are presented in Table 4.

Table 4. Estimated daily intake (EDI) of trace elements in vegetables

Plant species	**EDI of Cu (mg/kg/day)**		**EDI of Mo (mg/kg/day)**	
	Male	**Female**	**Male**	**Female**
Potato	**0.0360**	**0.0420**	**0.0798**	**0.0931**
Carrot	0.0074	0.0087	**0.0089**	**0.0104**
Bean	**0.0189**	**0.0220**	**0.0753**	**0.0879**
Fennel	0.0039	0.0046	**0.0066**	**0.0077**
Pumpkin	0.0056	0.0066	**0.0124**	**0.0144**
Cumulative daily intake	**0.0718**	**0.0839**	**0.183**	**0.2135**
Reference values	**0.01**		**0.005**	

Note: *Exceeded EDI values are bolded.*

The estimated daily intakes of Mo for all investigated vegetables exceeded the reference value (0.005 mg/kg/day). In contrast to this, the EDI values of Cu exceeded the reference value (0.01 mg/kg/day) only for potato and bean. Meanwhile, when considering the combined consumption of investigated vegetables, the estimated cumulative daily intakes exceeded the reference values both for Cu and Mo.

In order to assess whether the investigated vegetables have a potential to pose non-carcinogenic health risks target hazard quotient (THQ) was assessed. If the value of THQ is less than 1, the risk of non-carcinogenic toxic effects is assumed to be low. The obtained outcomes for THQ assessment are presented in Figure 1.

According to presented data (Figure 1) the ranking orders of THQ both for Mo and Cu in vegetables were as follows: potato > bean > carrot > pumpkin > fennel. The THQ values for Mo were more than safety level (THQ>1) for all investigated vegetables. In contrast to this, the THQ values of Cu were more than 1 only in case of potato and bean consumption. It is crucial to underline, that for potato and bean THQ values of Mo were more than 15. From human health point of view, this indicates that consumption of these food items has a high potential to pose adverse health effects to local population.

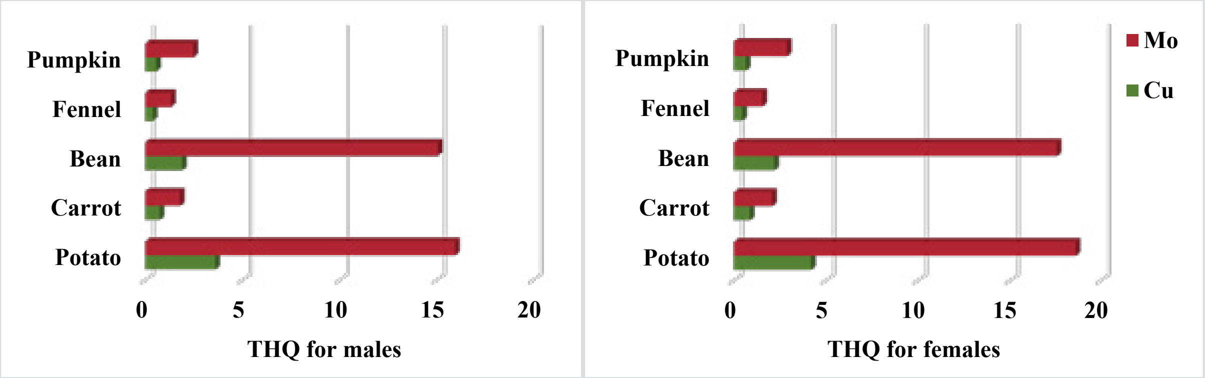

Fig. 1 Target hazard quotients (THQs) of trace elements.

CONCLUSIONS

The investigation of soil-to-plant transfer of Cu and Mo indicated poor response of studied vegetables towards these element uptakes. Meanwhile, health risk assessment of Cu and Mo indicated that local population would experience significant health risks if they only ingested these two metals from all studied vegetables. So, the main outcomes of this study provided some insight for health risk assessment of potentially toxic trace elements (Mo and Cu) and served as a basis for comparison to other mining regions in Armenia.

LITERATURE

Adamo, P., Iavazzo, P., Albanese, S., Agrelli, D., De Vivo, B., Lima, A., 2014: Bioavailability and soil-to-plant transfer factors as indicators of potentially toxic element contamination in agricultural soils. Sci Total Environ, 500, 11-22.
Armstat (Statistical Committee RA) 2016: Available at http://armstatbank.am/pxweb/en/ArmStatBank/ArmStatBank__7%20Food%20Security/FS-1-2016.px/table/tableViewLayout2/?rxid=002cc9e9-1bc8-4ae6-aaa3-40c0e377450a).
ATSDR 2004: Toxicological Profile for Copper. Update. Agency for Toxic Substances and Diseases Registry, Centers for Disease Control, Atlanta, GA, USA. Available at https://www.atsdr.cdc.gov/toxprofiles/tp.asp?idD206&tidD37.
Ding, Q., Cheng, G., Wang, Y., Zhuang, D., 2017: Effects of natural factors on the spatial distribution of heavy metals in soils surrounding mining regions. Sci Total Environ 578:577–85.
Li, X., Li, Z., Lin, C.J., Bi, X., Liu, J., Feng, X., Wu, T., 2018): Health risks of heavy metal exposure through vegetable consumption near a large-scale Pb/Zn smelter in central China. Ecotoxicology and environmental safety, 161, 99 – 110.
Saghatelyan, A.K., Gevorgyan, V.S., Arevshatyan, S.H., Sahakyan, L.V., 2008: Ecological and Geochemical Assessment of Environmnetal State of the City of Kajaran. Yerevan.
Saghatelyan, A.K., Sahakyan, L.V., Menchinskaya, O.V., Zangiyeva, T.D., Kajtukov, M.Z., Uzdenova, Z.H., 2010: Medical geology in connection to mining. Medical Geology in Russia and the NIS, 242 – 247.
Tepanosyan, G., Sahakyan, L., Belyaeva, O., Asmaryan, S., Saghatelyan, A., 2018: Continuous impact of mining activities on soil heavy metals levels and human health. Sci Total Environ, 639, 900.
US EPA 1992: Molybdenum; CASRN 7439-98-7, Washington, DC, USA. Available at https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm?substance_nmbr=425.
US EPA 1997: Exposure Factors Handbook. EPA/600/P-95/002F. Washington, DC, USA. Available at https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deidD12464.
WHO/FAO 2008: Dietary Exposure Assessment of Chemicals in Food. Annapolis, Maryland, USA. Available at http://apps.who.int/iris/bitstream/10665/44027/1/9789241597470_eng.pdf.
Pipoyan, D., Beglaryan, M., Costantini, L., Molinari, R., Merendino, N., 2018: Risk assessment of population exposure to toxic trace elements via consumption of vegetables and fruits grown in some mining areas of Armenia. Human Ecol Risk Assess: An Int J 24(2):317 – 30.

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TRACE ELEMENTS CONCENTRATION IN SELECTED URBAN SOILS OF THE RUSSIAN ARCTIC

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Soils play a crucial role in Arctic ecosystems functioning determining their geochemical regime directly through accumulation, migration and transformation of energy and matter. Increasing rates of anthropogenic forcing on natural and urban ecosystems in the Arctic requires development of more detailed environmental monitoring. In this context, studying of background trace elements contents seems to be actual goal. In addition, soils play very significant role for various ecosystem services (Morel et al., 2015).

On the one hand, trace elements are naturally present in parent materials and soils occurring in the form of sulfides, oxides, silicates, and carbonates (Antcibor et al., 2014). At the same time trace metals are considered as the major group of anthropogenic contaminants in soils. Studies conducted earlier, showed that trace metals can reach the Arctic by different paths both anthropogenic and natural origin (Akeredolu et al., 1994; Barrie, 1985, 1992; Rahn al., 1997; Rovinskiy et al., 1995; Thomas et al., 1992). Metallurgical and energy industries are usually accompanied by the emission of acid-forming substances. These substances can be transported over long distances and can contribute leaching of such labile elements as aluminum, cadmium, zinc (Nikitina et al., 2015).

Studying of pollutant behavior in both urban and natural soils seems to be one of the most important issues for investigations in further decades. Such investigations could be used for making accurate risk assessments concerning such aspects as human health and long-term ecological effects. Approaches to establishment of limit values and identifying priorities concerning the remediation of contaminated sites could be also developed (Linde, 2005). Data concerning the trace elements content in soil of the Arctic is limited and should be state as insufficient. Evaluation of anthropogenic impacts on Arctic ecosystems requires not only background levels of trace metals, but also landscape distribution of elements in permafrost-affected soils in relation to soil properties (Antcibor et al., 2014).

This study is aimed to evaluation of trace elements content of urban soils in Yamal region and Murmansk.

Our investigation isconducted on the territory of Yamal autonomous region within the settlements (Aksarka, Kharsaim, Kharp, Labytnangi, Salekhard) and Murmansk. Both regions are referred to the zone of discontinuous permafrost.

Table 1. General field information on studied key plots

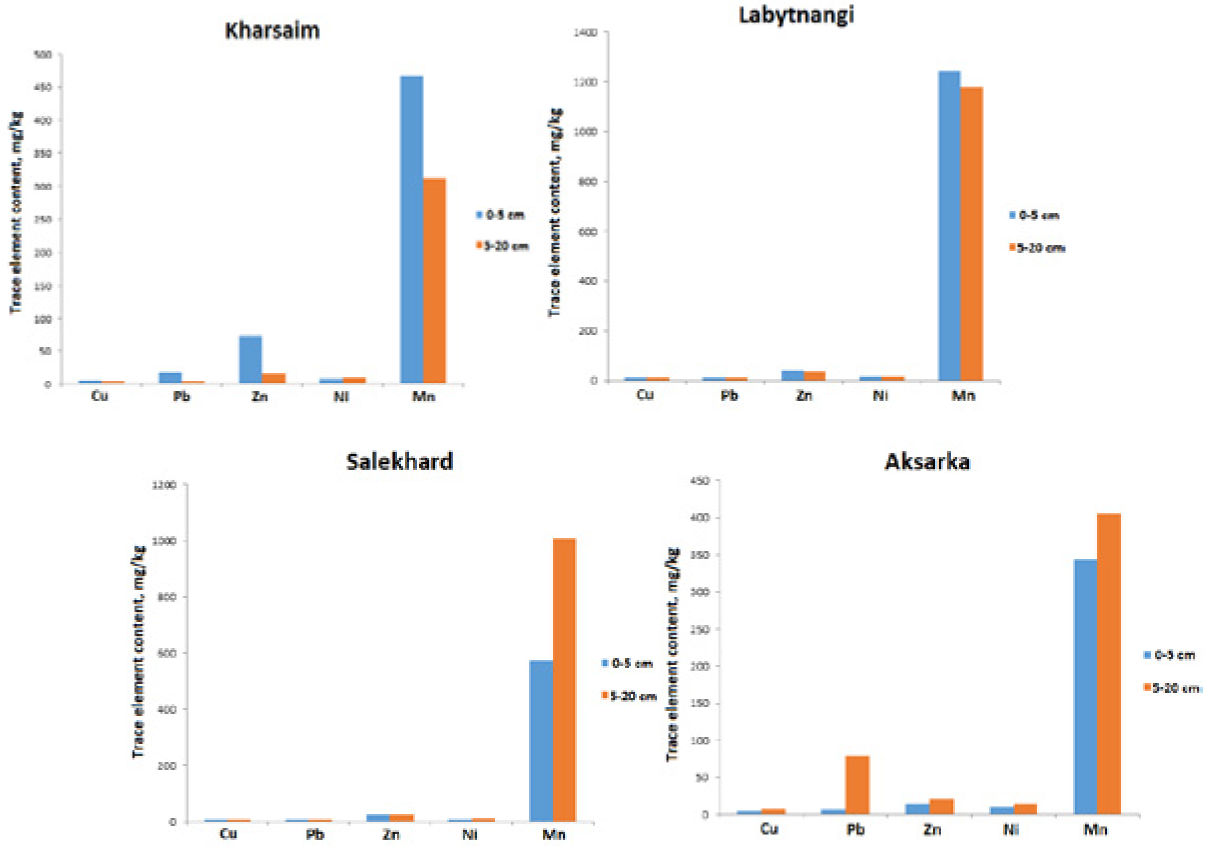
Key plot	Geographical coordinates	Functional zone/Landscape description	Name of the soils in WRB (2014); Russian soil classification system (2008)
Aksarka	N 66°33′54,3′′ E 67°48′04,8′′	Recreational functional zone	Urbic Technosol; Urbanozem
Kharsaim	N 66°35′54,7′′ E 67°18′34,2′′	Recreational functional zone	Urbic Technosol; Urbanozem
Salekhard	N 66°33′31,9′′ E 66°34′07,2′′	Residential functional zone	Urbic Technosol; Urbanozem
Labytnangi	N 66°40′01,1′′ E 66°20′59,6′′	Industrial functional zone	Urbic Technosol; Technozem
Kharp	N 66°48′34,0′′ E 65° 47′08,0′′	Industrial functional zone	Urbic Technosol; Technozem
Murmansk	N 68°58′45′′ E 33°05′33′′	Recreational (x2)/Industrial/Residential functional zone	Urbic Technosol/Histic gleyic Podsol/Urbic Technosol/Entic Podzol; Torfyano-stratozem/Torfyano-Podzol gleeviy/Urbo-stratozem/Torfyano-Podbur gleeviy

Soil classification was conducted according to “Classification and diagnostics of Russian soils” (Shishov et al., 2004) and World Reference Base for Soil resources (FAO, 2014). Detailed description of studied key plots is given in Table 1.

Ecotoxicological state of Russian Arctic cities is underestimated. That is why this study was aimed to investigate trace metals content in soils of both Yamal and Murmansk urban environments, and to deduce profile trends of distribution trace metals in permafrost-affected soils of studied urban areas. During the investigation 12 sites in Yamal region and four sites in Murmansk were studied.Samples were taken from a depth of 0-5 cm and 5-20 cm. Soil samples have been collected in industrial (Labytnangi, Kharp, Murmank), residential (Salekhard), recreational functional zones (Aksarka, Kharsaim, Murmansk). Laboratory analysis was conducted in the Komi Scientific Centre Laboratory of the Russian Academy of Sciences. Trace elements contents (Pb, Cu, Ni, Zn, Mn) were determined with an X-ray fluorescent analyzer "Spectroscan-MAX" (OST 10-259-2000).The values obtained were compared with the permissible concentrations and maximum allowable concentrations adopted in Russia named in GN 2.1.7.2511-09 (GN 2.1.7.2511-09), GN 2.1.7.2041- 06 (GN 2.1.7.2041-06) and SanPin 42-128-4433-87 (SanPiN 42-128-4433-87).

Results on trace elements content for investigated key plots in urban environments of Yamal region and Murmansk are summarized in Figure 2. The highest concentrations for Cu, Zn, Ni were found in the Kharp key plot which seems to be caused by existing chrome-processing factory. The highest median values for Pb were found in soil samples from Aksarka and Labytnangi key plots. Soil samples from Kharsaim and Kharp key plots were characterized by the highest median values for Zn. This can be explained by geological origin and high regional background concentration element for this trace element (Moskovchenko, 2010).

Soil samples collected in Murmansk are characterized by highest medians in Pb, Ni and Mn in topsoil horizons, and Mn in lower horizons (*Mur1 and Mur3* – recreational functional zone); Mn and Zn (*Mur2* – industrial functional zone); Mn and Ni in topsoil horizon, Mn and Zn in lower horizon (*Mur4 – residential industrial zone)*. Since soil samples in Murmansk were collected from less-disturbed soils (compared to highly human-mixed soil material in settlements of Yamal autonomous region) profile distribution of trace elements seems to be similar to those in natural soils of the Arctic region reported in previous works (Tomashunas, Abakumov, 2014; Moskovchenko, 2010; Nikitina et al., 2015). It means that the highest contents of trace elements occur in histic topsoil horizons or on the biogeochemical barriers (which can developed on the active layer-permafrost border or in redoximorphic conditions).



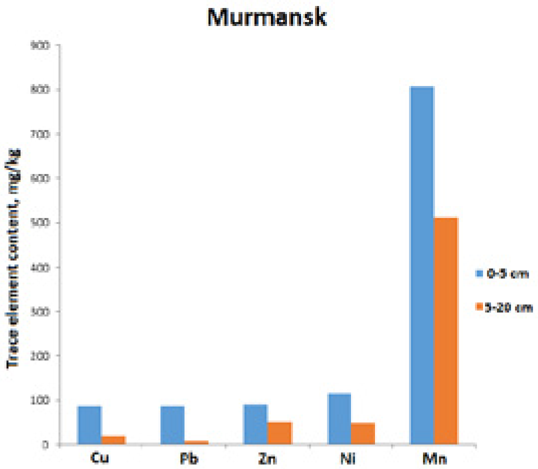


Fig. 2 Trace elements content in urban soils of Yamal region and Murmansk

It has been also performed calculation of Saet´s index (Zc). During its calculation it was used not only average arithmetic values of coefficient of concentration (Kk), but also its average geometric values. Most of the soil samples are characterized by non-hazardous (Zc <16) levels of total soil contamination. It characterizes soils as unpolluted. Saet´s index has been determined at levels of (16 < Zc < 32, moderately dangerous level) just in few soil samples from Aksarka and Kharp. The rest soil samples are characterized by Zc<16 (undangerous level of contamination).

Degradation of permafrost could alter the behaviour of trace elements in soils. It will affect the rates of accumulation, transformation, translocation, leaching and transportation of trace elements and other pollutants within the permafrost-affected landscapes. Consequently, ecosystem services provided by urban soils should be investigated in context of predicted climate change.

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LITERATURE

Akeredolu, F. A., Barrie, L. A., Olson, M. P., Oikawa, K. K., Pacyna, J. M., and Keeler, G. J. 1994. The flux of anthropogenic trace metals into the Arctic from the mid-latitudes in 1979/80, Atmos. Environ., 28, 1557–1572

Antcibor I., Eschenbach A., Zubrzycki S., Kutzbach L., Bolshiyanov D., Pfeiffer E.-M. Trace metal distribution in pristine permafrost-affected soils of the Lena River delta and its hinterland, northern Siberia, Russia. Biogeosciences, 11, 1–15, 2014

Barrie, L. A., Gregor, D., Hargrave, B., Lake, R., Muir, D., Shearer, R., Tracey, B., and Bildeman, T.: Arctic contaminants: sources, occurrence and pathways, Sci. Total Environ., 122, 1–74, 1992.

GN 2.1.7.2511-09. Approximate allowable concentrations of chemical substances in soils. [Orientirovochnodopustimyekontsentratsii (ODK) khimicheskikhveshchestv v pochve]. (in Russian)

GN 2.1.7.2041-06. Maximum allowable concentrations of chemical substances in soils. [Predel’no dopustimye kontsentratsii (PDK) khimicheskikh veshchestv v pochve]. (in Russian).

Linde M. Trace metals in urban soils. Diss. (sammanfattning/summary). Uppsala : Sveriges lantbruksuniv., Acta Universitatis agriculturae Sueciae, 1652–6880 ; 2005:111.

Nikitina M., Popova L., Korobicina J., Efremova O., Trofimova A., Nakvasina E., Volkov A., 2015. Environmental Status of the Arctic Soils. J. Elem., 20(3): 643-651. DOI: 10.5601/jelem.2014.19.4.743

Morel J.,Chenu C., Lorenz K., 2015. Ecosystem services provided by soils of urban, industrial, traffic, mining, and military areas (SUITMAs). J Soils Sediments, 15:1659–1666

Moskovchenko, D. V. (2010): Landscape geochemistry of the North of West Siberian Plain:structural-functional organization of matter in geosystems and problems of ecodiagnostics.Dissert; Saint Petersburg, 394 pp (in Russian).

OST 10-259-2000. Pochvy.Rentgenofluorescentnoe opredelenie valovogo soderzhania tyazhelyh metallov. (in Russian).

Rahn K. A., Tomza U., and Khodzher T. V.: An event of long-range transport of Siberian aerosol to Tiksi, Russia, J. Aerosol Sci., Elsevier Science, 28, Suppl. 1, s465–s466, 1997.

Reimann, C., Filzmoser, P., Garrett, R., and Dutter, R.: Statistical data analysis explained (Applied environmental statistics with R), John Wiley & Sons, Ltd, 2008

Rovinsky, F., Pastuchov, B., Bouyvolov, Y., and Burtseva, L.: Present day state of background pollution of the natural environment in the Russian Arctic in the region of the Ust-Lena Reserve, Sci. Total Environ. 160/161 193–199, 1995.

SanPiN 42-128-4433-87. Sanitary norms for available concentrations of chemical compounds in soils. [Sanitarnye normy dopustimykh kontsentratsiy khimicheskikh veshchestv v pochve]. (in Russian).

Shishov L.L. et al. 2004. Classification and diagnostics for Russian soils (in Russian). Oykumena, 342p.

Thomas, D. J., Tracey, B., Marshall, H., and Norstrom, R. J.: Arctic terrestrial ecosystem contamination, Sci. Total Environ., Elsevier Science Publishers, 122, 135–164, 1992.

Tomashunas V.M., Abakumov E.V. Soderzhanie tyazhelyh metallov v pochvah poluostrova Yamal i ostrova Beliy. Gigiena I sanitaria. 2014, 6: 26–5. (in Russian).

World reference base for soil resources. FAO. 2014. 181 p.

INFLUENCE OF TWO AMENDMENTS ON PHYTO- AND SANITARY AVAILABILITY OF METALS IN HIGHLY CONTAMINATED SOILS: A GREENHOUSE STUDY

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KEYWORDS
Contaminated soils, biochar, iron grit, metals, ryegrass, phytoavailability, oral bioaccessibility

ABSTRACT

Soil is an essential and non-renewable resource which can perform a high number of economic, social and environmental functions as biomass production, source of raw materials or protection of humans and environment (Blum, 2005). However, the soil functionality becomes increasingly compromised due to contaminations caused by human activities. In 2006 and in 39 countries, the European Environmental Agency inventoried approximately 3 million of sites where pollutant activities occurred with more than 1.8 million potentially contaminated sites (CGDD 2013). In 2012, the most frequently identified contaminants were metals (35 %), hydrocarbons (24 %) and polycyclic aromatic hydrocarbons (11 %).

Until recently, the most common remediation technique was the excavation of contaminated soil and its disposal as landfill. However, this kind of method is considered inappropriate because it generates considerable disturbances, is expensive and economically unfeasible on a large scale. Thus, other remediation techniques (*ex* and *in situ*) have been developed to overcome these disadvantages. Among them, a technique consists in adding inorganic or organic amendments to the contaminated soils in order to decrease the mobility and bioavailability of pollutants in soils (Kumpiene et al., 2008; Vangronsveld et al., 2009; Bolan et al., 2014; Nejad et al., 2017). The most often used amendments are phosphate compounds, liming materials, metal oxides and biochars, used alone or in combination (Waterlot et al., 2017; Lahori et al., 2017; Oustrière et al., 2017).

The goal of the present work consists in evaluating the ability of two amendments (woody biochar and iron grit, used alone or in combination) to immobilize Cd, Cu, Pb, and Zn in contaminated soils under greenhouse conditions.

Two metal contaminated soils with different physico-chemical parameters were used in this study (Table 1). The first one, named MAZ, was collected in a brownfield located on an old settling basin where residues from a plastic industry were deposited (Mazingarbe, France). The second one, named ME, is an agricultural soil contaminated by past atmospheric emissions from lead smelter (Evin-Malmaison, France).

Tab. 1 Physico-chemical characteristics of the two soils studied

	Cd (mg kg^{-1} DW)	Pb (mg kg^{-1} DW)	Zn (mg kg^{-1} DW)	Cu (mg kg^{-1} DW)	pH$_{water}$	C$_{org}$ (g kg^{-1})	CaCO$_3$ (g kg^{-1} DW)
MAZ	4.8	84.7	658	86.3	7.9	17.9	438.7
ME	15.3	812	1016	37.3	7.5	48.0	4.1

The first amendment used was a woody biochar (BC) made from hardwood plants (hornbeam, beech and oak) at 400°C during 12 h (La Carbonerie, Crissey, France). The second amendment was iron grit (IG), provided by Arena (GH120, Marquette-lez-Lille, France).

The pot experiment consisted in four treatments for each soil: 1) untreated soil (T), 2) soil + 2 % BC (BC), 3) soil + 1 % IG (IG) and, 4) soil + 2 % BC + 1 % IG (BC/IG). After watering, the pots (2.1 kg of soil) were placed under semi-controlled conditions in a greenhouse during 5 weeks for equilibrium. Then, 1.5 g of ryegrass (*Lolium perenne* L. var. Cantalou) were sown per pot. They were watered regularly and shoots were harvested 6 weeks after sowing.

The aerial biomass and Cd, Pb, Zn and Cu concentrations in ryegrass shoots were determined. The sanitary availability of metals in soils was evaluated by *in vitro* oral bioaccessibility test, using the Unified Bioaccessibility Method (UBM; Wragg et al. 2011). The UBM test consisted of two parallel sequential extractions and provided information on the metal availability in the gastric (G) and gastrointestinal (GO) phases.

The Table 2 presents the aerial biomass of ryegrass for the two soils studied. In the MAZ soil, the input of iron grit alone positively affected the plant biomass by increasing it from 8.43 to 9.83 g pot^{-1}. The biochar alone or in combination with iron grit did not statistically affect the ryegrass biomass. In the ME soil, no treatment modified the plant biomass.

Tab. 2 Aerial biomass of ryegrass (g pot^{-1} DW) cultivated in the MAZ and ME soils. “T” corresponds to the non-amended soils and “BC”, “IG” and “BC/IG” to the soils amended with: the woody biochar, the iron grit and the mix biochar and iron grit, respectively (n = 3). Capital letters compare the different treatments for the MAZ soil and lower letters for the ME soil. Different letters correspond to values statistically different ($p < 0.05$)

	MAZ	ME
T	8.43 ± 0.33 ^{A}	8.21 ± 0.49 ^{a}
BC	9.50 ± 0.66 ^{AB}	8.02 ± 0.26 ^{a}
IG	9.83 ± 0.29 ^{B}	8.50 ± 0.23 ^{a}
BC/IG	9.60 ± 0.72 ^{AB}	8.66 ± 0.66 ^{a}

The Fig. 1 presents the concentrations of Cd, Cu and Zn (mg kg^{-1} DW) in ryegrass in the two soils studied following the different amendments. The Pb concentrations in plants were under the limit detection for all the conditions. In the MAZ soil, the only observed effect was a decrease of Cu concentrations following the input of iron grit alone or in combination with biochar. In the ME soil, the three amendments decreased Cd concentrations in ryegrass with a more important decrease with iron grit alone or in combination with biochar. Moreover, only the iron grit alone or in combination with biochar decreased Cu and Zn accumulation in ryegrass.

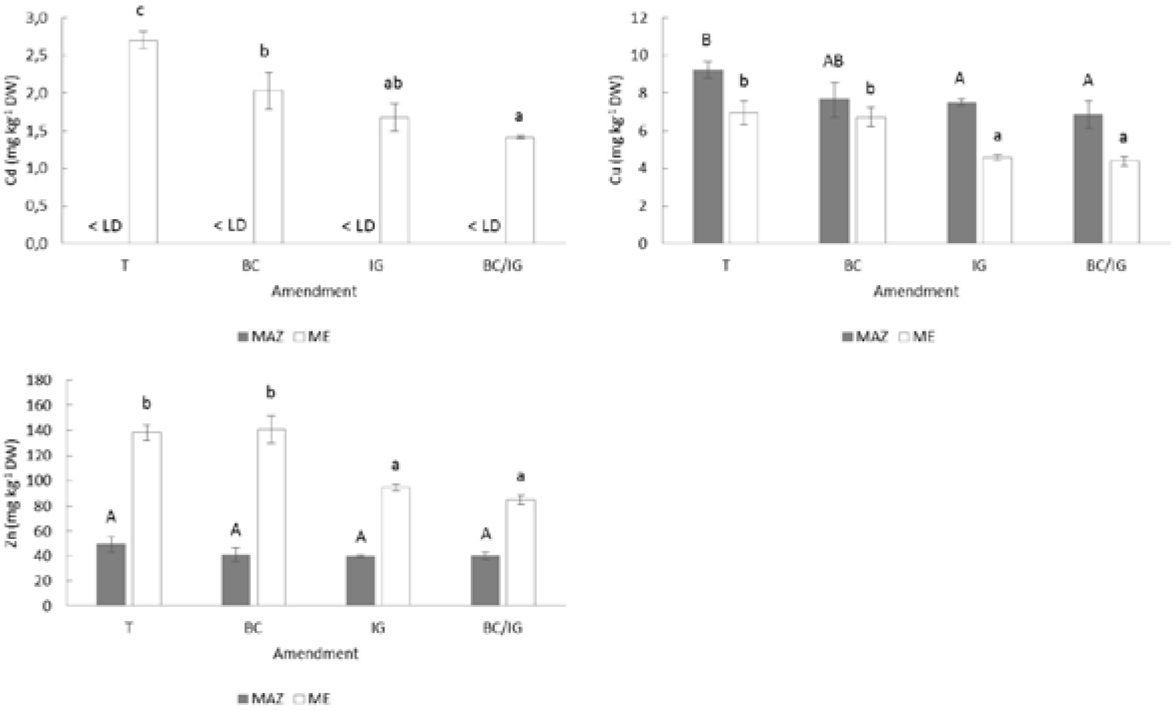

Fig. 1 Concentrations of Cd, Cu and Zn (mg kg^{-1} DW) in aerial part of ryegrass in the MAZ and ME soils. “T” corresponds to the non-amended soils and “BC”, “IG” and “BC/IG” to the soils amended with: the woody biochar, the iron grit and the mix biochar and iron grit, respectively (n = 3). Capital letters compare the different treatments in the MAZ soil and lower letters in the ME soil. Different letters correspond to values statistically different ($p < 0.05$)

The Fig. 2 presents the oral bioaccessibility of Cd, Pb and Zn in the two soils studied following the different amendments. In the MAZ soil, the input of biochar alone or in combination with iron grit always increased the bioaccessibility of the three metals in the gastric phase. When the iron grit was added alone, an effect was only observed for Zn with a decrease of its bioaccessibility. In the gastrointestinal phase, no effect was observed for the three metals and the three amendments.

In the gastric phase, for ME, the only observed effect was an increase of Pb bioaccessibility following iron grit amendment. In the gastrointestinal phase, the input of iron grit alone or in combination with biochar decreased the Cd bioaccessibility but increased the Zn bioaccessibility.

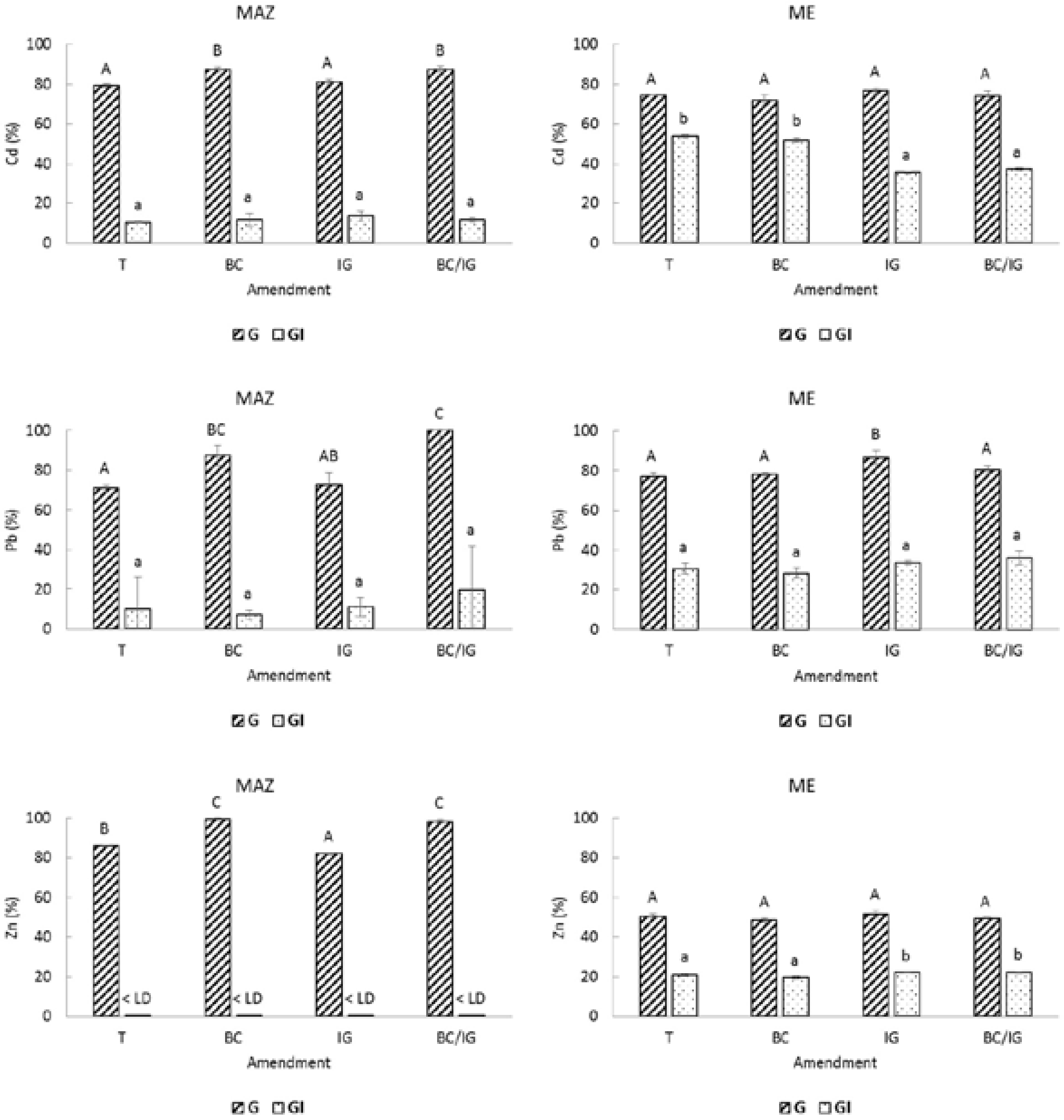

Fig. 2 **Cd, Pb, and Zn oral bioaccessibility in the gastric (G) and gastrointestinal (GI) phases (results expressed as the percentage of the pseudototal soil trace element concentrations) in the MAZ and ME soils. "T" corresponds to the non-amended soils and "BC", "IG" and "BC/IG" to the soils amended with: the woody biochar, the iron grit and the mix biochar and iron grit, respectively (n = 3). Capital letters compare the different treatments in the gastric phase and lower letters in the gastrointestinal phase. Different letters correspond to values statistically different ($p < 0.05$)**

In conclusion, the effects of amendments depended on the metal but also on the soil used. These differences are due to the physico-chemical parameters of the soils. Moreover, if focusing on metal phytoavailability, the input of iron grit alone or in combination with biochar was more efficient. However, from the point of view of sanitary availability, the three amendments have increased, in some case, the bioaccessibility of the three metals. The results highlighted the importance of testing different parameters before applying amendment in the field. Indeed, even if an amendment has a positive impact on metal phytoavailability, it can have a negative impact on other parameters, like sanitary bioaccessibility in this case. Thus, more attention should be paid on this parameter before applying amendment in the field.

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LITERATURE

Blum WE. (2005). Functions of soil for society and the environment. *Reviews in Environmental Science and Bio/Technology*, 4(3), 75 – 79.

Bolan N., Kunhikrishnan A., Thangarajan R., Kumpiene J., Park J., Makino T., ... & Scheckel K. (2014). Remediation of heavy metal (loid) s contaminated soils–to mobilize or to immobilize? *Journal of Hazardous Materials*, 266, 141 – 166.

CGDD (2013) Basol : Un panorama des sites et sols pollués ou potentiellement pollués nécessitant une action des pouvoirs publics, Etudes & documents. Ministère de l'Ecologie, du développement durable et de l'Energie. Paris

Kumpiene J., Lagerkvist A., Maurice C. (2008) Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments – A review. *Waste Management*, 28(1), 215 – 225.

Lahori AH., Zhang Z., Guo Z., Mahar A., Li R., Awasthi M. K., ... & Zhao J. (2017). Potential use of lime combined with additives on (im) mobilization and phytoavailability of heavy metals from Pb/Zn smelter contaminated soils. *Ecotoxicology and environmental safety*, 145, 313 – 323.

Nejad ZD., Jung MC., & Kim KH. (2017). Remediation of soils contaminated with heavy metals with an emphasis on immobilization technology. *Environmental geochemistry and health*, 1 – 27.

Oustriere N., Marchand L., Rosette G., Friesl-Hanl W., & Mench M. (2017). Wood-derived-biochar combined with compost or iron grit for in situ stabilization of Cd, Pb, and Zn in a contaminated soil. *Environmental Science and Pollution Research*, 24(8), 7468 – 7481.

Vangronsveld J., Herzig R., Weyens N., Boulet J., Adriaensen K., Ruttens A., ... & Mench M. (2009). Phytoremediation of contaminated soils and groundwater: lessons from the field. *Environmental Science and Pollution Research*, 16(7), 765 – 794.

Waterlot C., Pruvot C., Marot F., & Douay F. (2017). Impact of a phosphate amendment on the environmental availability and phytoavailability of Cd and Pb in moderately and highly carbonated kitchen garden soils. *Pedosphere*, 27(3), 588 – 605.

Wragg J, Cave M, Basta N, Brandon E, Casteel S, Denys S, Gron C, Oomen A, Reimer K, Tack K, van de Wiele T (2011) An inter-laboratory trial of the unified BARGE bioaccessibility method for arsenic, cadmium and lead in soil. *Science of The Total Environment* 409:4016–4030

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ROLE OF HYPERACCUMULATORS IN PHYTOMANAGEMENT OF METAL CONTAMINATED SITES

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KEYWORDS

Agromining, Heavy metals, Hyperaccumulators, Phytoextraction, Phytomining, Phytoremediation, Phytostabilization, Resource recovery

INTRODUCTION

According to the Status of the World's Soil Resources Report, soil pollution has been identified as main soil threats affecting soils and their ecosystem services. Currently, we are facing a global soil crisis as the world's arable land available per person has decreased from about 0.45 to 0.25 ha whereas the population has almost tripled over the last 50 years (FAO 2011) and an increase in food demand by 70 % in 2050 with 220,000 new mouths to feed every day with the existing land area. Hence, several remediation technologies were adopted for cleaning the contaminated sites. Based on the global awareness of soil quality, several reports are existed to the extent of contaminated sites/soil pollution and possible remediation methods globally (FAO 2018). Further, UNEP are involved to develop a concrete solution to address these issues under the framework of Sustainable Development. Depending upon the site condition and type of the contaminants, several phytotechnologies has been used. In addition to reclamate the contaminated environments, the by-products obtained from these phytotechnologies are added benefits to the stakeholders. 'Phytomining' has been deployed to extract ores from the hyperaccumulators using pyrolysis. 'Agromining' which could provide local communities with an alternative type of agriculture on degraded lands; farming not for food crops, but for metals such as nickel (Ni).

EXTENT OF GLOBAL SOIL CONTAMINATION

According to the Status of the World's Soil Resources Report (SWSR), soil pollution is one of the major soil threats affecting global soil resources and their ecosystem services. Recently, United Nations Environmental Assembly (UNEA-3) taking stringent action plans and programmes through various collaborations to address and manage the soil pollution. This agreement was globally accepted for more than 170 countries to develop concrete solutions to address the causes and impacts of soil pollution. Soil pollution as the third most important threat to soil functions in Europe and Eurasia, fourth in North Africa, fifth in Asia, seventh in the Northwest Pacific, eighth in North America, and ninth in sub-Saharan Africa and Latin America. According to the FAO-ITPS (2015), 19 percent of its agricultural soils are categorized as polluted in China (CCICED, 2015), approximately 3 million potentially contaminated sites in the European Economic Area (EEA, 2014), more than 1,300 polluted sites in USA (US EPA, 2013) and 80,000 contaminated sites are existing in Australia (DECA, 2010).

Previous abandoned mining lands are one of the major sources of pollutants as there were poor laws governing the mining operations and management of abandoned mine sites. Recently, The United States, Canada, Australia and China were established mine reclamation bond programs to ensure that reclamation of the mined area is completed (Cheng and Skousen, 2017). According to the Bureau of Land Management, approximately 550,000 abandoned mine sites including gold, coal and others in the United States have generated 45 billion tons of mine wastes (US EPA, 2004) and the clean up cost estimated as 32 to 72 billion US dollars. Approximately 20% of these sites have either been remediated, or have reclamation actions planned or are ongoing or do not require further action, whereas the remaining 80 % require further investigation and/or remediation. Superfund Green Remediation strategies has been implemented in US to minimize the impacts under CERCLA. Canada has an estimation of more than 10,000 abandoned mines including the Giant gold mine, Britannia copper mine, Kam Kotia copper and zinc mine and Gunnar uranium mine and mill site (Venkateswarlu *et al.*, 2016). Towards sustainable mining, Canada established the Green Mining Initiative (GMI) to develop green technologies, mining processes and innovations for energy efficiency and effective stabilization methods to limit the metal mobility in the environment (Green Mining Initiative, 2013). Recently, the online inventory system of NOAMI

(National Orphaned and Abandoned Mines Initiative) project catalogued the orphaned and abandoned mines under four categories (Class A, B, C and O) and six statuses ('inactive,' 'neglected,' 'abandoned,' 'legacy,' 'terminated' and 'unknown') across Canada. According to the Mineral Policy Institute 2016 Report, Australia has 431 operating mines, 1373 historic mines and 50,000 abandoned mines scattered across the country (Roche and Judd, 2016). Remediation strategies has been initiated in Collingwood Park Mine, Mount Morgan Mine, Mount Oxide Mine, Texas Silver Mine, Federation La Perouse Mine at Croydon, Horn Island mine sites, Herberton mine sites, Charters Towers mine sites, Gympie mine sites, New Hope coal mine and Calliope Park mine sites. Further, lack of rehabilitation and reliable data are the bottlenecks of reclamation. Only a smaller number (21) of mines have been fully rehabilitated and formally relinquished in Australian states (ABC News, 2017). In Europe, EU mine inventory programme PECOMINES Project and PADRE (Partnership for Acid Drainage Remediation in Europe) focuses on remediation issues pertaining to AMD releases in the vicinity of mines in European countries. According to the Department of Agriculture and Rural Development in Gauteng, the South African province is estimated to be having about 6150 officially listed abandoned mines that lie dormant across the country. Among the 297 abandoned mine sites in India, IBM recommended 82 sites for reclamation and rehabilitation of such abandoned mine sites in India. Energy developers around the globe are pushing to transform abandoned mines into hydroelectric storage facilities to stockpile wind and solar power. Recently, Ministry of New and Renewable Energy (MNRE) has identified the possibility of geothermal energy for power production from these abandoned mine sites especially 42 coal mines under the Son-Narmada-Tapti (SONATA) lineament zones in the state of Madhya Pradesh, Chhattisgarh and Jharkhand as well as four abandones coal mine in Godavari provinces especially in Andhra Pradesh (http://mnre.gov.in). IBM has initiated the remediation action plan for abandoned mine sites in association with TERI and NALCO especially remediation of red mud. Mining activities alone in China by more than 8000 national and 230,000 private companies resulted in creation of 200,000 km^2 of derelict land which includes the loss of 370,000 ha of agricultural land. However, only 25 % of the degraded land has been reclaimed in China (Liu, 2011). On the other hand, USA and Australia have reclaimed 80 % of the degraded lands based on the reclamation bonding system (Luo and Wang, 2010). According to Mine Reclamation Corporation (MIRECO) data, among the 2089 abondoned mine sites throughout the Korea, reclamation activities was enforced only 12 % of the mines (MIRECO, 2014). The lack of exact database and soil contamination map by specific pollutants like heavy metals in most of the developing and developed nations are major bottleneck for planning the remediation or reclamation plan for metal contaminated and mine sites.

ROLE OF HYPERACCUMULATORS IN METAL CONTAMINATED SOILS

Phytoremediation, an eco-friendly, cost effective diverse collection of plant-based green technology was deployed globally to remediate the moderate to low contaminated sites. Although several categories of phytotechnologies followed to remove the contaminants, phytoextraction and phytostabilization have been commonly utilized for mine site reclamation studies. Hyperaccumulators – are the ideal candidate for remediation of metal contaminated sites including mine site reclamation. Such plants are able to accumulate higher amount of heavy metal in the aboveground parts especially in the leaves (ie., vacuolar sequestration) under natural environmental conditions. Therefore, hyperaccumulators can be used as a model plant for exploring the unidentified gap in the metal uptake, translocation and accumulation as well as evolution and adaptation mechanism in extreme environmental conditions.

Globally, More than 75 % of hyperaccumulators are naturally occurred in Ni-enriched serpentine (ultramafic) soils in New Caledona, Malaysia, Phillipines, Brazil, Cuba and Southeast Asia belongs to genera *Alyssum* (Brassicaceae) and *Phyllanthus* (Phyllanthaceae). Similarly, Cu and Co-enriched soils are predominantly existed in Copper Hills in the DR Congo. Recently, Reeves *et al.* (2017) highlighted the significance of global hyperaccumulator database including the information about the taxonomy, distribution, ecology, collection records, analytical data and references for other studies for a particular species. The threshold criteria of each heavy metal were designated as follows: Cd, Th and Se (100 mg kg^{-1}), Cu, Co and Cr (300 mg kg^{-1}), Ni, As and Pb (1000 mg kg^{-1}), Zn (3000 mg kg^{-1}) and Mn (10,000 mg kg^{-1}) grown under natural conditions (van der Ent *et al*., 2013). However, most of the studies pertaining to the identification of hyperaccumulators were conducted either in artificial hydroponics and/or 'metal-spiked' soils under controlled conditions with unrealistic environmental concentrations and these plants are unable to survive under natural extreme environmental conditions. Globally 721 hyperaccumulator species listed in the global database (Reeves *et al*., 2017) and the number of plants for each metal as follows: 523 (Ni), 53 (Cu), 42 (Co), Mn (42), Se (41), Zn (20), Pb (8), Cd (7), As (5), Th (2) and Cr (1). Among these recorded database for hyperaccumulators, most of the species belong to Brassicaceae (83 species) and Phyllanthaceae (59 species) families. Species richness and endemism are the two key criteria to designate the 'biodiversity hot spots' and the 'global hyperaccumulator hot spots' was evident in Cuba, New Caledona, Turkey, Brazil, Indonesia, Philippines and Malaysia (Reeves *et al*., 2017). The protection of indigenous hyperaccumulators is need for the hour as small fractions of these plants are prone to logging, fires and mining. In this scenario, a ‘Hyperaccumulator Garden’ has been established by Sabah Park, Malaysia to conserve germplasm of rare hyperaccumulator plants and to support scientific study of these plants. Recently, two new Ni hyperaccumulators viz., *Actephila alanbakeri* (van der Ent *et al*., 2016) and *Phyllanthus rufuschaneyi* (Bouman *et al*., 2018) were identified from Sabah, Malaysia and the names designated the pioneering scientists in the field of phytoremediation Prof. Alan JM Baker and Prof. Rufus Chaney, respectively.

PHYTOMINING AND AGROMINING

The extraction of metal ore from the biomass of hyperaccumulator plants by pyrolysis is known as phytomining. The successful phytomining strategies were implemented in USA (Li *et al*., 2003) and Albania (Bani *et al*., 2015) using Ni hyperaccumulators. The indigenous plants are ideal candidates for Ni phytomining as their ability to adapt the local climatic and edaphic conditions with more than 1% of Ni accumulated in the aboveground biomass. Hyperaccumulators can also be used as ‘metal crops’ in agromining strategies to generate metal rich biomass for commercial value. Such practice can be useful for small scale farmers to attain economic benefits especially in low income countries. Field trials for phytoextraction of Cd were successfully conducted in Zhejiang and Hunan Provinces, PR China using *Sedum plumbizincicola* with co-cropping of *Zea mays* (Sterckeman and Puschenreiter, 2018). The recently identified Ni hyperaccumulator *P. rufuschaneyi* has fulfill several key criteria for hyperaccumulators including high biomass, fastest growth rate, rapid re-growth after coppicing, excellent tolerance and higher Ni accumulation in whole biomass of the plant. The ashed biomass contains 12.7 Wt% Ni and this material can also be used for producing high purity Ni salts for electrochemical industry (Vaughan *et al*., 2017). In a recent review by Kidd *et al*. (2018) has extensively demonstrated the various aspects of the sustainable agromining practices in agricultural ultramific soils andhighlighted the Agronickel and LIFE-Agromine - are the two major EU projects which are mainly focused to implement the Agromining strategy in a large scale.

In conclusion, identification of suitable metallophyte communities and conservation of endemic hyperaccumulator species richness is need for the hour to sustain these strategies.

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LITERATURE

ABC News, 2017: Mining report finds 60,000 abandoned sites, lack of rehabilitation and unreliable data [online], 16 February.

Bani, A., Echevarria, G., Zhang, X., Benizri, E., Laubie, B., Morel, J-L., Simonnot, M-O., 2015: The effect of plant density in nickel-phytomining field experiments with *Alyssum murale* in Albania. Aust. J. Bot. 63:72–77.

Bouman, R., van Welzen, P., Sumail, S., Echevarria, G., Erskine, P.D., van der Ent, A., 2018: Phyllanthus rufuschaneyi: a new nickel hyperaccumulator from Sabah (Borneo Island) with potential for tropical agromining. Bot. Stud. 59:9

CCICED, 2015: Special Policy Study on Soil Pollution Management. China Council for International Cooperation on Environment and Development.

Cheng, L., Skousen, J.G., 2017: Comparison of international mine reclamation bonding systems with recommendations for China, Int. J. Coal Sci. Technol. 1 – 13.

DECA, 2010: Assessment Levels for Soil, Sediment and Water. p. 56. No. 4. Australia, Department of Environment and Conservation.

EEA, 2014: Progress in management of contaminated sites. European Environment Agency.

FAO & ITPS, 2015: Status of the World’s Soil Resources (SWSR) – Main Report. Rome, Italy, Food and Agriculture Organization of the United Nations and Intergovernmental Technical Panel on Soils.

FAO, 2011: The State of the World’s Land and Water Resources for Food and Agriculture (SOLAW)–Managing Systems at Risk; Food and Agriculture Organization of the United Nations: Rome, Italy; Earthscan: London, UK, 2011.

Food and Agricultural Organization (FAO), 2018: Soil Pollution: A Hidden Reality, FAO, Rome, Italy.
Green Mining Initiative, 2013: Natural Resources Canada, http://www.nrcan.gc.ca/mining-materials/green-mining/8178.

Jaffre, T., Reeves, R.D., Baker, A.J.M., Schat, H., van der Ent, A., 2018: The discovery of nickel hyperaccumulation in the New Caledonian tree *Pycnandra acuminata* 40 years on: an introduction to a Virtual Issue. New Phytol. 218:397 – 400.

Kidd, P.S., Bani, A., Benizri, E., Gonnelli, C., Hazotte, C., Kisser, J., Konstantinou, M., Kuppens, T., Kyrkas, D., Laubie, B., Malina, R., Morel, J-L., Olcay, H., Pardo, T., Pons, M-N., Prieto-Fernández, A., Puschenreiter, M., Quintela-Sabarís, C., Ridard, C., Rodríguez-Garrido, B., Rosenkranz, T., Rozpądek, P., Saad, R., Selvi, F., Simonnot, M-O., Tognacchini, A., Turnau, K., Wazny, R., Witters, N., Echevarria, G., 2018: Developing sustainable agromining systems in agricultural ultramafic soils for nickel recovery. Front. Env. Sci. doi: 10.3389/fenvs.2018.00044

Li, Y-M., Chaney, R., Brewer, E., Roseberg, R., Angle, J.S., Baker, A.J.M., Reeves, R.D., Nelkin, J., 2003: Development of a technology for commercial phytoextraction of nickel: economic and technical considerations. Plant Soil 249:107–115.

Liu, Z., 2011: To give land life and vigor - Interpretation of ‘‘Land reclamation ordinance’’ by the director of policy and regulations of the Ministry of Land and Resources. Land Resour. Commun. 5:12–13.

Luo, M., Wang, J., 2010: The enlightenment to China from the construction of land reclamation system and the research of science and technology in Australia. China Land 4:51–53.

MIRECO (Mine Reclamation Corp. in Korea): 2013 Yearbook of MIRECO Statistics. pp. 5–11, 138–165. Mine Reclamation Corp., Republic of Korea Press, 2014.

Reeves, R.D., Baker, A.J.M., Jaffré, T., Erskine, P.D., Echevarria, G., van der Ent, A., 2017: A global database for plants that hyperaccumulate metal and metalloid trace elements. New Phytol. 218:407 – 411.

Roche, C., Judd, S., 2016: Ground truths: taking responsibility for Australia’s mining legacies [online], 38 p, Mineral Policy Institute.

Sterckeman, T., Puschenreiter, M., 2018: Phytoextraction of Cadmium: Feasibility in Field Applications and Potential Use of Harvested Biomass. In: Agromining: Farming for Metals – Extracting Unconventional Resources Using Plants, van der Ent, A., Echevarria, G., Baker, A.J.M., Morel, J-L., (Eds), Springer Nature, Switzerland.

US Environmental Protection Agency (USEPA), 2004: Abandoned mine lands team: reference notebook. www.epa.gov/aml/tech/amlref.pdf.

US EPA, 2013: Protecting and restoring land: Making a visible difference in communities: OSWER FY13 end of year accomplishments report. p. 47.

van der Ent, A., Baker, A.J.M., Reeves, R.D., Pollard, A.J., Schat, H., 2013. Hyperaccumulators of metal and metalloid trace elements: facts and fiction. Plant Soil 362:319–334.

van der Ent, A., van Balgooy, M., van Welzen, P., 2016: *Actephila alanbakeri* (Phyllanthaceae): a new nickel hyperaccumulating plant species from localised ultramafic outcrops in Sabah (Malaysia). Bot. Stud. 57:6.

Vaughan, J., Riggio, J., Chen, J., Peng, H., Harris, H.H., van der Ent, A., 2017: Characterisation and hydrometallurgical processing of nickel from tropical agromined bio-ore. Hydrometallurgy 169:346–355.

Venkateswarlu, K., Nirola, R., Kuppusamy, S., Thavamani, P., Ravi Naidu, Megharaj, M., 2016: Abandoned metalliferous mines: ecological impacts and potential approaches for reclamation. Rev. Environ. Sci. Biotechnol. 15:327 – 354.

IMPORTANCE OF ENVIRONMENTAL AND TOXICOLOGICAL AVAILABILITIES OF CD AND PB IN MANAGEMENT OF DREDGED SEDIMENTS

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KEYWORDS

Dredged material, anthroposol, metals, chemical extraction, oral bioaccessibility

ABSTRACT

Sediment management is a growing problem in areas sensitive to soil water erosion. Dredging operations on waterways are necessary to maintain navigation and limit flooding. However, they generate considerable amounts of sediment that may present inorganic and/or organic pollutants of various origins (agricultural, domestic, urban and/or industrial). For a long time, because of quantities, qualities and cost of treatment the main management solution consisted to transport the dredged sediments in specific disposal sites where they are subjected to meteorological conditions and oxidation. By drying a process of pedogenesis is set up and spontaneous vegetation can develop for creating an anthroposol (Capilla *et al*. 2006). Long considered as landfills, particular attention has been devoted to their requalification provided that the environmental and health risks are in accordance with the intended use. Many studies have focused on the environmental availability of these disposal sites, in particular to study the soil-plant and soil-aquifer transfer of metallic contaminants (Huguet *et al*. 2015; Lions *et al*. 2010). However, these studies were focused on a single site and did not take into account the toxicological availability of metals to better assess human exposure through particle ingestion, which is the main exposure pathway for people visiting these sites. To improve knowledge on the environmental and toxicological availabilities of Cd and Pb in the disposal dredged sediments, 67 anthroposol samples from 12 management sites located in northern France (figure 1) were selected according to their physicochemical parameters and degree of contamination in both metals. According to the heterogeneity of this matrix (Capilla *et al*. 2006; Vandecasteele 2003), each sample was considered independent. This study focused on these metallic elements for two reasons: (i) their high environmental and health toxicity, (ii) their presence at high concentrations in sediments located in areas with high industrial and agricultural activities (Tchounwou *et al*. 2012).

On each topsol sample, pH and the total concentrations of carbonates ($CaCO_3$), total organic carbon (TOC), assimilable phosphorus (P_2O_5) and free Fe-, Mn-, Al-oxides were measured. The environmental availability of Cd and Pb was determined using sequential extractions according to modified BCR protocol (Waterlot *et al*. 2012). That consists of four successive extractions with increasing strength reagents. These extractions produced four fractions in which Cd and Pb are distributed according to the phase targeted by the reagent Each fraction was noted as fraction F1, F2, F3, or F4 and defined respectively as: (a) exchangeable, water- and acid-soluble, (b) reducible (bound to oxyhydroxydes more or less crystallised), (c) oxidizable (bound to organic matter), and (d) residual (bound to silicates). The toxicological availability was measured by the UBM (Unified Barge Method) test. This *in vitro* test, developed by BARGE (the Bioaccessibility Research Group of Europe), aimed to simulate the behaviour of Cd and Pb when passing through the gastrointestinal tract to estimate the solubilizable fraction after an ingestion of particles. This test consisted of two successive extractions in synthetic digestive solutions (saliva, gastric, duodenal and biliary solutions) and allowed to assess the bioaccessible concentrations of metals in the gastric phase (G) and then in the gastrointestinal phase (GI). Except for the pH which was performed on the fraction < 2 mm all other analyses were carried out on the fraction < 250 μm.

The results of the characterization are presented in Figure 1. The pH of the anthroposols studied were neutral to slightly acidic and had a low dispersion (from 6.6 to 7.7). The $CaCO_3$ and TOC concentrations ranged from 0 to 678 g kg^{-1} and 16 to 216 g kg^{-1}, respectively. For free oxides, the values were from 3.1 to 73.7 g kg^{-1}, 0.02 to 1.42 g kg^{-1} and 0.06 to 2.79 g kg^{-1} for Fe, Mn and Al, respectively. The P_2O_5 concentrations varied from 0.03 to 1.77 g kg^{-1} and the pseudototal concentrations of Cd and Pb were from 0.9 to 104 mg kg^{-1} and from 33 to 1949 mg kg^{-1}, respectively. These results highlighted the high variation in terms of physicochemical parameters and a large scale of contamination.

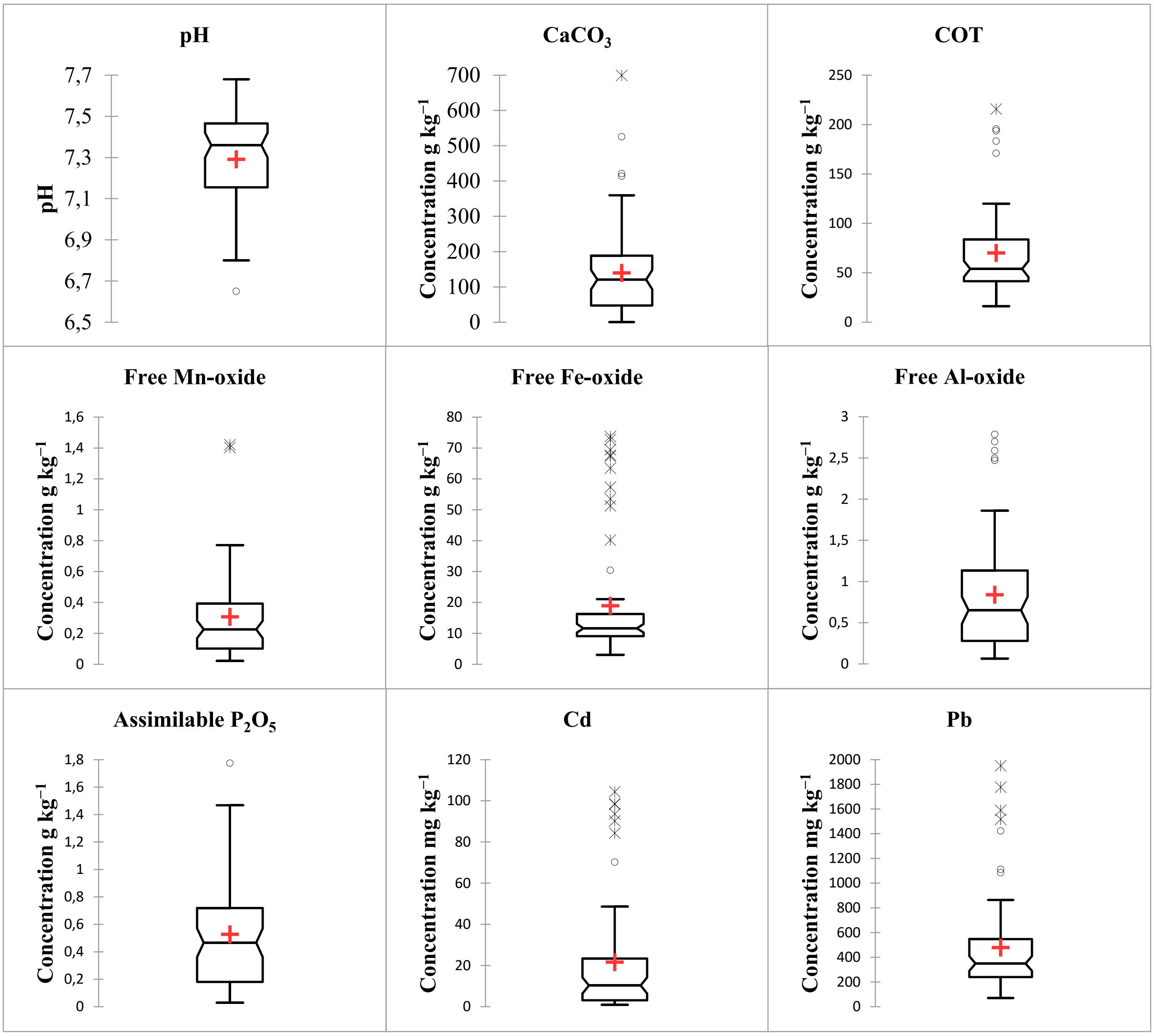

Fig. 1 Box plot of pH; concentration of $CaCO_3$, COT, assimilable P_2O_5, free Fe, Mn-, Al-oxide expressed on g kg^{-1} and pseudototal concentration of Cd and Pb expressed on mg kg^{-1}

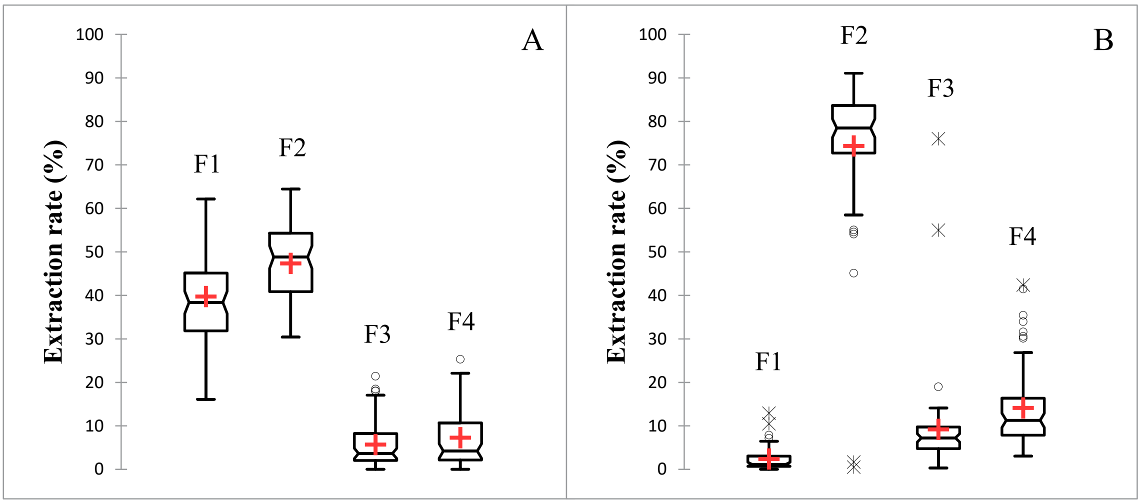

Fig. 2 Box plot of Cd (A) and Pb (B) (expressed in % of pseudototal concentrations) in the four fractions of the sequential extraction. F1 = Exchangeable + bound to carbonate, F2 = Reducible, F3 = Oxidisable, F4 = Residual

For the UBM test results (table 1), the elemental concentrations extracted from samples within the simulated G and GI phases were, on average, 16.4 and 9.9 mg kg^{-1} for Cd, and 303 and 99 mg kg^{-1} for Pb. A large gradient of bioaccessible Cd and Pb was observed in both phases, as reported for pseudototal concentrations. For both metals, G extractions showed a higher bioaccessibility than GI extractions. During the transition between the stomach and the intestine, a high decrease in bioaccessible concentrations was observed. This could be explained by a higher pH and a rich carbonate environment in the gastrointestinal solution that could induce the stabilization of some of the elements passed in solution during the G phase through reabsorption, complexation or precipitation processes (Basta *et al*. 2000).

Table. 1 Bioaccessible concentrations of Cd and Pb (expressed in mg kg^{-1}) in the gastric (G) and gastrointestinal (GI) phases in the anthroposols. Mean, standard deviation (SD), minimum and maximum are given for the 67 samples. ND = No Detection

	Cd G mg kg^{-1}	Cd GI mg kg^{-1}	Pb G mg kg^{-1}	Pb GI mg kg^{-1}
Minimum	0.47	0.22	33	ND
Median	7.28	4.63	246	74
Mean	16.5	9.94	303	99
Maximum	108.8	49.2	1309	433
SD (n-1)	25.0	13.6	268	96

In term of extraction percentages in the G and GI phases (figure 3), the values ranged respectively from 27 to 100 % and from 12 to 68 % for Cd. For Pb, the values ranged from 33 to 100 % and from 0 to 47 % for G and GI phases, respectively.

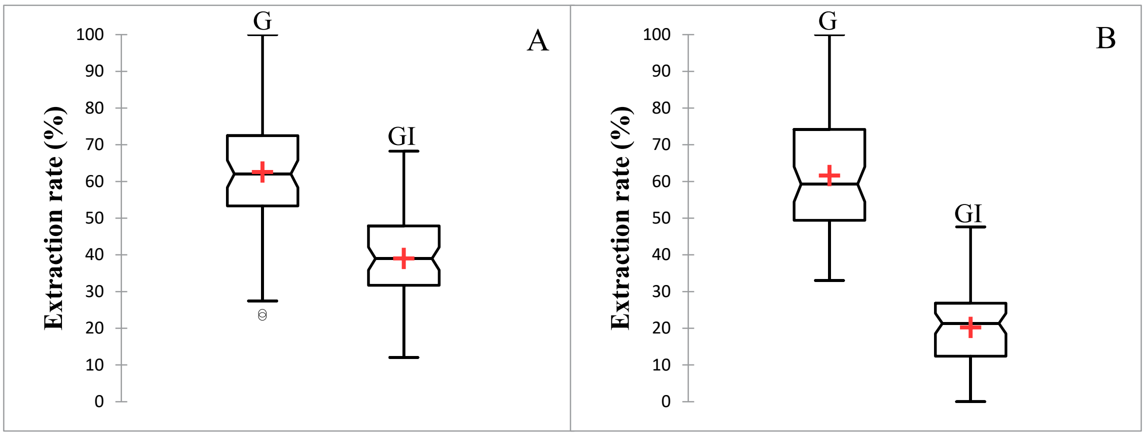

Fig. 3 Box plot of bioaccessibility of Cd (A) and Pb (B) in gastric (G) and gastrointestinal (GI) phases (expressed in % of pseudototal concentrations)

In conclusion, this study showed that anthroposols from dredged sediment are complex matrices that present high variability in terms of physicochemical parameters and a large scale of contamination. Sequential extractions highlighted a higher environmental availability for Cd than for Pb. A high heterogeneity was observed in bioaccessible concentrations and extraction rates in the UBM test. In phase G, both metals showed a similar behavior but a greater decrease was observed for Pb in phase GI indicating a higher availability of Cd. Now environmental availability is widely studied during the management of these contaminated sites, this is not the case for toxicological availability. In a further investigation, it seems important to integrate the notion of bioaccessibility to better assess the human exposure and risks. Finally, because this matrix studied is very heterogeneous, it will be interesting to identify the physicochemical parameters of these anthroposols that influence the oral bioaccessibility of contaminants.

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LITERATURE

Basta, Nicholas, and R. Gradwohl. 2000. "Estimation of Cd, Pb, and Zn Bioavailability in Smelter-Contaminated Soils by a Sequential Extraction Procedure." *Journal of Soil Contamination* 9 (2): 149 – 64.
Capilla, Xavier, Christophe Schwartz, Jean-Philippe Bedell, Thibault Sterckeman, Yves Perrodin, and Jean-Louis Morel. 2006. "Physicochemical and Biological Characterisation of Different Dredged Sediment Deposit Sites in France." *Environmental Pollution* 143 (1): 106 – 16.
Huguet, Séphanie, Marie-Pierre Isaure, Valérie Bert, Agnès Laboudigue, Olivier Proux, Anne-Marie Flank, Delphine Vantelon, and Géraldine Sarret. 2015. "Fate of Cadmium in the Rhizosphere of Arabidopsis Halleri Grown in a Contaminated Dredged Sediment." *Science of The Total Environment* 536 (December): 468 – 80.
Lions, Julie, Valérie Guérin, Philippe Bataillard, Jan van der Lee, and Agnès Laboudigue. 2010. "Metal Availability in a Highly Contaminated, Dredged-Sediment Disposal Site: Field Measurements and Geochemical Modeling." *Environmental Pollution* 158 (9): 2857 – 64.
Tchounwou, Paul B, Clement G Yedjou, Anita K Patlolla, and Dwayne J Sutton. 2012. "Heavy Metals Toxicity and the Environment." *EXS* 101: 133 – 64.
Vandecasteele, B. 2003. "Temporal-Spatial Trends in Heavy Metal Contents in Sediment-Derived Soils along the Sea Scheldt River (Belgium)." *Environmental Pollution* 122 (1): 7 – 18.
Waterlot, Christophe, Géraldine Bidar, Christelle Pruvot, and Francis Douay. 2012. "Effects of Grinding and Shaking on Cd, Pb and Zn Distribution in Anthropogenically Impacted Soils." *Talanta* 98 (August): 185 – 96.

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AGENDA

INTERNATIONAL CONFERENCE CONTAMINATED SITES 2018
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3	**Agnieszka Baran** Poland	THE USE OF CHEMICAL INDICATORS AND BIOASSAYS FOR AN ASSESSMENT OF ECOLOGICAL RISK IN CONTAMINATED BOTTOM SEDIMENTS
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BACTERIAL COMMUNITY IN SOIL CONTAMINATED WITH CHROMIUM

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KEYWORDS
Metagenomic, soil microbial diversity, 16S rRNA, next-generation sequencing, metals

ABSTRACT

The application of industrial wastes can contribute for increasing contamination with metals (Sousa et al., 2017). Chromium (Cr) is one of the metals that could accumulate in soil with application of wastes and, in long-term, this accumulation in soil can alter the bacterial structure and diversity (Nakatani et al., 2011). Thus, we used the next-generation sequencing to assess the structure and diversity of bacterial communities in soils contaminated with Cr. Sites with different concentration of Cr were selected: 5, 30, 50, 100, and 150 mg kg^{-1} Cr. Soil samples were collected at 0-20 cm depth and the bacterial community was assessed.

The sequences were affiliated to 22 bacterial phyla, 113 families, and 99 genera within the all evaluated sites. Ten phyla were considered most abundant with percentages of OTUs above 1% (Actinobacteria, Proteobacteria, Firmicutes, Chloroflexi, Planctomycetes, Acidobacteria, Gemmatimonadetes, Verrumicrobia, Nitrospirae, and Bacteriodetes) (Fig. 1). Specifically, there was a slight shift in abundance of some phyla according to treatments. Although non-significant, Proteobacteria decreased while Firmicutes increased with the application of CTS as compared with the unamended soil.

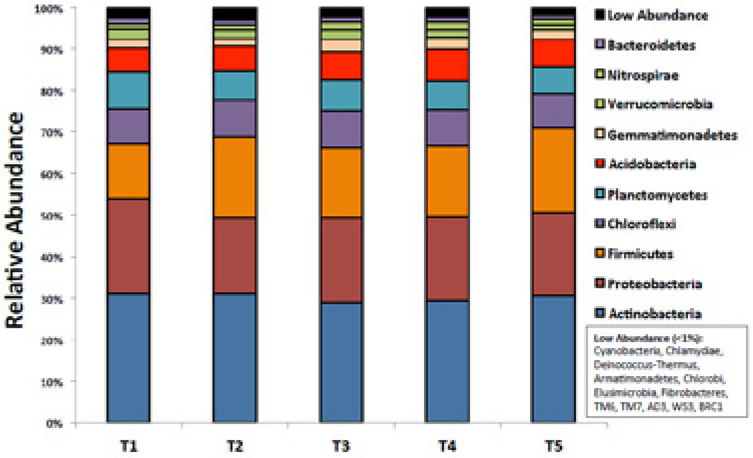

Fig. 1 Taxonomic composition of the bacterial community in soils. T1 – 5 mg kg^{-1} Cr; T2 – 30 mg kg^{-1} Cr; T3 – 50 mg kg^{-1} Cr; T4 – 100 mg kg^{-1} Cr; T5 – 150 mg kg^{-1} Cr

The relative abundance of six bacterial genera differed significantly between amended (CTS-treated soil) and unamended soil (without CTS) (Fig. 2). Thus, the relative abundance of Bacillus, Paenibacillus, Symbiobacterium, Clostridium, Microlunatus, and Actinomadura increased significantly after application of CTS as compared with unamended soil. Consistently, Bacillus, Paenibacillus, Symbiobacterium, and Clostridium showed an increasing relative abundance with increasing CTS

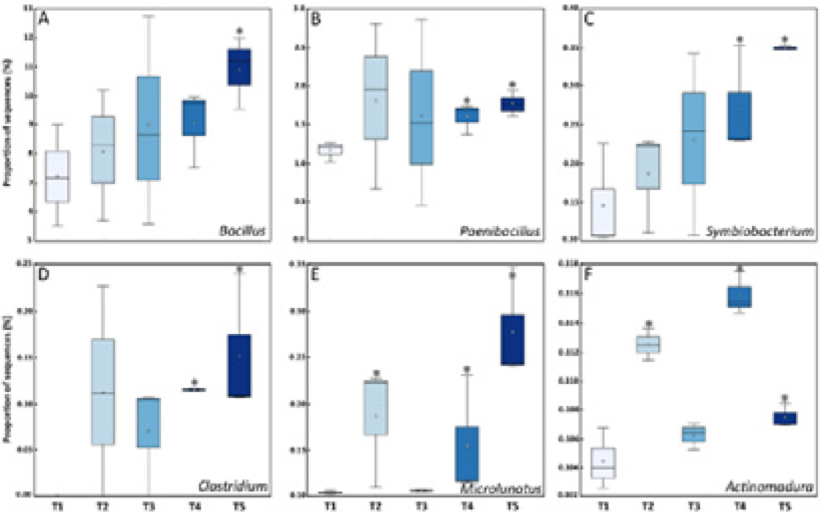

Fig. 2 Most abundant bacterial genera in soil. T1 – 5 mg kg^{-1} Cr; T2 – 30 mg kg^{-1} Cr; T3 – 50 mg kg^{-1} Cr; T4 – 100 mg kg^{-1} Cr; T5 – 150 mg kg^{-1} Cr

Finally, this study showed that contamination of Cr has a primary effect on the structure and composition of bacterial communities. Negatively, it suggests alteration in the bacterial diversity and community. Positively, it permits to select specific bacterial groups able to resist and potentially biodegrade Cr. This study found different bacterial groups more resistant to Cr, such as Actinobacteria, Proteobacteria and Firmicutes.

LITERATURE

Nakatani, A.S., et al., 2011. Changes in the genetic structure of Bacteria and microbial activity in an agricultural soil amended with tannery sludge. Soil Biology & Biochemistry. 43,106–114

Sousa, R. S., Santos, V. M., Melo, W. J., Nunes, L. A. P. L., Van den Brink, P. J., Araújo, A. S. F. 2017.Time-dependent effect of composted tannery sludge on the chemical and microbial properties of soil. Ecotoxicology 26, 1366–1377.

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THE USE OF CHEMICAL INDICATORS AND BIOASSAYS FOR AN ASSESSMENT OF ECOLOGICAL RISK IN CONTAMINATED BOTTOM SEDIMENTS

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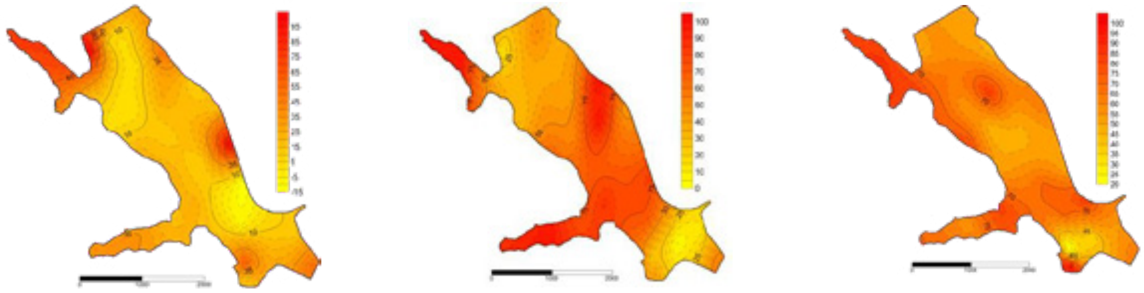
KEYWORDS
Bottom sediments, contaminants, chemical indicators, biotests, risk assessment

ABSTRACT

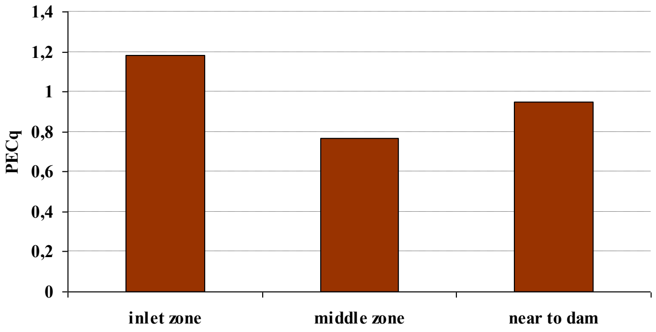
The aim of the study was presented the ecological risk associated with heavy metal, PAHs and dioxin concentration in the bottom sediment on the basis of their ecotoxicological properties. The bottom sediment originated from the Rybnik reservoir situated in the Silesian provinces (south Poland). The reservoir is located in one of the most industrialized areas of Poland (the Upper Silesian District), which affects the contamination of the sediments. The sources of sediment contamination include: treated industrial sewage emitted by the Rybnik power plant, municipal sewage, rain wastewaters, sewage from the water treatment plant, cooling tower blowdowns, and dry precipitation. Four bioassays were used to assess the bottom sediments ecotoxicity: Phytotoxkit (*Sinapis alba, Lepidium sativum*, *Sorghum saccharatum*), Ostracodtoxkit (*Heterocypris incongruens*), Microtox (*Vibrio fischeri*) and respiration. The concentrations of pollutants in bottom sediments were compared with the consensus-based sediment quality guideline values (SOQs). In addition, the mean PEC quotient (PECq) was calculated. The contents of heavy metals, PAHs and dioxin in sediments demonstrate that these pollutants have a good affinity for organic matter in the Rybnik reservoir sediments. Sediments of the Rybnik reservoir are toxic, but the test organisms showed a different sensitivity. The integration of ecotoxicological and chemicals methods is necessary for an appropriate ecological risk assessment.

Fig. 1 Localization of Rybnik Reservoir



Roots growth inhibition of *S. alba* Growth inhibition of *H. incongruens* Luminescence inhibition of *V. fischeri*

Fig. 2 Distribution of sediment toxicity for individual test organisms (PE%)



PECq: non-adverse effect (PECq <0.1), slightly adverse effect (0.1 < PECq <0.5), moderate effect (0.5< PECq<1.0) and heavy effect (PECq > 1.0) to the benthic fauna

Fig. 3 The mean PEC quotient (PECq – 8 metals) for the sediments

LITERATURE

Baran A. et al. 2017. Environmental Science and Pollution Research, 24, (29), 23180–23195.

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CHANGES IN COPPER SPECIATION IN LONG-TERM CONTAMINATED SOIL

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KEYWORDS

Transformation, Haplic Chernozem, Cu, easily and poorly soluble compounds, long-term incubation experiment

ABSTRACT

The contamination of soils with heavy metals (HMs) from anthropogenic sources is inevitably accompanied by the transformation of HM forms. HMs are present in the soil in easily and hardly soluble forms, which obviously pose different environmental hazards, because the mobility and bioavailability of HMs strongly depend on their chemical forms. The easily soluble forms can effectively react with soil components, while the hardly soluble forms are subject to dissolution due to further transformation (Bauer et al., 2018). However, the transformation of HMs coming into the soil in the form of different chemical compounds was studied in few long-term experiments only (Bauer et al., 2018; Voegelin et al., 2005). The mechanisms of decreasing or increasing extractability of HMs added to soils over time are unclear. The aim of this work was to study features of Cu speciation in the soil contaminated with easily and hardly soluble metal compounds in a long-term incubation experiment.

A 5-year-long model experiment was established to study the transformation of anthropogenic Cu compounds in Haplic Chernozem. The soil has the following physical and chemical parameters: Corg 3.7 %; $CaCO_3$ 0.1 %; pH_{H_2O} 7.3; cation exchange capacity 37.1 cmol(+) kg^{-1}; exchangeable cations (cmol(+) kg^{-1}): Ca^{2+} 31.0, Mg^{2+} 4.5; physical clay (particles <0.01 mm) 53.1 %; clay (particles <0.001 mm) 32.4 %. The original uncontaminated soil (1 kg) was passed through a 1-mm sieve and placed in plastic pots with a ceramsite drainage layer on the bottom. Nitrates and oxides Cu compounds were then separately added to the pots at concentrations of 300 mg Cu kg^{-1}. Soil was maintained at 60% of water holding capacity during the experiment by the regular application of distilled water to the pots. Contaminated soil was exposed at room temperature and natural lighting for 5 years. The collection of soil samples for analysis was performed every year. Selective extractions were employed to study the mobile Cu forms (Minkina et al. 2008): (1) exchangeable Cu form (extraction for 18 h, using a 1 N solution of NH_4OAc with pH 4.8 and a solid-to-liquid phase ratio of 1: 10); (2) organically bound forms and complex compounds of Cu together with its exchangeable forms (extraction for 18 h, using a 1 N solution of NH_4OAc with 1% EDTA disodium salt at pH 4.8 and a solid-to-liquid phase ratio of 1 : 10). The concentrations of the metal in complex compounds were calculated from the difference between the concentrations in extracts (2) and (1); (3) Cu bound to amorphous compounds and carbonates (shaking for 1 h with 1 M HCl at a solid-to-liquid phase ratio of 1:10). The difference between the contents of metal in the 1 N HCl and 1 N NH_4OAc extracts corresponds to the amount of metal bound to carbonates and Fe–Mn hydroxides). The extracts analyzed by atomic absorption spectrophotometry. The sum of exchangeable, complex, and specifically sorbed forms represents loosely bound compounds (LBC). These are the most important forms in ecological terms, which are capable to enter adjacent areas and plants in particular.

It shown that in uncontaminated soil samples (control) the concentration of Cu indicates to the stability of soil and equilibrium of the processes occurring in the soil (Tab. 1). The Cu LBC content in the control samples did not exceed 7% of total Cu content. During the 5-year-long experiment, the Cu LBC content remained almost unchanged, which indicated the stability of processes occurring in the soil and the absence of anthropogenic soil contamination.

Compounds of metal	**LBC (mg kg^{-1})** **exchangeable /complex /specifically absorbed (% of the LBC)**				
	years				
	1	**2**	**3**	**4**	**5**
Control	2.5 12/12/76	2.9 10/10/80	2.0 10/10/80	2.6 12/12/76	2.7 11/11/78
$Cu(NO_3)_2$	140.9 20/33/47	132.3 15/31/54	119.9 13/30/57	97.5 10/31/59	99.5 8/30/62
CuO	17.5 11/15/74	35.2 12/15/73	41.4 11/14/75	50.2 10/14/76	55.3 10/14/76

Tab. 1 Changes in the content and composition of Cu loosely bound compounds (LBC) in Halpic Chernozem during 5 years of incubation in the form of different compounds

Differences in the content of extractable Cu WBCs depending on the chemical composition of compounds added to the soil were revealed. The total concentration of Cu LBCs in the soil contaminated with nitrate of metal rapidly decreased already during the first year of the experiment; later the Cu LBC content decreased relatively slowly during the entire period of observations. The extractable LBC content in the contaminated soils significantly exceeded the extractable LBC content in the control soil samples during all years of the experiment.
The concentration of extractable Cu LBC in soils contaminated with Zn oxide during the experiment was significantly lower than in soils contaminated with easily soluble metal forms (Tab. 1). This was primarily related to the relatively lower solubility of these compounds and the kinetics of their dissolution in the soil. The thermodynamic solubility products (Ksp) of $ZnNO_3$ (Ksp=0.40) is way more than of ZnO (Ksp=20.32). As in the case of soil contamination with Cu nitrate, equilibrium is not reached during 5 years. On the other hand, the mobility of Cu added in the form of easily soluble salt decreases with time, but the concentration of Cu LBC after the addition of Cu oxide continues to increase (Tab. 1). Analysis shows that the Cu content in different fractions of LBCs in the control samples is lower than in the contaminated soils. The distribution of Cu in the studied LBC fractions remains similar in all cases: exchangeable form ≤ complexed form < specifically sorbed form. Thus, the largest amount of loosely bound Cu is concentrated in the so-called specifically sorbed form.
The fractional composition of Cu in the uncontaminated original soil does almost not change over time, while it significantly alters in the contaminated samples during the entire incubation time. The relative content of exchangeable and complexed Cu forms in the soils contaminated with nitrate of metal decreases over time, while the content of specifically sorbed forms increases gradually.
Thus, transformation of Cu added to the soil with easily and poorly soluble compounds can be assessed from changes in the metals LBCs of the soil over time. The easily soluble forms of Cu can effectively react with soil components, while the poorly soluble forms are subject to dissolution due to further transformation. Therefore, the metal oxides in the soil should induce a lower environmental hazard than easily soluble salts.

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LITERATURE

Bauer, T., Pinskii, D., Minkina, T., Mandzhieva, S., Burachevskaya, M., Kalinitchenko, V., Barakhov, A. 2018: Stabilization dynamics of easily and poorly soluble Zn compounds in the soil. Geochemistry: Exploration, Environment, Analysis. DOI: 10.1144/geochem2017 – 086.
Minkina, T.M., Motuzova, G.V., Nazarenko, O.G., Kryshchenko, V.S., Mandzhieva, S.S. 2008: Forms of heavy metal compounds in soils of the steppe zone. European Journal of Soil Science, 41, 708 – 716.
Voegelin, A., Pfister, S., Scheinost, A.C., Marcus, M.A., Kretzshmar, R. 2005: Changes in zinc speciation in field soil after contamination with zinc oxide. Environ. Sci. Technol. 39 (17), 6616 – 6623.

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MONITORING OF GROUNDWATER BODY IN DRINI I BARDHË RIVER BASIN IN KOSOVO

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KEYWORDS
Monitoring, Kosovo, groundwater, surface water, risk, agglomeration influences

INTRODUCTION

The article focuses on methodology and results of groundwater and surface water monitoring in western part of Kosovo, including geophysical survey in Drini I Bardhë River Basin in Kosovo. Main activity of the monitoring was to obtain real hydrogeological data from pre-defined areas in Drini I Bardhë River Basin with special focus on agglomeration influences (waste water, agriculture etc.).

METHODOLOGY

GEOtest, a.s. was commissioned by the Ministry of the Environment and Spatial Planning of the Republic of Kosovo (the Employer) to perform Geophysical Investigation of Groundwater Resources in Drini I Bardhë River Basin in Kosovo, where:

- Part A is focused on Geophysical Investigation in the true sense,
- Part B is focused on Groundwater Body Characterization,
- Part C is focused on Delineation of Agglomerations in the Drini I Bardhë River Basin.

Groundwater body characterization comprises technical condition inventory, sampling and analytical works. Groundwater abstractions were carried out on objects lying nearby proposed geophysical measurement. Taken samples mostly represent shallow quarter groundwater structures. One sample was taken from Drini river representing surface water. Nearby the selected sites measured by using geophysical methods (LOT A) were not existing any boreholes.

Fig. 1 Groundwater bodies in Kosovo with sampled points

Fieldwork was carried out in August 2017, 29 sampling points were inventoried and used for the collection of parameters such as location, owner, material, covering, type of use, geometry of sampling points (diameter, measuring site above level, depth), groundwater level, thickness of groundwater body, measuring of coordinates by GPS, on site measuring of parameters – temperature, pH, electrical conductivity (EC), incl. color, odor, contamination.

CONCLUSION AND RECOMMENDATION

29 samples of groundwater from shallow aquifer and surface water was taken at selected places across all the river basin of Drini I Bardhë.

Thickness of aquifers in Drini I Bardhë river basin is, based on geophysical investigation, approximately 23 meters depth (6 – 40 meters). Thickness of an each aquifer depends on geological (proluvial cones, cretaceous flysch, fluvial gravels, neogene sandy sediments overlain by fluvial sediments and valley sediments) and hydrogeological (karst, porous, fissured) conditions.

Based on field survey and on finding the current state of affairs we recommend followings:

- Completing and harmonization of legislation with the EU acquis as it is mentioned in chapter 2.1. EU Legislation and its Transposition
- Prepare administration of the strategies and plans for the river basins on state level:
    - Establish the river basin authorities
    - Prepare the river basin management plans
    - Do a management plan for the protection and regulation of river beds
    - Establish a protected areas and protection zones
- Prepare wastewater treatment strategy plan, build WWTPs
    - Compile cadaster data on water polluters
    - Construction of wastewater treatment plants (WWTPs) and canalization system
- Based on EU Directive 2000/60/EC do a regularly quality and quantity monitoring of surface water and groundwater:
    - Upgrading surface water monitoring networks, add more stations
    - Creating a groundwater-monitoring network
        - Drill new monitoring boreholes
        - Refine the results of geophysical investigations based on new information from new boreholes (geological description, water level, thickness of aquifer(s)
    - Interpret and present data on quality and quantity based on Directives regulations
- Protect the surface water. Be focused on main pollution sources and consider measures against:
    - Urban wastewater discharges
    - Direct industrial discharges from large industrial installations
    - Agriculture activities (surface runoff, soil erosion, artificial drainage flow, leaching of fertilizers)
    - Waste management (landfills, dumps, storages – chemical fluxes in leachate)
    - Contaminated sites (brownfields, industrial zones, military activities, fuel storage, freight railway stations, i.e.)
    - Impacts of mining (mine waste water, quarries, deposits, heaps)
    - Other negative influences on water pollution (e.g. dredging of river sediments, fish farming)
- Protect the groundwater, the main objectives are essentially:
    - Estimation and identification of significant water abstraction for urban, industrial, agricultural and other uses, including seasonal variations and total annual demand, and of loss of water in distribution systems.
    - Implement the measures to prevent or limit the input of pollutants into groundwater and to prevent the deterioration of the status of the groundwater body (quantitative and also qualitative status)
    - Protect, enhance and restore all bodies of groundwater, and ensure a balance between abstraction and recharge of groundwater, with the aim of achieving good groundwater status
    - Reverse any significant and sustained upward trends in the concentration of any pollutant resulting from the impact of human activity in order to progressively reduce pollution of groundwater

LITERATURE

Bartoň, J., Duras, R., Oprchal, J., 2017: Kosovo Environmental Programme, Geophysical Investigation of Groundwater Resources in Drini I Bardhë River Basin, GEOtest, a.s., Brno

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EXAMINATION OF THE SOIL POROSITY AND ITS PHYSICO-CHEMICAL PROPERTIES

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KEYWORDS
soil, degradation, climate change, porosity.

Soil is a product of the action of pedogenetic processes that are due to the continuous, joint and interdependent effect of heterogeneous pedogenetic factors. From the pedogenetic factors we would mention: the relief with different altitude, exposure and inclination, the hydrographic conditions, the geological formations with different age and composition, the presence of several climates, and various plant associations. Soil is an extremely complex and variable medium. The soil structure plays a significant role in determining its ability to perform its functions. Any damage to the soil structure damages other environmental media and ecosystems. Soil is susceptible to serious degradation. This includes erosion, the reduction of organic matter, local and diffuse contamination, imprinting, reducing biodiversity, salinization, flooding, etc. In combination, all these degradations can lead, in arid and sub-climatic climatic conditions to desertification. The effects on soil caused by human activities are constantly increasing, causing serious socio-economic consequences. A major challenge is to prevent soil degradation. This must be achieved through specific measures of the soil protection and management policy, as well as the incorporation of soil protection issues into other sectoral policies, i.e. in agriculture, forestry, water management, transportation, etc. In this paper the porosity and physico-chemical properties of the soil will be examined.

INTRODUCTION

Soil represents a three-dimensional dynamic natural body with a very complex composition which depends primarily on the composition of the parent substrate (rocks) and the organic residues from which it formed. The composition of the soil can be observed as a multi-phase system, composed of a solid, liquid and gas phase. The solid phase occupies 50 % (vol.) of the soil and is a mixture of organic and inorganic substances that compose the skeleton of the soil, which, in turn, contains pores filled with liquid and gas, the ratio of which varies depending on humidity. The solid phase consists mainly of inorganic matter (more than 80 %), but there are also soils dominated by organic matter. In fact, the optimal soil for growing plants should contain about 45 % non-organic matter, 5 % organic, 24 % water and 25 % air.

The dual role of the soil, or on the other hand to serve as a waste collector, may be disturbed by human activities. In fact, often despite the fact that man's activity is aimed at improving soil properties, it still leads to pollution. Thus, for example, by adding large quantities of fertilizers in order to increase yields, the role of the filter may be disturbed, and the drainage water containing excess salted salts from the fertilizer will lead to secondary soil salinization.

CHEMICAL CHARACTERISTICS OF THE SOIL

The chemical properties of the soil include: reaction of soil solution, buffering, redox potential and composition of soil solution.

Water in soils is not pure water. It has dissolved various mineral and organic substances. Therefore it is called a soil solution. The soil solution contains biogenic micro and macro elements (O, H, C, N, K, Ca, Mg, S, Mn, Cu, Fe, Zn, Mo), useful for plants (Si, Cl, Na), stimulative (Al, Ba, Br, P, Co, Si), and toxic elements.

Dissolved substances in the soil solution come from the soil itself (solid and gaseous phase) and precipitation. Soil solution participates in all physical, physico-chemical and biochemical processes in the soil. It is very important for the nutrition of plants, as well as for the life of the plant because the root of the plant is in constant contact with the soil solution.

PHYSICAL PROPERTIES OF THE SOIL

The physical properties of the soil wich are significant are: the structure, specific gravity, soil porosity, and physico-mechanical properties.

Soil structure

The ability of soils to form aggregates is called structural, and the aggregates obtained by soil tillage are called structural aggregates.

Formation of structural aggregates is called aggregation, and destruction desaggregation. If structural aggregates are stable in water, and have dimensions of 0.25 to 1 mm in the form of a grain, then the process is called granulation.

Structural aggregates have different sizes and shapes. By size they are divided into: microstructural < 0.25 mm, macrostructural > 0.25 mm. Three types of structure are distinguished: one-particle, coherent and aggregate structure One-particle structure has soils with a rough mechanical composition. In them, mechanical elements do not have the ability to bond to each other. The coherent (massive) structure is characterized by a balanced arrangement of mechanical elements interconnected in a compact mass. Aggregate structure, characterized by a division of the soil mass of fragments that are clearly bounded by all sides, and composed of interconnected primary particles. These aggregates are called structural. Structural aggregates are three-dimensional bodies and can occur in various forms, namely: plate, primitive, polyhedral, and spheroidal.

Aggregates according to form can be grouped into three main groups: cubo-morphic (polyhedral and spheroidal), prismodomorphic (prismatic) and laminomorphic (plate or leaf). The soil structure is shown in figure 1.

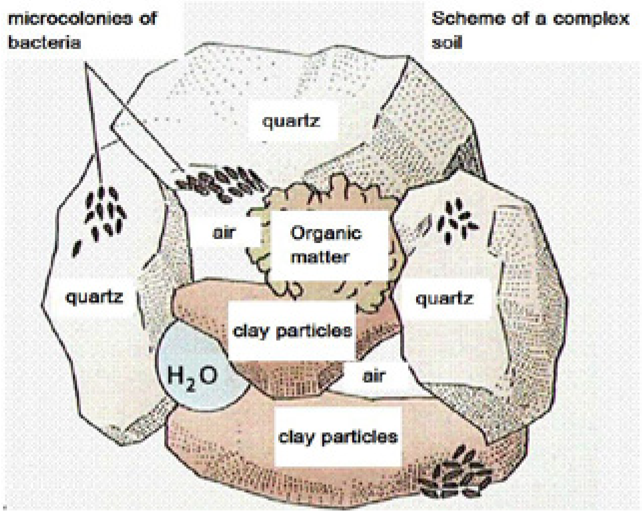

Fig. 1 Soil structure

Aggregates can be natural and artificial. The natural ones were created in the course of subgenesis, and the artificial ones were created with the influence of humans. To form structural aggregates in the soil, colloidal particles have a great influence, which in the process of coagulation blast clay, dust and sand into smaller aggregates. Stability of structural aggregates means the ability to counter the destructive effect of water. Mechanical stability of aggregates represents resistance to mechanical destruction (friction).

The soil structure depends on its fertility, i. e. the water, air and heat regime of the soil, the availability of nutrients and water for plants and microorganisms.

Specific soil density. There are two types of specific soil density: true and volume. A true or actual specific density is the weight of 1 cm^3 soil without pores, expressed in grams. This specific density does not depend on the size of the particles and their compactness, but on the mineralogical composition and the content of organic matter. The actual specific soil density is usually 2.6 to 2.7. It is the density of the solid phase of the soil. The volume specific density is the weight of 1 cm^3 of dry soil in a natural state (with pores) expressed in grams. This specific density depends on the actual specific density and the porosity.

Fig. 2 Specific soil density

Porosity of the soil

When the primary particles are blocked in structural agregates, they remain gaps because they do not touch with entire surface. Gaps that occur between soil particles and aggregates are called soil pores. The total volume of the pores expressed in weight percent is called soil porosity. The soil porosity usually ranges from 40 to 60 %. Depending on the size, the pores can be: micropores < 50 microns and macropores > 10 microns. Pores, in the soil can be capillary and non-capillary. In the capillary pores the water is retained, and in the non-capillary air. The soils, depending on the total porosity, are divided into: porous: > 45 %, slightly porous: 30 to 45 %, nonporous: < 30 %. The soil porosity depends on the mechanical composition, structure, content of organic matter, compactness, processing, etc. From the porosity of the soil depend the water, air and heat properties of the soil, fertility, etc.

Physico-mechanical properties of the soil

Soil consistency means the ability to change the condition in different amounts of water, under the influence of cohesion forces and adhesion. There are following forms of consistency: viscous, slurry – the soil flows under the influence of the Earth's weigh, sticky – the soil adheres to certain objects, plastic – the soil can be modeled, soft – the soil is crushed between fingers and hard – the soil is strongly bound, heavy and hard and does not break between fingers. The consistency of the soil depends on the type and content of the clay and the amount of water. Stickiness plasticity and crushing are consistency on moist soil. The stickiness of the soil means the property to stick to other objects. Depending on the degree of stickiness, the soils can be non-sticky, poorly sticky, sticky and very sticky. Plasticity of soil means the property can be modeled under the influence of external forces. The plasticity of the soil depends on the content of the clay, the mineral composition of the clay, the type of absorbed ions, and the amount of organic matter. Depending on the degree of plasticity, the soils can be non-plastic, low-plastic, plastic and very plastic. Under soil crushing, it is a property to break down the soil under the influence of mechanical forces.

CONCLUSION

On the basis of the presented material it can be concluded that one soil is quality if it meets the above components. Today, soils that are mostly contaminated by heavy metals near industrial facilities, and waste materials are examined. The environmental protection departments take all measures for remediation of the soils and their reuse.

LITERATURE

Филиповски, Ѓ., 1995: Почвите на Република Македонија, Том I, МАНУ, Скопје.
Филиповски, Ѓ., 2001: Почвите на Република македонија Том V, МАНУ, Скопје.
Цекова, Б., 2010: ХЕМИСКО ТЕХНОЛОШКО ИСПИТУВАЊЕ НА МАТЕРИЈАЛИТЕ, Скопје.
Cekova, B., Zlatanovic, V., 1994: Determination of the pollution of a water by consumption of $KMnO_4$, p. 84, SYMPOSIUM PROCEEDING BUDAPEST, Second International Symposium and Exhibition on Environmental Contamination in Central and eastern Europe, Budapest, Hungary.
Јовановиќ, Виторович, О., Рекалич, В., 1999: Испитивање у технолошкој производњни са практикумом за вежбе , Белград, Србија.

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PROJECTS OF THE SLOVAK ENVIRONMENT AGENCY RELATED TO CONTAMINATED SITES

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

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

OPERATIONAL PROGRAMME 'ENVIRONMENT' (2007 – 2013)

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

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

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

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

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

Within these groups, the following activities can be supported:
Group I: Monitoring and investigating contaminated sites and producing hazard analyses:
A. projects focused on the production of hazard analyses, remediation feasibility studies and inspections of contaminated sites
B. projects focused on the study of high-priority likely contaminated sites
C. projects focused on thorough and repeated investigation of the most hazardous contaminated sites, in line with the established priorities
D. regional studies of the environmental impacts of contaminated sites

E. projects focused on the development of monitoring systems for the most hazardous contaminated sites, in line with the established priorities
Group II: Remediation of the most hazardous sites of environmental contamination:
A. projects focused on the remediation of contaminated sites that present a major hazard to human health and the environment, in line with the established priorities
Group III: Finalisation of the Environmental Contamination Information System (ECIS):
A. implementation of the ECIS as a component of the government's information system
B. preparation of the Atlas of Remediation Methods as a component of the ECIS
C. projects focused on public relations, public awareness and promotion of activities related to the remediation of contaminated sites

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

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

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

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

BASIC INFORMATION ABOUT PROJECTS

1. **Project title**	**REGIONÁLNE ŠTÚDIE HODNOTENIA DOPADOV ENVIRONMENTÁLNYCH ZÁŤAŽÍ NA ŽIVOTNÉ PROSTREDIE PRE VYBRANÉ KRAJE (REGIÓNY)** STUDIES ASSESSING THE ENVIRONMENTAL IMPACT OF CONTAMINATED SITES IN SELECTED REGIONS
Acronym	STUDIEEZ
Main objective of the project	• assess the environmental impacts of contaminated sites in Slovakia's individual regions
Specific objectives	• develop a unified rubric of methods for regional studies of the impacts of

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

Fig. 1 Environmental Contamination in Predajná, Slovakia.

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

2. **Project title**	**DOBUDOVANIE INFORMAČNÉHO SYSTÉMU ENVIRONMENTÁLNYCH ZÁŤAŽÍ** FINALISATION OF THE ENVIRONMENTAL CONTAMINATION INFORMATION SYSTEM
Acronym	DOBUDISEZ
Main objective of the project	• finalise the Environmental Contamination Information System • carry out an informational/educational campaign in the form of regular informational and instructional trainings
Finantial tool	The Cohesion Fund of the European Union within the Operational Programme 'Environment' 2007 – 2013
Project duration	09/2009 – 09/2014

Total eligible expenditure	922,733.88 €
Project code (ITMS)	24140110017
Project manager	Katarína Paluchová
E-mail	katarina.paluchova@sazp.sk
Web	http://www.sazp.sk/public/index/go.php?id=1746

[Integrated Monitoring of Pollution Sources]: MV-2A

[Integrated Monitoring of Pollution Sources]: MV-2A (Status information: 12/08/2014)

Name and number of monitoring object:	MV-2A; 1229675348
Name and number of monitoring location:	Dump level EVO Vojany; 1238211888
Property type:	unknown
The owner and his LE identifier:	Slovak power, as, ID: 35829052

Coordinates: S-JTSK (1268188, 210990) ; WGS 84 [48.554765, 21.971964] ;

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

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

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

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

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

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

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

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

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

Number of accomplished information and public awareness activities of the project – 5.

LITERATURE

1. FRANKOVSKÁ, J., KORDÍK, J., SLANINKA, I., JURKOVIČ, Ľ., GREIF, V., ŠOTTNÍK, P., DANANAJ, I., MIKITA, S., DERCOVÁ, K., JÁNOVÁ, V., 2010: Atlas sanačných metód environmentálnych záťaží [Atlas of Remediation Methods for Contaminated Sites]. Dionýz Štúr State Geological Institute, Bratislava. ISBN 978-80-89343-39-3.
2. Problematika environmentálnych záťaží na Slovensku [The Issue of Environmental Contamination in Slovakia]. Slovak Environmental Agency, Banská Bystrica, 2010. ISBN 978-80-88850-98-4.
3. www.minzp.sk
4. www.opzp.sk
5. www.enviroportal.sk
6. www.sazp.sk

THE IMPACT OF NATURAL AND SUPPORTED ATTENUATION ON PRECIPITATION OF FE-OXYHYDROXIDES FROM SURFACE WATERS CONTAMINATED BY MINING WATERS

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KEY WORDS
Mining waters, natural and supported attenuation, remediation method, oxyhydroxides

ABSTRACT

The aim of our research was to compare the efficiency of natural and supported attenuation as a remediation method for the removal of potentially toxic elements from mining waters flowing out of deposits with sulfide mineralization. Samples for this research were taken from sites where abandoned deposits of sulfide ores pose a danger to the environment in the form of increased concentrations of some potentially toxic elements (As, Sb, Ni, Hg) in waters flowing out of abandoned mines. These were the Smolník, Poproč, Dúbrava and Slovinky sites, where the main risk pose the As and Sb elements, and the Merník site, where increased concentrations of Hg and Ni were found. As part of our research we have successfully proved that natural attenuation is an effective remediation method for mining waters contaminated by potentially toxic elements, and that the supported attenuation greatly accelerates the process of precipitation of secondary mineral phases in the form of Fe oxyhydroxides and also helps to increase the amounts of these precipitates.

METHODOLOGY

First set of samples consisted of mining water taken from locality Poproč. We used the following two procedures to determine the amount of Fe ochre precipitates. At the first procedure (November 2016), we filled two 100-liter plastic barrels by mining water from the Agnes adit and after 48 hours in field conditions, we separated the sediment (iron ochre precipitates) created on the bottom and the walls of the barrel from water. After transferring to the laboratory, the ochre precipitates were dried and weighed. Second measurement of the amount of Fe ochres took place in October 2017. We took two 9.5-liter samples of mining water from the Agnes adit and two 9.5-liter samples of water from the drainage channel approximately 100 m from the adit mouth. The samples were transferred to the laboratory and the first sample from both sampling points was immediately filtered through a 0.45 µm filter. The second samples were aerated by air compressor for three days in order to perfect the oxidation and obtain the maximum amount of Fe oxyhydroxide precipitates. After that, we filtered the water through a 0.45 µm filter and the separated precipitates were dried and weighed.

The second set of samples consisted of samples of mining waters taken from Smolník, Poproč, Dúbrava, Slovinky and Merník localities. After the samples were taken, basic physicochemical parameters were measured, and the waters were sent to the laboratory for analysis. Other samples of the same waters were then transferred to the laboratory where they were left to sediment for 10 days and then filtered through 0.45 µm filter. After drying, we weighed the amounts of precipitated mineral phases (tab. 1).

RESULTS

From both barrels containing the water from locality Poproč we separated basically the same amount of material – namely 4.28 g and 4.29 g which translates to 0.0428 g of precipitated material per liter of water. It is obvious that this is a large amount of material, which reflects to the abundance of ochres accumulated in the vicinity of the examined abandoned adit. If the composition of the water flowing out of the adit and the surrounding conditions were unchanging (remaining the same as on the day of sampling), up to 18.5 kg of Fe ochres can be generated per day with the flow of 5 liters per second of mining water flowing out of the Agnes adit. This can lead to amounts as high as 6 750 kg of precipitates per year.

Sedimentation from mining water taken from the Agnes adit mouth without aeration produced 0.0838 g of Fe oxyhydroxides which represents 0.009 g/l. After 3 days of aeration, we collected 0.5031 g of precipitates from the whole volume of the sample, which equals to 0.053 g/l. Increased aeration thus increased the formation and precipitation of Fe oxyhydroxides up to 6 times, from 9 mg/l to 53 mg/l. No significant differences in the amount of precipitated material were found in the water sample from the drainage channel taken from a bigger distance from the Agnes adit. Without aeration, we collected 0.221 g of the precipitates from the whole sample volume, representing 0.023 g/l. After aeration, the amount of sediment from the whole sample volume increased to 0.53 g, corresponding to 0.056 g/l. The results confirmed that the water from the drainage channel after passing approximately 100 meters from the adit mouth was partially aerated and was in contact with the bottom of the channel and other surrounding factors. Therefore, without additional aeration, we were able to collect only 23 mg of solid phase (precipitates) in the laboratory. After intensive aeration under laboratory conditions, up to 56 mg of precipitates from each liter of water was collected on the filter, meaning that precipitation was increased and accelerated. The total amount of precipitates collected from both samples (at the adit mouth and 100 m from the adit mouth) after aeration under laboratory conditions is virtually equal. If the amount of water flowing from the Agnes adit was 5 l/s on average, and other conditions would stay the same, there could be 8 830 kg of Fe oxyhydroxides generated annually.

As part of the further study of oxyhydroxide precipitates from mining waters, samples from Smolník, Poproč, Dúbrava, Slovinky and Merník localities were taken. The sample volumes and the amounts of precipitates are presented in table 1.

	Sample volume [ml]	Amount of precipitate [g]	g/l	Fe [mg/l]
SMOLNÍK	2 830	0.7169	0.2533	222.4055
POPROČ	2 605	0.101	0.0388	15.9321
DÚBRAVA	5 290	0.0218	0.0041	<DL
SLOVINKY	11 000	0.0838	0.0076	2.4744
MERNÍK - V1	810	0.0384	0.0474	0.0870
MERNÍK - V2	880	0.2704	0.3073	0.0520

Tab. 1: Overview of the quantitative and qualitative characteristics of the samples

The largest amount of oxyhydroxide precipitates produced by sedimentation under laboratory conditions was recorded in the sample SMOLNÍK. From a sample volume of 2 830 ml, we collected 0.7169 g of precipitates by filtration, which equals to 0.2533 g/l. On the contrary, the smallest amount of precipitate was obtained from the sample DÚBRAVA, where 0.0218 g of precipitates were collected from the sample volume of 5 290 ml, which equals to 0.0041 g/l. This finding also corresponds with the Fe content measured in water samples.

From the results presented in table 1, we can see that the more Fe the water sample contains, the more iron oxyhydroxides can precipitate from the water. Exceptions are the samples MERNÍK – V1 and MERNÍK – V2, where the Fe content in water samples was relatively low. The reason for the higher proportion of solids filtered from these samples despite the low Fe content will be a subject of further research.

CONCLUSIONS

In our research, we have successfully proven, that supported attenuation is more effective than natural attenuation, and that supported attenuation leads to increased and accelerated precipitation of secondary mineral phases in the form of Fe oxyhydroxides, which serve as an effective absorbent for removing potentially toxic elements from iron-rich mining waters. Also, we have proven the fact, that the higher the content of Fe in the mining water, the more iron-oxyhydroxide precipitates could be sedimented from the water.

ACKNOWLEDGEMENTS

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THE LEAD COMPOUNDS IN THE SOIL IN CONDITIONS OF AIR POLLUTION

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KEYWORDS
Haplic Chernozem, Miller's method, lead, fractional distribution, compound forms

ABSTRACT

The fractional composition of Pb in Haplic Chernozem under effect of long-term technogenic emission from Novocherkassk State Power Plant was studied. Analysis of the Pb compounds in the soils was carried out by Miller's method sequential fractionation in the modification of Berti, Jacobs (Berti, Jacobs, 1996). The method allows to extract water-soluble heavy metal forms, bound to Mn oxides, bound to amorphous and crystallized Fe forms. Monitoring plots were situated at different distance from the Power Plant. The soil located at distance up to 1.6 km has been exposed to active influence of aerosol emission, and effect of plant emission decreased significantly from 1.6 up to 15.0 km from the factory. The major part of Pb (66 %) was retained in the primary and secondary minerals in uncontaminated soil. The highest increase in Pb percentage was observed in the organic matter from 8 % to 27 % and most mobile fractions from 2 % to 4 % in contaminated soil. The Pb percentage increased from 5 % to 12 % in the fractions bound to amorphous Fe oxides while its share in the fractions of crystalline Fe forms decreased.

Soil is a foundation for plant life and any toxic substances contained in them can affect humans through the food chain. The enterprises of the power industry worked by coal are one of the active sources of environmental pollution with heavy metals. One of the biggest power industry in the South of Russia is Novocherkassk State Power Plant. The atmospheric emissions contain heavy metals including Pb.
Monitoring plots are occupied by Haplic Chernozem (WRB 2006) at a distance of 1.6 and 15,0 km along the main North-West direction wind from Power Plant (Rostov region, Russia). Soil was sampled from the humus-accumulative A1 horizon (0–20 cm). The soil had the following properties (g kg^{-1}) at a distance of 1.6 and 15,0 km respectively: C_{org} 0.45 and 0.42; $CaCO_3$ 0.07; physical clay 5.5 and 5.4; clay 3.0 and 3.1; pH_{H_2O} 7.4 and 7.6; exchangeable bases (cmol kg^{-1}): Ca^{2+} 32.0 and 32.1, Mg^{2+} 6.0 and 5.9, Na^{+} 0.06 (Vorob'eva 2006).
Analysis of the Cu compounds in the soils was carried out by Miller's method modified by Berti & Jacobs (1996). The method distinguishes between 8 different fractions: 1. water-soluble (Deionized water); 2. exchangeable (0.5 M $Ca(NO_3)_2$); 3. bound to carbonates (0.44 M CH_3COOH); 4. Mn oxide (0.1 M $NH_2OH{\cdot}HCl$ + 0.01 M HNO_3); 5. organic matter (0.1 M $Na_4P_2O_7$); 6. non-crystalline (amorphous) Fe oxide (0.175 M $(NH_4)_2C_2O_4$ + 0.1 M $H_2C_2O_4$ (oxalate reagent)); 7. Crystalline Fe oxide (oxalate reagent, ultraviolet irradiation); 8. Residual (HF, $HClO_4$, HNO_3).
The total Pb content in the soils of model experiment was determined by X-ray fluorescence on spectroscan "MAKC-GV". Analysis of Pb content in soil extracts was performed by atomic absorption spectrophotometry (AAS).

The total content of Pb in the Haplic Chernozem located at a distance of 1.6 km from the Power Plant corresponds to the background levels (Minkina et al. 2014). The total Pb contents in the studied soils were close to the sum of fractions of this metal (Table 1).

Distance from Plant, km	Fractions									Total content
	water soluble	exchangeable	bound to carbonates	bound to Mn	bound to organic matter	bound to amorphous Fe oxides	bound to crystalline Fe oxides	residual	sum	
15.0	0,4±0,1	0,6±0,1	1,6±0,3	0,9±0,4	2,0±0,3	1,2±0,2	1,8±0,4	16,6±3,8	26,6±2,0	28.0±1,8
1.6	1,2±0,1	2,4±0,5	8,0±1,3	1,4±0,5	17,4±3,7	7,5±1,5	3,4±0,6	23,7±5,3	67,2±6,9	68.0±7,5

Table 1. Fractional composition of Pb in Haplic Chernozem determined by the Miller method modified by Berti and Jacobs (1996), mg kg^{-1} (*n* = 9)

It is found that the soil located at a distance of 1.6 km from the Power Plant is exposed to active influence of aerosol emission. At a distance of 15.0 km from the Plant, its impact on the soil is reduced significantly.

Primary and secondary minerals significantly contributed to the fixation of Pb in the uncontaminated soil (located at a distance 15.0 km) (66 %) (Table 1). The relative content of Pb was 8 % in the fraction bound to organic matter, 7 % in the fraction bound to crystalline Fe oxides, 6% in the fraction bound to carbonates, 4% in the fraction bound to Mn. The least amount of Pb (2 %) was noted in the water-soluble and exchangeable fractions.

The Pb distribution of fraction forms in the uncontaminated Haplic Chernozem (Table 1) was determined: residual Pb > Pb bound to organic matter > Pb bound to crystalline Fe oxides > Pb bound to carbonates > Pb bound to amorphous Fe oxides > Pb bound to Mn > exchangeable Pb > water-soluble Pb.

In the contaminated soil (located at a distance 1.6 km) resulted in an increase in the relative contents of Pb fractions: the exchangeable fraction increased in twofold (4 %), the fraction bound to carbonates in twofold (12 %), and the fraction bound to amorphous Fe oxides in 2.4 times (12 %). The highest increase in Pb percentage was observed in the organic matter (up to 27 %). At the same time, Pb percentage in the residual fraction is reduced.

Thus, organic matter, nonsilicate iron and carbonates compounds are the main components that retain Pb coming into the soil at aerosol pollution. The contamination of soil results in an increase in the content of Pb bound to amorphous Fe forms. In contaminated soil, the relative content of metal in the residual fraction decreases and the percentage of the most mobile metal fractions increases.

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LITERATURE

Berti, W.R. & Jacobs, L.W. 1996. Chemistry and phytotoxicity of soil trace elements from repeated sewage sludge applications. Journal of Environmental Quality, 25, 1025–1032.

Minkina, T.M., Mandzhieva, S.S., Motusova, G.V., Burachevskaya, M.V., Nazarenko, O.G., Sushkova, S.S., Kızılkaya, R. 2014. Heavy metal compounds in a soil of technogenic zone as indicate of its ecological state. Eur. Soil Sci., 44, 144 – 151.

Vorob'eva, L. A. 2006. Theory and Practice Chemical Analysis of Soils, pp. 1–400, GEOS, Moscow (in Russian).

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CONSTRUCTION OF PLANT FOR WASTEWATER TREATMENT

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KEYWORDS
wastewater, water pollution, wastewater treatment plants

ABSTRACT

The term contaminated waters means waters that have changed their original composition by introducing harmful substances whose presence has caused a change in the physical, chemical, biological and bacteriological properties of the water, where it becomes dangerous for use and has limited use. “Wastewater” comes from households, human and animal waste, industrial enterprises, atmospheric precipitation and from the infiltration of groundwater. Waste water is in principle water from the water supply system that expires after its use by the community. It is 99.94 % water by mass. The remaining 0.06 % is a substance that is dissolved or mixed in water. To a large extent, it is the same amount of water that leads to the community and is contaminated on different grounds. The efficient operation and management of the wastewater treatment plant (WWTP) requires a thorough knowledge of the composition of the water that flows (the influent), the purified water (effluent), and the internal process flows by the experts (operators) who lead the process purification. In order to gain this knowledge, the operator determines the characteristics of raw sewage and other flows by collecting and analyzing representative samples throughout the plant.

INTRODUCTION

Wastewater is any water used once for different uses (existential or industrial), which has undergone changes in its quality. Wastewater consists of water in a liquid state, littered with waste from human activities in the household, commercial and industrial activities, agriculture, and covers a wide range of potentially harmful pollutants (contaminants/pollutants) to the environment. Sewage drainage is a synonym for wastewater contaminated with urgent feces, although it is often used to mark wastewater from households, communal waste water or liquid waste from the industry's disposal (discharged) through pipes (sewer networks).

ORIGIN OF WASTEWATER

Every human activity, unconditionally, resulting in separation of waste water, ie, contaminants found in wastewater can be of various origins:

1. Human waste (faeces and urine, used toilet paper, handkerchiefs, and other unwanted fluids), known as black water, commonly from sinks.
2. Ejectings from septic tanks and/or sewage treatment plants (processing)
3. Water used for the maintenance of personal hygiene – (washing clothes, washing the floor), is known as gray water
4. Rainwater (water collected after rainfall on the roofs, yards (usually this water is pure water but contains traces of oil
5. Subsoil water (infiltrated into the sewage system)
6. Additionally formed fluids from a domestic source – (drinks, cooking oil, pesticide lubricating oils, paints, liquid cleaning agents)
7. Consequences of floods in urban areas (from streets, car parks, sidewalks) – that water usually contains oils, animal droppings, soil, residues from fuel and rubber, metals from the outer parts of vehicles
8. Salt water additives (large amounts of salts and other compounds containing a large amount of soluble salts
9. Direct additions of river waters (high content of microbial)
10. Drainage after storm drainage (so-called cars, bicycles, trees)

RELEVANT LEGAL ACTS OF EU LEGISLATION

In the course of the implementation of the project "Wastewater Treatment Plant on the territory of the Municipality of Strumica", particular consideration should be given to:

The EIA Directive (85/337 / EEC), as amended in 1997, 2003, 2009, codified version, ie Directive 2011/92 / EC, which was last amended in 2014 with the Directive 2014/52 / EC, Directive on urban waters (91/271 / EEC), Water Framework Directive (2000/60 / EC), Directive 6/278 / EEC on the protection of the environment, in particular soil from the use of sludge in agriculture, (2006/118 / EC).

TREATMENT OF WASTEWATER

Purification of wastewater is carried out in wastewater treatment plants (Figure 1), which are designed depending on the location, the quantity of waste water. Waste water treatment can be divided into 4 (four) main groups: Mechanical purification, biological treatment, treatment and use of sludge, small purification **devices.**

Figure 1. Appearance of wastewater treatment plants

According to the operations carried out in the treatment plants, they are divided into 3 main operations: Primary, secondary and tertiary wastewater treatment. In the process of primary wastewater treatment, the suspended and emulsified substances are removed by means of deposition, filtration and flotation. In the secondary treatment of wastewater, colloidal and parts of dissolved organic matter are removed chemically and biologically, and by tertiary treatment, the residual pollution from the type of organic matter, pathogens and toxic substances is lagging behind.

One of the most modern wastewater treatment plants in the Republic of Macedonia was the purification plant in Strumica, which was designed according to EU regulations. The installation and operation of this refining station provides sufficient quantity of high quality drinking water to the population, reduction of water losses in the water supply network, increasing the share of households connected to the water network through the rehabilitation of the existing construction of new water supply systems. The installed facilities at the Purification Station (Figure 2), located in the village of Sachevo, on an area of 55 thousand square meters, cover the city of Strumica with 53,419 inhabitants and 12 settlements, with a daily sewage capacity of 9,458 m3.

Figure 2. Appearance of the purification plant in city Strumica

The purification station in Strumica in its constituent part of the facilities includes the following: sludge reception station from septic tanks, grilles for large and small waste, inlet pump station, aeration grid compartments with grid, inlet for distribution of incoming sewage and return active sludge, distributive chamber to the secondary sedimentary trough, secondary sedimentation troughs, pumping station for return active sludge and surplus sludge, gravity thickener sludge, sludge storage tank, sludge drainage, pump station for waste water from the installation itself, smell control (reduction) plan.

CONCLUSION

Having in mind the complexity in the interconnection of water, man, economy and the natural environment, the promotion of scientific research in this area is of great importance. In addition to developing technical, biological and legal research, it is also necessary to develop hydro-economic research that can solve quite practical problems related to the qualitative and quantitative management of existing water supplies. Nowadays the most economical way of wastewater treatment, the first place, holds the biological treatment.

LITERATURE

Water Environment Federation: Operation of Municipal Waste Water Treatment Plants, McGraw-Hill, 2008; Operation of Wastewater Treatment Plants, Volume 1, 6th Edition, Chapter 6, “Trickling Filters; California State University, Sacramento, 1988; WEF:Developing Source Control Programs for Commercial and Industrial Wastewater, WEF Press, 1996;Industrial Wastewater Management,Treatment and Disposal Task Force of the Water Environment Federation: Industrial Wastewater Management, Treatment and Disposal, McGraw-Hill, 2008.

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PRELIMINARY INVESTIGATIONS REGARDING THE POTENTIAL OF HUMIC SUBSTANCES TO EXTRACT NICKEL FROM CONTAMINATED SOIL

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KEYWORDS
Soil remediation, humic substances, nickel, mining areas.

ABSTRACT

Effective soil remediation at contaminated mining sites very often needs customized remediation technologies due to the characteristics of the soil and the content and types of pollutants. Among other technologies, soil washing prove to be a valid and effective technology to remove heavy metals from multi-metal polluted soil. However, there is a need for inexpensive and environmentally-friendly soil washing agents to extract heavy metals from contaminated soil. Thus, in this study, a series of remediation experiments using a 2% solution of humic substances extracted from Leonardite were performed in order to quantitatively evaluate the feasibility of using this natural washing agent to remove nickel from soil collected from "Larga de Sus" mine (Zlatna, Romania). In the investigated experimental conditions, the preliminary results showed that natural humic substances are able to remove more than 94% nickel from contaminated soil after 12 hours of stirring. Best extraction yield (56.3 %) of the washing technology was obtained after six hours of stirring indicating that humic substances are suitable to be used as washing agents to remove nickel from contaminated soil.

AIMS AND BACKGROUND

Heavy metals persist for a long time in soil causing severe environmental problems and risks on human health, through the introduction of non biodegradable heavy metals from soil in the food chain (Khalid et al., 2017). Thus, remediation of soil contaminated with heavy metals is necessary. Currently, soil washing that generally uses chemical solutions to extract heavy metals, is one of the few effective treatment alternatives for the elimination of heavy metals from highly contaminated soils such the ones nearby mining areas (Dermont et al., 2008). The overall objective of any soil remediation approach is to create a final solution that is protective of human health and the environment (Wuana and Okieimen, 2011). Thus, the main objective of the present study, was to evaluate the feasibility of using natural and eco-friendly humic substances extracted from Leonardite as washing agent to remove nickel from soil collected from "Larga de Sus" mine (Zlatna town, Romania) with the scope of finding a substitute of synthetic chemicals generally used in soil washing technology.

EXPERIMENTAL AND RESULTS

For soil washing experiment a soil sample from 10–90 cm depth was collected from a pasture located at about 800 meters downstream the "Larga de Sus" mine. The concentration of Ni from collected soil was determined by atomic adsorption spectrometry (AAS). Soil sample was processed according to procedure described in SR ISO 11464:1998. A humic substance sample extracted from German Leonardite (commercially found as Powhumus WSG-85) was investigated in the present study as potential extracting agent for Ni found in soil collected from "Larga de Sus" mine. The soil washing experiments using humic substances were conducted at a liquid/solid ratio (L/S ratio) of 8:1 (mL/g) in a 100 ml batch reactor with continuous orbital rotation-oscillation stirring at 100 oscillations/minute. Polluted soil was stirred with 2% humic solution for different time intervals (360, 720, 1440 min) then samples were collected, filtered through 0.45 μm pore size filter and concentration of Ni in the supernatants and treated soil samples was measured through AAS.

Effectiveness of the extraction method was quantitatively determined using extraction yield, according to the following equation (Sur et al., 2018):

$$\eta\ (\%) = m_e/m_i * 100$$

where: m_e is the extracted pollutant concentration (mgkg^{-1}); m_i is the initial pollutant concentration present in the soil (mgkg^{-1}).

Percent of metal removed was also quantitatively determinated using the next equation (Wuana et al. 2010):

$$Percent\ of\ metal\ removal\ (\%) = (C_l * V_l)/(C_s * m_s) * 100$$

where: C_l and C_s = concentration of metal in supernatant (mgL^{-1}) and soil (mgkg^{-1}); V_l = volume of supernatant (L) and m_S = dry mass of the soil (kg).

The variation of concentration (conc.) of Ni in soil and supernatant, extraction yield of Ni from soil and percent of metal removed from soil along investigated stirring time (up to 1440 min) is ilustrated in Fig.1.

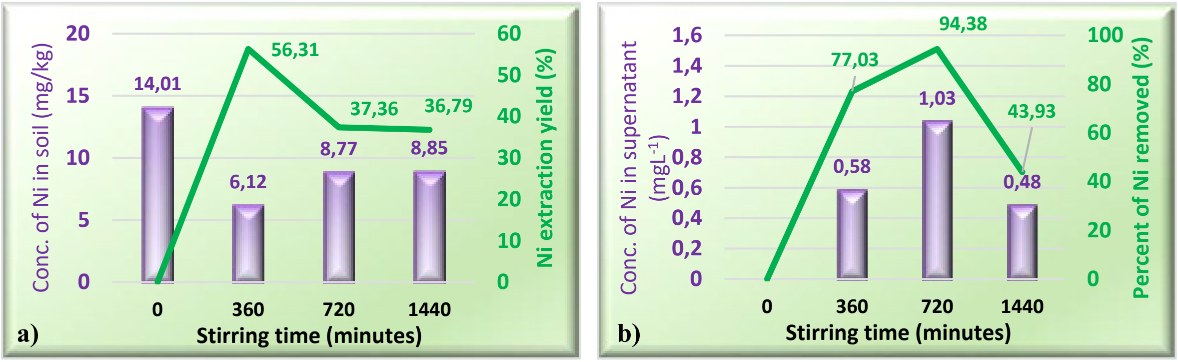

Fig. 1 a) Variation of concentration of Ni in soil and extraction yield of Ni from soil during stirring time; b) Variation of concentration of Ni in supernatant and percent of Ni removed from soil during stirring time.

As it can be seen in Fig. 1a, concentration of Ni from soil decrease to less than half of its initial value (14.01 $mgkg^{-1}$) after 360 min of stirring, with an extraction yield of the washing technology of 56.3%. Congruent, the concentration of Ni in supernatant increase with stirring time to 1.03 mgL^{-1} after 720 min of stirring, while percent of Ni removed from soil was 94,38%. The best results were obtained at shorter stirring times, indicating the high efficiency and rapidity of the applied soil washing technology.

CONCLUSIONS

In the investigated experimental conditions, the results indicate that natural humic substances are able to remove more than 94% nickel from contaminated soil collected from “Larga de Sus” mine after 12 hours of stirring. The best extraction yield (56.3%) of the soil washing technology was obtained after 6 hours of stirring indicating the rapidity of the soil remediation. Results revealed a high potential of humic substances to be used as washing agent to extract nickel from contaminated soil.

LITERATURE

Dermont, G., Bergeron, M., Mercier, G., Richer-Lafl`eche, M., 2008: Soil washing for metal removal: A review of physical/chemical technologies and field applications. Journal of Hazardous Materials, 152: 1–31.
Khalid, S., Shahid, M., KhanNiazi, N., Murtaza, B., Bibi, I., Dumat, C., 2017: A comparison of technologies for remediation of heavy metal contaminated soils. Journal of Geochemical Exploration, 182: 247–268.
SR ISO 11464: 1998 Soil quality - Pretreatment of samples for physico-chemical analysis.
Sur, I.M., Micle, V., Gabor, T. 2018. Heavy metals removal by bioleaching using Thiobacillus ferrooxidans. Romanian Biotechnological Letters 23(2): 13409-13416.
Wuana, R. A. and Okieimen, F. E., 2011: Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. ISRN Ecology 11: 1–20.
Wuana, R.A., Okieimen, F.E., Imborvungu, J.A, 2010: Removal of heavy metals from a contaminated soil using organic chelating acids. Int. J. Environ. Sci. Tech 7 (3): 485–496.

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BIOREMEDIATION OF POLYCHLORINATED BIPHENYLS (PCBs): INTEGRATION OF BIOTECHNOLOGY AND NANOTECHNOLOGY APPROACHES

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KEYWORDS

Bacteria, bio-nano-remediation, nano-bio-remediation, nano-zerovalent iron (nZVI), polychlorinated biphenyls

ABSTRACT

PCBs are a group of hydrophobic, toxic substances with tendency to persist in organic matter of soils and adipose tissues of animals. As their removal from the environment is essential, many technologies for their elimination have been introduced into practice. Integration of nanotechnology and biotechnology we studied using sequential application of nano-bio and bio-nano approaches. The first approach implies the addition of reductive nanoscale zerovalent iron particles (nZVI) and a subsequent inoculation with a bacterial strain isolated from the PCB-contaminated sediment with the suitable degradation ability. The second approach involves a reverse assay. The background for used bacterial strains regarding isolation, identification and bioaugmentation can be find in our previous papers (Dudášová et al., 2014; Murínová and Dercová, 2014; Dercová et al., 2015; Horváthová et al., 2018a; Horváthová et al., 2018b; Lászlová et al., 2016; Lászlová et al., 2018) and the background for using of iron nanoparticles in some latest review papers (Fu et al., 2014; Kumari and Singh, 2016; Stefaniuk et al., 2016; Zhao et al., 2016).

The reductive dehalogenation of PCBs using nanoparticles and biodegradation of PCBs using bacteria are two different processes regarding the oxygen supply. The former process is inhibited by oxygen, whereas aerobic degradation of PCBs by bacteria requires oxygen. Due to this reason, the individual processes were performed in two different apparatuses. Experiments were performed in the defined minimal mineral media artificially spiked with PCBs technical mixture Delor 103) and in the real PCB-contaminated river sediment sampled from the surroundings of the former PCB manufacturing facility historically contaminated with PCBs, mainly with Delor 103. The process was started by bioremediation, which was carried out in 500 ml cultivation flasks with the addition of PCBs (100 mg/ml) and bacterial inocula (1 g/l) at 28°C. After 14 days, contents of the whole flask were transferred to 100 ml closable glass bottles and nZVI suspension was added. Cultivation with nZVI lasted another 14 days and the residual PCBs were extracted with n-hexane and indicator PCB congeners were subsequently analyzed by GC-ECD. The reverse order was tested as well: the addition of nanoparticles followed by inoculation of bacteria. The toxicity of nZVI towards the cells was evaluated using the relevant bacterial strains and a short-term germination test with a plant *Sinapsis alba.*

Sequential application in the order „nZVI → bacteria“ (nano-bio approach) appeared to be more effective than bacteria→nZVI (bio-nano approach). The integration of nZVI followed by the bacterial strain *Stenotrophomonas maltophilia* removed 95 % and by the bacterial strain *Ochrobactrum anthropi* removed almost 99 % of the total indicator PCB congeners. Application of the reverse order also resulted in the removal of PCBs, however to a lower extent. The elimination rate was slightly higher in comparison with biodegradation by the relevant single strains. To determine the toxicity of nZVI suspension, concentrations 0.5; 1; 5 and 7 g/l were tested. The used bacteria were more sensitive in comparison with *S. alba*, whereas the growth of both strains was observed only at concentration 0.5 g/l of nZVI, while the germination of *S. alba* was totally inhibited only at 7 g/l.

The applied innovative integration of nano-bio-remediation performed under microcosm´s conditions revealed effective elimination of PCBs, which is applicable also in the field conditions. It is important to note that the process in the trial experiments may be influenced also by other environmental factors, which implies that a scale-up experiment should be performed.

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REFERENCES

Dercová, K., Lászlová, K., Dudášová, H., Murínová, S., Balaščáková, M., Škarba, J., 2015: The hierarchy in selection of bioremediation techniques: the potentials of utilizing bacterial degraders. Chemické Listy 109: 279 – 288.

Dudášová, H., Lukáčová, L., Murínová, S., Puškárová, A., Pangallo, D., Dercová, K., 2014: Bacterial strains isolated from PCB-contaminated sediments and their use for bioaugmentation strategy in microcosms. Journal of Basic Microbiology 54(4): 253 – 260.

Fu, F., Dionysiou, D.D., Liu, H., 2014: The use of zero-valent iron for groundwater remediation and wastewater treatment: a review. Journal of Hazardous Materials 267: 194 – 205.

Horváthová, H., Lászlová, K., Dercová, K., 2018a: Bioremediation of PCB-contaminated shallow river sediments: The efficacy of biodegradation using individual bacterial strains and their consortia. Chemosphere 193: 270 – 277.

Horváthová, H., Lászlová, K., Dercová, K., 2018b: The remediation potential of bacterial mixed cultures for the biodegradation of polychlorinated biphenyls (PCBs) (under revision)

Kumari B., Singh D.P., 2016: A review on multifaced application of nanoparticles in the field of bioremediation of petroleum hydrocarbons. Ecological Engineering 97: 98 – 105.

Lászlová, K., Dercová, K., Horváthová, H., Murínová, S., Škarba, J., Dudášová, H., 2016: Assisted bioremediation approaches – biostimulation and bioaugmentation – used in the removal of organochlorinated pollutants from the contaminated bottom sediments. International Journal of Environmental Research 10(3): 367 – 378

Lászlová, K., Dudášová, H., Olejníková, P., Horváthová, G., Velická, Z., Horváthová H., Dercová, K., 2018: The application of biosurfactants in bioremediation of the aged sediment contaminated with polychlorinated biphenyls. Water, Air, & Soil Pollution 229: 219.

Murínová, S., Dercová, K., 2014: Potential use of newly isolated bacterial strain Ochrobactrum anthropi in bioremediation of polychlorinated biphenyls. Water, Air, & Soil Pollution 225: 1980.

Stefaniuk, M., Oleszczuk, P., Ok, Y.S., 2016: Review of nanozerovalent iron (nZVI): from synthesis to environmental application. Chemical Engineering Journal 287: 618 – 632.

Zhao, X., Liu, W., Cai, Z., Han, B., Qian, T., Zhao, D., 2016: An overwiev of preparation and application of stabilized zero-valent iron nanoparticles for soil and groundwater remediation. Water Research 100: 245 – 266.

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THE IMPACT OF TECHNOGENIC POLLUTION ON HERBACEOUS PLANT COMMUNITIES

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KEYWORDS
Plant, soil, contamination, heavy metal, transformation, bioavailability

ABSTRACT

The effect of different metals forms content in the soil and technogenic emissions level on the input of Pb, Zn, Cd, Cu, Mn, Cr, and Ni into herbaceous plants of the different families has been studied. Correlation between the heavy metals (HM) accumulation in different plant species and the distance from the emission source has revealed. High technogenic emissions level has impact on the metals mobile forms in the soil, the main element sources in plants. Another HM distribution factor in the above and underground plants parts include the individual physiological features of different plants determining their barrier function. It has proposed to evaluate herbaceous plants resistance parameters by the acropetal coefficient, which characterizes the input of pollutants at the root–aboveground organs boundary, and the accumulation factor values. *Elytrigia repens* is most resistant to the contamination with Pb, Cr, Zn, Mn, Ni, and Cu. *Ambrosia artemisiifolia (L.), Artemisia austriaca (Pall. ex. Wild.), Achillea nobilis (L.), and Tanacetum vulgare (L.)* are HM accumulators.

INTRODUCTION

The studies on input of heavy metals (HM) to plants are very important practical aspects of scientific research. First, the plants were considered as an intermediate reservoir for HM translocation from water, air and especially from soil to human body, and the accumulation of heavy metals along the food chain is a serious threat for animal and human health. In this case, the methods are required to prevent the input of heavy metals at toxic concentration. The increased concentration of heavy metals is rather toxic for plants and for this reason, a number of problems raises to determine the plant response to an excessive HM amount in soil. In the third place, the possible use of plants as bioindicators for the environment contamination with heavy metals should be thoroughly studied (Minkina et al., 2012). Every metal taken up by plants for a long period is accumulated in them to a definite level, above which significant harmful changes occur in the plant quality. Adverse consequences of such accumulation were manifested in time, depending on technogenic loads and the response of the soil-plant system to heavy metals. In this context, long-term stationary observations serve as a valuable source of information.

The heavy metals of interest in the present study are Cr, Ni, Mn, Cd, Cu, Pb and Zn. The long-term monitoring allowed evaluating their accumulation in grasslands located at technogenic territories.

MATERIAL AND METHODS

The objects of research are abandoned sites of grasslands near Novocherkassk power station (NPS) in Rostov region (Russia). The latter is known as a region of intensive agricultural production and industrial center. The enterprises of mining and manufacturing industry, power engineering, and metallurgy are basic sources for heavy metal contamination of the environment. Novocherkassk power station is one of the largest stations in Russia to be a source of pollutant discharges not only in Novocherkassk but also in the entire region.

Ten monitoring plots were prepared from the NPS (1.0–20.0 km). A relatively greater number of plots were arranged in the "main direction" from the NPS according to the prevailing wind direction to the northwest of the pollution source through the residential areas of the city of Novocherkassk (plots 4, 5, 8, 9 and 10) (Minkina et al., 2013).

The majority of the soils of monitoring plots were ordinary chernozems; the low-humus calcareous sandy alluvial meadow soil, which had a light texture and a low cation exchange capacity (CEC), and the low-humus silty clayey meadow-chernozemic floodplain soil with a high CEC that differed from the control soils.

Plant sampling was taken to analyze the averaged samples of grass harvest at monitoring sites; under study was a terrestrial part of such plants as *Elytrigia repense, Artemisia austriaca, Achillea millefolium, Tanacetum vulgare, Ambrosia artemisiifolia, Cichorium intybus*. Since 2000 the soil and plant sampling has being taken yearly in the second half of June in the period of the active plant growth and development.

General analytical procedures

The total contents of Cr, Ni, Mn, Cd, Cu, Zn and Pb in the soils were determined with the X-ray fluorescence method.

The HM compounds classified as loosely bound were transferred to solution by means of parallel extractions using the following reagents (Minkina et al., 2008): 1 N ammonium acetate buffer (NH_4Ac) pH 4.8 (soil : solution ratio 1 : 10, extraction time 18 h) capable of solubilizing the exchangeable forms of metals characterizing their "actual" mobility. 1 % EDTA solution in NH_4Ac with pH 4.8 (soil : solution ratio 1 : 10, extraction time 18 h), which supposedly solubilizes the relatively unstable complex compounds of metals together with their exchangeable forms. The concentrations of the metals in the complex compounds were calculated by the difference between the metal concentrations in extracts 2 and 1. The acid soluble metal compounds extracted with 1 N HCl (soil : solution ratio 1 : 10, extraction time 1 h) characterize the reserve of the mobile metal compounds in the soil. They are supposedly represented by the metal ions capable of exchange and by the specifically absorbed compounds including the Fe and Mn retained by the amorphous oxides and carbonates. The amount of specifically absorbed metal compounds was calculated by the difference between the metal concentrations in the HCl and NH_4Ac extracts. Under study were exchangeable, complex and specifically sorbed HM compounds represented a group of loosely bound ones to be the most important from ecological viewpoint and capable to enter adjacent areas and the plants in particular.

The concentration of HMs in the plants was determined using the wet combustion in a mixture of HNO_3 and HCl at 450°C. The content of heavy metals in extracts from soils and plants was determined by FAAS.

RESULTS AND DISCUSSION

To obtain a clearly expressed picture about the environmental situation at the territory within the influence zone of the above power station, it was necessary to determine the available relationship in distribution of heavy metals in soils and plants at the studied sites of grasslands.

HM total content at sites № 9 and № 10 located far from the power station does not exceed the maximum permissible concentration (MPC). The background content of Pb accounting for 25 mg kg^{-1} is in soil at the site № 9, while the site № 10 located in 500 m from a motor highway is contaminated with Pb largely. The content of loosely bound compounds and especially the most mobile exchangeable and complex ones is insignificant in soils of these monitoring sites and well agrees with their average content in grass plants of the given region.

The average Ni content in plants shows a change from 0.1 to 5.0 mg kg^{-1} dry mass, being varied from 1.3 to 1.5 mg kg^{-1} in wild grasses and 0.47 to 1.99 mg kg^{-1} in cultural ones. The total Ni content in plants varies in the range of 0.8–4.0 mg kg^{-1} at the entire territory of the region. The concentration of Mn, Cd, Cu, Zn and Pb in plants is 20–300, 0.05–03, 1.8–10, 30 and 1.5–2.1 mg kg^{-1} respectively (Kabata-Pendias, 2004).

Due to the effects exerted by discharges of the power station the total content of heavy metals proves to be increased in soils located near this contamination source along the line of wind rose (sites № 4, 5, 8) and at the site №6. The amount of loosely bound compounds increases as well. The total content of Cu, Pb, Zn and Cd and the content of their exchangeable compounds exceed the maximum allowable limit in these soils.

The plants at the sites located near the power station (within 5 km from the source) are contaminated with Ni, Cu, Zn and Pb, thus exceeding the maximum permissible concentration in the terrestrial part of grass plants. It is worth emphasizing that the plants at the site № 10 located in a distance of 20 km from the power station but near the motor highway, reveal an increased content of Pb by 3 times as compared to those grown at the site № 9. It exceeds the concentration of this metal allowed in plants by 2.4 times. The maximum content of HM in plants may be presented in the following way: Zn > Mn > Cu > Pb > Ni > Cd

The HM accumulation by plants is affected by soil properties. The concentration of Cd, Ni, Mn, Zn and Cu in plants grown on the meadow-chernozem soil (site № 3) is lower by 1.2–2.6 times than that on alluvial meadow sand soil (site № 2) characterized by insignificant buffering capacity to heavy metals.

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REFERENCES

Kabata-Pendias, A., 2004: Soil-plant transfer of trace elements – an environmental issue. Geoderma. 122 (2 – 4), 143 – 149.

Minkina, T.M., Motusova, G.V., Mandzhieva, S.S., Nazarenko, O.G., 2012: Ecological resistance of the soil-plant system to contamination by heavy metals. Journal of Geochemical Exploration. 123, 33 – 40.

Minkina, T.M., Motuzova, G.V., Mandzhieva, S.S., Nazarenko, O.G., Burachevskaya, M.V., Antonenko, E.M., 2013: Fractional and Group Composition of the Mn, Cr, Ni, and Cd compounds in the soils of technogenic landscapes in the impact zone of the Novocherkassk Power Station. Eurasian Soil Science. 46 (4), 375–385.

Minkina, T.M., Motuzova, G.V., Nazarenko, O.G., Kryshchenko, V.S., Mandzhieva, S.S., 2008: Combined approach for fractioning metal compounds in Soils. Eurasian Soil Science. 41 (11), 1170–1178.

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OBSERVATIONS FROM THE MONITORING OF ENVIRONMENTAL BURDENS OF THE CHEMIKA AND GUMON PLANTS IN BRATISLAVA, SLOVAKIA

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KEYWORDS

Bratislava, groundwater, monitoring, pollution, environmental burdens, Apollo refinery, Chemika and Gumon plants

ABSTRACT

In the capital of Slovakia, Bratislava, the industrial part of the city used to be located near the Danube River in the past. In addition, the Apollo refinery, Chemika and Gumon plants were located in this area as well.

The refinery was destroyed by the US army in 1944. These factories were in operation until the beginning of the 21st century. Since then, oil pollution has spread out of the refinery and has been diversified with chemical leakage from the Chemika and Gumon plants, mainly represented by chlorinated hydrocarbons or polycyclic aromatic hydrocarbons. Since the 1950s, many surveys have been carried out at the site (Auxt et al., 2002). In the period of 2004 and 2006, a remediation was carried out, however, only one of two planned remediation stages was implemented. Remediation has sufficiently reduced the content of contaminants in the soil and groundwater, nevertheless, the absence of the second stage of remediation is the reason for the still present contaminants in the area. Since 2014, the State Geological Institute of Dionýz Štúr has carried out the monitoring (Kordík et al., 2015). The oil phase is measured and observed in four boreholes (VN4-5 – in the premises of the Chemika plant, VN5-2, VN5-5, VN5-6 – in the premises of the Gumon plant).

Well	**OSFP August 2015 [cm]**	**OSFP October 2015 [cm]**	**OSFP August 2016 [cm]**	**OSFP October 2016 [cm]**	**OSFP March 2017 [cm]**	**OSFP June 2017 [cm]**	**OSFP September 2017 [cm]**
VN4-2	Film OS	Film OS	-	Spills OS	-	-	-
VN4-4	Film OS	Turbidity	Film OS	Film OS	-	-	-
VN4-5	9	11	6.28	9	6.51	6.71	6.76
VN4-7	Turbidity	Film OS	Film OS	Film OS	Film OS	Film OS	Film OS
VR4-1	-	Film OS	Film OS	-	-	-	-
VN5-1	-	Film OS	-	-	-	Odour	-
VN5-2	13	11	7.9	2	8.2	8.42	-
VN5-5	-	Film OS	-	1	6.13	6.31	8.3
VN5-6	-	Film OS	Film OS	0.1	Film OS	Film OS	6.39
VN5-7	-	Film OS	Weak film OS	0.1	Film OS	Film OS	Film OS
VR5-1	-	-	-	-			Film OS

Tab. 1 Free phase of oil substances thickness measured during the monitoring campaigns in 2015, 2016 and 2017

Note: OS – oil substances, OSFP – oil substances free phase

Fig.1 Withdrawn groundwater sample from the VN4-5 borehole polluted by the oil substances (Jantáková, 2017)

The predicted way of pollution spreading was through the rock environment and groundwater. The pollution was concentrated within the aquifer. It can be stated that the pollution has spread to areas previously remediated due to precipitation and groundwater flow. Nowadays, the area has become interesting for investors, therefore, massive investment in construction has recently begun (Jantáková, 2017). This construction could either prevent or make remediation impossible in the future.

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LITERATURE

Auxt, A., Šuchová, M., Murín, M., et al., 2002: Partial final report – ecological solution of the Košická - Landererová Area in Bratislava. Remediation of the ecological burden in the wider area of the industrial zone of the former Apollo refinery. Partial task: Risk analysis (risk assessment). HES – COMGEO spol. s r.o., Banská Bystrica. Manuscript – Archive of SGIDŠ Bratislava.

Jantáková, N., 2017: Monitoring of the impact of selected environmental sites in Bratislava area. Master thesis. Bratislava. 71 p.

Kordík, J., Slaninka, I., Bačová, N., et al., 2015: Monitoring of environmental burdens on selected locations of the Slovak Republic. Final report. SGIDŠ Bratislava. 252 p.

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APPLICATION OF LICHENES IN THE ENVIRONMENT

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KEYWORDS
secondary metabolites, lichen, lipic acid, atomic absorption, chemical analysis

ABSTRACT

Today, different forms of environmental threat are one of the main environmental factors pollution. Pollution causes a disturbed condition characterized by qualitative and quantitative changes in the physical, chemical and biological properties of the basic components (water, air, soil, food) of the environment. The sensitivity of the pollutant to the polluted air is known for a long time. Particularly sensitive to the increased concentration of SO_2, which is the largest polluter in the urban environment. The specificity of the lichens is that they are very sensitive to the reduced air quality. Secondary metabolites are commonly located in the extracellular sites where they appear as surface crystals; they are easily extracted with: acetone, ethanol or some other organic solvent, or a combination thereof in a suitable ratio to the mixture. Secondary metabolites are unusual compounds with a low molecular weight. Secondary products can serve to protect the thalus from other organisms and antibiotics.The most sensitive organisms are Gram – positive bacteria, fungi, and more than half of the lichen species have products capable of antibiosis.Active supernatants are lipic acid, semi – trivial acid derivatives, aliphatic acids, orcosin-based depsidins and depsidons. The protection of lipid acid from visible light should be minimal and larger than UV light. Uralic acid is often a major component of the lichen, for this purpose in our examination will be examined the lichens by determining the chemical and granulometric composition, heavy metals by atomic absorption and the determination of total mineral matter and sand content.

INTRODUCTION

In accordance with the continuous development of the food, pharmaceutical, cosmetic and chemical industries and stricter quality requirements for finished products, the substance of certain synthetic products and import components with natural products of vegetable origin is of particular interest. On the territory of R. Macedonia as a central part of the Balkan Peninsula collide with a large number of taxa. The rich complex composition of the lichen flora, its quantitative distribution in our region, the high demand for dry plant material from lichen flora abroad, as well as the fact that they have not yet been studied in the direction of separation, characterization and application of their components, are the main prerequisites for the usefulness of studying from plant representatives. Today, plants are used as raw materials to produce a large number of products that cannot be obtained by synthetic route, and are an important raw material and for the extraction of many active substances important for the preparation of various preparations. Lichens are lower thallophytic plants, represent symbiosis between algae and fungi and vegetate on various substrates such as: soil, stems and branches of different trees and stones. With the intense analysis and study of the lichen and their secondary metabolites from the beginning of this century, it is possible to use them for different purposes. Out of the number of representatives of the lichens in the Republic of Macedonia, the most common species are from the genera Ervernia and Pamelia.

LICHEN MORPHOLOGY AND THEIR CHARACTERISTICS

Lichens are symbiotic organisms that are composed of fungi, most commonly from the family of Ascomycetina and algae of the genus Cyanobacteriopyta or Chlorophuta. The usefulness of this common symbiosis also has the two members of this symbiosis because they complement one another and allow one to survive. The algae carries photosynthesis and supplies the fungus with organic matter, while the fungus with the aid of hyphae absorbs water from the substrate along with minerals and salts. The exchange of substances between algae and fungi is carried out through their cell walls. Fungi are considered to be builders of lichens because they prevail in a quantitative sense. In the composition of some lichens, the bacteria azotofixators, as a third symbiotic, enter. Lichens should not be understood as a simple symbiosis of two different organisms, because during their long lasting existence they function as the only organism with special properties, which are not typical for symbiotic partners. This is why the lichens occupy a separate systematic place, derived from other systemic groups in microbiology. Because of this, the lichens occupy a special systemic place, separated from other systemic groups in microbiology. Fungi – participants in the lichens, usually ascomycetes or basomycetes, while algae are single-celled green or blue-green. The lichen thalus has been built in its own way, morphologically, from a few millimeters to a hundred centimeters. By color are gray, green, whitish, in different shades of yellow or orange can meet. The intensity of the color may be strong in some cases, so that the lichen is dark brown or almost black. Coloring comes from the special kind of lichen acids that the lichen itself creates, not the fungus itself or algae itself. Lichens differ in anatomy. In some lichens, the thalus is evenly built of scattered hyphae, in which there are also evenly distributed algae – homomeric type of construction (Figure 1). In the heteromeric type of lichens (Figure 2), fungus hybrids are distributed in the surface layers, building a rather compact, protective part while the algae is located in the central part. Because they are located on the surface of the organism, fungi protect the lichen from excessive overheating and lighting.

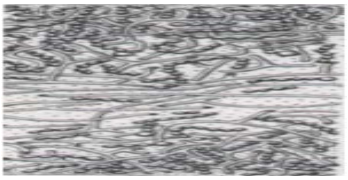

Fig. 1 Heteromeric lichen

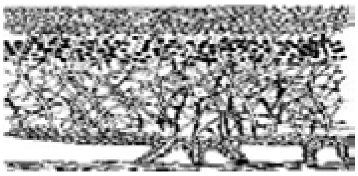

Fig. 2 Homemere lichen

Fig. 3 Cross-section through the thymus of the lichen Hypogymnia physodes. SEM micrographs

The reproduction of lichens is different. In some cases, the lichen, as the only organism, multiplies with special vegetative growths, built of two components morphologically differently shaped, sideburns that, when tearing off a solid foundation, the radiance and the insides, penetrate into a new lichen, completely identical to the lichen-parent. In other cases, each component of the lichen is proliferated in a characteristic manner, and after sprouting, if no adequate flow is obtained, the fungus or algae does not continue the individual development (Figure 3). Because the lichens are a kind of very complex symbiosis, built over a long period of time, the constituents are highly customized to each other, and in relation to the surrounding environment. As a result of the long-standing evolution, more than 20000 different types of lichens have been created. Their systatic division is based on the belongings of mushrooms: Ascolichenes. Basidiiolichenes. In our country, it is primarily deprived of the Ascolichenes group.

EXPERIMENTAL PART

Determination of dry mass content

Sample	Empty vegeglas (g)	Vegeglas with sample after drying (g)	Vegeglas with sample before drying (g)	Dry mass (%)
1	34,2841	36,0115	36,2090	89,7
2	31,0896	32,8455	33,0589	89,19

Tab. 1 Content on total dry mass

The average percentage of dry mass is 89.44 %.

Determination of total mineral matter (ash)

Sample	Empty porcelain pot (g)	Pot with sample before ignition (g)	Pot with sample after ignition (g)	Ash (%)
1	31,4647	33,4640	31,5316	3,35
2	38,7485	40,7474	38,8222	3,68

Tab. 2 Ash content

The mean value of ash is 3.52 %.

Determination of sand content in Usnea barbata

Sample	Empty porcelain pot (g)	Pot with sample before ignition (g)	Pot with sample after ignition (g)	Sand (%)
1	31,4647	32,6430	31,4759	0,9505
2	38,7485	40,0016	38,7606	0,9736

Tab. 3 The content of sand

The average value of sand is 0.9620 %.

LICHEN AS BILOGICAL INDICATORS OF AIR QUALITY

The sensitivity of the lichen of polluted air has been known for a long time. As early as the middle of the 19th century, the reduction of lichens from the Luxembourg Park in Paris was the cause of severe air pollution in that area. Since then, many studies have been done in urban areas and industrial areas around the world, they have confirmed exceptional selectivity of lichens to different levels of air quality. Particularly sensitive to the increased concentration of SO_2, which is the largest pollutant in urban city areas. The specificity of the lichens is that they are very sensitive to the reduced air quality. Many European countries use mosses and lichens as bioindicators for this purpose since the beginning of 1960. During national and multinational research on the deposition of metals from the atmosphere. For the first time, the method of using mosses and lichens as bioindicators of air pollution was introduced and developed on the territory of Scandinavia in the late 1960s. The first nationwide survey was launched in the territory of Sweden, Norway and Denmark in the early 1970s and 1980s. During the 1980s, a survey was launched covering all Nordic countries, and in the 1990s the survey covered most European countries. Lichens are symbiotic organisms composed of fungus (fungi) and green algae or blue-green bacteria. Lichens differ from the higher plants in that they do not have a root system, and the necessary nutrients provide them from wet and dry substrates, most often through plants. These characteristics make the lichens suitable for bioindicators for the spatial and temporal assessment of atmospheric pollution in a particular area. In general, there are three basic mechanisms of absorption of metal ions of the lichens: intercellular absorption through ion exchange process, intercellular accumulation, capture of fine particles containing high metal content. The accumulation of metals in the tissue of the lichen tissue over time can alter during the accumulation phase and gradual release. The processes of absorption of metals in lichens affect: pH of the environment (background acidity), seasonal changes, geographical variability, soil dust. The most commonly used types of lichens as bioindicators are those of the genus Hypogymnia sp. (Hypogymnia physodes) Parmelia sp. (Parmelia sulcata and Parmelia caperata), as well as species of the genus Cladonia sp. of the territory of the Republic Macedonia widespread species of the genus epiphytic lichen Evernia sp. (Evernia prunastri), for which a bioindicator for such issues is suitable.

Different morphological and physiological characteristics between mosses and lichens usually reflect the differences in the ability to “consume” the metals from the atmosphere. The surface constitution of the mosses is different from that of the lichens. They have a very large area and are with a dense constitution. The surface in most lichens is more abundant and not so dense than in mosses. A large number of studies have shown that epiphytic lichens more accumulate heavy metals expressed on a dry mass than the mosses. The reason for this difference may be due to the variation in the ability to accumulate under different conditions or due to the effect of precipitation in the epiphytic lichen. Lichens also accumulate soluble heavy metals (Hg, Pb), which are continuously recycled back into the atmosphere, much more efficiently than the mosses. Unlike lichens, mosses are much easier to accumulate atmospheric dust.

CONCLUSION

Contraindications for the use of lichens have not yet been fully understood by science. Allergic reactions to individual components. Nor can the possibility of individual intolerance be ruled out. Lichen-based preparations are not recommended for pregnant and lactating women - the potential for side effects. Before starting treatment, you should consult a doctor or pharmacist. Lichens should be consumed in small quantities because they are quite rich in carbohydrates, and organic acids. Because lichens are similar to mushrooms that change their color, it is necessary to choose their own sorting and sorting families, families and types of lichens, because many of them easily change color and take in a similar kind of lichens that have different characteristics and actions of the human body.

REFERENCES

Групче, Р., 1986: “Ботаника’’, Просветно Дело, Скопје.
Damic, M., 1985: „Praktikum iz Biohemije“, Beograd.
Jacobs, J., A, 1985: Lichenogist.
Honegger, R., Ultrastructural studies in lichanes II. Mucobiont and photobionat cell wall surface layers and layeres and adhering crystalline lichen products in four Parmeliaceae. New Putol

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COMPARISON OF THE DYNAMICS OF SELECTED PHYSICAL AND PHYSICOCHEMICAL PROPERTIES DURING COMPOSTING OF TWO DIFFERENT WASTES PRODUCED FROM SOLID MUNICIPAL WASTES AND BIOMASS PRODUCED FROM ENERGETIC PLANTS

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KEYWORDS
MSW compost, CEC, compost maturity

ABSTRACT

The aim of the research was to analyze the composting process, in the aspect of changes of some physical and physicochemical properties of the organic part of municipal solid waste and biomass of willow and hay mixture. In the compost produced from biomass of willow and hay mixture, the thermophilic phase was achieved later than in the compost produced from municipal waste and lasted much shorter. The dynamics of changes in CEC values in relation to the base value of the initial materials of both tested composts was higher for MSW compost than for compost from willow biomass. The dynamics of pH changes was similar in the tested types of compost and was rather small during the process of composting, regardless of the type of organic residues and initial reaction. Both compost from willow and municipal wastes showed similar values pH for single based dynamics indexes – 1.12 and 1.11 respectively at the end of composting process.

INTRODUCTION

Composting is a part of the oxidative processes of biological and biochemical transformations that occur under strictly defined temperature, humidity and pH conditions, as well as C/N ratio. The most important aspect in the production of compost is to ensure the proper course of the organic matter transformation process, so that the product obtained does not pose a threat when it is introduced into the soil environment and brings tangible benefits in the form of a positive impact on plant growth and development [1].

Accurate knowledge and understanding of the transformation of organic matter, which takes place in the composting process, as well as a proper assessment of the stability and maturity of compost, are necessary for the effective use of composts. The direction of organic matter transformation during the process depends on the type of composted material.

The aim of the research was to analyze the composting process, in the aspect of changes of some physical and physicochemical properties of the organic part of municipal solid waste and biomass of willow and hay mixture.

MATERIALS AND METHODS

The objects of the research were composts produced from: mixtures of biomass of hay and energy willow (BWC) and organic part of municipal solid waste (MSWC), obtained according DANO technology [4]. For laboratory tests mixed samples were collected in different phases of compost maturity, which represented the initial material of both composts and after: 1, 37, 54, 71, 130 and 167 days of composting, corresponding to different stages of their maturity. On the basis of the collected material, moisture was determined (by weight-drying method), the pH of the water extract (in the ratio 1:10), potentiometrically, the exchange capacity (CEC) by the Harada and Inoko method [3]. The results were statistically analyzed using Statistica 13. Correlation coefficients between individual parameters were calculated as well as indexes of dynamics of changes in the tested parameters.

RESULTS AND DISCUSSION

One of the important factors for the correct course of composting and also one of the most important physical criteria for assessing compost maturity and at the same time is a measurable indicator of the intensity of biotransformation processes occurring during composting process [2]. In the compost produced from biomass of willow and hay mixture, the thermophilic phase was reached after 13 days of composting and lasted for 14 days (Fig. 1).

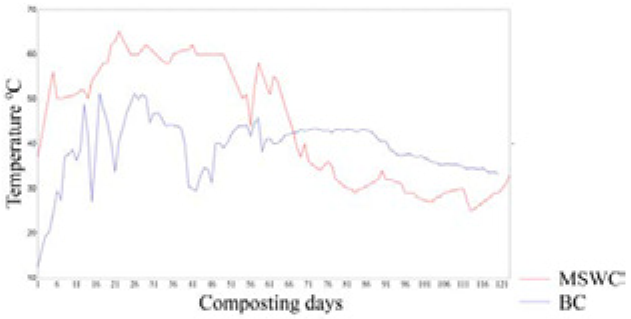

Fig. 1 Temperature changes during composting of MSWC and BC

In the compost from municipal waste, the thermophilic phase was reached after only 5 days and lasted much longer, for as much as 40 days. Experiments carried out so far have allowed us to conclude that there is a strict negative correlation between temperature and oxygen concentration [5].

The analyzes carried out showed that there was a difference in pH of the aqueous extracts between the tested composts. BC was characterized by an acid reaction (pH 5.3 – 6.0), while the MSWC pH exceeded 7.0 (Table 1). The increase of pH during composting indicates the course of ammonification processes, especially in the thermophilic phase of composting, when especially in compost (MSWC) there is a marked change in pH in the alkaline direction (from 6.9 to 7.9). After the thermophilic phase, both composts still show a small increase in pH (Table 1). The difference of CEC values observed between tested composts at various stages of maturation is related to the type of organic residues (Table 1). Interesting results have been obtained by calculating the dynamics of changes in CEC values in relation to the base value of the initial materials of both tested composts (Table 1).

Composting days	Single based dynamics indexes for BC		Single based dynamics indexes for MSWC	
	pH	CEC	pH	CEC
1	1.00	1.00	1.00	1.00
37	1.02	0.71	1.08	1.45
54	1.04	1.09	1.15	1.65
71	1.06	1.48	1.12	1.58
130	1.09	1.29	1.21	1.80
167	1.12	1.39	1.11	1.94

Table 1. Single based dynamic indexes for BC and MSWC

The dynamics (an increase in both cases) was higher for MSW compost than for compost from willow biomass although in both experiments a temporary decrease of dynamic intensity was observed, after 54 days in MSW compost and after 71 days in willow biomass compost. Both compost from willow and municipal wastes showed similar values for single based dynamics indexes – 1.12 and 1.11 respectively at the end of composting process. It can be concluded that transformation of organic matter and mineral components during composting process expressively slowed down after reaching a certain stage of maturity.

LITERATURE

1. Chen H., Dou J., Xu H., 2017: Remediation of Cr(VI)-contaminated soil with co-composting of three different biomass solid wastes. Journal of Soils and Sediments.
2. Drozd J., Licznar M., 2004: Changes of physical and physicochemical properties during composting of municipal waste in various conditions. In: Composts from municipal waste - production use and their impact on the environment (in Polish). Red. Drozd J., PTSH, Wrocław, 120 – 129.
3. Harada Y., Inoko A., 1980: The measurement of the cation-exchange capacity of composts for the estimation of the degree of maturity, Soil Science and Plant Nutrition, 26:1, 127-134.
4. Rosik-Dulewska Cz., 2002: Basics of waste management (in Polish).
5. Tiquia S.M., 2002: Evolution of extracellular enzyme activities during manure composting. Journal of Applied Microbiology, Vol. 92, 764 – 775

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STUDY ON THE EFFECTIVENESS OF MICROCLIMATE COOLING SYSTEMS IN A TOXIC ENVIRONMENT

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KEYWORDS

Contamination, impermeable protective clothing, heat stress, cooling vest, strain indicators.

ABSTRACT

The present study was conducted in order to evaluate efficiency of a personal body cooling systems based on ventilation technologies and its effects on test subject's physiological suitability during exertional heat stress in hot environment and usage of impermeable CBRN protective suit. Performed results are based on realized tests in especially unique designed testing ground. Six male test subjects were subjected to exertional heat stress test consisted of two cycles of specific working activities in hot environment. As a physiological strain indicator the following parameters have been determined: mean skin temperature, auditive temperature, heart rate and sweat rate. Results confirmed that cooling vest worn under the impermeable protective clothes was able to attenuate the physiological strain levels during exercise, when compared to identical exposure without the cooling system.

INTRODUCTION

Compensated heat stress (CHS) occurs when the heat loss is in balance with its production. It is possible to reach core temperature equilibrium (steady-state) at given physical activity. Compensated heat stress is usually present in most of the dedicated military tasks.

Uncompensated heat stress (UCHS) occurs when demands for disclosure of heat (sweat evaporation) overcome the evaporative capacity of the specific environment. During uncompensed heat stress, the body cannot achieve steady state core temperature, so it rises until it reaches physiological limits. Heat exhaustion in terms UCHS occurs at relatively low value of core temperature. In cases of inadequate cooling (caused by insufficient evaporation of sweat), skin temperature remains high. Bloodstream is relocated to expanded skin vascular compartment in order to remove the heat from inside the body, which reduces the minute volume and increases heart rate. Uncompensated heat stress extremely reduces physical performance, so these conditions demand special regimes of work and rest cycles, with the use of active cooling during breaks.

Contemporary military activities request the best possible physiological comfort of soldiers. Considering this, different systems for body cooling have been developed so far, with a main purpose to increase comfort as well as to reduce thermal stress. Military applications of cooling systems bring numerous additional benefits, such as increased mission duration, de- crease in hydration needs, improved mental acuity and maintained physical performance. Generally, cooling systems can be classified in five basic groups: evaporative cooling products, products based on phase change materials (PCM), compressed air systems, liquid circulation systems, and thermoelectric systems.

The application of particular cooling system type depends of many factors, such as cooling garment weight, readiness, cooling capacity, heat removal rate, compatibility, possibility for the monitoring and control by the wearer, environmental conditions, durability, and portability.

Protective characteristics of body protection means depend on the type of protection materials and specificity of contamination applied. In the context of current development and production of cloth designed to protect the body from highly toxic substances (HTS), more types of protective materials are made. They can be classified into two main groups. In the first are insulating materials based on elastomer or thermoplastics, and in the second are thin carbon sorption materials which found application in the production of protective filtration suits.

The basic advantage of the insulating materials is reflected in good protective properties against HTS, with a lack of permeability to air and sweat, what can cause the prerequisites for heat stress phenomenon. The use of these funds, in activities of medium and high intensity in hot conditions leads to rapid heat build-up in the body and heat load of users, so the time of their wearing is limited in depending on the external ambient temperature.

Testing of physiological suitability under field conditions represents a logical continuation of tests of protective equipment physiological suitability in laboratory conditions. The goal of these tests was to build a unique field polygon, the area where shall be made testing of the body cooling system function in real terms of their use.

CONCLUSION

Methodology used in this study and experimental protocols where carried out in accordance with contemporary standards in area of thermal strain evaluation by physiological measurements (ISO 9886), with respect to prescribed measures of medical supervision of subjects exposed to extreme hot environment (ISO 12894). All field tests were conducted using high performance equipment, with technical features that enable to measure, monitor and record necessary physiological parameters in real time. Among other things, validity of results confirming engagement of sufficient number of test subjects (volunteers) with similar anthropometric parameters, selected according to strict criteria from a larger number of potential participants.

LITERATURE

Moran D.S., et al., A Physiological Strain Index to Evaluate Heat Stress, Am J Physiol, 275 (1998), July, pp. 129–134;

Kenney W., Heat Flux and Storage in Hot Environments, Int J Sports Med, 19 (1998), 2, pp. 92 – 95;

Teal W., Microclimate Cooling, Chemical Biological Individual Protection Conference, US Army Natick Solder Center, Natick, Mass., USA, 2006;

Fatah A.A., et al., Guide for the Selection of Personal Protective Equipment for Emergency First Responders, 2nd ed., Washington, D. C., USA, 2007;

ISO 9886: Ergonomics – evaluation of thermal strain by psychological measurements (2008);

ISO 12894 (E): Ergonomics of the thermal environment – Medical supervision of individuals exposed to extreme hot or cold environment, (2008);

http://www.arcticheat.com.au

http://www.texascoolvest.com

http://www.firstlinetech.com

http://www.entrak.de

PORTABLE X-RAY FLUORESCENCE ANALYZER: AN EXCELLENT TOOL FOR PRELIMINARY EXPLORATION AND SCREENING OF CONTAMINATED SITES

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KEYWORDS
X-ray fluorescence, portable analyzer, environmental screening, monitoring, contaminated sites

ABSTRACT

X-ray fluorescence (XRF) ranks among the methods of elemental analysis (atomic spectrometry), which is currently an integral part of analytical methods not only in research but also in many production processes. The purpose of the development of portable XRF analyzers was the effort to on-site diagnose of various materials composition based on screening of elemental composition (quality control). However these devices are increasingly being used in the environmental field as well. Based on representation of elements in various environmental matrices (soil, sludge, wastes, sediments, etc.), the degree of contamination can be estimated. In the presented study, Delta Premium spectrometer from Canadian company Innov-X (Fig. 1) was used for determination of the extent of contamination on several sites. By setting the appropriate mode, the analyzer can determine wide range of chemical elements (P, S, K, Cl, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Sr, Zr, Mo, Ag, Cd, Sn, Sb, W, Hg, Pb, Bi, Th, U) during 2 minutes in a wide dynamic range at concentrations ranging from ppm to practically 100 %. The accreditation process has found that the uncertainty of the instrument's determination ranged from 25 % to 50 %, depending on the sample treatment. Obviously, by measuring in field conditions, this uncertainty will change much more significantly, but the purpose of field measurements is above all comparison with background samples.

Fig. 1 Portable XRF spectrometer

The principle of the method consists in interaction of highly-energy (primary or incident) x-ray beam with the sample and the subsequent measurement and evaluation of the secondary (fluorescence) x-ray beams emitted by the sample (Fig. 2). During analysis, materials are excited using a high-energy incident beam of short wavelength X-ray radiation and become ionized. Inner electrons are ejected from lower energy orbitals (usually the K and L orbitals), making atoms in the sample unstable until the electron holes are filled by electrons from outer orbitals with higher energy. When an electron moves from a high energy orbital to a lower energy orbital, energy is released in the form of X-rays that are characteristic of the type of atom present. Continuous ionization of the sample and absorption of energy from the incident beam allows for analysis of the complex X-ray spectrum emitted by the excited material.

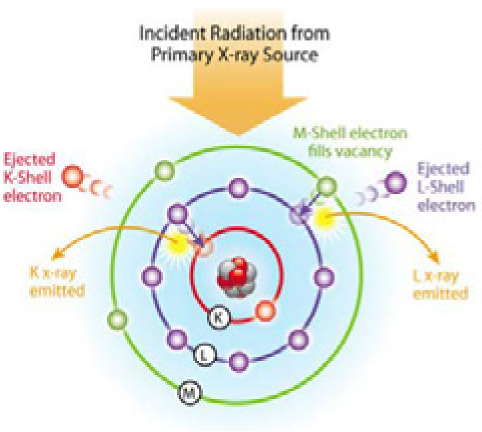
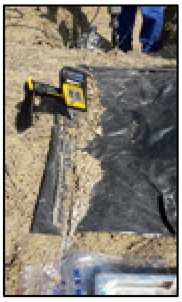


Fig. 2a Principle of X-ray fluorescence

Fig. 2b Principle of XRF spectrometer

PRACTICAL APPLICATIONS OF XRF SPECTROMETER

Landfill of obsolete organochlorine pesticides, Nubarashen – Armenia

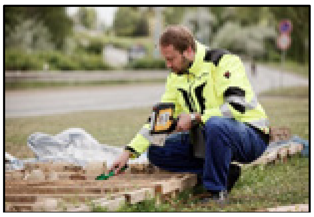


Outdated and unsecured landfill from the 1980s containing of about 600 m^3 of pure organochlorine pesticides (OCPs), including strongly contaminated surrounding soil. In the past, landfill was illegally opened and the contamination was expanded to the surface and surroundings. In the summer of 2017 a site survey was conducted to precisely detect the location of clean OCPs and determine the current range of contamination by using DELTA Premium Analyzer. Due to the fact that these were chlorinated organic substances, during the measurements, attention was paid mainly to the element Cl and also to elements S, Zn, Cu, Ni, Cr, Hg and As, which were also largely detected in clean pesticides taken from the landfill. For this purpose, network of about 200 surface measuring points was realized in the area of the landfill and its surroundings. Based on the detection and representation of the selected elements, the extent and level of surface contamination was subsequently determined and processed to a map form. On the basis of obtained results, a technological process of elimination of the old ecological burden and decontamination of the area will be proposed.

Controlled removing of soil contaminated by chromium

Locality of former automotive factory where the old building with chroming facility was located. Walls and floor of the building were heavily contaminated by Cr^{6+}. The roof of the building was damaged and due to precipitations there was a long-lasting significant contamination of both the soil bedrock under the building and its surroundings as well as the saturated zone of the rock environment in a depth of about 20 m. In the most contaminated places below the object, concentrations about units of g/kg of Cr were detected. Majority of this contamination was formed by Cr^{6+}. The design of remediation precautions at this site included the removal of the most contaminated soil layers and the subsequent creation of an impermeable clay barrier followed by the in-situ remediation of the saturated zone. By using XRF analyzer was possible do a measuring network during dredging works. On the basis of the obtained results, the removal of contaminated soil could be coordinated and controlled effectively directly in the field.

Exploration of municipal and industrial landfills – detection of wastes



CONCLUSIONS

Portable XRF analyzer is excellent tool for preliminary and supplementary monitoring of contaminated sites. Thanks to its mobility, a real-time field exploration can be conducted. The data obtained from the concrete point and at the given time thus can be much more informative than data obtained from conventional sampling (including transport of samples to laboratories and their subsequent laboratory analysis). From the point of view of comparative evaluation and the ability to quick acquisition of relevant data directly in the field and real time, portable XRF analyzers are a very effective tool for carrying out the exploration and determining the extent of contamination. Only a few practical applications have been listed in this study, but it is obvious that the potential of these devices is much wider, not only in the field of ecology. Except for quality control of various materials and waste detection, this device has a significant potential for use in mining, geochemistry, geological exploration, etc. Although manipulation and measurement with this device are relatively user friendly, there is a very important aspect consisting in the experiences, knowledge and resolving ability of operators who interpret obtained data and decide on their relevance in relation to specific sectors and application areas.

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SOIL CONTAMINATION BY THE PRESENCE OF CHROMIUM AND TEMPORAL EFFECTS ON BACTERIAL COMMUNITY

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KEYWORDS
Microbiome, pollution soil, metagenomic, remediation, bacterial diversity.

ABSTRACT

Composted tannery sludge (CTS) has promoted shifts in soil chemical properties and, therefore, could affect the soil bacterial community, mainly due the presence of chromium and salts. This study assessed the effect of CTS on soil bacterial community over time at diversity and abundance levels. CTS was applied at five rates (0, 2.5, 5, 10 and 20 t/ha) and bacterial community was evaluated for 180 days. Cr and soil pH were the main chemical variables influenced by CTS amendment showing weight (b_k) higher than 1.0. Cr was the main chemical element that increased more significantly and its increase with the application of CTS can be harmful to the soil and the plants (Sousa et al., 2017; Miranda et al., 2018).

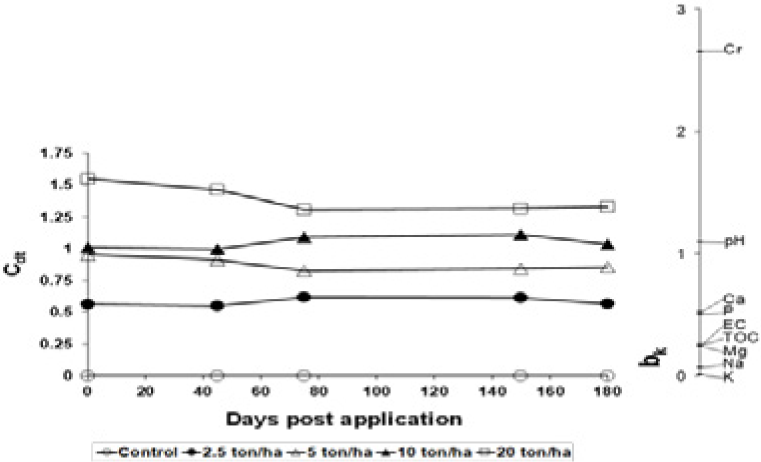

Fig. 1 Principal response curve diagram of physico-chemical data set indicating the effects of the CTS into the soil. The lines represent the course of the treatment levels in time. Cr-chromium; pH-soil pH; Ca- calcium; P-phosphorus; EC-electric conductivity; TOC-total organic carbon; Mg-magnesium; Na-sodium; K-potassium.

The principal curve response (PRC) analysis showed that the most abundant phyla were not influenced by CTS rates over time. While the analysis of bacterial community showed some of the less abundant phyla being influenced by the CTS rates (Figure 2). Namely, phyla AD3, Tenericutes and Verrumicrobia were negatively influenced by CTS over time, which can be explained by the strict relationship between these organisms with pH, organic carbon, nitrogen and electric conductivity[14], showing greater abundance in sites with low concentrations of C and N and salinity, although AD3 showed higher abundance in soil with higher pH (Tas et al., 2014).

The redundancy analyses for bacterial class (Figure 3) showed the relationship between the significant chemical properties and bacterial community of soil after CTS amendment over time. Therefore, there was a shifting in the bacterial community over time with the application of composted tannery sludge. Our study has shown that the less abundant bacterial groups were more influenced by CTS than those most abundant bacterial groups, and that these bacterial groups were drove by soil chemical properties, mainly Cr and soil pH. It is known that these organisms, are sensitive to the presence of organic matter in the environment, presenting variable responses to the pH and availability of nutrients (Navarrete et al., 2013). Metal stress affects sensitive species (Gans et al., 2005). and decreases their competition ability, resulting in an increase in abundance of metal-resistant species capable of adapting to stress and filling up the empty niches in order to maintain ecological stability (functional redundancy)

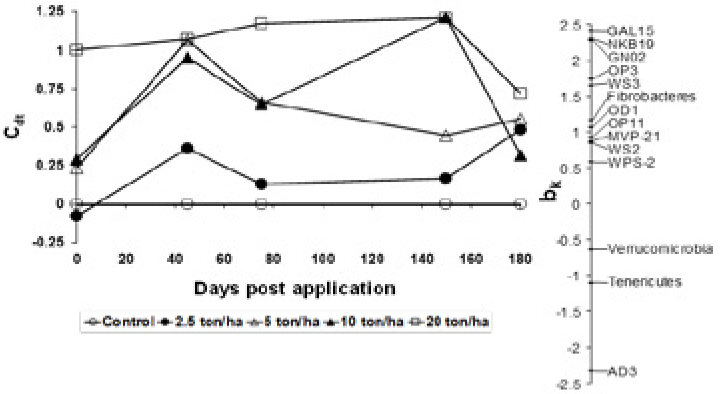

Fig. 2 Principal Response Curves between biological characteristics at Phyla level and treatments with tannery sludge (ton/ha^{-1}). The weight (b_k) can be interpreted as the affinity of the Phyla with the Principal Response Curves (c_{dt}).

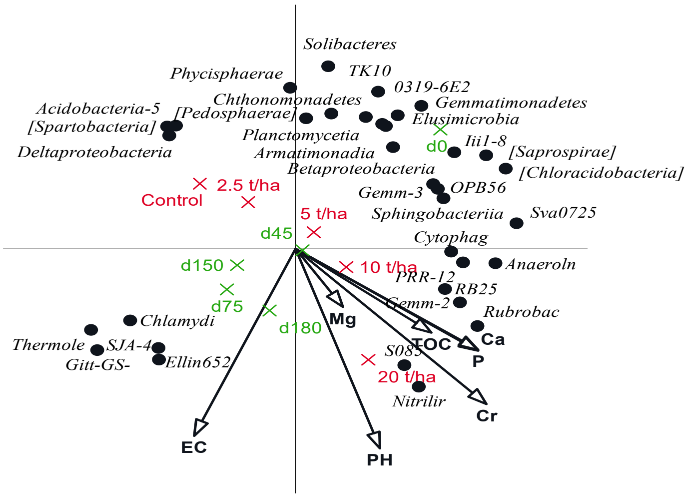

Fig. 3 Redundancy analysis diagram (RDA) of correlations between significant physico-chemical proprieties and OUT's at the Class level. Rates of CTS (2.5, 5, 10 and 20 t/ha^{-1}); Time of sampling in days (0, 45, 75, 150 and 180); Total organic carbon – TOC; P – phosphorus; Ca – calcium; Cr – Chromium; pH – soil pH; EC –electric conductivity.

LITERATURE

Sousa, R. S., Santos, V. M., Melo, W. J., Nunes, L. A. P. L., Van den Brink, P. J., Araújo, A. S. F. Time-dependent effect of composted tannery sludge on the chemical and microbial properties of soil. Ecotoxicology 26, 1366 – 1377 (2017). Miranda, A. R. L. de, et al. Responses of soil bacterial community after seventh yearly applications of composted tannery sludge. Geoderma 318, 1 – 8 (2018). Tas, N., Presta, E., McFarland, J. W., Wickland, K., et al. The ISME Journal 8, 1904 – 1919 (2014). Navarrete, A. A., Kuramae, E. E., de Hollander, M. et al. Acidobacterial community responses to agricultural management of soybean in Amazon forest soils. FEMS Microbiol Ecol, 83, 607 – 21 (2013). Gans, J., M. Wolinsky, J. Dunbar. Computation improvements reveal great bacterial diversity and high metal toxicity in soil. Science 309, 1387 – 1390 (2005).

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CHANGES OF SOIL QUALITY IN THE VICINITY OF THE EUROPE'S LARGEST COPPER ORE TAILINGS IMPOUNDMENT

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KEYWORDS
Tailing management, soil quality, metal-enriched particles

INTRODUCTION

Poland is one of the world's largest producers of cooper. The Polish copper industry is based on extraction and processing of the largest European deposits of copper ores, within area known as Polish Copper Basin. The Polish Copper Basin is located in southwestern Poland and is composed of two parts: North Sudetic Trough and Fore-Sudetic Monocline (Karczewska et al. 2017). The low concentration of Cu in the ores implies the need of preconcentration prior to smelting processes. Currently, all tailings, produced as byproducts of Cu ores flotation are hydraulically transferred to the large central tailings management site – Żelazny Most (Fig. 1) which is the largest European and one of the world's largest object of this type. It is surrounded by a 14.3 km long ring-dam, which height ranges between 41 and 65 m.

Fig. 1 Localization of Żelazny Most tailing impoundment

WIND EROSION AND SOIL QUALITY MONITORING

Tailings deposited in the Żelazny Most have texture of fine sand and silt sand which become dry after sedimentation and create wide "beaches" in the outer part of impoundment. Also, shell of the dam is built of relative coarse tailings with the texture of sand and silt sand. Dry tailings are exposed to wind erosion and conditions that favor this type of erosion occur normally in 10 % – 20 % of the time in a year, i.e., in 35 – 75 days. Therefore, the blowing-out of metal-enriched particles into surrounding areas is one of the main environmental concerns (Angełow et al. 2000, Monograph, 2007, Baran et al. 2013, Karczewska et al. 2017). However, the monitoring of soils surrounding the Żelazny Most continued since 1997 shows that content of heavy metals depends on the distance from the dam (Fig. 2). Mean concentration of Cu, Pb, Zn and As in topsoil are stable or even decrease. Since 2005 slight increase in concentration Cu and Zn was noticed. However, it's related to presence of forests which large surfaces were planted in area of landfill, in a so-called "sanitary protection zone". Forests retain more dust than bare surface, therefore absorbed dust along with fall of leaves is deposited in the litter and then in soil surface. During last 20 years mean value noticed for Cu ranges from 16.1 to 24.1 mg/kg, for Pb – 16.2 to 28,2 mg/kg, Zn- 25.5 to 40.5 mg/kg, and for As – 3.2 to 4.0 mg/kg. It's worth of emphasizing that the concentration of all metal under study remained below the legal threshold levels established in Poland.

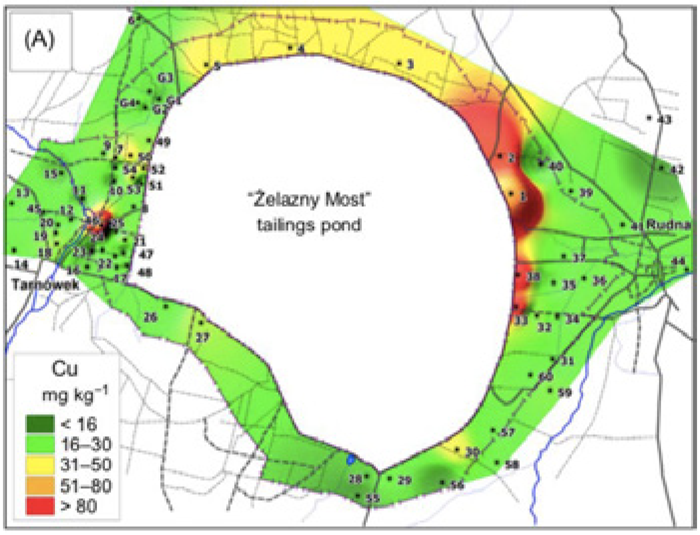

Fig. 2 Map of monitoring network around Żelazny Most impoundment. Data gained from monitoring illustrating Cu distribution in soils (Kabała et al. reports, 1995–2014)

ANTI-DUSTING TREATMENTS

The facts that concentrations of heavy metals in soils surrounding are stable and remained below the legal threshold levels confirm that anti-dusting treatments on the landfill are highly effective. The following treatments are applied on the study area: 1) covering dry beaches and dam surfaces with aqueous solution of bitumen emulsion, 2) water curtains on dams at windy days, 3) dam slopes covering with turf.

Effectiveness of anti-dusting treatments it's all the more important due to decision to expand the Żelazny Most tailing impoundment.

CONCLUSIONS

The Żelazny Most tailing management site is the largest European objet of this type. The soil quality monitoring shows that concentrations of heavy metals (Cu, Pb, Zn, As) are remained below the legal threshold levels established in Poland. Thus, these concentrations do not create environmental risk and therefore there is no need for remediation.

LITERATURE

Angełow, Z., Chodak, T., Kabała, C., Kaszubkiewicz, J., Szerszeń, L., 2000. Effect of Żelazny Most tailings impoundment on the surrounding soil environment. Rocz. Akad. Roln. Pozn. 56, 327–339 (in Polish, with English abstract).

Baran, A., Zaleski, T., Kulikowski, E., Wieczorek, J., 2015. Hydrophysical and biological properties of sandy substrata enriched with hydrogel. Pol. J. Environ. Stud. 24 (6), 2355–2362.

Kabała, C., Jezierski, P., Chodak, T., Kaszubkiewicz, J., Gałka, B., Waroszewski, J., Reports 1995–2014. Documentation on the Content of Heavy Metals in Soils in the Vicinity of Disposal Site 'Żelazny Most' with Special Focus on the Village Tarnówek. Reports from soil monitoring, 1995–2014. Unpublished materials (in Polish).

Karczewska A., Kaszubkiewicz J., Kabała C., Jezierski P., Spiak Z., Szopka K., 2017. Tailings Impoundments of Polish Cooper Mining Industry – Environmental Effects, Risk Assessment and Reclamation. Chapter 6 in Assessment, Restoration and Reclamation of Mining Influenced Soils, Elsevier.

Monograph, 2007. KGHM Polska Miedź SA, second ed. KGHM Cuprum, Lubin-Wrocław (in Polish).

NEW FACTS AND CONTEXTS FOUND IN THE INVESTIGATION OF THE SPREAD OF POLLUTION NOT ONLY IN THE AREA OF CHZJD LANDFILL IN BRATISLAVA

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KEYWORDS

contaminants, contaminated sites, groundwater, landfill

ABSTRACT

Ladfill of „Chemické závody Juraja Dimitrova“ (CHZJD) located in territory of capital city Bratislava has become the subject of increased attention among public and scientific sphere in recent years. During exploratory work in 2014 and 2015 the transfer of pollutants from the landfill to a city district Vrakuňa and to the area further beyond Bratislava city was confirmed. That area is initial part of the biggest groundwater reservoir in Slovakia - Žitný ostrov.

Subsequently with previous findings about this site and the pollution that is present there, the pollution issue of the site in question was further elaborated in the ongoing research project. One of the project activities involve broadening knowledge and gaining facts that can help provide more comprehensive view of the site and consequently contribute to the protection of the ground water of Žitný ostrov. In the work of Machlica and Stojkovová 2017 potential ways of pollution spreading were identified based on the study of historical maps, topography and morphology of the area concerned.

The data from historical records were compared with data from Slovnaft's monitoring network, which runs a regular long-term monitoring of selected substances, which could be potentially related to Slovnaft´s activities in a wide area on the east of the landfill. It has been found that monitoring has revealed a cloud of chlorinated hydrocarbons slowly moving in south-east direction from Bratislava city, which probably originates with high probability partly from CHZJD landfill.

Date of sample collection	Place of sample collection	Volatile chlorinated hydrocarbons – cis 1,2 dichloroethene (µg / l)	Volatile hydrocarbons aromatic – chlorobenzene (µg / l)	Volatile chlorinated hydrocarbons – tetrachloroethene (PCE) (µg / l)	Volatile chlorinated hydrocarbons – trichlorethylene (TCE) (µg /	**TCE and PCE**	OCP – hexachlorocyclohexane (alfa)(µg/l)	Pesticídes – atrazine (µg/l)	Pesticídes – chloridazon (µg/l)	Pesticídes – prometryn (µg/l)	**All Pesticídes**
19.7.2017	č.1, Modricová 15	<0,5	<0,3	**37,80**	**2,90**	**40,70**	0,041	0,05	<0,1	0,09	0,14
31.7.2017	Hradská 46/A,	<0,5	<0,3	**40,30**	**3,70**	**44,00**	0,047	0,05	<0,1	**0,12**	0,17
31.7.2017	Majerská 4A,	**6,20**	**29,20**	**36,20**	**5,80**	**42,00**	0,106	**0,17**	**79,00**	**10,00**	**89,17**
31.7.2017	Priehradná 77,	<0,5	<0,3	**18,50**	<0,5	**18,50**	0,057	0,08	<0,1	0,07	0,15
31.7.2017	Brezová 29,	<0,5	<0,3	**11,30**	<0,5	**11,30**	0,037	<0,05	<0,1	0,09	0,09
31.7.2017	Orgovánová 2,	<0,5	**18,00**	**53,20**	**5,40**	**58,60**	0,153	**0,17**	**21,00**	**1,60**	**22,77**
31.7.2017	Podpriehradná 5,	<0,5	**5,50**	**63,00**	**5,90**	**68,90**	**0,10**	**0,14**	**6,60**	**0,90**	**7,64**
31.7.2017	Majerská – záhrady 20244,	<0,5	<0,3	**31,00**	<0,5	**31,00**	0,013	0,07	<0,1	**0,21**	0,28
31.7.2017	Majerská – záhrady 20452,	<0,5	<0,3	**28,90**	<0,5	**28,90**	0,01	0,06	<0,1	**0,12**	0,18
31.7.2017	Ráztočná 13,	**4,40**	**2,20**	**42,30**	**4,80**	**47,10**	0,084	**0,14**	**23,00**	**3,20**	**26,34**
1.8.2017	Na piesku – záhrady - roh Mlynské luhy,	<0,5	<0,3	**71,30**	**2,80**	**74,10**	0,032	<0,05	<0,1	0,03	0,03
1.8.2017	Parcelná 6,	<0,5	<0,3	**12,20**	<0,5	**12,20**	<0,01	<0,05	<0,1	<0,03	

Table 1. Selection of contaminants and their concentrations in the area out of landfill CHZJD based on publicly available data published by VÚVH 2017

Due to harmful nature of the substances in the CHZDJ and as a result of public pressure Ministry of the Environment of the Slovak Republic (MŽPSR) assigned the task to VÚVH (Water Research Institute), which carried out sampling of water from the wells. The occurrence of a wide range of pollutants was found not only in the direction of the groundwater flow under the landfill but also in the areas outside of it based on sampling results (Table 1). However, chlorinated hydrocarbons and pesticides have been found in two urban areas, particularly in Vrakuňa, with concentrations exceeding the drinking water limits. However, screening analyses show occurrence of wide range of different specific substances such as benzthiazole and its various derivatives, terc-butyl cresol, terc-butyl alcohol, chlorobenzene, triazine and organochlorine pesticides / herbicides. Due to better migration capacity of triazine pesticides, they were found in much larger quantities than organochlorine.

The above results confirmed increased concentration of pollutants at the sites of predisposing flow of ground water reported by Machlica and Stojkovova in 2017. These are water samples from Podpriehradna, Orgovanova, Majerska and Ráztočná streets, which are in one line with former old river arm of the Malý Dunaj river. The concentration of chlorinated hydrocarbons ranges from 40 to 70 μg / l, which is **4 to 7 times more than the limit of TCE + PCE** (limit 10 μg / l according to Decree 247/2017). In the case of a pesticide indicator (the sum of pesticides) (limit of 0.5 μg / l according to Decree 247/2017), the Majerska street **has exceeded the limit up to 178 times.**

The observed sampling results clearly show that they far exceed legal limits for drinking water in these wells. Screening results of other substances normally not determined in water analysis show that there are specific substances such as benzthiazole and its various derivatives, pesticides, herbicides, benzene compounds and many others contained in the water samples. For many of the identified substances sufficient information is missing in scientific sources to determine their level of hazard, toxicity or carcinogenicity, which is also reflected in their absence in the legislative framework of the substances that should be determined in drinking water analysis. Sampling of water carried out by VÚVH (Water Research Institute) helped identify new findings that support previous assumptions.

Benzthiazole is in particular interest from the list of contaminants. It is a chemical compound that is also used as an additive in the rubber industry. This substance also occurs at the CHZJD landfill site and it is a specific substance that is not normally found in the environment. Due to its widespread occurrence in groundwater under the landfill, benzthiazole and its derivatives could be considered as a kind of marker for determining the extent of migration of pollution from the landfill site. However, after our focusing on benzothiazole the occurrence of benzthiazole it was previously found out by Bartal et al. 2008. He identified the presence of benzthiazole in sediments of waste channel in the area of the Bratislava city district Nové Mesto. According to the authors, the channel is dry for most part of the year, but after ground water levels rise due to increased precipitation, more pollutants are leached into the ground water from river sediments, which transport them further in the direction of flow in the channel as well as thanks to transitions of ground waters. This polluted waste channel is located north of the landfill, so the question arises whether the source of benzthiazole is only a CHZJD landfill or other source too.

For more complex analysis of the conditions it would be necessary to carry out several more water samplings and analysis of samples in a wider area, not just directly under the CHZJD landfill but also further upstream before ground waters meet the landfill in their flow direction.

For the future it would be useful if SHMÚ or VÚVH has also included benzthiazole and its derivatives in their permanent ground water monitoring network not only in the area under the landfill, but also in the territory of the Bratislava city in the district of Nové Mesto.

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LITERATURE

Bartal, M., Vrána, B., Krascsenits, Z., Katona, G. 2008: Traces of Industrial Contaminants-I, Bratislava – Nové Mesto, Bratislava – Mestská, Hydrochemia 2008, Conference Proceedings, p.239 – 242, Slovak republic

Decree N.247/2017 of the Ministry of Health of the Slovak Republic laying down details on drinking water quality, drinking water quality control, monitoring and risk management of drinking water supply

Machlica, A., Stojkovová, D. 2017: Targeted research at the CHZD landfill in the context of the proposed remedial measures, Contaminated sites 2017, Štrbské Pleso, Conference Proceedings, Slovak republic

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CURRENT STATUS AND DEVELOPMENT OF SOIL PARAMETERS ON CONTAMINATED SOIL USED FOR PLANTING FAST GROWING WILLOW

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KEYWORDS
Contamination, energetic crops, soil monitoring, remediation

ABSTRACT

A new soil function, which is the use of agricultural outputs for energy purposes, was added to the primary production function of agriculture. Sustainable development associated with the efficient use of natural resources is to ensure that the exploitation of natural resources and the related impact on the environment as well as on the soil quality does not exceed the carrying capacity. Dynamic monitoring of selected indicators of soil quality (Kobza et al., 2014) was realized in a special network of sites on soil used for planting fast growing willow (Salix viminalis). Monitoring of the locality Kuchyna, contaminated Fluvisol (Fig. 1) is running since 2010 year.

Fig. 1 Contaminated site Kuchyna, Mollic Fluvisol

Evaluation and monitoring of soil quality indicators is an essential part in new ways of using agricultural land for energy purposes. In the monitoring of agricultural land used to grow energy crops, we have determined a negative trend in soil pH (decrease in pH) as well as in the content of available macronutrients (P, K, Mg), which was most pronounced for phosphorus (Table 1).

Parameter		**Soil depth 0 – 10 cm**		**Soil depth 35 – 45 cm**	
		2010 year	**2017 year**	**2010 year**	**2017 year**
pH in H_2O		5,81	5,27	5,80	5,46
pH in $CaCl_2$		5,23	5,08	5,31	5,17
Cox v %		2,318	2,62	1,958	2,482
Q^4_6		4,09	4,23	3,910	4,17
Macronutrients in mg.kg^{-1} (Mehlich III.)	P	73,70	34,84	43,50	24,62
	K	163,00	151,10	106,00	93,90
	Mg	92,70	88,28	119,00	99,50
Trace elements in soil in mg.kg^{-1} (total content in aqua regia)	Cd	1,016	0,602	0,822	0,632
	Zn	199,000	131,000	287,000	122,000
	Ni	51,500	34,300	69,600	32,500
Trace elements in soil in mg.kg^{-1} (1 M NH_4NO_3)	Cd	0,009	0,046	-	-
	Zn	0,320	1,060	-	-

	Ni	0,176	0,352	-	-
Trace elements in a plant in mg.kg^{-1}	Cd	7,154	4,730	-	-
	Zn	250,000	188,000	-	-

Tab. 1 Soil quality indicators

The willow belongs to potentially resistant crops due to the high content of risk elements.We have seen positive changes in the case of risk trace elements content in the soil. Remediation capability of willows was manifested with significant reduction of cadmium, zinc and nickel content in soil. Total cadmium content decreased by 41 %, zinc content by 34 % and nickel content by 33 % (Figure 2).

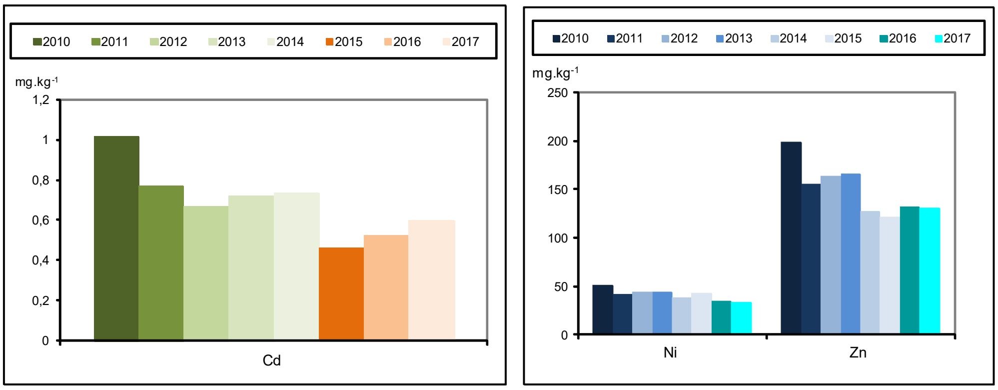

Fig. 2 Risk trace elements content in soil

In the case of cadmium and zinc, the content of this element in 2017 despite the continuing downward trend is still above limit according to Decree 59/2013 MPRV SR, which amends the Soil Act 220/2004 Z.z .. The cultivation of energy crops in line with environmental standards, allows for the efficient use of mainly less productive agricultural land as well as degraded agricultural land (contaminated with inorganic pollutants). The agroecosystem based on soil is multifunctional in all conditions, both in terms of its processes and functions and services Rapid-growing willow on agricultural land can positively influence regulatory agroecosystem services, climate control (sequestration of atmospheric CO2), soil purification (phytoremediation effect) as well as regulation of water regime (Makovníková et al., 2017) and thus allowing the use of degraded soils.

LITERATURE

Kobza J., Barančíková G., Dodok R., Hrivňáková K., Makovníková J., Pálka B., Pavlenda P., Schlosserová J., Styk J., Širáň M. 2014. Monitoring pôd SR. (Soil monitoring of Slovakia). NPPC – VUPOP Bratislava, 252 p. ISBN 978-80-8163-004-0.
Makovníková, J. - Barančíková, G. - Pálka, B. 2007. Approach to the assessment of transport risk of inorganic pollutants based on the immobilisation capability of soil. In Plant, Soil and Environment, vol.53, 2007, č. 8, s.365 – 373
Makovníková J, Pálka B, Širáň M, Kanianska R, Kizeková M, Jaďuďová J. Modelovanie a hodnotenie agroekosystémových služieb. Banská Bystrica: Belianum; 2017, 150 pp., ISBN 978-80-557-1242-0. Slovak

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INVESTIGATION CONCERNING EX-SITU BIOREMEDIATION OF PETROLEUM HYDROCARBONS CONTAMINATED SOILS

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KEYWORDS
aeration, bioremediation, moisture, microorganism, petroleum hydrocarbons, soil.

ABSTRACT

The bioremediation of petroleum hydrocarbons-polluted soils was studied by an ex-situ, lab-scale, biopile experiment with different parameters: aeration rate (1 h day-1 and 2 h day-1), soil moisture (44 % and 60 %) and microorganisms consortia addition (320 mL and 640 mL). The trial was conducted using 8 treatment cells, each having different parameters, and one control cell for 18 weeks on soil containing 7600 ± 400 mg kg-1 total petroleum hydrocarbons, taken from a former petroleum product warehouse in Sfantu Gheorghe, Covasna County (Romania). A bioremediation yield up to 76 % was obtained in the test cells, while in the control cell the reduction of petroleum hydrocarbons content by 16 % was attributed to natural attenuation. The results also revealed an accentuated decrease in TPH concentrations after 4 weeks of treatment, irrespective of the treatment conditions.

INTRODUCTION

Environmental pollution by PHC has become a global environmental problem. The success of bioremediation depends on a number of factors: the affected area, type and concentration of PHC, site characteristics (soil pH, temperature, humidity, nutrients and oxygen availability), available time and financial resources.

The objective of the study was the determination of optimal parameters of the ex-situ bioremediation process for PHC contaminated soils using an experimental set-up that controls the aeration time, soil moisture and microorganism content.

MATERIALS AND METHODS

For the laboratory experiment, about 150 kg of soil from 0–120 cm depth was collected from a former oil product depot situated on the outskirts of Sfântu Gheorghe, Covasna County (Romania).

Plastic boxes were used as laboratory treatment cells. In the treatment cells two perforated PVC pipes were introduced into the gravel layer to provide the aeration of the soil by pumping air from a compressor at a flow rate of 0.03 m^3min^{-1}/cell. The aeration for cells 1, 2, 5 and 6 was performed for 1 h day^{-1}, divided into 6 rounds of 10 minutes, while for cells 3, 4, 7 and 8 was performed for 2 h day^{-1}, divided into 6 rounds of 20 minutes each. Each cell has an aeration rate of 0.03 m^3min^{-1}. Throughout the experiment, the soil moisture was constantly: 44 % (cells 2, 3, 6, 7), respectively 60 % (cells 1, 4, 5, 8). The temperature at which the laboratory experiments were conducted ranged between 20–22 °C.

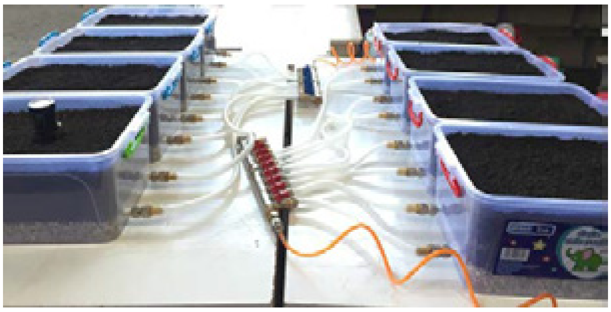

Fig. 1 Experimental set-up

RESULTS AND DISCUSSION

The average TPH concentration in the test soil determined by analyzing 5 replicates of a composite samples was 7600±400 mg kg^{-1}. This value was considered as the initial TPH content for each biopile. The initial TPH concentration exceeded approximately 3 times the intervention threshold for less sensitive soil uses (2000 mg kg^{-1}) set by the Romanian legislation (Order 756/1997), thus requiring remediation.

The evaluation of the effectiveness of the depollution process was performed by determining the yield for each cell. In the cells (cells 5 to 8) in which 640 mL of microorganism solution were added showed yields above 67 % (Fig. 2). The highest bioremediation yield (74–76 %) was observed in cells using 640 mL of microorganisms and 44 % moisture content (cell 6 and cell 7). Cells with low amount of microorganism addition (320 mL) showed yields below 60 %. Regarding aeration, the results show that the aeration duration is not so important because only a small difference was observed by comparing the efficiency of the two aeration regimes.

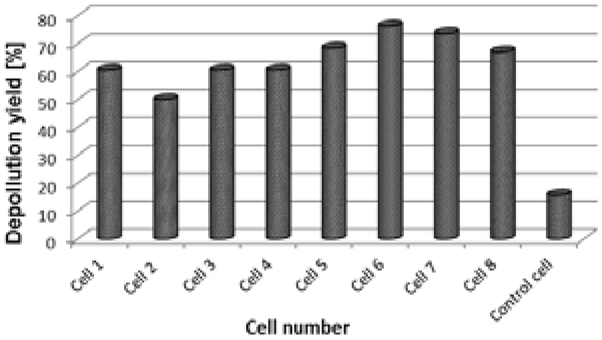

Fig. 2 Variation of the bioremediation yield in function of the experimental conditions

CONCLUSIONS

The polluted area of the former warehouse of petroleum products of Sfântu Gheorghe, Covasna County (Romania) was chosen as a study area because it requires remediation actions. A number of 8 test and 1 control cells were prepared for biopile experiments. The TPH decrease was higher in case of a 2 h day^{-1} aeration than in case of a 1 h day^{-1} aeration. The amount of microorganism solution used also influenced the yield of bioremediation, more significant reduction of TPH being observed in the case of the amount of microorganism solution of 40 mL/kg soil. Moreover, significant TPH decrease was found at 44 % moisture. In the case of cells where a higher amount of microorganism solution was added, it can be observed that aeration is not such an important factor in the evolution of the TPH concentration, the differences between the TPH concentrations being very small, but aeration is very useful for samples with less microorganisms. After 18 weeks of treatment, the results obtained showed a bioremediation yield ranging between 60 % and 76 %. The highest yield was obtained at 2 h day^{-1} aeration, 44 % moisture and 640 mL microorganism solution. Following research on the cells subject to decontamination process, it can be concluded that a TPH-polluted soil can be effectively decontaminated by performing an aeration over a longer time period or by adding a larger amount of solution loaded with microorganisms. By following optimal treatment parameters, which must be adapted to the specific conditions related to soil and pollutant characteristics, the ex-situ bioremediation process could be applied with good results.

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LITERATURE

Valer Micle, V. Sur, I.M., Criste, A. Senila, M., Levei, E., Marinescu, M., Cristorean, C., Rogozan G.C., 2018. Lab-scale experimental investigation concerning ex-situ bioremediation of petroleum hydrocarbons-contaminated soils, Soil and Sediment Contamination: An International Journal, DOI: 10.1080/15320383.2018.1503229

Adegbola, G.M., Eniola, K.I.T., Opasola, O.A., 2014. Isolation and identification of indigenous hydrocarbon tolerant bacteria from soil contaminated with used engine oil in Ogbomoso, Nigeria; Adv. App. Sci. Res. 5(3), 420–422.

Berar (Sur), I.M., Micle, V., Avram, S., Şenilă, M., Oros, V., 2012. Bioleaching of some heavy metals from polluted soils, Environ. Eng. Manag. J. 11(8), 1389–1393.

Order no. 756 of 11.03.1997 approving the regulations on environmental pollution assessment, Official Gazette no. 303 of 11/06/1997 (Ordin nr. 756/1997 pentru aprobarea Reglementării privind evaluarea poluării mediului, published in Romanian).

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FIELD HYDROGEOLOGICAL CENTER PÁTEK OPPORTUNITY FOR UNIQUE RESEARCH AND DEVELOPMENT IN ENVIRONMENTAL ENGINEERING

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Field hydrogeology, groundwater, survey, research and development, environmental engineering

The contribution presents a unique field infrastructure designed, constructed and operated for real-environment research and development applications. It presents geological, environmental and hydrogeological conditions on the site, the history of the site and consequently its current use. The field hydrogeological center (further Center) is then presented by particular realizations in the field of research and development. Examples of activities include the development of a chemical remediation method based on the principles of green chemistry, a unique tracer test and a set of experiments that improved on-line monitoring of hydrogeological parameters. The contribution is also intended as a collaborative offer, especially with academic partners in new projects with focus in environmental engineering and geological sciences.

MOTIVATION

Hydrogeologic field methods are essential tools, how to study hydrogeological relations in the environment, how to improve technical solution, and how to improve knowledge and skills of hydrogeological students and hydrogeologists as well. Only field experience might amplify theoretical background taught in classroom, planned and calculated in research and development project, or designed in project office. Field of groundwater, modelling, and theoretical studies rely desperately on data. Approaches how to collect data, knowledge about details of uncertainties in data collecting, and data interpretation represent crucial way how to make effort to “visualize” groundwater and subsruface. In fact, groundwater is simply the subsurface water that fully saturates pores or cracks in soil and rocks. Most groundwater is contained in and moves through the pore spaces between rock particles or in fractures and fissures in rocks. When the pore spaces become saturated with water, the water is groundwater [1]. Main motivation of the Center operation has been to create simple infrastructure with detailed geological and hydrogeological survey which enables to present what is groundwater, which ways may be used for its quality improvement, and to test methods how to describe groundwater profile more precious and objective using new results and technological concepts. Basic idea relies on willingness to cooperate by using this special field infrastructure in acceleration of field hydrogeological and other field which are in close connection under environmental and material sciences.

Fig. 1 geographical location of THCP

GENERAL DESCRIPTION

The Center is located in village of Pátek (50 km east from Prague, 3 km northeast from Poděbrady). Particularly, Center occupies central part of the village, on the left bank of Sánský kanál (channel). Its area represents about 2 000 m^2, average altitude of the site is 191 m above sea level. In 50th of the last century, STYL company began industrial production of stain removers, adhesive materials, paints and varnishes, and filling for lighters. After political changes in 1989, its production declined and real estate, where STYL conducted business, was restituted to origin owners. Environmental survey (2003) of the site showed serious groundwater contamination by chlorinated hydrocarbons. Ten years ago, remediation project (Since 2013 pump&treat approach to groundwater, pumping in 3 boreholes, compact stripper, and injection of clean water combined by injections of bacterial suspension with iron particles in 14 injection boreholes to accelerate bioremediation) in order to minimize CHC contamination started. After application of all planned measures, the site reached acceptable environmental standards [2].

The geological structure of the site is formed by Cretaceous sediments. The bottom layers are represented by Cenomanian grey-white sandstone in thickness about 20 m. They create Poděbrady spa structure with mineralized groundwater. Cenoman layers are covered by Turonian grey marlite in thickness about 90 m. Quarternary sediment are represented by sandy clays and sandy loams in thickness about 3 m. Turon sediments which create the main aquifer for Center are characterized by crack permeability. Main hydrogeological characteristics are represented by following parameters: groundwater level 1-2 m below the surface, coefficient of hydraulic conductivity kf = 10^{-6} to 10^{-7} m/s and real groundwater flow velocity is circa 10 m/year. From chemical point of view groundwater of the site belongs to Ca-Na-HCO_3-SO_4 type, with neutral to slightly alkaline chemical reactions. Sodium, manganese, ammonium, chloride, sulfate, CHSK-Mn and totally dissolved solids are increased [3].

FIELD CENTER

Center is operated by TERAMED, s.r.o. This company is responsible for technical, legal, and environmental issues resulting from activities realized on the site of Center (Fig. 1). Recently, the site about 2000 m^2 has been equipped by approximately 20 hydrogeological boreholes with complete documentation including geological, hydrogeological, and chemical characteristics. One of the biggest advantages of Center for scientific and testing purposes is long-run time path of detailed monitoring covering more than 10 years of similar survey activities carried out on the site of recent Center. There is rare opportunity to add some new boreholes however this change has to be without undesired influence on Center as whole. The prototype of the stripping tower represents a link to remediation technologies and methods and allows for further improvement of the concept of separative elimination of contaminants from groundwater. There is a complete system of distribution devices, pumps and their regulation. The Center location has its own weather station that monitors weather data on the site. At the same time it is connected to the wireless data transmission system, similar to the monitoring of physical and chemical parameters of groundwater. The system allows you to visit the collection of collected data on both your computer and your mobile phone. The proximity of the watercourse creates a remarkable hydrogeological situation in terms of preferential paths and flow directions. TERAMED, s.r.o. is the guarantor of systematic sampling, sample logistics, installation of special technical and technological units and their control. Wireless data is ready to connect other sensors and gauges whose analytical signal is digitible.

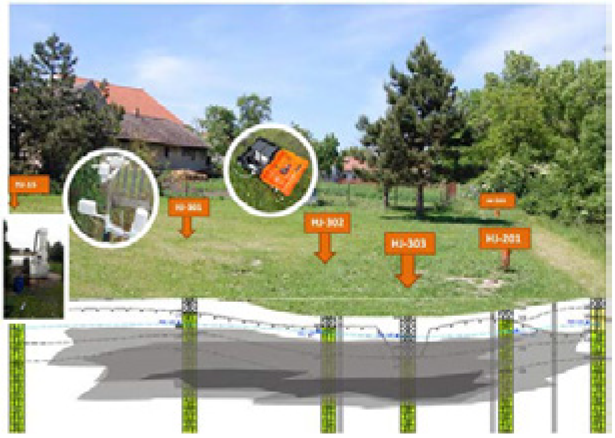

Fig. 2 cross section of Center with view on its surface

Table 1 Overview about activities

Infrastructure	*Purpose*	*Application*
Hydrogeological boreholes	HG survey, pumps, monitoring	material and device testing for hydrogeology
Stripping tower	improvement of conventional technology for contaminant removal	sorption material testing
Meteorological station	continual record of meteorological situation	experimental support
Pumping tests	velocity of GW	in different HG projects
Groundwater radar	knowledge about GW parameters	experimental support, quality check
Wireless data transfer and storage	immediate possibility to know the situation	multiple possibilities for data collecting which is user friendly
GW sample collecting and storage	real samples for scientific and testing purposes	service for science and testing
Geomicrobiological field lab	microbial monitoring	biotechnological and ecological issues

EXAMPLES OF ACTIVITIES

The first project, which was significantly contributed by the terrain infrastructure of Center, was the Eureka project called TRAIN (E! 6310). Its goal was to develop a preparation based on iron microparticles in the form of its hydrated oxides, which were subsequently colonized by iron-reducing bacteria. In particular, the result of the project was applied to the DCE-stall and to the residual contamination with chlorinated ethylenes with a lower number of chlorine atoms. The project was part of an Israeli partner AB Industrial Recycling Technologies, a renowned environmental engineering company with an international overlap.

Knowledge of geological, hydrogeological and chemical conditions has led to the idea of trying to exploit this potential in adapting the technology of tracer application to describe the chemically contaminated site (Eurostars-2, E 10016). Originally, the technology used for prospection of oil deposits (PITT) has been modified and tested under real conditions. The project's guarantee is the Norwegian company IFE, representing the respected partner for the state, the mining and petrochemical companies in the global dimension.

The presence of minor residual contamination has also helped to make all the tests in an operational environment in the case of a project initiated by the CHEMCOMEX, a.s. in co-operation with Czech Technical University in Prague (CTU), University of Chemical Technology in Prague (UCT) and the Institute of Macromolecular Chemistry, Czech Academy of Science. The latter institution has developed unique membrane hollow fiber contactors through which a remediation gas consisting of a mixture including, but not limited to, hydrogen as a source of reducing equivalent, electron donor and energy source for a wide range of microorganisms, including those that completely dehalogenate chlorinated ethylenes reductively. UCT has provided detailed microbiological analysis of the environment based on metagemomics (Illumina) and the CTU has developed a system for wireless parameter monitoring and regulation of remediation gas.

The protection of groundwater and the effort to provide these very valuable water resources opened the way for pilot demonstrations of the partial solutions of the project (TH02030622) involving CHEMCOMEX, a.s. and the Faculty of Civil Engineering of CTU, whose solution should reach a user-friendly, reliable and environmentally friendly hydrogeological seal in a compact form for a simple and one-time installation.

A Czech engineering company NEOGENE s.r.o. has used the site to finalize an automatic stripping tower designed for the needs of conventional remediation technologies, with emphasis on material and system innovation. The Center environment has demonstrated its use as a test polygon for technological solutions based on structural changes following major improvements to existing technical advances.

The site also provided conditions for testing the results of the binary prediction kit for the prediction of pollution with impacts on the reproduction of higher organisms, and a detailed metagenomic survey of the present microbial settlement from the taxonomic and functional point of view (TH02030957).

Table 2 Scope of cooperation

Activities	*Partneship*	*Examples*
national cooperation	Center (TERAMED) project partner, cooperation with companies, research centers, and universities	TAČR (Alfa, Epsilon, Théta), MPO (Trio), OPPIK Aplikace
international cooperation	Center (TERAMED) project partner, cooperation with companies, research centers, and universities	H2020, Eureka, Eurostars
subcontracting	for running project with complete service	stripping tower development
excursion for students	scientific and technical universities, field lectures	field trips, practical and field classes
visitors from public	consultancy how to deal with water	excursion

OPPORTUNITIES

Center is a field workplace that offers opportunities (Tab. 2) to apply hydrogeologically oriented R&D projects, both in the form of project partnerships as well as in the long-term cooperation and subcontracting. Within the framework of the didactic task, it is ready to enable field training for students, science, construction and technology colleges. It also offers its capacities for long-term testing of instruments and materials. Another level of use is the possibility of professional excursions for the general public.

LITERATURE

[1] Moore, J., Moore, J. (2002). Field Hydrogeology. Boca Raton: CRC Press.

[2] Pilný V. (2011) Update of the risk assessment in the premises of STYL, Village Pátek, CHEMCOMEX Praha, a.s.

[3] Pilný V. (2015) Final report, Remediation of former STYL company, MS CHEMCOMEX Praha, a.s.

PROPOSAL OF REMEDIATION OF MORAVA RIVER FLOODPLAIN CONTAMINATED BY CHLORINATED HYDROCARBONS

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KEYWORDS
Chlorinated hydrocarbons, contamination, groundwater, risk analyze, remediation

ABSTRACT

Due to historical leakage of chlorinated ethenes from the SIGMA Lutín Company a soil and groundwater has been contaminated. At present, contamination extends groundwater along a 5 km (longitudinal), 1–2 km (in the transverse direction) and 25 m (in thickness). Groundwater is bound on a quaternary aquifer of the floodplain of the Morava river. The spread of contaminants is approximately 50 m per year. The highest concentrations of key contaminants within impacted area are follows: PCE 70 – 152 $\mu g.l^{-1}$, TCE 52,9 – 266 $\mu g.l^{-1}$, 1,2-cis-DCE 45,2 – 122 $\mu g.l^{-1}$, VC 61 – 150 $\mu g.l^{-1}$.

The area affected by the contamination is inhabited with more than 4,000 people and intensively used for agricultural purposes (about 120 hectares). The use of groundwater is mainly for irrigation as well as domestic water and also for agricultural and industrial production. The Morava floodplain represents a reservoir of groundwater served as a source of drinking water and is therefore also protected by law. A supply wells potentially affected by contaminants spreading could offer in totally over 80 $l.s^{-1}$ of drinking groundwater. Evaluation of risk analyze showed that a specific active remediation activity is necessary to eliminate health risk for inhabitants and keep sustainable quality of groundwater used for water supplies.

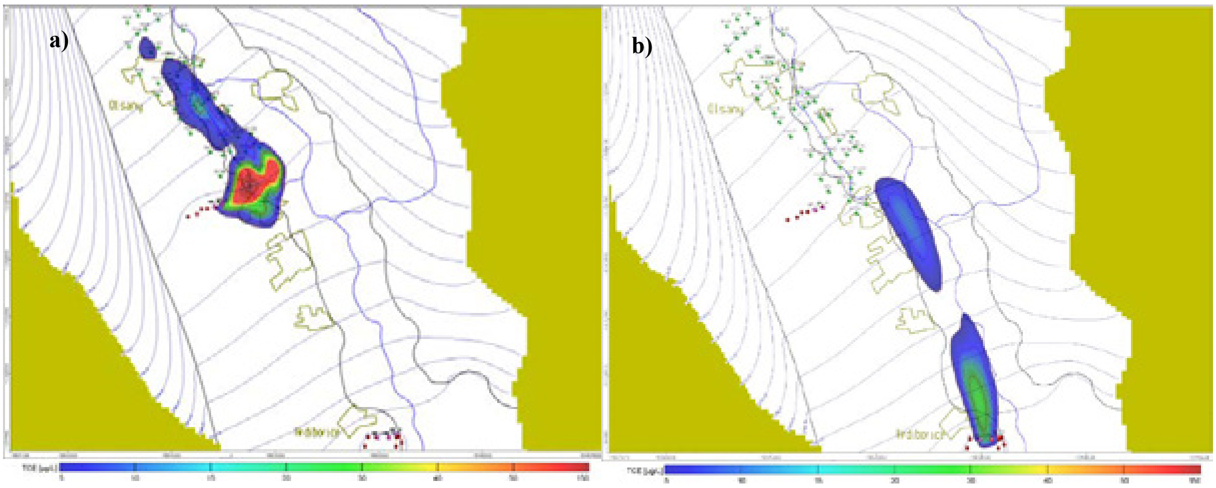
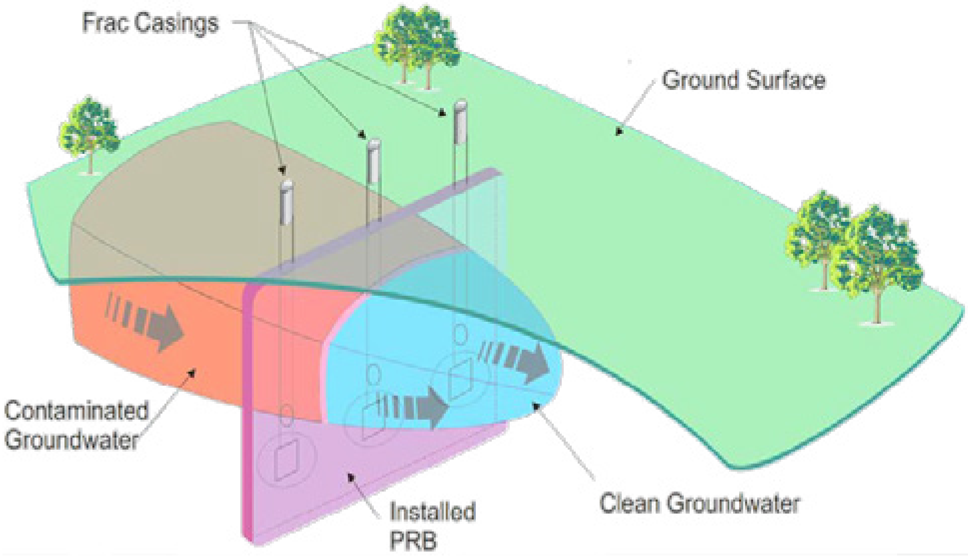


Fig. 1 Scenarios from hydraulic and transport modeling: a) TCE – situation after 8 years by pumping14,4 $l.s^{-1}$of groundwater, b) TCE – situation after 75 years by pumping 4,8 $l.s^{-1}$ of groundwater (Musil et al., 2012)

According of given target limits for the impacted area it is necessary to remediate above 40 200 000 m^3 of aquifer, it represents one of the largest remediation activities in Czech Republic. To remediate this huge contamination a methods of biological reductive dehalogenation (BED) with in-situ chemical reduction (ISCR) has been chosen like the best approach. The aim of these two remediation techniques is to support grow of a local microorganism which are able to degrade chlorinated hydrocarbons. A potential of selected remediation techniques has been proved by pilot testing directly on site. To create required reductive conditions for degradation of chlorinated ethenes, an appropriate substrate will be systematically applied in to the aquifer. This will be done by application of organic substrate and nutrients through injection boreholes. The boreholes will be installed along three line in perpendicular direction on the axis of the contamination cloud. To improve the initial conditions the ISCR remediation technique with target application of zero-valent iron will be used.



(Source: GeoSierra Environmental, Inc.)

Fig. 2 Conceptual scheme of in situ remediation technique

By pilot testing of remediation directly on site it was possible to obtained information about some limitations and possible improvements of planned remediation. This knowledge is already integrated in the final remediation approach described in a Feasibility study and in a Pre Project-documentation. To remediate the area impacted by chlorinated hydrocarbons is expected in 20 years' time-line with total cost about 9 mil. Euro.

LITERATURE

Musil, V., Polák, M., Veleba, P., 2012: Completion of exploration pollution in the vicinity of the village Olšany and verification of appropriate remediation technologies. Final Report II. stages of work. Dekonta. Praha

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LABORATORY TESTING OF BIOCHAR AND/OR NANO ZERO-VALENT IRON FOR REMEDIATION OF METAL-CONTAMINATED SOIL

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KEYWORDS
Biochar, nano zero-valent iron, soil remediation, risk metal(loid)s, stabilisation

INTRODUCTION

The District of Příbram in the Czech Republic is historically known for mining and smelting of silver and lead. The first evidence of such activities comes from 1311 (Dostál et al., 2006). However, this metallurgical tradition caused serious contamination by potentially toxic metals and metalloids in the Litavka River (downstream of the smelter) and consequently to the adjacent soils (Ettler et al., 2006).

Soil contamination represents a significant threat to ecosystems and humans in almost every part of the world. For this reason, various types of soil treatments and other remediation techniques have been studied (Jiang et al., 2018). Biochar (BC) and nano zero-valent iron (nZVI) have gained a lot of attention due to their promising results towards immobilisation of risk metal(loid)s. According to Cha et al. (2016), BC is an efficient sorbent of organic and inorganic contaminants while it can improve soil properties and increase the fertility. Nano zero-valent iron can also adsorb various pollutants and presents high reduction ability (Peng et al., 2017). Although they both have been efficiently used for water decontamination, their effectiveness in soils is yet to be discovered. Therefore, nZVI, BC and their combination was applied into metal(loid)-contaminated soil in this study to assess the potentials and drawbacks of the amendments in terms of soil remediation.

MATERIALS AND METHODS

Fig. 1 Map of the contaminated area in relevance to its position in the world. The sampling site (in the alluvium of the Litavka River) is indicated with red dots in both maps.

Soil samples from the alluvium of the Litavka River (Fig. 1) were collected from the depth of 0-20 cm. *Aqua regia* extraction revealed highly elevated concentrations of Zn (3082 mg/kg) and Pb (3854 mg/kg), while As, Cd, Cr, Cu and Ni were present to a smaller extent. In the present research, BC and nZVI were applied in the experimental soil as follows: i) 2 wt.% BC, ii) 2 wt.% nZVI, iii) 1 wt.% BC + 1 wt.% nZVI, and iv) 2 wt.% nZVI activated in ammonium oxalate solution. All soil treatments were incubated individually for 1 month before further testing.

For the evaluation of the amendments, numerous extractions including *aqua regia*, sequential extraction, and simple extractions in water and $CaCl_2$ were conducted. Physico-chemical parameters such as pH and Eh were measured as well. In addition, pot experiment and soil pore water sampling was performed in several different time steps to assess the actual metal/metalloid availability. Major and trace elements were analysed using inductively coupled plasma optical emission spectrometry (ICP OES). Organic carbon and major anions were analysed using ion chromatography and carbon analyser, respectively, when applicable. The purpose was to determine the effectiveness of the above mentioned soil amendments by comparing the soil characteristics to a non-amended (control) soil sample. Scanning electron microscopy coupled with energy dispersive X-Ray spectroscopy (SEM/EDS) was also implemented on control and amended soil samples.

RESULTS AND DISCUSSION

According to the initial results of the chemical extractions, none of the tested soil treatments proved to be significantly efficient for the risk metal(loid)s stabilisation. Physico-chemical parameters and carbon contents were not significantly different when comparing the amended and non-amended samples. In contrast, pore water sampling showed some promising results, all of the treated samples had significantly lower concentrations than the control for at least one risk element. Moreover, sorption on Fe and Mn oxides was often observed in the treated samples, as indicated by SEM/EDS. Therefore, the addition of sorbents may provoke indirect positive effects related to newly formed Mn oxides, responsible for extensive metal sorption. Low efficiency of the tested sorbents will lead to necessary improvements of the amendment characteristics by using different surface modifications. Therefore, further research needs to be conducted in this field.

LITERATURE

Cha, J. S., Park, S. H., Jung, S. C., Ryu, C., Jeon, J. K., Shin, M. C., & Park, Y. K. (2016). Production and utilization of biochar: a review. Journal of Industrial and Engineering Chemistry, 40, 1–15.

Dostál, J., Kunický, Z. & Vurm, K. (2006). 220 let olověné a stříbrné hutě Příbram 1786 – 2006 - 220-year Anniversary of the Silver and Lead Smelting Works in Příbram.

Ettler, V., Mihaljevič, M., Šebek, O., Molek, M., Grygar, T., & Zeman, J. (2006). Geochemical and Pb isotopic evidence for sources and dispersal of metal contamination in stream sediments from the mining and smelting district of Příbram, Czech Republic. Environmental pollution, 142(3), 409–417.

Jiang, D., Zeng, G., Huang, D., Chen, M., Zhang, C., Huang, C., & Wan, J. (2018). Remediation of contaminated soils by enhanced nanoscale zero valent iron. Environmental research, 163, 217–227.

Peng, X., Liu, X., Zhou, Y., Peng, B., Tang, L., Luo, L., Yao, B., Deng, Y., Tang, J., & Zeng, G. (2017). New insights into the activity of a biochar supported nanoscale zerovalent iron composite and nanoscale zero valent iron under anaerobic or aerobic conditions. RSC Advances 7, 8755-8761.

THE INVESTIGATION OF Zn SPECIATION IN MAN-TRANSFORMED SOILS OF THE ANOMALY ZONES OF THE SOUTHERN URAL AND LOWER DON (RUSSIA)

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KEYWORDS
Speciation, Spolic Technosols, Zn, XANES, EXAFS

ABSTRACT

The accumulation and speciation of Zn technogenically man-transformed soils within the anomaly zone of the Southern Ural and Lower Don were studied using a direct nondestructive physical methods, including X-ray diffraction (XRD) and X-ray absorption spectroscopy (XANES and EXAFS).

Studies were performed in long-term contaminated soils of the Karabash smelter zone's (Southern Ural territory, Russia) and the sediment pond of the chemical plant near city of Kamensk-Shakhtinskii (Lower Don region, Russia). Copper smelters are enterprises causing the maximal environmental damage; among them are the Karabashmed Company (Karabash copper smelter (KCS)) in the Southern Urals (Gashkina et al. 2015; Minkina et al., 2018; Udachin et al. 2003). During the entire active operation period of the KCS since 1910, technogenic zones have formed on the adjacent area of 30 km^2 (Fig. 1). The city of Kamensk-Shakhtinskii in Rostov oblast (Russia) is an example of the destructive impact of long-term anthropogenic activity on adjacent land and aquatic ecosystems. The construction of a large industrial center with chemical plants and production facilities in the city in the 1950s resulted in the installation of sediment ponds and sludge reservoirs in the Severskii Donets river valley. Natural lakes in the Severskii Donets floodplain were used for this purpose. Regular discharge of industrial effluents to these lakes and accidental releases directly to the floodplain landscapes continued to the mid-1990s. As a result, natural ecosystems were destroyed, and the technogenic lakes receiving industrial wastes and sludge collectors were transformed to extremely hazardous sources of secondary environmental contamination.

Fig. 1 Technogenic desert in the Karabash smelter zone's

Monitoring plots with high levels of technogenic pollution adjacent to the investigated objects were selected. Technogenically transformed soils on monitoring plots are classified as Spolic Technosols (IUSS, 2015). The total concentration of Zn in soils were determined by X-ray fluorescence method with a MAKC-GV spectroscane. XRD, XANES and EXAFS spectra were collected at the Zn K-edge (9659 eV) on the beamline “Structural Materials Science” (Chernyshov et al., 2009) of the Kurchatov Synchrotron Radiation Source (National Research Center “Kurchatov Institute”, Moscow, Russia) with the storage ring operating at 2.5-GeV

beam energy and beam currents between 70 and 90 mA. EXAFS data were analyzed using the Viper and IFEFFIT 1.2.11 data analysis packages.

It was found that the total content of Zn in Spolic Technosols was about 11000-66000 mg/kg, which exceeded clark for the lithosphere by hundreds of times. The study of the molecular-structural organization in soils adjacent to the Karabashmed copper smelter of (Southern Ural territory) allowed determining the type of the local surrounding of Zn coordinated to six oxygen atoms forming a distorted octahedron. From the fitting results of the EXAFS data, the lengths of the Zn–O bonds were found to be similar to those in $ZnSO_4$. The fitting results of the EXAFS data Spolic Technosols near the sediment pond of the chemical plant (Lower Don region) revealed 70% of Zn–S (close to ZnS) bonds and 30% of Zn–O bonds (Minkina et al., 2018). Studies of metal speciation are extremely relevant for correct assessment of risk/toxicity of soils from inorganic pollutants.

ACKNOWLEDGEMENTS: Financial Support: Russian Science Foundation Project No. 16-14-10217.

LITERATURE

Chernyshov, A.A., Veligzhanin, A.A., Zubavichus, Y.V., 2009: Structural materials science end-station at the Kurchatov Synchrotron radiation Source: recent instrumentation upgrades and experimental results. Nucl. Instr. Meth. Phys. Res. A. 603, 95–98.

Gashkina, N.A., Tatsii, Yu.G., Udachin, V.N., Aminov, P.G., 2015: Biogeochemical indication of environmental contamination: A case study of a large copper smelter. Geochem Int. 53(3), 253–264.

IUSS Working Group WRB. World reference base for soil resources 2014, update 2015, 2015: International soil classification system for naming soils and creating legends for soil maps. World soil resources reports, FAO, Rome, issue 106.

Minkina, T.M., Linnik, V.G., Nevidomskaya, D.G., Bauer, T.V., Mandzhieva, S.S., Khoroshavin, V.Y., 2018: Forms of Cu (II), Zn (II), and Pb (II) compounds in technogenically transformed soils adjacent to the Karabashmed copper smelter. J. Soils Sedim. 6, 2217–2228.

Minkina, T., Nevidomskaya, D., Bauer, T., Shuvaeva V., Soldatov, A., Mandzhieva , S., Zubavichus, Y., Trigub, A., 2018: Determining the speciation of Zn in soils around the sediment ponds of chemical plants by XRD and XAFS spectroscopy and sequential extraction. Science of the Total Environment. 634, 1165–1173.

Udachin, V., Williamson, B.J., Purvis, O.W., Dubbin, W., Brooks, S., Herrington, R.J., Spiro, B., Coste, B., Mikhailova, I., 2003: Assessment of environmental impacts of active smelter operations and abandoned mines in Karabash, Ural Mountains of Russia. Sustain Dev. 11(3), 133–142.

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THE EFFECTS OF HUMIC SUBSTANCES ON ADSORPTION OF HEAVY METALS BY CLAY MINERALS

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KEYWORDS
fulvic acids; bentonite; heavy metals; ternary systems; adsorption

Large specific surface area, chemical and mechanical stability, layered structure, and high cation exchange capacities make clay minarals exceedingly effective in adsorbing a wide range of environmental pollutants. The edges and faces of clay particles can accumulate cationic, anionic, non-ionic and polar contaminants from the liquid phase. They accumulate on clay surfaces leading to their immobilisation through the process of ion exchange, coordination, electrostatic attraction or ion-dipole interaction. Pollutants can also be held through H-bonding, van der Waals interactions and hydrophobic bonding. Both Brönsted- and Lewis-type acidity in clay minerals can also boost the adsorption capacity of contaminants (Perelomov et al., 2016).

Humic substances are the major organic components of soils. Humic substances provide important sources of dissolved adsorbent organic ligands and, therefore, are expected to influence the bioavailibility and mobility of metals in soil, sediments, and aquatic systems. With respect to the potential toxicity of heavy metals, adsorption by humic substances reduce metal uptake by organisms.

Humcic substances interact with clay minerals to form organo-mineral complexes and composites. Humic substances can significantly alter the characteristics of mineral surfaces, particularly heavy metal sorption (Giannakopoulos et al., 2006). Organic coatings by humic acids significantly affect the surface electrostatic properties of clays and, hence, influence clay sorption characteristics (Murphy et al., 1990,). The physicochemical mechanisms of the sorption of humics on mineral surfaces are the subject of intensive investigation (Perelomov et al., 2017).

In the literature, there are many contradictory data concerning the influence of fulvic acids on the absorption of heavy metals. Evidently, the interaction conditions (pH and ionic strength), as well as the presence in the composition of fulvic acids of various functional groups, are of great importance. Humic acid, added to bentonite, increased the sorption capacity for Cd and Pb, especially at high Pb concentrations. The coating with fulvic acid had a smaller effect on absorption due to its high solubility (Zhang et al., 2015). We investigated the adsorption of lead by sodium bentonite in the presence of model objects – organic acids with different functional groups – citric acid and lysine. The amount of lead absorbed by sodium bentonite was reduced in the presence of citric acid, both with the simultaneous addition of metal and acid, and in the case when the acid was added 2 hours before the metal. A possible reason for this was the formation of lead complexes with citrates, which had a less affinity for the surface of the mineral, as well as the dissolution of the lead carbonate – hydrocercussite mineral in an acidic environment. The introduction of lysine together with lead did not change the metal absorption by bentonite, and 2 hours before lead – reduced its sorption (Perelomov et al., 2016).

Adsorption of heavy metals (Pb, Zn, Cu and Ni) by bentonite and bentonite in the presence of natural and oxidized fulvic acids from peat was studied. Mesotrophic sphagnum peat from Tula region, Russia, was used for humic substances extraction in accordance with procedure as described by Stevenson (Stevenson, 1994). Samples of peat humic substances were oxidized by Elbs persulfate oxidation reaction (Sethna, 1951). The FTIR and NMR spectra of fulvic acids used were obtained. Bentonite from company BentoGroupMinerals, which is a part of the group of companies Auri, was used. The raw material base of the company is the Sarigyukhskoye deposit, which is being developed by the Ijevan Bentonite Combine (Republic of Armenia). For experiment fulvic acids solution with pH 4,5 and concentration of 0,2 g L^{-1} was used. Sorption experiment was carried out at heavy metals concentration 4 mmol L^{-1} and ratio solid:solution as 0,2 to 25. The supernatant of each sample was collected by filtering through acetate membranes syringe filter (pore size <0.2 μm) and the heavy metals concentrations were determined by ICP OES (spectrometer Perkin Elmer Optima 5300 DV) at wavelengths 222.778 nm for Cu, 217.000 nm for Pb, 213.857 nm for Zn and 221.648 nm for Ni. The amount of each heavy metal adsorbed was calculated by the difference between the amount of heavy metal added and that remaining in the supernatant.

The adsorption of studied heavy metal by bentonite and bentonite in the presence of natural and oxidized fulvic acids is shown in Figure 1.

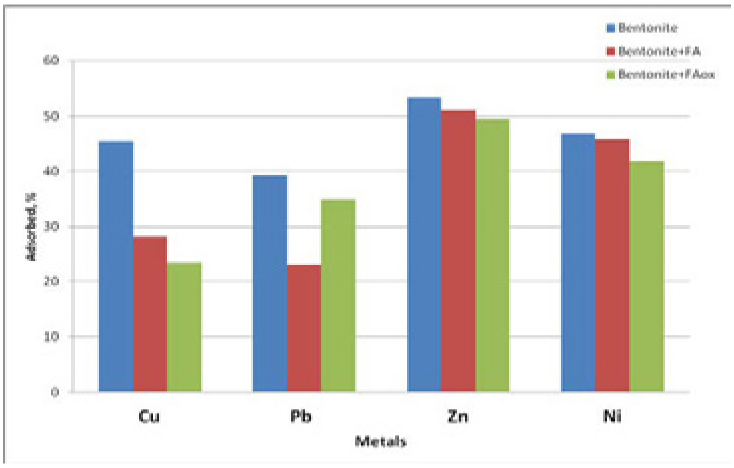

Fig. 1 Adsorption of heavy metal by bentonite and bentonite in the presence of natural and oxidized fulvic acids

The sorption of heavy metals by bentonite under the experimental conditions was from 39 % for lead to 53 % for zinc from the initial concentration (4 mmol L^{-1}). Sorption of copper and nickel was 45 % and 47 %, respectively. The presence of natural peat fulvic acids led to an increase in the content of all heavy metals in an equilibrium solution. Lead absorption decreased to 23 %, copper to 28 %, zinc to 51 % and nickel to 46 %. Thus, the formation of complexes of fulvic acids with these metals is possible, which have a lower chemical affinity for the surface of bentonite. Oxidized fulvic acids further reduced the sorption of metals, with the exception of lead. The effect of fulvic acids on the sorption of heavy metals depended on the type of metal. The maximum decrease was observed for copper in the presence of oxidized fulvic acids and for lead in the presence of natural fulvic acids. For zinc and nickel the decrease in adsorption compared to the mineral was insignificant. The reason for the insignificant decrease in the adsorption of these two metals by bentonite in the presence of fulvic acids can be both the good sorption capacity of their complexes by clay and the difficulty in the formation of their complex compounds with fulvic acids. The first reason seems more likely to us, because FTIR spectrometry and NMR data indicate the presence of a large number of functional groups in fulvic acids responsible for the formation of complex compounds with cations of heavy metals.

Effect of humic substances on the adsorption of heavy metal cations by clays realized in different ways depending on the complexing ability of organic ligands with the cation and the affinity of the metal, ligand and complex of “metal – ligand” to the surface of the clay mineral. Acidity and ionic strength of the soil solution, the degree of clay mineral surface coating by humus organic substances had great importance for the absorption of metals.

Thus, the use of bentonite clays and products based on them as remediants requires consideration of the presence of organic substances.

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LITERATURE

Giannakopoulos E., Stathi P., Dimos K., Gournis D., Sanakis Y., Deligiannakis Y. (2006) Adsorption and Radical Stabilization of Humic-Acid Analogues and $Pb2^+$ on Restricted Phyllomorphous Clay, Langmuir, 22, 6863–6873.

Murphy E., Zachara J., Smith S. (1990) Influence of Mineral-Bound Humic Substances on the Sorption of Hydrophobic Organic Compounds, Environ. Sci. Technol. 24, 1507–1516.

Perelomov L., Chilachava K., Shvykin A., Atroschenko Yu. (2017) The Effects of Humus Organic Matter on Absorption of Trace Elements by Clay Minerals, Agrochimia, 2, 99–107.

Perelomov L., Sarkar B., Rahman M.M., Goryacheva A., Naidu R. (2016) Uptake of lead by Na-exchanged and Al-pillared bentonite in the presence of organic acids with different functional groups, Appl. Clay Sci. V. 119, 417–423.

Sethna S.M. (1951) The Elbs persulfate oxidation. Chem. Revs., 49, 91.

Stevenson F.J. (1982). Humus chemistry. John Wiley & Sons, New York.

Zhang W., Zheng J., Zheng P., Tsang D.C.W., Qiu R. (2015) The roles of humic substances in the interactions of phenanthrene and heavy metals on the bentonite surface, J. Soils Sediments, 15, 7, 1463–1472.

RISK ANALYSIS OF WASTE DUMP IN AREA OF VOTICE, CENTRAL BOHEMIAN REGION

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KEYWORDS
Contaminant, quarry, groundwater pollution, environmental impact assessment, risk analysis

ABSTRACT

The problems with water or soil contamination form the former national companies are extended throughout the Czech Republic. This paper is about one in central Bohemian Region, near the town Votice. There is an old quarry south of the Votice which has been loaded with different waste from 1980´s. This waste was with certainty from tesla, National Company, which was focused on electrical production. There is also a second probable source, the chemical industry in the town.

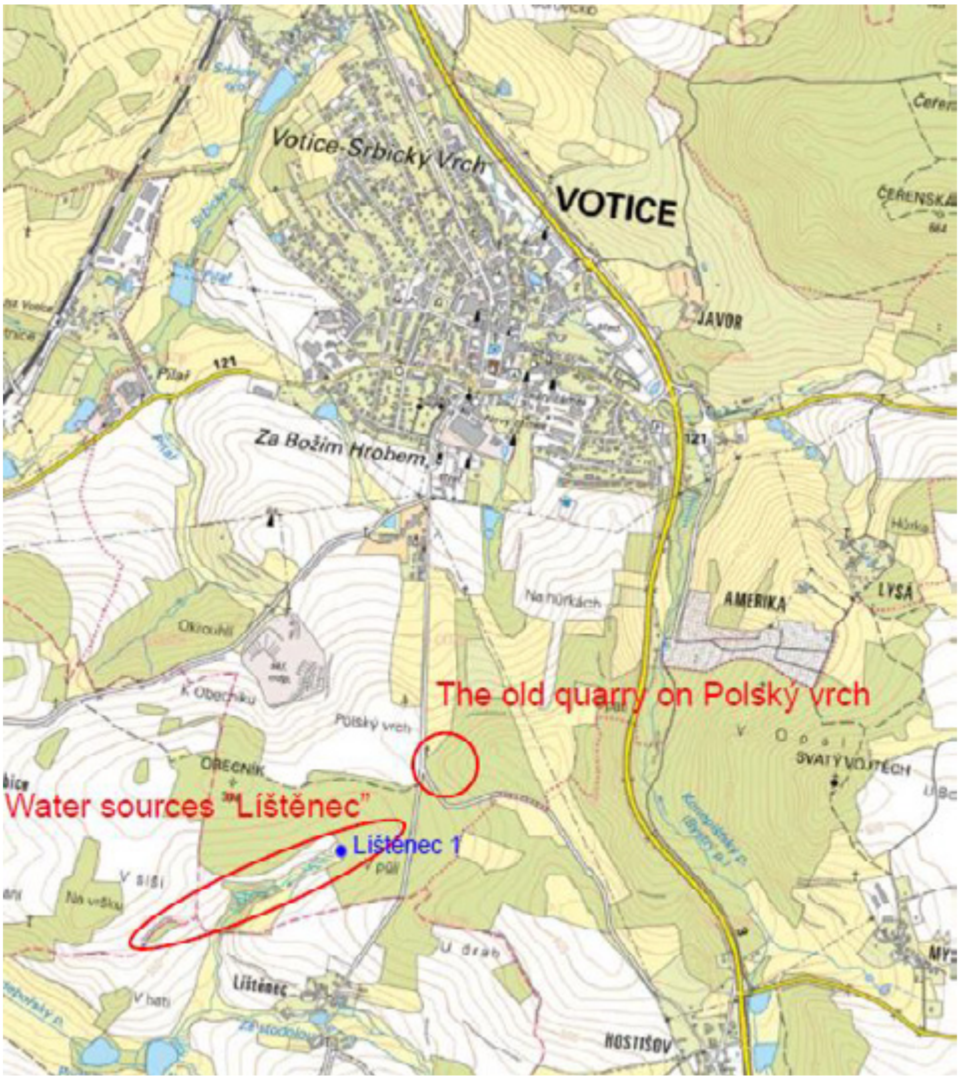

Fig. 1 Situation of the old quarry and water sources

This quarry is situated on the top of Polský vrch. South west of this hill is an area of water source for the town water supply. In one on this sources – Líštěnec 1 have been detected chlorinated hydrocarbons, especially trichloroethylene and tetrachloroethylene, for more than three years. This water source was shut down because the concentration of chlorinated hydrocarbons is higher than legislative limits for drinking water.

This risk analysis confirms presence of waste in the old quarry and also spreading of chlorinated hydrocarbons towards the water sources. The only way how to get rid of this contamination is to take off the waste in the quarry in the first place and after that started with remediation of polluted groundwater.

Fig. 2 The old quarry

Fig. 3 Contaminated materials

Fig. 4 Contaminated materials

This project is supported by European Union Operational Programme Environment, Priority Axis 3, Waste management and material flows, environmental burden and risks.

LITERATURE

Potočárová, L. 2017: Risk analysis of waste dump in area of Votice. Final report. Vodní zdroje Ekomonitor, s.r.o

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ENVIRONMENTAL REPERCUSSIONS OF HYDROPOWER PLANTS IN THE BALKAN

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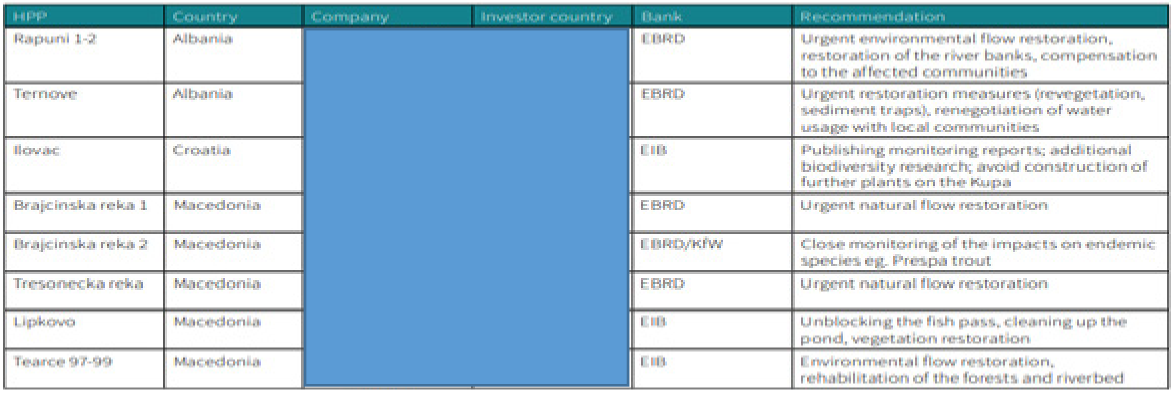
KEYWORDS

Balkan, hydropower, contamination, alternative energy, environmental assessment, protection

ABSTRACT

In the Balkan in the recent years several thousand Greenfield plants have been opened, 73 of which in Macedonia, and counting. Small stations contribute with only 3.4 % of all the hydro-power compared to the large scale plants, yet they are rapidly being set as a more economical alternative to the sizable plants. Experts from the field of Environmental Protection warn that these small plants cause tremendous damages and changes in the ecosystem as they destroy the natural habitats of living creatures, devastate the biodiversity, lower the vegetation, alter the landscape, contribute to erosion and change for good the living conditions of the living organisms, humans included. Another major concern is that an increasing number of Greenfield plants not just in Macedonia but in the Balkan as well, are being set in protected areas such as national parks which means that the possible repercussions in such projects are even higher as protected areas usually safeguard endemic species and have very fragile biotic and abiotic factors. The question is– how can we differentiate where the negative effects of hydro-power stop and the positive fact arises, which is that after all, hydro-power represents a renewable and environmentally friendly resource as it does not waste or lose water in the process and even controls flooding?

Greenfield plants in the Balkan region are slowly capturing every river that meets the minimum requirements. However, this means that construction areas are being assembled in natural habitats in 4 phases, each done with heavy machinery, many infrastructures and extensive equipment, which pollute the biotic factors and change gravely the abiotic ones. According to the official documents provided by the constructors, every necessary measure will be taken in order to minimize the negative effects of the projects, however plenty of irreversible negative effects have been recorded by independent experts. The following image is a set of recommendations given by experts who visited several of the Greenfield plants and noticed the changes to the environment and the wildlife the HPPs were creating.



HPP	Country	Company	Investor country	Bank	Recommendation
Rapuni 1-2	Albania	[redacted]	[redacted]	EBRD	Urgent environmental flow restoration, restoration of the river banks, compensation to the affected communities
Ternove	Albania	[redacted]	[redacted]	EBRD	Urgent restoration measures (revegetation, sediment traps), renegotiation of water usage with local communities
Ilovac	Croatia	[redacted]	[redacted]	EIB	Publishing monitoring reports; additional biodiversity research; avoid construction of further plants on the Kupa
Brajcinska reka 1	Macedonia	[redacted]	[redacted]	EBRD	Urgent natural flow restoration
Brajcinska reka 2	Macedonia	[redacted]	[redacted]	EBRD/KfW	Close monitoring of the impacts on endemic species eg. Prespa trout
Tresonecka reka	Macedonia	[redacted]	[redacted]	EBRD	Urgent natural flow restoration
Lipkovo	Macedonia	[redacted]	[redacted]	EIB	Unblocking the fish pass, cleaning up the pond, vegetation restoration
Tearce 97-99	Macedonia	[redacted]	[redacted]	EIB	Environmental flow restoration, rehabilitation of the forests and riverbed

Tab.1 Set of recommendations by experts

Source: CEE Bankwatch Network (Broken Rivers report)

According to the international law and regulations of construction processes, every investor and the executional company have to provide a detailed study – *Evaluation of the Influence on the Environment* and EBRD[1], being the main investor of the Greenfield plants in the Balkan, in its guidelines states*: "A good understanding of the nature of aquatic ecosystems (habitats, riparian flora, macroinvertebrates, fish, aquatic and semi-aquatic mammals and amphibians) is the basis for an assessment of the impacts of a hydropower scheme on these ecosystems"*, however the joint team of independent researchers proved that little prior field research was done. As a result, completely opposite of their guidelines, the field research showed that the HPP cascade system (typical for small HPP) and the joint settlements such as tunnels, reservoirs, roads, dams, building and electrical equipment, done to erect the

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[1] European Bank of Reconstruction and Development

HPPs, led to deteriorated water quality. For example, the pristine wild rivers in Macedonia are known to host macroinvertebrates such as the *Bombina variegata,* which live in pure, potable, oxygen rich, rapid waters, however their population is decreased as a result of the water contamination done by the settlements. Nevertheless that according to the EU Habitats Directive, an assessment of the biodiversity has to be supplied, it is especially worrisome how some of these HPPs are built in *Emerald zones* and possible future *Natura 2000 sites*[2] . How will this be possible considering that the HPPs have been built in national parks and protected areas which host endemic species and very fragile biodiversity, is unknown, considering that 2 endemic species are lost because their habitat is contaminated and many others are highly endangered. Furthermore, erosion around the HPPs is noted and loads of constructional waste such as concrete blocks and other waste material are dumped in the riverbed or around the site which also creates deposits of metals and other substances.

Figure 35: Culvert

Figure 36: Riverbed filled with branches and excavated materials

Fig 1. The natural and residual flow of the rivers is being compromised by artificial obstacles and contaminated by construction materials. (Source: Broken rivers report)

The following photos show that except for the obvious natural degradation as a result of the constructional work, erosion is also caused, which under wind and other natural factors contaminate the rivers with sediments.

Fig.2 Photos demonstrating the contamination of pristine wild rivers (Left – Upper Sana river, Right – Langarica river)

These sights are becoming often in the Balkan under the wave of financing new 2 638 HPPs which are planned or already being built. The unique network these rivers create, underlines the threats for the existence of aquatic life and potable water in the Balkan region as the chain effect stretches out throughout the region. If the countries want to increase the level of renewable energy but do not want to jeopardize the environment and the pristine rivers, they have to stop building in protected areas, areas with high biodiversity and respect the standards for minimum required residual flow, which now is not done. The waste management is also done very poorly which results in unnecessary and avoidable contamination of the areas connected to the dams.

LITERATURE

Vejnovic,Igor. Broken rivers: The impacts of European-financed small hydropower plants on pristine Balkan landscapes. December 2017

Schwarz, Ulrich., Hydropower Projects on the Balkan Rivers – Update. September 2015

Vejnovic, Igor; Gallop, Pippa. Financing for hydropower in protected areas in Southeast Europe: 2018 update. March 2018

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[2] According to the status of the Balkan countries as possible future EU members.

RECLAMATION OF RESERVOIR SEDIMENTS POLLUTED BY METALS BY CO-MIXING WITH WASTE

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KEYWORDS
Bottom sediments, heavy metals, mobility, waste, soil amendment

ABSTRACT

Bottom sediments accumulate high concentrations of heavy metals released by industrial activities, transported, sewage outfalls, urban and industrial runoff, and atmospheric precipitation. In this case, the most suitable technique for the management of contaminated sediments by metals is to immobilize contaminants in the solid phase by chemical stabilization because these techniques reduce the bioavailability of metals. Moreover environmental utilization of sediments is of the most promising alternative due to beneficial properties of sediments rich in clay, silt, organic matter, nutrients (macro- and micronutrition), and microbial activity therein. The aim of the study was to assess content and mobility of heavy metals in the mixtures of bottom sediments and sludge from paper production in the aspect of soil environment standards. Mixture of sediments and as a soil amendment, has an economical and environmental value.

Treatment	Zn	Cd	Pb	Cu	Cr	Ni
	mg · kg^{-1} d.m.					
100% S	3796	58.2	300	62.6	29.9	42.3
50% S + 50% SPP	1702	26.3	133	29.9	14.5	11.6

Table 1. Content of heavy metals in the mixture of bottom sediments (S) and sludge from paper production (SPP)

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NEW LOW-COST ADSORBENT FROM FISH SCALES CARP MODIFIED BY NANOPARTICLES OF CERIUM DIOXIDE TO REMOVE As(V) IONS FROM WATER

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KEYWORDS
Arsenate, adsorption isotherms, drinking water, carp scale, CeO_2 nanoparticles

ABSTRACT

The possibility of using porous carp fish scales (Cyprinus carpio) modified with cerium for the removal of As(V) ion from aqueous solution was investigated in this study. The synthesis consisted of chemical and thermal treatment in order to convert the fish scales into the porous fish scales covered by cerium nanoparticles (FS-CeO_2). The porosity and the content of the CeO_2 nanoparticles may be controlled in synthesized porous adsorbent by changing the reaction conditions. The reaction parameters were optimized using the response surface methodology (RSM) where the output is the result of the adsorbent capacity. A highly efficient material (FS-CeO_2) with a capacity of 78.12 mg g^{-1} (Langmuir isothermal model) was obtained to remove As (V) ions from the drinking water. The adsorption studies were conducted as a function of pH, contact time, mass of adsorbent and temperature. The best adsorption of arsenate ions was achieved for pH value between 4.0 and 6.0.

INTRODUCTION

Due to the material availability in a large quantity, the fish scales are nowadays considered only as a bio waste [1]. Development of material(s) and/or technique(s) for removal of disparate aquatic pollutants provides multiple contributions to the environmental protection. Cerium is known as a rather cost-effective element with large reserves among the other rare earth elements [2]. It has been reported a high adsorption capacity for the anions removal. The modification of fish scale by CeO_2 nanoparticles is studied as a new low-cost adsorbent for arsenate removal from water.

EXPERIMENTAL

The ratio of initial amount of $CeCl_3$ and the carbonization temperature was optimized in order to achieve a high adsorptive material for the removal of As(V) ions from the water. Synthesized FS-CeO_2 adsorbent is characterized using FTIR and BET techniques, and the zeta potential was also determined. Adsorption experiments were carried out in batch conditions, with the initial concentration of As(V) solutions ($C_0 = 5.78$ mg L^{-1}) and the adsorbent masses from 100 to 500 mg L^{-1}. In order to investigate the effects of pH on the adsorption of As(V) ions, the initial pH value of the solution was varied between 4.0 and 12.0. Thermodynamic adsorption experiments were performed at 25, 35 and 45 °C. The effect of contact time on the adsorption of ions As(V) was monitored over interval of 10–90 minutes. The number of adsorbed ions is calculated from the difference between the initial and the equilibrium concentration.

RESULTS AND DISCUSSION

The influence of the pH value, the adsorbent mass and the adsorption time are shown in Figure 1. The adsorption data for arsenate at 25, 35 and 45 °C are fitted to Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin isotherm models whose results are given in Table 1. Experimental data were used to model adsorption kinetics using pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion kinetic models. The results showed that the adsorption of As(V) ions onto FS-CeO_2 followed the pseudo-second-order kinetic model and Freundlich isotherm models. According to the Freundlich isotherm, the mechanism of As(V) ions adsorption onto CeO_2-HPC could be described by heterogenous adsorption, where the adsorbed ions/molecules had different enthalpies and adsorption activation energies. The n value from the Freundlich isotherm is a measure of the adsorption intensity or surface heterogeneity. Values of n close to zero indicate a highly heterogeneous surface. The value n < 1 (Table 1) implies a chemisorption process, whereas the higher value is an indication of cooperative adsorption, i.e., physisorption and chemisorption, with different contribution at different steps of the equilibration of the system [3].

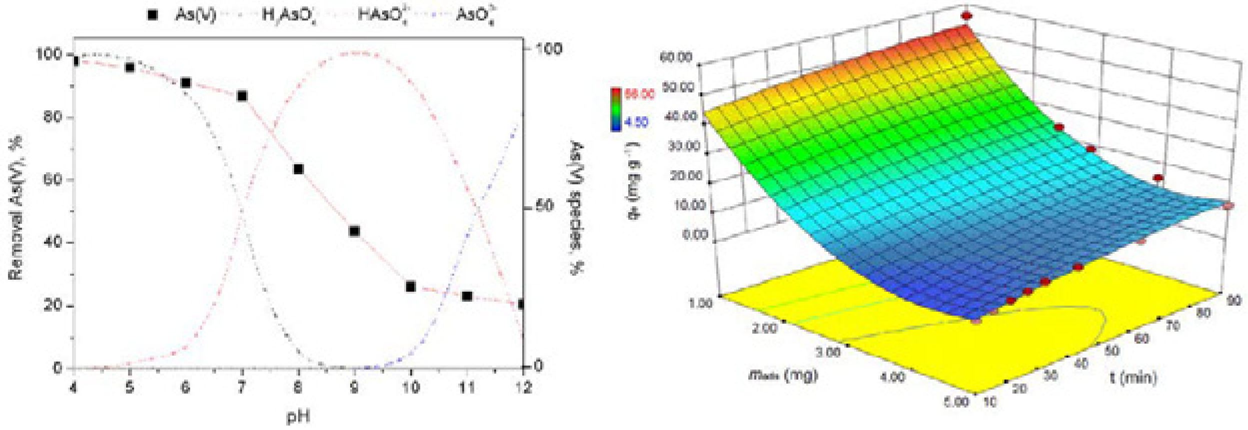

Figure 1. The influence of ph values (a), adsorbent mass and adsorption time (b) on the adsorption process ($C_{i[As(V)]}$ = 5.78 mg L^{-1}, *m/V* = 100 - 500 mg L^{-1}, pH = 4-12, *t* = 10–90 min)

Thermodynamic parameters, including the Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) changes, indicated that the present adsorption process was feasible, spontaneous and endothermic in the temperature range of 25-45 °C [3].

Table 1. Adsorption isotherm parameters for As(V) adsorption on the FS-CeO_2 ($C_{i[As(V)]}$ = 5.78 mg L^{-1}, *m/V* = 100 – 500 mg L^{-1}, pH = 4)

Isotherm model and model parameters		Temperature		
		298 K	308 K	318 K
Langmuir isotherm	q_m (mg g^{-1})	78.12	79.82	81.44
	K_L (L mg^{-1})	4.865	4.858	4.836
	K_L (L mol^{-1})	364530	363981	363323
	R^2	0.980	0.977	0.967
Freundlich isotherm	K_F (mg g^{-1}) (dm^3 mg^{-1})$^{1/n}$	95.629	98.426	102.011
	$1/n$	0.600	0.606	0.613
	R^2	**0.995**	**0.996**	**0.998**
Temkin isotherm	A_T (dm^3 g^{-1})	53.090	53.606	54.519
	b_T	16.26	16.42	16.58
	B (kJ mol^{-1})	152.41	156.00	159.52
	R^2	0.969	0.965	0.957
Dubinin-Radushkevich isotherm	q_m (mg g^{-1})	59.48	60.00	60.35
	K_{ad} (mol^2 kJ^{-2})	7.140	7.130	7.12
	Ea (kJ mol^{-1})	8.369	8.374	8.377
	R^2	0.990	0.976	0.975

CONCLUSION

In the present work, cerium dioxide nanoparticles supported onto a high porous fish scales FS-CeO_2 has been investigated for As(v) removal. The mechanism of As(v) adsorption by FS-CeO_2 involves physisorption and chemisorption processes. The adsorption capacity depends on the pH value, temperature, specific surface area, pore volume and diameter. Synthesized low cost adsorbent, in addition to its high efficiency, has meet other eco standards – potential waste material is used as a new medium for environmental protection.

REFERENCE

[1] Bajić, Z.; Đokić, V.; Veličković, Z.; Vuruna, M.; Ristić M.; Ben Issa N.; Marinković, A. Equilibrium, kinetic and thermodynamic studies on removal of Cd(II), Pb(II) and As(V) from wastewater using carp (cyprinus carpio) scales *Dig. J. Nanomater. Bios.* **2013.** 8 (4), 1581–1590

[2] Peng, X., Luan, Z., Ding, J., Di, Y., Li, Y., Tian B., Ceria nanoparticles supported on carbon nanotubes for the removal of arsenate from water, *Materials Letters* **2005**. 59, 399–403

[3] Karanac, M.; Đolić, M.; Veličković, Z.; Kapidžić, A.; Ivanovski, V.; Mitrić, M.; Marinković, A. Efficient multistep arsenate removal onto magnetite modified fly ash *J. Environ. Manage.***2018.** 224, 263–276 DOI: 10.1016/j.jenvman.2018.07.051

HEALTH AND ECOLOGICAL RISK ASSESSMENT OF HEAVY METALS POLLUTION IN MINING REGION: A CASE STUDY FROM MALOPOLSKA (SOUTHERN POLAND)

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KEYWORDS

Soils, zinc, cadmium, lead, biotests, health risk assessment

ABSTRACT

Intensive anthropopressure have released heavy metals into the environment, threatening human and ecosystem health. The aim of the study was to assess of ecological and health risks of heavy metals exposure from soil in the Malopolska area (southern Poland). Human health risks were assessed by adapting US EPA methodology. Three biotests: Phytotoxkit, Ostracodtoxkit and Microtox were used in the assessment of soil ecotoxicity. The investigation of 320 soil samples from the differently used areas (grassland, arable land, forest, wasteland) revealed very high variation in the metal content in the soils. We found that pollution of Malopolska soils with zinc, cadmium and lead is moderate. Generally, a point source of metal pollution was noted in the study area. The highest content of zinc, cadmium and lead was found in the north-western part of the area – the industrial zones (mining-metallurgical activity). The hazard index (HI) obtained for the metals were generally below 1, indicating no adverse health effects to most unlikely. Ecological risk assessment revealed that 34 % of the soils was characterised by a low, 31 % by moderate, 15 % by high and 9 % by very high risk. The lack of ecological risk I revealed in 11 % of the soils. Moreover, that the areas of north-western Malopolska are most exposed to chemical degradation connected with soil contamination by heavy metals.

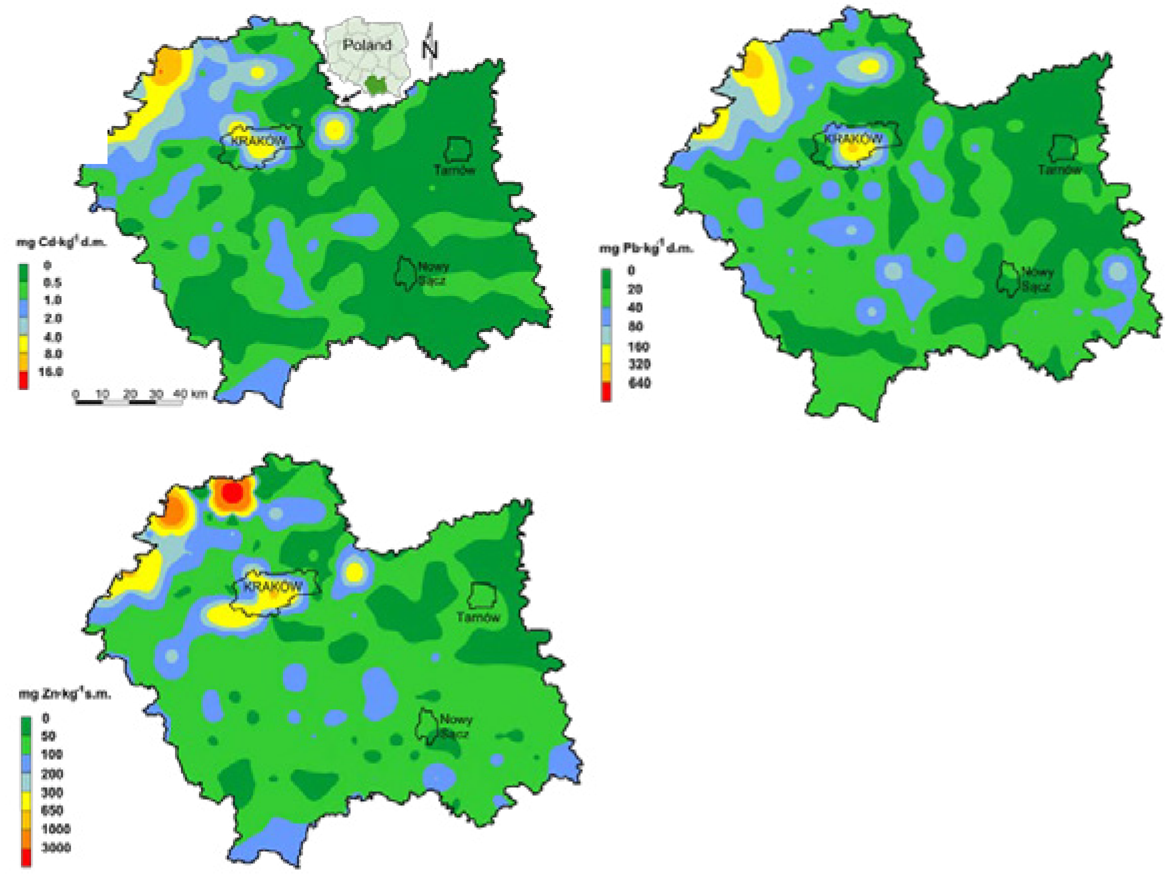

Fig 1. Total content of heavy metals in the soils of study area

LITERATURE

Wieczorek J. et al. 2018. Assessment of the pollution and ecological risk of lead and cadmium in soils. Environmental Geochemistry and Health, doi.org/10.1007/s10653-018-0100-5, Baran A. et al.2018. Potential ecological risk assessment and predicting zinc accumulation in soils. Environmental Geochemistry and Health, doi.org/10.1007/s10653-017-9924-7

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ANALYSIS OF MICROBIOLOGICAL SUCCESSION IN CHRONOSEQUENCES OF CONTAMINATED OVERBURDEN ROCK DUMPS OF KURSK MAGNETIC ANOMALY (KURSK, RUSSIA) USING 454 PYROSEQUENCING

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ABSTRACT

The study of the process of soil formation is an important task both for understanding soil evolution, and for the development of methods for the restoration of soil resources. Often, the soil genesis is closely associated with the evolution of the soil microbiome, since it is microorganisms that play a key role in ensuring the cycles of the basic biogenic elements, in the processes of destruction of organic matter, and in the formation of soil organic matter. In this respect, promising model objects are soil chronosequences in which the process of soil restoration can be observed in development within certain time intervals. An expedition to the region of the Kursk Magnetic Anomaly was organized to study the process of primary soil formation in the conditions of technogenic landscapes. Soil-forming rocks in the area of Mikhailovsky mining complex (KMA) were tertiary Callovian clays (Upper Jurassic). DNA extraction was performed using the PowerSoil® DNA Isolation Kit (MO BIO, USA), which included the step of mechanical destruction of a soil sample using abrasive materials (Mobio Laboratories, USA). The destruction of the soil sample was carried out on a Precellys 24 homogenizer (Bertin Technologies, France). The purity of isolation and the amount of isolated DNA were checked by electrophoresis in 1 % agarose in 0.5x TAE buffer. The average DNA concentration in the sample was 50 ng/ml. The purified DNA preparations (10-15 ng) were used as templates in the PCR reaction (temperature profile: 95°C – 30 s, 50°C – 30 s, 72°C – 30 s, 30 cycles in total) using Encyclo polymerase (Eurogen, Russia) and universal primers to the V4 variable region of the 16S rRNA gene: F515 (GTGCCAGCMGCCGCGGTAA) and R806 (GGACTACVSGGGTATCTAAT). To assess biodiversity and conduct comparative analysis of communities, the parameters of α- and β-diversity were calculated. The α-diversity was assessed using the index of species richness (the number of OTUs in the sample) and the Shannon index. The reliability of differences in α-diversity indices among microbiomes was assessed using the t-test. Soils of investigated dumps were presented mainly by weak developed profiles of Leptosols with well pronounced accumulation of organic matter in the topsoil. Not essential alteration of soil agrochemical properties as well as fine earth structure and texture composition was reveled. The species composition of the vegetation communities (table 1) was various for different age dumps. On the very initial staged dumps were dominated by grass, while the sparse forests with dominance of birch and poplar were typical for older stages.

When analyzing the taxonomic structure of the microbiome, 29 bacterial and 2 archaeal phyla were found in soil samples of the dumps. 0.5 % of the sequences (on average) were not identified to the domain level. Among the bacteria in the community, representatives of phyla *Proteobacteria* (41.7 % on average), *Actinobacteria* (34 %), *Chloroflexi* (10.4 %), *Gemmatimonadetes* (4.5 %), *Acidobacteria* (2.5 %), *Bacteroidetes* (2 %), *Planctomycetes* (1,1 %); other phyla on average did not exceed 1 % per library. When comparing the early and late stages of microbial succession with increasing age of the dump, the percentage and taxonomic diversity of bacteria from phyla *Actinobacteria, Chloroflexi* and *Acidobacteria* increase in the community, while the proportion of such phyla as *Proteobacteria, Gemmatimonadetes* and *Bacteroides* decreases. Also, with increasing age of the dump, the number of archaea belonging to the phyla *Crenarchaeota* and *Euryarchaeota* decreases almost to zero. The decrease in the number of archaea may be due to the replacement of their ecological niches (in particular, for the representatives of the phylum *Crenarchaeota*, it is the participation in nitrification processes) by bacteria in a more developed type of microbial community.

Changes in the taxonomic composition of the bacterial community are associated with the transition from an unstable stage of development of an ecosystem characterized by the dominance of copiotrophic microorganisms (for example, bacteria from the genus *Pseudomonas*, bacteria from the family *Enterobacteriaceae*) to the climax type of a community with a predominance of actinobacteria, the presence and high biodiversity of which indicate an effective process of transformation of soil organic matter (Goldfarb et al., 2011). In the 50-year-old dumps, the proportion of streptomycetes and nocardia increases, in particular, a reliable increase in the proportion in the community ($p<0.05$) was found for families *Micromonosporaceae, Nocardioidaceae, Microbacteriaceae*, as well as bacteria of the family *Gaiellaceae* and order *Solirubrobacterales* typical in the soil of areas with a high

value of the hydrothermal coefficient. The highest number of nucleotide sequences of the 16S rRNA gene in the analyzed amplicone libraries was shown to belong to proteobacteria from the *Comamonadaceae* family. All of them showed the greatest similarity with the nucleotide sequences of the typical strain of *Delftia tsuruhatensis*. It is known that this microorganism is often associated with contaminated and technogenically disturbed soils, as well as with the microbial community of activated sludge. The active participation of these bacteria in soil-forming processes was also confirmed by a peak-like change in their representation in the samples. For example, the number of these bacteria started to increase already in the 10-year-old dumps and reached a maximum in the 35-year-old dumps, after which it decreased. It can be assumed that active microbiological succession processes occur even 35 years after the formation of the dump. This conclusion is confirmed by the analysis of the alpha and beta diversity of the studied microbiomes (Table 1).

Table 1. Indicators of alpha diversity of microbiomes inhabiting dumps of different ages. CL_1,2,3 - designation of dumps of various ages, 1 - 10 years, 2 - 35 years, 3 - 50 years.

	Cl-1	Cl-2	Cl-3
Observed OTUs*	373.3±139.0	370.3±49.7	466.3±9.6
PD_Faith**	38.6±10.5	35.6±3.9	39.5±0.6
Shannon***	6.5±0.9	6.6±0.6	7.6±0.1

* Observed OTUs – total number of operational taxonomic units, ** PD_Faith – an indicator of the phylogenetic diversity of Faith, *** Shannon - Shannon Index

The multidimensional scaling of the distance matrix between the samples under study shows that the taxonomic structure of microbiomes differed qualitatively and quantitatively in dumps of different ages. At the same time, the 10-year-old and 35-year-old dumps were characterized by similar parameters of alpha diversity (Table 1), which indicates a transitional (unstable) stage of ecosystem development. The number of species in the community, as well as the Shannon index, increase only in the 50-year-old dumps which, according to these indirect indicators, can be characterized as the final phase of microbiological succession. Thus, based on the analysis of microbiological diversity, we showed that technogenic dumps formed by clay textured overburden rocks in the KMA region are a favorable substrate for the development of microorganisms already at the earliest stages of soil formation. Even in 10 years old embryonic humus enriched soils microbial communities demonstrate a relatively high level of biological diversity. However, the increase in biodiversity indicators and the transition to a stable (climax) type of community were observed only 50 years after the formation of the dumps. This process is characterized by the replacement of copiotrophic forms of microorganisms by oligotrophic ones, among which the main role is played by various types of actinobacteria.

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