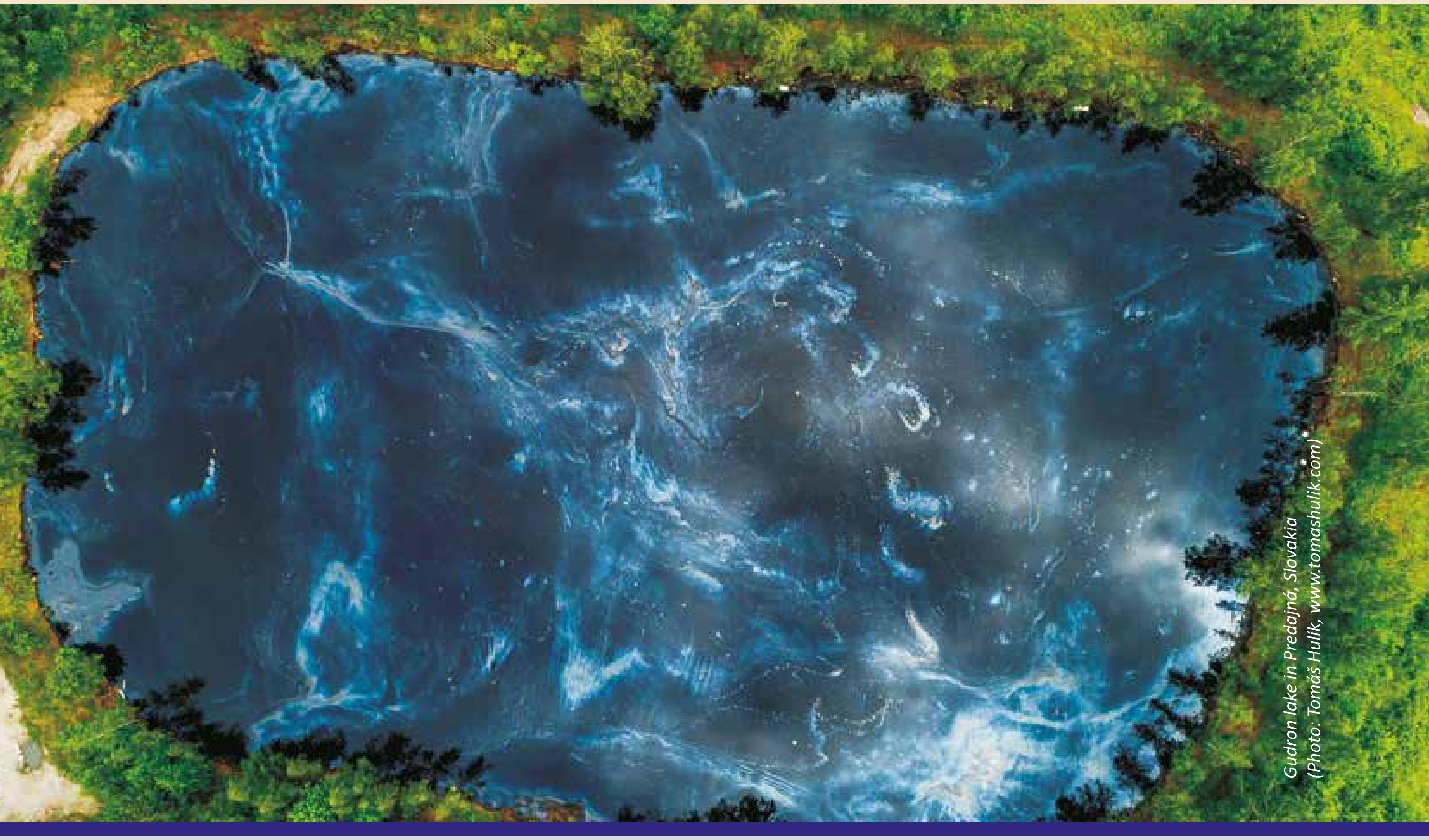
INTERNATIONAL CONFERENCE
CONTAMINATED SITES
ZNEČISTENÉ ÚZEMIA
MEDZINÁRODNÁ KONFERENCIA

Ministry of Environment of the Slovak Republic
Slovak Environment Agency

INTERNATIONAL CONFERENCE
CONTAMINATED SITES 2022
SENEC | SLOVAK REPUBLIC | 12 – 14 OCTOBER 2022



Gudron lake in Predajná, Slovakia
(Photo: Tomáš Hulík, www.tomashulik.com)

CONFERENCE PROCEEDINGS

OP KŽP

European Union
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MINISTRY
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OP KŽP

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CONTENTS

PROGRESS IN MANAGEMENT OF CONTAMINATED SITES IN THE REPUBLIC OF SERBIA 2021

Dragana Vidojevic[1], Nemanja Jevtic[2]

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KEYWORDS
Contaminated sites, management, dumpsites, cadaster

ABSTRACT

This study presents a current situation in management of contaminated sites in Serbia. In 2015 the Ministry of Environmental Protection adopted the Law on Soil protection, which was the basis for the establishment of a comprehensive legal framework for the management of contaminated sites in the Republic of Serbia. Based on the latest State of the Environment Report for 2020 (SEPA, 2021) in the territory of the Republic of Serbia there are 213 sites identified as either potentially contaminated or contaminated. Waste disposal sites have the largest share of 71.83 % in the total number of sites.

INTRODUCTION

The primary authority responsible for the environment management and policy at the national level in Serbia is the Ministry of Environmental Protection. Under jurisdiction of the Ministry is the Serbian Environmental Protection Agency (SEPA) and the Inspectorate while on the territory of the Autonomous Province of Vojvodina jurisdiction has also the Provincial Secretariat for Urban Planning and Environmental Protection.

The Republic of Serbia has adopted a considerable number of environmental laws, which are helping her to make a considerable progress towards the objective of “approximation” to the EU legislation, in view of the Serbia’s overall goal of joining the European Union in the future. The main principles of EU environmental laws are already transposed into the Serbian legislation. In order to improve the management of contaminated sites in Serbia, the Ministry of Environmental Protection in the period 2015-2021 adopted the legal framework that enables progress in management of contaminated sites (Figure 1).

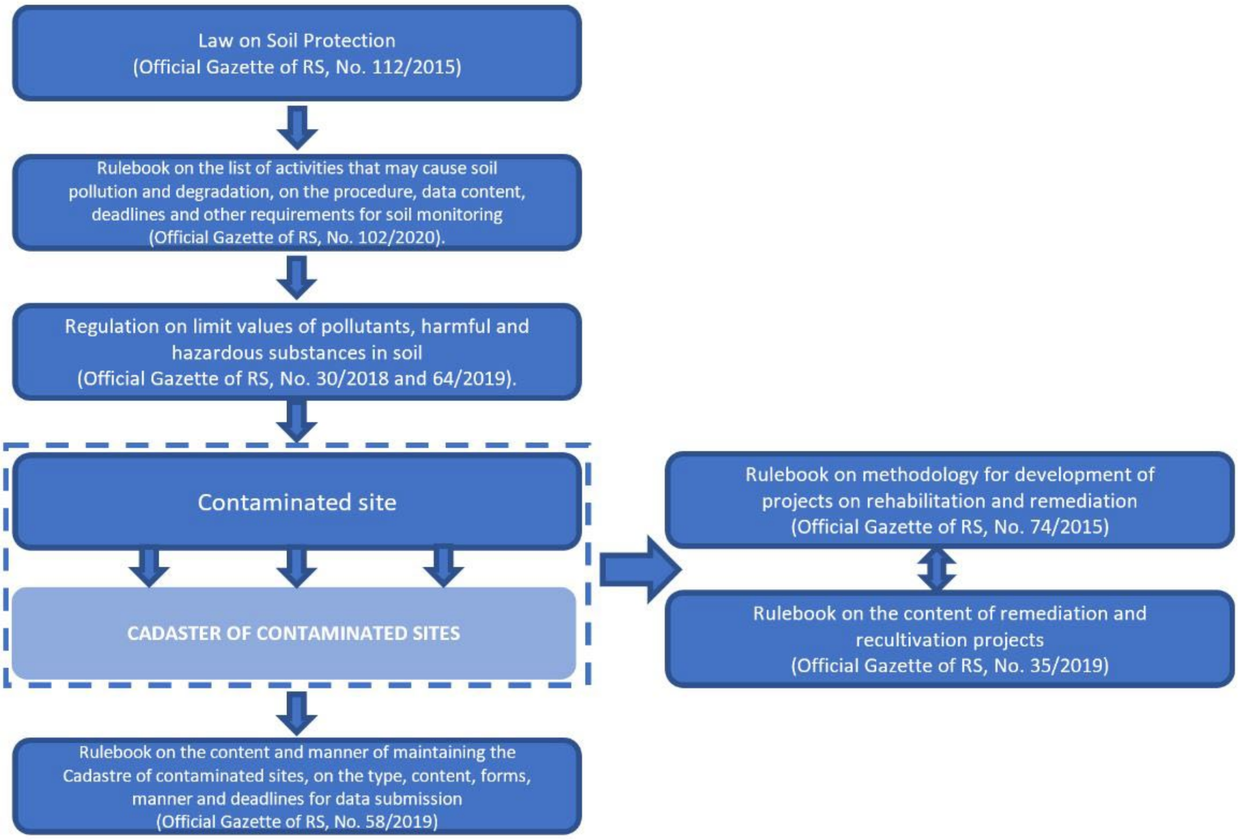

Figure 1. Legal framework for contaminated sites management in Serbia

RESULTS AND DISCUSSION

Based on the data submitted to the Cadastre of contaminated sites, 213 sites were identified in the Republic of Serbia where activities that are carried out are regulated by the Rulebook on the list of activities that may cause soil pollution and degradation, on the procedure, data content, deadlines, and other requirements for soil monitoring ("Official Gazette of RS", No. 102/2020). Out of the total number of reported sites, the report on soil monitoring was submitted by 21 companies (State of the Environment Report for 2020, SEPA, 2021).

SEPA reported that total of 850,000 tons of municipal waste was landfilled at twelve sanitary landfills in Serbia, covering 42% of the population of the Republic of Serbia in 2021. This is significantly increase of accessibility to sanitary disposal of solid municipal waste, compare with 2016, where sanitary landfilling was available only for 14% of the population. Despite such great progress in the population's accessibility to sanitary landfills, a considerable amount of waste is still disposed on dumpsites. Those sites have the largest share in the identified contaminated sites – 71.83% (Figure 2).

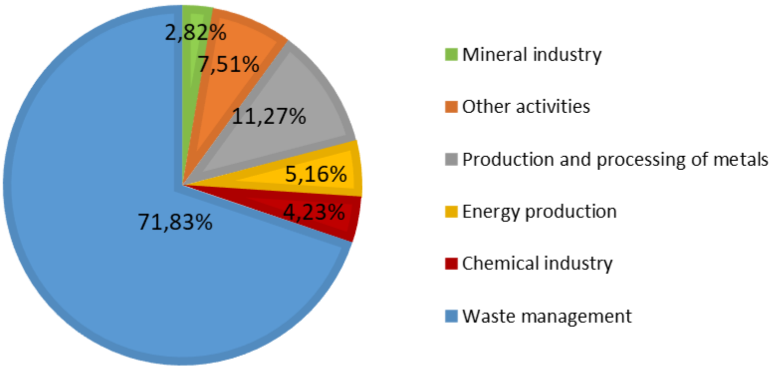

Figure 2. Share of main localised sources of soil pollution in the total number of identified sites (%)

SOIL ANALISYS IN THE SURROUNDINGS OF DUMPSITES IN VOJVODINA REGION

In Vojvodina Region, the Provincial Secretariat for Urban Planning and Environmental Protection examined the degree of endangerment of non-agricultural land from chemical pollution in 30 municipalities and cities, at 113 illegal dumpsites. A total of 1,130 soil samples were analysed (State of the Environment Report for 2020, SEPA, 2021).

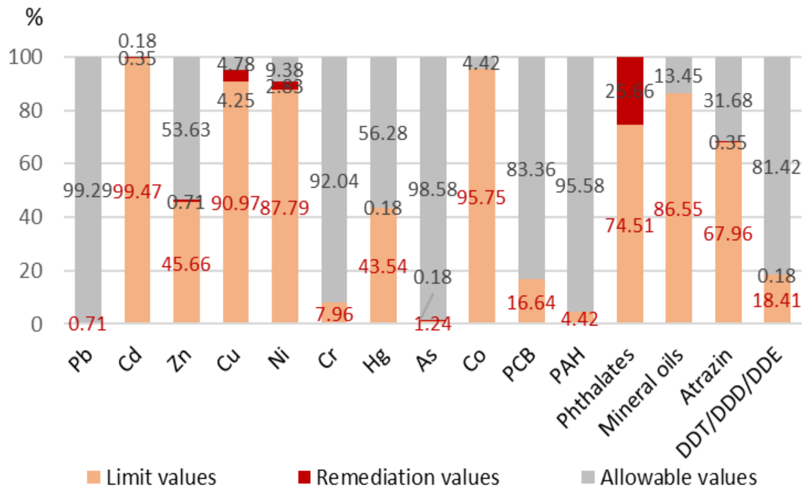

Figure 3. Percentage of exceedances at depths of 0-30 cm in the central points of the dumpsites

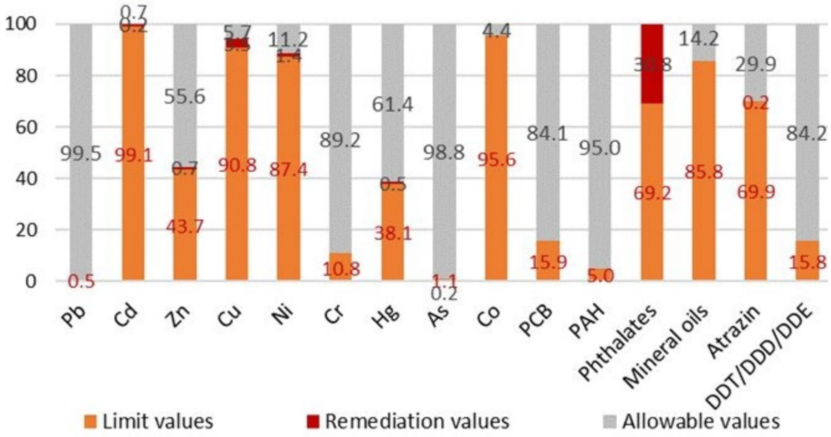

Figure 4. Percentage of exceedances at depths of 30-60 cm in the central points of the dumpsites

The analysis of heavy metal content in soil samples showed that remediation values were exceeded for cadmium, zinc, copper, nickel, mercury, and arsenic.

Analysis of the pesticide content and their metabolites in soil samples showed that remediation values were exceeded for DDE/DDD/DDT and atrazine. Concentrations of total PCBs, PAHs and mineral oils exceeded the limit values, but did not exceed the remediation values. Analysis of the content of phthalate esters shows that the content of phthalate esters is higher than the remediation value in 319 out of a total of 1,130 samples (Figures 3, 4 and 5). The analyses were conducted in accordance with the Regulation on limit values of pollutants, harmful and hazardous substances in soil ("Official Gazette of RS", No. 30/2018 and 64/2019).

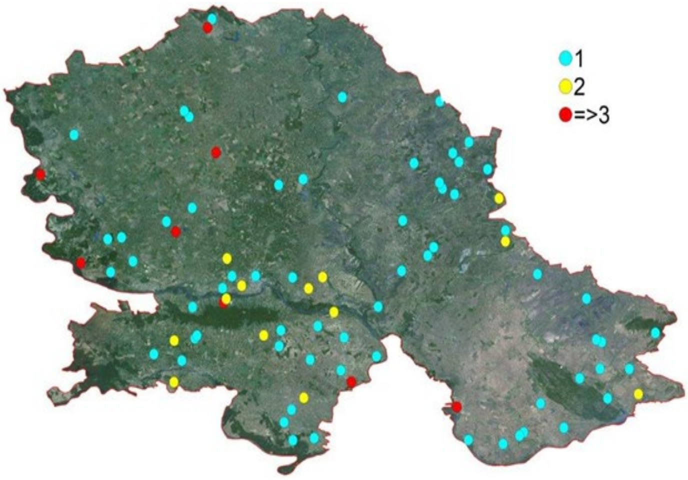

Figure 5. Contaminated sites where remediation values (RV) of individual elements were exceeded

CONCLUSION

The results of improved legislation and cooperation between different UN Agencies and ministries in the projects related to contaminated sites on the territory of the Republic of Serbia include the improved contaminated sites data management and developed capacity for the investigation of contaminated sites. Inadequate waste disposal still represents the most significant localized source of soil pollution in the Republic of Serbia.

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[2] Law on Soil Protection (“Official Gazette of RS”, No. 112/2015)

[3] Rulebook on the list of activities that may cause soil pollution and degradation, on the procedure, data content, deadlines, and other requirements for soil monitoring (“Official Gazette of RS”, No. 102/2020).

[4] Regulation on limit values of pollutants, harmful and hazardous substances in soil (“Official Gazette of RS”, No. 30/2018 and 64/2019).

[5] Rulebook on the content and manner of maintaining the Cadastre of contaminated sites, on the type, content, forms, manner, and deadlines for data submission (“Official Gazette of RS”, No. 58/2019).

[6] Rulebook on methodology for development of projects on rehabilitation and remediation (“Official Gazette of RS“, No. 74/2015).

[7] Rulebook on the content of remediation and recultivation projects (“Official Gazette of RS“, No. 35/2019).

THE FIRST NATIONAL DATABASE OF POTENTIALLY CONTAMINATED SITES (PCSS) IN SLOVENIA AND A MODEL APPROACH FOR DETERMINING PRIORITY TREATMENT

Barbara Lampič[1], Nejc Bobovnik[1], Helena Grčman[2], Lea Rebernik[1], Blaž Repe[1], Katja Vintar Mally[1], Tajan Trobec[1], Marko Zupan[2]
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ABSTRACT

The very first potentially contaminated sites (PCSs) database in Slovenia was established in 2021 and included 532 sites. In 2022, it was supplemented and expanded to a total of 671 PCSs. The identified PCSs were spatially located and displayed in the ArcGIS Online web application. In addition, we developed a simple modelling approach to evaluate the priority treatment of PCSs. Within the model, we defined four sets of criteria related to population, soil, water, and environmental protection, as well as nine indicators that enabled us to classify each site into one of five priority treatment categories based on the environmental sensitivity of the area. The final calculation was made using the multicriteria decision support model.

KEY WORDS

PCSs database, model approach, online application for monitoring PCSs, Slovenia

Most European countries have established a comprehensive management system for potentially contaminated sites (PCSs), which includes PCSs identification, preliminary surveys, detailed site investigation and finally implementation of mitigation measures. In Slovenia the Ministry of the Environment and Spatial Planning is responsible for managing a database of PCSs due to binding regulations on waste and water protection (especially drinking water sources). In 2022 we started with the activities to expand and supplement the PCSs database. This represents the first step towards further implementation of measures for PCSs remediation. An application in ArcGIS Online environment was designed, a tool which serves as a monitoring system (for various attributes) and for better and easier data management. A large amount of collected data at the level of individual PCS will enable faster identification of contaminated sites and locations that are more environmentally susceptible for potential contamination. The transparency of the data will ensure the communication between different departments as well as raise public awareness on the topic.

The PCSs database, established in 2021 received an extension and upgrade a year later. In 2022 it was supplemented with various sources and existing databases (for example Database of closed industrial landfills, Database of closed municipal landfills, IED operators etc.) and thus now includes 671 sites (532 sites in 2021).

To ensure consistency, all sites were drawn as a polygon using the same procedure. Simultaneously we also defined attributes for their monitoring, relying to a great extent on foreign practices and examples, thus defining more than 60 attributes related to PCSs identification (identifier, name, status etc.), location (region, municipality, water area, cadastral municipality, plot etc.), characteristics and description (a series of attributes presenting the properties of each PCS), pollution (sources of pollution, the presence of known pollutants in soil and water etc.), implementation of measures and monitoring (types of implementation of measures and monitoring).

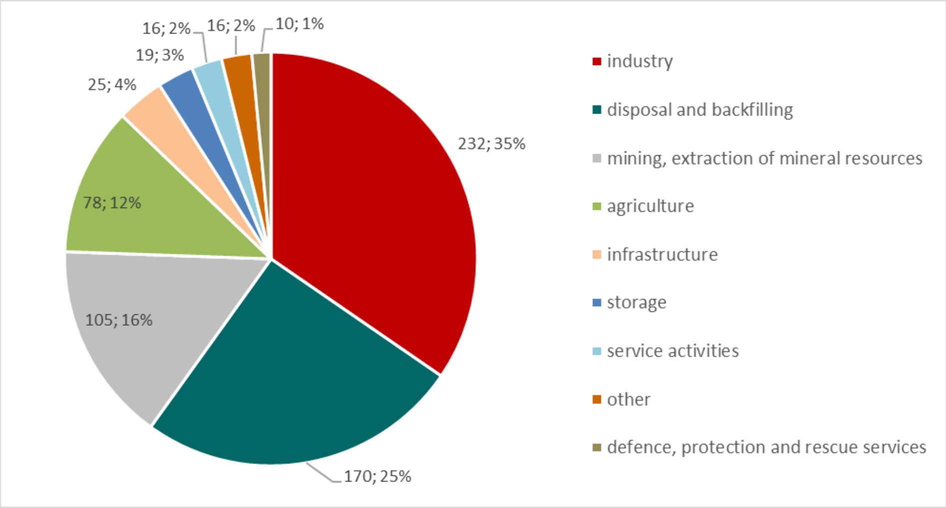

Figure 1. The structure of PCSs in Slovenia by the main source of pollution (number and share of PCSs) (Potentially contaminated … 2022).

The structure of Slovenian PCSs regarding the main source of pollution (Figure 1) is comparable to the EEA-39 level (Progress in management … 2021). The two main sources are industry and disposal and backfilling, while mining and extraction of mineral resources represents the third most common source in Slovenia (in EEA-39 it is storage). In Slovenia we can notice some regional differences, mostly related to the past and current economic development of the regions. There are also some differences between urban and rural areas. The predominant types of pollution in rural areas are agriculture and mining, extraction of mineral resources, while in urban areas industry and disposal and backfilling predominate.

We have developed a relatively straight forward and robust decision support model for priority treatment evaluation, which enables classifying of PCSs according to their environmental sensitivity.

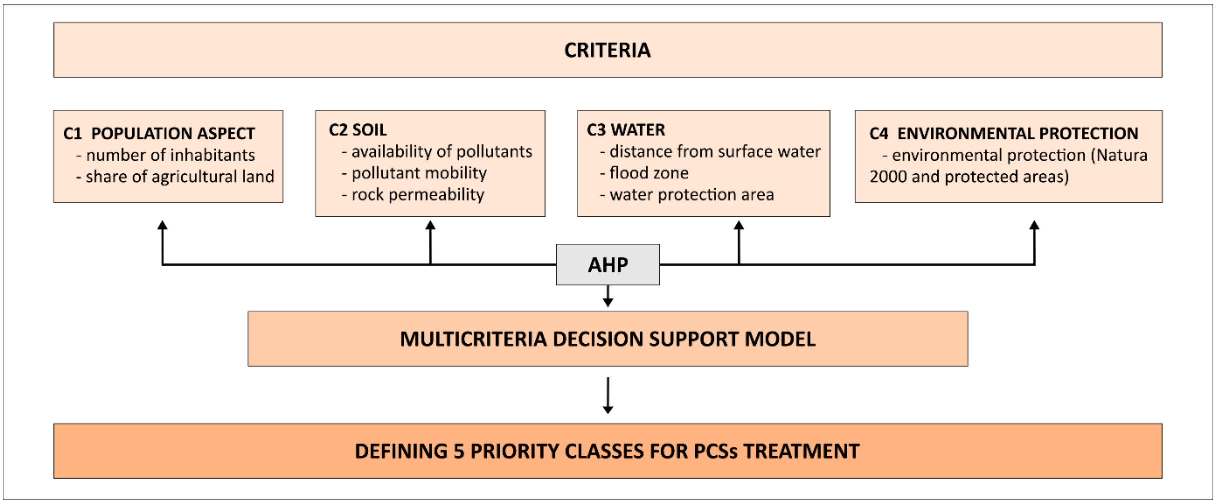

Figure 2. The model for classifying and prioritizing PCSs in Slovenia based on environmental sensitivity.

The model includes four sets of criteria (C1, C2, C3 and C4), within which we identified a total of nine indicators (Figure 2). C1 is the population aspect, and the two indicators determine the potential threat to population health and evaluate the potential risk for contaminants to enter the food chain. C2 focuses on the soil. Three indicators define the properties of the soil and the permeability of the rocks, which affect the transfer of pollutants into the food chain or affect the mobility of pollutants and the possibility of their transfer into the groundwater. In C3 (water) indicators assess the threat that PCSs pose as a potential source of pollution to surface waters, to the spread of pollution during floods, and to the contamination of drinking water resources. Finally, in C4 (environmental protection), we used an indicator to calculate the presence of the various protection regimes.

Using the analytical hierarchy process (AHP) we weighted individual sets of criteria, highlighting their relative importance in relation to other sets of criteria from the environmental sensitivity point of view. The calculated weights (Figure 3) show that the sensitivity of PCSs to pollution is most influenced by sets of criteria related to water (0.44) and soil (0.31). Together, they account for as much as 3/4 of the total impact.

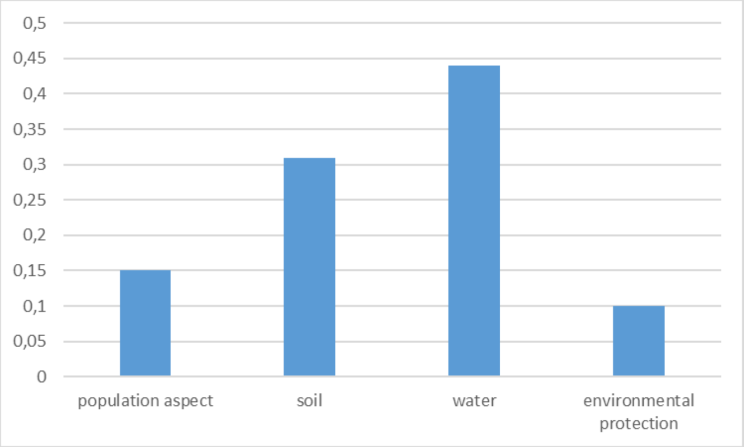

Figure 3. Final weights of individual sets of criteria in the multicriteria decision-support process for priority treatment of PCSs.

Based on the sets of criteria and corresponding indicators, we used the multicriteria decision support model to define five priority classes (Figure 4) for PCSs treatment based on the environmental sensitivity of the site and its surrounding area. The PCS prioritization is intended for decision makers to design and implement measures or decisions for site investigations (and later risk assessments), and to conduct feasibility studies. The PCS classification and prioritization model showed that most PCSs (296) are classified as intermediate priority, followed by those with low priority (183). Only 21 PCSs are classified as urgent priority and should be addressed immediately by decision makers.

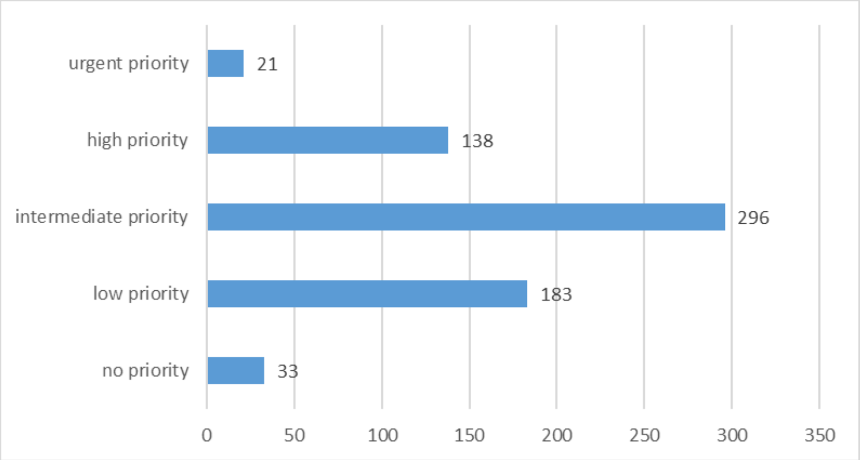

Figure 4. Priority for future treatment of PCSs based on the environmental sensitivity of PCS site and its surrounding area.

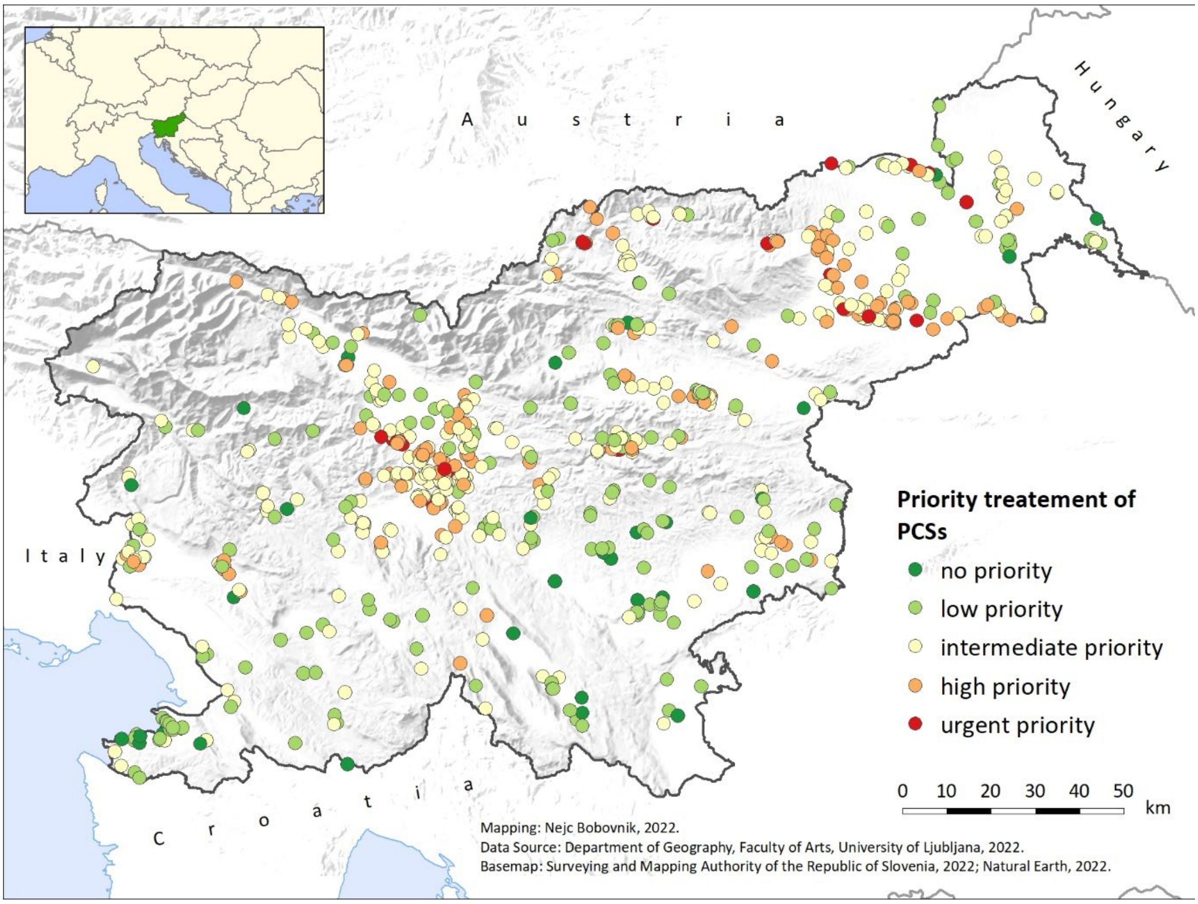

Figure 5. Spatial distribution of PCSs in Slovenia classified by priority treatment

The Slovenian PCSs database is new and not complete yet, but a quick review and the first analysis of the environmental sensitivity show the need for further activities. Several major environmental disasters in recent years (e.g., several fires) in these sites only confirm the need for a prudent placement of activities in space and a systematic approach to the implementation of measures on PCSs.

ACKNOWLEDGMENT

The data and conclusions presented are the result of a project funded by the Ministry of Environment and Spatial Planning of the Republic of Slovenia (2021 and 2022).

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INFORMATION SYSTEM OF CONTAMINATED SITES IN SLOVAKIA

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KEYWORDS
Contaminated site, web services, system integration, data integration, atlas of remediation methods

ABSTRACT

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

The basic components of ISCS are stated in the regulation of the Slovak Ministry of the Environment, no. 51/2008 as amended, which implements the geological law.
They are:
a) A national program for the remediation of environmental contamination
b) A register of documents related to contaminated sites.
c) A register of contaminated sites, consisting of:
    1. Section A - comprising records of potentially contaminated sites,
    2. Section B – comprising records of contaminated sites,
    3. Section C – comprising records of remediated and reclaimed localities.

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

1. An Enviroportal, which serves as the common internet access point designed to provide environmental information and E-services. In terms of a development conception of IS at the Ministry of Environment of the Slovak Republic, for the years 2014 to 2019, it is defined as a second-level portal of the Central Government Portal

2. A Register of contaminated sites, supporting the content of ISCS. It records the life cycle of contaminated sites (CS) and all information resulting as a consequence of processes defined by Act no. 409/2011. The register enables the search and subsequent presentation of descriptive information on CS in the form of lists, reports and registration sheets or information can be displayed in the form of maps and spatial data positioning on these maps

3. An Atlas of remediation methods, completed in 2011 by the State Geological Institute of Dionýz Štúr. Contains a series of remediation methods for the elimination of contaminated sites and is accessible to the general public in the form of a web application. The application enables the user to search for information according to the type of remediation method and contaminating substance. It interactively connects to remediated localities contained in the Register of contaminated sites, including appropriate methods of remediation applied at the given localities.

4. An Integrated application interface which accesses, via the ISCS, information held in other data sources consisting of relevant databases and registers of the public administration information system. This concerns an interface (SOAP API, OGC Web Services, and ArcGIS REST API) which enables the exchange of records between registers of data sources and the ISCS. Mutual communication of the application interface for administration of these records runs in real-time and is independent of the active participation of users.

RELEVANT WEBSITES

An Enviroportal: https://www.enviroportal.sk/environmentalne-temy/environmentalne-zataze
A register of contaminated sites - Web form application: https://envirozataze.enviroportal.sk/
A register of contaminated sites - Web map application: https://envirozataze.enviroportal.sk/Mapa/
An atlas of remediation methods: https://envirozataze.enviroportal.sk/Atlas-sanacnych-metod
Application programming interface (API)
- SOAP API: https://envirozataze.enviroportal.sk/LicenciaAtributoveUdaje.aspx
- OGC Web Services, ArcGIS REST API : https://envirozataze.enviroportal.sk/LicenciaPriestoroveUdaje.aspx

Examples of some data integration in ISCS
- Register of landfill sites: https://envirozataze.enviroportal.sk/ZaznListSkladky.aspx?RegistracneCislo=4657
- Integrated monitoring of point pollution sources: https://envirozataze.enviroportal.sk/MonitorovacieObjekty.aspx?Id_Zataz=-1&Id_Zaradenie=-1&Id_Lokalita=265420&Id_Objekt=1240275998
- Soil monitoring sites: https://envirozataze.enviroportal.sk/CmsPoda.aspx?IdLokalita=400003

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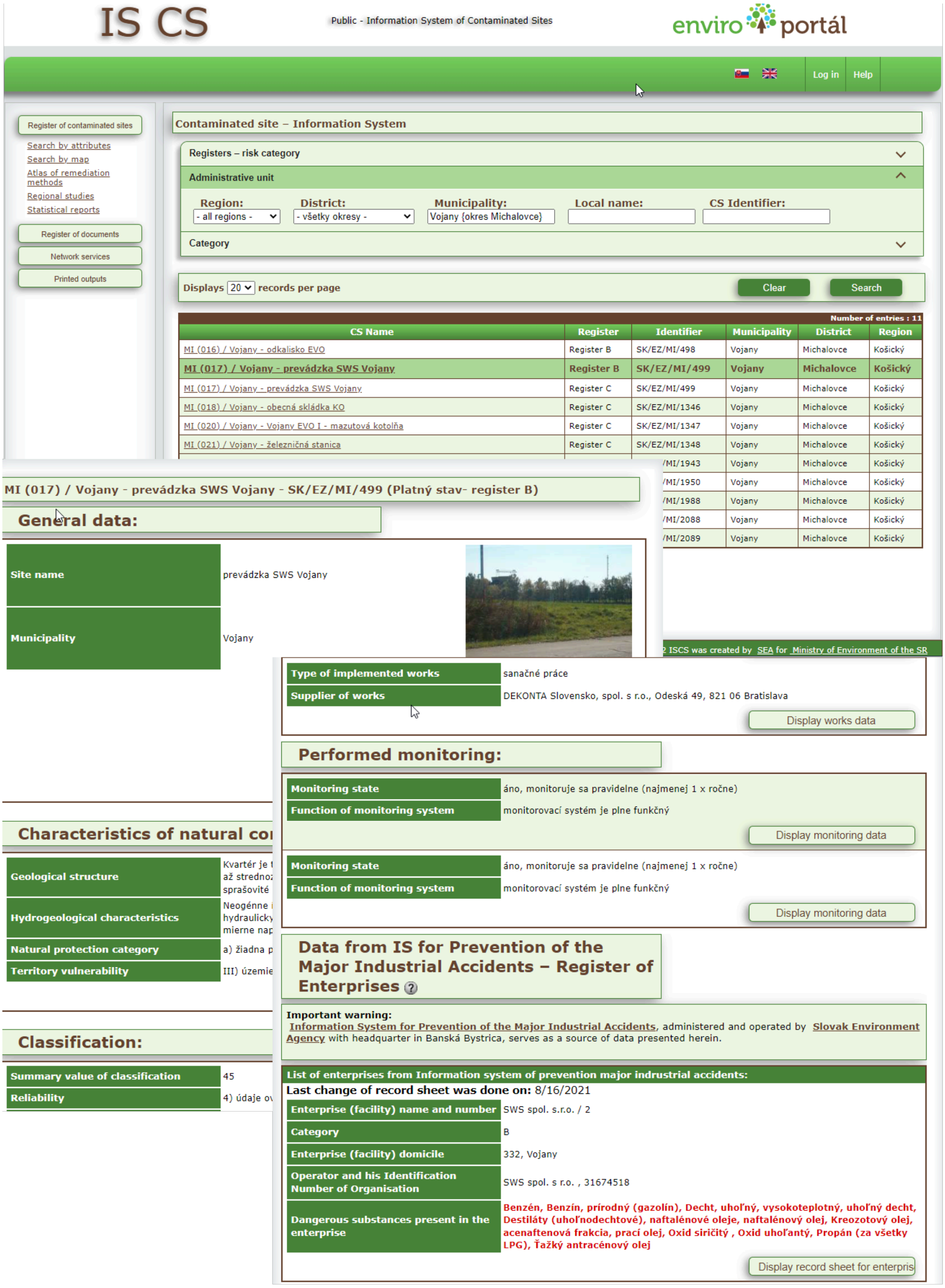


Region: - all regions -
District: - všetky okresy -
Municipality: Vojany {okres Michalovce}
Local name:
CS Identifier:

Displays 20 records per page

Number of entries : 11

CS Name	Register	Identifier	Municipality	District	Region
MI (016) / Vojany - odkalisko EVO	Register B	SK/EZ/MI/498	Vojany	Michalovce	Košický
MI (017) / Vojany - prevádzka SWS Vojany	**Register B**	**SK/EZ/MI/499**	**Vojany**	**Michalovce**	**Košický**
MI (017) / Vojany - prevádzka SWS Vojany	Register C	SK/EZ/MI/499	Vojany	Michalovce	Košický
MI (018) / Vojany - obecná skládka KO	Register C	SK/EZ/MI/1346	Vojany	Michalovce	Košický
MI (020) / Vojany - Vojany EVO I - mazutová kotolňa	Register C	SK/EZ/MI/1347	Vojany	Michalovce	Košický
MI (021) / Vojany - železničná stanica	Register C	SK/EZ/MI/1348	Vojany	Michalovce	Košický
		/MI/1943	Vojany	Michalovce	Košický
		/MI/1950	Vojany	Michalovce	Košický
		/MI/1988	Vojany	Michalovce	Košický
		/MI/2088	Vojany	Michalovce	Košický
		/MI/2089	Vojany	Michalovce	Košický

MI (017) / Vojany - prevádzka SWS Vojany - SK/EZ/MI/499 (Platný stav- register B)

General data:

Site name	prevádzka SWS Vojany
Municipality	Vojany

Characteristics of natural co

Geological structure	Kvartér je t až strednoz sprašovité
Hydrogeological characteristics	Neogénne i hydraulicky mierne nap
Natural protection category	a) žiadna p
Territory vulnerability	III) územie

Classification:

Summary value of classification	45
Reliability	4) údaje ov

Type of implemented works	sanačné práce
Supplier of works	DEKONTA Slovensko, spol. s r.o., Odeská 49, 821 06 Bratislava

Performed monitoring:

Monitoring state	áno, monitoruje sa pravidelne (najmenej 1 x ročne)
Function of monitoring system	monitorovací systém je plne funkčný

Monitoring state	áno, monitoruje sa pravidelne (najmenej 1 x ročne)
Function of monitoring system	monitorovací systém je plne funkčný

Data from IS for Prevention of the Major Industrial Accidents – Register of Enterprises

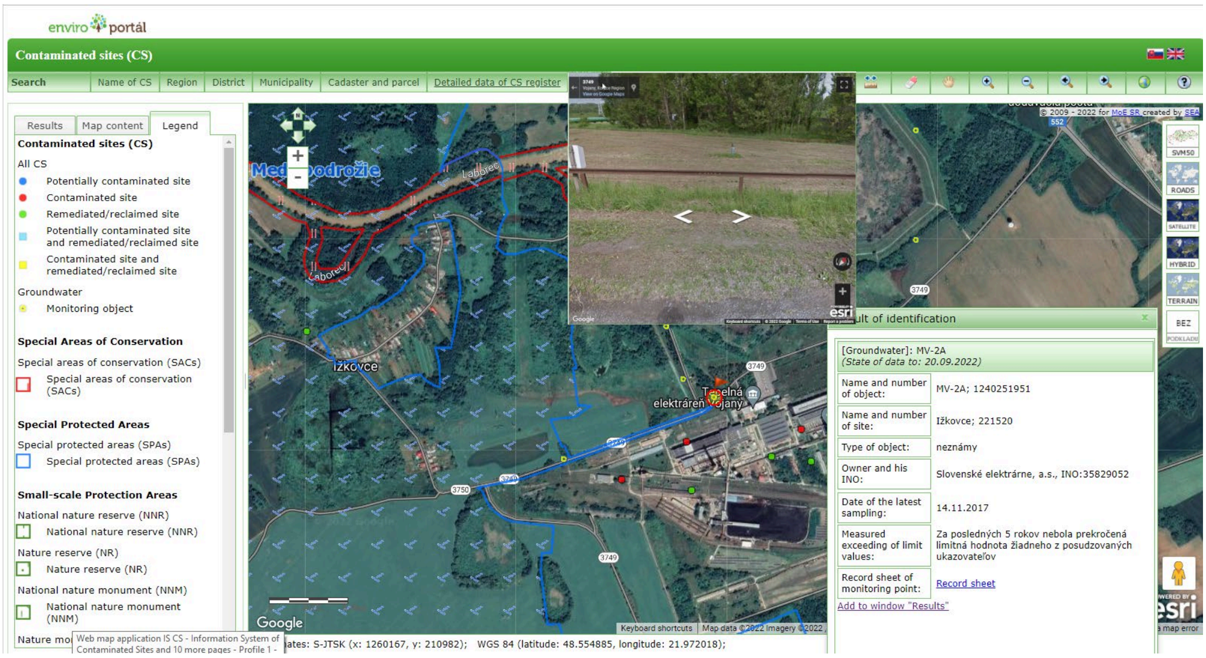
Important warning:
Information System for Prevention of the Major Industrial Accidents, administered and operated by Slovak Environment Agency with headquarter in Banská Bystrica, serves as a source of data presented herein.

List of enterprises from Information system of prevention major indrustrial accidents:

Last change of record sheet was done on: 8/16/2021

Enterprise (facility) name and number	SWS spol. s.r.o. / 2
Category	B
Enterprise (facility) domicile	332, Vojany
Operator and his Identification Number of Organisation	SWS spol. s r.o. , 31674518
Dangerous substances present in the enterprise	**Benzén, Benzín, prírodný (gazolín), Decht, uhoľný, vysokoteplotný, uhoľný decht, Destiláty (uhoľnodechtové), naftalénové oleje, naftalénový olej, Kreozotový olej, acenaftenová frakcia, prací olej, Oxid siričitý , Oxid uhoľantý, Propán (za všetky LPG), Ťažký antracénový olej**

Figure 1. Web form application – search contaminated sites in the municipality "Vojany". Display detailed information about the contaminated site "MI (017) / Vojany - prevádzka SWS Vojany - SK/EZ/MI/499"



[Groundwater]: MV-2A
(State of data to: 20.09.2022)

Name and number of object:	MV-2A; 1240251951
Name and number of site:	Ižkovce; 221520
Type of object:	neznámy
Owner and his INO:	Slovenské elektrárne, a.s., INO:35829052
Date of the latest sampling:	14.11.2017
Measured exceeding of limit values:	Za posledných 5 rokov nebola prekročená limitná hodnota žiadneho z posudzovaných ukazovateľov
Record sheet of monitoring point:	Record sheet

Add to window "Results"

ates: S-JTSK (x: 1260167, y: 210982); WGS 84 (latitude: 48.554885, longitude: 21.972018);

Figure 2. Web map application – 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 (2089)/Vojany - The western edge of the operational building EVO I, EVO II and the surrounding area)

THE INVENTORY OF CONTAMINATED SITES IN THE CZECH REPUBLIC (NIKM 2019-2021)

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KEYWORDS

Contaminated sites, inventory, remote sensing, methodology, registration of contaminated sites, SEKM – System for registration of contaminated sites

ABSTRACT

The complete National inventory of contaminated sites (NIKM) took place in the years 2009 – 2021 in two phases, both co-financed from the EU Cohesion fund. The basic goal of NIKM was the capture and basic evaluation of the most complete number of contaminated sites/potentially contaminated sites (CSs hereinafter) on the territory of the entire country. The 1st stage of NIKM focused on the methodology of the inventory, its testing and collection of the main data sources. The 2nd stage of NIKM (2018-2021) was completed on 31.12.2021. CENIA teams and suppliers selected via public tender participated in the project. 30,020 CSs or CSs clues were inspected of which 8,643 sites were evaluated as CSs. From other sources, 1491 newly evaluated localities were registered. In result, a total of 10,134 assessed CSs were registered. These sites have a record at least in the scope of the summary form, including the evaluated priority of needed corrective measures. In addition, maps of CSs distributions in the 205 municipalities with extended powers ("small districts") of 14 regions were processed, for each of the three priority categories (A, P, N). The result of NIKM is the filled in System for registration of contaminated sites (SEKM) (10,134 records), 14 inventory reports for individual regions and the Inventory Report for the Czech Republic.

THE CONCEPT OF INTENTION AND THE STAGES OF INVENTORY

In 2008, the Ministry of the Environment (MoE) developed and implemented a plan to include the inventory of contaminated sites in the topics of the Operational Program Environment (OPE). From the beginning, two separate stages were envisaged, the first of which was to be focused on the creation of a technical and organizational background and on the preparation and practical testing of all inventory tools and methodological procedures in three test areas. The second stage was supposed to consist of the proper inventory, i.e., the collection, processing and evaluation of data using functional apparatus and verified methodologies developed in the first stage. In the development of the project all respective EU documents, first of all the Thematic Strategy for Soil Protection [1], Proposal for a Soil Protection Directive (withdrawn in 2014) [2] and the INSPIRE Directive 2007/2/EC [3] were taken into account.

In the autumn of 2008, CENIA submitted the project of the 1st stage of NIKM to a specific call of the OPE. The goal was to create a unified database, to develop a methodology for the identification and inventory of CSs, to prepare procedures and manuals, to verify the functionality of the outputs, including the technical background for the 2nd stage of the project. Based on the background analyses and syntheses a methodology of the inventory was formulated, which was subsequently verified in test areas (3 squares of 50 x 50 kilometres).

PROJECT OF THE 2ND STAGE OF NIKM

After the end of the 1st stage, for organizational reasons, it was not possible to immediately start the 2nd stage of NIKM in the OPE period 2007-2013. The project was fortunately included for implementation in the following program period 2014-2020. The relevant call was published on 01/03/2017. CENIA again submitted an application including project documentation [4]. The decision to provide the subsidy was issued in May 2017. The amount of total eligible data according to the decision was CZK 116,627,180 (EUR 4,665,087), of which 85% - CZK 99,133,103.68 (EUR 3 965 324) was co-financing from the EU FS and 15% - CZK 17,494,077.12 (EUR 699,763) from our own resources (CENIA/MoE). The project implementation started with CENIA works in January 2018. In the course of 2018, a public contract for "NIKM2 Supply of Inventory Works" was announced and evaluated. The main phase of the project implementation took place in the period 1/3/2019 – 31/12/2021.

CENIA WORK AND PROJECT TASKS OF THE 2ND STAGE PROVIDED BY CONTRACTORS

CENIA was involved in the project in the role of project management and in the support of inventory using Remote Sensing (RS) methods [5] [6]. In this role, CENIA processed a data layer of CSs clues before the start of the area inventory in 2018.

The project was divided into 5 project tasks, of which 3 were provided by the supplier:

- The area inventory was provided by the consortium "DEKONTA, VZ Ekomonitor, GEOtest – NIKM 2". The work included initial analysis, data collection, data evaluation, inventory synthesis, project progress evaluation, report development, and publication of results.
- The inventory administration within the SEKM database [7] [8] including verification and validation of records and user support was provided by ProGeo Consulting Ltd.
- The supervision was assured by Jiří Tylčer. The content was a continuous control of the compliance of work with the methodology, audit and control activities, incl. output opponent assessments.

NIKM INVESTIGATION TEAM AND CSS INVENTORY METHODOLOGY

A total of 77 workers were involved in the solution. 57 of them were involved in area inventory. 3 workers were involved in the task of the SEKM/NIKM Administration, one supervisor provided external control. 16 workers were engaged within the CENIA tasks (7 in project management and 9 in inventory support using RS methods).

The methodological basis form two basic documents: "Inventory Methodology" with conceptual principles and "Inventory Manual" [4] with details of the procedures (step description and instructions). At the beginning of the implementation phase, an introductory training session was held for twenty team leaders. During the project, 6 mapper's manuals were published detailing the methodological procedures. Two certified methodologies [9] [10] were processed as a secondary follow-up output. In November 2019, during the shutdown of SEKM due to the migration of the data warehouse from SEKM 2 to SEKM 3, four consultation days / training seminars were organized for company teams for which also 13 methodological modifications were issued. Three more methodical meetings were organized, incl. seminars during the project.

INPUT CONTENT OF THE CENTRAL DATA WAREHOUSE

The SEKM central data warehouse is the core of the entire structured and distributed data warehouse, which ensures editing, storage, and management of CSs data through applications. The input content was prepared by transforming and merging partial data sources about CSs. It contained 30,020 locations (incl. 12,993 SEKM records and RS clues (17,038 locations). During the inventory, the SEKM data warehouse was completed with records of newly discovered CSs. All records from this input content of the central data warehouse were checked, updated, and evaluated or excluded as irrelevant or duplicated to other locations.

EFFECTIVENESS OF AREA INVENTORY

To complete the view of the effectiveness of the comprehensive inventory, it is necessary to include in the evaluation also data from the data layer of RS clues, which at the beginning of the inventory contained 17,038 CSs clues obtained by RS methods. From this number, 1,804 records of evaluated sites were created. Also included in this task are completely new localities detected during the area inventory with a number of 1,491 records - see the summary in Table 1.

Table 1. Summary of basic process data of the Contaminated Sites Inventory

	SEKM records			RS clues and records			New CSs records	Input records total	Output records total	Excluded records total
Records	SEKM input	evaluated	excluded	RS input	evaluated	excluded				
Input data as of 02/2019	12,982			17,038				30020		
Output data as of 31/12/2021		6,839			1,804		1,491		**10,134**	
Excluded records as of 31/12/2021			6,143			15,234				21,377

Findings, identified main problems and recommendations arising from the implementation of the project and from the work in SEKM3 are summarized in the final reports of the project [11] [12] and in conference contributions [13] [14].

THE MAIN CHARACTERISTICS OF THE TERRITORIAL DISTRIBUTION OF CONTAMINATED SITES

In the Report on the inventory in the territory of Czechia [11], the general characteristics of the distribution of CSs are described in detail. Below are the main conclusions:

Distribution in relation to industrial areas and cultural and economic centres

The dominant occurrence of CSs is in areas where industrial production was and still is concentrated, or in places where dangerous substances were handled and accidental or systematic leaks into the rock environment occurred due to their careless handling. These are, for example, the industrial areas along the river Elbe, the coal basins on the Northwest, the area of the Upper and Lower Moravian Valleys and the Moravian Gate. CSs are also accumulated in places of economic and cultural centres within the Czech Republic - in the capital city of Prague and Brno including their surroundings, in Ostrava and Pilsen.

Occurrence of CSs in agricultural areas

A smaller number of CSs are located in regions with agricultural production – e.g., the South Bohemian and the Vysočina regions, partially also the South Moravian region. The Karlovy Vary region in the west also has a low density of CSs.

Regions with the highest CSs density

The capital city of Prague has the highest density of CSs due to a small area of the city. The Olomouc and Moravian-Silesian regions have a higher density of CSs. There are several reasons: (1) the concentration of mining and heavy industry in and around Ostrava, (2) the concentration of industrial production in the area of the Upper and Lower Moravian Valleys and the Moravian Gate.

In the CSs density maps (see Figure 1), the main features of the CSs distribution are evident. In 14 posters [15], we evaluated the basic features of CSs distribution according to priority categories up to the “small districts” level.

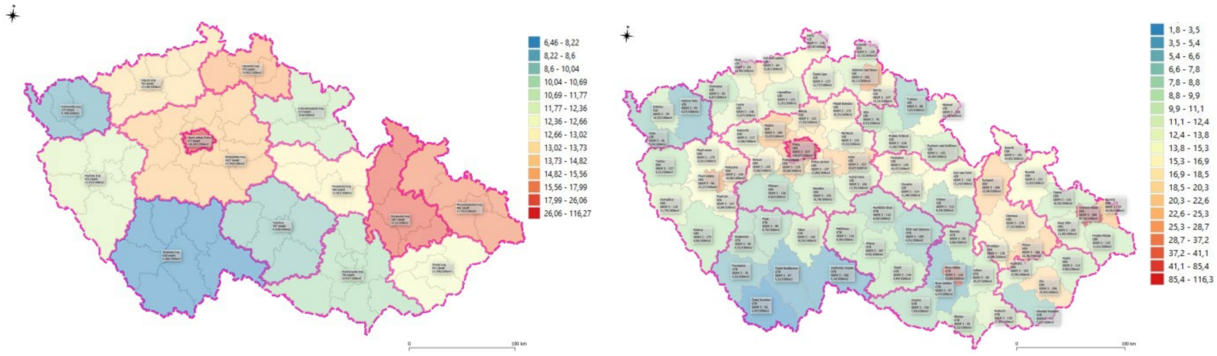

Figure 1. Numbers and densities of CSs in 14 regions and 76 districts

Colour scale legend: CSs density expressed as the number of CSs per 100 square kilometres.

PLANS AND FORMS OF CENIA ACTIVITIES FOR THE SUSTAINABILITY PERIOD OF THE NIKM2 PROJECT

During the five-year project sustainability, the results and SEKM data will be extracted for publishing and conference activities and for the CENIA research program. The maintenance of the SEKM database will be supported. Topics such as evaluation of remediation costs, evaluation of remediation technologies, analysis of knowledge about CSs in spatial planning and legal problems of CSs registration will be proposed for grant programs.

MAIN OUTPUTS OF THE PROJECT

Project results include the completed SEKM database, 14 reports on the inventory in individual regions, and the report on the inventory on the territory of the Czech Republic. In the territory of the Czech Republic, a total of 30,020 locations or indications were checked from the two basic sources of the IS SEKM and RS, of which 8,643 locations were evaluated as CSs. The remaining 21,377 sites or indications were excluded, or found not to be CSs. An additional 1,491 assessed CSs were identified from other sources, i.e. there are a total of 10,134 assessed CSs in Czechia as of December 2021. These CSs have a processed record in the SEKM database, at least in the scope of the so-called summary form, including the evaluated priority of corrective measures.

More than 70% of sites (7,102 out of 10,134 sites in total) are evaluated as sites with insufficient information on contamination, on the possible spread of contamination and on the possible consequences of contamination, for which it is not yet possible to define the method and scope of remedial measures. At approximately 30% of locations (a total of 3,032 out of 10,134 locations) the work associated with the removal of the old ecological load has either been carried out, is in progress, or is being prepared, or it was not necessary to carry it out at all.

With regard to **the site type,** municipal waste landfills predominate, which make up almost 46% of CSs. Over 17% of CSs of the contaminated area CSs type, i.e. sites where multiple activities occurred concurrently, which led to the creation of an old ecological burden. More than 10% of CSs are places where petroleum substances were manipulated and where substances systematically leaked into the rock environment. These three types of sites make up almost ¾ of all CSs.

As to **the urgency of the solution**, a total of 446 CSs require a timely solution (survey or implementation of corrective measures). Out of the total number, these CSs occupy 4.40% of all evaluated CSs.

Status and financing of corrective actions: At 667 CSs (approx. 6.5%), remedial work is in progress or is about to start or has been interrupted/was not successful. In total, for more than 72.5%, corrective measures are not yet known, and for the remaining some 21% of locations, measures are not necessary or have been completed. Funding of remedial measures is needed for 8,024 CSs (no funding is needed for the remaining 2,110 evaluated CSs). Out of 8,024 CSs, funding is not secured for 6,757 locations (approx. 84%). For the remaining 1,267 CSs, financing for at least one of the stages of remmediation is or has been secured. Financing is most often from the Ministry of Finance through environmental contracts, from EU funds (OPE), from the budgets of the municipalities, cities, regions, from other ministries' funds, state-owned enterprises or from private sources.

CONCLUSIONS

(1) Project implementation work was completed by / 31/12/2021 totalling costs of CZK 116,741,353 (EUR 4,669,654) and with fulfilment of the project indicator by up to 112% (10,134 evaluated CSs).
(2) In the following 5-year period, the results of the project will be maintained by CENIA - the grant recipient.
(3) Support for the sustainability of the SEKM IS in order to use the results of the inventory as a priority tool for the relevant authorities to effectively manage the process of the gradual reduction of old burdens, for the needs of spatial planning and reporting of various types .

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USE OF INFORMATION SYSTEMS AND SURVEY RESULTS OF CONTAMINATED AREAS FOR THE PURPOSE OF RISK ASSESSMENT AND GROUNDWATER STATUS WITHIN THE MEANING OF THE WATER FRAMEWORK DIRECTIVE

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KEYWORDS
groundwater bodies, pollution sources, contaminated sites

ABSTRACT

Directive 2000/60/EC of the European Parliament and of the Council (WFD) requires the adoption of specific measures to prevent and limit groundwater pollution [1]. For this purpose, the characterization of the sources of pollution, the assessment of the chemical status and the risk of not achieving environmental objectives are also required. One of the important factors involved in these assessments are environmental burdens, which belong to the most important point sources of groundwater pollution, mainly due to their spatial density and variety of contaminants. The evaluation of the potential pressure of point sources on groundwater quality and chemical status of groundwater bodies was carried out based on data from two databases in Slovakia, that are interconnected:

1. Register of Contaminated Sites, that is part of the Information System of Contaminated Sites (IS CS), managed by the Slovak Environmental Agency,
2. Database of Integrated Monitoring of Pollution Sources (IMPS), managed by Water Research Institute.

Important point sources of pollution in terms of negative impact on groundwater quality are mainly contaminated sites (CS). In November 2020, the Register of Contaminated Sites contained 1 817 locations with contaminated sites divided into three groups – potential, confirmed and remediated CS. Waste management facilities, especially municipal waste landfills and industrial waste landfills, have the largest share in the creation of CS. Common contaminants in the CS with very high potential impact on groundwater quality were non-polar extractable substances, chlorinated aliphatic hydrocarbons and metals such as arsenic, cadmium or antimony. The assessment of the CS impacts on groundwater included the value of the risk of contamination spreading into and through groundwater, and groundwater vulnerability. Out of the total number of 929 potential CS, 194 CS (i.e. 20.9%) were classified with very high and 236 CS (i.e. 25.4%) with high potential impact on groundwater, and out of 310 confirmed CS, 98 (i.e. 31.6%) were classified with a very high and 100 CS (i.e. 32.3%) with a high potential impact on groundwater quality. The largest number of CS with a very high potential impact on groundwater quality are located in Quaternary groundwater body (GWB) SK1000500P – *Intergranular aquifer, alluvial sediments of the lower reaches of the Váh river and its tributaries* (20 CS). However, the highest density of CS per square kilometer was in Quaternary GWB SK1001300P – *Intergranular aquifer, alluvial sediments of Topľa river and its tributaries* (8 CS per 100 km^2). The results of the potential impact of CS on groundwater quality in Quaternary and Pre-Quaternary GWB are depicted in Fig. 1.

Another group of point sources of pollution that could affect the groundwater quality in GWB are pollution sources (PS), the owners/operators of which are obliged to monitor the impact of PS on groundwater and voluntarily report the monitoring results to the IMPS database. In June 2022, the IMPS database contained data from 2 322 monitoring objects from 159 owners (industrial

enterprises, waste dumps, sewage sludge, contaminated sites, etc.). In the PS with very high potential impact on groundwater quality were detected contaminants as nitrogen compounds, metals or polycyclic aromatic hydrocarbons. The risk of the spread of contamination from PS into the groundwater was evaluated based on the comparison of the average concentration of the contaminant in the years 2007-2018 with the limits (quality standards for groundwater, threshold values, indication criteria and intervention criteria). The classification also included an expert assessment of the given location, groundwater vulnerability and the evolution of the contaminant concentration in time. Out of the total number of 88 PS, 27 PS (i.e. 30.7%) were assessed as having a very high and 23 PS (i.e. 26.1%) as having a high potential impact on groundwater quality (Fig. 2). The largest number of PS with a very high potential impact on groundwater are located in the Quaternary GWB SK1000500P (5 PS) and Pre-Quaternary SK2001000P – *Intergranular aquifer, central part of the Danube Basin and its offspurs* (5 PS). Moreover, the highest density of PS per square kilometer was in the Quaternary GWB SK1000500P.

The results of the potential impact of contaminated sites and pollution sources on groundwater quality in Quaternary and pre-Quaternary GWB were presented in more details in the report (Kučerová et al., 2020) [2].

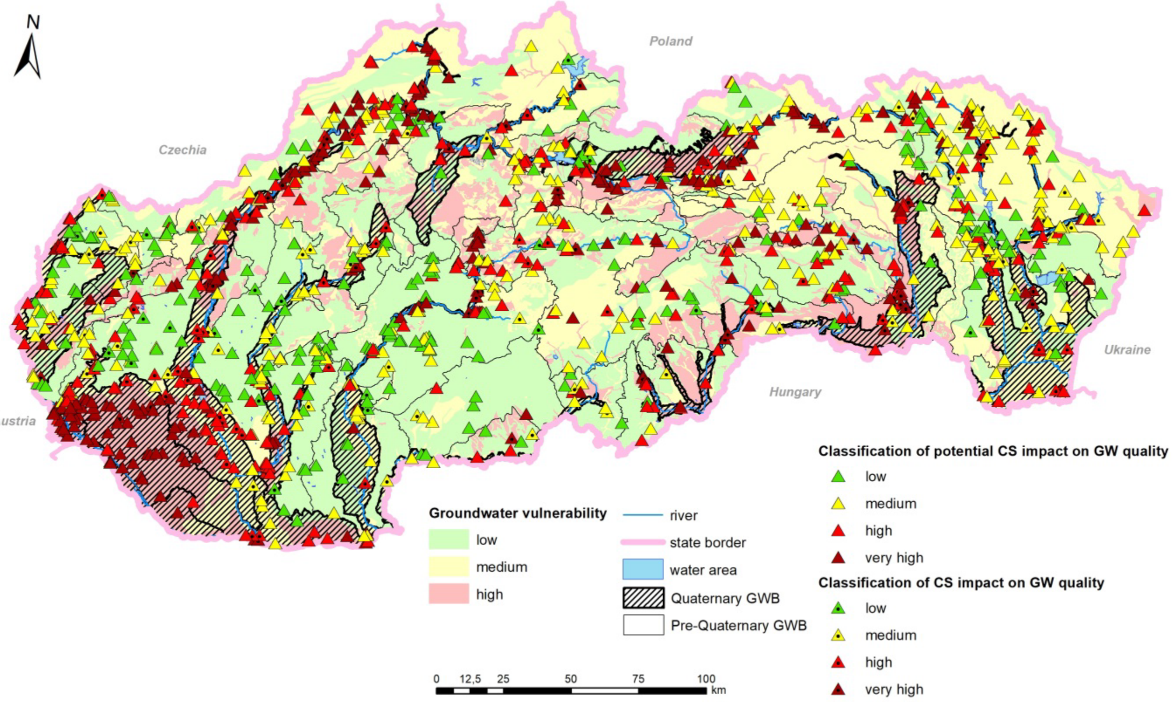

Figure 1. Potential impact of contaminated sites (CS) on groundwater (GW) quality in Slovakia (classification from November 2020) GWB – groundwater body

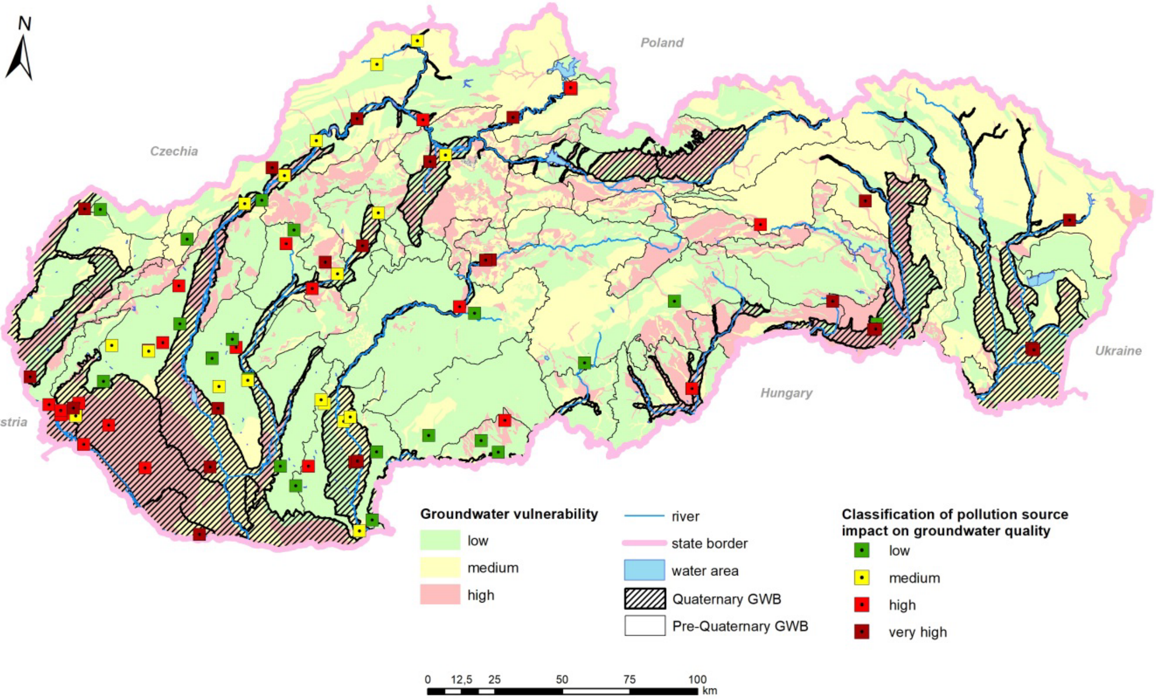

Figure 2. Potential impact of pollution sources on groundwater quality in Slovakia (classification from 2007 - 2018) GWB – groundwater body

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THE DRAFT OF THE DEVELOPMENT PRINCIPLES ACCORDING TO THE BUILDING ACT IN RELATION TO THE MINING ACT

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KEYWORDS
Construction law, mining law, mining claim, minerals, planning the development of the territory

ABSTRACT

The Czech Mining Authority stake a claim its standpoints to politics of territorial development and to the principles of territorial development from the view of the protection and utilization of mineral resources. An information system of the raw materials SURIS is one of the important source of information for the opinion and includes still active mining claims and mining claims with terminated activities. There are databases of territorial analytical data according to the Building Act as a source of data for the so-called phenomenon No 64 – „old burdens and contaminated areas“ and this phenomenon was used during the finishing national inventory of contaminated sites of the Czech Republic. SURIS as a part of the Geological Information System could be used like as a source of information of the phenomenon No. 64 – “old burdens and contaminated areas” for the national inventory of contaminated sites of the Czech Republic.

The State Mining Administration is a relevant authority in land-use planning activities and one of the competences concerns principles of territorial development.

The Czech Mining Authority stake a claim its standpoints to politics of territorial development and to the principles of territorial development from the view of the protection and utilization of mineral resources (§ 15, par. 2 on ACT No. 44/1988 Coll., on the protection and utilization of mineral resources (The Mining Act)) [1]. The Czech Mining Authority as a relevant authority can set an assessment – an acceptance of a suggestion, an acceptance of a suggestion with the conditions or a nonacceptance of a suggestion.

An information system of the raw materials SURIS is one of the important source of information for the opinion. SURIS includes a lot of spatial information and also still active mining claims and mining claims with terminated activities. Each object has its own identification number and it is possible to find basic information about mining claims e.g. the operator, mining, minerals. SURIS is a part of the Geological Information System (GeoIS) operated by the Czech Geological Survey.

https://mapy.geology.cz/suris/

Pursuant to The Mining Act mineral resources consist of deposits of reserved minerals (hereinafter referred to as "reserved deposits"). Mineral resources within the territory of the Czech Republic are owned by the Czech Republic. Deposit of non-reserved minerals constitutes an integral part of the land. In practice, this means that the deposit of non-reserved minerals is owned by the owner of the land.

In the past, mining areas with terminated activities sometimes became places with illegally disposed waste and could also be part of brownfields. Such sites must therefore be taken into account when planning the development of an entire administrative territories, the use of the land after remediation and reclamation, the placement of new projects and possible changes in land use.

And what are the possibilities of applying the opinion of the Czech Mining Authority when drawing up the draft of the development principles?

The draft of the development principles is procured by the regional office upon the assignment or the report on the development principles implementation according § 37, par. 2 on ACT No. 183/2006 Coll., on town and country planning and building code (The Building Act) [2], that is publicly discussed and agreed with all the relevant authorities, i.e. also with the Czech Mining Authority. Regional office shall ensure the assessment of the impacts on the area sustainable development to the draft of the development principles.

Regional office notifies of the place and time of the joint debate on the draft of the development principles. The regional office calls upon the relevant authorities to submit the assessments within the time limit laid down by law. There are not taken into account the assessments and remarks of the administrative regions, which are submitted later. This „concentration principle“ is applied at all stages of the acquisition of the principles of territorial development.

The public hearing of the modified and assessed draft principles of territorial development after a joint debate, including the assessment of the impacts on the area sustainable development, is announced by the regional office by a public notice (§ 39, par. 1 on ACT No. 183/2006 Coll.).

In the frame of the public hearing the Czech Mining Authority as the relevant authority sets an assessment on the parts of the solution that have been changed since the joint debate (§ 37, par. 2 on ACT No. 183/2006 Coll.).

The Regional office evaluates the results of the debate and prepares a draft decision on objections and a draft evaluation of comments with regard to public interests. It shall forward the proposals to the authorities concerned and invite them to submit their assessment within the stipulated period. If the relevant authority does not apply its assessment within the stipulated period, it is applied that the relevant authority agrees with the submitted draft. If necessary, the regional office shall ensure that the draft of the development principles is modified in accordance with the results of the public debate (§ 39, par. 4 on ACT No. 183/2006 Coll.).

The development principles can be updated using the above-mentioned procedure, or a shortened procedure according to the Building Act. For the development principles in practice, a shortened procedure is not often used, in contrast to a procurement of a changes of a territorial plans, where this shortened procedure is more common. The principles of a development principles must be viewed from a supra-regional level, in all its aspects (intentions, limits, problems, etc.).

At the regional level, the territory is dealt with by spatial plans and regulatory plans. In their acquisition or in the acquisition of their changes a spatial analysis documents are used, which are part of spatial planning documents. Municipalities with extended jurisdiction (ORP) and regions must obtain territorial analytical documents, their content is determined by a legal regulation (Decree No. 500/2006 Coll., on planning analytical materials, town and country planning documentation and the method of recording town and country planning activity) [3]. The Ministry for Regional Development of the Czech Republic can acquire territorial analytical documents and has acquired them for the entire territory of the whole Czech Republic.

There are databases of territorial analytical data by remote access through municipalities with extended powers (ORP), including a survey of sustainable development of the territory and an analysis of the sustainable development of the territory according to the Building Act and they are also a source of data for the so-called phenomenon No 64 – „old burdens and contaminated areas“ (annex 1, part A on ACT No. 183/2006 Coll.). The phenomenon No. 64 – “old burdens and contaminated areas” and its utilization for a planning documentation of ORP was used during the finishing national inventory of contaminated sites of the Czech Republic.

SURIS as a part of the Geological Information System (GeoIS) could be used like as a source of information of the phenomenon No. 64 – “old burdens and contaminated areas” for national inventory of contaminated sites of the Czech Republic.

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REMEDIATION FEASIBILITY STUDY OF A FLOODPLAIN OF MORAVA RIVER IN CZECH REPUBLIC CONTAMINATED BY CHLORINATED ETHENES

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KEYWORDS
Contamination, chlorinated solvents, feasibility study, remediation, groundwater, biological reductive dehalogenation

ABSTRACT

The feasibility study had the task of identifying, evaluating and comparing the variants of remedial measures that would lead to ensuring the required level of risk reduction from groundwater contamination by old ecological load at the Olšany near Prostějov city. The origin of the burden is closely related to industrial production on the premises of SIGMA Lutín, a. s., where degreasers based on chlorinated hydrocarbons were used during production. Chlorinated hydrocarbons, which in the past infiltrated through the unsaturated zone into the groundwater at the company's premises in Lutín, continued to spread in the direction of the groundwater flow, when they reached the village of Olšany near Prostějov city and further to the village of Dubany. The contaminated area and its surroundings are used very intensively for water management purposes, there are several important sources of drinking water.

The source of the pollution was already removed by previous remedial works during the 1990s. From investigations in 2008, it was found that the contamination cloud was separated from the original source and the contamination cloud slowly migrated in a southeasterly direction through the saturated zone (Cahlíková Z. et al., 2008). The shape of the contamination cloud appeared roughly elliptical, with the fact that the front of the contamination cloud was significantly extended in the east and southeast direction and did not completely copy the general direction of the groundwater flow. The location and extent of the contamination cloud is expressed in Fig. 1. Based on the results of the mathematical model, the contamination can reach as far as the village of Hrdibořice (by pumping groundwater from the local catchment area). Pollution was detected only within the saturated zone. The highest concentrations of chlorinated ethenes (ClU higher than 100 µg.l-1) were found in the following wells: MV-19 134.4 µg.l-1, MV-20 158.01 µg.l-1, MV-24 132, 72 µg.l-1, MV-33 195.54 µg.l-1, MV-35 130.71 µg.l-1, MV-37 293.35 µg.l-1, LO7 171.1 µg.l -1, LO15 175.49 µg.l-1 and LO17 158.58 µg.l-1. The most extensive of all pollutants is the DCE contamination cloud, primarily and completely dominantly 1,2-cis-DCE. Also, the average concentration in all samples taken is the highest.

The conclusions of the updated risk analysis (Veleba and Musil, 2012) showed that without an active remedial intervention leading to a reduction in the content of chlorinated hydrocarbons in the groundwater, it is not possible to eliminate the health risks for the residents of the villages of Olšany near Prostějov, Hablov and Dubany na Hané, as well as the risk of deterioration of quality groundwater (endangerment of the catchment areas of Dubany na Haná and Hrdibořice).

For ClU remediation in the saturated zone three possible technologies were verified (Musil et al., 2012):

- reduction of contaminants using a suspension of Fe nanoparticles (NZVI),
- biological reductive dehalogenation – BRD,
- airsparging combined with venting.

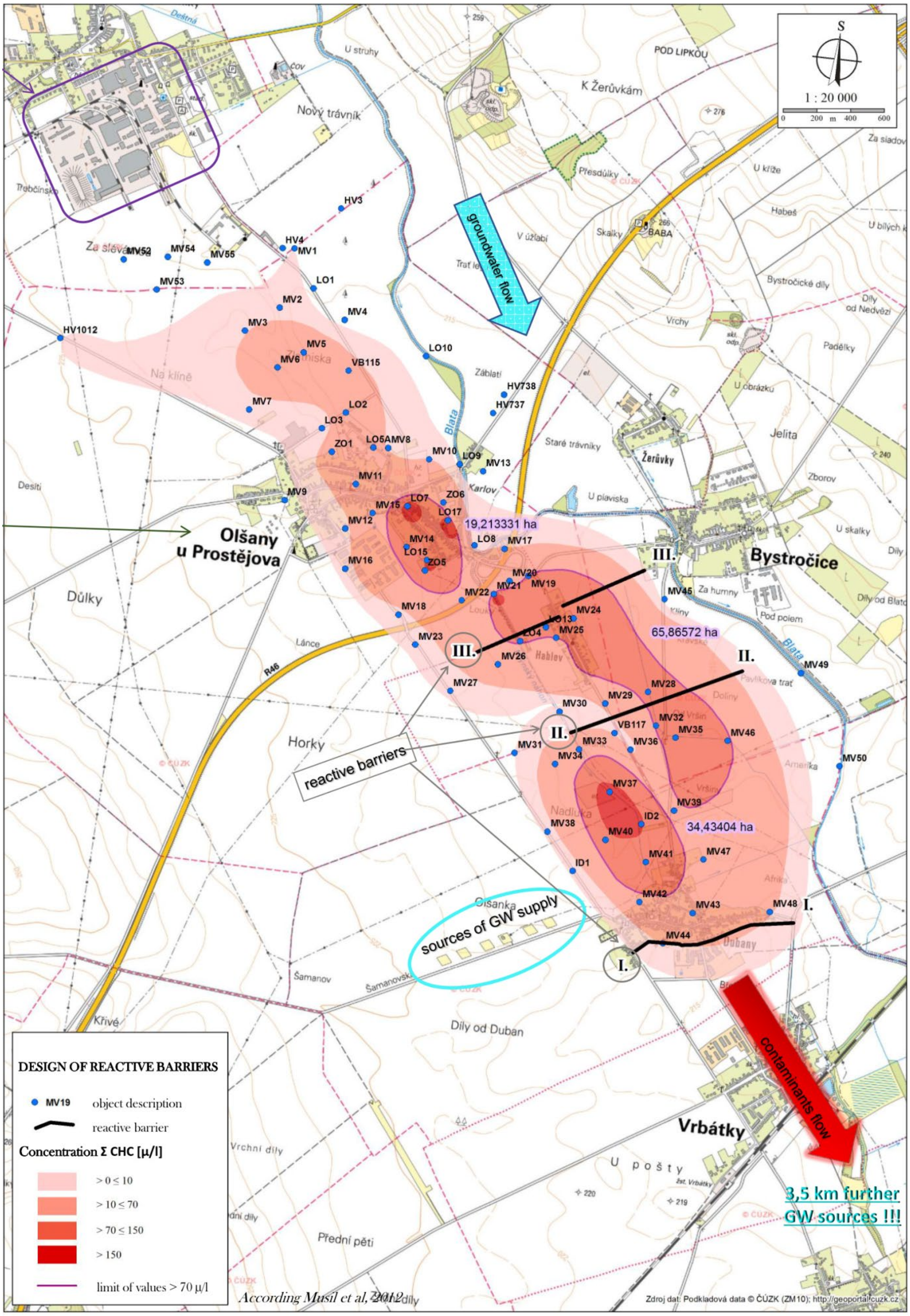

Figure 1. The location and extent of the contamination cloud

The feasibility study identified and assessed the basic conceptual variants of remedial activities from which a decontamination or remediation of contaminated saturated zone was as the only rationally justified conceptual approach selected. Based on the knowledge of the natural conditions, type and level of pollution in the Olšany area and on the basis of experience from similar locations, suitable techniques and technologies were identified to enable the desired goals of reducing contamination to be achieved. (Tab. 1).

Table 1. Identification of appropriate remediation technologies

Technik	**Technologies**
Targeted remediation of the saturated zone	
Pump and treat of groundwater	Remediation of groundwater by the method of pumping and cleaning (stripping) in lines of remediation wells
Venting + airsparging	Remediation of groundwater using the airsparging method with subsequent extraction of soil air by venting in the lines of airsparging and venting wells
Biological reductive dehalogenation (BRD)	Remediation of groundwater by the method of biological reduction of ClU in situ by regular application of whey in the lines of injection wells
Chemical reduction in situ by NZVI	Remediation of groundwater by chemical reduction of ClU in situ by regular application of nano-iron in the lines of injection wells
Chemical oxidation in situ (ISCO)	Remediation of groundwater by the method of chemical oxidation in situ (ISCO; e.g. application of hydrogen peroxide, permanganate, etc.) in lines of injection wells
Full-scale remediation of the saturated zone – in the entire area of the contamination cloud	
Remediation methods of groundwater decontamination - pump and treat, venting + air sparging, BRD, NZVI, ISCO	Remediation of groundwater in the entire area of the contamination cloud using the same methods as for targeted remediation, but on a much larger scale

After a detailed assessment of the selected remedial options, the option including: (i) **installation of a system of injection wells in three lines perpendicular to the axis of the contamination cloud** and (ii) **remediation of the saturated zone using the BRD method in combination with the in-situ chemical reduction (ISCR) method** was evaluated as the most suitable solution.

The principle of the method consists in supporting natural biodegradation by autochthonous organisms in the environment. By regularly applying a suitable substrate into the saturated zone, reducing conditions will be created. These condition are suitable for decomposition processes (degradation) of chlorinated hydrocarbons down to ethane gas (PCE → TCE → DCE → VC → ethen → ethan).

The remediation intervention procedure is based on the systematic application of organic substrate and nutrients to injection wells installed in three lines in a direction perpendicular to the axis of the contamination cloud (Fig. 2). The initialization of reducing conditions will be made by injecting a suspension of zero-valent Fe into the selected line of wells.

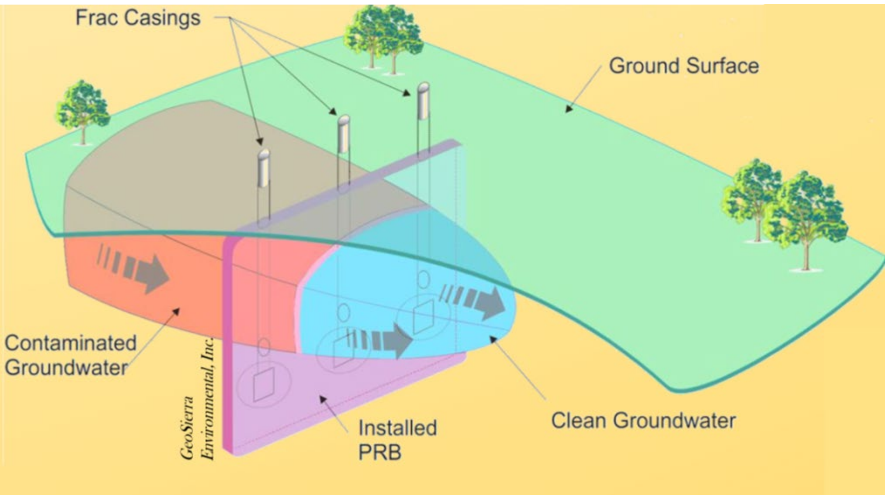

Figure 2. Model of permeable reduction barrier (http://www.geosierraenv.com/prb.html)

The main reasons for choosing this variant (NZVI + BRD) were:

- significant reduction of pollution in groundwater. From the long-term, or even in the medium-term perspective, there will be a reduction of health risks for their recipients (inhabitants of the affected municipalities) as well as the elimination of environmental risks, mainly related to the threat to the catchment area of Hrdibořice and Dubany na Hané.
- meeting the target parameters of the remediation activity. It can be assumed that, in the conditions of the given locality, the target will be reached in about 15-20 years.
- preventing the occurrence of the so-called "rebounding" effect, when after the remedial intervention is completed, there is a significant increase in ClU concentration due to a change in the equilibrium state in the system groundwater - contaminant - soil in a dynamic and natural state due to the presence of residual contamination
- by optimally combining both methods, it is possible to increase the effectiveness of the BRD method or to achieve remediation goals in a shorter time interval.
- there is no need for the groundwater pumping. The method requires only regular remediation monitoring and post-remediation monitoring.

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WATER AND SOIL ENVIRONMENTAL RISK ASSESSMENT IN LITHUANIA

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KEYWORDS
Contaminated sites, water pollution, environmental risk, soil pollution, Lithuania

ABSTRACT

Contamination can severely reduce soil and water quality and threaten human health or the environment. (Perez, Eugenio, 2018) estimated that potentially polluting activities have taken or are still taking place on approximately 2.8 million sites in the EU. At EU level, 650 000 of these sites have been registered in national or regional inventories, 65 500 contaminated sites already have been remediated (Fig. 1). Lithuania has registered 12 341 sites where potentially polluting activities have taken or are taking place, and already has remediated or applied aftercare measures on 96 sites. Lithuania has carried out a thorough mapping of potentially contaminated sites (Fig. 2). Thus contaminated sites remediating under the 'National environment protection strategy'(2015) and 'Management plan of contaminated sites for 2013-2023' (2015), approved by the Minister of Environmentof Lithuania Republic, is one of priority in Lithuania. Contamination of Lithuania's sites emerged from both previously and currently pursued industrial, commercial and intensive agricultural activity and various chemicals and toxic substances used in them (Vasarevicius *et al.*, 2015). Out of potential objects of contamination in Lithuania, 39% are the objects accumulating and regenerating pollution materials, around 30% – cattle-breeding objects and around 31% – industrial, energy, transport and service objects (Vasarevičius et al., 2013).

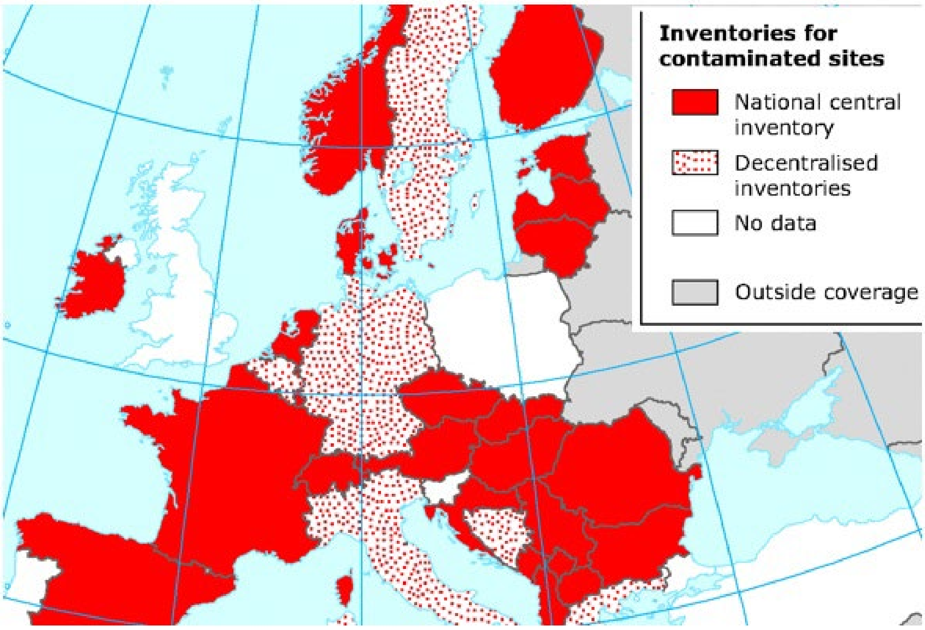

Figure 1. Inventories of contaminated sites (EEA, 2014)

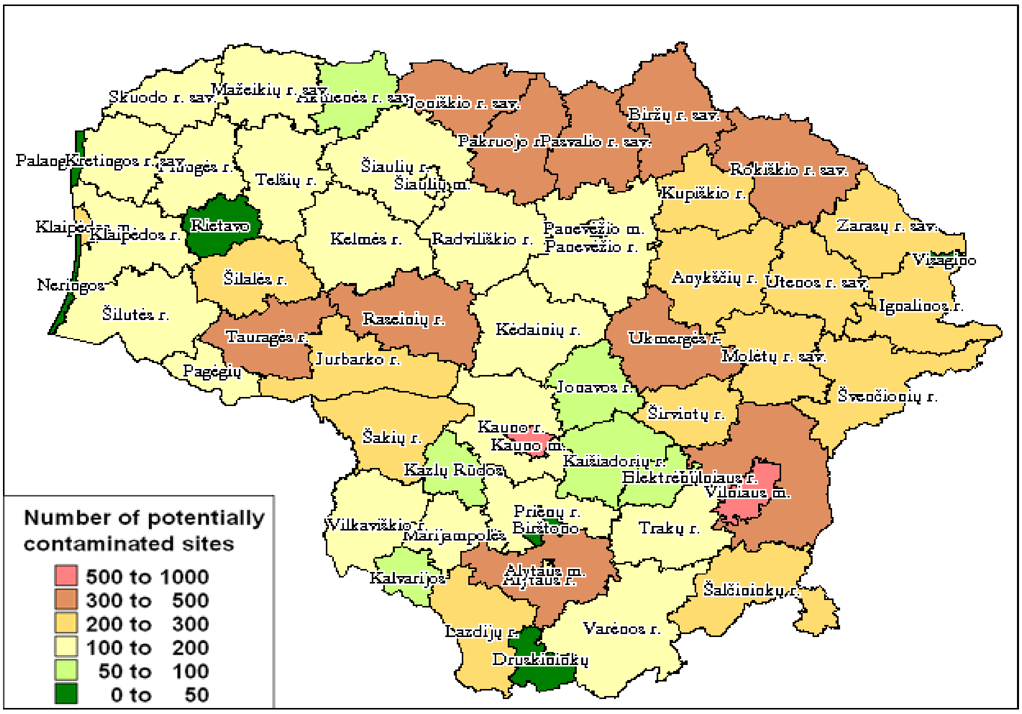

Figure 2. Inventory of potentially contaminated Sites (Lithuanian Geological Survey, 2017)

According on the data of the Geochemical Atlas of Europe, Lithuania should be classified as one of the cleanest countries in Europe in terms of the heavy metal content in soil. The general geo-hygienic status of natural soils of Lithuania is good, with a deficiency of biologically significant elements observed in some regions (National environmental..., 2016). Requirements for the investigation and rehabilitation of potentially contaminated sites in Lithuania are regulated by Law on Ecological Investigations prepared to protect human health from a negative influence of contaminated sites, to protect soil and groundwater from potential contamination during activities when hazardous materials are used and for reducing a negative influence on soil, groundwater as well as the status of ecosystems related to such environmental components (Kadunas et al. 2006). The influence of land use on contamination level, potential objects of environmental contamination may be attributed to a certain type of contamination: – objects of industry, energy, transport and services (e.g. technical fields, oil bases, boiler-houses); – objects to compiling contaminated materials and their regeneration (e.g. untidy or destroyed former warehouses for pesticides); – objects to cattle-breeding (e.g. large quantities of construction remains) (Baltrenas et al. 2011). The soil is critically important for the survival of land-based life, but at the same time, soil has a considerable capacity to retain and concentrate chemicals. Various factors (contamination, unbalanced fertilisation, etc.) result in the increase of soil acidity. Approximately 19% of Lithuanian agricultural areas are acid, and almost one million hectares are prone to acidification. Lithuanian soil with increased acidity may become less fertile as its capacity to preserve nutrients decreases. In order to increase soil fertility, farmers may begin using more fertilisers, which may in turn lead to higher soil and water contamination. An inventory of 11,136 potentially contaminated sites was established by 2012, which, based on a preliminary assessment, measured 2,500 ha. The contamination of about 49% of the affected sites attributed to the group of extremely dangerous areas and of some 41% of the sites attributed to the group of dangerous areas exceeds the permissible values (National environmental..., 2016). The implementation of existing legislative and regulatory frameworks (e.g. the Integrated Pollution Prevention and Control Directive, Landfill Directive, Water Framework Directive) helps to prevent new contamination of soil. However, efforts must still be made to deal with historical soil contamination (EEA, 2014). Rehabilitation of degraded soil, mostly focusing on the management of brownfields and contaminated sites, with due consideration to the current and expected needs of land use and soil restoration costs (National environmental..., 2016). Law on Environmental

Monitoring (1997) regulates not only the state environmental monitoring, but also the requirement applicable to economic entities (the potential polluters) to carry out the monitoring of the impact on the environment as well as groundwater. The surface layer of the soil is a barrier protecting subsoil water against pollution with different chemical substances. By the extent of soil pollution, it could be judged about the risk of subsoil water pollution (Vasarevičius, Greičiūte, 2004). Nowadays, soil and groundwater may be polluted by approx. 11 thousand contaminated sites in Lithuania, and approx. 4.5 thousand of them the potential for pollution is very high. The total estimated area of polluted land is about 0.43 % territories of the country. However, in contaminated sites the allowable limits are not exceeded (Bukantis *et al*., 2013).

Groundwater is the main source of drinking water in Lithuania. Deep layers of water bodies are used for the extraction of drinking water; however, protection of groundwater against anthropogenic impacts is inadequate. In Lithuania, the status of most groundwater basins is good (National environmental..., 2016). However according to the Lithuanian Geological Survey (LGS), 349 sources of concentrated contamination have been already registered in the sanitary protection zones of water bodies, though it represents only a small part of the truth. Therefore, a more detailed inspection of the sources of concentrated pollution is needed to establish danger to groundwater, and the means of prevention can be used for minimizing it (Kadunas et al. 2006). In 2012- 2013, the water of 1/3 of dug shaftwells was contaminated with nitrites and/or nitrates and non-compliant with the drinking water safety and quality requirements. Presently, the major potential polluters of groundwater bodies are sources of diffuse pollution (such as plant production, intensive livestock, poultry farms, etc (National environmental..., 2016). The measures implementing the Nitrates Directive are set out in the water field development program for the year 2017-2023 and implementation plan of the water field development program for the year 2017-2023. According to the last report on the implementation of the Nitrates Directive (2012-2015), nitrate levels in surface water and groundwater remain low in Lithuania. In the context of the Nitrates Directive, Lithuania applies mandatory measures on its whole territory. The measures implementing the Nitrates Directive are set out in the water field development program for the year 2017-2023 and implementation plan of the water field development program for the year 2017-2023. Overall, according to the last report on the implementation of the Nitrates Directive (referring to the period 2012-2015), nitrate levels in surface water and groundwater remain low in Lithuania. However, eutrophication of surface freshwater remains problematic, with a slight increase of stations reported in eutrophic and hypertrophic status, from 47 % to 49 %. Under the Nitrates Directive report for 2012-2015, Lithuania also reported that nitrate concentrations in surface water are not likely to decrease if no additional measures are taken to reduce pollution (The EU Environmental..., 2019). It should be ensured that dangerous chemicals do not exceed the maximum permissible concentration in water bodies; also, efforts should be made to reduce and/or discontinue water pollution with environmentally hazardous substances. The use of plant protection substances containing biocides, pesticides, fungicides or other chemicals or chemical products should be well-balanced and innovative plant protection technologies should be promoted (National environmental..., 2016).

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UPDATED RISK ANALYSIS OF THE UNIPETROL LITVÍNOV LANDFILL AREAS

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KEYWORDS

Risk Assessment, contamination, risk analysis, groundwater, surface water

ABSTRACT

The updated Risk Analysis (RA) focused on landfilling areas located directly eastward of petrochemical facility Chempark ORLEN Unipetrol RPA, s.r.o. in Litvínov (CZE) and comprising of multiple ash dumps, two lime-sludge landfills, and solid waste and liquid waste (lagoons) landfills. History of the site is dated back to 1939, when the Nazi founded the petrochemical facility for coal hydrogenation. Landfilling of the terrain continued until 1980's, serving the needs of ever growing chemical industry.

Two major Risk-recipients represent medium sized creek, running in N-S-SW direction and draining water from the entire area to Bílina River (tributary of Elbe River), and large effluent-lacking Lake Most created by flooding of former surface coal mine, directly southward from target area.

Overall hydraulic conditions of the area are greatly affected by past and recent anthropogenic activity, including long history of deep coal mining (many mining works unmapped or unrecognizable), mine-water pumping, surface coal mining, soil heap dumping, tailings dams' construction, water streams diverting, and drainage systems operation.

Target area has been studied thoroughly since 1994 by multiple reconnaissance studies for full or partial risk analyses, which have defined following contaminants of interest: Ammonia-nitrogen (N_{amon}), petroleum hydrocarbons, aromatic hydrocarbons, phenols, arsenic (As), fluorides (F^-), and sodium (Na).

Present updated RA has two main objectives: 1) To assess the option of extending time-frame for complete remediation of the area, as defined by Czech Environmental Inspectorate (CEI). 2) To verify effectiveness of all applied and projected remediation efforts with respect to reaching remediation limits derived by riskiness of particular sites in the area and to recommend eventual adjustments in methodology and/or defined remediation limits.

INTRODUCTION

The area of ORLEN Unipetrol Litvínov ash dumps (Fig. 1) was studied for the purpose of actualized risk assessment composition. The target area is largely made up of former waste dumps from the chemical industry. Due to undermining and land subsidence of the area, landfills' construction and due to dumping activities, the original villages of Kopisty and Růžodol had to be demolished. Such dynamic development since the World War II led to the creation of partial landfills, bounded usually by bulk dams. However, depending on the current operation and land surface development, particular dumps' boundaries were shifted and the dumps increased in size and/or partially overlapped.

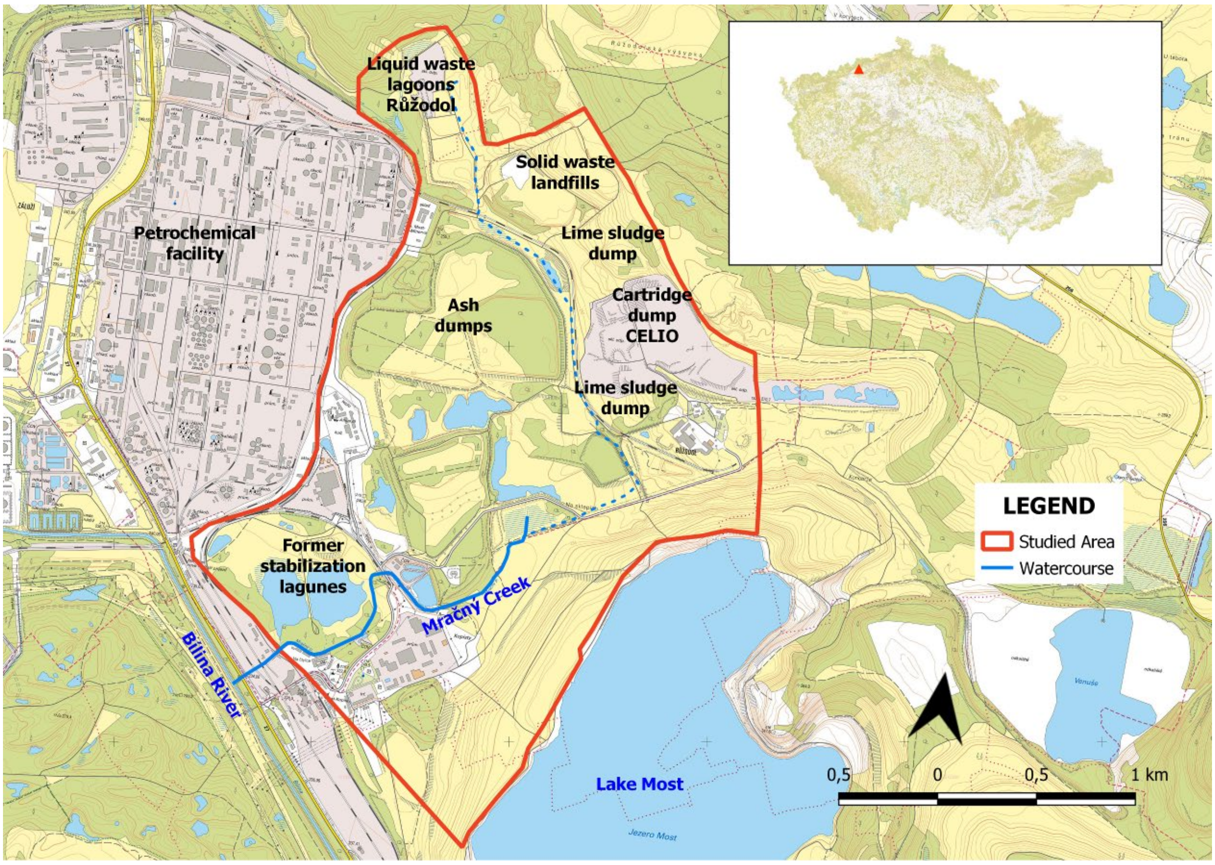

Figure 1. Target area of the Risk assessment analysis

The area belongs to the Most basin, its originally flat surface is severely affected by former coal mining, industrial activities and waste dumping (especially ash floating). In present, parts of the devastated area have been reclaimed, including several tracts of the studied area and the flooding of former Ležáky surface coal mine, giving the origin to the Lake Most. Geologically, the area belongs to the Mostecká part of North-bohemian basin, with the Palaeozoic crystalline bedrock (orthogneiss) and Mesozoic and Tertiary sedimentary fill (conglomerates, quartzites, sandstones, marlstones, lignite, and clays). The main hydrogeological unit at risk is the shallow aquifer spanning over quaternary silty- to sandy gravels, the upper regelation zone of the underlying clay and including the dumped mining tailings and wastes (ashes, soot, etc.). The secondary aquifer in the area lies in the strata majorly affected by the deep coal mining. Both aquifers are separated by the isolating unit of tertiary clays and siltstones (100 – 200 m thick) with the hydraulic conductivity coefficient ranging from 10^{-10} to 10^{-11} m/s. The potential vertical hydraulic connection between the two main aquifers may be caused by the old mine workings. Major surface water recipient is the Mračný Creek draining its waters from the Růžodol tailing dump drainage system to the Bílina River.

The dumped wastes comprise of several major types: Winkler combustion residue (incompletely combusted ground coke from gas production), float dusts, slags and ashes, coal soot, lime sludge (Fig. 2), petroleum residues (Fig. 3), and various municipal and industrial wastes. The major pollutants of interest are ammonia nitrogen (N_{amon} – global contaminant of the whole area; introduced by chemical waste liquid dumping; locally reaching concentrations 10^4 mg/l in groundwater and releasing free ammonia in $pH > 9$), petroleum and aromatic hydrocarbons (PAH, BTEX – local contaminants) in petroleum sludge dumps and in float ash dumps' groundwater, petroleum sludge (local contaminant), arsenic (As; regional contaminant due to coal mining and industrial utilization), and phenols (lime sludge from phenol manufacturing – local contaminant).

In this study, ammonia nitrogen represents the sum concentration of ammonium ions (NH_4^+) and non-dissociated ammonia (NH_3) dissolved in groundwater, since the relative abundance of both these forms fluctuates widely in the diverse groundwater conditions of the landfill area. Further, although the concentrations of N_{amon} adsorbed in the rock matrix were scarcely determined, it has been demonstrated that for high N_{amon} contents, the standard analytical protocol of extraction into water leachate is not sufficient. Thus, new methodology of acid leachate extraction has been developed and successfully tested.

The risk analysis included preliminary conceptual model describing relevant exposure scenarios, pollutant transport pathways (groundwater flushing, volatilization, rain water flushing, drainage system leakage, etc.), and risk recipients (human health, environment).

Figure 2. Example of lime sludge dump (left), lime sludge consistency in drill core (center), and typical purple color of phenolic solution submerged tertiary clays in lime sludge underlying strata (right).

Figure 3. Example of petroleum sludge hotspot and the sludge consistency.

DISCUSSION

For the purpose of up-to-date information acquisition, an additional survey was conducted at selected sites of the area with drilling works and core sampling, groundwater and surface water sampling and hydrological measurements. Five petroleum sludge hotspots were identified and the sludge was sampled for toxicological analyses and energetic potential analysis. Additionally, zoological survey investigating environmental diversity of the entire area was conducted.

Based on previous studies' and reports' background research and on current survey results, the aerial and spatial extent of contamination was summarized. Specifically, the nitrogen forms' concentrations, petroleum hydrocarbons concentrations, BTEX, phenols, As, F^-, and Na concentrations were discussed. The mass balance of residual contamination is shown in Table 1. For energy use purposes, the total amount of petroleum sludge at the defined hotspots was investigated, yielding the range of 947 – 1209 m^3 of petroleum sludge. The lime sludge mass balance was determined for eventual economic utilization, yielding the total amount of 158 550 m^3 present.

Migration and transport of target pollutants were discussed with groundwater flow and pollutant transport modelling. Especially in case of N_{amon}, historically accepted scenarios of pollutant plume migration were corrected, displaying greater effect of natural attenuation processes with significant portion of ammonia volatilization into unsaturated zone and atmosphere. Analysis of N_{amon} plume center-of-gravity migration showed insignificant shifts in position between the years 2008 and 2012 (cca 20 m): the plume center-of-gravity movement is lower than the variance error of N_{amon} concentrations in monitored wells during particular monitoring campaigns.

Table 1: Pollutant mass balance

Aquifer		*** N_{amon}**	**benzene**	**ethylbenzene**	**+ phenols**	**As**
		kg	**kg**	**kg**	**kg**	**kg**
Quarternary	Dissolved	** 576 000	22	8	1 453	119
	Sorbed	8 578 000	252	286	56 624	
Ashes	Dissolved		30	18	191	317
	sorbed	8 338 000	203	381	4 332	
Vadose zone		3 926 000	Globally insufficient data and geochemical characteristics			
Total		**21 418 000**	**506**	**694**	**62 600**	**436**

* N_{amon} mass balance acquired from former studies (Zamrazilová a kol. 2016).

** Mass balance dissolved in groundwater was determined together for quarternary and ash aquifer.

\+ Phenol mass balance does not include the lime sludge underlying strata, where no monitorable aquifer exists (the dumps are founded directly on clay izolator).

The following risk recipients were identified: 1) workers and employees conducting the remediation works; 2) public (the area is transected by local bicycle path); 3) surface watercourses, rain sewers, and drainage systems; 4) water ecosystems, terrestrial ecosystems, and wildlife. The major transport pathways were defined as 1) volatilization and inhalation (BTEX, ammonia); 2) direct dermal contact, accidental ingestion or inhalation by human; 3) rain water infiltration and groundwater flushing at surface effluents and lagoons. The human health risks were evaluated with respect to U.S. EPS standards using the R coefficient of riskiness. The environmental risks were evaluated at sites where contamination spreads to the surroundings of the assessed area or to surface waters, where watercourse and water body bottom and bank sediments are contaminated, where the drainage bases of the territory are affected, or where ecosystem components are affected. Such area with demonstrated soil, underground or surface water contamination exceeds 2 km^2. This fact alone is serious from the ecological risk assessment point of view. Due to the area mining and industrial history, the quality of the ecosystem is fundamentally affected. However, the whole landfill area hosts great number of bird, amphibian, reptile, and mammal species.

CONCLUSION

The risk analysis conclusions are based on several uncertainties and limitations that have potential of affecting the presented outcomes: 1) hydraulic data are influenced (among others) by the geologic composition of anthropogenically altered environment; 2) contaminant transport and attenuation considerations are further affected by lack of detailed sorption data in differing hydrogeological conditions, detailed TOC data, or short history of appropriate sampling methodology (acid extraction); 3) numeric modeling considerations omit non-global contaminants (As, petroleum hydrocarbons, F$^-$, etc.), do not account for unsaturated zone or potentially present preferential flow paths; 4) pollutant mass balance lacks detailed data in vadose as well as saturated zone; 5) monitoring methodology varied widely throughout the site assessment history.

The current state of the pollution migration from landfills can be considered stable, current extent of contamination plumes is determined by their limits in the form of drainage boundaries (surface waters, drainage systems), or their balanced reaction zones at the plume migration fronts.

No health risk was detected for the evaluated real exposure scenarios in the studied area. This is based mainly on the character of the area, historically and publically infamous for the industrial landfilling, discouraging local public from visiting. The non-carcinogenic risk value (HQ) was exceeded only in the sum of HQ of individual C_{10}-C_{40} in dermal contact with petroleum sludge. However, neither real risk was assumed in this case, as the result rather corresponds to an overestimation due to the entry of constant input maximum concentrations for all C_{10}-C_{40} fractions. The actual hazard rate will be lower in real terms, with HQ < 1.

Environmental risks were verified at 9 of the 17 exposure scenarios.

Based on the findings that 1) majority of the N_{amon} plume has the potential of slow volatilization and 2) the N_{amon} plume migration is limited, the original intent to cap the ash dumps with impermeable (clay) cover limiting rainwater infiltration was abandoned. In the context of current land use and according to the applicable spatial planning, the ammonia contamination does not pose any health or environmental risk.

The present petroleum sludge and lime sludge wastes were suggested for economical use in cement production with feasibility study necessarily preceding the project drafting and realization.

For each particular part of the studied area exhibiting identified environmental risk, the recommended remediation limits were actualized and specified in groundwater and soil matrices. Specific points of remediation limits verification were defined in each of the sites.

Further remediation measures were suggested at particular sites including excavations (petroleum and lime sludge), landscaping, and groundwater recharge prevention, drainage of rain water, repairing of present drainage systems, preventing formation of seasonal water bodies (lagoons), monitoring and further surveys for detailed mapping of present wastes.

The two main objectives of this Risk analysis actualization were fulfilled with the following conclusions: 1) the overall state of the area is stable. There is no acute health or ecological risk expected in extending the deadline for the implementation of corrective measures; 2) the planned remedy works were evaluated in the light of the actualized Risk analysis findings. In some cases, the current recommendations differ from previous projected remediation efforts.

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REPRESENTATIVE CONCENTRATIONS IN QUANTITATIVE RISK ASSESSMENT

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KEYWORDS

Quantitative health risk assessment, reference concentrations, concentration isolines, risk isolines

ABSTRACT

The paper describes and illustrates alternative possibilities of simplifying quantitative on-site risk assessment in cases when the data set of concentrations of contaminants was obtained by biased sampling, which complicates statistical evaluation and determination of representative concentrations by conventional methods.

INTRODUCTION

So called representative concentrations (RC) of pollutants in soil, groundwater and soil air are one of the basic input parameters for quantitative assessment of health risks from contamination. Determination of RC is one of the most important outputs of the pollution investigation interpretation.

Most of methodological guidelines for the assessment of risks from soil contamination deal in details with the issue of determining representative concentrations by statistical processing of concentration data from the site investigation (for Example US EPA 1989, 1999, 2000, DEQ 2002).

In any case, the input data for the RC determination are required to meet the strict criteria of statistical representativeness. In the first place, the sampling points must be distributed in a statistically random manner throughout the area to be investigated, and there must be a certain minimum number of samples in relation to the extent of the site. In case of more complicated sites, it is recommended to divide the area to several sub-units to eliminate certain types of variability. Each of these sub-units is then sampled and evaluated separately including the RC determination. The division of the site into sub-units should be based primarily on some prior knowledge on the distribution of contamination throughout the site, on preliminary indications of hotspot locations.

In real world, site contamination data is typically obtained by biased sampling, which is primarily focused on identifying hotspots and delineating the extent of contamination plumes. Sampling points are not systematically distributed throughout the exposure domain which precludes the use of statistical methods for data evaluation. Covering the entire area of interest by systematic sampling is generally unrealistic for economic reasons.

Subdividing a site into several quasi-homogeneous units - as discussed above - is often problematic. In practice, it encounters difficulties especially in complex sites with combined contamination and multiple pollution hotspots, with different ways of using parts of the site, with morphological and geological variability of the area, etc.

In many cases, it is possible to avoid the indicated complications in the specification of RC by completely abandoning their determination and proceeding in one of two ways, which allow to directly define the subareas with a different risk levels within the whole site. These two ways are:

(a) Contour lines of contaminant concentrations based on data from sampling are constructed using geostatistical methods (kriging). The isoline of the calculated limit concentration, corresponding to the selected threshold level of acceptable risk, is then inserted into the resulting image.

(b) The risk corresponding to the concentration of the contaminant at the given sampling point is calculated individually for each sampling point. Obtained values are then used to directly plot the ILCR or HQ isolines (for carcinogenic or non-carcinogenic risks) by kriging. An isoline corresponding to the selected threshold level of acceptable risk can be simply inserted into the resulting pattern. The limit concentration corresponding to this isoline can be easily derived.

The latter procedure also allows the construction of summary risk isolines for cases when more pollutants from a given exposure domain contribute to the exposure along the same exposure pathways. If a broader range of contaminants is involved in the site pollution, it is recommended to simplify the risk assessment by first identifying the so-called priority contaminants that contribute decisively to the potential health risks (e.g. more than 90% - see US EPA 1989). Experience shows that usually no more than two or three contaminants contribute decisively to the total risk, even in case of multispectral contamination.

I would like to illustrate the advantages of the described procedures with two examples.

EXAMPLE 1:
The first example is from the large site of the former chemical plant. It had changed its production profile several times within more than one century of its activities. There were two big fire accidents during its history and the plant was also bombed during the2nd WW. The site is affected by extensive and multispectral soil and groundwater pollution... The site has a very attractive location in terms of commercial usage. The example deals only with on-site risk interpretation issue in this article.

Pollution of the near-surface soil layer (0 – 1 m below the surface) represents the potential health risk for future site users though an unintentional soil ingestion, direct contact and inhalation of soil dust particles. Emissions of soil air polluted by volatiles are another source of health risk.

The synthesis of the on-site risk assessment is illustrated in the figure 1, which presents contours of areas with unacceptable risks for future site users both from the surface soil pollution and from soil air emissions. As can be seen, both types of risks mostly overlap. It was easy to derive these threshold risk contours from concentration isolines constructed for priority contaminants both of the near-surface soil layer and soil air.

It can be seen that this way of risk interpretation directly suggests possibilities for optimising risk reduction measures. There is an opportunity to exploit a significant part of the site without the need to implement any risk reduction measures. In areas with excess health risk from surface soil contamination, the risk for site users can be eliminated by locating there buildings with solid floors and/or covering them with hard surfaces. Again, no special risk reduction measures are necessary. Areas with above-limit risks from emissions of volatile substances must be completely excluded from use or may only be used for activities involving limited staff presence (e.g. open areas for long-term storage of certain commodities).

EXAMPLE 2:
This example illustrates the case of a large unused site in the middle of a luxury residential area of a large city. The site is understandably very attractive to developers. For many years it has been the site of industrial production, resulting in extensive and deep contamination of soil and groundwater. A detail site Investigation has shown that the priority contaminants are tetrachloroethylene (PCE) and trichloroethylene (TCE).
Cumulative on-site risks to potential future residents from emissions of these two priority pollutants were calculated for each documentation point. The results are illustrated in the figure 2.
The possibility of active contamination of the site is unfeasible for economic reasons due to the great depth to which the contamination extends.

However, the presented graphical interpretation of the risk assessment documents that at least the peripheral parts of the site can already be used for residential development and other large parts of the site can already be exploited for less demanding functional uses. Model calculations show that there is a chance that natural attenuation will reduce emissions and thus also the site usage limitations in future.

SUMMARY AND CONCLUSIONS

The paper presents and illustrates possibilities of avoiding difficulties with determination of representative concentrations for quantitative assessment of on-site risks from soil contamination, especially for more complex and larger sites and for datasets from non-random (biased) sampling. The outlined approaches to assessing risks from soil contamination offer these possibilities:

a) simplification of the risk quantification process;
b) more precise and illustrative determination of the health risk distribution throughout the site area;
c) more flexibility in delineating sub-parts of the site suitable for different types of functional use;
d) more flexibility in designing necessary risk reduction measures for sub-areas of the site.

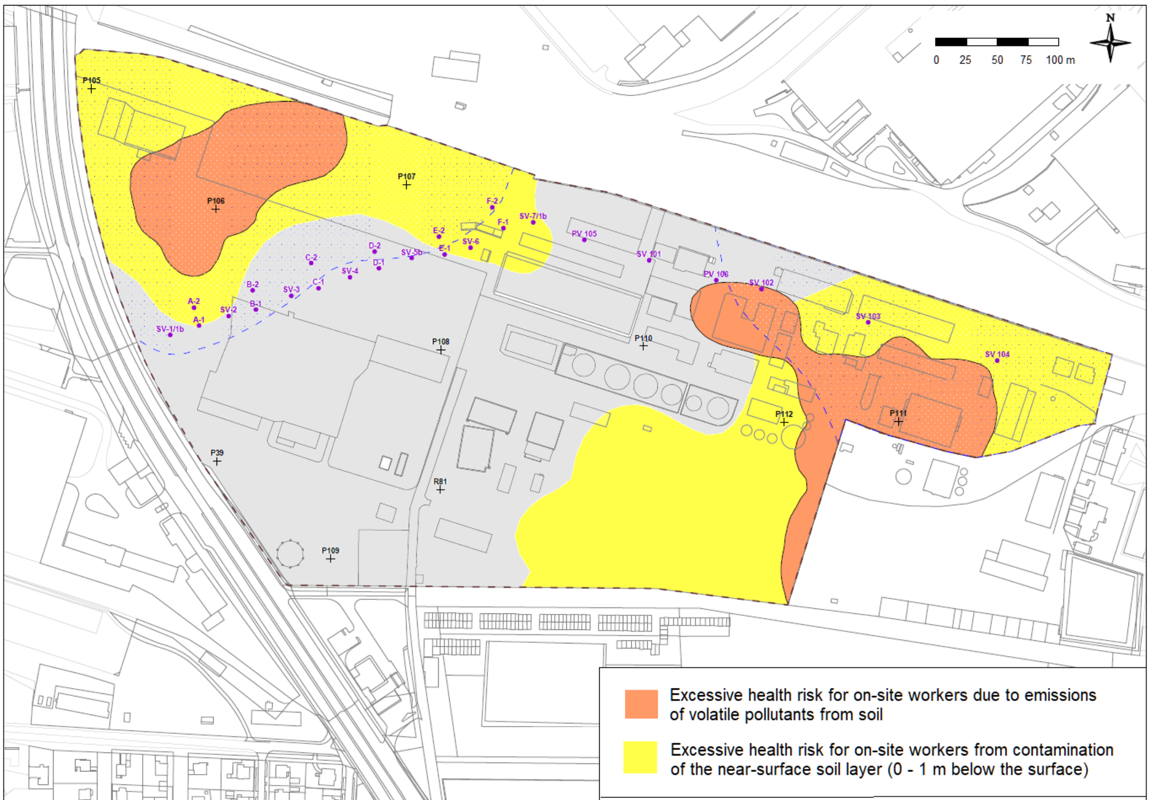

Figure 1
Delineation of the excessive on-site risks

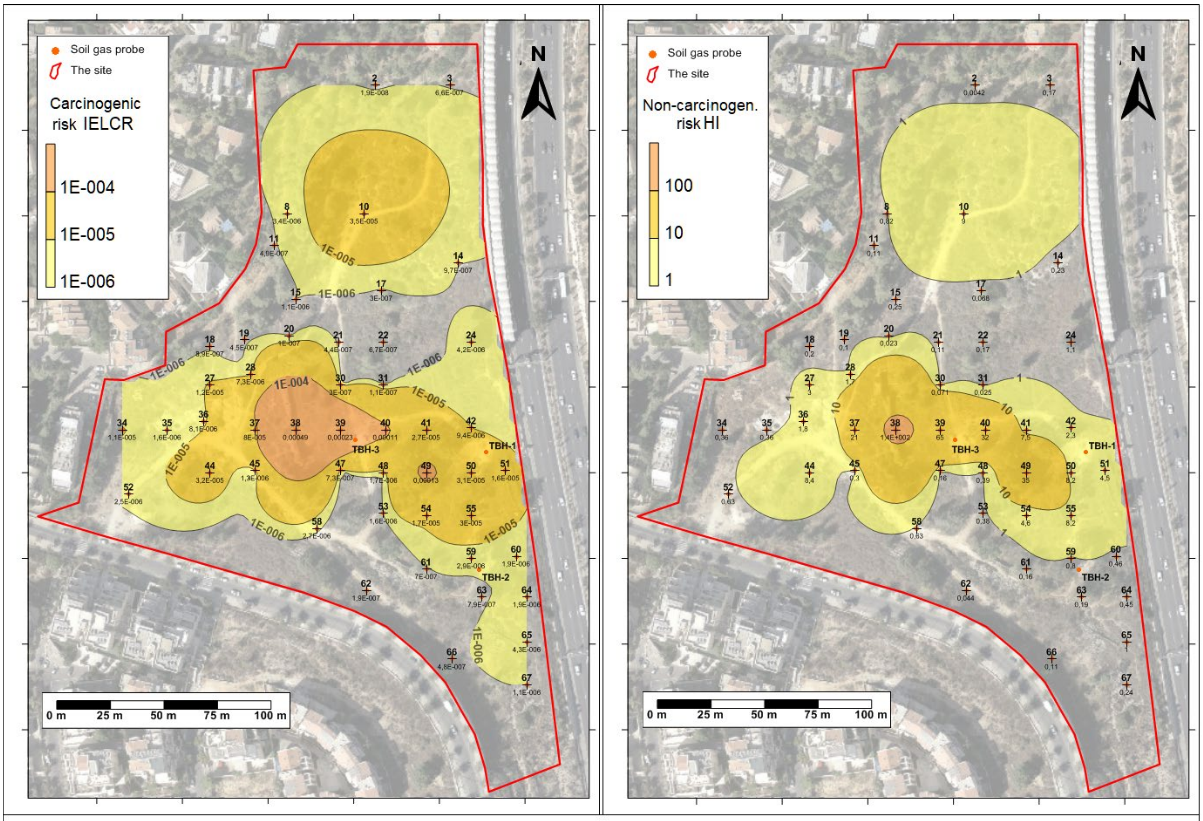

Figure 2: Cumulative on-site risks for residents from emissions of PCE and TCE from soil

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USING A NOVEL INDEX TO FIND THE MOST APPROPRIATE AGGREGATION FUNCTIONS FOR COMPOSITE HAZARD RATING OF A WASTE DISPOSAL SITE

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KEYWORDS
Composite hazard rating, Clustering index, Aggregation function, municipal waste, waste dumps, Ambiguity, Eclipsity

ABSTRACT

A waste disposal site has a number of hazards associated with it e.g. contamination of groundwater, surface water and air. These hazards can be repersented by individual hazard ratings. To have ease in decision-making, a composite hazard rating is required. The study selects thirteen aggregation functions from the literature and assesses them for ambiguity and eclipsity on a set of 27 sites with continuously varying site characteristics. Finally, the clustering index is employed to investigate the clustering of composite ratings for the group of 27 sites. The non-ambiguous and non-eclipsed function having minimum clustering index is finally selected as the most appropriate aggregation function.

1 Introduction

Hazard rating systems provide easy-to-understand mechanism to assess the hazards from a waste disposal sites on a relative basis [1]. In general, all the hazard rating systems first estimate the individual hazard ratings for various hazards, but only some of them combine these into a composite rating for a site. A composite hazard rating is easy to communicate among all the stakeholders and can make distinction among a number of dump sites for prioritization for closure. Aggregation is one of the most important step in developing an aggregated index and has been widely investigated in the literature concerning environmental engineering including water, air and solid waste [2] [3], [4],. It may sometimes lead to over-simplification and/or distortion of the information to be conveyed. Most of the studies in literature focus on minimizing eclipsing and ambiguity while selecting the aggregation function [4] [5]. However, for a composite hazard rating to serve its purpose, the composite hazard scores for a group of sites with varying characteristics should not be clustered in a narrow range. For such cases, we need a parameter that looks at the range as well as the scores for the in-between sites.

The clustering index has been already applied for assessing the clustering of scores for individual sites [6]. Clustering index measures the clustering of scores for a given set of waste sites. The manuscript attempts to employ clustering to find a suitable aggregation function for composite hazard rating of a municipal waste site.

2 Methodology

The selection of aggregation functions for determining composite hazard rating consists of the following steps: (i) finding aggregation functions in literature for assessment; (ii) application of individual new/modified rating systems to different cases of municipal waste sites (Table 1); (iii) application of various aggregation functions compiled from literature to determine composite hazard rating of municipal waste sites from step 2; (iv) screening of aggregation methods using ambiguity and eclipsity; (v) further evaluation of non-ambiguous, non-eclipsed aggregation functions using clustering; (vi) selection of the aggregation method for composite hazard rating.

Table 1. Individual hazard ratings for sites S-1 to S-27 from new hazard rating system

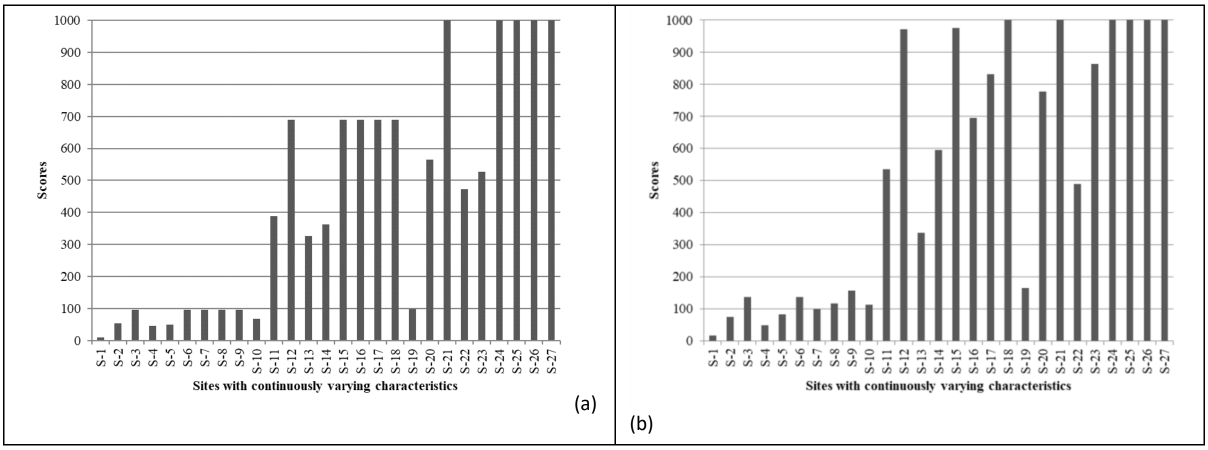
Site No.	**GW@**	**SW#**	**Air$**	**Site No.**	**GW@**	**SW#**	**Air$**
S-1	9	9	9	S-15	326	611	689
S-2	9	55	50	S-16	689	55	62
S-3	9	96	95	S-17	689	293	363
S-4	46	8	9	S-18	689	539	689
S-5	46	48	50	S-19	96	98	90
S-6	46	86	95	S-20	96	564	527
S-7	97	8	9	S-21	96	990	1000
S-8	97	41	50	S-22	473	81	90
S-9	97	76	95	S-23	473	494	527
S-10	66	67	62	S-24	473	886	1000
S-11	66	389	363	S-25	1000	80	90
S-12	66	683	689	S-26	1000	425	527
S-13	326	56	62	S-27	1000	782	1000
S-14	326	341	363				

3 Result and discussion

A number of aggregation functions have been reported in literature namely Aggregation method; Maxima; Average or Simple Addition; Weighted Sum; Unweighted multiplicative function; Weighted multiplicative or weighted geometric mean function; Root sum power function; Weighted root sum power function; Root Mean Square; Weighted root mean square function; Unweighted ambiguity and eclipsity free function r=0.4; Weighted ambiguity and eclipsity free function r =0.4; Subindex powered weight function and CEPI aggregation function. A set of 27 waste sites having continuously varying characteristics was used to select suitable function for determination of composite hazard rating. Sites from S-1 to S-27 have been categorized into three groups. Site characteristics for source, pathway and receptor components vary from best to worst for these sites [7].

Initially, individual ratings for groundwater, surface water and air were determined for these 27 sites (i.e. S-1 to S-27) using the newly proposed/modified rating systems [6, 8, 9]. Afterwards, the composite hazard rating scores for the 27 sites were determined using various aggregation functions. Next step was the screening of functions showing eclipsity and ambiguity.

Ambiguous functions are the ones in which the aggregated value exceeds the critical level without any of the subcomponents' rating exceeding the critical levels. The functions found ambiguous were maxima, root sum power function and Unweighted ambiguity and eclipsity free function (r=0.4), as shown in Fig. 1.

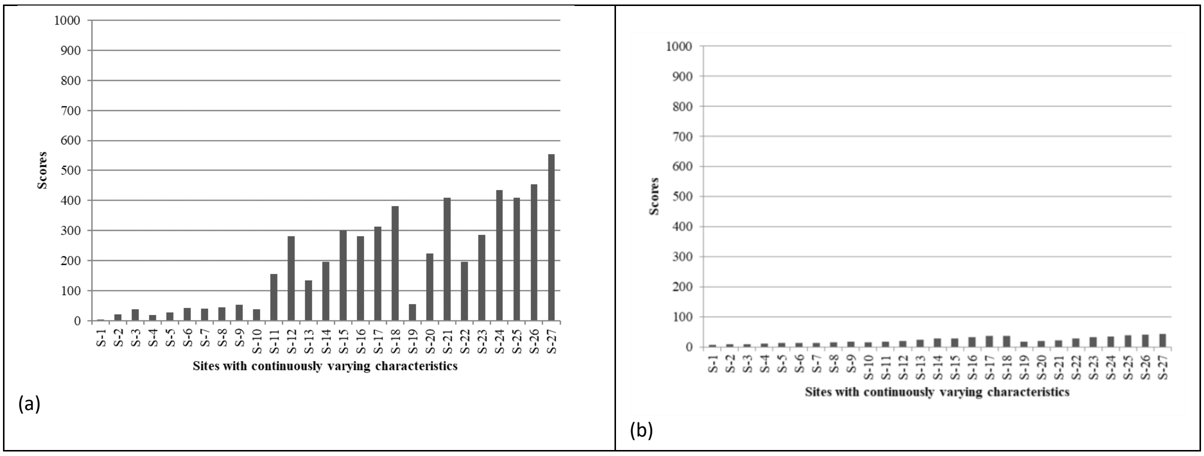


(a)

(b)

Figure 1. Composite scores showing ambiguity using (a) maxima, (b) root sum power function

Eclipsed functions are the ones in which the where the aggregate index does not exceed the critical level despite one or more of the sub-components' value exceeding the critical levels. Weighted root mean Square function, Subindex powered weight function and multiplicative aggregation functions (unweighted and weighted) have been considered as eclipsed (Fig. 2).



(a)

(b)

Figure 2. Composite scores showing eclipsity using (a) Weighted root mean Square function, (b) Subindex powered weight function

The aggregation functions found to be free from ambiguity and eclipsity are Simple Addition function, weighted sum aggregation, Root mean Square, Wt. ambiguity & eclipsity free (r=0.4) and Weighted root sum power function. These initially selected functions were further analysed using clustering index.

In this step, the clustering indices are determined for the non-ambiguous, non-eclisped aggregation functions [6]. Table 2 shows the clustering indices of these aggregation functions. The range of clustering indices for these functions varies from 0.433 to 0.506. Among the initially selection functions, root mean Square shows the minimum clustering index of 0.433.

Table 2. Clustering indices of initially selected aggregation functions

Aggregation function	**Clustering index**
Weighted sum aggregation	0.477
Weighted root sum power function	0.483
Root mean square sum	0.433
Wt. ambiguity & eclipsity free r=0.4	0.477
Simple addition	0.437

Aggregation function	Clustering index
CEPI Aggregation	0.506

4 Conclusions

The present study has dealt with the development of a composite hazard rating system and priority of closure. A review of the aggregation functions reported in the literature has been presented followed by their application to 27 waste dump sites. A total of thirteen different aggregation functions from the literature, were applied to MSW dumps with varying characteristics to determine composite ratings. Out of the thirteen aggregation functions, only six functions were found to be non-ambiguous and non-eclipsed. As the clustering index of the root mean square function is the minimum, it has been demonstrated to give the best measure of composite hazard rating.

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ASSESSMENT OF WATER RESOURCES CONTAMINATION NEAR LANDFILL USING LWPI MEASURE

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KEYWORDS
Landfill water pollution index (LWPI), Landfill leachate, Surface water, Classification, contaminant, contaminated sites, groundwater, environmental impact assessment

ABSTRACT
In this study, water contamination near a municipal solid waste dumpsite due to leachate leakage to nearby water resources was investigated. For this purpose, the analyses of physicochemical, heavy metals and microbial parameters were performed around Tabriz dumpsite located near Tabriz city, Iran. Three surface water and six groundwater resources were monitored during wet and dry seasons.

Since the water resources (i.e., surface water and groundwater) in the region are subjected to leachate pollution, in an effort, the scale of the surface water and groundwater pollution due to the generated leachate in the last 20 years was investigated. However, water pollution assessment needs the interpretation of numerous water quality data with complex and non-linear relationship between data, so, LWPI measure with only ten physicochemical parameters was used to quickly and effectively streamline the numerous data and discern pollution rate, with spatially and temporally water quality analysis data.

The results indicated low water quality in both surface water and groundwater due to leachate penetration. Surface water and groundwater samples close to the dumpsite showed the most pollution impact according to LWPI measure.

Introduction

Lack of fresh water resources is one of the main challenges in the recent century. Due to shortage of sufficient available water resources, especially in arid and semi-arid areas, the protection of existing water resources has the prime importance. Municipal waste and landfilling is one of the main cause of water pollution around the world. Landfills and dumpsites are potential water pollution sources due to leachate generation which migrates into the water bodies [1]. Water pollution due to the leachate migration is considered as a serious environmental threat, and is dependent on leachate age, solid waste degradation rate, composition and amount of the leachate, landfill location, distance from water bodies, soil type, climatic conditions, and etc [2]. Water pollution has been reported as a potential health problem, and a good number of studies have developed various measures to properly monitor water quality [3]. The use of such measures reduces the difficulties of processing numerous water quality indicators, and can be helpful in diagnosing diverse sources of pollution. Some of these measures are mentioned as follows: World Health Organization (WHO) standards for drinking water [3], Horton’s water quality index (WQI) as a rating to show the composite influence of different water quality parameters [4], Brown’s index as the modified WQI with much greater precision in selecting parameters [5], multiplicative water quality index [6], and The Oregon Water Quality Index (OWQI) [7]. Although the latter index can help to assess the water quality management activities more effectively, it should not be adopted for evaluation of water resources in a strongly polluted landfill area[2]. She introduced a Landfill Water Pollution Index (LWPI), to evaluate water pollution due to landfill leachate. LWPI provides a convenient and appropriate measure to recognize water pollution with landfill source which has been applied in the recent studies e.g., [1, 2, 8, 9]. Our study lies on evaluation of LWPI performance (using 10 water quality parameters) on dumpsite of Tabriz city.

Study area

Tabriz is the capital city of East Azerbaijan province at north-west of Iran. The weather is semi-arid with regular seasons. The annual precipitation of Tabriz is around 280 mm, and mostly falls in wet seasons (i.e., October to April). The average temperature during summer and winter times is 25 and 2 °C, respectively. Based on geological foundation of the region, the area is covered by a sand formation which is underlain by a complex of boulder clay.

The dumpsite of the city which is located in north-west of Tabriz at the valley of the mountainous region with the area of approximately 70 ha has been operated since 1997, see Fig. 1. The quantity of the generated waste is roughly 1200 ton per day, which like other developing countries mostly consists of organic materials. Almost all the waste that is transferred to the dumpsite is deposited (Fig.1).

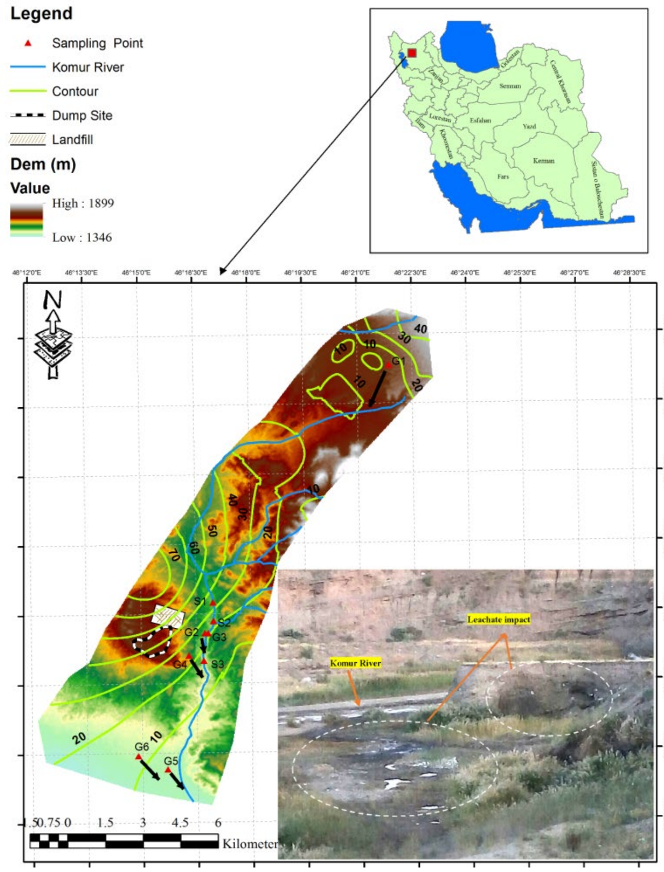

Figure 1. Contaminated sites in Tabriz landfill

Results and discussion

The pH value of the leachate sample from Tabriz dumpsite showed an alkaline nature, indicating that the dumpsite could be classified as mature to old stage [10].

Although the pH values for all groundwater samples are within the range of WHO standards [11], the inflow groundwater pH (G1) was less than the values near the landfill (G2 and G3), moreover, in the far away outflows (i.e., G4 and G5) the pH range was shown to be decrease due to distance from the landfill. The observed pH in the surface water showed increasing trend; so that the S1 sample as the inflow had value less than neutral, but S2 sample, despite being inflow as well showed an increase in pH value proportion to S1. Such increase might be due to the existence of a chicken slaughterhouse before landfill, which probably enters its wastewater illegally to the nearest surface water. The sample S2 was taken from the surface water exactly in the vicinity of slaughterhouse, where there were not any other pollution resource such as plants or even any kind of buildings. Moreover, the samples S1 and S3 were taken from the locations before and after the slaughterhouse, where the increased pH source in S2 is probably due to slaughterhouse. Furthermore, in the history of the google earth map, there is a probable pollution track of wastewater from slaughterhouse, which drains to the Komur River.

Overall, the LWPI results in Table 1 declare the increasing trend in surface water and groundwater when approaching the dumpsite.

Table 1. Calculated LWPI for surface and ground water impacted by Tabriz dumpsite leachate

Season	**Wet season**									**Dry season**								
Sampling points	**S1**	**S2**	**S3**	**G1**	**G2**	**G3**	**G4**	**G5**	**G6**	**S1**	**S2**	**S3**	**G1**	**G2**	**G3**	**G4**	**G5**	**G6**
LWPI	3.6	6.1	17.2	1	1.5	1.6	42.5	2.5	1.5	3.5	4.5	6.5	0.9	1.4	1.4	30.1	1.5	1.2

According to the pollution range division, the surface water was highly polluted even at inflow, however, the leachate impact at outflow of the landfill was increased due to dumpsite effect. In case of groundwater, the LWPI values at sampling points before and after G4 were reported to be less than 2, but in sample G4, LWPI had been dramatically increased to above 30.

In spite of higher variation of ground elevation between dumpsite (located at a mountainous area) and G4 well (located near the Komur River), G4 well is impacted immensely by leachate that corresponds to quantity and quality of leachate and the sandy soil type of the region. The reason for the S3 pollution is dependent on leachate and contaminated runoffs during precipitation, which originated from highlands and passed through the dumpsite and end at Komur River.

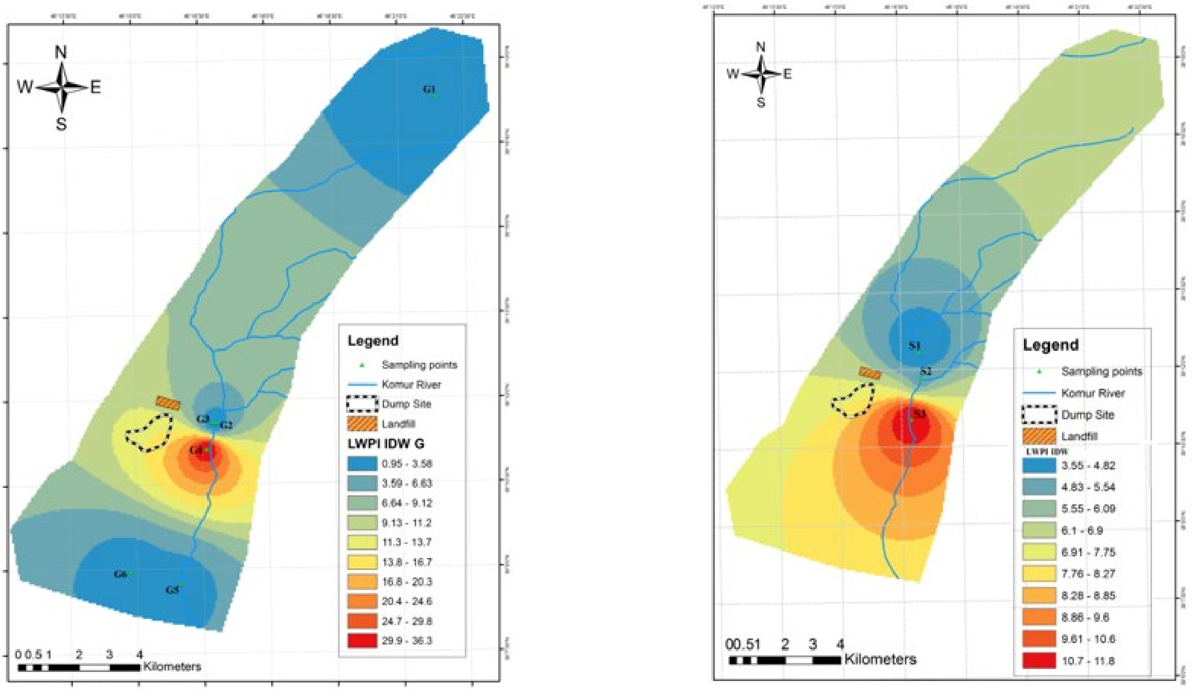

Figure 2. Spatial water pollution interpolation by IDW method according to LWPI a) Groundwater b) Surface water.

Conclusion

The LWPI as an indicator to determine water pollution with the source of landfill leachate revealed that Tabriz city dumpsite had the most negative impact on the surface water and groundwater at S3 and G4 sampling points. The temporal evaluation of water pollution indicated that during the wet season, the LWPI values were higher than dry season, because precipitation and runoff transport contaminations.

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CURRENT HYGIENIC STATE OF AGRICULTURAL SOILS IN KROMPACHY – RUDŇANY REGION

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KEYWORDS
Soil monitoring, soil contamination, risk elements, Krompachy – Rudňany area, Slovakia

ABSTRACT

Krompachy – Rudňany region belongs to the most contaminated sites in Slovakia. Therefore soil survey in more details based on national soil monitoring system was conducted in 2016 year. Current hygienic condition on agricultural land (mostly greenland) has been evaluated. Soil survey consists of 14 monitoring sites where topsoil (depth of 0 - 10 cm) and subsoil (depth of 30 - 40 cm) were sampled and analysed. Basic risk elements were extracted by aqua regia (Cd, Pb, Cu, Zn, Cr, Ni, As, Co) and Hg (total content using AMA analyzer) in chemical laboratory of National Agricultural and Food Centre – Soil Science and Conservation Research Institute in Bratislava.

Based on obtained results the main risk elements in Krompachy – Rudňany region were determined. The most risk elements on agricultural soils of Krompachy – Rudňany region are extended in the following order: Hg, As, Cu, Co, Zn, Ni, Pb and Cd. Contaminated sites are mostly situated in the industrial (metalurgical) areas (anthropogenic impact) and also are affected by occurrence of geochemical anomalies (geogenic impact), as well.

INTRODUCTION

The contaminated region Rudňany-Gelnica is situated on the north edge of Volovské vrchy (hills) in Rudňany and Poráč fold. The paper gives an evaluation of the load of risk elements in agricultural soils around Rudňany and Krompachy in the 2016 year. This area belongs to the most sensitive areas in Slovakia. As the main causes of soil pollution according to Valko et al. 2011 can be identified here by:

- geological threats to soil from historical maining activities;
- risk elements from metalurgy waste deposits;
- geogenic sources influenced by geochemical anomalies occurrence.

The results of above causes is high to very high concentration of risk elements. The most significant is mercury, which is running here in the range 0.11 – 33.5 mg.kg^{-1} (Fargašová, 2009). Namely, thermic processing of ores rich in mercury in Rudňany region was characteristic since 1899 year. Later, after 1991 year the mining activities have been slowly finished. In comparison with Rudňany, in Krompachy region the Slovak electrical factory belong to the main polluter with emitting about 90% of total emissions in Krompachy (Hronec, 2008). Cambisols are predominated soil type on acid metamorphic rocks (pH/KCl 3.6 – 5.7), which are situated on 87.20 % of evaluated agricultural area (Kobza, et al., 2019a). These soils are medium deep to shallow mostly covered by extensive grassland also there are abandoned soils covered by bushes and trees.

METHODOLOGY

The obtained results are evaluated on the basis of soil monitoring system in Slovakia and soil survey in more details, which has been sampling in 2016 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 were selected 14 monitoring sites on agricultural land in Krompachy – Rudňany area. Monitoring sites have been sampled from topsoil (0 - 10 cm) and subsoil (30 – 40 cm). 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 were analysed (Cd, Cr, Pb, Ni, Zn, Cu, Co extracted with aqua regia) and Hg (total content – using AMA analyzer). Obtained results were evaluated using by standard statistical procedures in a GIS environment.

RESULTS AND DISCUSSION

The distribution of risk elements on agricultural soils (topsoil and subsoil) in Krompachy – Rudňany region is given in the following Tables 1 and 2.

Table 1. Content of risk elements (mg.kg^{-1}) extracted with aqua regia in topsoil of agricultural land (0 – 10 cm) in Krompachy-Rudňany region

4.1 Elements 4.2 Statistics	5 As	Cd	Co	Cr	Cu	Ni	Pb	Zn	Hg^1
x	**129.15**	0.60	**17.20**	46.70	**143.10**	39.00	41.30	**171.10**	**12.20**
Xmin	16.60	0.20	7.60	22.30	31.20	17.10	13.80	48.70	0.46
Xmax	259.00	2.10	38.00	119.00	497.00	83.00	112.00	495.00	83.60
Sd	85.50	0.50	8.30	31.10	135.50	20.10	28.80	137.60	24.30
Vc (%)	66.00	84.90	48.40	66.60	94.60	51.50	69.70	80.40	198.80
n	14	14	14	14	14	14	14	14	14

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), **bold** – above-limit values

Table 2. Content of risk elements (mg.kg^{-1}) extracted with aqua regia in subsoil of agricultural soils (30 – 40 cm) in Krompachy-Rudňany region

5.1 Elements 5.2 Statistics	6 As	Cd	Co	Cr	Cu	Ni	Pb	Zn	Hg^1
6.1 x	**87.70**	0.30	**16.50**	42.20	52.30	35.60	14.70	79.00	**1.80**
6.2 Xmin	17.00	0.10	4.60	8.80	11.80	12.70	7.00	28.70	0.10
6.3 Xmax	533.00	0.40	42.40	114.00	124.00	70.70	28.70	166.00	8.40
6.4 Sd	130.40	0.10	9.60	28.40	31.20	17.20	7.30	41.40	2.50
6.5 Vc (%)	148.60	41.60	58,40	67.30	59.80	48.20	49.90	52.40	136.20
6.6 n	14	14	14	14	14	14	14	14	14

Explanations: see Tab. 1

Location of Krompachy – Rudňany region in Slovakia and distribution of risk elements on monitoring sites which exceed valid hygienic limits for Slovakia (MPRV SR, 2013) are illustrated in the following Figs. 1 and 2.

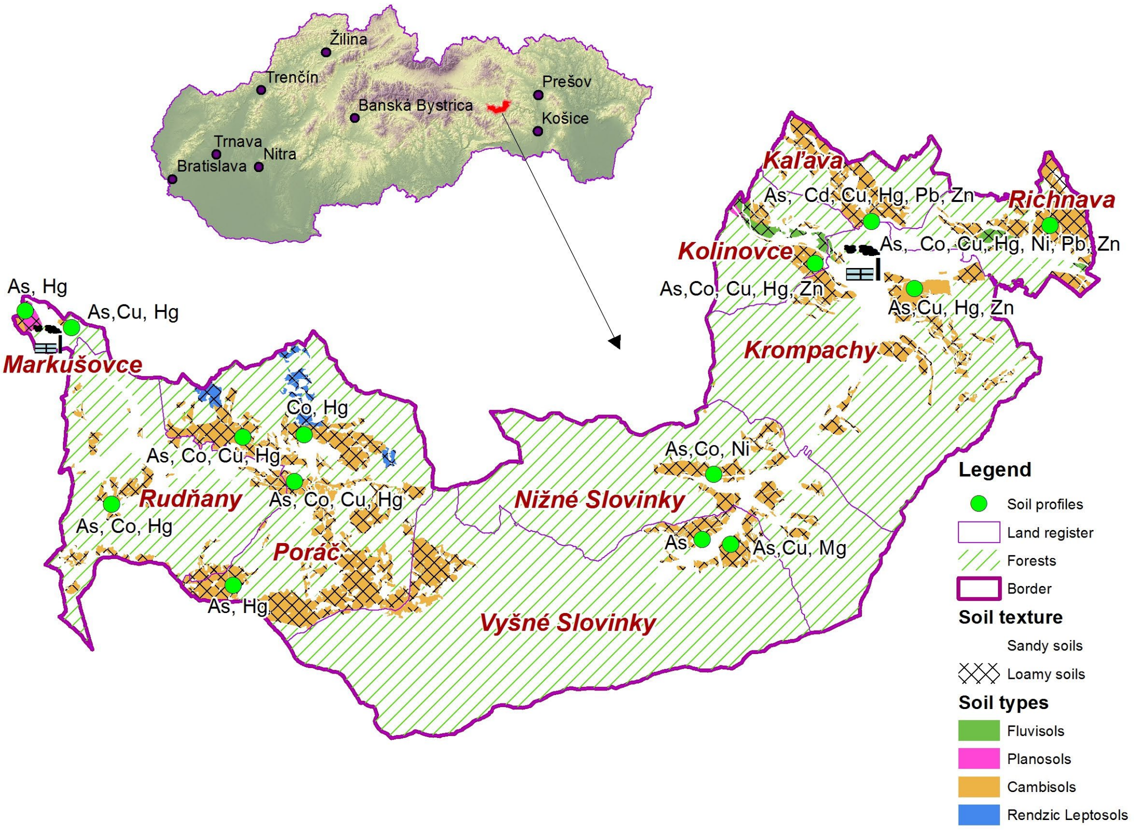

Figure 1. and 2. Krompachy – Rudňany region and distribution of above-limit values of risk elements on agricultural land

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, Wedepohl, 1995). 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). Average content of arsenic exceed the valid hygienic limit for Slovakia (MPRV SR, 2013) in topsoil and in subsoil, as well (Tables 1 and 2). It is an important risk element practically in all evaluated monitoring sites (Fig. 2). Content of arsenic is higher in topsoil in comparisom with subsoil, but it is more variable element in subsoil (Vc = 148.60 % opposite topsoil where Vc = 66 %), where the highest maximum value of As was measured. It depends mostly on geogenic influence.

Average values of **cadmium** in topsoil and subsoil in evaluated area is lower than hygienic limit. Increased value of Cd was indicated only in Kaľava surroundings (Fig. 2). Higher values of Cd were measured in topsoil where are the measured values also more variable. In this case it could be caused probably by anthropogenic input (probably by the influence of emissions from Slovak electrical factory in Krompachy (Kobza et al., 2019b).

Average content of **cobalt** in topsoil and subsoil slightly exceeds the hygienic value (MPRV SR, 2013) – (Tables 1 and 2) and it is higher than average content of Co in agricultural soils in Slovakia which is 8.80 mg.kg^{-1} (Kobza et al., 2014) and in agricultural soils in Czech Republic is 14 mg.kg^{-1} (Poláková et al., 2011). The variability of cobalt is the lowest from among the evaluated risk elements. Difference in Co content between topsoil and subsoil is not wide, what was also confirmed at evaluated of agricultural soils in Slovakia (Kobza et al., 2014). In addition, it may be said that anthropogenic input of cobalt in soils of Krompachy – Rudňany area is not significant.

Average content of **chromium** content in topsoil and subsoil is very low. It means the content of chromium in soil profile is even-tempered and reflects mostly the natural distribution of chromium in evaluated soils, what was also confirmed in agricultural soils of Slovakia (Kobza et al., 2014).

Position of **copper** in comparison with chromium is rather different. The highest content of copper is strongly higher in topsoil (143.10 mg.kg^{-1}, where average value of Cu exceeds the valid hygienic limit for Slovakia (MPRV SR, 2013). In this area it is caused by industrial input of copper because in the last century (1937 – 1938 years) Krompachy smelter started producing copper (Očvára et al., 1987).

Average content of **nicke**l in topsoil and subsoil is lower (39 – 35.60 mg.kg^{-1}) than valid hygienic limit for predominated loamy soils (50 mg.kg^{-1}). Increased values of Ni were indicated only in Richnava and Nižné Slovinky surroundings (Fig. 2). In comparison with average content of Ni in agricultural soils of Slovakia (29.43 mg.kg^{-1}) (Kobza et al., 2014), in this case it is probably only increased background value of Ni. Finally, similar values of Ni in agricultural and forest land of Slovakia were found out also by Čurlík and Šefčík, 1999 (on average 25 mg.kg^{-1}).

Average content of **lead** in topsoil and subsoil is lower than valid hygienic limit (MPRV SR, 2013). Increased values of Pb were indicated only in Kaľava and Richnava surroundings (Fig. 2).

High content of **zinc** was determined in topsoil (on average 171.10 mg.kg^{-1}). Its content in agricultural soils in Slovakia is running in the range 40 – 120 mg.kg^{-1}) (Kobza et al., 2014). Content of Zn in subsoil is significantly lower (Tab. 2). Zinc is rather variable in topsoil and in subsoil (Coefficient of variability is higher than 50 %). According to our latest results about 36 % of agricultural land of evaluated area is affected by zinc (Kobza et al., 2019a).

Average content of **mercury** in agricultural soils of Krompachy – Rudňany region is strongly high as a result of natural mineralogical composition (occurrence of cinabarite – HgS) and hazards from metalurgy where the mercury rich ores were processed. The high variability (the highest from among the evaluated risk elements) is characteristic for mercury in evaluated soils (>100 %) (Tables 1 and 2) caused by volatility of Hg, what was also confirmed in our previous work (Kobza et al., 2014).

CONCLUSIONS

Based on obtained results the most risk elements on agricultural soils of Krompachy – Rudňany region are in the following order: Hg, As, Cu, Co, Zn, Ni, Pb and Cd. Contaminated sites are mostly situated in the industrial (metalurgical) areas (anthropogenic impact) and also are affected by occurrence of geochemical anomalies, as well. Finally, it may be said that despite the cessation of industrial activities, the unfavourable hygienic situation persists and therefore it will be necessary this poor hygienic condition of soils to monitor also in the future.

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ARSENIC

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SUMMARY

Gold-arsenic, arsenic and gold-antimony deposits in Georgia are of significant economic importance. Realgar As_4S_4 - Orpiment As_4S_6 (Lukhuni, Racha) and Arsenopyrite FeAsS (Tsana, Svaneti) ores of Georgia are unique in the world. The arsenic content in these ores is particularly high and reaches an average of 12%. Although the mining of arsenic deposits have temporarily ceased, important volumes of As containing industrial wastes are present at the various mining sites, located at the *Racha, Svaneti.*

Arsenic has long been known because of its acute and long-term toxicity. It occurs in soil and minerals and it may enter air, water and land through wind-blown dust and water run-off. It causes serious pollution when it enters rivers or ground water, and it is a particular problem where either of these sources are used as drinking water supplies. Although the mining facilities are now out of operations, the environmental pollution resulting from the former activities is still acting. Recent studies have shown that the content of arsenic in the soils around the factory were 20 to 30 times those of background levels. However, the nature, importance and extent of the environmental effects of the As mining in Georgia are very poorly known.

This article intends to assess the environmental impact of the arsenic -As mining and to evaluate the various approaches for remediation/rehabilitation of the mining sites, considering the socio-economic context of the county.

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 [1]. The most common of the arsenic minerals is arsenopyrite FeAsS, Realgar As_4S_4 , orpiment As_2S_3. 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 [2].

The occurrence of As mineral deposits in Georgia Gold-arsenic, arsenic and gold-antimony deposits in Georgia are of significant economic importance.

Realgar 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 (Realgar As_4S_4- Orpiment As_4S_6(Lukhuni, Racha)) do not contain impurity elements. 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.[3] 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.

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.

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, Georgia) 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. 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 [4,5]. 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.

The behaviour of As in the environment

As in water Arsenic in drinking water is a major public health problem threatening the lives of over 140 million people word wide. The acute toxicity of arsenic in high concentration has been known about for centuries, but only recently has strong adverse effect on health been associated with long-term exposure to even very low concentrations. Over the past few decades, naturally occurring arsenic has been discovered in groundwater used to supply drinking water in many countries on all continents. Long-term exposure to arsenic in drinking-water is causally related to increased risks of cancer in the skin, lungs, bladder and kidney, as well as other skin changes such as hyperkeratosis and pigmentation changes. These effects have been demonstrated in many studies using different study designs. Exposure–response relationships and high risks have been observed for each of these end-points. Extensive information concerning health effects of ingestion of inorganic arsenic in drinking-water comes from a series of studies performed in Taiwan. In the late 1960s, exposure to arsenic from drinking-water was suggested to be the cause of BFD). The effects have been most thoroughly studied in Taiwan but there is considerable evidence from studies on populations in other countries, mainly in Georgia as well. The dissolved forms of arsenic in the water column include arsenate, arsenite, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). Some As (III) and As (V) species can interchange oxidation states depending on Eh, pH and biological processes . Some arsenic species have an affinity for clay mineral surfaces and organic matter, and this can affect their environmental behaviour. Methylation and demethylation reactions are also important transformations controlling the mobilization and subsequent distribution of arsenicals. Transport and partitioning of arsenic in water depends on the chemical form of the arsenic and on interactions with other materials present. Arsenic may be adsorbed from water on to clays, iron oxides, aluminium hydroxides, manganese compounds and organic material). The distribution and transport of arsenic in sediment is a complex process that depends on water quality, native biota and sediment type. There is a potential for arsenic release when there is fluctuation in Eh, pH, soluble arsenic concentration and sediment organic content. When an arsenic containing material comes in contact with water, substantial amounts of arsenic can be released into the environment. If the material is present in deeper formations, arsenic can be brought to the surface by thermal springs. When the arsenic bearing formation is near the surface, weathering and erosion release substantial amount of arsenic into the environment. Arsenic either accumulates in soils and sediments, or is diluted in natural waters. Streams and glaciers can transport arsenic over distances of several 100 kilometers. In soils, sediments, and relatively stagnant, particle rich waters, arsenic typically binds to iron or aluminum oxyhydroxides and to clay minerals. Under certain conditions it can be remobilized, for example, if the pH increases to above 7.5, or when the absence of oxygen leads to iron reducing conditions

As in the air Arsenic is released into the air by volcanoes, through weathering of arsenic-containing minerals and ores, and by commercial or industrial processes. Some arsenic compounds are relatively volatile and consequently contribute significant fluxes in the atmosphere. It has been estimated that the atmospheric flux of As is about 73 540 tons/year of which 60% is of natural origin and the rest is derived from anthropogenic sources. Arsenic is primarily emitted into the atmosphere by high-temperature processes such as coal-fired power generation, smelting, burning vegetation and volcanism. Natural low-temperature biomethylation and microbial reduction also release arsenic into the atmosphere; microorganisms can form volatile methylated derivatives of arsenic under both aerobic and anaerobic conditions, and can reduce arsenic compounds to release arsine gas. Arsenic released to air exists mainly in the form of particulate matter. These particles are dispersed by the wind to a varying extent, depending on their size, and the particles are returned to the earth by wet

or dry deposition. Arsines that are released from microbial sources in soils or sediments undergo oxidation in the air, reconverting the arsenic to less volatile forms that settle back to the ground. A case of lung cancer associated with exposure to arsenical dust was brought to the notice of the British Factory Department, and some further cases were detected in the early 1940s. These reports were followed by an investigation of the matter, and a remarkably elevated relative cancer mortality rate from lung and skin cancer was observed in a sheep-dip factory manufacturing sodium arsenite.
In Racha and Svaneti region arsenic was 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.
Assessment of the presence of As in soils Arsenic from weathered rock and soil may be transported by wind or water erosion. However, because many arsenic compounds tend to adsorb to soils, leaching usually results in transportation over only short distances in soil. However, rainwater or snowmelt may leach soluble forms into surface water or groundwater, and soil microorganisms may reduce a small amount to volatile forms (arsines) . Under reducing conditions, arsenite dominates in soil but elemental arsenic and arsine can also be present. Arsenic would be present in well-drained soils as $H_2AsO_4^-$ if the soil was acidic or as $HAsO_4^{2-}$ if the soil was alkaline. Oxidation, reduction, adsorption, dissolution, precipitation and volatilization of arsenic reactions commonly occur in soil. In the porewater of aerobic soils arsenate is the dominant arsenic species, with small quantities of arsenite and MMA in mineralized areas. Natural levels in soils usually range from 1 to 40 mg/kg, but pesticide application or waste disposal can produce much higher values. The highest concentrations of arsenic in Racha & Svaneti soil tend to be associated with mining waste.

Proposal of remediation technologies
Remediation technologies should be proposed aiming at minimization of risk at waste disposal sites.

Removal of Arsenic from water
Several remediation approaches for removing arsenic for municipal water supplies are common. These include: oxidation and stripping, coagulation, precipitation, and filtration using iron and aluminum salts, lime softening, ion exchange resins, membrane processes (e.g. reverse osmosis), adsorption onto commercially-available alumina, activated carbon, activated bauxite, or Granular Ferric Hydroxide. A new system, Electrochemical Arsenic Removal (ECAR) has been developed at Lawrence Berkeley Laboratory is now being tried in the field both in India and in Bangladesh. In many cases, there are plans to solve the problem by developing new springs and groundwater sources, which is relatively expensive .In some places it may be possible to remove the arsenic by oxidation of the aquifer. This is the aim of the Subterranean Arsenic Removal (SAR) technology proposed by Mukherjee of Kolkata, India. They claim" This technology can transform the way arsenic is removed from groundwater in Ganges, Brahmaputra and Mekong delta where the arsenic is of arsenopyrite origin, saving millions of lives. This includes affected areas of India, Bangladesh, Cambodia, Nepal, Vietnam and Thailand. The technology is about to be implemented in Cambodia and Burkina Faso with the help of Royal University of Phnom Penh and ‘Friends in Action International’ respectively, subject to proper research. The technology is scalable from a production capacity of 10,000 liters/day (USD 4,000) to 1,00,000 liters/day (USD 20,000) for each plant, catering to the drinking water needs of 2000 to 20000 people, depending on the soil & water conditions." A couple of years ago Harvey tried experiments along these lines with limited success. The information from well water surveys such as that of the British Geological Survey and Mott MacDonald shows that many deep wells, greater than 150 meters in depth, are free of arsenic. This seems to be confirmed by more detailed studies from an MIT/BUET (and others) group and a Columbia University group. Dhaka and the southern part of Bangladesh (where salt water enters the shallow aquifer)are mostly free of arsenic. [6] The reason appears to be that there is a clay layer below the aquifer from which most tube wells take their water and these deep wells tap a lower aquifer. But this is not true, for example, in Jessore where there is no clay layer. It is claimed that these deep wells are cheaper than most other alternatives. As of 2009 this has been the major mitigation solution and is supported by the funding

agencies, World Bank and UNICEF and the Department of Public Health Engineering (DPHE). More important, however, is that these retain much of the simplicity of the "ordinary" tube wells and require less care in construction and less maintenance than other solutions. A comparison of the Bangladesh government reports in 2002 and 2006 shows the increased confidence in deep tube wells as the preferred solution for75% of the country.

But there are potential problems that should be considered in any implementation:
- if such wells are dug carelessly, and not properly grouted, there is a possibility of "shunting" the aquifers and allowing water from the higher aquifer to contaminate the lower aquifer.
- it is unsure whether the lower aquifer is a "closed" aquifer from a hydro geologic point of view or whether it is as easily recharged as the upper aquifer.
- It is unclear whether, in a longer term, pumping from these wells would increase the arsenic level.

2. Removal of Arsenic from soils

Low cost in-situ chemical fixation treatment is designed to react contaminated soils directly with treatment solutions to cause the formation of insoluble arsenic-bearing phases and thereby decrease the environmental leachability of arsenic. Combinations of ferrous sulfate, potassium permanganate and calcium carbonate used as major reagents for the chemical fixation solutions. Sequential leaching with an extraction fluid described in the EPA synthetic precipitation leaching procedure (SPLP) used to simulate the long-term leaching behavior of treated soils under natural conditions.

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)-orpiment(As_4S_6) and arsenopyrite FeAsS ores of Georgia and from the residuals of pyrometallurgical processing. 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. 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. The heterotrophic *Thiobacillus ferrooxidans* strain has been used for the purpose[7-9]. The proposed methods 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. The obtained extract is the best isolated substance to produce not only high purity arsenic for semiconductor systems, but also other products such as arsenic trioxide, antimony trioxide, sulphur, silver, gold [10-13], which are the main precursors of a novel materials. The most important ones are antibacterial arsenic Nano composites[14].

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LESSONS LEARNED IN REMEDIATION OF THE MOST POLLUTED SITE IN LATVIA – INCUKALNS ACID TAR PONDS

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KEYWORDS
Historically contaminated sites, pollution, innovations, risk assessment, risk management

ABSTRACT

Historically contaminated sites ”Inčukalns acid tar ponds” were established and operated as two waste dumpsites - Northern pond and Southern pond – from fifties to eighties of 20th century. Waste from the oil lubrication production, medical, perfume oil production and other chemical product production plants containing mixture of used lubricating oils and sulphuric acid tar was dumped in a sand quarries without any bottom and side insulation. The industries that produced the waste do not exist anymore and thus “polluter pays principle” cannot be applied to implementation of the remediation project. Waste material is extremely complex substance due to variety of physical and chemical processes that took place in the ponds. The dumpsite was closed in 1986, since then the leachate from both acid tar ponds has infiltrated into the groundwater and artesian waters of 70 – 90 m depth and migrated north towards the Gauja river. The distribution range of contaminated ground waters: for the Northern pond – approximately 150 ha, for Southern pond – approximately 140 ha. [1]

Figure 1. Threats to birds from acid tar [1]

Remediation of Incukalns acid tar ponds started more than 10 years ago and it is financially biggest environmental project in Baltics. Implementation of the project is assigned to State Environmental Service of Latvia. The aim of the project is to prevent further spreading of pollutants, especially acid tar waste matter emissions from source of pollution on groundwater, surface water and soil. The main activities focus on elimination of the pollution sources in Southern and Northern acid tar ponds thus minimising the negative effects and improving environmental quality in the future.

Figure 2. Remediation of Southern acid tar pond [1]

Remediation projects are usually complex, individual, and multidisciplinary due to close interactions between social, economical and environmental dimensions, Incukalns acid tar pond remediation project is not exception. During the implementation of the project different physical, geological, technical and administrative challenges such as atypical chemical and physical properties of acid tar, malfunctioning technologies, non-specific regulation framework and other emerged demanding to come up with more and more inovative and corresponding solutions. The risk management over the project implementation stage has been very crucial especially if there has been a lack of sufficient feasibility studies in project preparation stage. Various methodologies, procedures and inovations have been implemented during the project such as pilotprojects for applied technologies, duplicating local laboratory on site, different control procedures and metodologies agreed with the parties involved etc.

Our experience shows that the key to success is communication, mutual cooperation and willingness not only to face challenges, but also to prevent possible problems in advance as in the project preparation stage as well as during the project implementation stage and aftercare period.

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PROJECT: HISTORY OF ANTROPOGENIC SEDIMENT CONTAMINATION IN INDUSTRIALIZED RIVER SYSTEMS (GRANT PROJECT: DSGS-2021)

EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání

MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

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KEYWORDS

Contamination history, fluvial sediments, stratigraphic analysis, caesium dating, sedimentary geochemistry, environmental risk assessment, magnetic susceptibility, organic pollution.

ABSTRACT

River systems are important pathways for transport, deposition and reworking of sediment in populated areas. River sediments are carriers of toxic elements (Cu, Zn, Pb, Hg, Cd, etc.), radioactive isotopes and organic compounds from agriculture, industry, municipal waste and transportation. Sediments of river channels, floodplains, abandoned meanders and dam reservoirs therefore act as sinks for anthropogenic contamination, which can be mobilized during floods, dam removals, and other interventions in water courses, and pose serious environmental hazards in the future. Despite the present-day efforts to reduce anthropogenic contamination from primary sources, the risk from old ecological burdens from the 18th to the 20th century persists. Goal of the project is to identify hotspots of old anthropogenic contamination in the Bečva, Lubina and Ondřejnice catchments, to and perform their environmental risk assessment.

INTRODUCTION

River systems sediments and lake sediments in many industrial areas may act as perennial or intermittent traps for anthropogenic contamination. Contamination history over the last few decades is of special significance for Central and Eastern Europe as it can reflect high pollutant levels from the second half of the twentieth century (Žák et al., 2009; Lecce and Pavlowsky, 2014). Significant sources of pollution from the machinery and chemical industry can be found on the Lubina River and Ondřejnice River - a right-hand tributaries of the Odra River (Frenštát pod Radhoštěm, Kopřivnice, Příbor) which is mainly contaminated by organic pollutants (POP), polycyclic aromatic hydrocarbons (PAU), pesticides together with heavy metals and radioactive elements (Heim and Schwarzbauer 2013), and especially in the Bečva River basin near Valašské Meziříčí. Some of these contaminants can be used as indirect proxy markers for dating these sediments (for example isotope ^{137}Cs). Until now, contamination in river sediments has not received much attention, as state-owned companies managing river basins in the Czech Republic are not obliged to study the historical pollution of the river systems. Due to this shortcoming, there is ample scope for academic research (Bábek et al., 2008; Faměra et al., 2018; Grygar et al., 2016).

Contaminants of natural origin enter the cycle due to erosion and are transported, reprocessed and re-deposited. So-called hot-spots affecting the geochemistry of the area are thus created. Another source of contamination is anthropogenic activity (industry, burning fossil fuels, mining, etc.). The carriers of contamination in these river and lake sediments are mainly organic material, fine-grained soil particles (Bábek et al., 2008) and ferromagnetic particles (technofossils) together with ferromagnetic minerals (magnetite, titanomagnetite, etc.), which can be formed by human activities (Faměra et al., 2021) and in a natural way.

The aim of this project is to analyze historical contamination in their depositional systems (reservoirs, river banks, ponds and floodplains).

Another goal will be to try to separate anthropogenic contamination from natural sources of ferromagnetic elements such as the ultramafic igneous rocks cropping out in the catchments of the studied rivers.

MATERIALS AND METHODS

Maps of historical and current locations of riverbeds and other water bodies were created in the QGIS program. Historical maps (II. and III. military mapping) and available orthophoto images (1954-2021) were used to compile these maps, as well as a digital relief model available from the ČUZK website. Based on these analyzes in the QGIS program, the most suitable sampling sites were selected.

The collected material came from six types of sedimentary environments:

1) Water bodies (lakes and ponds)
2) Defunct water bodies (old lakes and historic ponds)
3) Oxbow lakes
4) River cliffs
5) Sediments of active river channel
6) Floodplain sediments

A slotted drill bit from the company Eijkelkamp (drill bit width: 4.0 cm; drill bit length: 1.0 m) was used to collect drill cores (old no longer existing historical ponds and lakes, oxbow lakes, active river channels and floodplain sediments). All the collected drill cores were already photographed in the field, lithologically described and divided into plastic bags at an interval of 2,0 cm. The samples were subsequently dried in the laboratory at a temperature of 40° C. After drying, the samples were analyzed in the laboratory.

Sampling from the river cliffs was carried out using a stainless steel shovel and segmented with the help of a stretched band at an interval of 4,0 cm along the entire length of the profile. Subsequently, the samples were stored in plastic bags and lithologically described. The profile was photographed directly in the field. In the laboratory, the samples were again dried at a temperature of 40°C.

Water bodies were sampled using a small inflatable boat and a piston sampler (Multisampler) for underwater sediment sampling (drill width: 4.0 cm; drill length 1.0 m). All the collected drill cores were photographed in the laboratory, lithologically described and divided in the interval of 2,0 cm at plastic bags. The samples were subsequently dried in the laboratory at a temperature of 40°C.

Samples were taken separately for the analysis of organic contaminants (POPs, PAHs, pharmaceuticals, pesticides, etc.) using either a slotted drill bit from the Eijkelkamp company (drilled samples from e.g. floodplain sediments) or a stainless steel shovel (samples coming directly from the active river channel). These samples were then wrapped in aluminium foil, sealed in plastic bags and then placed in a portable car refrigerator. After the completion of the field work, the samples were immediately sent for laboratory analysis at the Department of Analytical Chemistry of the Faculty of Science, UP.

In the laboratory phase of the research, the weight of the dried samples was measured and the following laboratory methods were measured: magnetic susceptibility, gamma spectrometry, granulometry, ED-XRF, spectral photometry, magnetic separation of particles and dating using the ^{14}C method.

ERT (Electrical Resistivity Tomography), DEMP (Dipole Electromagnetic Profiling) and GPR (Georadar) geophysical measurements were carried out too.

PERFORMED AND PLANED ACTIVITIES

In the period from 1. 1. 2022 to 30. 9. 2022 a total of 34 borehole samplings of river sediments were carried out (Tab. 1.). In total, there are 1473 samples. All samples taken from river sediments were analyzed by magnetic susceptibility, gamma spectrometry, and almost half of the drill cores were grind and measured by ED-XRF, spectral photometry, and granulometry. Several samples were also sent for ^{14}C isotope dating. Measurement of other methods is still ongoing.

Furthermore, samples were taken for the analysis of organic pollutants. These subscriptions are still ongoing.

Furthermore, 6 drill cores were taken from water bodies in the floodplains of the studied rivers (Tab. 1). In total, there are 345 samples. Currently, these samples are being dried in the laboratory.

ERT (Electrical Resistivity Tomography), DEMP (Dipole Electromagnetic Profiling) and GPR (Georadar) geophysical measurements have been carried out at one selected location and further measurements will follow.

Table 1. Number of cores taken according to the sedimentation environment and localities.

Sedimentary environment	**River Bečva**	**River Ondřejnice**	**River Lubina**
Active river channel	3	1	4
Floodplain sediments	5	-	4
Oxbow leaks	6	1	3
River cliffs	2	1	-
Water bodies	3	-	3
Defunct water bodies	4	-	-

GOALS OF PROJECT

1) Identification of the main outbreaks of contaminated sediments along the studied watercourses
2) Calculation of the rate of accumulation of contaminated sediments based on historical data and dating of 14C and 137Cs
3) Description of contamination time by toxic material and organic pollutants
4) Distinguishing signals of contaminants from natural and anthropogenic sources

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REMEDIATION OF A FORMER MINE TECHNOSOL HIGHLY CONTAMINATED WITH AS AND PB USING (IN) ORGANIC AMENDMENTS COMBINED WITH SALIX SPECIES: A 5-YEAR FIELD STUDY

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KEYWORDS
Mine, Metal(loid)s, Biochar, Compost, Iron sulfate, Willows, Phytomanagement

ABSTRACT

The huge amount of wastes, contaminated by metals and metalloids, generated by the past and present mining extraction activities presents a big issue, due to the high toxicity of metal(loid)s which endangers the environment (*e.g.,* loss of biodiversity) and human health (*e.g.,* cancers, chronic diseases) [1]. An environment-friendly solution to remediate such contaminated sites has developed and attracted research interest, phytomanagement. This process has two outcomes: remediate the soil and produce biomass with a market value [2]. It relies on the growth of the plants, which is often hampered by the poor fertility and high contamination levels in these areas. Soil fertility can be improved through the application of amendments to the soil, such as biochar (product of pyrolysis of biomass under low oxygen conditions) [3], compost [4], and iron-based products [5]. Such amendments showed positive results when applied to polluted soil in greenhouse experiments: increase of soil pH, ameliorate soil organic matter content and nutrient availability, and reduction of metal(loid) mobility and availability, leading to an improvement of plant growth [6]. However, long-term field testing of those amendments is still scarce. Moreover, in addition to amendments, it is crucial to select species that will produce a high biomass and with a reduced translocation of metal(loid)s to their upper parts. In this regard, several willow species showed potential, although the accumulation and translocation of metal(loid)s were affected by soil amendments [7,8]. In this context, a field experiment was implemented to evaluate the effect of three amendments, alone or combined, to ameliorate soil fertility, lower metal(loid) toxicity, and improve willow growth. The final aim was to determine which combination of amendment-willow species allows the valorization of the produced biomass for industrial purposes, based on the regulations.

The field experiment has been implemented 5 years ago on a former mine technosol, located in Pontgibaud (France). The study focused on the second settling pond, which is highly contaminated with As and Pb, has an acidic pH, a low organic matter content and nutrient availability (Table 1). A 202 m² plot was implemented and subdivided into four plots (9.6 m x 4.5 m) separated by 1 m. The four treatments, each one corresponding to a bloc, were: (i) 2 % biochar (PB), (ii) 5 % compost (PC), (iii) 2 % biochar + 5 % compost (PBC), and (iv) 2 % biochar + 5 % compost + 0.15 % iron sulfate (PBCS) (Figure 1). The biochar was made from hardwood biomass pyrolyzed at 500 °C, the compost was a commercial product, Algoflash (culture medium NF U 44-551), made from peat moss, softwood

bark, green compost, and seaweed, and the iron sulfate was a commercial product (E-Leclerc) (Table 1). Amendments were incorporated at 25 cm depth, on March 31st, 2017. Each bloc was subdivided into three: the first subplot (4.5 m x 4.8 m) was vegetated by 4 willow species, the second subplot (2 m x 4.8 m) was sown with *Trifolium repens*, and the third subplot (2 m x 4.8 m) was left unvegetated to evaluate natural revegetation. The tested willow species were *Salix purpurea*, *Salix alba*, *Salix triandra,* and *Salix viminalis*. Inside the subplot, 42 rooted cuttings (85 days old) were placed in a randomized design.

Table 1. Pontgibaud soil and amendments physico-chemical properties. ND = not determined. Data from [9]

	Pontgibaud	Compost	Biochar	Iron sulfate
pH	4.82 ± 0.01	7.40 ± 0.02	8.46 ± 0.01	2.58 ± 0.00
Electrical Conductivity (µS.cm^{-1})	68 ± 1	801 ± 24	302 ± 1	ND
Water Holding Capacity (%)	29.80 ± 0.47	312 ± 9	212 ± 4	ND
Total [As] (mg.kg^{-1})	1068 ± 20	ND	ND	ND
Total [Fe] (mg.kg^{-1})	6325 ± 114	ND	ND	ND
Total [Pb] (mg.kg^{-1})	23387 ± 1020	ND	ND	ND
NH_4N0_3 [As] (mg.kg^{-1})	2.29 ± 0.25	0.7 ± 0.3	0.9 ± 0.1	16.5 ± 0.5
NH_4N0_3 [Pb] (mg.kg^{-1})	4198 ± 134	0.4 ± 0.0	1.6 ± 0.1	22.2 ± 0.9
NH_4N0_3 [Fe] (mg.kg^{-1})	0.02 ± 0.02	1 ± 0	18 ± 5	23265 ± 299

Six months after the amendment application, soil samples were collected using a 2 x 2 m grid, and analyzed for pH, OM content, P and K availability, and As, Fe, and Pb soil fractions. Only the results of the non-vegetated subplot will be discussed. Leaves were sampled after 18 months of growth for As and Pb measurement, while the entire stem biomass production was harvested after 22 months and 55 months for dry biomass assessment, and As and Pb measurement.

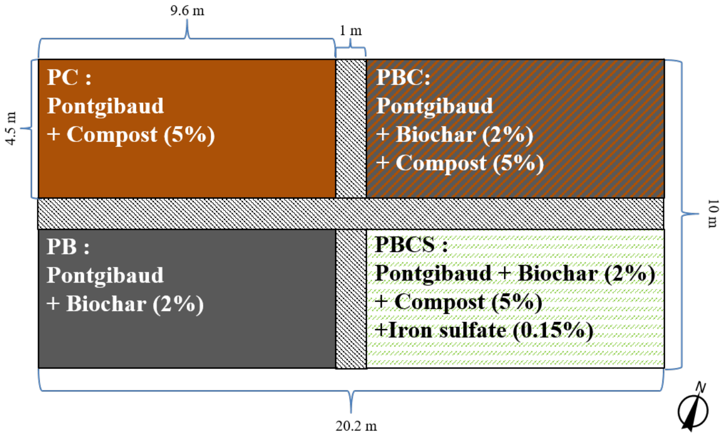

Figure 1. Experiment set-up

After six months, soil pH was the highest in the treatment containing both biochar and compost (pH 7.1), while the other three treatments had lower but similar pH (pH 5.5 on average), which were higher than non-amended soil. Organic carbon content was also increased by the amendments, with the highest value measured in PBC (6.5 %, compared to 0.3 % in the control). Potassium availability was improved in the amended conditions, especially when biochar and compost were added together (98-fold).

At the first cut, Species, Treatment and Species x Treatment effects were significant. The highest fresh weights were recorded on the bloc amended with biochar and compost, Among the 4 genotypes, *Salix triandra* presented the highest biomass production (Figure 2). At the second cut, fresh biomass was lower for all species on PB and PC and for *Salix triandra* and *Salix purpurea* on PBC and PBCS. The highest biomass was again recorded on PBC treatment. Among the species, the lowest biomass was measured for *Salix purpurea*, and the highest for *Salix alba*, although this species did not significantly differ from the other two.

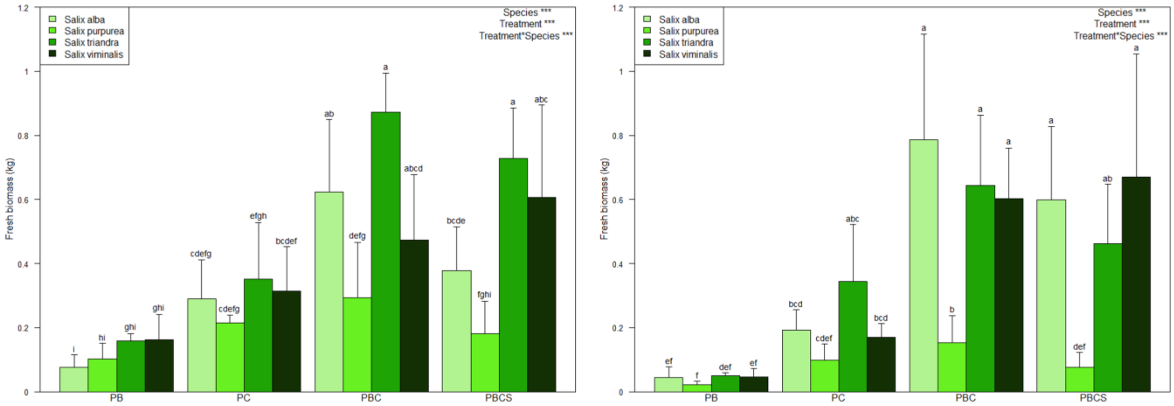

Figure 2. Fresh biomass (kg) produced by the different willow species on the four treatments after 22 months (left) and 55 months (right).

In the leaves sampled after 18 months, species, treatment and their interaction had no effect on As concentrations while the effect was highly significant for lead. On average, leaf Pb concentrations were the highest in the treatment PBCS and the lowest in PBC, and the highest concentrations were measured in *Salix alba* and the lowest in *Salix triandra*.

In February 2019, when the stems were sampled, arsenic concentrations were the highest in *Salix purpurea* while the species *Salix alba* and *Salix viminalis* presented concentrations below the quantification limit when grown on PB and PBC. The maximal permissible As concentration for a classification 2910-B (allowing the use of by-products as combustibles) is 5 mg.kg^{-1}, and stem concentration was below this threshold in six cases: *Salix alba* on PB, PBC, *Salix viminalis* on PB, PBC, *Salix triandra* on PC, PBCS. Lead concentrations were the highest in *Salix alba* and on average, the lowest concentrations were measured in PB treatment. In most cases, concentrations were below permissible limits for the 2910-B classification (50 mg.kg^{-1} Pb). In the second sampling, most Pb concentrations were below permissible. The lowest values were measured in *Salix purpurea* and *Salix triandra*, and in compost amended plots.

In conclusion, *Salix triandra*, on the biochar-compost-iron sulfate treatment, presented a high biomass production, associated with As and Pb concentrations in the upper parts below the threshold value to use it for energy production, adding an economical benefit to the process. This long-term field study demonstrates the potential of organic amendment association with iron sulfate to remediate highly contaminated soil, as well as the potential to produce energy from the biomass.

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MERCURY CONTENTS IN LARGEMOUTH BASS (*MICROPTERUS SALMOIDES*) FROM THE VALDEAZOGUES RIVER, ALMADÉN HG MINING DISTRICT, SOUTH CENTRAL SPAIN

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KEYWORDS

Potentially toxic elements (PTE), Mercury, fish, *Micropterus salmoides*, mining-related Pollution, Almadén, Spain.

ABSTRACT

The Almadén district has been the World's largest producer of mercury (Hg), for more than 2000 years. The mining activity in the district ceased some 20 years ago; however, the generalized pollution of soils and stream sediments, as well as the atmospheric emissions from these and other sources, still represent possibilities to toxify the human food chain. The Valdeazogues river crosses completely the district, with some 150 km^2 extension, and including a huge mine, three mines of median importance, and up to 60 points where cinnabar (HgS) has been recognized.

Largemouth bass (*Micropterus salmoides*) is a carnivorous freshwater gamefish, very common along the Valdeazogues river. For years it was fished to complement the diet of the local inhabitants, although nowadays is not so common to consume it. We obtained 28 specimens, with sizes between 69 and 335 mm and weight between 11 and 552 gr, in a transect from the El Entredicho open pit to a site downstream the district (some 36.3 km). The specimens were analyzed for total Hg using atomic absorption spectrometry with Zeeman effect.

Results show important variations throughout the transect; the largest fish in terms of weight and length had the highest Hg concentration (5246 ng g^{-1}), much higher than the fish with the lowest concentration (473.2 ng g^{-1}), which was not the specimen with the lowest size. Besides, as we go downstream the Valdeazogues River, moving away from the Entredicho Mine (considered to be the main source of contamination), Hg concentrations drops considerably until stabilizing at approximately 1200 - 1500 ng g^{-1}.

INTRODUCTION

The presence of Hg in the environment is a Worldwide concern, since this element bioaccumulates in the human food chain, in particular though the bioaccumulation and biomagnification in fish (Fitzgerald and Clarkson, 1991). Inorganic Hg can be transformed into methylmercury ($[CH_3Hg]^+$) throughout physicochemical and biological reactions, occurring in riverine areas: this organic chemical form of Hg has a high toxicity (Craig, 1986), and it is bioconcentrated in fish, and strongly biomagnificated in carnivorous fish, such as *Micropterus salmoides* (Clarkson, 1990).

Mining areas can be considered as 'natural laboratories', with the possibility to study in detail the Hg environmental cycling as well as the possibilities of this element to affect general population. The Almaden Hg mining district is one of the best possible example of such type of areas, since it has been exploited for mor than 2000 years, producing almost one third of total world's production of this element (285,000 t), so important for industry during long periods of the XVI to XX Centuries.

Several toxicity events, and in particular Minamata bay incident (Harada, 1982) caused the decrease and cessation of industrial applications of Hg, and the closure of the Almadén mine in year 2002, although remediation actions had to wait until 2008. But the Almadén district is not only the Almadén mine. Hernández et al. (1999) describe the geology and mining history of the area. Almadenejos is a locality located some 15 km to the East of Almadén, and it is the site of other smaller but still significant Hg ore deposits, exploited in different moments of history; furthermore, in the complete district, with some 150 km^2 extension, the presence of cinnabar has been identified in some 60 sites. The Valdeazogues river starts some 30 km to the East of El Entredicho, an open pit which is located westernmost in the mining area, and goes through all the mining area, receiving Hg polluted inputs from diverse tributaries.

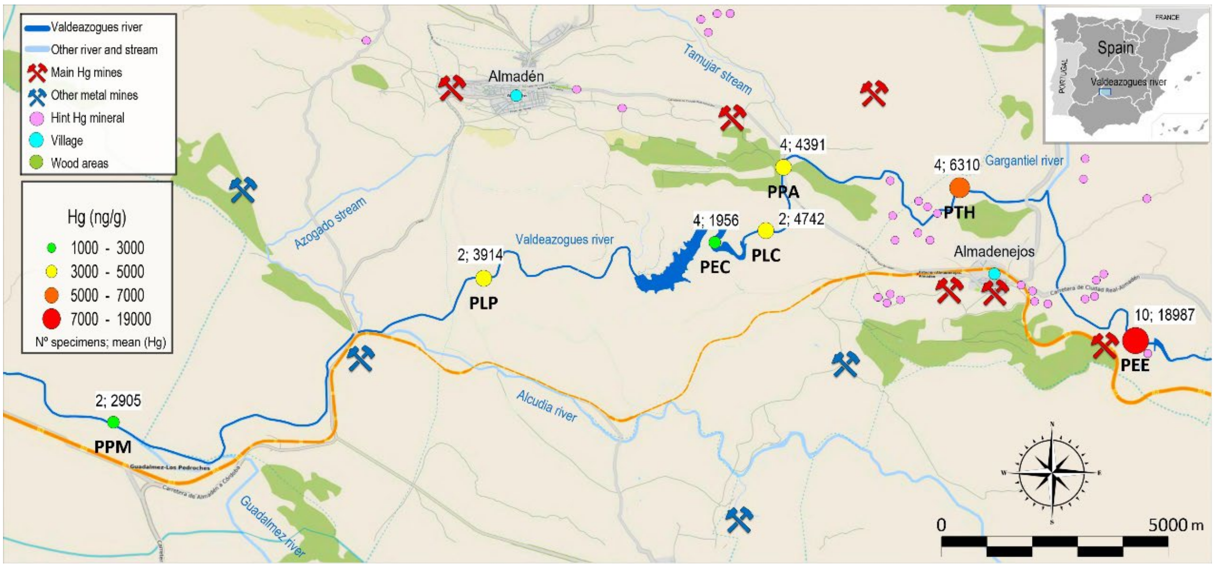
In the present study we have analysed the presence of mercury along the Valdeazogues river, in terms of total Hg contents in Largemouth bass (*Micropterus salmoides*). This is an exotic species in the area, introduced in the XX Century from North America. Its expansion in fluviatile environments has produced serious survival concerns to local species, and so this one is considered as an invasive species.

STUDY AREA

The Almadén Hg mining district is, from the geological point of view, characterized by detritic successions of Palaeozoic age, with frequent mafic magmatic presence (Hernández et al., 1999). The Hg deposits correspond to different typologies, being the most important one the Almadén mine, of stratabound type.

METHODOLOGY

The sampling of the *Micropterus salmoides* specimens, in the sites shown in Figure 1, was carried out by conventional fishing, at first hours in the morning and though the evening, when these fish have their higher activity.



For each specimen, the information referred to the characteristics of the sampling/fishing site, dimensions, and weight of each one was annotated. Every fish was individually introduced in separated plastic zipbags and conserved in portable fridge for less than 5 hours. Once in the laboratory, the specimens were frozen at -20ºC, prior to freeze-drying.

Analysis of total Hg concentrations was carried out using a LUMEX RA-915, using both raw samples and freeze-dried samples. Raw samples were just unfrozen while freeze-drying was carried out using a TELSTAR CRYODOS device, at -50ºC and pressure < 0,4 mbar. In a first approach, we analysed separately the specimen's head, the central fish muscle, and the muscle from the tail. The results were similar (see Table 1), and then we decided to analyse only the muscle from the central part for being the most homogeneous (RSD:5.3%).

Table 1. Results of Hg analysis of different parts of the body of one on the specimens. SD: Standard deviation, RDS: relative SD.

Sample	**Hg (ng.g^{-1})**	**SD**	**RSD**	**Relative spread (%)**
PPA-1-head	1,562	177.8	11.4	21.9
PPA-1-tail	1,530	121.5	7.9	15.8
PPA-1-center	1,660	87.4	5.3	9.5

RESULTS AND DISCUSSION

The results, shown in Table 2, evidence significative differences in Hg concentration (general range: 473 to 5,246 mg kg^{-1}) along the Valdeazogues river transect. The highest values have been found in the specimens from El Entredicho open pit, located to the East of the area, and decrease downstream. Average values corresponding to the different sampling sites are shown in Figure 2. The highest ones correspond to El Entredicho open pit (PEE in Figure 2), being much higher than the highest values measured by Rimondi et al. (2012) in the Paglia River, located downstream of the Monte Amiata Hg mining district (Siena province, Italy), with highest concentrations ranging 1,600 to 12,000 mg kg^{-1}. Concentrations in the rest of our sampling sites enter in this range, with variability probably related with variations in the Hg concentrations in the water and in the bottom sediments produced by diverse inputs from tributaries streams. Particularly low are the concentrations found in the Castilseras reservoir, possibly due to an effect of deposition of Hg-loaded particles in this quiet water environment (García-Ordiales et al., 2016, 2017).

Table 2. Concentrations of total Hg in the specimens, by locality. Hg1: measured in raw samples; Hg2: measured after freeze-drying.

Sample	**Hg1** (mg.kg^{-1})	**SD**	**Hg2** (mg.kg^{-1})	**SD**	**Weight (g)**
PPA-1	1,660	87.4	5,529	400.0	207
PPA-2	1,076	55.3	4,008	118.7	127
PPA-3	1,078	147.6	4,050	247.7	135
PPA-4	1,195	0.8	3,975	400.4	259
PTH-1	1,162	68.8	3,868	362.1	80
PTH-2	1,287	106.5	5,621	720.7	179
PTH-3	2,058	84	9,490	910.5	173
PTH-4	1,536	110.8	6,260	385.1	232
PEE-1	5,272	494.5	19,590	2439.0	178
PEE-2	4,666	61.9	18,840	366.9	228
PEE-3	4,754	54.6	18,320	561.5	198
PEE-4	6,099	865.5	23,840	741.3	440
PEE-5	5,246	148.7	24,500	2005.0	552
PEE-6	7,613	538.5	21,500	3288.0	420
PEE-7	3,115	313.6	14,480	1498.0	14
PEE-8	5,115	972.1	14,040	491.2	18
PEE-9	4,452	428.5	12,400	959.1	11
PEE-10	5,433	487.4	22,360	332.7	194
PLP-1	1,163	86.1	4,197	383.5	271
PLP-2	970	89.6	3,631	417.3	353
PLC-1	1,352	52.8	3,888	116.5	144

Sample	**Hg1** (mg.kg^{-1})	**SD**	**Hg2** (mg.kg^{-1})	**SD**	**Weight (g)**
PLC-2	7,811	27.5	5,596	1110.0	162
PEC-1	473	101.6	1,933	329.7	120
PEC-2	600	100.9	1,656	1135.0	118
PEC-3	530	67.2	1,919	172.1	97
PEC-4	605	14.6	2,316	106.2	90
PPM-1	1,056	97.4	2,926	197.0	190
PPM-2	932	91.5	2,883	2068.0	238

Considering well proven that methylmercury (MeHg) in fish represents > 90% of total Hg (Rimondi et al., 2012 and references within), it is very important to highlight that all the measured total Hg concentrations imply MeHg well above the USEPA fish muscle standard recommended to protect human health (300 ng g^{-1}, wet weight).

CONCLUSIONS

The main conclusion of this study is that total Hg concentrations measured in the edible muscle of Largemouth bass (*Micropterus salmoides*) in a transect of the Valdeazogues River, crosscutting the Almadén mercury mining district, contains concentrations of the toxic Hg high enough to affect the health of possible consumers. Highest concentrations have been found in a derelict open pit (El Entredicho mine), located upstream in the transect, and the lowest, in the Castilseras reservoir, located in the central part of the transect. The rest of samples show variable concentrations, possible conditioned by local inputs affecting the pollution of water and streams sediments.

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SOIL AND SEDIMENT CAPPING WITH ACTIVE GEOCOMPOSITES FOR SITE REMEDIATION

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KEYWORDS
Active Geocomposites, Remediation, Landfills, Contaminated Sites

ABSTRACT

Anthropogenic contaminants enter our environment in a variety of ways. The chemical industry with its products for many applications (automotive, food, plastics, pharmaceutical, construction materials industries etc.) is a key driver behind our modern-day achievements. However, harmful by-products also arise during production. Similarly, the steel, oil and gas industries brought prosperity, but with sites along rivers, contaminants reached sediments in the river for decades. The steadily growing requirements in environmental protection increase the demand for innovative products and technical solutions. With growing public attention, contaminated sites have come to focus and have thus triggered large-scale remediation projects. In order to treat a wide range of contaminants such as mineral oils and oil-based products, volatile organic compounds (VOC), polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) etc. active geocomposites have been developed.

1. Active Geocomposites

Active geocomposites are systems in which at least one active material (active layer) is placed between two geosynthetics layers (carrier layers) to prevent a spread of specific contaminants. The structure and different granular active materials are shown in Figure 1.

Figure 1. Exploded view of an active geosynthetic composite

Using active composites enables the installation of a layer of active materials faster, with more ease and as a safer process. Moreover, a constant active layer thickness is ensured over the whole covered area. The materials that can be used as an active layer in geosynthetic composites can vary. Mostly used are products such as activated carbon, which has been used in the chemical industry since the 1920s and organophilic clay, which is used in the oil and gas industry to treat oil contaminated process waters. Activated carbon uses its large inner surface area to bind the contaminants via adsorption. This enormous surface area is a result of the microporous structure of the material, which is roughly sketched in Figure 2. The different pores are classified by pore diameter: macro pore > 50 nm, meso pore > 2 nm and < 50 nm, micro pore < 2nm. The percentage in which the different pore types occur depend especially on the base material. If the base material already has a fine carbon structure, like for example coconut shell then the manufactured activated carbon will have a larger amount of micro pores. A fine porous structure of course has its limitations against larger molecules, for example oil. These materials can block the pore network and reduce the adsorption capacity. Other starting materials for activated carbon can be wood, bituminous coal or other materials with a carbon base structure.

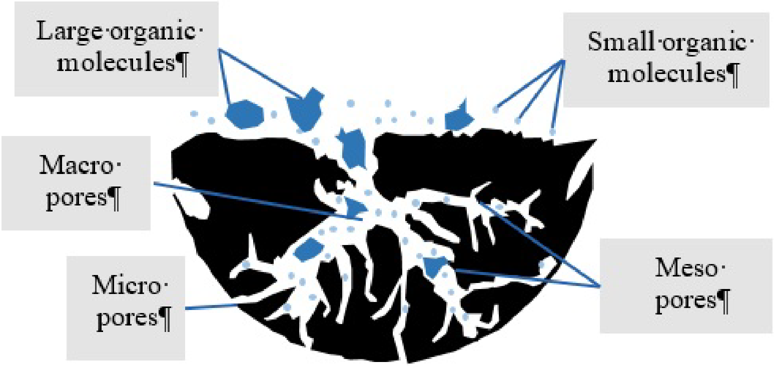

Figure 2. Micro porous structure of activated carbon

Organophilic clays are surface-modified clays that have been shown to be effective adsorbents for insoluble and partially insoluble compounds like creosote or coal tar. The production of organophilic clays replaces the surface cation of bentonite or hectorite clay with an organic molecule. Quaternary amines based upon tallow are the most commonly used organic compound. The resulting clay is oleophilic, hydrophobic and permeable. A properly compounded organophilic clay will exhibit minimal swelling upon organic adsorption and maintain high permeability. (Olsta et al., 2010) In treatment of produced water from offshore crude oil production, organophilic clays have removed polycyclic aromatic hydrocarbons to non-detect levels (Darlington, 2002).

Other potential applications arise with zeolites that are used in water treatment to remove nitrates and metals such as lead, zinc and copper (Thomas & Crittenden, 1998). Zero valent Iron has also been successfully used in permeable reactive barriers for dechlorination of chlorinated hydrocarbons and the reductive precipitation of Chromium(VI) to Chromium(III) shows possible applications (Powell et al., 2002). Tests at HUESKER with Ion Exchange Resin have shown good results in column tests against leachates of PFAS contaminated soil. An active geocomposite with activated carbon was used in the remediation of the K20 contaminated site in Austria.

2. K20 contaminated Site Remediation Project

The K20, a former company landfill, lies roughly one kilometre south of the Austrian town of Brückl in the lower part of the Gurktal valley in Carenthia. Between 1926 and 1981, it was used for the disposal of carbide lime, chlorinated hydrocarbons (CHC) and mercury-polluted waste (Austrian Federal State of Carinthia, 2016). The deposited CHCs mainly comprise tetrachloroethylene, trichloroethylene, hexachlorobutadiene, hexachloroethane and hexachlorobenzene. The total quantity of CHCs was estimated at some 100 – 1.000 to (UBA, 2003). An aerial photo of the K20 site is shown in Figure 3. As of 1995, various remediation works were performed in tandem with the ongoing evidence-collecting measures (Kraiger, 2016). In 2003, in the wake of further investigations, K20 was classed as a priority 1 site to push for a quick remediation (Austrian Federal State of Carinthia, 2016).

Figure 3. K20 contaminated site (as 28.3.2017) during remediation works

In December 2009, a notice was issued by the Governor of the Austrian Federal State of Carinthia for remediation of the K20 site through the continuous and complete clearance of all landfill materials. Depending on their pollutant content, these were to be recycled, treated or disposed of. In 2012, with the necessary preparations completed, the clearance works commenced and approx. 150.000 t of material, including some 100.000 t lime sludge, were removed. In November 2014, when hexachlorobenzene was detected – among other things, in locally produced food – near the cement plant entrusted with recycling the polluted lime sludge, clearance of the contaminated site was discontinued. The conclusion reached following a new pan-European call for tenders for transportation and treatment of the polluted lime sludge was that "no project involving continued site clearance could offer legal, technical, time or cost certainty" (Austrian Federal State of Carinthia, 2016). Containment of the contamination had already been considered as a remediation option in the first analysis performed by G.U.T (Gruppe Umwelt + Technik GmbH) in 2008. The disadvantage of this procedure is that it involves a permanent monitoring and maintenance regime for the containment, and that the potential pollution is left in place.

In addition to measures below the water table (cut-off wall to enclose contamination), the containment contracts awarded by the authorities included an innovative, multifunctional cover lining system. It comprised of an 11 kg/m² calcium geosynthetic clay liner, an LDPE membrane with integral CHC-proof aluminium layer, a drainage element and a 2 kg/m² active geocomposite with activated carbon, as shown in Figure 4. This system constitutes a practically impenetrable barrier for gaseous CHC emissions. The activate geocomposite is installed below the membrane in order to reduce the CHC concentrations acting on the membrane and slow down the associated diffusion momentum. HUESKER's active geocomposite Tektoseal® Active AC unlocks completely new areas of application for activated carbon – a widely and successfully deployed high-performance adsorption agent. The geotextiles in Tektoseal Active AC guarantee the mechanical stability of the active layer. This allows simple and rapid installation of the product. At the same time, the active layer is fully protected against erosion caused by water or inclinations. The lining system also incorporates horizontal suction pipes on two levels, above and below the sealing. Soil air is continuously exhausted from the lower extract layer and passed through a cleaning unit. The upper extract layer is used for monitoring purposes, though can also be exhausted if necessary. A special requirement for the installation process is that there is minimal interference with the existing landfill body to shape the surface profile. After finishing the remediation works the hazardous waste site will look like a usual green hill. Due to the special topography of the site there are inclinations up to 70° that need to be sealed. To enable a long term stability of the whole sealing system geo grids are used.

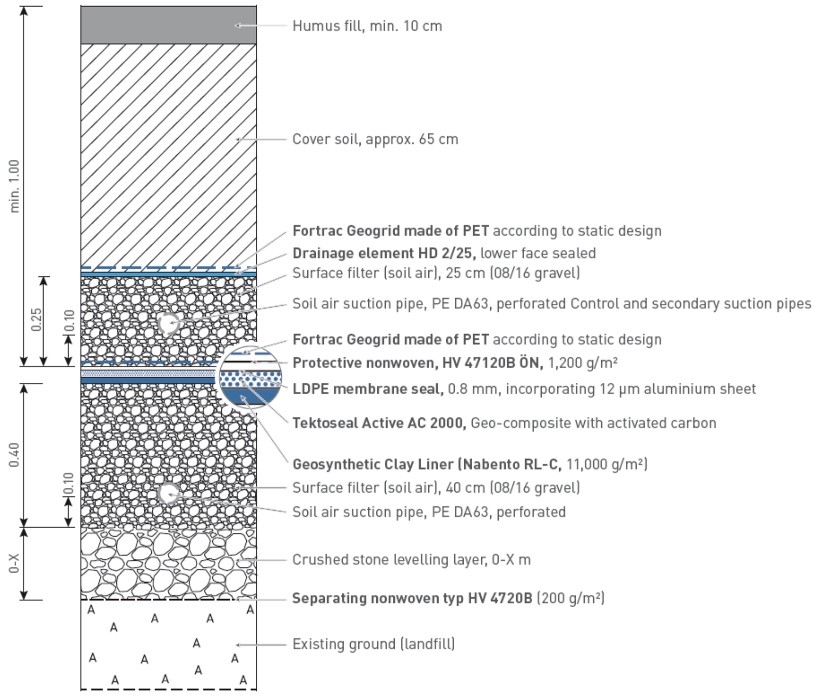

Figure 4. Cross section of the surface sealing system

3. Conclusion

As there is no universal solution to the problems posed by contaminated sites, designers and engineers need a "toolkit" from which they can select the most suitable measures. The multifunctional active cover lining described in this paper, for use in the containment of contamination, represents a new tool in this kit. Specific site factors can be readily accommodated through the variation of materials or their quantities.

From an ecological perspective, there is currently no alternative to the containment solution for the K20 contaminated site. It eliminates the need for long-distance transportation, possibly to neighbouring countries, and prevents any local pollution through emissions during loading and movement. Thousands of truck journeys are now unnecessary. The cover lining will protect against both the ingress of precipitation and wind loads.

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LYSIMETER RESEARCH – NEW EXPERIMENTS

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KEYWORDS
lysimeter, contaminant, contaminated sites, groundwater, waste, microbiology, biochemistry, Tychy, Poland

ABSTRACT

Lysimeter tests are an ideal supplement to monitoring research performed in the region of landfills. This study presents results of an interdisciplinary lysimeter experiment that used hydrogeological, biochemical and microbiological approaches to evaluate the process of leaching pollutants from waste. The obtained results of leachate tests indicate that the EC value was as high as 31 mS / cm with high concentrations of chlorides and sulphates. The microbiological tests confirm the seasonality. The number of heterotrophic bacteria was higher from spring to autumn. The analysis of the ability to utilize nitrogen and phosphorus sources showed seasonal differences in the use of substrates containing these biogenic elements. It was observed that nitrogen-containing compounds were most intensively used in winter and the least in spring while phosphorus compounds were the most intensively oxidized in summer. Lysimeter studies can play a helpful role in the construction of landfills.

INTRODUCTION

Municipal landfills are real and potential pollution sources for groundwater since the lots of contaminants, especially xenobiotics, are hardly biodegradable (Esmaeilian et al., 2018). Recycling such materials as metals, plastics, and glass is obligatory but still, 90% of municipal waste is dumped in Poland, while in the USA about 50% (Mukherjee et al., 2014). The most important issue connected with landfilling is the leaching of the salts and trace elements and their migration to groundwater. This situation is typical for landfills without any liner systems but also in the case of damaged materials (Taylor et al., 2004; Rykala and Dabrowska, 2020). In this context, groundwater quality monitoring is needed with the assessment of typical physicochemical pollution indicators and also microbiological parameters (Yanez, et al., 2006). Additional research like static and dynamic tests should be performed for a better understanding of the leaching mechanism and the total charges of pollutants possible to migrate to groundwater (Arain et al., 2008; Hesbach et al., 2010).

Especially important is that lysimeter research combines hydrogeological and biological aspects of landfilling and waste management (Bilgili, et al. 2006) which can be extended by measurements from sensors and the artificial inteligence methods (Polap et al., 2022).

The lysimeter studies carried out at the University of Silesia were comprehensive - hydrogeological tests (physicochemical analyzes of the leachate and precipitation recharging the lysimeter), microbiological tests (determining the structure of the microbial population) and biochemical tests (assessment of the metabolic diversity of the microbial population and its changes over time) were taken into account.

This paper aims to investigate the characteristics of the process of leaching pollutants from municipal landfill waste with 19 05 99 European Waste Code in the lysimeter experiment.

MATERIAL AND METHODS

Wastes with the initial moisture equal to 69.5% that have undergone the D5 disposal process were used in the research. The lysimeter experiment operated for about 400 days from the end of November 2018 until the end of December 2019. The inner diameter of the lysimeter was 0.4 m and the height 1.8m. The volume of medium-compacted municipal waste was about 130 liters (Fig. 1).

Figure 1. Lysimeter test stand

During the experiment, the lysimeter was precipitated with natural precipitation and artificially supplied with distilled water. The total volume of infiltrated rain was about 119 l, artificial supply was about 33 l and the volume of leachates was about 96 l. In each month the values of specific electrolytic conductivity, temperature, pH, Eh, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Al^{3+}, Mn^{6+}, Ni^{2+}, Cu^{2+}, Sr^{2+}, As^{3+}, Sb^{3+}, B^{3+}, Zn^{2+}, F^-, Cd^{2+}, Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}, N Kjeldahl, TOC, SiO_2, and alkalinity were determined. Additionally, 9 physicochemical analyzes of rain were performed in order to determine the potential influence of the chemical composition of rain on the composition of the leachate. Microbiologically, the leachate was tested for the determination of the total number of mesophilic and psychrophilic microorganisms, the determination of the total number of Escherichia coli and coliforms, enterococci, Pseudomonas aeruginosa and Clostridium perfringens. The seasonal metabolic changes of microorganisms in the leachate of waste dumps were determined using Biolog® 96-well EcoPlates™. All tests were carried out in accordance with the relevant standards. Physicochemical analyzes were performed in a certified laboratory, and other research was carried out at the Institute of Biology, Biotechnology and Environmental Protection of the University of Silesia.

RESULTS

In the analyzed leachates, high values of electrical conductivity were measured, reaching even 31 mS/cm. These values are comparable to the typical conductivities in leachate from municipal landfills (Dabrowska et al., 2018).

The chemical composition of the leachate was determined primarily by high concentrations of bicarbonates, chlorides and sulphates (Fig. 2). The dominant cations are Ca, Mg, Na and K. The greatest leachability was observed in the case of sulphates and chlorides. Of the remaining parameters, no high concentrations were observed. Metals like Ba, Cr, Cu, Ni, Al, Mn show a decrease in the content during the experiment. However, in the case of Ba, Ca, Cu and Mn, the concentration of these components in precipitation may be a dozen or even more percent of their concentration in the leachate.

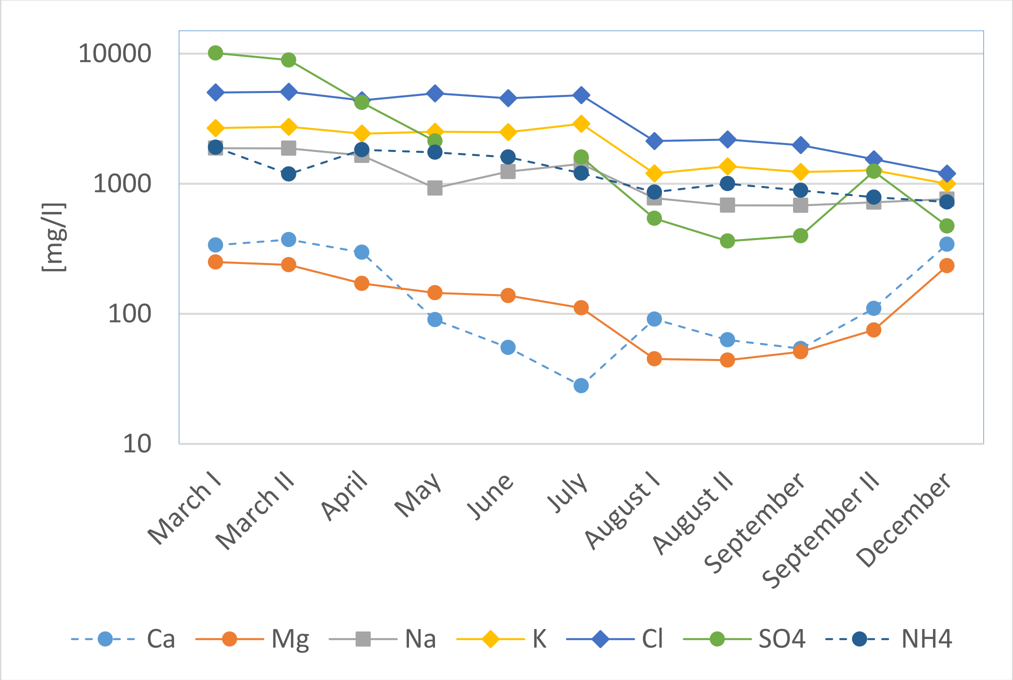

Figure 2. Selected chemical parameters values in leachates from a lysimeter filled with municipal waste

The electrical conductivity of rainfall samples varied in the range of 15-163 µS / cm. The chemical composition of precipitation was dominated by hydrocarbonates, sulfates and calcium. The concentration of N-NH_4 was also distinct in the hydrochemical type of precipitation (up to 2.8 mg/l).

The microbiological analyses showed seasonality. From spring to autumn, the number of mesophils was at the same level (10^7 CFU cm^{-3}) and was higher than in winter (10^5 CFU cm^{-3}). A similar situation occurred in the case of psychrophilic microorganisms isolated from the leachate in spring and autumn (10^7 CFU cm^{-3}) with the lowest number in winter (10^5 CFU cm^{-3}). The differentiation in the structure and functioning of the eluted microbiome was similar to the changes in physicochemical parameters. In the spring-autumn period, the weather conditions favored the development of pathogenic microorganisms: Escherichia coli, Salmonella sp., Enterobacter sp., Enterococcus sp.

Obtained results confirm the increase of microbial activity in spring and autumn and the highest functional diversity and substrate richness indices. In the summer, the utilization of labile carbon sources represented mainly by carbohydrates in Eco Plate was observed, while the decomposition of more complex carbon sources such as surfactants increased in the winter. The analysis of the ability to utilize nitrogen showed the enhanced microbial N use in winter. The highest oxidation of phosphorus compounds in summer was observed, which can be connected with intensive metabolism of phosphate leachate compounds by phosphorus-solubilizing bacteria (Dabrowska et al., 2022).

CONLCUSIONS

An interdisciplinary lysimeter experiment has shown that this type of research can be conducted to reflect the conditions in municipal landfills. Most of the eluted physicochemical parameters decrease with time. This suggests rapid leaching of pollution. Among the advantages of lysimeter studies, the possibility of assessing the influence of atmospheric factors and oxygen access on the chemical and bacteriological composition as well as the determination of seasonal metabolic changes in the effluent microorganisms deserves attention. Thanks to this type of research, it is also possible to prepare forecasts specifying the time and scope of the negative impact on the soil and water environment.

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ELECTRICAL CONDUCTIVITY ESTIMATION IN LYSIMETERIC TEST AT A LANDFILL SITE USING TRANSFER LEARNING APPROACH

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KEYWORDS
Landfill leachate, Lysimeter, Artificial Neural Network (ANN), Tychy-Urbanowice landfill

ABSTRACT

Predicting leachate pollutants is of prime importance in detecting the amount of pollution in water resources adjacent to sources of leakage. In this study, Electrical Conductivity (EC) as a physicochemical water pollution with the possibility of portable measurement was used as an indicator of leachate quality for the Tychy-Urbanowice operating and closed landfill complex. In order to simulate landfill conditions, two lysimeter experiments were conducted simultaneously by means of sensors to detect the EC, waste temperature, and waste moisture for the open lysimeter. Since the EC parameter, was missing in one of the lysimeters Artificial neural network-based transfer learning method was used to fill the EC value in a lysimeter with missing values. For this purpose, the EC parameters of the first lysimeter were estimated using the meteorological data. Afterwards, the missing EC parameters were simulated via the transfer learning method system to recognize and apply previously learned knowledge and skills in the lysimeter with complete sets of data.

INTRODUCTION

The capability of data-driven approaches, such as ANN, was validated in environmental engineering problems dealing with unclear physics and non-linear conditions (Nourani, 2012). In relation to this, Karaca and Özkaya (2006) developed an ANN model for modeling leachate generation in a landfill site using the daily meteorological data and observed leachate rate. The proposed model was able to significantly predict the daily leachate flow rate. Bagheri et al. (2017) used ANN and fuzzy logic to simulate the leachate leakage rate into the groundwater aquifer. The results were an indicator of the efficiency of the obtained models for predicting and evaluating the impacts of a leachate.

In order to investigate landfill leachate, on-site measurements are inevitable. However, landfills are faced with special structural conditions, such as instability of slopes or lack of access to deep buried layers, which threaten the possibility of on-site measuring. In this way, installing sensors to record the physicochemical properties of landfills seems to be a time-consuming and costly process. Therefore, in this study, lysimetric tests were conducted to simulate landfill conditions. Moreover, ANN models were developed to analyze the relationships between the recorded pollutant (i.e., EC) and hydro-environmental parameters of the landfill, taking meteorological and satellite data into consideration.

Due to technical and economic constraints, it is usually impossible to collect data from all available lysimeters in landfill sites for some periods, as was the case in this study of two lysimeters at the Tychy-Urbanowice landfill site. Since the conditions of the lysimeters were equal in this instance, the Transfer Learning (TL) method could be used to estimate the missing EC of the closed lysimeter by employing the models developed for the open lysimeter.

STUDY AREA

The lysimeter test stand is located next to the system of landfills in Tychy-Urbanowice.This system consists of two landfills: an active one (site I) and an abandoned one (sites II, III). The lysimeters were intended to simulate the operational phase of the inactive landfill and to show the differences in the leachate occurring due to the infiltration by precipitation water.

Lysimeter (I) was supplied with distilled water, with the leachate filled up to the volume of monthly precipitation afterwards to simulate the operating landfill condition. The lysimeters were covered with several layers of perforated foil to restrict the supply of air. Covering the waste with layers of foil was intended to imitate the covers over the top of the waste dump. The closed lysimeter (Lysimeter (II)) was recharged by rainfall or with distilled water with a volume equal to the average monthly rainfall calculated on the basis of rainfall volume measurements for this landfill in the period 2004-2009 with technology for treating the waste with leachate (Dąbrowska et al., 2019).

ARTIFICIAL NEURAL NETWORK (ANN)

The three-layer Feed-Forward Neural Network (FFNN) structure with back propagation algorithm was utilized to predict the EC parameter since this structure has shown a better performance in environmental issues (Maier & Dandy, 2000). Due to the favorable rate of convergence, the Levenberg-Marquardt scheme of a back propagation algorithm was used to train the ANN (Haykin, 1994; Kisi, 2004; Nourani, 2012). Respecting the data pre-processing method, scaling the data between 0 and 1, a hyperbolic Tangent sigmoid (Tansig) was used as an activation function (Nourani, 2012). The number of hidden neurons, as well as the epoch number, are of pivotal importance in determining the proper structure of the ANN model; for this purpose, the trial-error procedure was conducted (Nourani et al., 2019).

TRANSFER LEARNING (TL)

The black-box model of the first lysimeter can be used in the second lysimeter to estimate the EC if the similarity between the two systems is proven. In other words, when the conditions of the lysimeters are equal and the only different is their amount of precipitation received, and also both lysimeters are the sub branches of the greater system (landfills), the TL method can be applied to transfer the developed models of the first lysimeter to the second lysimeter (by implementing the second lysimeter's data as the inputs of the models).

RESULTS AND DISCUSSION

Considering that EC arises from ions in water, EC consequently rises when bacterial activity increases (as soluble materials increase in the leachate), as does leachate production. Therefore, it is necessary to examine not only the linear relationships (CC) but also the nonlinear relationships (AI) to find the connection between moisture, temperature, and EC (see Table 1,2, and 3).

Table 1. The results of CC feature extraction methods

parameters	SM_{100}	SM_{200}	P	ST_{100}	ST_{200}	T_{mean}
M_{I-a}	0.36	0.68	0.09	0.39	0.24	0.59
M_{I-b}	0.15	0.54	0.06	0.58	0.78	0.72
T_{I-a}	-0.35	0.11	0.09	0.87	0.78	0.95
T_{I-b}	-0.32	0.15	0.09	0.87	0.78	0.95
EC_{I-a}	0.58	0.54	0.12	0.02	-0.12	0.22
EC_{I-b}	0.58	0.75	0.12	0.02	-0.12	0.22

Considering the CC results (Table 1), it can be seen that at depths of 100cm to 200cm, the results demonstrated a strong correlation between the internal moisture content of the lysimeters and the soil moisture retrieved from the satellite as external data. In addition, as depth decreases, the linear correlation gradually declines, since some borderline factors, such as evaporation, affect the amount of moisture at these depths, reducing the linear correlation.

Table 2. The results of internal parameter relation analysis using ANN

MODEL	INPUTS	OUTPUT	DC		RMSE (NORMALIZED)	
			Calibration	Verification	Calibration	Verification
ANN	$M_{I\text{-}a}$	$EC_{I\text{-}a}$	0.75	0.75	0.10	0.10
	$M_{I\text{-}a}, T_{I\text{-}a}$	$EC_{I\text{-}a}$	0.79	0.76	0.09	0.10
	$M_{I\text{-}b}$	$EC_{I\text{-}b}$	0.85	0.79	0.08	0.09
	$M_{I\text{-}b}, T_{I\text{-}b}$	$EC_{I\text{-}b}$	0.88	0.86	0.07	0.09

Regarding the results of the sensitivity analysis between the lysimetric data (Table 2), it was clear that the moisture content of the lysimeters had a significant influence on the variation rate of the EC over time. Moreover, since the temperature parameter is one of the key factors in the evaporation and reaction rate within the waste, using the temperature and moisture of the lysimeters together as inputs increased the models' performance by 5.3% and 3.4%.

The results of the sensitivity analysis (Table 3) indicated that the soil moisture contents obtained from satellites within the depths of 40-100cm and 100-200cm have an acceptable correlation with the moisture content of the lysimeters. Hence, if the synoptic station data were not available or sufficient, the satellite data could be a viable alternative for this purpose, since the satellites have covered almost all countries for over 70 years.

Tab. 3 The results of external parameters and moisture relation analysis by ANN

Model	Input Combinations	Outputs							
		$M_{I\text{-}a}$				$M_{I\text{-}b}$			
		DC		RMSE (m^3/m^3)		DC		RMSE (m^3/m^3)	
		C[a]	V[b]	C[a]	V[b]	C[a]	V[b]	C[a]	V[b]
ANN	$ST_{100}, ST_{200}, SM_{100}, SM_{200}$	0.93	0.94	0.04	0.04	0.94	0.96	0.04	0.05
	All effective parameters	0.95	0.93	0.03	0.06	0.96	0.97	0.03	0.04

[a] Calibration, [b] Verification

Based on the obtained results, the internal moisture parameter is the dominant parameter affecting the EC changes. Moreover, regarding the CC and the sensitivity analysis results, the external parameters affecting internal moisture are also known. Therefore, we developed a model for predicting EC with the same inputs as the optimum inputs from the sensitivity analysis.

Model	Input Combination	Outputs							
		$EC_{I\text{-}a}$				$EC_{I\text{-}b}$			
		DC		RMSE (m^3/m^3)		DC		RMSE (m^3/m^3)	
		C[a]	V[b]	C[a]	V[b]	C[a]	V[b]	C[a]	V[b]
ANN	$ST_{100}, ST_{200}, SM_{100}, SM_{200}$	0.66	0.62	0.59	0.69	0.72	0.65	0.50	0.68
	All effective parameters	0.62	0.61	0.66	0.68	0.69	0.66	0.56	0.67

[a] Calibration, [b] Verification

With regard to the conditions of the lysimeters (open or closed), the only difference is in the precipitation parameter. Therefore, it can be concluded that if the precipitation parameter over the test period entered into the system is considered as a very low or zero value for the closed lysimeter, and the soil moisture parameter is set to be the daily average of 6 years (period of 2004-2009) corresponding to the operating years of the landfill, the trained models for the first lysimeter can be used to estimate the EC of the second lysimeter. To demonstrate this, the EC for the second lysimeter was predicted using the first lysimeter's EC as the target of the models. The results of the EC estimation for lysimeter (II) are depicted in Table 4.

CONCLUSIONS

In this paper, the EC parameter, as an indicator of landfill leachate pollution with the capability of portable measurements, was estimated by implementing ANN. For this purpose, a lysimetric experiment was carried out with two lysimeters to simulate the operating and closed landfills of Tychy-Urbanowice.

The results of the data analysis indicated that:

- The inner moisture parameter is the dominant factor in EC fluctuations
- The moisture of the lysimeters could be predicted using external data
- External temperature and soil temperature revealed a potent relationship with the temperature of the lysimeters.

Subsequently, the EC parameters of the first lysimeter were estimated using satellite and synoptic data. Following this, the missing EC parameters were simulated via the transfer learning method.

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FULL-SCALE APPLICATION IN ITALY OF THE EHC® LIQUID TECHNOLOGY FOR THE COMBINED ISCR AND ERD TREATMENT OF AN AEROBIC AQUIFER IMPACTED WITH TETRACHLOROMETHANE AND CHLOROFORM

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KEYWORDS
Enhanced Reductive Dechlorination, Aquifer, Tetrachloromethane, Chloroform, Hexavalent Chromium, Bioremediation, In Situ Chemical Reduction, Lecithin.

ABSTRACT

EHC® Liquid Reagent is a combined product for the in situ chemical reduction (ISCR) and enhanced anaerobic bioremediation (ERD) treatment of aquifers contaminated by organochlorine organic compounds and heavy metals such as hexavalent chromium. Once in the water table, EHC Liquid technology rapidly generates enhanced reducing conditions, favoring both biotic and abiotic dechlorination reactions (Adamson et. al., 1999). The product is composed of a cysteined organo-ferrous component and a fermentable substrate based on lecithin; commercially branded as ELS® Microemulsion. Both components are easy to mix, dilute and inject into the stratum.

This innovative technology was successfully applied to a highly-industrialized site in northern Italy, where groundwater was historically contaminated with tetrachloromethane (> 10 ppb), chloroform (> 10 ppb), hexavalent chromium (> 2 ppb) and, to a lesser extent, PCE and TCE.

After approximately 15 months from injection of EHC® Liquid into the groundwater in the main source area, the concentrations of CT and CF contaminants are rapidly reduced, compared to the pre-treatment concentrations, until the target values of treatment are reached in the main piezometers monitoring in the area, also highlighting the establishment of clear and enhanced biotic and abiotic reducing conditions.

DESCRIPTION OF THE TREATMENT AREA

Based on the results of an extensive Risk Analysis, the intervention area was contaminated both with regard to the aquifer and unsaturated soils. Impacted area was approximately 2000 m^2 with a 17 meters thickness between the saturated and unsaturated zones. Groundwater was affected by high concentrations of chloroform and tetrachloromethane, while unsaturated soils were only affected by chloroform. The following actions were selected as an initial intervention phase:

- Hydraulic containment barrier (Pump & Treat)
- Soil Vapor Extraction (SVE) technology for the reclamation of unsaturated soils contaminated with chloroform.

Monitoring data trends showed a significant reduction of CT and CF concentrations in groundwater during the first years of operation (P&T and SVE). However, in September 2017, values measured in groundwater for CT and CF were still highly above the site-specific reclamation target values (66 µg / L for CT and 65 µg / L for CF). In addition, there was some evidence of degradation anaerobic catabolites (i.e. DCM and CM) along with concentrations of TCE and CrVI present in the solution (Penny C. et. al., 2000).

Therefore, given an asymptotic trend of those contaminating concentrations with values above the calculated CSR (site-specific reclamation target values), the client opted to apply EHC Liquid reagent; an in-situ treatment technology developed to establish both biotic and abiotic reduction processes in groundwater.

Pre-treatment stratum (September 2017) of CT and CF concentration distributions shown in Figure 1 and Figure 2.

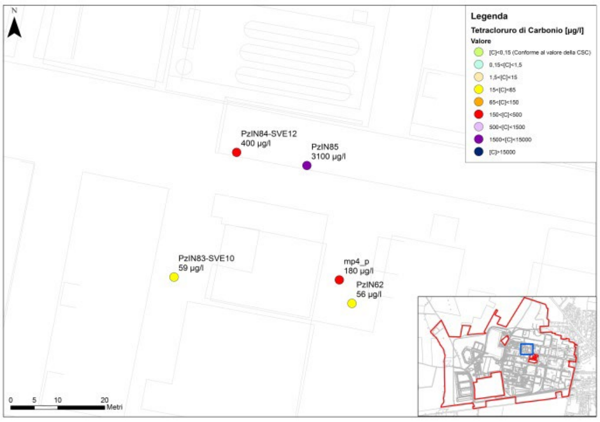

Figure 1. Pre-treatment CT concentration in the source zone (September 2017)

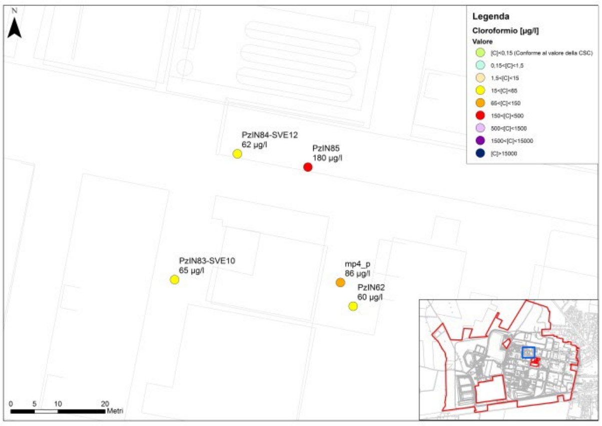

Figure 2. Pre-treatment CF concentration in the source zone (September 2017)

The contaminated superficial aquifer consists of a coarse sand with permeability between 3.6 x 10^{-4} and 1 x 10^{-4} m / s. Consequently, linear velocity of the groundwater flow is equal to about 284 m / year, considering a hydraulic gradient equal to about 0.3% and an effective porosity of the saturated medium of 12%. The piezometric surface is located 8 meters from the surface, while the base of the aquifer, represented by a layering of compact clay, is 17 m from the ground. Furthermore, before treatment, the aquifer showed naturally occurring aerobic conditions (Eh ≈ 50 mV, DO ≈ 7 mg / L) and an average sulphate content of about 70 mg / L and pH values in the neutrality range (pH ≈ 7.3).

FULL-SCALE APPLICATION

In December 2017, approximately 8568 kg of concentrated ELS product was emulsified with 10% dilution water along with 1960 kg of a cysteinate organo-ferrous compound. It was then injected under pressure (≈ 7 bar) in the stratum through 28 fixed injection points (Manchette tubs) and distributed in the saturated source area (Figure 3). The main objective established in the reclamation plan was to obtain compliance with site-specific CSR limits (CT = 66 µg / L, CF = 65 µg / L) at the monitoring points present in the treatment area.

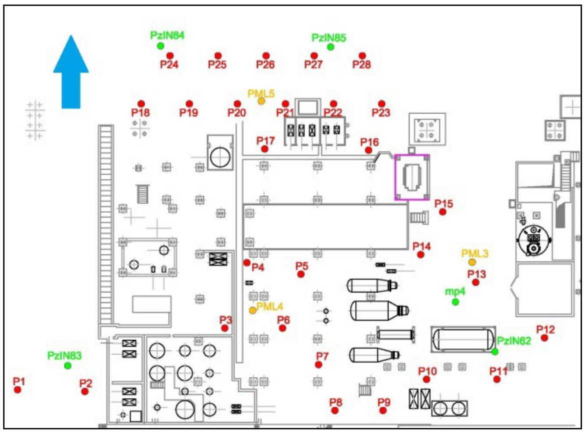

Figure 3. Grid of the injection points (in red) and monitoring points (in green and orange) together with the stratum-direction.

RESULTS

Approximately 15 months after the EHC Liquid reagent was injected into the stratum, the remediation targets were achieved in all the treatment area's monitoring piezometers. Figure 4 shows how the concentrations of CT and CF in the stratum have decreased below the treatment targets in two of the main control piezometers, thus showing a reduction of more than 98% in only 15 months of treatment.

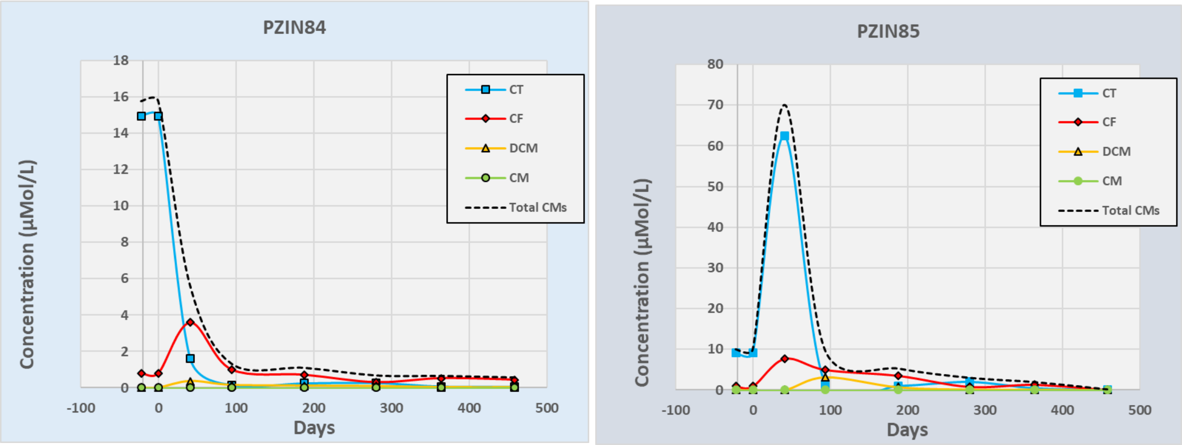

Figure 4. Concentrations of chlorinated methane in stratum in two monitoring points in the treatment area before and after EHC Liquid injection performed in December 2017.

In addition, the concentration levels of degradation catabolites, such as DCM and CM, remained below the detection limits in almost all the treatment area's monitoring points, with the exception of a few downstream piezometers in the first year of treatment. This confirmed the establishment of complete enhanced reductive dechlorination processes throughout the treated aquifer (Lee et al., 1999). Furthermore, through a sampling at different depths, the same reclamation trend was observed and the degradation process in the various portions of the treated aquifer verified.

Finally, all monitoring sites located in the enhanced anaerobic treatment zone indicated the complete elimination of hexavalent chromium concentrations in solution (Figure 5).

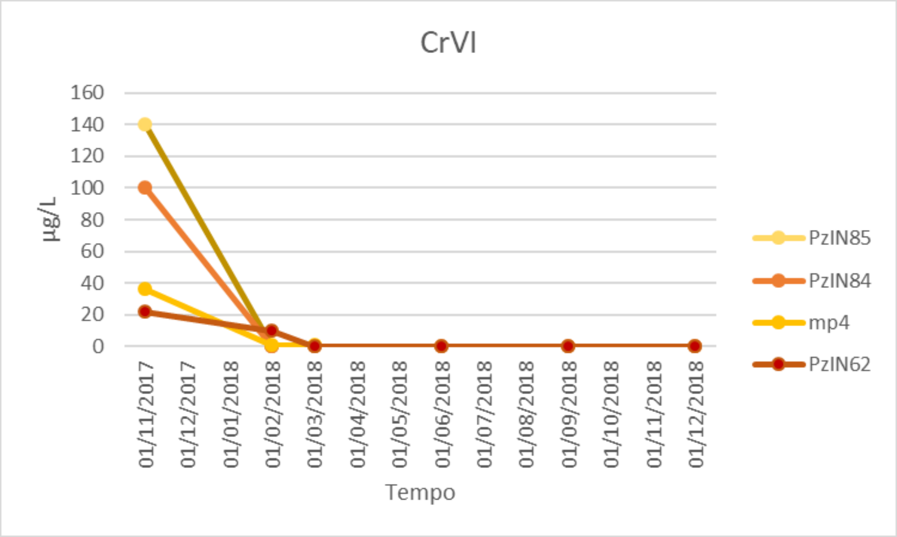

Figure 5. Evolution of hexavalent chromium concentrations in groundwater at the main monitoring points in the treatment area before and after the EHC Liquid injection performed in December 2017.

In order to determine if the piezometers were actually under the influence of EHC Liquid reagent, and to demonstrate the actual distribution of the reagent in all the areas subject to reclamation, we sampled the parameters of the aquifer field, including Fe (II) and Mn (Lewis et. Al., 2000). A significant increase in the concentrations of Fe (II) and Mn in solution were observed in all the monitoring piezometers present in the treatment area, confirming the correct distribution of the reagent in the stratum and the establishment of enhanced anaerobic conditions. In particular, maximum concentrations of Mn and Fe (II) of 8.1 and 36 mg / L were monitored.

Additionally, a significant decrease in the oxidation-reductive potential (ORP) was observed up to negative values at all the monitoring points of the treatment area, as well as a decrease in the concentrations of the sulfates in solution, on average equal to one order of magnitude compared to the pre-treatment values between 50 and 100 mg / L, demonstrating the establishment of sulfate-reducing conditions. A similar decreasing trend was also monitored for dissolved oxygen concentrations.

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LIFE SOURCE PROJECT: TESTING INNOVATIVE TECHNOLOGIES TO ENHANCE PFAS POLLUTED GROUNDWATER TREATMENT

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KEYWORDS
PFAS, groundwater remediation, pump and treat, phytoremediation, electroxidation, Surface Active Foam Fractionation, Anion Exchange filters

ABSTRACT

Introduction

The LIFE SOuRCE (Demonstration and evaluation of Sustainable On-site Remediation technologies for PFAS-ContaminatEd groundwater) is a European project funded by the LIFE Programme, which objective is to develop a cost-effective solution for on-site remediation of PFAS (per- and polyfluoroalkyl substances) polluted groundwater. PFAS are a group of more than 5,000 chemicals that are extremely stable in the environment (OECD/UNEP, 2013). Because of this stability, they present all over the world and are connected to the increase of multiple pathologies like kidney cancer. In response to the high risk posted by these compound, the European Union has issued the new Framework Directive for Drinking Water (EU – DWFD), setting the limits to 0.1 µg/l for individual PFAS and 0.5 µg/l for PFAS in total (EU Commission, 2018).

Despite their high presence in groundwater (Goldenman et al., 2019), treatment technologies – specially if implemented individually - are still expensive and not effective with all types of PFAS. Granular Activated Carbon (GAC) remains one of the most used technologies for on-site remediation of PFAS. However, its costs increase for large volumes of water, and its efficiency is lower for short chain PFAS. Therefore, there is a pressing necessity for alternative costs-effective solutions to remediate PFAS pollution in groundwater.

In response to this context, the LIFE SOuRCE project aims to demonstrate and optimize a modular treatment train, that should reduce costs, increase efficiency and result in complete destruction. The solution is based on a pump-and-treat scheme and the combination of four on-site PFAS remediation technologies: Surface Active Foam Fractionation (SAFF), Anion EXchange filter (AEX), Electrochemical Oxidation (EO), and Phytoremediation (PHYTO). The objective with the combination of the technologies is to reach removal rates higher than 99 % long-chain PFAS and 95 % short-chain PFAS, while reducing costs for large volumes of treated water (0.1 €/m^3).

The solution will be tested in two demo sites in Spain and Sweden. Both sites have different geological setting, climatic conditions, and groundwater matrixes, which allows testing different modular combinations of the mentioned technologies in a treatment train adapted to each case. The

Swedish site is located at the Hovgården land field in Uppsala. Groundwater in this site is polluted by a combination of compounds, among them PFAS. On the other hand, the Spanish site is solely polluted by PFAS resulting from the use of firefighting foams. The Swedish site will be treated combining the SAFF with Phytoremedaition and EO; while the Spanish site will be treated using a combination of SAFF, AEX and EO.

However, before being able to operate the system on site, bench scale tests were done individually for some of the technologies. Bach experiments with three different AEX resins were performed to select the most efficient one and select a regeneration strategy to be implemented at the Spanish pilot site. Experiments using an EO cell were performed to optimize PFAS disintegration from the regeneration solutions. Results were used to design the Spanish pilot scale treatment train.

AEX batch experiments

Anion Exchange Resins have been identified as one of the most effective treatment techniques to remove PFAS from water (Boyer et al., 2021). Although GAC is one of the most used technologies for PFAS removal, recent publications conclude that anion exchange resins are more effective for both long- and short-chain PFAS (Gagliano et al., 2020).

The types of resins available in the market increase every year, being Purolite one of the main manufacturer of resins compatible with PFAS removal. Many of them have been tested over the last decade (Boyer et al., 2021). Recent publications highlight two of them, Purolite PFA694 (Franke et al., 2021) and Purolite A532E (Zaggia, 2016). Additional PFAS specific resins, like the A592EBF, are advertised by Purolite

One of the key factors for the economic viability of AEX applications, is the regeneration of the resins. Despite its importance, AEX regeneration is less studied than removal capacity. Zaggia (2016) testes 11 different regeneration solutions with the A532E resin. They concluded regeneration solutions based on methanol or ethanol were more effective than solutions based only in inorganic salts.

Based on the identified knowledge gaps and overall project objectives, three bench scale test were designed to first, select from the three identified resins from Purolite (PFA694, A532E and A592EBF) the most suited for PFAs removal; second, estimate the adsorption capacity of the most suitable resin; and third, select the most efficient regeneration solution for the selected resin. The three experiments were done using groundwater extracted from the Spanish site spiked for the three PFAS with higher concentrations in the field.

For the first test, the three different resins and GAC were left in contact with the spiked water during four different periods (2.5min, 5 min, 15 min and 2h) to analyse the kinetics of adsorption. Results (Fig. 1) show that, as expected, the PFAS specific resin (PFA694) is the only one reaching equilibrium quicker than GAC.

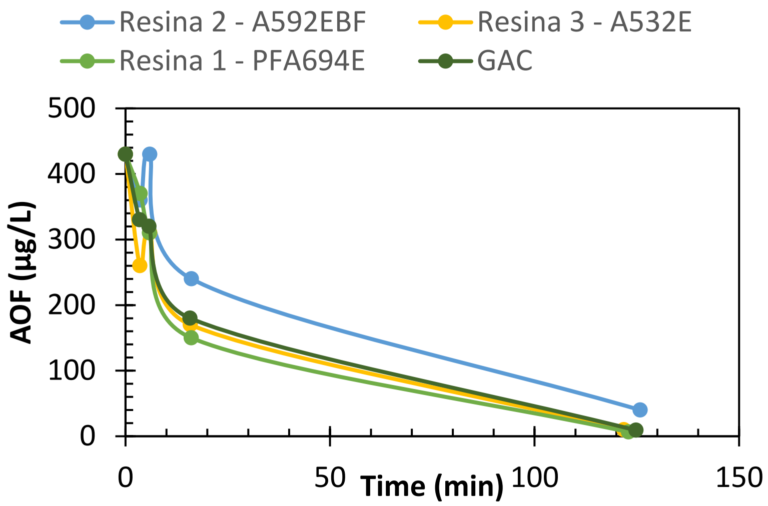

Figure 1. Kinetics of the three different resins and GAC adsorbing AOF (Adsorbable Organic Fluoride).

The second experiment was performed leaving in contact different amount of the PFAS-specific resin during 24 hours with the spiked groundwater. The objective was to estimate the capacity of the resin to adsorb the spiked PFAS, however only the 6:2FTS reached full saturation.

A final experiment was performed to select the resins regeneration solution. Two cycles of regeneration were performed on the PFAS-specific resin, to observe the reduction in the adsorption capacity after being regenerated two times. Results (Fig. 2) show that the two regeneration solutions based on methanol and ethanol have a higher regeneration capacity. Differences between these two regeneration solution are not significant, at least for just two regeneration cycles.

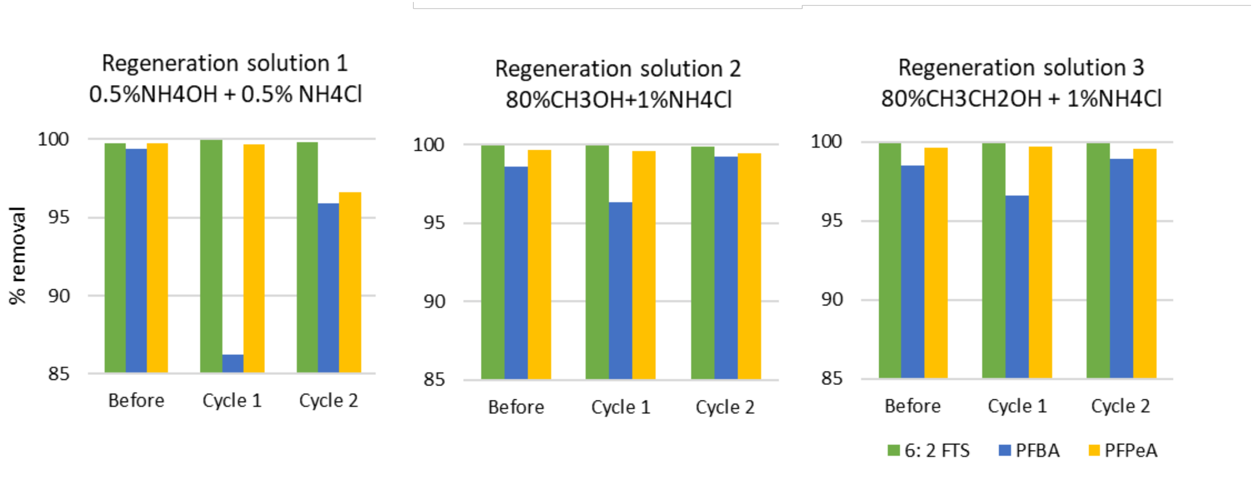

Figure 2. Adsorption capacity of the resin PFA694E after two regeneration cycles with three different regeneration solutions.

EO experiments

Boron Doped Diamond electrodes (BDD) are a relatively new technology (Schaefer et al, 2017). Because of their high voltage and corrosion resistance, these types of electrodes have been shown to be one of very few methods to decompose PFAS (Ross et al., 2018). BDD will be used to destroy PFAS concentrated in the regeneration solutions used to regenerate the resins. Nine experiments were performed treating the three regeneration solutions resulting from the above-described experiment, with three different intensities (5, 15 and 25 A). Unfortunately, at the moment of writing this extended abstract, samples from the experiment are being analysed at commercial labs, thus results are not available yet.

Discussion and conclusions

The performed bench scales tests allowed us to select the most efficient resin for treating groundwater polluted only by PFAS, estimate the design parameters for the pilot scale treatment and select the most effective regeneration strategy. As expected, PFA694E is the selected resin. The most efficient regeneration solutions are also those identified in literature, although difference among both solutions (based on ethanol and methanol respectively) are not significant. Imminent results from electrooxidation tests may help identifying any difference in the treatment efficiency among regeneration solution which could help selecting one over the other. In any case, the combination of both technologies will allow us to comply with the circular economy objective, reusing waste, while ensuring complete destroy of PFAS, at the LIFE SOuRCE Spanish pilot scale test.

Acknowledgements

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UTILIZATION OF ENERGY CROP *MISCANTHUS × GIGANTEUS* BIOMASS CULTIVATED IN THE POST-MINING AND POST-MILITARY SOILS

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KEYWORDS

Miscanthus × giganteus, marginal&contaminated sites, biomass processing, bioproducts

ABSTRACT

CORNET project MiscanValue (2020-2022) implies application of the energy crop *Miscanthus × giganteus (M×g)* for revitalisation of post-mining and post-military localities ensuring sustainable utilisation of biomass to fibres and pulp. The project ensures a complete Miscanthus value chain from sustainable land management through cultivation, harvest, and storage of biomass to its processing to fibres, pulp, fibrous materials, and packaging paper. The produced during these stages Miscanthus waste is utilised by pyrolysis to biochar with its utilisation in the fields.

The current report introduces the results of multiyear growing of *M×g* at the post-mining land in Chomutov, the Czech Republic, amended by different soil amendments. During two vegetation season the improving of the soil health and enhancing biomass has been established which was the biggest when biochar at dose of 10% was incorporated to the soil. The Best Available Practice of Miscanthus utilisation and Quick test for Miscanthus biomass processes to bioproducts were developed. The peculiarities of processing the Miscanthus biomass to fibrous and insulation materials using thermomechanical (TMP) and chemo-thermomechanical pulp (CTMP) processes were investigated. The laboratory sheets were received with the produced Miscanthus TMP (0.02 and 0.2 mm) in 5, 10, and 20% blends with a corrugating medium. The results of the project will be summed up in a full value chain of Miscanthus biomass as a valuable input to the implementation of EU Bioeconomy strategy.

The robustness and physiological characteristics of *M×g* like a deep, dense, and extensive root system, allow the crop to adapt to various soil and environmental conditions[1]. The crop has a relatively high biomass yield [2-3] and cellulose content compared with other lignocellulose

bioenergy crops [4], which makes it one of the most promising feed stocks for the production of biofuels [5] and bioproducts: fibres, insulation materials, and papers [6]. Cultivation of Miscanthus on the slightly contaminated or marginal lands has environmental and economic benefits: in addition to the remediation potential [7-9], the plant demonstrates high efficiency in carbon sequestration [10].
In the current study the utilization of *M×g* at the post-mining land in Chomutov, the Czech Republic has been tested at the soils with different incorporated amendments, i.e.: biochar in two doses 5 and 10% (BD1 and BD2), sewage sludge (SS), digestate (D), and hemicellulose waste (HW). The experiment has been provided since 2021 at the field scale and *M×g* growing parameters, harvest value and changes of the soil microbial communities (with focus on nematodes) have been evaluated. The samples were collected three times during vegetation: right after soil amending (May), at the mid-vegetation (July), and at the end of vegetation (October). Results showed that the nematodes community associated with crop growing was sensitive to the type of applied amendments which had a different influence on soil nematodes' food web. Out of five amendments tested, SS vs D favoured a more stable nematode community maturity status, which would give a snapshot of the soil health condition. Some controversy was detected on the impact on nematode during adding BD1, BD2, and HW. BD2 increased the biomass yield and positively impacted the soil nematode community structure. The second-year 2022 monitoring of the impact of amendments to nematode communities is underway.
A comparison of enzymatic activity of samples of undisturbed soil (next to the Miscanthus field) and samples of soils with different treatment by soil amendments was accomplished for 2021 plantation; the depth of sampling was 20 cm. Basal respiration was determined using the colorimetric method; results are presented in Fig. 1. Respiration was increased in case of amendment of the soil by BD2.

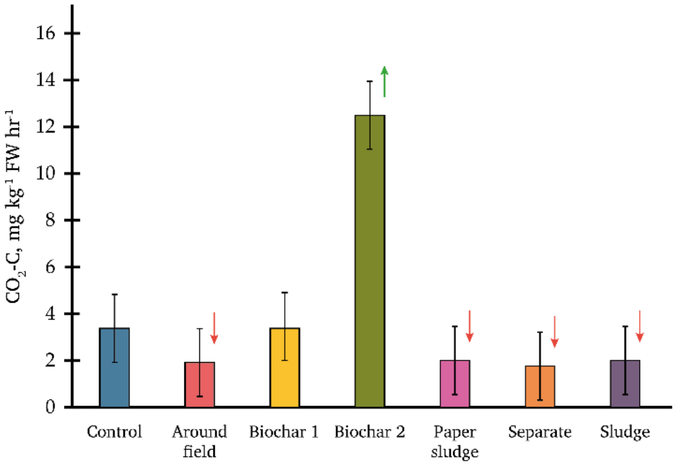

Figure 1. Basal respiration of the soil. Arrows indicate significantly higher or lower values (p <0.05) in comparison to control (t-test, n = 3)

The diversification of the feedstock deposit in the paper and fibrous material industries and the increasing sharing of non-wooden materials is within the demand of bioeconomy encouraging the production of renewable biological resources and processing to vital products. The replacement of cost increasing virgin and recycled fibre pulp qualities by natural alternatives is urgent. High yields with prominent content of lignocellulose make *M×g* an excellent feedstock for producing fibre-based materials [6].
The peculiarities of converting the Miscanthus biomass to fibrous and insulation materials using thermomechanical (TMP) and chemo-thermomechanical pulp (CTMP) processes were investigated. In a first process step, a straw shredder was used for shredding and the material was then passed twice over a vibrating screen with a mesh size of 12 mm. In the TMP process, Miscanthus material was continuously processed in the refiner at 4 bars. The cooking temperature was 140 °C. The grinding disc spacing was varied between and 0.14; 0.3 as well as 0.5 mm. In another process, CTMP pulp was produced for further processing into papers (Fig. 2).

Figure 2. CTMP laboratory pulp

The pulps (TMP, CTMP) were characterized accordingly (fiber length distribution over fiber fractions). Laboratory sheets were produced from the Miscanthus biomass produced at the marginal land-former landfill). The Miscanthus TMP (0.02 and 0.2 mm) in 5, 10, and 20% blends with a corrugating medium were produced. The resulted particle board are presented at Fig. 3.

Figure 3. Particle board produced from Miscanthus biomass cultivated at the land field

The full value chain of *M×g* biomass starting from production stage via converting to isolation material, pulp and packaging paper is undeway.

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MOBILITY OF ZN IN A METAL-ENRICHED SLUDGE SOIL AMENDED WITH BIOCHAR AND/OR COMPOST; COMPARISON BETWEEN A POT AND RECIRCULATING COLUMN LEACHING TESTS

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KEY WORDS
Biochar, compost, zinc, pore water, metal leaching

ABSTRACT

Organic amendments to contaminated soils are a remediation method to regulate metal(loid) leaching to waters and uptake to crops. In this study a wood-derived biochar and/or green waste compost was amended to a Zn-rich agricultural soil (~450 mg kg^{-1} total Zn, derived from legacy sludge application). A pot experiment with barley and pea crops in amended soil was run for 100 days, simultaneously measuring Zn in soil pore waters and its uptake to crops. An assessment was made of leaching of Zn via a linked column test that recirculated soil leachates.

Concentrations of Zn in pore waters were reduced from ∼2 mg l^{-1} in soil without amendment to ∼1 mg l^{-1} following the addition of 5% (vol.) biochar and compost, which was reduced further (∼0.5 mg l^{-1}) in the presence of crops. Barley Zn content was maintained or enhanced by all soil amendments. The leaching column test revealed that biochar raised pH ~2 units above that of the soil alone, and ~1 unit greater than the compost amendment and Zn leachate concentrations were reduced from ~8 mg l^{-1} from soil alone to < 0.05 mg l^{-1} after biochar amendment. Conversely, compost resulted in net mobilisation of Zn from soil.

This study demonstrates that the biochar and compost addition to a Zn rich agricultural soil was able to reduce pore water Zn considerably, especially in the presence of a barley crop. Compared to compost, biochar was the more efficient sorbent of Zn.

INTRODUCTION

A common source of heavy metals to land has been the application of metal-rich organic wastes such as sewage sludges. Their application in the UK was historically based on an EU wide ban on at-sea disposal in the 1990s, and also due to their ability to improve physical, biological and chemical properties of soils (Suman, 1991). A legacy of historic applications of metal rich sludges to agricultural soils exists in the form of metal enriched soils. Previous studies on UK soils having received repeated application of metal enriched sludges have demonstrated reduced yields of cereal and legume crops from enhanced soil metal concentrations in excess of 200 mg kg-1 (Bhogal et al., 2003). Zinc is of particular interest in such sludge amended systems as its mobility has been shown to be subject to less influence from sludge-derived dissolved organic matter (DOM) than other metals, such as Cd, Cu and Ni (Antoniadis and Alloway, 2002; Ashworth and Alloway, 2004). Therefore, Zn longevity in topsoils after sludge application is uncertain (Alloway and Jackson (1991) and could be such greater than that of other metals.

One intervention to regulate metal mobility from extant Zn in soils is the application of amendment. Applying composts, biochars and other organic (and inorganic) materials to metal enriched soils are now established methods of adjusting soil geochemical parameters to regulate metal solubility and soil-plant transfer. Numerous studies exist where composts and biochar alone or combined have been shown to impact metal solubility and plant uptake to an extent when mixed into metal rich soils (Fanguiero et al., 2018).

In order to understand the overarching mechanisms involved in Zn transport in amended soils, the objectives of this study were to; 1) determine the effects of compost and biochar amendment on Zn mobility and crop uptake in a sludge-impacted agricultural soil; 2) elucidate the primary mechanisms affecting any measured changes in Zn leaching resulting from amendment, 3) discuss the findings in relation to the application of compost and/or biochar to manage environmental risk associated with elevated concentrations of Zn in soils.

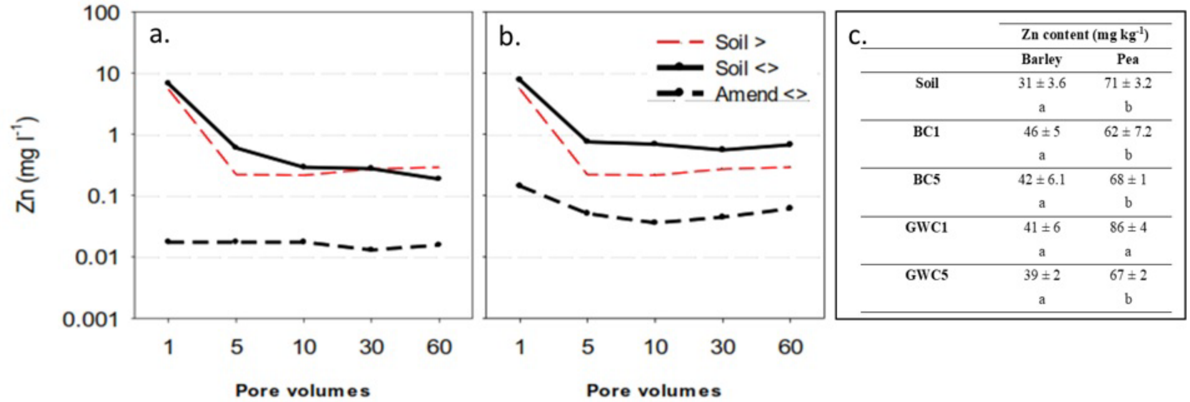
MATERIALS & METHODS

Soil was sampled from Hartwood Home Farm, 30km east of Glasgow, in the village of Hartwood (Lanarkshire, UK). The soils here are classified as poorly drained gleys ('Eutric Stagnosol' under WRB classification system) of the Rowanhill and Caprington series, with sand, silt and clay proportions of 59, 20 and 21% respectively (Gibbs et al; 2006). Soil was sampled from the experimental field plots having received the highest dosage of a Zn rich sludge cake (6000 mg kg-1 total Zn) applied annually from 1994-1997, resulting in a total soil Zn concentration of c. 450 mg kg-1 (Gibbs et al; 2006).
Initially a pot experiment was set-up with two organic amendments mixed with the soil. Amendments were selected for this experiment, with proven efficacy for reducing the concentrations of metal(loid)s in soil solutions and reducing plant uptake (for example; Beesley & Dickinson, 2011). The first was biochar (BC) originating from hardwood off chippings (Oak, Ash, Sycamore and Birch) from saw milling, pyrolyzed at 400°C in a steel ring furnace from Bodfari Charcoal (Denbighshire, UK). The second was composted mixed green (GWC) waste produced in accordance with PAS 100 quality criteria (The British Standards Institution (BSI)), obtained from Keenans (Aberdeenshire, UK). In the pot test they were added at 1 and 5% by volume (denoted 1 and 5 here).

The second experimental procedures physically separated soil from the tested amendments so that only the solutes from soil and amendments were in contact. To achieve this, leaching columns were operated in a closed loop manner, recirculating leachates from one column containing the contaminated soil (denoted 'soil') to another column containing the tested amendments (denoted 'Amend').

RESULTS AND DISCUSSION

Both amendments significantly reduced pore water Zn compared to the non-amended soil. The furthest, reduction in pore water Zn concentration was achieved by 5% doses of both biochar (BC) and compost (GWC) resulting in pore water Zn concentrations of c.1 mg l^{-1}. Unlike pH and DOC, on the column tests Zn curves did not converge by the termination of the test indicating that retention of Zn must have occurred within the columns containing the amendments (Figure 1). Thus both BC and GWC can be deemed to have immobilised Zn in solution, though BC was an order of magnitude more efficient. A divergence occurred at 60 v/vpore leaching in the case of GWC (Figure 1b), which is not the case for BC (Figure 1a) indicating that feedback from GWC (of DOC) to soil resulted in some re-mobilisation of Zn from soil which was not the case for BC. Combined with the greater efficiency for reducing Zn in solution this means that BC both acts as a sorbent for Zn and, in its feedback effects to soil, does not re-mobilise Zn.
For crops, head content of Zn in barley was increased by all soil amendments, though not significantly in any case (Figure 1c), indicating that the amendments were unlikely to result in Zn becoming more bioavailable in the tested soil.



	Zn content (mg kg^{-1})	
	Barley	Pea
Soil	31 ± 3.6 a	71 ± 3.2 b
BC1	46 ± 5 a	62 ± 7.2 b
BC5	42 ± 6.1 a	68 ± 1 b
GWC1	41 ± 6 a	86 ± 4 a
GWC5	39 ± 2 a	67 ± 2 b

Figure 1. a) leaching column curves for biochar (BC), b) green waste compost (GWC) and c) table of crop Zn uptake under the influence of the amendments

CONCLUSIONS

This study demonstrated, through contrasting methodologies, that the amendment of a Zn-rich agricultural soil with biochar or compost can affect a substantial reduction in potentially leachable Zn without reducing crop uptake of Zn. Furthermore, the combined amendment and cropping was shown to reduce Zn concentrations in soil pore waters furthest. Coupled with fact that Zn immobilisation by the tested biochar was highly efficient, and unlikely to be easily reversible, the findings are significant with regards to the future management of agricultural soils impacted by legacy metal-rich sludge applications. uptake, which alludes to the purposing of sludge-impacted soils for fortified crop growth. Further investigations at the field scale are now required.

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HEAVY METAL TOLERANCE AND PESTICIDE DEGRADATION BY TWO SOIL BACTERIA ISOLATED FROM AGRICULTURAL FIELD OF WEST BENGAL, INDIA- A BIOREMEDIATION APPROACH

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KEYWORDS
Bioremediation. Carbendazim, Heavy metal, Imidacloprid, Methomyl, Pesticide, Plasmid

ABSTRACT

Two soil bacteria, Disha A (*Bacillus cereus*) and Disha B (*Bacillus safensis*),were isolated from pesticide-contaminated crop field in Baruipur, West Bengal, India, showing tolerance against several pesticides and heavy metals. Both of these soil isolates could not be grown in mineral salt medium (MSM) but proficiently grown in MSM supplemented with pesticide (carbendazim/ methomyl/ imidacloprid), indicating the involvement of pesticide usage as a carbon/nitrogen source. The HPLC studies pointed out the efficient degradation of these pesticides by both bacteria. *B. safensis* degraded more amount of imidacloprid (82.48%) and carbendazim (88.93%) than *B. cereus,* 49.12% and 78.07%, respectively, whereas *B. cereus* exhibited slightly better degradation (88.25%) of methomyl in comparison to *B.safensis* (77.5%). Both bacteria tolerated various concentrations of heavy metals, viz. cadmium, cobalt, copper, lead, molybdenum and zinc but not mercury andthe highest tolerance level (1500 µg ml^{-1}) shown against lead and molybdenum. Both bacteria contained a single plasmid. The plasmid-cured *B. cereus* strains did not tolerate any tested pesticide, whereas the wild and cured *B. safensis* strains tolerated all the tested pesticides. So, possibly the pesticide tolerance gene(s) of *B. cereus* are plasmid-dependent but genomic in *B. safensis.*The experiments of plasmid curing did not influence the heavy metal tolerance potential of both bacteria. The consequent transformation experiments also suggested the genomic nature of heavy metal tolerance genes in both the isolates, whereas pesticide resistance genes are plasmid-dependent in *B. cereus* but genomic in *B. safensis.*

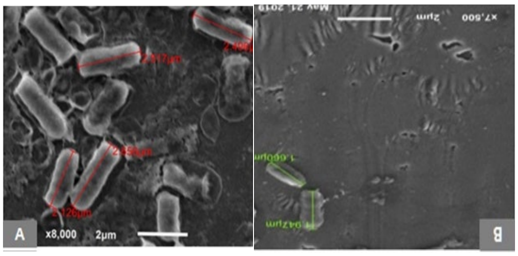

Figure 1 A) Scanning electron micrograph of Disha A (B. cereus)B) Scanning electron micrograph of Disha B (B. safensis).

Agricultural practices heavily depend on chemical pesticides and chemical fertilizer to feed the ever-increasing population in recent years throughout the globe, including India. The unwarranted use of these chemicals ultimately poses a severe threat of pesticide and heavy metal pollution, affecting present as well as future generations. To diminish the pollution effect, searching for beneficial microbes with bioremediation potentialities is an endeavour for environmentalmicrobiologists. In the present investigation, seventeen pesticide-tolerantbacterial strainswere initially isolated from thirty-three soil samples collected from pesticide-infested agricultural fields of West Bengal, India.From these soil isolates, finally, two rod-shaped, Gram-positive bacteria (Disha A and Disha B) are chosenfor thorough investigation due to their tolerance against three pesticides and various metals.The scanning electron micrograph of both the strains is presented in Fig. 1.These rod-shaped bacteria are Gram-positive in nature and spore-former. Both the isolates were characterized biochemically followed by 16s rDNA sequencing, suggesting theclose similarity of Disha A and Disha B with *Bacillus cereus*ATCC 14579 and *Bacillus safensis*FO36B ATCC BAA-1126, respectively (Roy and Das, 2017). The 16S rDNA sequences of bacterial strains were deposited in NCBI with the accession numbers KY094642 for Disha A and KY094643 for Disha B. These bacterial strainshave been deposited in the National Centre for Industrial Microorganisms (NCIM), Pune, India and the accession numbers areNCIM 5557 for*B. cereus*and NCIM 5558 for *B. safensis*.

Though these bacteria can grow generally in Nutrient broth and LB medium but could not grow in the mineral salt medium (MSM).However, growth was observed when MSM was supplemented with any of the three tested pesticides,.It is assumed that the degraded product(s) of pesticides acted as carbon and/ nitrogen source,thus helping the bacteriato grow efficiently in the presence of the pesticide(s).*B. safensis* grew better in the carbendazim/imidacloprid-supplemented MSM medium, whereas *B. cereus* grew better in the methomyl-supplemented medium.

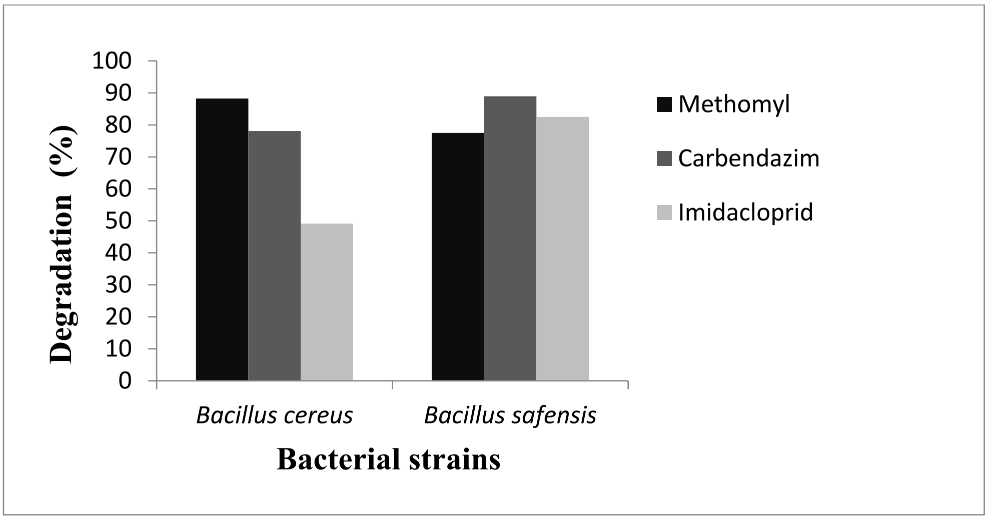

Fig. 2 Comparative degradation of different pesticides as evidenced by HPLC by B. cereus and B. safensis.

Some metals like molybdenum, lead, zinc, copper, cobalt, and cadmium were tolerated by both *B.cereus* and *B.safensis* in the current investigation; however, mercury was not (Table 1). The metal resistance was similar in both microorganisms. The optimum tolerable concentrationis 1500 mg ml^{-1}for molybdenum and lead, 700 mg ml^{-1} for zinc, 500 mg ml^{-1} for copper and cobalt, and 250 mg ml^{-1} for cadmium for both bacterial species. Heavy metal-resistant bacteria are supposed to be an indicator of heavy metal pollution and can help with biogeochemical cycling and ecosystem remediation (Rahaman and Singh 2018).

Different research groups reported that the presence of plasmids in various bacterial species like*Bacillus, Citrobacter, Pseudomonas*, Enterobacter and *Escherichia* might be accountable for pesticide tolerance and resistance todifferent metals and antibiotics(Anjum et al. 2012; Efe 2020). The present investigation found that both the *B. cereus* and *B. safensis* possessed a single 1.5 kb (approx.) plasmid. To know the involvement of plasmid in metal resistance and pesticide tolerance, curing of plasmids was done by some curing agents like crystal violet, acridine orange, and SDS.Here in the presence of 500 µg/mlacridine orange, 70-80% curing frequency is observed, followed by crystal violet (63-72%), whereas SDS showed only 22-28% curing frequency.

In the present study, both thewild B*acillus strains* tolerated and degraded all three tested pesticides,as evidenced by HPLC with different efficiencies(Fig. 2) . Theplasmid-cured strain of *B. cereus* could not tolerate any pesticide.

However, the cured strains of *B. safensis* could tolerate all the pesticides.Again, all the tested cured and wild bacterial strains can tolerate different concentrations of heavy metals except mercury (Table-1) So, the heavy metal resistance gene(s) of both the bacteria are not plasmid-dependent; however, the pesticide tolerance gene(s) of *B. cereus* is plasmid-borne but genomic in *B. safensis*. In the present study, amoxicillin resistance was used as a marker character, and the MIC value was 500 µg/ml. The wild strain of *B. cereus* and *B. safensis* were able to grow individually in the presence of amoxicillin (500 µg/ml), but cured strains were unable. So both *B. cereus* and *B. safensis* carry the amoxicillin-resistant gene in their plasmid*.* Seiler and Berendonk (2012) concluded that various heavy metals, viz. mercury, copper, zinc and cadmium, when arriving at the environment and gathering to critical concentrations, can trigger co-selection of antibiotic resistance.

Table 1. Metal tolerance of wild and plasmid-cured B. cereus and B. safensis at different concentration

Bacterial strains	Molybdenum (µg/ml)	Lead (µg/ml)	Zinc (µg/ml)	Copper (µg/ml)	Cobalt (µg/ml)	Cadmium (µg/ml)	Mercury (µg/ml)
B. safensis (Wild)	1500	1500	700	500	500	300	Nil
B. safensis (Plasmid-cured)	1500	1500	700	500	500	300	Nil
B. cereus (Wild))	1500	1500	700	500	500	300	Nil
B. cereus (Plasmid-cured)	1500	1500	700	500	500	300	Nil

For confirmationof the presence of metal/pesticide resistance genes in plasmid or chromosome, both the bacterial plasmids were transformed separately into plasmid-less *E. coli* strain*.* The isolated plasmids from transformed *E. coli* cells showed similar R_f values to those ofdonor plasmids. The colonies that received the *B. cereus* plasmids were able to grow in pesticides (0.2% imidacloprid or 0.2% carbendazim) supplemented NA medium but which received the *B. safensis* plasmids were unable to grow in any of the pesticides supplemented media [Data not shown]. It was also found that after plasmid curing, the growth of *B.cereus*was hampered but no such effect was observed in *Bsafensi.*indicating the plasmid-dependent growth of *B*., *cereus*. Considering all these observations, it can be concluded that, in *B. cereus,* plasmid genes wereresponsible forpesticide tolerance, but not for theheavy metal tolerance, whereas both pesticide and heavy metal tolerance genes in *B. safensis* were genomic in nature.

According to Malik et al. (2008), the transfer of conjugative plasmids containing independent replicons, which might elicit desirable factors, is the most potentgene transfer strategy, particularly in polluted soil. Heavy metal resistance genes can be found in chromosomal DNA, plasmids, or both (Nies and Brown 1997). Plasmid-dependent pesticide tolerance was reported by some researchers in some bacterial strains like *Enterococcus faecalis* and *Pseudomonas aeruginosa,Staphylococcus aureus* etc. (Maheswari et al., 2010).). According to Yu et al. (2018), the Chromosomal DNA mediated heavy metal tolerance mechanism was found in *Stenotrophomonas maltophilia.*In *Stenotrophomonas* sp. MA5, Agarwal et al. (2019) discovered a transposon-derived mer operon capable of mercury detoxification. Within the genome of this bacterial species, they revealed several gene determinants for resistance to heavy metals and antibiotics.A carbofuran degrading plasmid less *Enterobacte*r sp. from soil was isolated and stated the involvement of chromosomal gene (s) in pesticide degradation (Ekram et al. 2020). Hawkins et al. (2019) argued that pesticide resistance capability might evolve under sturdy evolutionary pressure due to the environmental (pesticide treated) changes and genomic DNA mutations or plasmid-mediated horizontal gene transfer being the most likely causes.

Restricted use of synthetic pesticides and different agrochemicals are essential for sustainable agricultural practices. The bioremediation approach is significantly more beneficial in the biodiversity niche when it comes to battling against agrochemicals-infested contaminated environments.Pesticide and heavy metal degrading/tolerating PGPRs are advantageous in bioremediation activities as they can be used as a disease management paradigm and plant growth promotion in heavily agrochemical-infested soil. For sustainable agricultural practices, the plasmid containing pesticide tolerant gene(s) of *B. cereus* may be exploited for developing native PGPR strains from contaminated soil through transformation, for better plant growth promoting aptitude and for pesticidedegradation and soil remediation,Combination of different multidisciplinary approachesfrom nanotechnology,material science, chemical engineering, biotechnology, and genetic engineering to diverse ecological and functional biological strategies might provide new dimensions in optimizingthe bioremediation of different agrochemicals, particularly by indigenous soil inhabiting PGPRs.

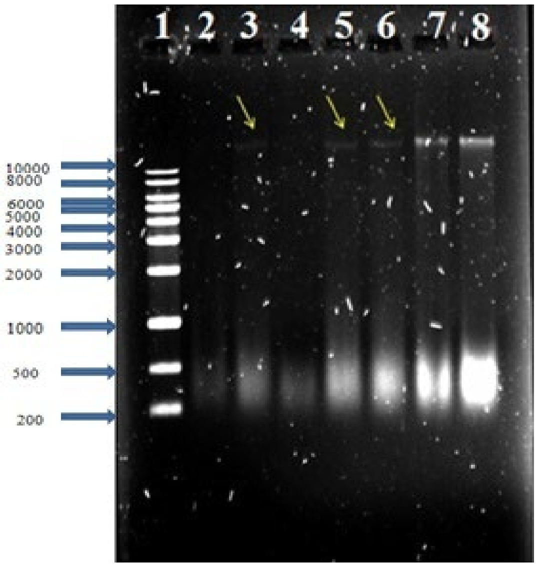

Figure 3. Plasmid profile of different wild and transformed cells. Lane 1- Marker DNA, Lane 2- Wild Strain of E.coli, Lane 3,4,5 and 6 showed transformed E. coli, Lane 7- Wild B. cereus and Lane 8- Wild B. safensis.

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HEAVY METAL PROFILES IN PADDY SOILS AND DIFFERENT RICE VARIETIES IN WESTERN TAMIL NADU, INDIA

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KEYWORDS

Oryza sativa, Heavy metals, Enrichment factor, Translocation factor, Food chain transfer

ABSTRACT

Rice is a staple food crop for more than 90% of Asian countries and half of the world's population. In addition to geogenic in nature, several anthropogenic activities also increased heavy metals in soils especially in paddy fields and rice plants. Currently, farmers followed modern agricultural practices especially for excess input of phosphatic fertilizers in order to increase the agricultural productivity to ensure the food security. The objectives of the present study are mainly focused on the heavy metal profiles of paddy soils and different rice varieties cultivated in Salem, Tamil Nadu, India. Although the accumulation of soil Fe was higher (ranged from 10.92 to 24.80 mg kg^{-1}), Pb and Mn in paddy soil were also significantly higher in all the rice varieties. Among the plant parts, the accumulation of heavy metals (Cd, Pb, Ni, Cu, Zn, Fe and Mn) was higher in roots for all the rice varieties. Compared to Amman variety, root Mn and Fe contents were nine and seven folds higher in Surichi, respectively. Further, nearly 7 and 31 fold higher Pb content in stems and leaves were evident in Bhavani, respectively. Cu content was 6 to 23 folds higher in stems, leaves and grains in Amman than the other varieties. Based on the enrichment factor (EF), Cd showed higher accumulation in both the roots and shoots of different rice varieties. Although the Cd and other metal contents in soils are within the permissible limits, the enrichment factor and translocation factor (TF) also showed that Cd, Pb and Ni was effectively transferred from soil to rice plants including grains is an 'early warning signal' for heavy metal transfer to human beings through food chain.

INTRODUCTION

Heavy metal pollution in agricultural soil is the most important worldwide concern which requires immediate attention. Rice (*Oryza sativa* L.) has become one of the three primary agricultural crops grown worldwide. Heavy metals are predominantly found in paddy soils, it gets accumulated in grains and various parts of rice plants and this factor is reported in different parts of the world. Natural concentration of heavy metals in soils tends to remain low. However, usual anthropogenic practices such as agrochemicals, urbanization, and industrial development are responsible for increasing the heavy metal concentration in the paddy soil [1]. Although India has one of the major rice grain producer and consumer, only limited studies has been carried out to determine the toxicity of heavy metals in the soil - rice system [2-4]. Therefore, the main objectives of the current study is to assess the concentrations of both the heavy metals (Cd, Pb, Ni, Cu, Fe, Zn and Mn) in paddy soil and different parts of rice plants in the dominantly paddy grown regions of Salem district, Tamil Nadu, India.

MATERIALS AND METHODS

SAMPLE COLLECTIONS

A total of 15 soil samples and five widely cultivated major *indica* rice varieties namely (*Bhavani*, *Idly Kundu*, *Amman*, *Thirupathi* and *Suruchi*) were collected from different paddy fields in Western Tamil Nadu, India. At each site, a total of three rice plants and the respective rhizosphere soil samples were collected diagonally. However, the rice plant samples were taken only at the mature phase of the plant, i.e., at the end of the yellow-ripe stage or at the beginning of the full-ripe stage when the rice grains are yellow and transparent. After that, the collected soil and plant samples were transported to the laboratory for further processing and analysis. In the laboratory, soil samples were air-dried at room temperature and homogenized using an agate mortar until it passed through a 2 mm mesh sieve and were stored in clean polyethylene individual bags. In the case of rice plants, samples were thoroughly washed with tap water followed by deionized water and oven-dried at 70 °C until a constant sample weight was established. Subsequently, the samples were homogenized using a stainless-steel mixer grinder and then packed in sealed zip-lock polyethylene bags until further analysis.

SOIL AND PLANT ANALYSES

Soil available metals (Fe, Mn, Cu, Ni, Pb, Zn, and Cd) were extracted using Diethylene Triamine Penta-Acetic acid (DTPA) following the method of Lindsay and Norvell [5]. In the case of rice plant samples, about 0.2 g of homogenized vegetal material was digested using a mixture of HNO_3:$HClO_4$ (4:1 v/v). Thereafter, metal concentrations in both the DTPA extracted soil and acid digested plant samples were determined using an ICP-MS (Inductively Coupled Plasma Mass Spectrometry) (Thermo Fisher Scientific, Model - iCAP Q).

RESULTS

SOIL METAL CONCENTRATIONS

The average soil metal concentrations (mg kg^{-1}) of all the studied heavy metals were found to be in the order of Fe (9.50 to 26.40) > Mn (1.50 to 15.95) > Cu (0.85 to 10.10) > Pb (0.55 to 4.10) > Zn (0.90 to 3.30) > Ni (0.30 to 1.60) > Cd (0.05 to 0.25) (Fig. 1). The soil Fe, Mn, Cu, Zn and Ni concentration obtained in this study exceeded the critical limits (of 4.5, 1.0, 0.2, 0.8 and 0.17 mg kg^{-1} for plant growth [5,]. In addition, the reported soil Cd and Pb content in the paddy fields were below the maximum allowable limits in soils stipulated by India (3-6; 250-500 mg kg^{-1}), China (0.6; 300 mg kg^{-1}), European standard (3.0; 300 mg kg^{-1}), and the USA (70; 400 mg kg^{-1}).

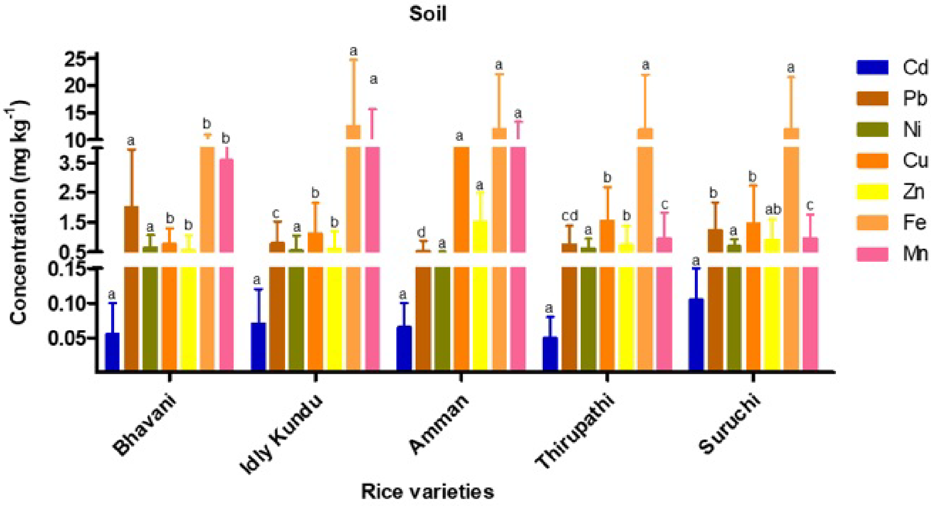

Figure 1. Heavy metal accumulation in paddy soil

HEAVY METAL ACCUMULATION IN RICE PLANT PARTS

The majority of the metals accumulated more in the roots than the aboveground plant parts. The order of heavy metal accumulation in roots, stems, and leaves was found to be Fe>Mn>Pb>Ni>Zn>Cu>Cd. Among the rice cultivars, root metal concentration was higher in Thirupathi (Cd and Zn), Suruchi (Ni, Fe and Mn), Bhavani (Pb) and Amman (Cu). On the other hand, higher stem and leaf metal concentrations were observed in Bhavani (Cd, Pb and Ni), Surichi (Ni, Zn and Mn), Amman (Cu) and Thirupathi (Fe). (Fig. 2).

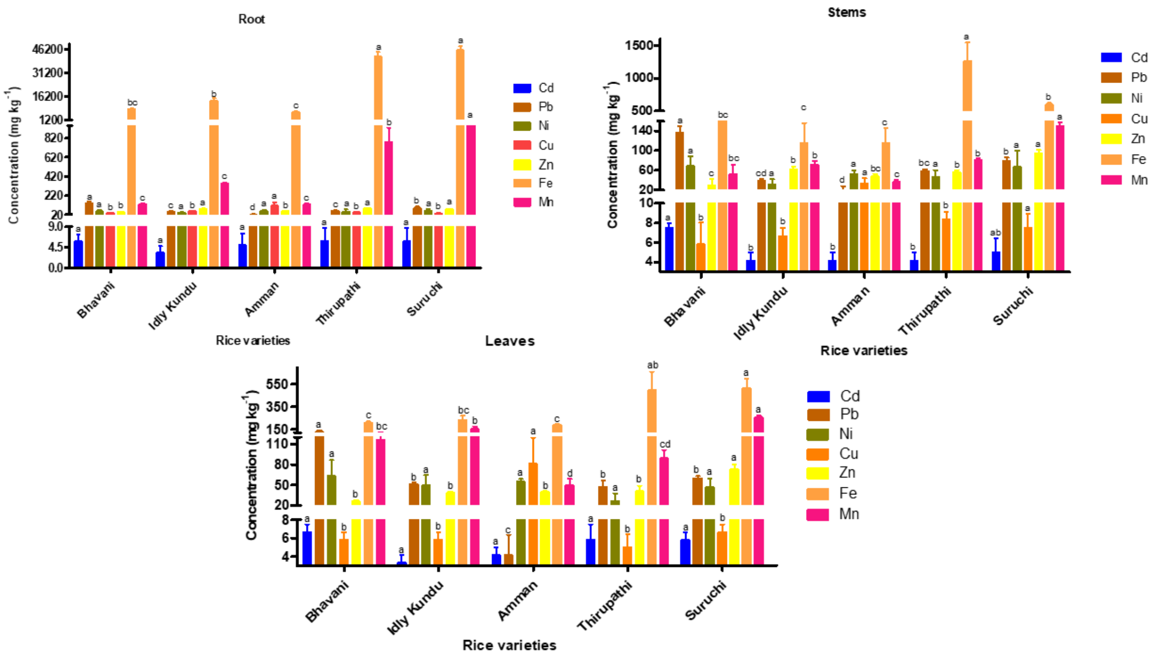

Figure 2. Heavy metal accumulation in different rice plant parts

The order of heavy metals in rice grains were Fe>Zn>Pb>Ni>Mn>Cu>Cd. Among the rice varieties, in addition to Fe, higher grain metal concentrations were evident in Bhavani (Pb), Idly Kundu (Pb, Ni and Zn), Amman (Cu and Mn), Thirupathi (Pb and Mn) and Surichi (Zn) (Fig. 3). The average concentrations of heavy metals especially in Cd in rice grains were exceeded the upper limit that has been imposed by CODEX and FAO/WHO [6].

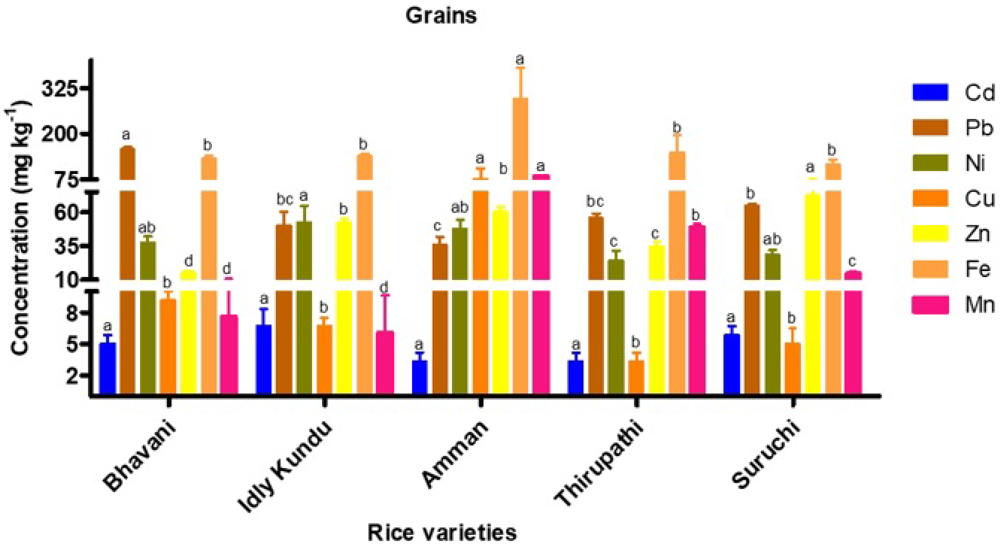

Figure 3. Heavy metal accumulation in rice grains

TRANSLOCATION FACTOR (TF) AND ENRICHMENT FACTOR (EF)

The TF values for Cd, Pb and Ni from soil to root showed >10 in all the studied rice varieties.

The TF values for Pb from leaves to grains were >1 in all the rice varieties and for Cd in both Idly Kundu and Surichi clearly indicated that these metals are effectively translocated and accumulated in aerial parts especially in rice grains. On the contrary, the TF values for Mn and Fe from leaves to grains were <1 in all the rice varieties studied except Amman (Fe). Based on the mean EF values, Cd, Pb, Ni, Zn and Fe categorized as ‘very severe enrichment’ in all the studied rice varieties.

CONCLUSION

The DTPA extracted heavy metal (Cu, Zn, Fe, Mn and Ni) concentrations in paddy soil samples were exceeded the maximum permissible limits. However, the concentrations of Cd and Pb in paddy soil were below the maximum allowable limits. On the other hand, the average heavy metal concentration in grains were above the maximum permissible limits especially for Cd and Pb. Based on the TF and EF values, these metals are efficiently translocated from roots to shoots especially in grains even though Cd and Pb was within the permissible limits in paddy soils. Thus, this type of findings could provide valuable evidence to the government and NGOs for formulating better strategies to alleviate metal contamination in agricultural soils and staple food crops. Presently, rice consumption is considered as a potential vector of metal transfer to humans, and it is an absolute demand to address the possible health risks.

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ENHANCED BIOREMEDIATION OF SOILS USING SUSTAINABLY PRODUCED ORGANIC SOIL AMENDMENTS

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ABSTRACT

Agricultural, industrial, and military activities have resulted in extensive contamination of soil at thousands of sites throughout the world. Over the past 25 years many of these sites have been successfully remediated using sustainably produced organic soil amendments. For contaminants most effectively destroyed under aerobic conditions the amendments are composed of processed plant materials and an emulsifying agent and offered under the tradename Terramend®. For contaminants more effectively degraded under anaerobic conditions microscale zero valent iron (ZVI) is added to the formulation and the tradename is Daramend®. Among the contaminants successfully treated using these soil amendments are petroleum hydrocarbons, PAHs, phthalates, chlorinated phenols, chlorinated herbicides, chlorinated pesticides, and organic explosive compounds. Treatment of soils with these reagents results in destruction of the targeted contaminants, rather than their immobilization, and allows reliable attainment of industrial and residential land use standards. This approach also provides a more economical, sustainable, alternative to excavation and off-site soil disposal. Large projects using these soil amendments have been completed in Canada, China, Colombia, El Salvador, Europe, and the United States. Treatment has been conducted both in situ without excavation, and on-site following soil excavation. The presentation will illustrate how changes in soil chemistry and microbial ecology following addition of the Terramend® or Daramend® reagents promotes destruction of soil contaminants. Results from bench-scale testing and full-scale projects will be presented and discussed including performance data and cost.

STUDY OF THE VEGETATION COVER OF AN ENVIRONMENT CONTAMINATED BY HEAVY METAL SULPHIDES: STRATEGIES AND SPECIFIC DISTRIBUTION

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KEYWORDS
Sulphide metals pollution; plant colonization strategies; pioner plants; nurse plants

ABSTRACT

After the extraction of sulfide minerals such as galena, sphalerite and pyrite for decades, the abandoned minesites are a sort of mosaic of different substrates related with the different activities carried out on mineral management and processing. After the exploitation time, a slow but steady natural colonization starts by a select group of species, resilient enough to the very harsh conditions. The presence of high levels of heavy metals, acidic pH and a poor water retention are the key limiting factors. The list of the species and their specific role in the colonization strategies have been studied with the aim of determining the physiological or ecological mechanisms involved in overcoming the environmental restrictions. *Phragmites australis* can be considered as a pioner species, colonizing first the substrate and creating the necessary conditions for other species to stablish themselves in the area. This species creates a shallow network of rhizomes that allows the accumulation of resources (organic matter, finer mineral particles, etc.) that will ease the germination and growth of other species, specially *Retama sphaerocarpa*.

We have observed some interspecific strategies that lead to the improvement of edaphic conditions, increasing the organic matter content, favoring compaction, water retention and some enzymatic activities linked to microbial activity. This study draws predictions on the hypothetical ability to gerenate resources by plants and how different soil types alter plant strategies to achieve a sustainable plant cover, despite trenchant environmental constraints.The general objective of this study is to gather knowledge to understand the relationship between soil properties and species distribution in harsh environment.

SUMARY

An abandon mine area is an excellent site to study the processes used by plants to overcome environmental constraints. In our work we have analyzed and quantified the small scale spatio-temporal patterns of colonization and the phenomena involved in both the advance of the vegetation cover and in the increase in biodiversity. Having knowledge about soil properties, microbial activity and composition (Ailstock, 2000; Gallego et al, 2021) and plant cover patterns as well as changes in the relation and structure of coexisting species, is crucial in determining the functionality of the ecosystem and to identify opportunities for management of the degraded lands (Bradley 2014).

Our studies are focused on a galena and sphalerite mine, abandoned since the middle of the 20th century (Mina de San Quintín, Ciudad Real, Spain). Currently it is an area of approximately 1.5 km^2 that stands out as an interruption of the landscape patterns. The vegetation cover is characteristic of these Alcudian slate and greywacke substrates, generally of the dehesa type, with a clear predominance of holm oak (*Quercus ilex*), sporadic presence of broom, and the spontaneous vegetation generally associated with this ecosystem (Table 1). Surrounding the minesite we find oak-scattered pastures dedicated to extensive sheep and cattle farming, alternated with cereal and olive plots and with a relative human presence. The minesite appears as a highly altered area with piles of rubble, mining tailings and scarce vegetation. Making a detailed study of the surface we identify the following areas (Fig 1):

TD: Totally Degraded areas. Characterized by the original soil has been totally removed or replaced by different materials.

Here we can find:

TDMG. Totally Degraded Mine Gangues: Large mounds of material several meters thick of sulphurous material extracted from the mine with ore richness lower than required to be extracted and processed (metallic sulphides around 2-5%). This material has ecological importance since they generate acid drainage due to the contact of sulfides with rainwater. Normally the acidic water percolates down to the impermeable base layers and then appears on the surface forming streams that end up affecting the surrounding area. Originally, a drainage channel was built to collect these runoffs and direct them to a nearby stream, characterized by a red color due to the presence of *Acidothiobacillus ferredoxidans* and the consequent ferric hydroxides. It is an area practically without vegetation with some isolated individuals of plants resistant to acidic substrate (Soil pH≈2.0) (**Table 1)**.

TDHT. Totally Degraded Heap of Tailings: With a surface of about 3000 m^2 this heap rises above the original level between 5 and 2 m. It is made up of a fine material coming from the grinding and subsequent extraction by physical decantation of the sulphide ores. The whole area consists of a deep substrate of fine material of silt and fine sand fractions, coming from the marly slates materials that surrounded the sulphurous veins. The resulting material is sulphides free. In this area a gradation of soil formation and compaction can be observed and studied. It has also been possible to observe the process of colonization of the lower parts through the years. *Phragmites australis* is the unique species homogeneously distributed throughout the whole covered area and it can be considered as a pioneer (Ait, 2004). The collaboration between the *Phragmites australis* and *Retama sphaerocarpa* species for said colonization has been studied.

PD: Partially Degraded areas. In this case, the soil has undergone gradual physical or chemical alterations but preserving its original composition and level. This alteration can be considered extreme, in the center of the mining area, or weaker, in the edge spaces. The disturbance may be due to the presence of non-native materials, mainly carried by the wind, contaminated liquid spills, acid drainage or soil compaction due to the continuous heavy hauling activity derived from mining processes.

We can find:

PDAD. Partially Degraded affected by Acid Drainage: It is an area affected by the acid drainage coming from the gangue deposits (**Fig. 2**). During the rainy season, the leached water from this material spreads over the flat and low-lying areas until it converges in a stream that empties into a nearby lagoon, outside the mining area. In the area affected by acid drainage we find very little vegetation and species that are very resistant to these conditions (**Fig. 3**). The vegetation is formed almost exclusively by patches of *Spergularia purpurea* and *Molineriella laevis*, perfectly associated and with a special location, leaving *S. purpurea* outside, in contact with acidic water (pH around 2.5). In places where conditions allow the formation of patches with a diameter greater than 1 m, the species *Micropirum tenellum* usually occupies the center.

PDLL. Partially Degraded Low-Level areas: Characterized by receiving materials from neighboring areas, specially, wind-borne fine material (clay and silk). A thin but impermeable layer is formed resulting harsh conditions for plant colonization. These areas flood in the wet season and dry up in summer. Due to these wet/dry cycles a salt crust appears in the surface. This area is colonized mainly by *Phragmites australis* and *Tamarix africana*, both of them resistant to high values of edaphic electric conductivity (10-16 dS/m). Processes closely linked to the evolution of natural ecosystems such as wind deposits of fine material, erosion by storm avalanches, colonization by pioneer species, etc, can be seen, measured and tracked. In general terms, the vegetal biodiversity is varied, and we can find species such as *Linum tenue, Retama sphaerocarpa*, *Centaurium eritraea, Hirschfeldia incana, Jasione montana* and *Thymus mastichina* among others.

PDCS. Partially Degraded Compacted Soil: Characterized by a deep alteration of the original substrate but keeping the original level. They are wide and irregular areas of gravel and loose sand, with a certain undulation with varied vegetation. Here we find a high incidence of therophytes, mainly *Molineriella laevis* and *Rumex bucephaloforus* as predominant species, accompanied by *Piptaptherum milliaceum* when edaphic conditions allow it. Allochthonous organic material, dumped in some areas, relieves the edaphic conditions and allows the appearance of new species such as *Holcus lanatus*.

PDME. Partially Degraded Marginal Edges: They are characterized by slightly disturbed soil. In these areas we find transitional vegetation with the most common ruderal species in the spaces surrounding the mining area. In this area, *Biscutella auriculata* and *Retama sphaerocarpa* are the most representative.

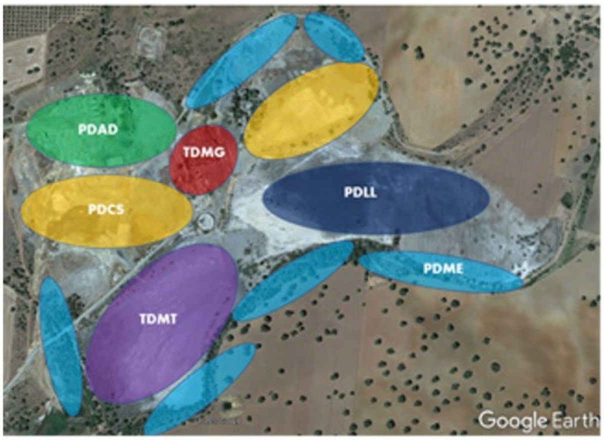

Figure 1. Defined areas

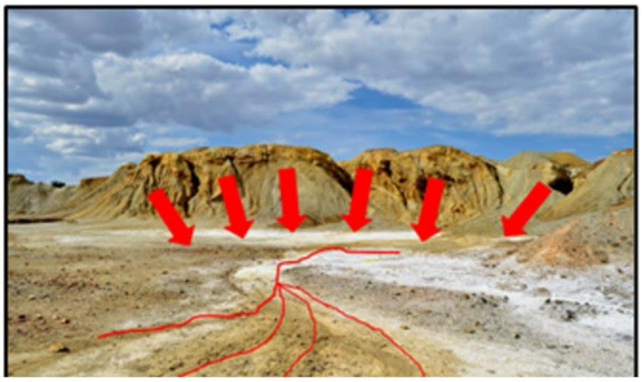

Figure 2. Acid drainage, coming from the gangue piles, affect the lower areas. Only scattered patches of Spergularia purpurea and Molineriella laevis can be found on this zone.

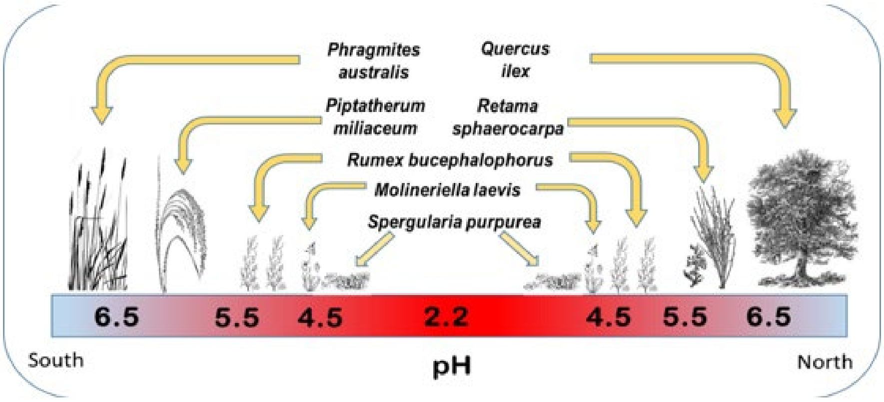

Figure 3. Plant cover transect across affected Acid Drainage zone (PDAD)

Table 1. Species distribution according with identified areas. TDMG: Totally Degraded Mine Gangues. TDHT: Totally Degraded Tailings Heap. PDAD: Partially Degraded affected by Acid Drainage. PDLL Partially Degraded Low-Level areas. PDCS: Partially Degraded Compacted Soil areas.PDME: Partially Degraded Marginal Edges areas. Presence: +++ abundant, forming tight communities; ++ dispersed individuals through a wide area; + isolate or rare individuals.

Species	TDMG	TDTR	PDAD	PDLL	PDCS	PDME
Aegilops triuncialis L.		+				
Asparagus acutifolius L.						+
Avena barbata Pott ex Link						++
Biscutella auriculata					++	+++
Bromus rubens L.		+		+	+	++
Campanula rapunculus L.						+
Carlina corymbosa L.						+
Carlina racemosa L.						+
Centaurium erythraea Rafin.		++		++	+	+
Cistus ladanifer L.						+
Crupina vulgaris Pers. ex Cass.						+
Daucus carota L.						+
Eryngium campestre L.				+	+	+
Helichrysum stoechas (L.) Moench.					+	++
Hirschfeldia incana (L.) Lagréze-F.	+	++		++	++	+
Holcus lanatus L.					+	
Jasione montana L.		+		+	++	++
Linum tenue Desf.		+		++		
Lomelosia stellata (L.) Raf.		+		+		++
Micropirum tenellum Link.			+		+	
Molineriella laevis (Brot.)			+++		+++	
Onopordum illyricum L.						+
Papaver roheas L.				+		+
*Petrorhagia nanteuilii (*Burnat)		+		+	+	++
Phragmites australis (Cav.) Trin.		+++		+++		
Piptatherum miliaceum (L.) Coss.			+	+	++	
Plantago coronopus L.					+	+
Quercus ilex L.						+
Retama sphaerocarpa (L.) Boiss.		+		+	+	++
Robinia pseudoacacia L.		+				+
Rumex bucephalophorus L.	+				+++	
Scabiosa atropurpurea L.		+		+		
Scrophularia canina L.		++				
Spergularia purpurea (Pers)	+		+++		+	
Serapias lingua L.						+
Tamarix africana Poir.				++		
Thymus mastichina (L.) L.		+		++	+	+
Species	**TDMG**	**TDTR**	**PDAD**	**PDLL**	**PDCS**	**PDME**
Thymus vulgaris L.		+				+
Trifolium arvense L.						+

Trifolium stellatum L.						+
Trifolium angustifolium L.						+
Trifolium campestre Schreb. in Sturm.						+

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RESEARCH ON THE DISTRIBUTION OF SLAG CONTAMINATION IN THE CAVE SYSTEM OF RUDICKÉ PROPADÁNÍ – BÝČÍ SKÁLA

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KEYWORDS
Slag contaminant, Rudické propadání, Býčí skála, cave system, ERT method

ABSTRACT

Rudické propadání – Býčí skála cave system in the Moravian Karst (Czech Republic) has currently over 15 km of corridors, six of which are active corridors of the Jedovnice creek. The stream erodes an old slag deposit [1, 2] near the Rudice Sinkhole and brings the slag into the cave system. Concentrations of leached metals in the karst waters are not too high, however, the slag if highly abrasive, clogs the cave system and mechanically damages speleothems [3]. A detailed mapping of the slag distribution contained in the sedimentary fill was carried out throughout the cave system. The sedimentary fill was sampled in 50 documentation points with 25-150 m step. Mechanical effects of slag on the cave environment were also documented (damage to the stalactites, grooves and potholes on the sinter crust). The extent of contamination was determined based on granulometric analysis of the slag separated from the sampled cave sediment. The thickness of sedimentary fill in the cave system was estimated using three profiles of an electrical resistivity tomography (ERT) survey. The principle of deposition, the proportion of slag and the grinding intensities of individual pieces vary with the distance from the Rudice Sinkhole. The distribution of slag pieces is uneven and depends on the morphology and hydrodynamics of the cave space. In the cave are also documented organic pond sediments layers, which are contaminated with heavy metals [3].

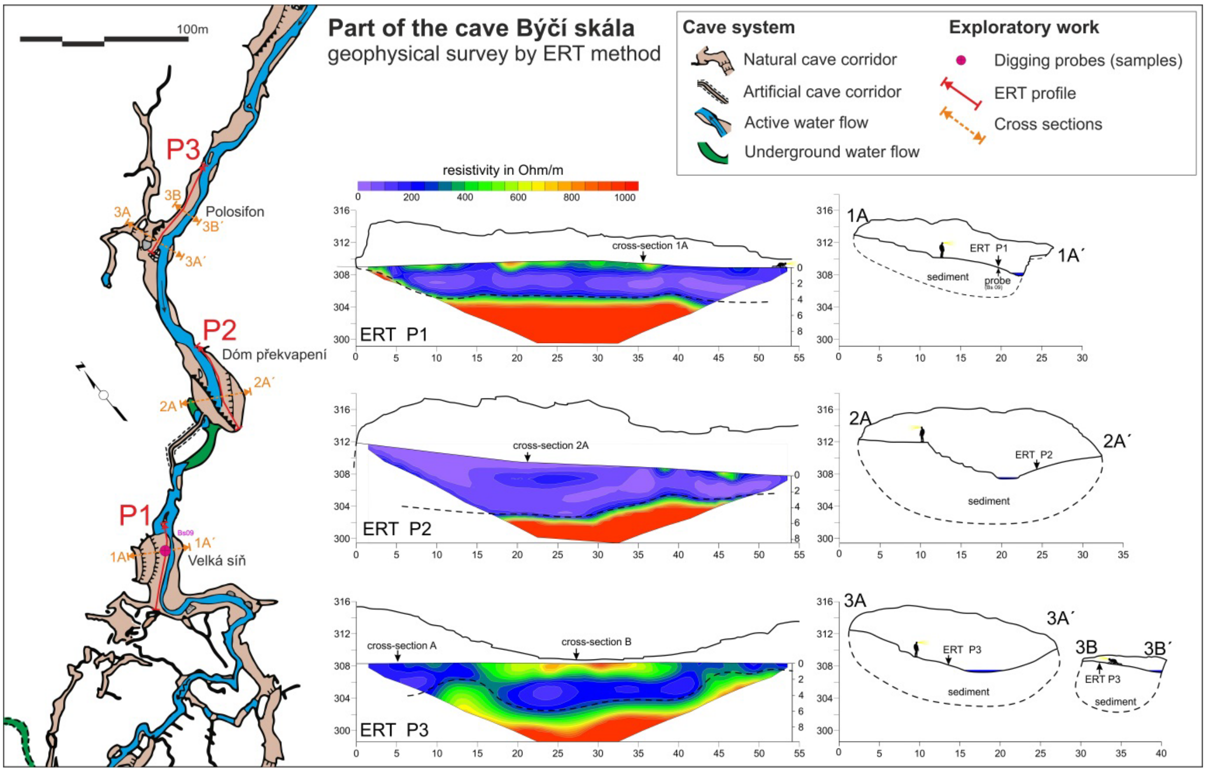

Figure 1. Interpretation of ERT method to determine the thickness of the sedimentary fill in the CS

A detailed mapping of the slag distribution within the sedimentary filling was performed. The cave was divided according to the estimated thickness of the sediment, using knowledge of cave sedimentation. It was suitably supplemented with dug probes. The main goal was to determine the depth distribution of slag. Secondary goal was to try to dig up sediment on the limestone bedrock, which has not yet succeeded. Therefore, the geophysical method ERT was used. ERT was used to estimate thicknesses of the sediment. The positions of the ERT profiles were selected in places with assumed maximum thickness of sediments. We considered a basic geophysical model which consists of 2 major quasi-homogeneous geoelectric layers: cave sediments saturated with water (low resistivity 0-400 ohm.m), and underlying limestone (high resistivity more than 400 ohm.m). The dashed black line indicates the interpreted interface (sediment vs. limestone). The thickness of sedimentary filling was estimated using ERT to be up to 8 m (ERT P2 in Fig. 1) at 3 places in the Býčí skála cave (Fig. 1).

It should be noted that the use of geoelectric methods in caves complicates the lateral reach of the method. The required half-space is not maintained here. Measurement negatively affects the electric current which passes through the walls and ceiling.

Mechanical effects of the slag material on the cave environment were also documented. These comprise mainly damage to the stalactites (grooves and potholes on the sinter crust). The extent of contamination was determined based on granulometric analysis of the slag separated from the sampled cave sediments. The cave sediments (poorly sorted angular to rounded clasts) contain sediments of culm, limestones, silicified sandstones (slůňáky), slag material, other anthropogenic material and organic matter such as bits of wood and dark mud. Deposition style and slag material content change with distance from the Rudice sinkhole [1, 2]. In the upper narrow and high canyon-like parts, thanks to the great energy of the Jedovnice stream, the slag is completely mixed with other sediment and deposited on the bottom of the stream in small areas of accumulation. From the Stará River tributary the depositional style changes into large flat alluvial deposits and terraces, similar to the lower parts of the cave system. Within the small terraces on the edges of the cave corridors, the slag material is dispersed in muddy or sandy sediments forming layers layers. This distribution can be attributed to deposition at higher water levels caused by spring melting, heavy rains or discharge of ponds. In some places there are layers with thicknesses up to 3 cm of organic dark sediment originating in the pond system in the vicinity of Jedovnice. In the Býčí skála cave, outside the riverbed itself, the slag material is usually only "sprinkled" on top of the cave sediments.

The slag material is formed by irregular clusts of various sizes (from millimeters to cobbles up to 20 cm). The clusts show evidence of heavy rounding during transport. Roundness increases with distance from the source area. The most abraded are cobbles at the end of the cave system in the Josefov valley. The distribution of slag material within the cave is heavily dependent of the corridor geometry and energy of the stream.

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GEOTECHNICAL STRUCTURES IN CONTAMINATED AREAS

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KEYWORDS
Geotechnical structures, structural reliability, remediation method

The choice of a suitable remediation method depends on the water and environmental conditions specific to the occurrence of different types of contaminants. Land and groundwater remediation is a complex problem. The most common solution is using a combination of several technologies and various ex-situ and in-situ methods. In contaminated areas, it is possible to create impermeable hydrodynamic barriers (sealing diaphragm walls), which serve to stop or direct the flow of water, or reactive barriers (PRB - permeable reactive barriers), which remove impurities from the water flow (Suthersan, 1997, Birke et al., 2003). Sealing diaphragm walls and other geotechnical remediation technologies are geotechnical structures and can be used as remediation method, e.g. passive barriers.

Geotechnical reliability

European standards - Eurocodes defines structural reliability as the ability of a structure to fulfil the specified requirements during the service life for which it has been designed; the notion covers safety, serviceability and durability. All structures must achieve a required level of reliability. In a more narrow sense of the word, reliability refers to the way uncertainties are dealt with in design and assessment by the use of partial factors or more advanced probabilistic methods. Ground model and geotechnical design model shall be used to verify the requirements for safety, serviceability, robustness and durability of geotechnical structures. Geotechnical reliability is based on the extent of the zone of influence. The zone of influence should consider the structure and its elements, any transient or persistent changes in ground conditions and also environmental impact, pollution according new revised Eurocode 7 (prEN 1997-1: 2022).

The Geotechnical Category is used as a tool in EN 1997 to obtain appropriate reliability. The concept of Geotechnical Category as the tool to ensure such level for the geotechnical structures. The Geotechnical Category (GC) of a geotechnical structure combines the consequence of failure of the structure (represented by its Consequence Class, CC) and the complexity of the ground (represented by the Geotechnical Complexity Class, GCC). The Geotechnical Complexity Class shall be selected using engineering judgement account complexity and uncertainty in the ground, groundwater conditions and ground interaction. All geotechnical structures in contaminated areas shall be classified as GCC 3 with higher complexity. Geotechnical Category shall be used to specify the extent and amount of the following measures:

- measures to achieve appropriate representation of parameters for design, including:
    - appropriate extent of ground investigation ;
    - validation of available information from Ground investigations;
    - validation of the Geotechnical Design Model;
- measures to achieve accuracy of the calculation models used and the interpretation of their results, including:
    - validation of calculation models;
- measures to ensure appropriate implementation of design according to procedures specified in the project documentation, including:

- supervision;
- inspection;
- monitoring;
- maintenance.

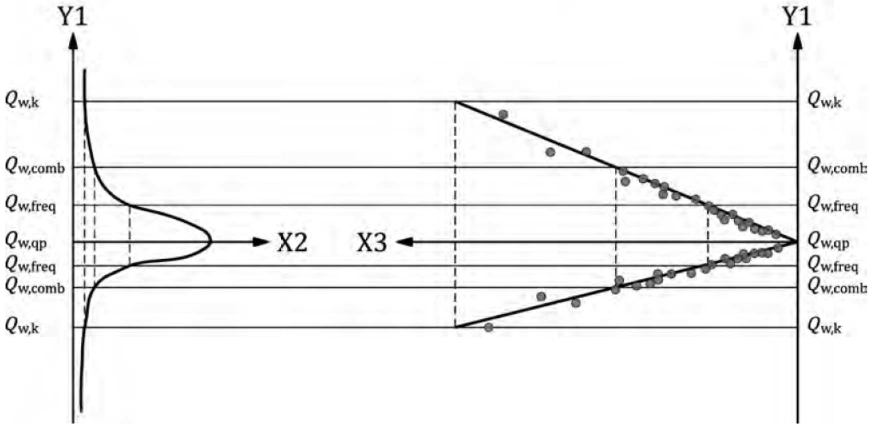
The adverse effects on the durability of the structure, of the following environmental influences on degradation, corrosion, leaching and erosion shall be considered:

- existing and future climate conditions due to precipitation, temperature and wind;
- freezing and/or thawing of groundwater and surface water;
- electro-chemical composition of ground, groundwater, surface water and any fill;
- salinity of ground, groundwater and surface water;
- mineralogical composition of the ground;
- change of physical, chemical and/or mineralogical composition in the ground;
- evaporation;
- any electrical current flowing in the ground;
- biological activity; and
- existing or potential contaminated ground, groundwater, or surface water.

The representative value of groundwater pressure $F_{\text{w,rep}}$ should be selected as either:

- a single permanent value, equal to the characteristic upper or lower value of groundwater pressure (whichever is more adverse according to the considered limit state);
- the combination of:
  - a permanent value, equal to the mean value of groundwater pressure, and
  - a variable value, equal to the representative value of the variation in groundwater pressure.

The values are based on an annual probability of exceedance of 2 % (which corresponds to a return period of 50 years). Figure 1 illustrates the different terms used to denote representative values of groundwater pressure.



Key: X1 t (time), X2 probability density (annual maximal), X3 log t return period, Y groundwater pressures, Piezometric levels, 1 higher values, 2 lower values.

Figure 1. The representative value of groundwater pressures- illustration of characteristic, combination, frequent, and quasi-permanent values (prEN 1997-1, 2022, prEN 1990:2021).

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EFFECTIVENESS OF SPECIFIC COOLING VESTS ON PHYSIOLOGICAL AND PERCEPTUAL RESPONSES OF FIRST RESPONDERS IN CONTAMINATED AREAS

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KEY WORDS
Protective equipment, cooling vest, temperature effects, heat stress, perceptual response

ABSTRACT

The present study was realized in order to evaluate the efficiency of modern cooling vest based on a different technologies and its effects on physiological and perceptual responses of first responders in contaminated areas. The all results are based on the different tests realized in the climatic chamber in the Military Medical Academy in Belgrade. Fifteen male volunteers were subjected to exertional heat stress test on a treadmill in hot environmental conditions (air temperature 40 °C). The tests were performed with professional solders (23.5 ± 2.3 years, 70 ± 8 kg, 178 ± 7 cm), without any cooling system (NoCOOL) and using the several cooling vests: Arctic Heat cooling system and Entrak. As physiological strain indicators, the following parameters have been determined during tests: mean skin temperature (Tsk), tympanic temperature (Tty) and heart rate (HR). For this purposes sweat rate (SwR) was calculated to determine the change in the water and electrolyte status. The obtained results confirmed that the contemporary cooling vest used in hot environment was able to attenuate the physiological strain levels and perceptual responses during exercise, when compared to the identical exposure without the cooling.

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 (Moran, 1998). 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.

Many activities request the best possible physiological comfort of first responders, especially in contaminated areas (Fatah, 2007). 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. Applications of cooling systems bring numerous additional benefits, such as increased mission duration, decrease in hydration needs, improved mental activity 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.

EXPERIMENTAL PART

Testing of physiological suitability under field conditions represents a logical continuation of tests of cooling vests physiological suitability in laboratory conditions (ISO9886, ISO 12894(E), 2008). Each subject performed two tests, both times wearing working uniform, with and without cooling vest over. In both cases, exercises performed under the same climatic conditions (temperature 40 °C, relative humidity 58 %, air speed < 0,3 m/s). Tympanic temperature was measured by conducting thermo-element TSD202A into the aural channel and investing as close as possible to the eardrum. This measurement was continually, with recording data every 10 seconds. Tthe mean body skin temperature (Tsk) was determined continually, mesuring of local body temperatures on four points, using transdusers types TSD202E and TS202F. Subjective assessment of the level of comfort was rated by each subject using the McGinnis scale for ergometry testing in the climatic chamber.

Figure 1. Snapshot vest recorded with standard and thermal imaging camera, after 30 minute of exercise

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 laboratory and field tests were conducted using high performance equipment, with technical features that enable to measure, monitor and record necessary physiological parameters in real time. The evaluation of the evaporative cooling system in this study found two important conclusions: in case of wearing cooling vest covering torso area, body core temperature (measured through tympanic temperature) grow slower, and mean body skin temperature is significantly lower. Moreover, heart rate values and subjective assessment of comfort levels point to the much expressed test subject's physiological stability, which is very important result from the aspect of confidence and efficiency in fulfilling the given professional activities. The results clearly identified the benefits of a cooling vest in lowering the thermal strain for the mounted test subjects.

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APPLICATION OF LOW-COST ADSORBENT BASED ON FLY ASH FOR THE REMOVAL OF DICHLORODIPHENYLTRICHLOROETHANE (DDT) FROM WATER

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KEYWORDS
Fly ash, adsorbent, dichlorodiphenyltrichloroethane, water, adsorption capacity

ABSTRACT

This paper investigates possible association between two large environmental problems. First is fly ash as a by-product resulting from the burning of coal in thermal power plants, and whose disposal requires large areas of land, huge amount of water and energy. It poses a major environmental and economic problem. Second problem is regarding pesticides that occur as contaminants in water sources, have adverse effects on human health due to their toxicity, carcinogenicity and mutagenicity, or cause aesthetic problems such as taste and odor. Hence, this paper investigates the feasibility of using fly ash as a cheap adsorbent for removing pesticides from water instead of using commercial activated carbon. This study recognizes that fly ash (FA) is a promising adsorbent for the removal of various contaminants. Fly ash from the Morava thermal power plant was simply chemically treated with lime yielding modified fly ash (MFA), which proved to be an effective adsorbent for the removal of organochlorine pesticide – Dichlorodiphenyltrichloroethane (DDT) from water. The lime content in fly ash was optimized with respect to the adsorption capacity of DDT using response surface method (RSM). The commercial software "Design expert 9" was used for this purpose. The maximum Langmuir capacity of the adsorbent for DDT was $4.489 \bullet 10^{-5}$ mol g^{-1} (15.9 mg g^{-1}) at 25 °C at the solution pH of 7. Adsorption kinetics was determined to be a second-order pseudo model and equilibrium was established after 90 minutes.

INTRODUCTION

There is an increasing demand for the development of efficient and economic adsorbents for treatment of water that are capable to remove removal toxic or hazardous organic contaminants. Organic pollutants such as pesticides and herbicides are increasingly present in wastewater. Pesticides and herbicides are life-threatening due to their toxicity, carcinogenicity and mutagenicity (Liu et al., 2011). Thermal Power Plants (TPP) actively produce and generate solid waste byproducts, such as fly and bottom ash. Many distinct benefits are found in the reuse of TTP solid wastes, among which are the zero cost materials (due to their byproduct origin), new added value of the product (from waste to the novel material), and multifunctional implementation. Fly and bottom ash present the most abundant waste material occured from the coal combustion, but also an effective adsorbent for different pollutants removal from the wastewaters (Karanac et al., 2018).

EXPERIMENTAL PART

The FA used in this study was obtained from the waste product of the Thermal Power Plant (TE) Morava, Serbia. Chemical activation of FA (lime addition) is performed in order to ensure better adsorption and mechanical properties of modified samples (MFA), which after use as an adsorbent is used in the production of building materials. Adsorption experiments were performed under batch conditions, according to the conditions given in Figure 1.

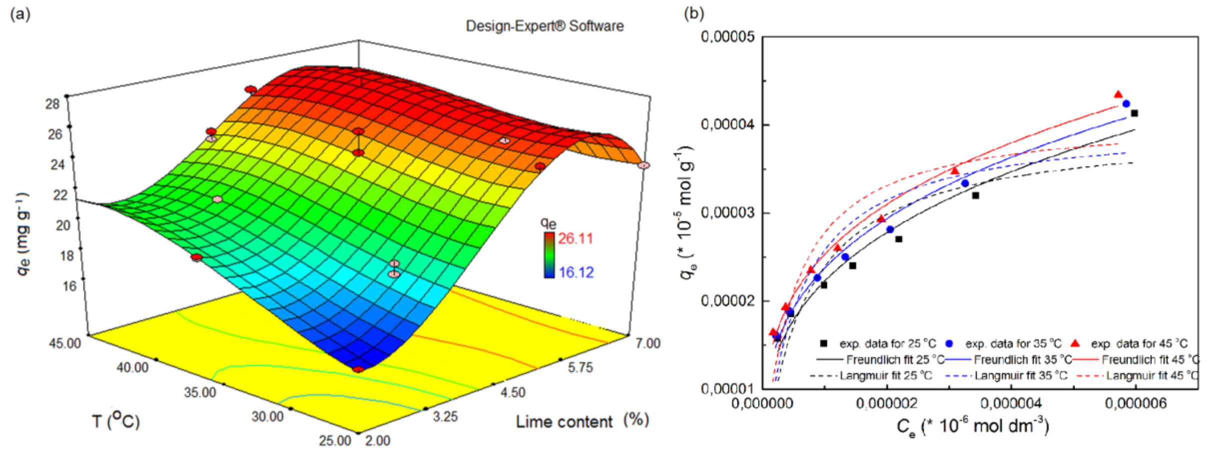

Figure 1. Contour diagram representing relation between capacity vs T and lime content (%) for MFA (a) and experimental plan and fitting of adsorption experimental data with Freundlich and Langmuir isotherm model adsorption of DDT on ***MFA (Experimental conditions: C_0 = 2.23*10^{-5} mol L^{-1}, dose adsorbent of 250 to 1250 mg L^{-1}, T=25, 35 and 45 °C, t=90 minutes)***

RESULTS AND DISCUSSION

Based on the regression coefficient (R), as well as the Δ*q* value (calculated standard error) for all model parameters, the experimental data are best described using pseudo-second-order kinetic model (PSO) and the Freundlich-isotherm model (Figure 1b). According to the Freundlich isotherm, the adsorption mechanism of DDT on MFA could be described by heterogeneous adsorption, where the adsorbed ions/molecules had different enthalpies and activation energies of adsorption (Karanac et al., 2018). Negative standard changes in free energy of adsorption (ΔG^0) and positive standard changes in entropy (ΔS^0) at all temperatures indicate that the adsorption reactions are spontaneous (Table 1). The decrease in Gibbs free energy (ΔG^0) with increasing temperature indicates that the spontaneity of the reaction increases. The obtained results free energy exchange indicate that chemisorption and physisorption are represented simultaneously in these case (Karanac et al., 2018).

Table 1. Calculated Gibbs free energy of adsorption, enthalpy and entropy for DDT adsorption on MFA

Δ*G*° (kJ mol^{-1})			Δ*H*° (kJ mol^{-1})	Δ*S*° (J mol^{-1} K^{-1})	R^2
25 °C	35 °C	45 °C			
-44.29	-46.11	-47.98	10.85	184.88	0.997

CONCLUSION

The present study dealt with the exploitation of FA as materials in its modified form with lime, named MFA. The optimization procedure for the adsorption experiment was conducted in order to postulate/select the most influential factor which contribute to adsorption efficiency. In the course of pollutant removal a number of independent/related processes are: the co-existence of physisorption, i.e., ion exchange, surface interactions, electrostatic attraction and chemisorption, i.e., surface complexation, which participate at different extent in overall process. Developed method designed for use of exhausted adsorbents gave a product with satisfactory mechanical properties in relation to filler free material, and their safe use in human environment was proved by the results from TCLP testing

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LEVELS OF SOIL CONTAMINATION IN VICINITIES OF THE RUSSIAN ANTARCTIC STATIONS

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KEYWORDS
Trace elements, soils, Antarctica, permafrost, environmental impact assessmen

ABSTRACT

Antarctica has experienced a significant anthropogenic forcing in recent years. It is vital to perform effective realization of environmental protection measures within the Environmental Protocol of Antarctic Treaty to save unique polar ecosystems. These measures should include environmental impact assessment, permanent monitoring of various components of natural ecosystems, such as soil. Soils play crucial role in deposition of different chemical compounds including pollutants. Soil in Antarctica has been impacted by anthropogenic activities such as chemical pollution (Aislabie et al. 2001; Balks et al. 2002; Claridge et al. 1995) physical disturbance of soil cover (Campbell et al. 1993; Campbell et al. 1998). Numerous studies focused on soil pollution by heavy metals and polycyclic aromatic hydrocarbons have been conducted in Western Antarctica, and only few investigations available for coastal oases of Eastern Antarctica (Gasparon, Matschullat 2006; Goldsworthy et al. 2003; Subhavana et al. 2019).

The aim of this work was to analyze the levels of 17 polycyclic aromatic hydrocarbons and eight trace elements in soils and soil-like bodies of both Eastern and Maritime Antarctica. Moreover, our work was aimed to determine the trends and reasons of anthropogenic pollution of Antarctic soils and characterization of accumulation levels of trace elements and PAHs.

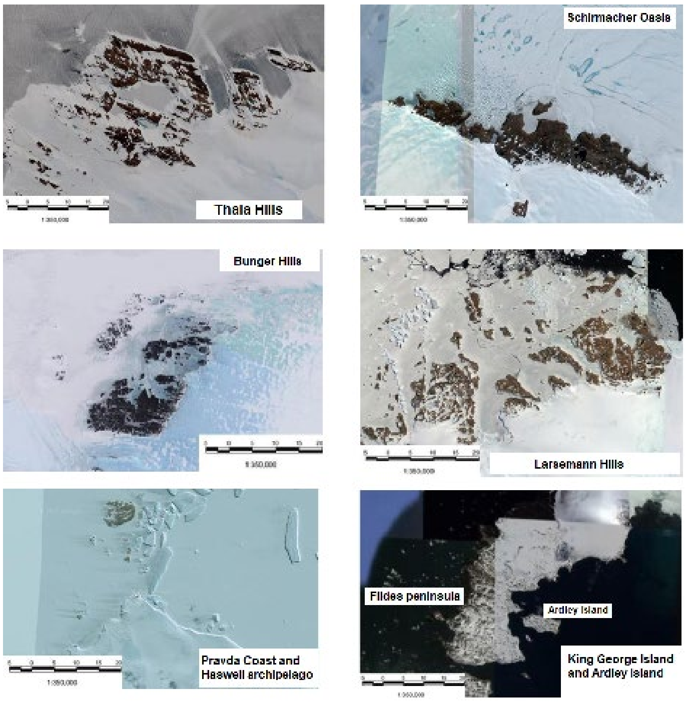

Figure 1. Study areas in Eastern and Maritime Antarctica (credits to ©Google Earth 2010)

It was found that Cu and Zn are the most abundant elements in all studied soils. The highest lead content has been described in soil from Bellingshausen station. However, this was much lower than previously described in polluted soils from Antarctic stations in Western Antarctica. Relatively high content of some metals (e.g., copper and zinc) was also found in more pristine sites indicating mineralogical origin of accumulation of particular metals. In general terms, obtained Igeo values for trace elements were under or slightly above the 0 level, indicating low to moderate pollution of the studied soils. This study contributes new data on trace element accumulation in soils strongly influenced by ornithogenic factor. Bioaccumulation of metals in seabirds occupying the highest position in the food chain occurs, transfer of bioaccumulated metals into terrestrial ecosystems through birds excreta should be investigated in more detail. Principal component analysis allowed to estimate the probable sources of specific trace metals and their relationship with soil variables. Arsenic accumulation in soils was significantly correlated with organic carbon content (TOC), nitrogen content (N), and fine earth content, whereas cadmium, copper, and zinc are in significant positive correlation with pH. Lead and zinc were found significantly correlated with each other suggesting the same source of their accumulation in studied area, i.e., local human-induced pollution. We suggest that use of pollution load index (PLI) is preferable when estimating pollution status of Antarctic soils, since other indices do not consider natural geochemical processes and geochemical background, therefore better reflecting specific conditions of soil forming.

Our results suggest that that in most of the studied soils, light PAHs which are the components of natural organic matter, are predominant. At the same time, some investigated sites, where soils showing the lowest sum of PAHs could be used as reference-sites for further ecological risk assessment research.

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SOURCES OF SOIL POLLUTION AND ITS HEAVY METAL CLEANING

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KEYWORDS
Sources of pollutants, soil, heavy metals, procedures for determination of heavy metals

ABSTRACT

Soil remediation is a measure for remediation of existing soil pollution in order to reduce the concentration of pollutants to a level that does not pose a danger to the environment and human health. So far, various approaches have been proposed for remediation of soil contaminated with metals. Some of these techniques, such as soil washing using separation methods and extraction with aqueous solution of surfactants and mineral acids, are the most widely used, while the technology of soil leaching with the help of chelates is in development. Soils differ in their capacity to hold heavy metals. From the point of view of aquatic ecosystems, a large amount of heavy metals accumulates and is detected especially at the mouths of rivers and on the shores of seas and oceans. The origin of heavy metals in natural soils comes exclusively from the lithosphere. Sources of the mineral part of the earth are the rocks and minerals that make up the Earth's crust. The eight elements (O, Si, Al, Fe, Ca, Na, K, Mg) make up 98.59% of the Earth's crust, and all others 1.41%. Concentration of heavy metals such as Co, Cr, Mn, Ni and V depends on the natural composition of the soil. This paper will list the sources of pollution with special reference to experimental data on the content of heavy metals in the soil.

INTRODUCTION

Soil is a medium that serves as a substrate for plant growth and nutrition. The soil has a complex structure and contains a large number of organic and inorganic substances, microorganisms, water, insects, gases. Soil pollution will have a direct impact on the proper development of plants, and thus on the entire ecosystem. Soil is generally defined as the top layer of the earth's surface and is a medium that is largely non-renewable. Soil is formed from mineral particles, organic matter, water, air and living organisms. The soil is an intermediary between the geosphere, the atmosphere and the hydrosphere. The intensive development of the food production industry today is in direct correlation with the needs of the population for healthy and quality food. On the other hand, the number of the population in the world is increasing intensively, and this leads to an increase in the needs for the production of quality agricultural crops that will be used for food. Due to the ever-increasing production of agricultural crops, there is an intense depletion of nutrients from the soil. This phenomenon contributes to a change in the physiological traits of plants grown on nutrient-depleted soils.

CAUSES OF SOIL POLLUTION

Soil pollution is caused by various chemicals that are present in higher concentrations than the equilibrium concentrations of those chemicals in the soil, the most common pollutants are: pesticides, herbicides, artificial fertilizers. The quality of the soil itself decreases, as a result of the accumulation of heavy metals that plants Furthermore, they cannot use them in biochemical reactions. Heavy metals include: sulfur, arsenic, nickel, cobalt, iron. The pollution will affect the functions of the soil and the nutrition of the plants, and thus the entire ecosystem. The increased accumulation of certain metals or chemical compounds stop or inhibit the plant's biomechanical processes. Most often, the pollution is caused by various incidents with toxic substances or oil, or by the discharge of waste from mines or metal industry. Agriculture and chemicals that - Local soil pollution is usually associated with mining, industrial facilities, landfills.

DIFFUSE POLLUTION OF SOILS

It is associated with atmospheric deposition (emissions from industry, traffic and agriculture), certain agricultural practices (inadequate use of fertilizers and pesticides) and inadequate recycling and treatment of waste and wastewater. Sealing of the soil, the scope of which also includes conversion of use, is a type of degradation that includes covering the soil with infrastructure such as the construction of residential buildings, roads, artificial reservoirs, etc. applied to agricultural land are the biggest polluters of the soil. artificial fertilizers, pesticides, herbicides. Today, artificial fertilizers, pesticides and herbicides are used everywhere in agriculture. In the beginning of the 20th century, intensive and mass production of these artificial fertilizers took place in order to obtain better yields in agriculture. With the mass use of these chemical agents, the bohemian composition of the plant is improved, they are protected from pests. Nowadays, in western developed countries, it is impossible to distinguish between the one obtained by chemical means and the one from organic production. Fortunately, the agricultural markets in the Republic of Macedonia are still at a satisfactory level for the quality of food that has been treated with chemical agents. The increased use of agrochemical techniques pollutes the soil, and part of the chemical components are also stored in the fruit of the plant (Figure 1).

Figure 1. Soil contaminated with heavy metals

Contamination of the soil from solid waste from mines, metallurgical and other industrial facilities. One of the ways of exploitation of coal, copper and nickel ore is open pits. The greatest damage occurs during the exploitation of coal for energy purposes, because it occurs in our valleys under fertile soils and under deep layers of loose sediments. The solid waste from mines in which Fe, Zn, Pb, Cr, Ni, Cu, etc. are extracted contains heavy metals and is processed by flotation. Contamination of soil with heavy metals can be natural and anthropogenic. Much more dangerous and intense is anthropogenic contamination, which can occur relatively quickly. To a large extent, anthropogenic contamination is carried out in the form of heavy metals that are available to plants. These forms are used by the plant and are therefore more toxic.

Figure 2. Soil

Table 1. Contamination of heavy metals (total concentration) in some soils in the Republic of North Macedonia (Ministry of Environment and Spatial Planning of the Republic of North Macedonia)

Heavy metals	Limit values of concentration of heavy metals in soil according to the European Community expressed in mg/kg	Concentration limit values for heavy metals in Germany expressed in mg/kg	Content of heavy metals in the examined soils from the Republic of Macedonia
Pb	50-300	100	4220 Reka Zletovica 54-6764 Veles 273-519 Drachevo (Skopje region)
Cd	1-3	1 - 1,5	4.1-16.6 Drachevo (Skopje region) 5.6-7.6 Kumanovska river
Zn	150 – 300	150 – 200	4083 Reka Zletovica 92-2105 Veles 652 Autocommand (Skopje region)
Ni	30 – 75	50	63.11-458.67 Trubarevo (Skopje region)
As	-	20 – 40	30.83 Kumanovska Reka
Cr	-	100	131.95 - 208.14 Trubarevo (Skopje region) 109.40-193.72 in black soil
Cu	50 – 140	60	395 Zletovica river

CONCLUSION

The health consequences of exposure to soil contamination vary greatly depending on the type of pollutant, the route of exposure, and the vulnerability of the exposed population. Chronic exposure to chromium, lead and other metals, petroleum, solvents, and many formulations of pesticides and herbicides can be carcinogenic., can cause congenital disorders or can cause other chronic health conditions. Nitrates and ammonia associated with manure from agricultural practices have also been identified as health hazards in soil and groundwater. Chronic exposure to benzene in sufficient concentrations is known to be associated with a higher incidence of leukemia. Mercury and cyclodienes are known to cause higher incidences of kidney damage. Polychlorinated biphenyls and cyclodienes are associated with liver toxicity. Organophosphates and carbonates can cause a chain reaction that leads to neuromuscular blockade. At sufficient doses, many soil contaminants can cause death by exposure through direct contact, inhalation, or ingestion of contaminants in groundwater contaminated through soil.

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ULTILIZATION OF THE ION-EXCHANGE ABILITY OF ZEOLITE 4A POROUS MATERIAL FOR PURIFICATION OF POLLUTED RIVER WATERS

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KEYWORDS
Zeolite 4A, ion exchange capacity, polluted rivers, heavy metals

ABSTRACT

Using the ion-exchange properties of zeolite, we will be able to remove heavy metals from industries that pollute water. Given that the procedure is very simple and economically viable, polluted rivers can be easily cleaned. The technological procedure for purification of water in polluted rivers is economically justified because zeolite 4A is synthesized from domestic raw materials. Water after use in industry and in mass consumption, often contains large amounts of impurities such as: sand, heavy metals, acids, alkalis, salts, pesticides, large amounts of organic matter, pathogenic microorganisms, radioactive materials, etc. Most of them are dangerous for human health because they often cause serious diseases, but also for the flora and fauna in rivers, lakes and oceans where these waters flow are a serious problem. Wastewater, before being released into nature, should be treated, as otherwise it will lead to pollution of clean ecological water, and can cause suffocation of flora and fauna. The adaptation of waste materials and the way it should be done depends on the quantity of pollution. The microporous structure of zeolites depends on the type and size of the geometric structures that are participants in the composition of the zeolite.

CHANGES IN THE CONCENTRATION OF POTENTIALLY TOXIC ELEMENTS IN PLANTS GROWN IN SOILS TREATED WITH NATURAL SORBENTS

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ABSTRACT

The effect of sorbents on the immobilization of potentially toxic elements (PEP) in soils from the Maximilian mine dump (Špania Dolina) was evaluated using the bioconcentration factor (BCF), which indicates the uptake of contaminants into a living organism from the environment or the soil substrate in which it is located. The sorbent was evaluated as effective if the BCF value was lower in plants grown on treated soils compared to the BCF determined in plants grown on untreated, control soil from the heap body. This indicated that the sorbent stabilized the PTP in the soil, and plants took up less of it in the aerial parts. BCF was determined and graphically represented using boxplots for 10 PTPs (Ba, Cr, As, Mn, Co, Ni, Ag, Zn, Pb, Cu). The results were commented according to the position of the BCF of the specific element relative to the control sample. Biochar had the most significant effect, which stabilized Cr, Mn, Co, Ni, Pb, Cu, bentonite had a positive effect on As and Ag, organozeolitic substrate on Zn.

The work was financially supported by grant VEGA 1/0291/19.

UTILIZING PRINCIPAL COMPONENT ANALYSIS (PCA), HIERARCHICAL CLUSTER ANALYSIS (HCA) AND SPECIATION CALCULATION FOR CONTAMINATED SITES ASSESSMENT OF PREDAJNÁ 1 AND PREDAJNÁ 2 LANDFILLS

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KEYWORDS
PCA, HCA, speciation calculation, groundwater pollution, Predajná landfills, Slovakia

ABSTRACT

This study reveals the state of groundwater quality in the vicinity of contaminated site in Central Slovakia and points to the suitability of using a combination of hydrogeochemical and statistical analyses to assess groundwater pollution.

MATERIALS AND METHODS

The study site is located near the village of Predajná in Central Slovakia, and is contaminated by acid tar, which leaked from the designated landfills Predajná 1 and 2 (Fig. 1) [1]. The inorganic pollution was evidenced by high values of EC and TDS, Na^+, Cl^-, and SO_4^{2-} ions, while organic pollution was represented by TOC and surfactants [2]. The study processed data obtained from monitoring of the twelve wells (BR1 - BR12) carried out in May 2019. Through hydrogeochemical analysis, Hierarchical Cluster Analysis (HCA) and Principal Components Analysis (PCA), relationships among the monitored parameters from the site were determined.

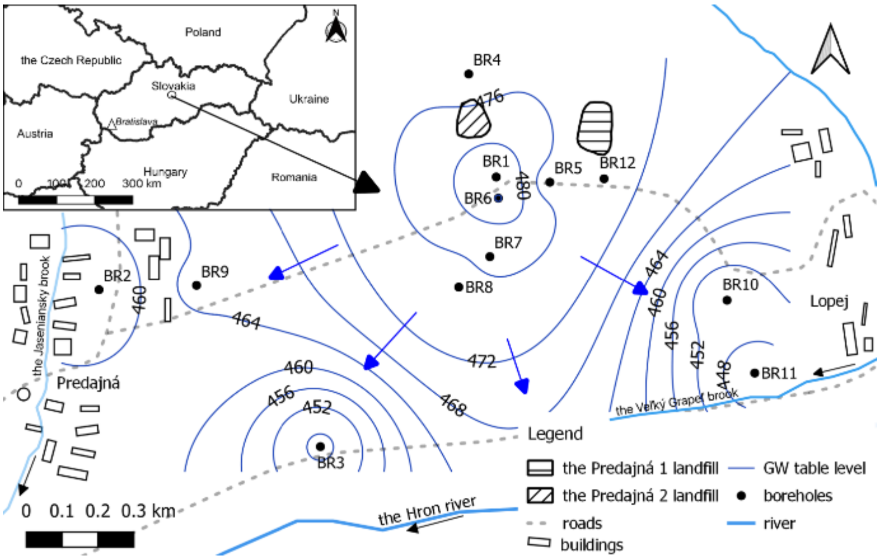

Figure 1. Map of the studied site, sampled boreholes BR1 - BR12 and flow pattern

RESULTS

Hydrogeochemical calculations pointed to the dissolution of carbonates as the dominant process of the formation of groundwater chemistry. The water is undersaturated with respect to gypsum although elevated sulphate concentrations have been reported in many boreholes.

The HCA indicated spatial relationships and hydrogeochemical properties of groundwater. The dendrogram (Fig. 2) shows the result of the HCA. The HCA created two main clusters (A and B) divided into three subgroups (I – III). Cluster 1 represents the most polluted well. The four wells are contained in cluster 2, in which the environmental pollution is demonstrated by slightly high TOC values exceeding the ID criterion given by Directive no. 1/2015-7. Cluster 3, formed by seven wells, has high TOC contents, exceeding IT [2].

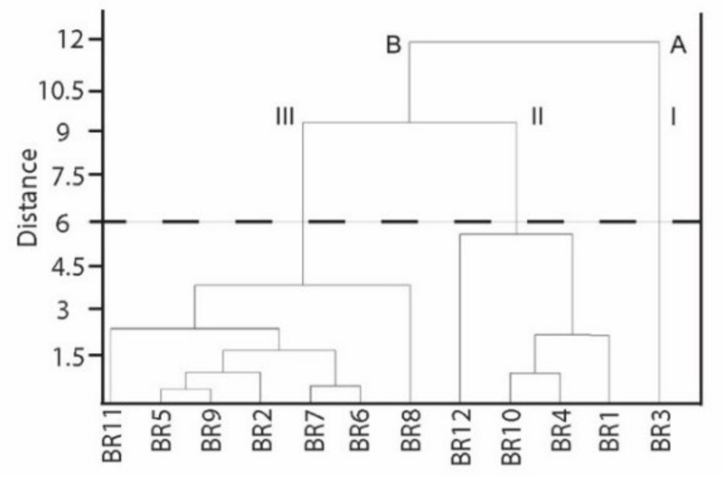

Figure 2. Hierarchical dendrogram of boreholes BR1 – BR12

The PCA achieved a significant dimensionality reduction of the original data set. The PCA using Kaiser normalization and VARIMAX rotation were performed. Based on the Kaiser criterion, the three first principal components (PC) were selected. The PCA explains 89.0% of the total variability in the data set using three principal components: PC1 corresponds to the dominant process of carbonate dissolution, PC2 represents inorganic contamination, and PC3 reveals the main indicators of organic pollution by acid tar (Tab. 1). The study demonstrated that a smaller number of examined variables obtained by PCA is enough to get a picture of groundwater quality and pollution caused by leaks from industrial waste landfills Predajná 1 and 2.

Table 1. Varimax rotated PCA loadings

Parameter	**Component**			**Parameter**	**Component**		
	1	**2**	**3**		**1**	**2**	**3**
pH	**-0.84**	0.12	-0.35	Cl^-	0.01	**0.83**	0.13
EC	0.37	**0.91**	0.08	Hardness	**0.94**	0.24	0.17
Na^+	-0.2	**0.95**	0.01	TOC	0.20	0.14	**0.95**
Ca^{2+}	**0.88**	0.30	0.24	Surfactants	0.42	0.13	**0.80**
Mg^{2+}	**0.97**	0.12	0.01	TDS	0.42	**0.89**	0.08
K^+	**-0.65**	0.55	0.35	Eigenvalue	6.59	3.45	1.49
HCO_3^-	**0.81**	0.23	0.24	% Variance	38.7	34.9	15.4
SO_4^{2-}	0.34	**0.86**	0.18	% Cumulative variance	38.7	73.6	89.0

CONCLUSIONS

Selected multivariate statistical analyses and hydrogeochemical analyses are suitable methods for processing data from the monitoring of contaminated sites. The results offer a more precise insight into the state of the selected contaminated site, the changes and relationships between the monitored objects and the physicochemical processes that take place in the waters. The results of this study suggest that combination of hydrogeochemical analysis and multivariate statistical methods such as PCA and HCA can provide valuable information about contamination at studied sites. Taken together, these findings highlighted a role of abovementioned methods that can be used as the preliminary step to building conceptual site models.

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WASTEWATER TREATMENT PLANT`S BACTERIA RESISTENT TO HIGH CONCENTRATIONS OF HEAVY METALS

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KEYWORDS
Trace elements, sewage sludge, urban wastewaters, microorganisms

ABSTRACT

One of the main global problems associated with industrial development and population growth is the increase in environmental pollution and wastewater generation from domestic activities or as a mixture of wastewater generated by household, industrial, and stormwater outflows. Around 330 billion m^3 of municipal wastewater generated universally per annum (Mateo-Sagasta et al., 2015). The percentage of the population living in urban areas is expected to increase significantly, from 55.3% in 2018 to 60.4% in 2030 (Zamparas, 2021) that will cause a further significant increase in the volume of wastewater.

Biological wastewater treatment consists in the cultivation of mixed microbial communities of activated sludge that consume wastewater components as nutrient substrates, thereby removing them from wastewater. The main product of the bioconversion of wastewater impurities is biologically purified water; the by-product is activated sludge biomass (Gottschalk, 1986). Utilization of inorganic pollutants is also effectively carried out by the activated sludge community because of biosorption and biotransformation processes. In this regard, strains of microorganisms that are part of activated sludge, which are capable of destroying organic matter and are resistant to high concentrations of heavy metals, are of great interest. Purpose of this investigation was isolation and study by molecular genetic methods strains of aerobic bacteria tolerant to high concentrations of heavy metals (Ni, Cd, Pb, Zn and Cu) from water and sludge of various parts of the sewage treatment facilities of a large city located in a temperate climate (Tula, Central Russia).

The elemental composition of the samples (water, suspension of sludge in the water of secondary sedimentation tank and media of digester) is shown in the Table 1. The water of the secondary sedimentation tank does not meet the standards for cadmium concentration accepted in Russian Federation (Table 1). For other elements, no excess concentrations in the water of the secondary sedimentation tank are observed. Thus, at the time of sampling, wastewater from the studied part of the treatment facilities was not contaminated with most heavy metals.

Amount of microorganisms (CFU) in sludge suspension from the secondary sedimentation tank was higher (2.8×10^6 cells/ml) in samples compared to water from the secondary sedimentation tank (2.4×10^5 cells/ml) and suspension from the digester (1.6×10^5 cells/ml). Based on the results of inoculation on a nutrient medium with HM, from the water and sludge of the secondary sedimentation tank bacteria were isolated that are resistant to the concentrations of Ni, Cd, Zn, Pb, Cu at 3 mM. No growth of colonies was noted on the medium with Co. Among cultivated bacteria,

some showed resistance to maximal concentrations (5 mM) of Pb and Zn. Only one HM-resistant strain, namely, to Ni (5 mM), was isolated from the digester. Some strains, developing on a medium enriched with heavy metals, changed the color of their colonies. From the isolated strains, 10 were selected for further identification.

Table 1. Concentrations of heavy metals in the media of the sewage treatment plant

Heavy metal	**Concentration, mg/l**			
	Maximum Permissible Concentrations for waters of household and cultural water use	**Secondary sedimentation tank (water)**	**Secondary sedimentation tank (suspension)**	**Digester (suspension)**
Cd	0.001	0.0053	0.0037	0.0186
Cu	1.0	0.0056	0.0037	0.0248
Ni	0.02	0.0089	0.0041	0.1204
Pb	0.01	<0.0001	0.0038	0.0050
Zn	1.0	0.0002	0.00001	0.0002

The results of phylogenetic analysis of 16S rRNA gene sequences showed that most of the isolated HM-tolerant strains belong to the genus *Pseudomonas* (Table 2). The exceptions are strains resistant to Ni from digester and strains resistant to Pb and Cu from sludge of the secondary sedimentation tank. It should be noted that the Zn-resistant *Pseudomonas gessardii* 9 strains also grew on a medium with a Cd concentration of 2 mM/l. Lead-resistant strains (*Pseudomonas brenneri* 7 and *Pseudomonas fragi* 6) grew on a medium containing 3 mM/l of Zn.

Table 2. Isolated strains of metal-tolerant bacteria from wastewater treatment plants

N	**Species**	**Source**	**Element**	**Maximal tolerance concentration**
1	*Serratia proteamaculans*	Digester	Ni	5 мМ
2	*Pseudomonas gessardii*	Secondary sedimentation tank (sludge)	Ni	3 мМ
3	*Pseudomonas fragi*	Secondary sedimentation tank (sludge)	Cd	3 мМ
4	*Pseudomonas fragi*	Secondary sedimentation tank (water)	Cd	3 мМ
5	*Serratia proteamaculans*	Secondary sedimentation tank (sludge)	Pb	5 мМ
6	*Pseudomonas fragi*	Secondary sedimentation tank (water)	Pb	3 мМ
7	*Pseudomonas brenneri*	Secondary sedimentation tank (water)	Pb	3 мМ
8	*Pseudomonas gessardii*	Secondary sedimentation tank (sludge)	Zn	5 мМ
9	*Pseudomonas gessardii*	Secondary sedimentation tank (water)	Zn	5 мМ
10	*Klebsiella pneumonia*	Secondary sedimentation tank (sludge)	Cu	3 мМ

Cultivation of nonpathogenic strains of these bacteria and their introduction into communities of other activated sludge microorganisms could possibly make the biological treatment of wastewater containing organic and inorganic pollutants more efficient.

This research was funded by the Russian Science Foundation grant No. 22-24-20074 (regional competition), held jointly with the authorities of the subject of the Russian Federation: Tula region (Agreement with the Government of the Tula region No. 2, April 19, 2022).

TRACE ELEMENTS IN THE ALLUVIAL SOILS WITH DIFFERENT TECHNOGENIC LOAD

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KEYWORDS
Heavy metals, floodplain, alluvial soils, soil properties, geochemical balance

ABSTRACT

Alluvial soils occupy 590 million hectares in the world and provide food for about 25% of the Earth's population (Basayigit and Senol, 2008). Fluvisols, have higher fertility compared to zonal soils due to the better supply of moisture, nutrients and good structure. Therefore they are used intensively in agriculture, primarily for growing vegetable crop that are most demanding on nutrition and moisturizing conditions. Recently, the problem of trace element contamination of alluvial soils has received more and more attention all over the world (Saint-Laurent et al., 2020). In this research concentrations and depth distribution of the trace elements (TE) total concentrations and their forms in fluvisols of Central Russian rivers with different technogenic load were studied and the soils use for safe agricultural products was assessed.

Alluvial soddy saturated soil of the Oka River, located to east of the town of Pushchino (Moscow region) (near 54°84` and 37°67`), was studied as floodplain soil with a relatively low regional technogenic load. The investigation of the concentrations and depth distribution of TE in alluvial meadow soil with high technogenic load was carried out in two plots in the floodplain of Upa river in the vicinity of industrial Tula city (near 54°17` and 37°67`). Sample preparation for determining the total TE content was carried out by processing of soils with concentrated acids HF, HNO_3 and HCl after mineralization of the samples in a muffle furnace. The extraction of mobile forms of TE was carried out with an ammonium acetate solution with pH 4.8. Extraction of Zn forms associated with various soil components was carried out according to the Tessier method (Tessier et al., 1979).

Comparison of the trace element content in precipitation and river runoff, studied for Upper Oka River Basin (Zolotareva, 2003) shows that, in general, the influx of Cu, Zn, Ni, Cd in the studied area with atmospheric precipitation is almost 2 times lower than their removal with river runoff, and the Pb balance is close to zero. TE input to the ecosystems mainly in soluble form, and output mainly with suspended matter. Moreover, the regional modules of atmospheric deposition of Mn and Cu are close to global, and the modules of deposition of Zn, Ni, Pb, Cd are 1.5–3 times higher than global ones. Previous researches show that in the studied area to each 1 m^2 of soil surface can be deposit with liquid precipitation and dust: 1776-18263 mg of Fe, 85-210.5 mg of Mn, 115-222 mg of Zn, 9.4-36 4 mg of Ni, 11.4-92.5 mg of Pb, and 2.1-19.2 mg of Cd (Uchvatov, 1994).

Evaluation of the main components of the input part of the TE geochemical balance in the agro-industrial landscape typical for the studied area (input of the elements with liquid and solid sediments, fertilizers, excluding income with crop residues and litter, seed, lime flour) with microelement losses due to various migration processes also shows that the current balance is negative, with the exception of Zn. 256-542 mg of Fe, 28-53 mg of Mn, 23-47.5 mg of zinc, 2.3-4.6 mg of Ni, 0.6-2 mg Pb and 0.05-0.23 mg Cd can be entered to arable soils per 1 m^2 due to the specific agricultural sources of TE. The supply of TE to the agricultural landscape is from 13% for Mn to 50-70% for the remaining elements in comparison with their removal from the landscape. At the same time, taking into account the above mentioned missing agricultural sources, the balance for almost all elements except iron, copper, lead and partially nickel becomes positive. For agricultural ecosystems where cereals are grown and technological erosion is absent, the balance of Cr, Ni and Zn is positive, Mn, Cu and Co are negative, Pb is approximately zero, or positive in some years. Replenishment of TE losses in the soil due to the application of mineral fertilizers does not exceed 15-35% of the total losses from the agricultural ecosystems (Uchvatov 1994).

The study of the TE content in soils of the Tula region showed their increased concentrations in the soils of cities in which industrial objects are located (Arlyapov et al., 2015). For ferrous metallurgy plants of Tula city typical metals of technogenic anomaly are: Ni, Mn, Pb, Cu, Zn. In the industrial centers of Tula and Novomoskovsk, the density of dust deposition, and, accordingly, the aerosol flux of TM exceeds the regional background by more than 3 times (Zolotareva, 2003). The most contrasting geochemical anomalies in the soils of Tula city are characteristic of the elements of the first class of environmental hazard: Pb, Zn and Hg. Halos with maximum levels of soil pollution are mainly located in the right-bank part of the city and are confined to industrial factories of machine-building and metallurgical profile and main transport highways of the city (Komissarov, 2007).

Our results show that in the studied alluvial soil of the Upa floodplain, located near the metallurgical industry, higher concentrations of total Fe, Zn, Cd and Ni are observed in comparison with fluvisol of Oka floodplain. Despite being on the outskirts of the industrial city, concentrations of most TE, with the exception of Zn and Fe, in the natural and arable fluvisol of Upa river is within the established State standards and clark values, which may be due to the predominance of the removal of these elements over the input. There are differences in the concentrations of trace elements in fluvisol depending on their localization in the various parts of the floodplain. We can conclude that the maximum amount of the main part of studied total TE (except Ni) in the top layer of alluvial soil of the Oka floodplain is characteristic of the riverbed floodplain. It is shown that despite the remoteness from industrial sources of metal emissions, the floodplain soil of the Oka can accumulates a significant amount of Zn and Fe as a result of the introduction of a bulk. For terraced part of the floodplain it is characterized by an increase in total and mobile Fe, Mn, Pb, mobile Cd concentrations in upper soil layer compared to the layer of central floodplain. In the fluvisol of Upa river under the meadow, more high amount of total Mn and Fe and more low concentrations of total Zn and Ni are observed in comparison with arable soils. The maximum concentrations of Mn, Fe, Pb and Cd mobile forms are in the upper layer of natural soil under meadow, which has the highest content of humus and physical clay and a salt pH close to neutral. Agricultural use can cause a change in depth distribution of total and mobile forms of trace elements, which is often expressed in their most uniform distribution. The increase in Zn concentrations in agricultural soil of the Upa floodplain is due to an increase in its content in conservative fractions and is safe for transition along food chains at the present soil conditions. Nonetheless, floodplain agricultural soils should be a permanent subject of environmental monitoring. Thus, the content, distribution and speciation of trace elements in alluvial soils with different technogenic loads depend not only on the scale of this load, but also on the soil properties and the ratio of the processes of metal input to and removal from the soils.

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EFFECTS OF NATURAL SORBENTS ON THE GERMINATION AND EARLY GROWTH OF GRASSES ON SOILS CONTAMINATED BY POTENTIALLY TOXIC ELEMENTS

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ABSTRACT

The reclamation of abandoned mining heaps rich in potentially toxic elements (PTEs) is critical for the environment. We carried out a laboratory experiment studying the effects of the addition of four natural sorbents (biochar, bentonite, chicken manure and organo-zeolitic substrate) to soils contaminated with PTEs, predominantly Cu, As and Sb, on the germination and growth of the autochthonous grasses Agrostis capillaris, A. stolonifera, Festuca rubra and Poa pratensis. The experiment used Petri dish tests with water extracts of contaminated soil and soil neutralized with the four sorbents. Standard indexes of the germination process were used (germination percentage, time required for 50% germination index, speed of emergence), and different values were found depending on the plant species and sorbent used. However, the percentage of seeds germinating was lower for each sorbent compared to the control (distilled water). The fresh mass values were positively stimulated by all sorbents. Electrolyte leakage was the highest in seedlings watered with an extract of untreated soil from the heap compared to extracts from treated soils and the control. This can be interpreted as eliminating the harmful effects of increased potentially toxic element (PTE) contents by sorbents, which can be useful in remediation processes.

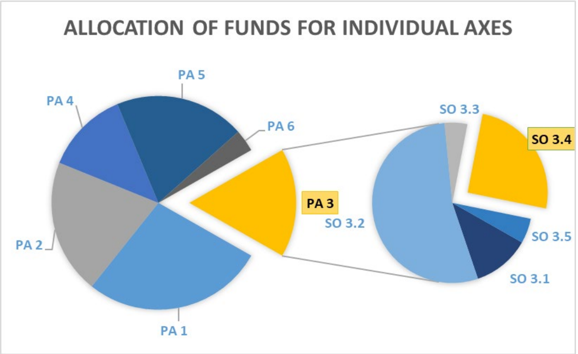
The work was financially supported by grant VEGA 1/0291/19.

OPERATIONAL PROGRAMME ENVIRONMENT 2014–2020

Martina Jiroutová, Hana Kroová, Lenka Zárubová
The State Environmental Fund of the Czech Republic

This programme contains six priority axes with a total allocation of EUR 2 789 613 540

Priority axis 3 – Specific objective 3.4: To complete the inventory and remove environmental burdens



programme allocation	2 789 613 540 €	100%
priority axis 3	458 819 995 €	16,45%
specific objective 3.4	**115 468 727 €**	**4,14%**

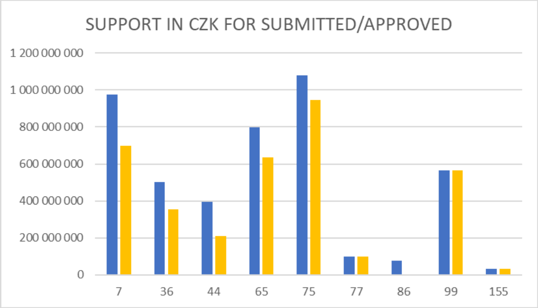
Supported activities:

- activity 3.4.1 – inventory of contaminated and potentially contaminated sites, categorization of contaminated site priority according risk
- activity 3.4.2 – implementation of exploratory work (including exploration works), risk analyses
- activity 3.4.3 – remediation of hazard contaminated sites

Financial support up to 85% of total eligible cost

call number	call allocation in CZK	number of submitted applications	EU support in CZK	**number of approved applications**	**EU support in CZK**
7	560 000 000	46	975 366 605	30	699 204 458
36	600 000 000	35	501 304 818	29	353 437 335
44	500 000 000	23	395 649 399	16	208 161 697
65	400 000 000	31	796 895 215	21	635 089 794
75	400 000 000	16	1 079 597 134	8	944 555 711
77*	150 000 000	1	99 133 104	1	99 133 104
86*	200 000 000	4	146 206 621	3	71 645 631
99	200 000 000	13	563 573 885	13	563 573 885
155	50 000 000	11	31 386 986	10	30 904 976
			total number of projects	**131**	**3 605 706 591**

**this is an ITI (Integrated Territorial Investment) call



Under the OPE 2014-2020

- 5 547 569.51 m^2 of land remediated
- 79 risk analyses prepared
- Inventories carried out for 10 134 sites

Project example:

Under activity 3.4.1. – inventory of contaminated and potentially contaminated sites, categorization of contaminated site priority according to severity, a project entitled “2nd Stage of the National

Inventory of Contaminated Sites” from contracting authority CENIA, the Czech Environmental Information Agency, with total eligible costs of CZK 116.627 million and a subsidy of CZK 99.133 million, was approved under the 77th call in OPE 2014 -2020. The actual final costs of the action were CZK 116.493 million.

The purpose of this action was to implement the project, comprising the elaboration of a comprehensive contaminated site database with priority ratings for the whole of the Czech Republic for long-term universal use. The project was launched in January 2018. The deadlines for the completion of the action (31 December 2021) and for the submission of the documentation for the final assessment of the action (1 August 2022) were met.

The binding indicator for the action was set at 9 053 inventoried sites with priority ratings. In spite of significant difficulties related to the COVID epidemic, the indicator was actually exceeded, and 10 134 sites were inventoried, with 446 sites receiving the highest risk rating and thus also the highest urgency for risk elimination or mitigation solutions.

Authorised entities can use the contaminated sites database to manage inventoried territories and to comply with legislative requirements relating to the environment.

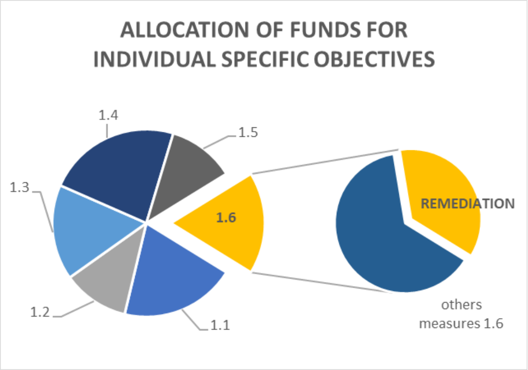
OPERATIONAL PROGRAMME ENVIRONMENT 2021-2027

This programme contains six specific objectives with a total allocation of EUR 2 390 195 324

Remediation and risk analysis fall under Specific objective 1.6: Enhancing protection and conservation of nature, biodiversity and green infrastructure, including in urban areas, and reducing all forms of pollution

Supported measures:

- Measure 1.6.11 Exploration of the extent of pollution of the rock environment and the associated risks, including the design of an effective solution
- Measure 1.6.12 Elimination of contamination risks to human health, water resources or ecosystems, and reclamation of old waste disposal sites



programme allocation	2 348 114 082 €	100%
specific objective 1.6	413 417 235 €	17,61%
remediation - measures 1.6.11 a 1.6.12	**150 510 263 €**	**6,41%**

DETAILED QUANTITATIVE RISK ASSESSMENT AT THE FORMER COMPRESSED GAS PLANT

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KEYWORDS

Risk Assessment, Compressed Gas Plant, Sampling, Contamination, Remediation

INTRODUCTION

The main objective of the survey was to identify and quantify the extent of soil, groundwater and surface water contamination and developing recommendations, including cost estimates and options for further investigation and, if necessary, proposing corrective action. The majority of historical objects of the former compressed gas plant were demolished in the past, however some of them still exist, such as a desulphurisation station, a heating plant building with residual asbestos, a mercury plant, cooling towers containing asbestos and coal handling routes. The site is planned to be developed for light industrial production with associated logistic facilities.

METHODOLOGY AND SCOPE OF WORK

All sampling work was carried out in accordance with the Methodological Guideline of the Ministry of the Environment – Sampling Work in Remediation Geology (12/2006). Sampling works included Soil sampling (17 pcs), Groundwater sampling (11 pcs), Surface water sampling (7 pcs incl. sumps and civil defence bunker), Sampling of Riverbed sediments (2 pcs), Sampling of Building structures (8 pcs) and Asbestos survey.

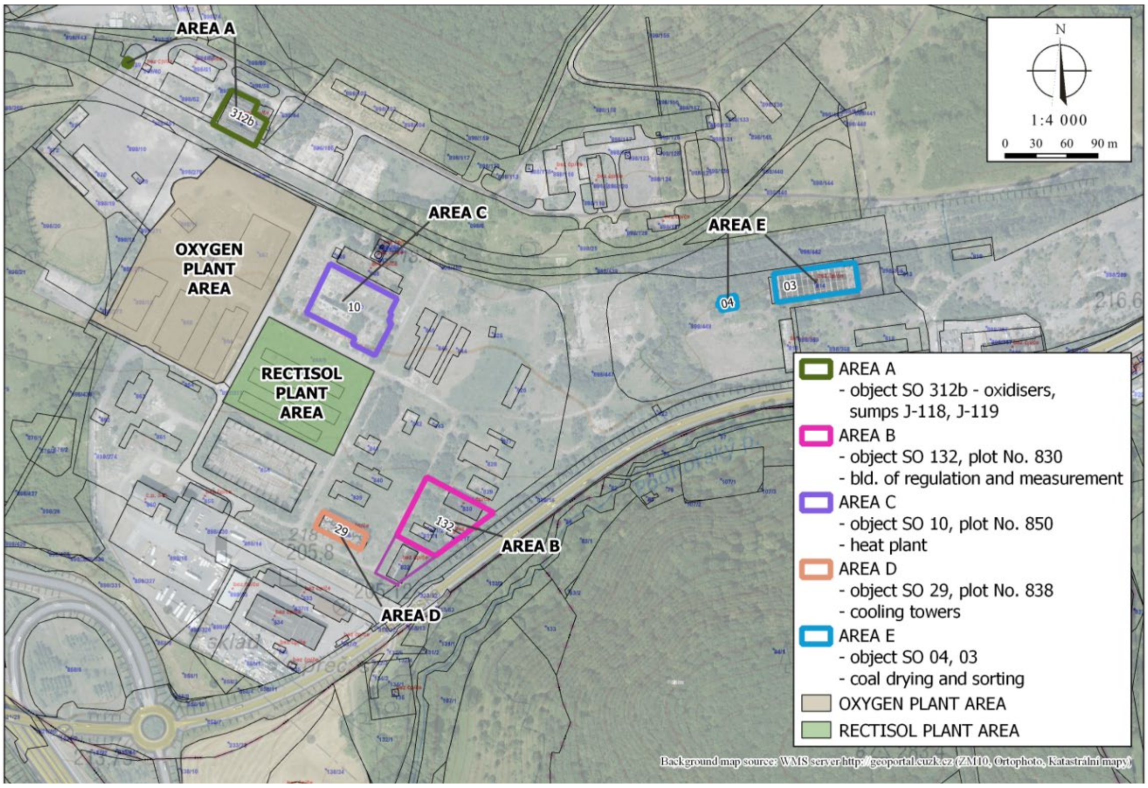

Figure 1. Areas and buildings with parcels of interest

SCOPE OF CONTAMINATION

The majority of old ecological burden has been removed; however, some remaining contamination still persists at the subject site.

The non-saturated zone

Sulphuric waste was verified in the area of oxidation and desulphurisation, in the object of the mercury plant and in three areas which contain asbestos (the former cooling towers, the former coal storage area and the heating plant building). Asbestos containing materials (ACM) are classified as hazardous waste.

The saturated zone

We verified the current contamination levels at the Oxidiser and Rectisol remediated outbreaks, which were completed in 2011. In the Oxidiser outbreak, remediation of CHC was carried out by the application of nano-iron supported by sodium lactate. Current groundwater sampling and the analysis of groundwater samples confirmed that the remediation limit has been reached.

Remediation of petroleum hydrocarbons (determined to be C_{10}-C_{40}) and BTEX was performed at the Rectisol outbreak. Current borehole sampling confirmed the presence of high concentrations of BTEX (maximum benzene concentration – 13930 µg/l). In addition, high concentrations of CHC were confirmed in the outbreak with a maximum 23462 µg/l, many times exceeding the remediation limit of 1000 µg/l. It is clear that remediation at this outbreak has not eliminated the source of contamination.

RECOMMENDED WORK

For the remediation of the site is recommended, i.e. the works mentioned in the Decision of the CEI, supplemented by groundwater remediation:

- disposal of sulphuric waste, the oxidiser and sulphur sumps (area A), contaminated constructions and soil (1 960 m^2);
- demolition and disposal of the mercury plant constructions and soil (building 132, area B);
- demolition and disposal of the cooling towers, construction debris containing asbestos and the heating plant. Asbestos objects were estimated at a total area of 11 770 m^2 (areas C, D and E);
- remediation of groundwater in the Rectisol facility (Area C):
    - pump and treat – pumping and cleaning of pumped water in a container decontamination station, located for this purpose on site. The purified water will be leached back by infiltration wells.
    - To support the biodegradation of petroleum hydrocarbons, macronutrients of ammonium salts and phosphates will be added to the infiltrated water or directly to the wells in accordance with the valid permit. If necessary, a complexing agent – citric acid – will be used to prevent the formation of deposits in the technology.
    - Supportive reductive dechlorination of CHC will take place using supporting substances (sodium lactate and nanoiron), which will be dosed into the infiltrated water.

Objectives of remediation intervention:

- to prevent undesired migration of the active substance to non-planned sites at the site of contamination
- to prevent undesired oxidation of the environment by infiltration of stripped (oxygenated) water
- to preserve the natural dynamics of groundwater and thus improve the conditions for the growth of microorganisms

We recommend the following work before the remediation work:

- Geophysical survey (georadar, DEMP, ERT),
- Pre-remediation investigation in the area of oxidation (oxidisers with sulphuric waste) to identify the exact scope of contamination

REFERENCE LIST

Bartoň, J., Sionová, P., Procházková, E., Vodičková, E., 2022: Detailed Quantitative Risk Assessment (RA) for Podhořský Park (Property of Tlaková plynárna Ústí nad Labem a.s.), GEOtest, a.s., Brno

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REDUCTIVE TECHNOLOGY USING RANEY ALLOY FOR QUICK AND EFFECTIVE DEGRADATION OF HALOGENATED ORGANIC COMPOUNDS IN CONTAMINATED WATERS

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KEYWORDS

Halogenated organic contaminants, wastewater, ground water, reductive reaction, hydrogenation metal catalysts, wastewater treatment

ABSTRACT

Halogenated organic compounds collectively referred as AOX (Adsorbable Organic Halides) are one of the most widespread groups of water contaminants (wastewaters, surface waters, ground waters). Reasons are both historical and industrial. Historical reasons include use of wide range of halogenated chemical compounds for preparation of solvents, degreasers, pesticides, flame retardants, and technical liquids in the past. Industrial reasons are that some of these substances are still used in many sectors of industry (paper, textile, chemical etc.). Due to their environmental persistence and potential toxicity, these substances have become subject of strict controls in surface and waste water. Therefore, there is a need of their elimination from these types of water. This can be achieved via utilization of fast and effective technologies.

This study is focused on development of technology based on strong reducing properties of Al-Ni 50:50 wt. % alloy (Raney alloy) in alkaline water environment for degradation of a wide range of halogenated organic compounds directly in contaminated waters. The mechanism involves the catalytic hydrodehalogenation reaction on the surface of porous nickel by the action of hydrogen gas produced in-situ during aluminium dissolution step (Fig. 1).

$$2\ Al(s) + 2\ NaOH(aq) + 6\ H_2O(l) \rightarrow 2\ Na[Al(OH)_4](aq) + 3\ H_2(g)$$

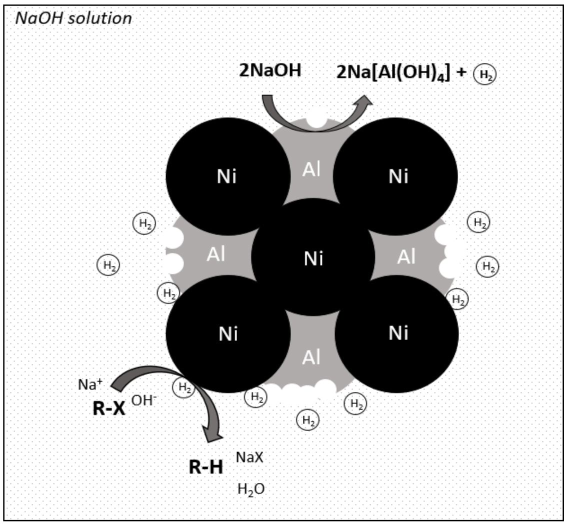

Figure 1. Principle of catalytic dehydrogenation

The proposed technology was subsequently applied for degradation of halogenated organic substances directly in contaminated waters under ambient temperature and atmospheric pressure. For purpose of verification, a special technological device (Fig. 2) for water treatment in large volumes was constructed and verified on model water samples as well as on a wide range of real waters (industrial wastewater, groundwater, landfill water). In all cases, significant degradation of all monitored halogenated contaminants, including even persistent forms, was observed within a few hours.

The use of Raney Al-Ni alloy for degradation of halogenated organic substances (AOX) directly in contaminated waters under alkaline conditions thus seems to be a very promising method especially for treatment of heavily contaminated waters.

Figure 2. Technological device for on-site application

ACKNOWLEDGEMENT

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ASSESSMENT OF THE SOIL ENVIRONMENTAL QUALITY FROM MITIDJA PLAIN, ALGERIA

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KEYWORDS
Mitidja plain, levels of contamination, pollution indices, soil quality, trace metals

ABSTRACT

The present study investigates the soil environmental quality from Mitidja plain using pollution index and pollution load index. A total of 180 composite topsoil samples were collected and analyzed for Cd, Cr, Cu, Fe, Ni, Pb and Zn. The results showed that soils samples were uncontaminated with Cr and Ni, and moderately contaminated with Cu, Cd, Pb and Zn. According to the spatial distribution map of pollution load index, 17% of the whole studied area was belonged to low contamination, while 70% and 13% were moderately and highly contaminated with trace metals, respectively. Overall, the studied area is classified as moderately contaminated. The highest levels of contamination have been observed near urban and industrial areas. The main sources of contamination appear to be related to traffic emissions, atmospheric deposition of particles, and wastes discharge. The results of this study can help the decision makers to implement suitable control measures.

INTRODUCTION

Trace metals (TM) in soils are derived from the parent material and human activities. Anthropogenic inputs in the terrestrial environment are associated with industrial and urban discharges, road traffic emissions, mines, smelters, and agricultural practices (Alloway 2012; Huang et al., 2013; Lineard et al., 2014). Environmental contamination by TM has become a worldwide concern due to their persistence, non-biodegradability, and potential risks to humans through the food chain (Nriagu and Pacyna 1988). Therefore, it is important nowadays to evaluate the soil quality and to distinguish natural concentrations of TM from abnormal concentrations (Reimann and Garrett 2005). This can be done by comparing the concentration of TM with the related environmental guidelines or by quantifying a pollution factor such as pollution index (PI) and pollution load index (PLI) (Luo et al., 2012). These indices help to determine whether the accumulation of TM was due to lithogenic source or the results of anthropogenic activities, and have a great importance for monitoring soil quality (Kowalska et al., 2018). Therefore, the main objective of the present study was to investigate the soil environmental quality of the Mitidja plain based on pollution indices.

MATERIALS AND METHODS

This study concerns the eastern part of the Mitidja plain with an area of 665 Km^2 and is considered one of the most fertile lands in Algeria. A total of 180 composite topsoil samples across the plain were collected and the concentrations of trace metals were determined by inductively coupled plasma (ICP) spectrometry following aqua regia extraction (HNO_3+HCl). The diagnosis of soil pollution with trace metals was assessed using the PI for each metal and the IPI for six metals (Chen et al., 2005; Guo et al., 2012). The PI of each metal was defined as the ratio of its concentration to the geochemical background value (GBV) of the corresponding metal in the earth´s crust (McLennan 2001) using equation 1, where C is the measured concentration of each trace metal, and S is the GBV

$$\mathrm{PI} = \frac{\mathrm{C}}{\mathrm{S}} \tag{1}$$

The IPI represents the overall degree of metal pollution in soils, and is calculated according to equation 2 where n is the number of metals considered.

$$\mathrm{IPI} = \frac{\sum_{\mathrm{i}=1}^{\mathrm{n}} \frac{\mathrm{C}}{\mathrm{S}}}{\mathrm{n}} \tag{2}$$

The PI of each metal was classified as either low (PI ≤ 1), moderate (1 < PI ≤ 3) or high contamination (PI > 3). Three levels of contamination were classified for trace metals based on their IPI values as follows: IPI ≤ 1, low contamination; 1 < IPI ≤ 2, moderate contamination; IPI > 2, high contamination.

RESULTS AND DISCUSSION

The PI values were Cd 0.52 - 10.68, Cr 0.16 - 1.78, Cu 0.13 - 12.41, Ni 0.12 - 1.63, Pb 0.50 - 23.1 and Zn 0.23 - 6.57. The mean PI of trace metals in the surface soils of the Mitidja plain decreased in the order:

Cu (2.51) > Cd (2.23) > Pb (2.07) > Zn (1.3) > Ni (0.77) > Cr (0.57)

The results of PI showed that Cu, Cd, Pb and Zn had been moderately influenced by anthropogenic activities, except for Ni and Cr. The overall IPI of all examined trace metals ranged from 0.43 to 5.76, with a mean value of 1.57. Approximately 17% of the samples were classified as having a low contamination level, with IPI values ≤ 1. About 70% of the samples showed moderate contamination levels with IPI values between 1 and 2, and finally 13% of all samples were highly contaminated with trace metals, with IPI values higher than 2. Overall, the studied area revealed moderate contamination. In comparison with other studies, the mean value of IPI obtained for Mitidja soils was similar to the reported in urban soils of Yibin City (mean 1.6, Guo et al., 2012) and lower than in urban soils of Beijing (mean 2.21, Chen et al., 2005). The spatial distribution of IPI is shown in Figure 1

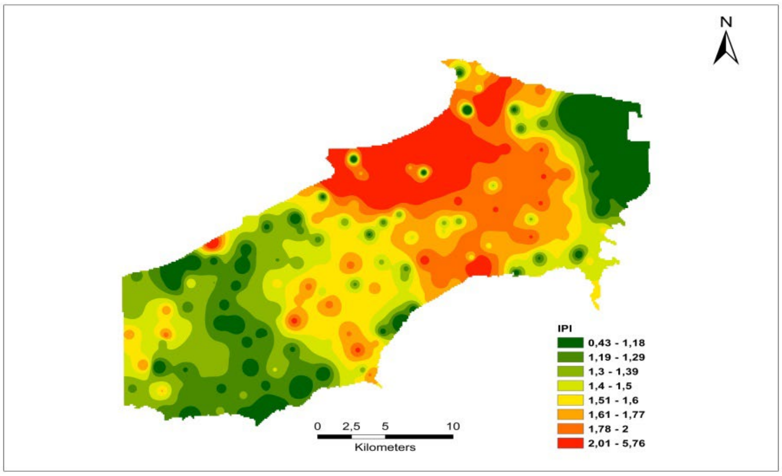

Figure 1. Spatial distribution of integrated pollution index of metals in soils of the Mitidja plain.

The soils with the least trace metals pollution were found mainly at the north eastern part of the plain, which could be attributed to the pedogenic material. The soils with the most trace metals pollution were observed at the north of the Mitidja plain, mainly close to industrial and urban areas of El Harrach, Dar El Baida and part of Rouiba districts where industrial activities include the production of plastics, hydrocarbons, petrochemicals, steel, cement, building materials, pharmaceuticals and electronic components. The atmospheric deposition of particles from industrial, vehicular emissions, and wastes from urban activities could be possible sources of these trace metals in the studied area.

CONCLUSION

The use of pollution indices has shown that the studied area is moderately contaminated by Cu, Cd, Pb and Zn.

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THE POSSIBILITY OF PLANTING THE FAST-GROWING TREE SPECIES AT THE LANDFILLS OF THE KOLUBARA MINING BASIN

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KEYWORDS
deposols, recultivation, woody cultures

ABSTRACT

The soil conditions in the surfaces produced by the surface mining of the ore, which need to be recultivated, are accompanied by numerous problems such as overwetting, lack of nutrients, poor functional activity, compaction and destruction of the soil texture.

On the surface mine of field "B" in the settlement of Prkosava within the Kolubara mining basin in the Republic of Serbia (Coordinate: 7453715;4916566), a landfill was formed on which an area of 7.6 ha of deposol land was set aside for the cultivation of woody crops [1] . One part of the separated area was leveled and two average samples were taken from this area and a pedological profile was opened. The second part was in existing condition, with numerous depressions in which water was retained, so that in some places it was overgrown with reeds, willows (*Salix sp.*) and poplars (*Populus sp.*).

In the composite samples sampled at the study site, the mechanical composition, main fertility parameters and content of the total forms of Mn, Cd, Pb, Ni, Cr, Zn, Cu, Co, were determined. It has been determined that the tested soil by texture belongs to clay and clayey loam. It is neutral to slightly acidic reaction, medium provided with humus, nitrogen and readily available potassium, while the availability of readily available phosphorus is low.

Table 1. Basic fertility parameters

N°	Coordinate		pH		$CaCO_3$	SOM	P_2O_5	K_2O
	x	y	(H_2O)	(1MKCl)	(%)	(%)	(mg 100 g^{-1})	(mg 100 g^{-1})
			SRPS ISO 1039(2007)		SRPS ISO 10693(2005)	According Kotzmann's method	According Egner-Riehm	
1	7453494	4916487	7.60	6.60	0.00	3.34	8.16	23.08
2	7453824	4916667	7.50	6.40	0.00	3.57	3.31	25.88

Table 2. Total contents of trace elements in soils under studied area

N°	Fe	Mn	Cu	Zn	Co	Cr	Pb	Ni	Cd	As
		(mg kg^{-1})								
	(%)	SRPS ISO 11047 (2004)								(mg kg^{-1})
1	25.00	548	22.28	66.9	21.06	127.10	26.59	139.80	0.48	8.82
2	31.17	505	22.66	71.20	19.87	144.20	32.61	145.60	0.47	8.21

Fe (%) and As (mg/kg) was determined by digestion with HNO_3 i H_2O_2 on ICP

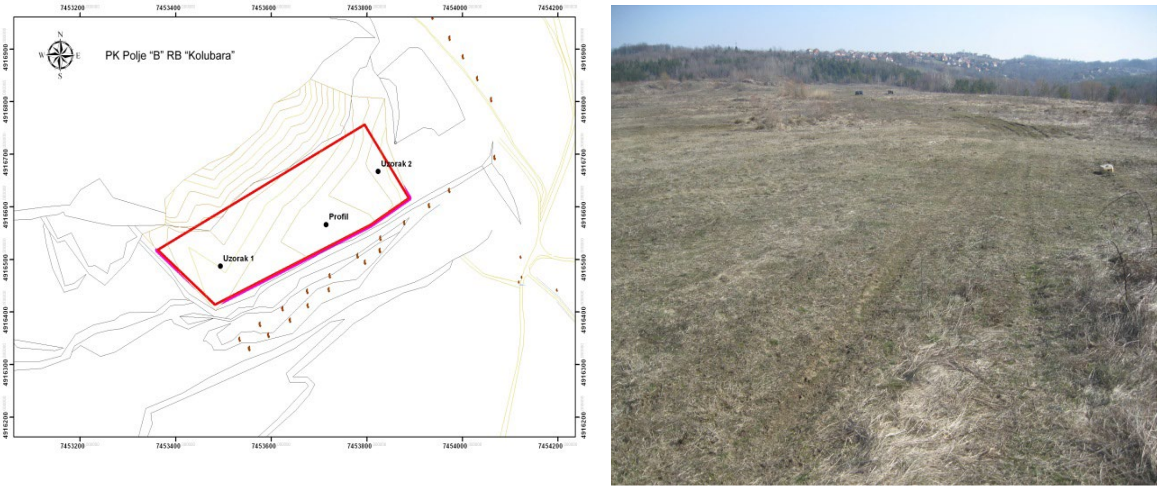

Figure 1. Location of studied area

Table 3. Particle-size distribution

Profil 1 Depth (cm)	Particle-size distribution (%)						Soil textural class
	Coarse sand >0.2mm	Fine sand 0.2-0.02mm	Silt 0.02-0.002mm	Clay <0.002mm	Total sand >0.02mm	*Silt+clay* <0.02mm	
	Method sieving and sedimentation						
0-18	1.7	24.7	22.6	51.0	26.4	73.6	G
18-43	2.9	26.2	26.6	44.3	29.1	70.9	G
43-118	5.5	25.8	31.0	37.7	31.3	68.7	Gl
118-140	12.1	26.5	25.9	35.5	38.6	61.4	Gl

Soil textural class – acording ISSS, [2]

Table 4. Maximum allowed concentrations of hazardous and harmful substances in the soil in the Republic of Serbia

Element/Rule book	Cd	Co	Cr	Mn	Ni	Pb	Zn	Cu	As
	(mg kg^{-1})#								
Official Gazette 23/1994[3]	3		100		50	100	300	100	25
Kastori et al.(1997) [4]				400*					
Ordinance - Official Gazette 51/2002 [5]		30*							

\# absolutely dry matter

The total content of hazardous and harmful substances tested is within the maximum permissible concentrations, except for Co, Ni and Cr, whose increased content comes from the geological substrate which has reached the surface by the deposition of tailings.

	mI, 0-18 cm, basically light-coloured (10YR7 / 1) interspersed with granular (7.5YR7 / 8) and gley stains (Gley18 / 2,510GY) Clay composition (G), has no clear structure. Not carbonate. Only in the first few cm permeated with veins of grass. Abruptly passes into

	mII, 18-43 cm, Marbled layer of dark brown color (10YR 6/1) mixed with granular-yellow stains (7.5YR 7/8 and 10YR 8/8) with gley mass (Gley1 8 / 2.5 10GY). Clay (G), unstructured, difficult to penetrate and permeable. Non-carbonate. It stands out very clearly
	mIII, 43-118 cm; The layer has a very mosaic appearance due to granular-yellow, brown and gley stains (10YR 7/1; 7,5YR 7/8; 10YR 8/8; Gley1 8 / 2,5 10GY) of clay loam composition (GI), not structured, more difficult to permeate. Non-carbonate. Transitions to
	mIV, 118-140 cm. Layer dominated by gley bluish-white (Gley 18 / 2.5GY), clay loam (GI). Unstructured, non-carbonate, water appears at 140 cm.

Figure 2. Pedological profile

Their impact on the cultivation of woody crops is not crucial. We believe that the conditions for the production and cultivation of woody crops are good, particularly of species from the association *Populeto - Salicetum* (poplar and willow), although success would also be good with the species *Robinia pseudoacacia* (acacia).

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TRACE ELEMENTS CONTENT IN SOILS AND INDIGENOUS MEDICINAL HERBS IN THE AREA OF HIGHLY DEVELOPED INDUSTRIAL ACTIVITY

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KEYWORDS
Extensive environmental pollution, industry, medicinal species, power plants, wild habitats

ABSTRACT

In rich flora of Serbia thrives a wide variety of indigenous medicinal species whose effectiveness is associated with their active constituents. One of the major quality problem is their high trace elements content that can be associated to extensive environmental pollution of their wild habitats, particularly when characterized by highly developed industrial activities. Aim of the study (Project TR 37006, year 2017; Project 451-03-68/2022-14/200011, year 2022) was to determine the trace elements contents in medicinal plants and in soils of their wild habitats.

Figure 1. Republic of Serbia, near Belgrade: Nikola Tesla Thermal Power Plants d.o.o. Obrenovac: Tent A (a) and Tent B (b); industrial-petrochemical complex HIP-Petrohemija a.d. Pančevo (c)

Nikola Tesla Thermal Power Plants d. o. o. Obrenovac (TENT A and TENT B) are very diverse in terms of relief and geological background of the primary vegetation and climate. The production complex of HIP - Petrohemija in Pančevo was built on approximately flat soil, raised on chernozem, with signs of glaying on the loess. The flora of Pančevo consists of wild and cultivated plants. The studied soil types, under all plant species sampled, were Calcic Gleysol (Obrenovac) and Humogley (Pančevo) [IUSS

Working Group WRB, 2015]. The samles of plants are colleted in the area of highly developed industrial and industrial-petrochemical activities: Obrenovac (*Cichorium intybus* L., *Plantago major* L., *Symphytum officinale* L., *Taraxacum officinale* F. H. Wigg) and Pančevo (*Matricaria chamomilla* L., *Melissa officinalis* L., *Mentha piperita* L, *Foeniculum vulgare* Mill). Soil and plant analyses were done according to ICP-OES methodology (Soltanpour et al., 1996).

Tab. 1 shows total levels of trace elements in the soil samples under studied plants from both Obrenovac and Pančevo. It corresponded to the usual levels in agricultural soils and were below the maximum permissible concentrations – MPC (OGRS, 2019).

Table 1. Total contents of trace elements in soils from Obrenovac and Pančevo under studied plants

Trace elements	**Total forms of trace elements (mg kg^{-1}) in soil under studied plant species**							
	C. intybus	***P. major***	***S. officinale***	***T. officinale***	***M. chamomilla***	***M. officinalis***	***M. piperita***	***F. vulgare***
Cd	0.56	0.57	0.55	0.48	0.71	0.69	0.63	0.70
Co	19.11	15.75	16.96	19.37	0.90	0.43	0.75	0.73
Cr	78.71	82.11	84.61	81.21	0.72	0.45	0.53	0.76
Cu	92.05	91.35	89.98	93.81	16.48	14.26	16.85	15.42
Fe	29920	31345	30160	34491	31560	22457	34103	24300
M	724.67	428.67	481.00	749.33	254.70	137.13	196.33	262.50
Ni	36.37	29.25	31.86	41.86	27.64	14.66	23.24	23.72
Pb	21.81	20.68	19.93	14.16	13.76	13.88	15.20	12.36
Zn	94.38	111.55	111.75	91.37	7.98	10.14	6.08	5.73
As	8.60	3.46	3.80	9.86	1.18	0.85	1.16	1.03

Fig. 1 shows the normal and toxic concentrations of trace elements (mg kg^{-1}) and As (µg kg^{-1}) in the plants aerial parts collected from the area of Obrenovac and Pančevo.

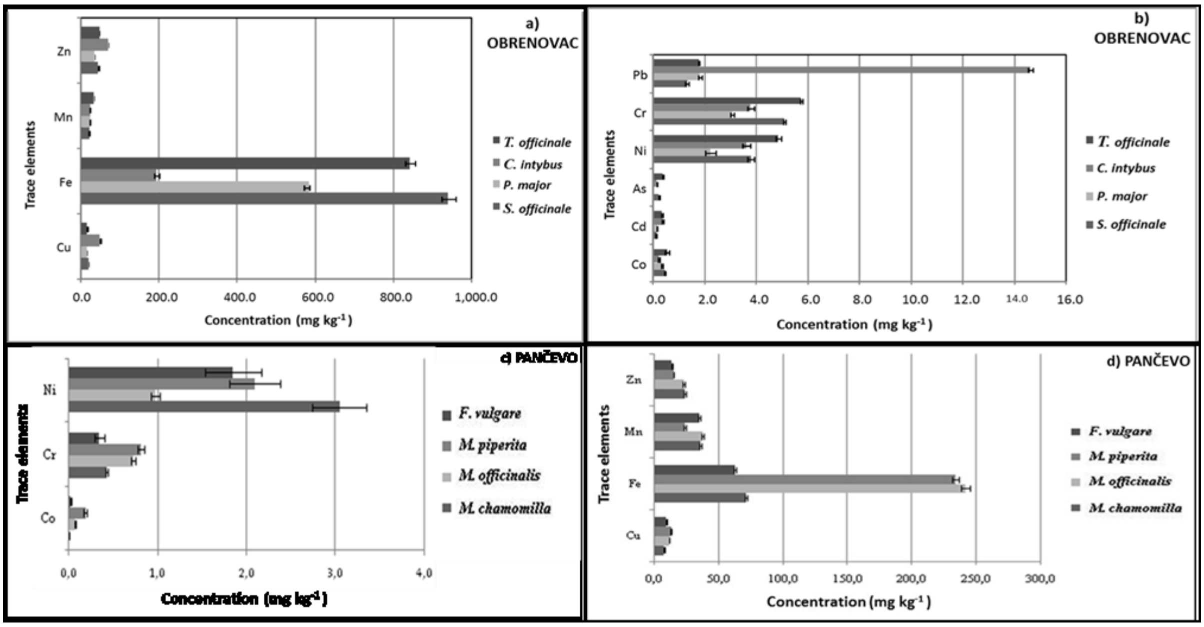

Figure 1. Trace elements content in plants collected from the area of Obrenovac (a, b) and Pančevo (c, d)

During the year 2017, the contents of Pb, As, Cd, Co, Mn, Ni and Zn in the herbs samples from Obrenovac were below MPC; Cr was toxic in all samples, Cu was toxic in *C. intybus* and *S. officinale*, and

Fe was toxic in *T. officinale*, *P. major* and *S. officinale*. The contents of trace elements in herbs from Pančevo were below MPC (Kastori et al., 1997), suggesting that they are with normal contents of trace elements suitable for further usage. It could be concluded that the herbs from Obrenovac growing site are, generally, not appropriate for further use.

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THE POTENTIAL OF *MISCANTHUS X GIGANTEUS* FOR REMEDIATION OF SITES CONTAMINATED WITH OIL-PRODUCTS

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KEYWORDS
Soil contamination, Total Petroleum Hydrocarbons, *Miscanthus x giganteus,* biomass, phytoremediation

ABSTRACT

The risk of soil contamination with oil-products continues to be a serious concern in Ukraine. Such contaminated localities formed by sites where the oil-products were spilled to the soil because of military operations, accidents of pulp broken or equipment damaging including transformer. Remediation of oil-contaminated sites by utilization phytoremediation with the second generation energy crop *Miscanthus x giganteus* and investigation of feasibility of biomass production have been the specific objectives of the current study.

The field research was conducted in 2016-2019 in village Ivanivna, Kharkiv region, Forest Steppe climatic zone of Ukraine. The site location is: Longitude – 36^0 42” 50.3, Latitude – 49^0 12” 21.2. Site has a surface 0,38 ha (Fig.1). Two research plots were under evaluation: plot contaminated by oil-products, mainly Total Petroleum Hydrocarbons (TPH) and not-contaminated plot (control). The level of contamination by TPH was analyzed using the Gravimetric method (https://meganorm.ru/Data2/1/4293807/4293807051.pdf). The content of TPH in the contaminated soil was 0,7 g/kg, although in Ukraine the limited value of TPH concentration for soil and water resources is uncertain. The second generation crop *Miscanthus x giganteus* was established at the contaminated and control sites in 2016 and annually the morphometric parameters, harvest biomass yield, and concentration of TPH in the plant’s tissues were monitored. The General Linear Model (GLM) was utilized for results evaluation.

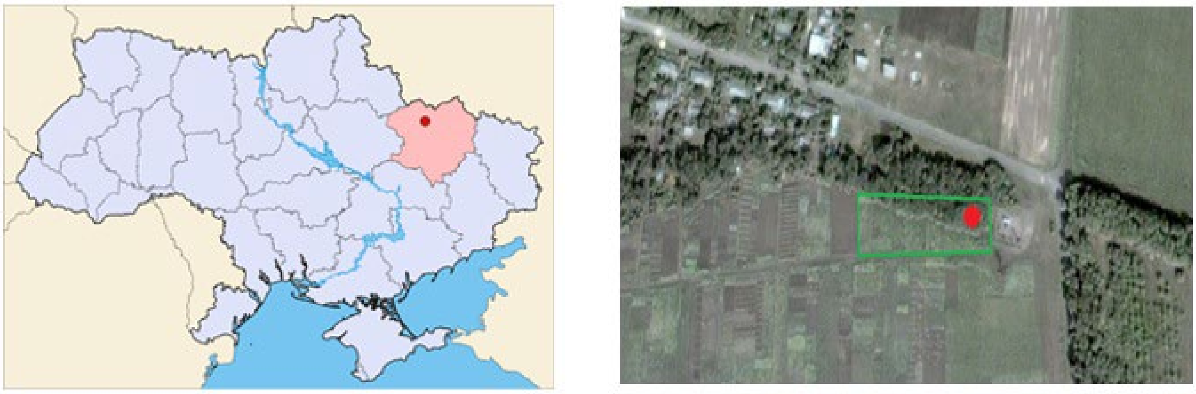

Figure 1. Location of the research site

The results of the GLM (Fig.2) indicated that the level of contamination ($F = 49.3$, $p < 0.001$),the year ($F = 2470.2$, $p < 0.001$), and their interaction ($F = 46.2$, $p < 0.001$) had a statistically significant effect on the morphometric parameters and dry mass yeild (DMY) of the crop. The decreasing of DMY was observed for the contaminated site in each of the monitored vegetative seasons. Oppositely, the gradual annual increase of DMY was recorded when the crop cultivated in the uncontaminated soil (control). When biomass was produced at the contaminated soil TPH were detected in roots and the above part biomass: the average concentration in the roots was 0,06 mg/kg for harvested years, and the average concentration in the above part was lower: 0,03 mg/kg for harvested years. The three year results confirmed the suitability of *Miscanthus x giganteusg* for phytoremediation of TPH contaminated soils. However, the economic value of obtained yield may reduce profit of the phytoremediation. The further feasibility study is needed to ensure the possibility of application of *Mxg* for phytoremediation of the oil-contaminated soils.

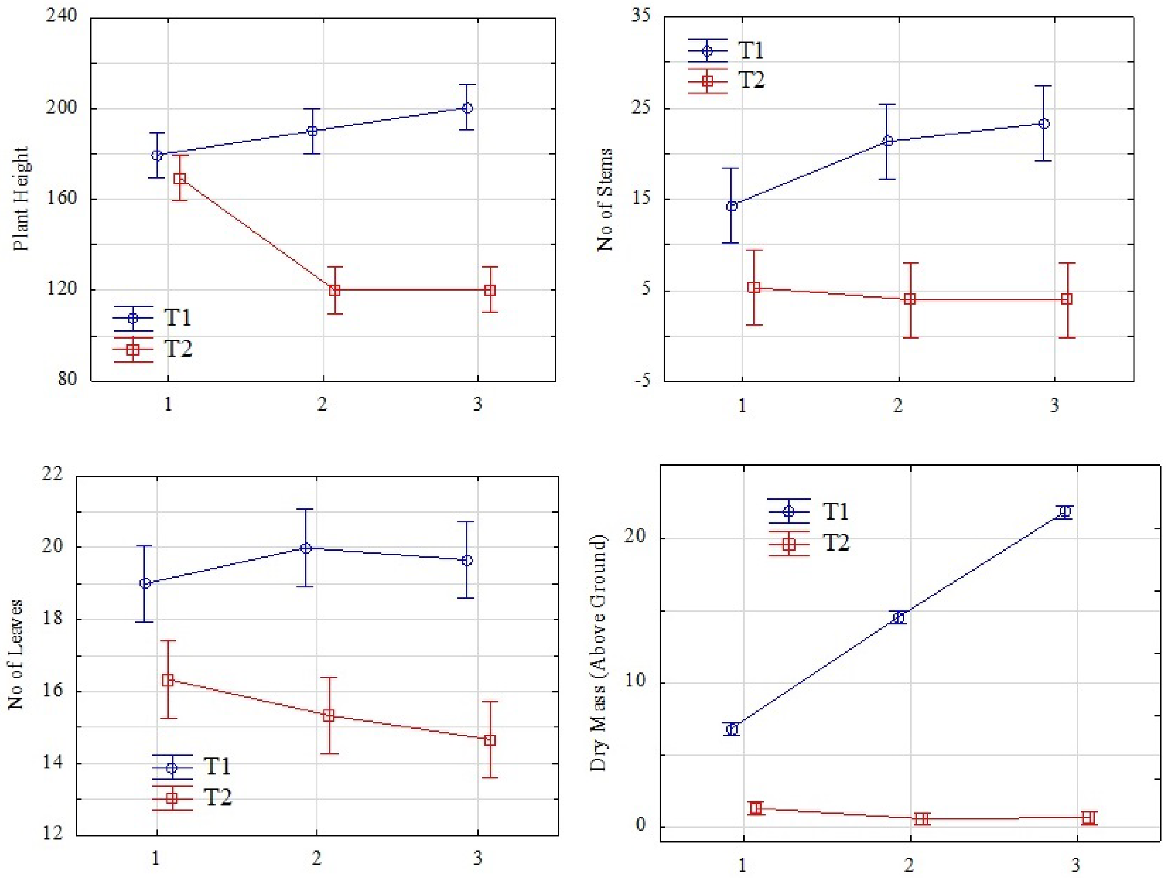

Figure 2. Response of morphometric traits to the soil contamination in the different years. T1 – control soil; T2 – soil contaminated by TPH

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RADIONUCLIDES AND DAMAGED SOILS OF EASTERN HERZEGOVINA

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KEY WORDS
Bosnia and Herzegovina, Gacko field, radionuclides

ABSTRACT

Soil is one of the most important natural resources. Soil represents a potential source of contamination of biota, which makes tracking of distribution of artificial radioactivity extremely important (Sarap, 2017).

Monitoring of any release of radioactivity material to the environment is necessary for environmental protection. Measurement of natural radioactivity in soil is very important to determine the amount of change of the natural background activity with time as a result of any radioactivity release (Sarap et al., 2012).

Republic of Srpska has about 0.85 ha of agricultural soil per capita, of which about 0.60 ha is arable (ploughland, gardens, orchards, vineyards, meadows) i.e. about 0.40 ha of ploughland and gardens. Currently, only about 0.20 ha per capita is cultivated. The above data show that the degree of utilization of the natural resources in Republic of Srpska is low with a trend of reduction. Throughout the world, the surface of 0.10 ha of arable land per capita is considered the lower limit (Agricultural Development Strategy of Republic of Srpska until 2015). Annual losses of soil, in Republic of Srpska, in the process of its destruction, amount to more than 1,500 hectares (Nature Protection Strategy of Republic of Srpska). In Bosnia and Herzegovina, according to NEAP's data for 2003, 900 ha disappears in open pits and 300 ha in dumps annually.

Gacko field is a karst field and is virtually the only oasis of arable land in the region studied. Nevertheless, nothing significant has been done in this area over the past decade to protect land resources from damage and permanent destruction. Coal mine and thermal power plant in Gacko field is a very important industrial facility not only for this region but also for the Republic of Srpska (Tunguz et al., 2014). The available data in the field of research of soil damage and destroyed farmland by various activities, where the exploatationof mineral resources by surface mining leads, date back to the period of 20 or 25 years ago. It is obvious that the lasting conflicts in interests and rights of soil disposal in the technical and in ecological areas are gaining in importance. This is one of the important motives for undertaking research activities in Herzegovina, to shed light, as much as possible, on the current situation in the interests of individual land users. Resulović, (2004) makes the most elaborate discussion about the issue of the destruction of agricultural soil in Bosnia and Herzegovina.

This issue is a challenge in terms of determining the damaged and destructed soils, defining a model of re-cultivation, implementing the measures for rehabilitation and reanimation of damaged farmland, as well as the definition of damaged and destroyed farmland in eastern Herzegovina.

Given that there are no specific regulations in the Republic of Srpska, the concentration of natural and produced radionuclides in samples from the working and living environment of thermal power plants, comparison with literature data from the region and the world is one way of evaluating the impact of the plant's operation on the soils.

In all soil samples, regardless of their origin and method of utilisation, it is possible to detect different levels of concentration of activities that originate from the presence of natural and artificial radionuclides. Given that a relatively large area was investigated, it is expected that the radionuclides will be detected in a wide range of sizes, because the composition of soil differs from one site to another. Arable land is formed by mixing the products of mechanical decomposition of rocks with an organic component, and the values of activity concentration of natural radioactive elements in rocks are known. Natural radionuclides are detected in the investigated samples: ^{210}Pb, ^{238}U, ^{235}U, ^{226}Ra, ^{232}Th, ^{40}K, and the produced radionuclide ^{137}Cs.

The results of gamma emitters spectrometry indicate that the concentrations of natural radionuclides are of the same order of magnitude, as in power plants in other countries. The results point to the necessity of regular monitoring of radioactivity in eastern Herzegovina in order to assess the impact of the technologically increased natural radioactivity. At the same time, the obtained results represent the initial basedata based on which could be predicted levelradioactivity since such studies have so far not been carried out in the Republic of Srpska.

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PRODUCTION OF BIOFUELS USING RAW ALGAE (*CHLORELA*)

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KEY WORDS
Biofuels, raw materials, production process, micro, mark, red, algae

Production and application of biofuels are gaining strategic importance in national economies because biofuels have positive effects in many areas (agriculture, energy, new technologies, protection of the human environment). The main advantage is that the import dependence on fossil fuels is reduced, the quantities of which are limited quantitatively, and are located in inaccessible areas in the world. However, other effects of the introduction of biofuels are appreciated in the world, such as: introduction of various energy technologies in a country and thus securing an energy future, reducing greenhouse gas emissions, revitalizing rural areas and increasing employment in all stages of biofuel production. Over the years, there have been efforts around the world to find alternative, environmentally friendly ways to obtain energy, ie to replace fossil fuels. The cultivation of micro and macro algae, green, brown and red algae has been found to be quite productive and efficient and are an environmentally viable way to produce biofuels and other derivatives. Some types of microalgae have been found to be suitable for obtaining biofuels due to the presence of lipids in them, while macroalgae are rich in polysaccharides so that by their fermentation process bioethanol can be obtained. This energy source has been shown to have a greater advantage than other energy sources. The use of algae in the production of biofuels is useful because they are beneficial to the environment, they reduce the emission of carbon dioxide (CO_2) in the air, because in contact with solar energy they get a food source, so algae is considered efficient and quality source of energy.

INTRODUCTION

Biofuel is a solid, liquid or gaseous fuel consisting of or derived from biomass. It can be used directly, for heating and electricity, or by processing it. It is obtained from any rapidly renewable carbon source. The most common raw material is plants. The term biofuel is a name for a fuel that belongs to or is produced by processing biomass (Biomass (Figure 1)-(organic matter) can be used to produce heat, fuels, and electricity. This is called bioenergy. Wood, the largest source of bioenergy , has been used for thousands of years to produce heat. But there are many other types of biomass, such as wood, plants, agricultural or forestry waste, as well as the organic components of industrial waste that can now be used as a source of energy , this also includes microorganisms). As such, biofuels are different from fossil fuels, they belong to renewable energy sources. Biofuels are also included in fuels obtained from by-products of other processes which, if not used, will be waste materials.

DIVISION OF BIOFUELS

Pure biofuels - wood - in different forms in the form of logs, wood chips (chips), twigs, briquettes, pellets, chipboards, etc., straw - can be in its casing or completely with the grain, hay - which currently has no practical application, other vegetable wastesLiquid, which are divided into several subgroups - alcoholic biofuels are alcoholic fuels that are produced from biomass (bioethanol, biomethanol, butanol can also be produced), bio-oils - this includes vegetable oils, biodiesel, biogas and wood gases that with Fischer -Tropical synthesis can be transformed into a liquid aggregate state, waste products - terminal depolymerization with it, methane and hydrocarbons are obtained from different types of waste, which are chemically similar to oil.Gaseous-biogas, any generator gases that are produced by processing biomass (wood gas), some distillation gases produced by processing biomass, hydrogen that can be produced by splitting any molecule of hydrocarbons.

RAW MATERIALS FOR OBTAINING BIOFUEL

Raw materials from which biofuel can be obtained are: algae, various types of microorganisms, coffee grounds, potato peels, sunflower, waste oils, sugar beets, soybeans and many others.

ALGAE AS RAW MATERIALS FOR THE PRODUCTION OF BIOFUEL

Throughout the years, there have been efforts in the world to find alternative, environmentally acceptable forms of obtaining energy, i.e. to replace fossil fuels. Cultivation of micro and macro algae, green, brown and red algae has been established that they are productive and efficient and are an environmentally profitable way to produce biofuels and other derivatives. It has been determined that some types of microalgae are suitable for obtaining biofuels due to the presence of lipids in them, while macroalgae are rich in polysaccharides, so bioethanol can be obtained through their fermentation process. It turned out that this source of energy is more advantageous than other sources of energy. There are over 1000 types of algae that are suitable for the production of biofuels, but only 100 of them are used. Some of these algae are shown in table 1.

Table 1. Chemical composition of some algae expressed as percentage of dry matter (%)

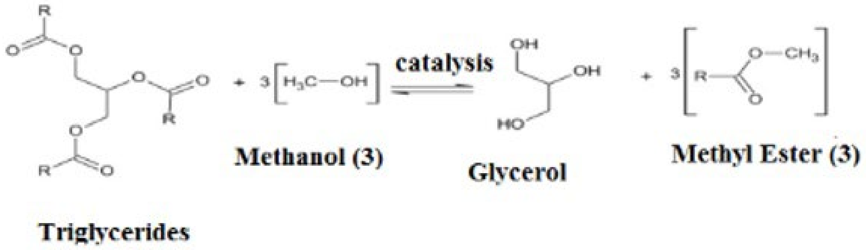
Species	Proteins	Carbohydrates	Fats and oils	Nucleic acids
Scendesmus obllquus	50 – 56	10 -17	12 -14	3-6
Scendesmus quardicauda	47	-	1.9	-
Scendesmus dimorphus	8 -18	21 – 52	16 -40	-
Chlamydomonas rheinhardii	48	17	21	-
Chlorella vulgaris	51 – 58	12 – 17	14 – 22	4 – 5
Chlorella pyrenoidosa	57	26	2	-
Spirogyra sp.	6 – 20	33 – 64	11 – 21	-
Dunallella bioculata	49	4	8	-
Dunallella salina	57	32	6	-
Euglena gracills	39 – 61	14 – 18	14 – 20	-
Prymnesium parvum	28 – 45	25 – 33	22 – 38	1 – 2
Tetraselmis maculata	52	15	3	-
Porphyrdium creuntum	28 – 39	40 – 57	9 – 14	-
Spirulina maxima	60 – 71	13 – 16	6 – 7	3 – 4,5
Synechoccus sp.	63	15	11	5
Anabalena cylindrica	43 – 56	25 – 30	4 – 7	-

Algae cultivation method: there are two basic ways of growing algae, that is, the outdoor pool system or the artificial indoor pool system. (Figure 3 and Figure 4).

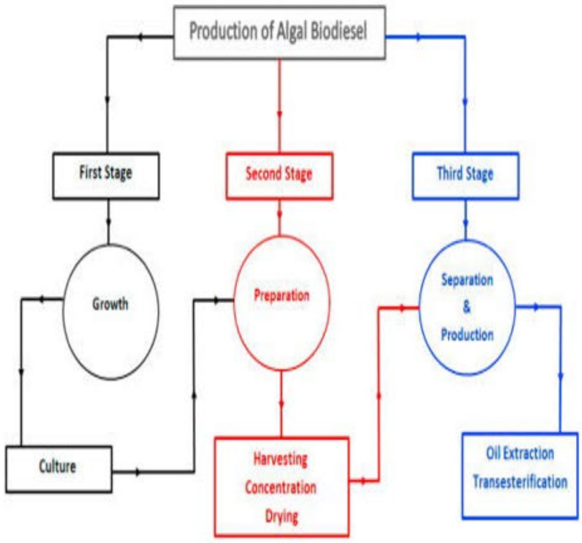
Figure 3. Open systems for growing algae

Figure 4. Closed systems for growing algae

In open ponds: they are problematic because it is difficult to control the distribution of species and the assemblage of a system that grows only one species without other intrusions. Bioreactors are better methods because they allow control of light, water quality and nutrient input. To supply nutrients in such systems, waste water from water treatment is often used which are combined algae cultivation systems. The advantage of this method is possible elimination of possible errors as a result of full control of the environment and production is feasible, anywhere in the world. The only drawback is the supply of sufficient amounts of sugar. Algae harvesting - the most used method is ultrasound-assisted extraction, which causes vibrations and tremors of the molecules in the algae, thereby contributing to a critical point, that is, bubbles are created and various types of media, steam and gas fill the voids. This method is performed using catalysts such as NaCl, or an ester (TAG) that is mixed with an alcohol such as methanol or ethanol, as a final product biodiesel mixed with glycerol that is further removed and can be used in the cosmetic industry for the production of soaps.



TECHNOLOGICAL PROCEDURE OF PRODUCTION OF BIOFUEL FROM ALGAE



CONCLUSION

Biofuel was born as a reason to save the environment from pollution and a perfect replacement for fossil fuels, it proved to be much more economically profitable than "black gold". For the production of biofuels, a very large area is needed for the production of the crops from which the biofuel will be obtained, thereby causing the disturbance of forests and grasslands, which disrupts biodiversity and the extinction of some types of plants and animals due to the disturbance of their habitats (disturbance of the ecosystem). On the other hand, there is a debate about whether food should be used as a source of energy for humans or whether it should be used as a raw material for the production of biofuels and their use in agriculture, public transport, and cars make life easier for a certain part of the population. the population of the Earth.

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INVESTIGATIONS ON THE EFFICIENCY OF SOME BIOPRODUCTS IN BIOLOGICAL CONTROL ASH [UNCINULA NECATOR (SCHW.)] IN HARDHI

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ABSTRACT

Grape production methods of biological agriculture started in Albania since 2001 and currently occupies an area of 25 ha for production of wine and table grapes. Biological vineyards are concentrated in 15 farms with 1-5 ha sized mainly in Durres, Tirana, etc. Kavaja. The main challenge during this period has been the implementation of practices and methods in accordance with the standards of biological agriculture to ensure sustainability and increase the efficiency of biological production in the vineyards. The main attention is focused on maintaining and enhancing soil fertility through the addition of organic matter and biological activity. Along with organic manure, widely applied in biological vineyards green fertilization, and plant covers mulçërimi with different organic materials to control weeds and maintain soil moisture. The choice of suitable cultivars is one of the important elements for the success of cultivation methods of biological agriculture. Protection from diseases and pests is one of important challenges, including that from the application of various agro-technical methods and to the application of biotechnological methods (sex pheromones, biological preparations) and treatments allowed by the standard preparations. Precisely this was and the purpose of taking this study on the effectiveness of certain study biofungicideve and efficiency comparison of control with that treatment Bio traditional farm in the village Bio Hajdar Kuçi Marikaj Tirana against powdery mildew [Uncinula necator (Schw.)] in grapevine.

FISHPOND SEDIMENT AS A FERTILIZER OR FEED SUPPLEMENT

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KEYWORDS
Fishpond sediment, utilization, fertilizer, fish feed

ABSTRACT

Fishpond sediment is rich in organic matter, nitrogen, phosphorus, macro and micronutrients, and therefore it can be used as a fertilizer for crop production and as a supplement in animal feed. Thermally treated sediment from three fishponds was used as a fertilizer in the production of peppers and as a supplement in fish feed. No significant difference was found in yield and quality between peppers fertilized with manure and those fertilized with thermally treated sediment. Furthermore, no significant differences were observed in the fish growth between fish fed with standard fodder mixture and those fed with fodder mixture with thermally treated sediment added.

INTRODUCTION

Global aquaculture fish production has been gradually increasing over the last 40 years. It has been estimated that its annual growth is on average 8.8% (Dròżdż et al., 2020). According to FAO (2014), aquaculture is one of the fastest growing industries, enabling the production of animal proteins worth 66.63 million tons per year. The production of freshwater aquaculture accounts for about 46 million tons/year, and marine about 2.7 million tons/year (FAO, 2016). It is estimated that in the European Union, aquaculture production in 2015 accounted for about 19.7% of total fish production or 1.6 million tons out of 106 million tons worldwide. It is considered that the largest producer of aquaculture fish is China with over 61 million tons or 58% of world production, followed by Indonesia with 15% of world production. The growth rate of aquaculture production is a result of the fish increased consumption due to the growth of the human population, enlarge urbanization and income.

Intensive fish farming and increased aquaculture production result with creation and accumulation of sediment in fishponds. Accumulation of sediment over time will result with a reduction in the depth of the fishponds, a reduction in their volume and limitation of the living space and movement of the fish. On the other hand, sediment accumulation means the accumulation of organic matter that can release toxic compounds such as hydrogen sulfide or nitrites. Also, the decomposition of organic matter by microorganisms can result with oxygen depletion and reduce its presence in the water, which negatively affects fish breeding, their well-being as well as yield and economic benefits (Muendo et al., 2014). Therefore, it is necessary to periodically clean the fishponds from the accumulated sediment. The treatment of the removed sediment is also the subject of a great deal of scientific research, because sediment contains unused organic matter and compounds such as methane (CH_4) or nitrous oxide (N_2O) that affect global warming (Ma et al., 2018). Fish pond sediments may contain undesirable substances such as heavy metals or pathogenic microorganisms, so its improper treatment and disposal can pose a danger to the environment and cause pollution of surface, groundwater and soil. However, fishpond sediments are also a rich source of nutrients (nitrogen, phosphorus, potassium) and can be used as fertilizers or as soil structure improvers (Rahman and Yakupitiyage, 2006). Due to its high content of organic compounds, it can also be used as a supplement to animal feed.

EXPERIMENTAL PART

Fishpond sediment as a fertilizer

The potential of fishpond sediment to be used as a fertilizer was observe during experimental analyses over pepper production. The sediment collected from the basins of three cold-water rainbow trout ponds in the Republic of Macedonia was first thermally treated at 100°C for 10 minutes and after that was used as fertilizer.

Due to the small quantity of sediment, mini-experiment over an area of 2 m^2 was made for pepper production. A pepper from the "Kurtovska kapija" variety was taken as a culture. Peppers fertilized with manure in the amount of 5 kg per 2 m^2 (control) and peppers fertilized with thermally treated sediment in the amount of 2.5 kg per 2 m^2 (treatment) were compared.

The results showed that in the production of peppers, the sediment as a fertilizer material showed somewhat lower results. On the plot in which manure was used as a fertilizer 12 kg of peppers were produced, while on the plot where sediment was used 10 kg of peppers were obtained. However, considering that the sediment was added in lower amount, it can be concluded that the sediment can yield very good results, and moreover, it is much cheaper than manure. On the other hand, with its extraction from pond wastewater, the environment (water, soil) from pollution is protected. Fishpond sediment beside as a fertilizer can be used to improve the characteristics of the soil (Rahman and Yakupitiyage, 2006). They proved that application of 30% of fishpond sediment improved the soil aggregate stability. The fishpond sediment can also be used in nurseries and green houses.

According to Boyd and Massaut (1999) fish pond sediments can accumulate different kind of risk substances such as fertilizers, heavy metals, oxidants, coagulants, pesticides, osmoregulators and probiotics. The substances with highest risk of contamination are heavy metals, algaecides, herbicides and insecticides. The authors emphasized that some of the microorganisms such as *Bacillus* sp., present in the sediment, can have a positive impact, because these bacteria can increase the decomposition of organic matter and can reduce the concentration of nitrogen. But care must be taken to avoid presence of pathogenic bacteria which can enter the fish ponds with low quality water or poorly treated waste water (Dròżdż et al., 2020). The risk in using fishpond sediment as a fertilizer also represents medicaments used for treating or supplementing the fish. Those are different kinds of antibiotics or therapeutics that can have negative effects on environment and living organisms or can have toxic effects on fish, consumers and aquatic environment especially if they are used in excessive quantities. It is considered that fishpond sediment composition can be treated more as a resource than as a waste.

When considering the sediment from fishponds as a fertilizer a care should be taken about the availability of the nutrient compounds. For example, phosphorus in fishpond sediments can be in different forms: water soluble, less soluble or insoluble form. Phosphorus can be adsorbed on the mud and can't be available. Potassium ions can be released in the pond water or part of the potassium could leach to dipper layers of the pond sediment, while the organic matter of the fishponds could improve soil physical and chemical condition, can improve soil texture by forming soil aggregations. Soil aeration could also be increased that helps soil to improve its infiltration. That is good for reduction of soil surface erosion and losses of its nutrients (Muendo et al., 2014).

Fishpond sediment in fish diet

In order to investigate the effect of including fishpond sediment in the fish diet, fish fed a standard fodder mixture from Macedonian origin (control) and fish fed a fodder mixture supplemented with

20% recycled fishpond sediment (treatment) were examined. 100 rainbow trout (*Oncorhynchus mykiss*) individuals with an initial weight of 120 g were tested.

The results showed that for the production of 1 kg of fish meat in the control treatment where fish fed with commercial feed, 2050 g of food were consumed, while in the treatment where the daily amount of food was combined with sediment in a quantity of 1650 g commercial feed + 400 g recycled sediment, 995 g of fish meat were produced. The difference was insignificant, but given the fact that the fish feed was reduced by 400 g, it can be concluded that in the production of fish meat there was a great saving in food without a significant decrease in the yield.

With this type of diet where thermally treated sediment was included, the production of fish meat becomes cheaper, since thermal processing of waste material has low energy consumption which is not higher than 2% of the price of fish food, which means that the production of fish meat is at least 16-18% cheaper.

Recycled fishpond sediment can be successfully used in agriculture in the production of peppers and in animal husbandry as a partial replacement of fish diet.

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ADSORPTION OF HEAVY METAL IONS FROM WATER WITH ENVIRONMENTALLY FRIENDLY SORBENT-BASED ON ELDER TREE CORE

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KEYWORDS

Heavy metals, water, adsorbent, elder tree core, optimization, *Sambucus nigra*

ABSTRACT

Pollution of water by heavy metals is one of the greatest global problems of mankind. Trends in sustainable production and green technologies lead to a reduction in pollution on the one hand, but the increase in living standards and population growth inevitably affect greater resource utilization. Thus, the higher goods production and the increase of the environmental pollution, amongst it water, is unavoidable. In this study, we investigated the possibility of using a new environmentally friendly adsorbent based on elder tree core, *Sambucus nigra* for the removal of heavy metal ions from water (Pb^{2+}, Cd^{2+}). The elder tree core *Sambucus nigra* elderberry tree has been modified by chemical oxidation of surface groups. The obtained adsorbent - (ChOxSN), was characterized and tested for the removal of Pb^{2+} and Cd^{2+} cations from water.

The results showed that the adsorption of Pb^{2+} and Cd^{2+} from water on the ChOxSN adsorbent followed the pseudo-second kinetic model and the Freundlich isothermal model. Thermodynamic parameters indicate the endothermic, feasible and spontaneous nature of the adsorption process.

INSTRUCTION

Due to the increased attention to pollution in the environment, including the presence of heavy metals in the water, discovering environmentally-friendly solutions gains great importance (Huang et al., 2014). Cellulose-based sorbents represent a promising option for reducing the presence of heavy metal ions in the water, primarily due to the abundance of feedstock and environmentally sustainable procedures for obtaining the sorbent material. Other properties of cellulose sorbents include renewability, biodegradability, strength and stiffness, easy modification, and biocompatibility; therefore, these sorbents show excellent extraction and enrichment performance for many analytes, and they offer multipurpose use potential for both organic and inorganic pollutants (Popović et al., 2020). Heavy metals, which can be seen as pollutants in the environment, are serious health and environmental problem because of their toxicity, non-biodegradability, and long half-life in the soil (Ram et al., 2000).

RESULTS AND DISCUSSION

The state of interactions/bonds on the adsorbate/adsorbent surface can be recorded by fitting experimental data with different adsorption isotherms. The results of modeling the adsorption of Pb^{2+} and Cd^{2+} ions on the tested adsorbents are given in figure 1.

The best fit of the Freundlich isotherm indicates that the mechanism of ion adsorption on the adsorbent can be described as heterogeneous adsorption, where the adsorbed ions/molecules have different enthalpies and activation energies of adsorption (Popović et al., 2020).

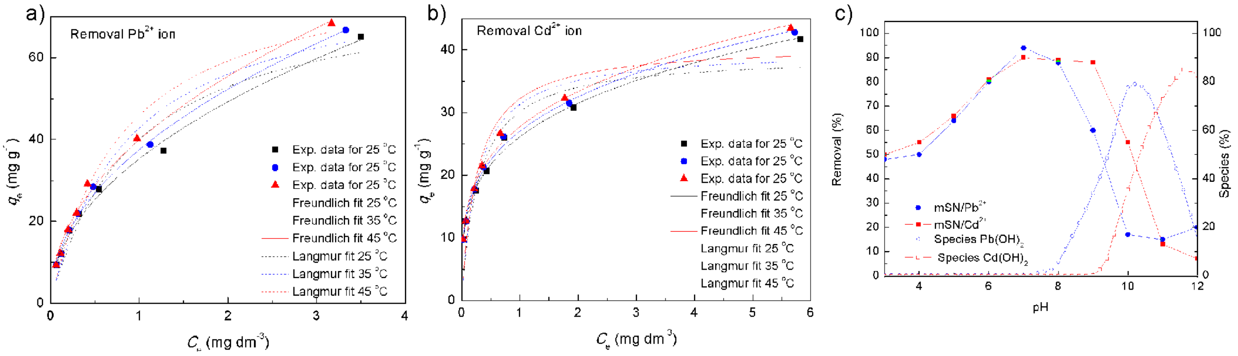

Figure 1. Presentation of the results of adsorption experiments with the best-fit isotherm models (solid line) for the removal of Pb^{2+} (a) and Cd^{2+} (b) ions and the display of the pH dependence of the adsorption of Pb^{2+} and Cd^{2+} ions on the adsorbent ChOxSN

The dependence of the adsorption capacity of ChOxSN on the experimental conditions is shown in Figure 2.

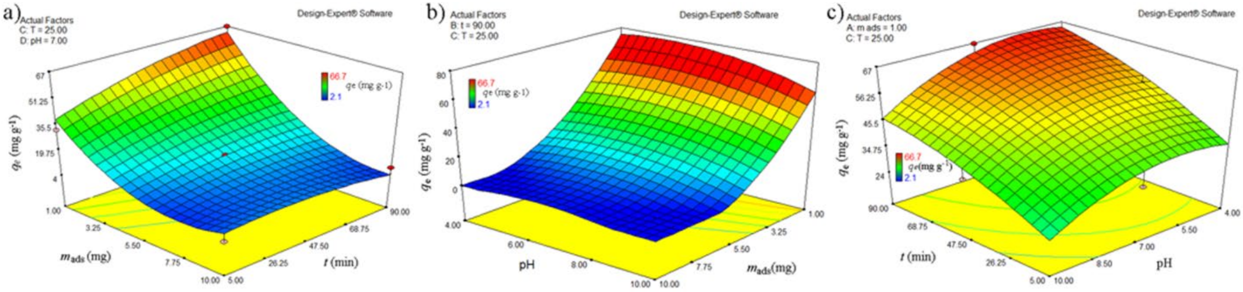

Figure 2. 3D plot of mutual dependence of the most influential variables of the adsorption process

CONCLUSION

In this work, a new adsorbent called ChOxSN was synthesized by chemical modification (oxidation) of the elder tree core. The obtained material was tested as an adsorbent for removing Pb^{2+} and Cd^{2+} from water and showed a satisfactory Langmuir adsorption capacity at 298 K of 76.012 and 43.321 mg g^{-1} respectively. The results showed that the adsorption of Pb^{2+} and Cd^{2+} from water on the ChOxSN adsorbent followed the pseudo-second kinetic model and the Freundlich isothermal model. Thermodynamic parameters indicate the endothermic, feasible and spontaneous nature of the adsorption process. The activation energy, free Gibbs energy and pH dependence indicate that the mechanism of sorbate binding to the adsorbent is simultaneously physisorption and chemisorption.

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MAPPING OF ANTHROPOGENIC CONTAMINATION OF SEDIMENTS OF DAM RESERVOIRS IN THE VÁH RIVER BASIN

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KEYWORDS
Contamination, sediments, reservoirs, the Váh River, drill core

ABSTRACT

Filling of dam reservoirs with sediment represents an important environmental and economic problem due to the financial costs associated with sediment extraction and the risk of anthropogenic sediment contamination. Due to the frequency of dam reservoirs, the Váh River offers an excellent opportunity to study the effects of dams on the transport, accumulation, architecture and composition of sediments. The paper presents the procedure of removing drilling cores from the dam reservoirs Hričov, Žilina and Nosice. Samples were taken using a floating drilling platform of our own design, which allows the collection of an intact sediment profile from the required depth according to the thickness of the sediment. Sampling in this way allows us to map the extent of contamination of the dam sediments from drilling cores taken directly from the bottom of water reservoirs and their quantitative and qualitative determination and evaluation using geological and geochemical methods without the need to drain the water reservoir, which eliminates degradation of complete sediment record when discharging reservoirs, when the sediment is often eroded by water running down its surface.

Figure 1. Floating drilling platform and taking the drill core from the bottom of the dam

As the longest river in Slovakia, the Váh River has 22 dams built on its 406 km course (on average one dam per 18.5 km). Within Slovakia, this is also an area with a higher concentration of industry. Due to the frequency of dam reservoirs and the very diverse geology, the Váh River offers an excellent opportunity to study the effects of damming on the transport, accumulation, architecture, composition and degree of sediment contamination.

Due to its vastness, the area of interest shows great dynamics of changes in the geological subsoil, basically it can be said that the geological structure of the subsoil changes every few kilometers. Despite this variability, the upper layer is eroded the most, so the washout material consists mainly of Quaternary sediments and recent soils, or anthropogenic deposits. The above applies in general with the exception of flood events and direct erosion of the exposed rock surface.

A floating drilling platform of our own construction (Figure 1) enables direct sampling of drill cores from the bottom of the reservoir to a water column depth of up to 50 m. The sampler (Uwitec, Austria) is suspended on a steel cable and works on the principle of gravity (core compaction does not occur). The cores were collected in plastic tubes and then kept in a cooling box until further processing (sectioning, drying, analysis...).

Field work was carried out at the Hričov, Žilina and Nosice dams. The aim was to collect sediments from different parts of the reservoir with the intention of obtaining a spatial idea of the distribution of sediments.

Drill cores were taken from the sediments directly from the bottom of individual dams using a floating drilling platform (Figure 1). Selected analytical, geological and chemical methods for the analysis of qualitative and quantitative parameters can be performed on the sediment samples taken in this way (Figure 2). The samples were measured for spectral reflectance (colorimetry), magnetic susceptibility, sediment dating using the event stratigraphy method by measuring ^{137}Cs content, particle size analysis, X-ray fluorescence analysis (XRF) and total organic carbon (TOC).

Figure 2. Photo documentation of the drill core from the Hričov dam with a visible change in the granular fraction of sedimentation

Sediment sampling using a floating drilling platform allows mapping the extent of contamination of dam sediments from drill cores taken directly from the bottom of water reservoirs and their quantitative and qualitative determination and evaluation using geological and geochemical methods without the need to drain the water reservoir, which eliminates the impairment of the complete sedimentary record during discharge, when sediment is often eroded by water flowing over its surface. It is thus possible to obtain samples from basically any place in the reservoir, regardless of the depth or access from the shore. However, the presence of a sufficient layer of fine-grained sediment is a must, as the sampling device is not able to take samples in sediments with a coarser grain fraction than sand (even this causes problems during sampling).

HISTORY OF ANTROPOGENIC SEDIMENT CONTAMINATION IN INDUSTRIALIZED RIVER SYSTEMS (GRANT PROJECT: DSGS-2021)

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KEYWORDS
Contamination, fluvial sediments, stratigraphic analysis, caesium dating

ABSTRACT

River systems are important pathways for transport, deposition and reworking of sediment in populated areas. River sediments are carriers of toxic elements (Cu, Zn, Pb, Hg, Cd, etc.), radioactive isotopes and organic compounds from agriculture, industry, municipal waste and transportation. Sediments of river channels, floodplains, abandoned meanders and dam reservoirs therefore act as sinks for anthropogenic contamination, which can be mobilized during floods, dam removals, and other interventions in water courses, and pose serious environmental hazards in the future. Despite the present-day efforts to reduce anthropogenic contamination from primary sources, the risk from old ecological burdens from the 18th to the 20th century persists. These sites were assessed and selected in the Odra and Bečva river basins, as it is an area with historical and current industrial activity, and the river basin also provides an opportunity to collect and analyse these sediments due to the presence of dead branches and abandoned meanders.

A slotted drill bit from the company Eijkelkamp (drill bit width: 4.0 cm; drill bit length: 1.0 m) was used to collect drill cores (**Fig. 1**) – old no longer existing historical ponds and lakes, oxbow lakes, active river channels and floodplain sediments. All the collected drill cores were photographed in the field, lithologically described and divided into plastic bags at an interval of 2,0 cm. The samples were subsequently dried in the laboratory.

Figure 1. Taking a sediment sample using a hand sampler

The dried samples were measured for the mass activity of the radioisotope ^{137}Cs, which serves for dating purposes – **event stratigraphy**, was measured in the individual samples. This measurement was provided by a GS-320 Shielded laboratory gamma spectrometer for laboratory measurement of gamma radiation spectra (mass activity, concentration of K, eU, eTh and mass activity of ^{137}Cs) with a 3x3" NaI(Tl) scintillation detector (manufactured by Exploranium Inc., Canada) with service PC and software.

The aim of measuring the mass activity of ^{137}CS is to determine the sediment deposition rate based on the Chernobyl accident in 1986, which released radioactive ^{137}CS into the atmosphere. This ^{137}CS was previously not commonly found in nature (a very small concentration was released into the atmosphere from nuclear bomb explosions during testing before the Chernobyl accident).

Based on the knowledge that the largest part of ^{137}Cs entered the atmosphere in our geographical area in 1986, the rate of sedimentation of individual profiles can be calculated – **event stratigraphy**.

The core OLD1 was taken near the village of Oldřichov by the river Bečva. This is an old meander that separated from the Bečva river around the 1950s. This old meander is located in an agricultural landscape between fields. Based on the data in the graph (**Fig. 2**), it can be seen that the largest concentrations of ^{137}Cs are at a depth of 72-74 cm (**Event 1**) and at a depth of 18-22 cm (**Event 2**) below the surface.

These concentrations can be interpreted so that, in the case of Event 1, it could be a primary fallout from the atmosphere (flush from the surroundings into the small sedimentary basin at the time of the Chernobyl accident), between Event 1 and Event 2 it is a relatively stable and uniform supply of ^{137}Cs concentration. Event 2 can have several explanations - for example, it could have been heavy rainfall over a short period of time, which brought a large amount of sediment into the sedimentary space in a short time.

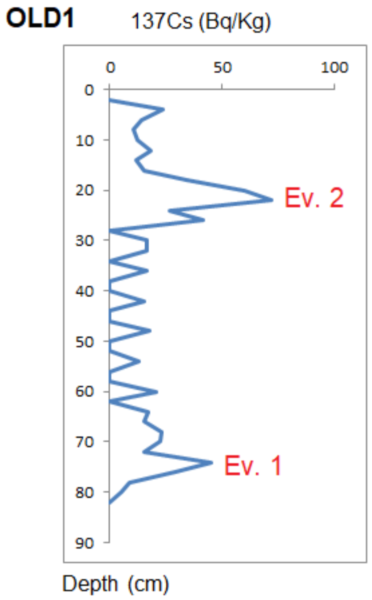

Figure 2. Cesium mass activity plot for core OLD1

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SULFIDATED ZERO-VALENT IRON NANOPARTICLES: PROPERTIES, REACTIVITY AND MIGRATION

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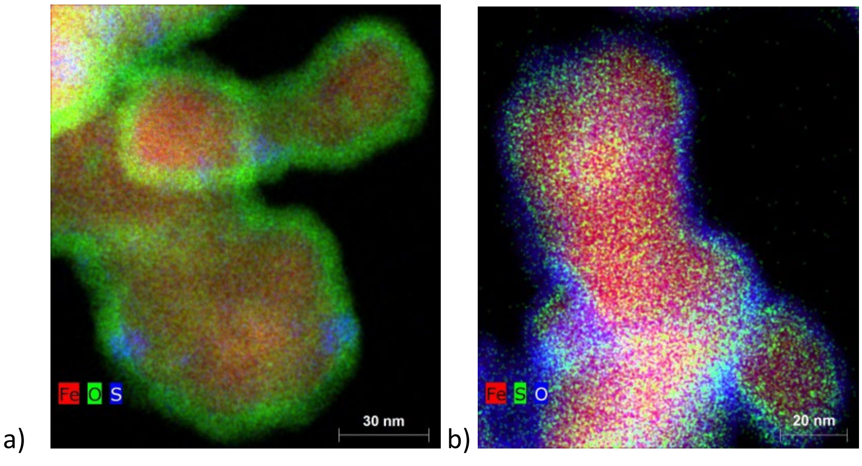
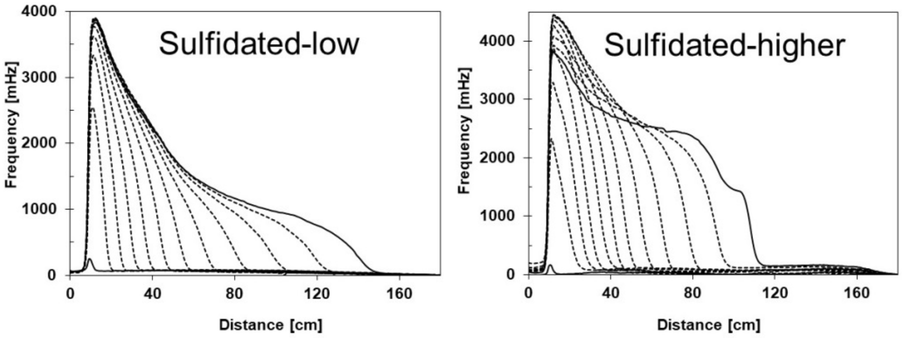
KEYWORDS
Zerovalent iron nanoparticles (nZVI), sulfidation, migration, reactivity, remediation

SULFIDATION AS A PART OF SURFACE MODIFICATION OF NZVI

To extend the application potential of the nanomaterials for remediation, it is necessary to increase their current offer with a variety of improved materials. We highlight a novel approach to the aqueous sulfidation of commercially available nano zerovalent Fe particles (nZVI) (**Figure 1a,b**). Sulfidated nZVI particles (S-nZVI) have a core-shell structure containing a metallic iron core and a poorly crystalline or amorphous sulfide shell around it. The thickness of the shell can be modified using different concentrations of sulfide during synthesis [1, 2]. Sulfidated core-shell structured nZVI has been recently tested for their migration properties and efficient removal of inorganic and organic contaminants from contaminated waters including chlorinated compounds (such as trichloroethylene – TCE) [1] or hexavalent chromium [2]. The impact of the dominant surface characteristics on the mobility of nZVI was studied in the model environment while simulating the real remediation conditions. A migration monitoring device (vertical geometry, length 2m, i.d. 20 mm) based on the ferromagnetic susceptibility measurement was developed for the direct non-destructive quantification of solid nZVI in porous media. Sulfidation of nZVI was confirmed as a process which is increasing the mobility of Fe nanoparticles depending on the surface layer thickness (**Figure 1c**). Enhancement of the reactivity of nZVI particles can be achieved by creating a uniform sulfide shell on nZVI particles. Modifying nZVI using the FeS shell is slowing down the reaction of nZVI with water and thus provides more electrons to the reaction with the contaminant. Such a surface modification of nZVI would bring a promising remedial agent allowing a wider application in the actual market.



a) b)



c.)

Figure 1. HR-TEM image of sulfidated nZVI: a) sulfidated pyrophoric nZVI, b) sulfidated nZVI with oxide shell, c) migration of S-nZVI with different surface layer thickness.

TCE REMOVAL USING S-nZVI

In general. the growth of the sulfide shell on nZVI increases the reactivity and mobility, and also significantly increases their selectivity during the process of pollutant removal in a contaminated environment. The reactivity during contaminant removal is demonstrated via the dechlorination ability of sulfidated nZVI. Sulfidated nZVI can effectively increase trichloroethylene removal up to 14 times compared with nZVI without modification (Figure 2). The degradation products observed were only fully dechlorinated compounds. Different thicknesses of the sulfide shell have an impact on the TCE removal rate. The optimal thickness of the shell is approximately 7.3 nm [1].

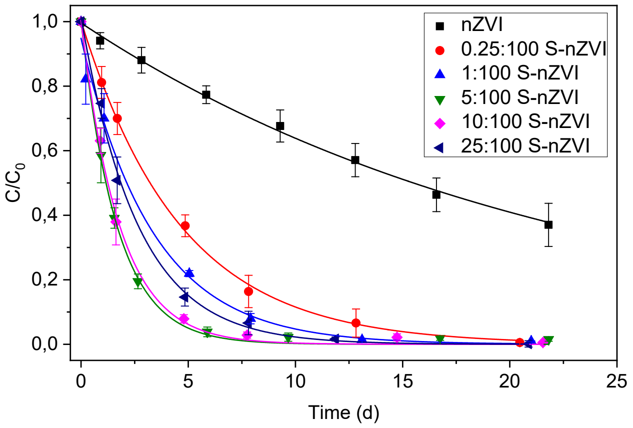


Figure 2. TCE removal using different sulfidated nZVI compared with pyrophoric nZVI in time.

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IMPORTANCE OF REGIONAL BASELINE LEVELS IN DERIVED THRESHOLD VALUES: AN EXAMPLE WITH DEEP MARINE SEDIMENTS

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KEYWORDS

Heavy metals, Baseline levels, Threshold levels, Statististics, Pristine sediments

ABSTRACT

International institutions have defined background or baseline levels to assess heavy metal concentrations on environmental compartments in order to use these calculated values as a reference for pollution control. This criterion for different environmental compartments, like marine sediments, is applied to evaluate the potential risk of pollutants in ecosystems. However, those values were established using samples collected in large areas which present specific geochemical conditions. Then there may be a lack of accuracy in the results when using these parameters in other local areas with its own peculiarities. In this context, this research used 15 sediment cores that were collected along the 400 km Asturian coastline, which is an area with representative lithological conditions for the Bay of Biscay, to determine more precise baseline levels for this area respect general levels. An evaluation of statistical and empirical methods was done to determine which method delivers the best results. Statistical methods such as mean±2SD and median±2* Median Absolut Deviation (MAD) are strongly influenced by outliers and data distributions which make these approaches less robust. Graphic techniques such as Cumulative Distribution Function (CDF) avoid the problems that asymmetrical data distributions may cause but introduce a certain level of subjectivity in the results due to the baseline values obtained depending on the researcher's experience. Finally, the Probability Curve (CP) method solves issues which may occur when using other techniques and allows one to establish baseline levels based on different percentiles. Regarding the features of the data analysed in this study, the baselines obtained via the CP method with the 95th percentile appear to be the most accurate for the study area. A wide variation has been found between the new baseline values and other international reference levels. Disparity between those levels and the baselines obtained in this study can be generated by samples, granulometric and geological factors. The notable increase is remarkable for Hg baseline values with respect to European OSPAR Background Concentration values (BCs) (0.05 μg g−1 and 0.6 μg g−1 respectively) and the huge different with National levels and new threshold levels emphasised the relevance of defining specific baselines and threshold levels based on quality samples, as the ones obtained in this study, not only allow to obtain more precise criteria for environmental studies, but also to propose new threshold levels for the protection of environmental ecosystems.

INTRODUCTION

Asturias is a region located in the north of Spain (southwest Europe) which is bordered to the north by the Cantabrian Sea, which defines the transition between the Atlantic Ocean and the Bay of Biscay. Regarding the geology, Asturias is composed of two main sets of bedrocks which are differentiated by an unconformity. The first main group crops out on the western zone which is characterised by sandstone, lutite and slate which are usually found in the orogen hinterlands, also this set of rocks crops out on the eastern part showing carbonate and siliciclastic lithologies. The second set of bedrocks is located in the central part of Asturias and is composed of a mix between limestone, sandstone, quartzite and lutite. This first set, which corresponds to the West-Asturian Leonese Zone (ZAOL) and the Cantabrian Zone (ZC), is composed of rocks from the Precambrian to Carboniferous geological periods, while the second main group of rocks were formed by Permian, Mesozoic and Tertiary materials. The geological materials previously described are also presented along the whole Cantabrian coast and as a result, Asturias may be a good representation of the geology settled on the coast of northern Spain.

In this context, this research attempts to determine baseline levels which could be used as preindustrial levels for environmental management for goberments or other organisms. These values were determined by means of of suitable samples and statistical approaches and compared with the legal background values with the aim of determining which is more appropriate for assessing criteria of sediments from Cantabrian coast. Additionally, this study is an attempt to adapt the threshold levels established, taking into account the particular geological conditions of the area which would allow for the development of better environmental assessments.

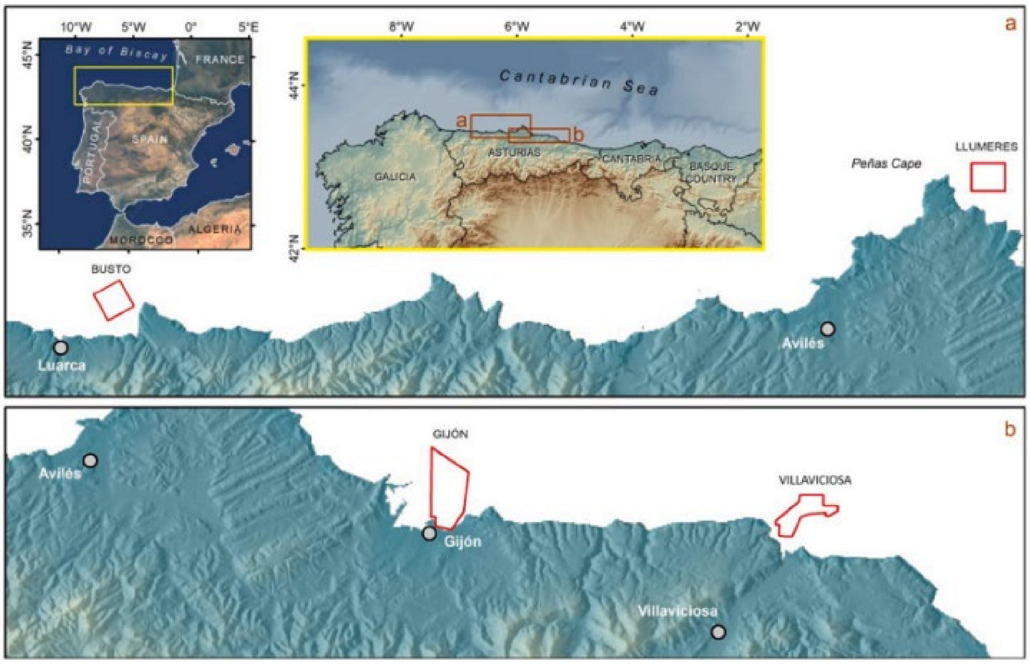

Figure 1. Study area and location of four sampling sites (total 16 vibrocore)

RESULTS AND DISCUSSION

The statistical summary of the metal (oid)s registered and analysed from the 16 cores is shown in Table 1 and the summary of the calculated baselines by different methods on 156 samples in the Table 2. Values reported for mean±2SD and median±2*Median Absolut deviation (MAD) correspond with the upper limit values of each metal (oid) ranges calculated using these methodologies. In this case, mean and standard deviation values are seriously affected by extremely high or extremely low values, and that is why this method is not accurate enough to determine a suitable geochemical baseline. With the aim of improving the mean±2SD method, some authors have recommended using the median and the median absolute deviation (MAD) rather than the standard deviation. However, the extreme values removed with both methods may be unrealistic if the dataset does not follow a symmetrical distribution. To solve this fact, Cumulative Distribution Function (CDF) method is a graphic technique which allows for the visualization of each single data value. Although this technique is quite robust, the task of deciding where is the inflection point in the curve, which correspond with the baseline level, corresponds to the investigator and depends on their own experience, that is why CDF entails a degree of subjectivity. Another way to represent CDF is to plot the Probability Curve (CP); some studies have suggested this method to establish the baseline values in 90th, 95th or 98th percentiles which may avoid the disadvantage of subjectivity. Table 3 shows the 90th, 95th and 98th percentiles for the metal (oid)s in this investigation. Selecting the 90th percentile could be interesting from an environmental point of view. However, this percentile could be a disadvantage since a considerable number of sites could exceed the 90th percentile values. Although the 98th percentile could reduce the number of sites which surpass the baseline level, it may also present disadvantages for environmental assessments as some samples may present a certain degree of contamination and, at the same time, they may be below that baseline. Thus, the 95th percentile appears to deliver the best results to establish the baseline values. Moreover, this percentile is not as conservative as the 90th percentile, nor does it define the too high baseline levels as the 98th percentile may do.

Table 1. Descriptive statistics of the element concentrations detected in the samples.

μg g^{-1}	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Mean	10.48	0.06	9.78	4.15	0.13	7.80	6.32	20.91
Median	10.50	0.05	6.00	2.85	0.06	5.80	5.30	17.75
Max	22.45	0.28	90.00	52.75	1.22	56.00	21.55	146.50
Min	2.18	0.01	2.00	1.25	0.01	0.60	1.80	4.00
SD	2.80	0.04	12.82	4.96	0.19	8.05	3.98	17.52

Table 2. Baselines of metal (oid)s obtained using several statistical methods.

μg g^{-1}	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Mean+2SD	16.1	0.15	34.6	11.1	0.65	36.6	17.6	65
Median+2MAD	12.8	0.1	15	6.4	0.28	25	16	49
CDF	14.9	0.1	21	6.5	0.27	15	12	38
CP (90th)	13.15	0.1	16.2	7.9	0.37	14.5	11.7	35
CP (95th)	14.7	0.12	39	11	0.6	26	14	47
CP (98th)	17.5	0.19	62	13	0.82	37	16	78

With the Baseline levels determined in this study, the geoaccumulation index (Igeo) was used with the aim of defining new Hg threshold levels for sediments due to this element presented baseline values greater than those recommended by the goverments. Indicators 1, 2 and 4 were selected to calculate new threshold levels in this study as they represent low, moderate and heavy contamination, respectively. Comparing Table 3 values one can observe that levels based on specific baselines are significantly higher than Spanish levels, as a result, environmental studies realised with spanish levels in this area should be adjusted to these background or baseline levels. It is therefore recommended to use threshold levels created by particular baselines with the aim of developing more accurate environmental studies.

Table 3. Hg Spanish levels and Hg threshold levels which this study proposed for coastal sediments

	No polluted	Moderate polluted	Highly polluted
Spanish levels	0.35	0.71	2.84
Present study	1.2	2.4	9.6

CONCLUSIONS

Comparisons developed with different statistical and empirical methods for obtaining baseline levels from the samples has proved that the Probability Curve (CP) method is the most robust. Regarding the CP method, baselines defined by their 95th percentile deliver the most accurate values for our cores, since these coincide perfectly with the breaks on the CP line. Baseline levels defined using this method surpasing the OSPAR reference value for Hg, which showed values twelve times higher than the Europena level due to the natural anomalies. The new baseline values defined in this study have caught the attention of the Spanish environmental agencies and are currently recalculating the threshold levels for this area due to this highlight the relevance of defining specific baselines and threshold levels for specific areas according to their particular geological characteristics.

PLANTS AND MACROMYCETES FROM AREAS AFFECTED BY ORE MINING – BIOCONCENTRATION FACTORS

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KEYWORDS
potentially toxic elements, ore mines, bioconcentration

ABSTRACT

Species of macrofungi were collected from extremely polluted sampling spots in the vicinity of abandoned ore mines in Slovakia. Concentrations of potentially toxic elements in plants and fungi were determined by ICP-MS and in soils and sediments by both ICP-MS and ICP-ES. Of the edible species the highest values of arsenic and cadmium were recorded in *Agaricus arvensis*, lead in *Imleria badia* and representatives of the genera *Boletus, Leccinum* and *Suillus* accumulated high levels of mercury. *Suillus* species also accumulated high levels of antimony and chromium. Bioconcentration factors were calculated for selected species and antimony, cadmium, and mercury were accumulated by most of the sampled species. Based on the results of our study, we can assume that the species *Cardamine amara* belongs to accumulators of potentially toxic elements.

INTRODUCTION

Substantial ore deposits and smaller occurrences are located in various zones of the Western Carpathians of Slovakia. Open adits outflows, weathering of dumps and non-isolated tailing impoundments cause many problems such as water, soil and stream sediments contamination. Bioaccumulation as such is defined as the process of sequential storage of a chemical in the cells of a living organism over a period of time. This type of absorption may occur because the product is absorbed faster than it can be used or because it cannot be metabolised. For any reason, if the accumulated product is harmful, it can become a problem for human health and the environment [1]. The aim of our study was to determine the bioconcentration factor of selected potentially toxic elements (PTE) in fungi and plants collected from the model area affected by ore mining.

RESULTS

In 2018-2022 basidiomycetes and plants were collected in 7 sampling areas. Accumulation of potentially toxic elements has been evaluated in basidiomycetes and plants growing in high polluted areas at the surroundings of abandoned ore mines in Slovakia. In selected samples of macromycetes, plants and corresponding soils contents of As, Sb, Cd, Cr, Hg, Cu, Zn, Na, P, Ni, Ag and Fe were measured, bioconcentration factors were calculated and health risk of consumption edible species estimated. The national, EU, or WHO limits (LV) for arsenic, cadmium, lead, and mercury in food have been exceeded in some of the edible fungal species. Detected values of chromium and antimony were relatively high compared to published data, too, though there were no limit values set. Of the edible macromycetes species the highest values of arsenic were recorded in *Lactarius deterrimus*, cadmium and antimony in *Suillus grevillei*, lead in *Leccinum piceinum*, mercury and chromium in *Marasmius oreades*. Antimony was accumulated by *Suillus* spp., cadmium was accumulated by all species except genera of the edible mushrooms *Leccinum*, *Lactarius*, and *Gomphidius*, and most of the species accumulated mercury except for *Gomphidius, Imleria* and *Lactarius,* copper was accumulated by *Boletus edulis* and *Cantharellus cibarius* and high content of manganese was recorded in *Gomphidius glutinosus.* All other elements were excluded by fungi.

Manganese values were increased in all plant species. Excess manganese in plant tissues can alter various processes, such as enzyme activity, absorption, translocation, and utilization of other mineral elements (Ca, Mg, Fe, and P), causing oxidative stress. The phytotoxicity of manganese, as well as the tolerance to an excess of this metal, is highly dependent on plant species and cultivars or genotypes within the species. We recorded the highest bioconcentration factor in iron, specifically in the species *Oxalis acetosella*. Iron and its oxidation states, especially Fe^{2+} and Fe^{3+}, participate in various soil reactions, significantly affecting the physical and chemical properties of the soil and thus the solubility and acceptability of nutrients by plants. The importance of iron for plants stems from its role in the formation of chlorophyll and in its participation in many enzymatic reactions. Its deficiency damages the mechanism of chlorophyll formation, and therefore on young leaves it manifests itself in chloritic spots between the veins of the leaves – chlorosis.

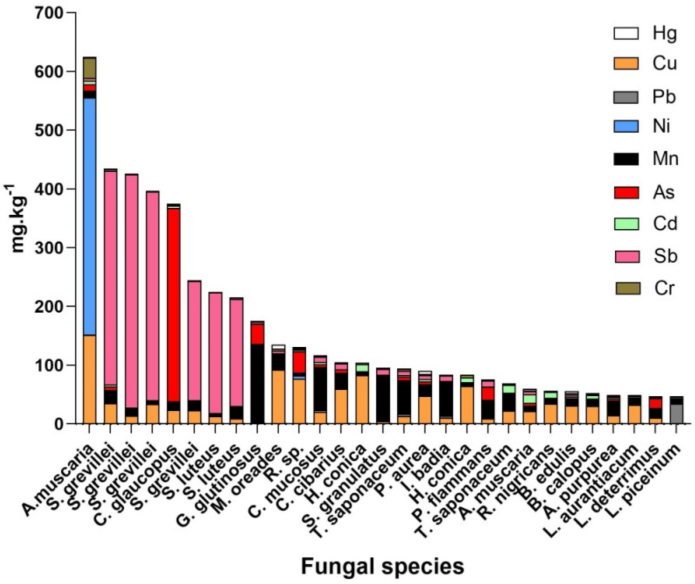

Figure 1. Contents of potentially toxic elements in basidiomycetes.

CONCLUSION

We do not recommend the consumption of edible mushrooms or the collection of medicinal herbs from the studied areas, as they may pose a risk of intoxication of the organism. These results can be the basis for further studies and the possibility of phytoremediation.

ACKNOWLEDGEMENTS

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NIKM – DISTRIBUTION OF THE CONTAMINATED SITES ON THE TERRITORY OF THE CZECH REPUBLIC

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SUMMARY

The National Inventory of Contaminated Sites (NIKM 2 project) was completed in December 2021. We present the output regarding the distribution of inventoried, contaminated and potentially contaminated sites (CSs) in 205 administrative districts - *Municipalities with Extended Powers* ("small districts"). The filled database of the Contaminated Sites Registration System (SEKM) [1] serves as the main source for the so-called *Planning Analytical Materials*, i.e., for spatial planning at the level of Municipalities with Extended Powers. Until now, incomplete documents on CSs were used. After the completion of the inventory, the updates of the territorial analytical documents in this matter can be based on relevant data.

KEYWORDS

Contaminated sites, inventory, methodology, registration of contaminated sites, Planning Analytical Materials, town and country planning

PROJECT RESULTS

On the territory of the Czech Republic, a total of 30,020 locations or indications were examined from two basic sources - from SEKM and from the use of remote sensing methods, of which 8643 sites were evaluated as CSs. The remaining 21,377 locations or clues were excluded. 1491 newly evaluated locations were registered from other sources. As of 31 December 2021, a total of 10,134 CSs (assessed locations) were registered in SEKM. These sites have a processed record in the SEKM database, at least in a so-called summary form, including the evaluated priority of further work progress. The result of the NIKM is a complete SEKM database (10,134 records as of 31/12/2021) and an evaluation of the inventory in the form of 14 reports on the inventory in individual regions [2] and the Report on the whole country’s territory [3]. Details on the localization of CSs according to priority categories are shown in 14 posters at www.cenia.cz [4].

Distribution of CSs in "small districts" and localization of CSs according to priority categories

For individual "small districts" in the regions, we present in the poster a graphic output capturing the density of CSs (expressed as number/100 km^2 - see Figure 1) and localization of CSs of all three priority categories evaluated according to the Methodological Instruction of the MoE No. 1/2021 [5]. Each assessed location is clearly categorized according to what further action is required depending on its presumed or verified contamination and the consequences or possible consequences of this contamination for human health and the environment. Three basic categories of locations are distinguished - contaminated (A), potentially contaminated (P) and/or non-contaminated (N) locations. Each of these three basic categories is broken down into even more detail. Category A sites are those where contamination represents an existing and confirmed problem. For sites P, contamination means a potential problem, there is not enough information for definitive conclusions. The actual severity of contamination must be verified by survey and/or risk analysis for this category. Locations of category N do not require any intervention.

Among the main benefits of the inventory is also a contribution to better spatial planning. SEKM data is used by the MoE as a basis for the so-called phenomenon 64, which is a requirement arising from the Building Act [6]. Compared to the generalized situation in regions and districts, the evaluation of individual "small districts" gives a more accurate idea of the territorial distribution of CSs, which is linked to the socio-economic and physical-geographical characteristics of the territory.

The requirements for spatial planning are regulated by the Building Act [6] and subsequent Decree [7]. The decree specifies in more detail the requirements of such documentation, incl. the list of 119 phenomena in the territorial analysis documents. For us, the most significant phenomenon is No. 64 - "old burden of territory and contaminated areas" and its use in spatial planning documentation "small districts". By law, the provider of data on phenomenon 64 is the Ministry of the Environment. The basis for fulfilling this duty are data on old ecological burdens now collected in the updated SEKM database. The New Building Act, coming into law on July 1st, 2023 [8] will not change the duties and the approach related to the spatial planning documentation of the current Building Act [6].

Territorial planning documentation should also deal with the recognition and solution of environmental and sustainability problems on the relevant territory. It consists of a valid spatial plan and various spatial planning documents, such as Planning Analytical Materials of municipalities and Municipalities with Extended Powers. "Small districts" are obliged to update Planning Analytical Materials every 4 years. Their fifth full update of the municipalities' Planning Analytical Materials was due by the end of 2020. According to the Building Act, these documents should be publicly available in the municipality's website with extended scope.

Update status of Planning Analytical Materials in Municipalities with Extended Powers

Among regions, the percentage of updates varies between 13.3% (Plzeňský Region) and 80% (Pardubický Region). As of August 2022, 116 updated materials were reported for the entire Czech Republic, i.e., 56.6% of all "small districts" – see table 1. For the entire territory of the Czech Republic a special portal in the field of town and country planning [9] can be used. It contains links to all web sites of 205 "small districts".

Table 1. Overview of updates of Planning Analytical Materials from Municipalities with Extended Powers by regions with the share of updated materials

13 regions and the Capital City of Prague			
Name of the region	Number of Municipalities with Extended Powers	5. update of the Planning Analytical Materials	% of updated materials
Prague	1	0	0,0
Středočeský	26	18	69,2
Jihočeský	17	11	64,7
Plzeňský	15	2	13,3
Karlovarský	7	5	71,4
Ústecký	16	11	68,8
Liberecký	10	6	60,0
Královéhradecký	15	9	60,0
Pardubický	15	12	80,0
Vysočina	15	8	53,3
Jihomoravský	21	11	52,4
Olomoucký	13	7	53,8
Zlínský	13	6	46,2
Moravskoslezský	22	10	45,5
Czech Republic	205 + 1	116	56,6

CONCLUSIONS

(1) The national inventory of CSs (the NIKM 2 project) was completed in December 2021.

(2) The completed database SEKM serves also as the main source for the so-called *Planning Analytical Materials*, to be used for their updating every 4 years.

(3) The last update due by the end of 2020 was not completed. Only 57% from 205 “small districts” have published them by the end of August 2022.
(4) The updates of the *Planning Analytical Materials* can now be based on the complete relevant data of NIKM / SEKM.

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QUICK TEST FOR CASCADING USAGE OF *MISCANTHUSXGIGANTEUS* BIOMASS CULTIVATED IN THE POST-MINING AND POST-MILITARY SOILS

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KEYWORDS
Miscanthusxgiganteus processing, value chain, contaminated sites, biochar, bioproducts

INTRODUCTION

The cultivation of *Miscanthusxgiganteus*, a C4 perennial non-food crop, in the post-mining and post-military soils permits to improve the soil health, to reduce emission of greenhouse gases, and to produce sufficient amount of biomass [1,2]. When *Mxg* is growing multiyear at such sites, the contaminants are mainly accumulated in the rhizomes thus the above ground biomass which has little or no contamination can be processed to fibrous and insulation materials, and packing paper. Subsequently, biochar can be obtained from *Mxg* residues and returned back to the agricultural process as a soil amendment for cultivation of the different crops, including Miscanthus.

In order to successfully process *Mxg* biomass to bioproducts and better understand the interconnection within the *Mxg* value chain (Figure 1) the Quick Test was created. It provides information about a general documentation of the full processes involved and points necessary analyses regarding the materials.

Figure 1 shows a general overview of the individual steps of *Mxg* utilization and the specific material cycle when using Miscanthus biomass produced at the marginal and slightly contaminated soils.

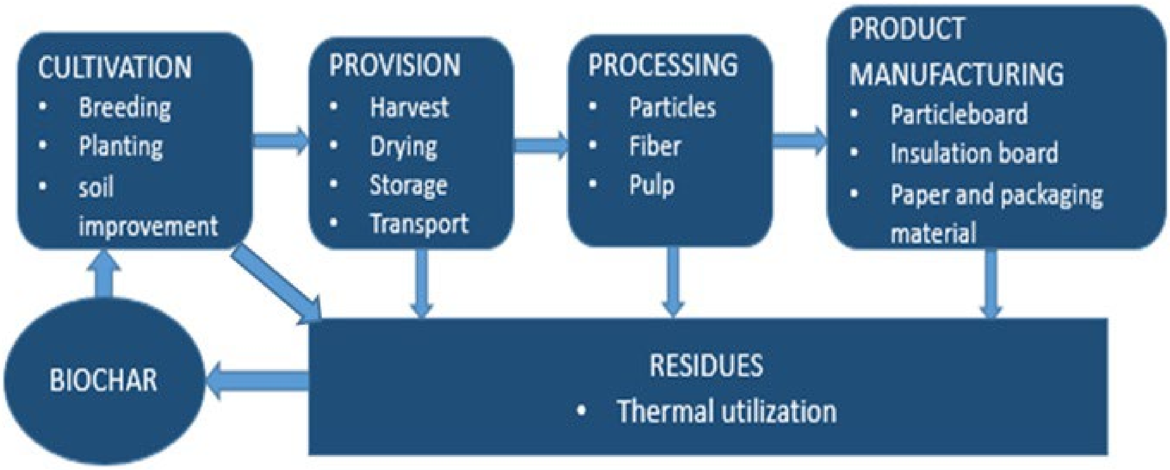

Figure 1. Miscanthus utilization from marginal and contaminated soils

THE QUICK TEST

The Quick Test highlights the different requests and processes for the successful conversion of the *Mxg* biomass to bioproducts. The cultivation of *Mxg* at the marginal and slightly contaminated soils involves complex knowledge about the plant in relation with the given local conditions. Soil has to be enriched with nutrients to support phytoremediation and to additionally increase the plant productivity. Harvest is recommended between February and March ("brown" harvest) due to the low moisture content (< 20 %) of *Mxg* which decreases biological activity during storage. After harvest, typical dryers for agricultural goods can be used for drying *Mxg* biomass. To transport the biomass, open trailers over short distances is recommended, whilst at high speeds (> 50 km/h), transport trailers must be tarpaulin-covered in order to avoid losses. The high lignin (approx. 12-13%) and cellulose content of *Mxg* is an important precondition for the conversion of plant's biomass to bioproducts. Particleboards from *Mxg* show the requested qualities when produced by the hot pressing and steam processes. Paper production is essentially a two-stage process in which the fibrous raw material is first converted into pulp and thereafter the pulp is processed into paper. Pulp can be produced by mechanical or thermochemical processes or their combination. The chemo-thermal mechanical pulping (CTMP) process is suitable for conversion of *Mxg* biomass itself or in combination with wood.

The residues accumulated during the cultivation of *Mxg* as well as during further processing of the biomass to fibers or particleboards can be converted to biochar using pyrolysis with a temperature of 600°C for 1-2hours [3]. The conversion of the *Mxg* residues into biochar offers an option for utilization within the value chain as a soil amendment to support phytoremediation and to increase the plant productivity [4].

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ADSORPTION OF FULVIC ACIDS AND THEIR COMPEXES WITH TRACE ELEMENTS BY CLAY MINERALS

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KEYWORDS
Classification, contaminant, contaminated sites, groundwater, environmental impact assessment, priority, risk, surface water

ABSTRACT

Clay minerals and humic substances are one of the most important components controlling the accumulation, mobility and bioavailability of nutrients and pollutants in soils (Perelomov et al., 2019, Perelomov et al., 2021). The composition and properties of these components and their interactions with each other affect the formation of the soil structure, the adsorption and transfer of nutrients and pollutants, and the development of erosion processes. The interaction of clay minerals with humic substances is a complex process that depends on the properties of the mineral and organic matter, as well as the soil and ecological conditions in which their interaction takes place. This paper presents the results the adsorption of peat's fulvic acids (FA) on two clay minerals (kaolinite and bentonite) in the presence of increasing concentrations of heavy metal cations (Pb or Zn) investigated by measurement of the optical density changes in the of equilibrium solutions.

Adsorption of fulvic acids on bentonite and kaolinite

A binding of FA-metal compounds by clay minerals is a complex phenomenon due to the chemical heterogeneity of FA, different properties of metal ions and the variability of environmental conditions. The results of studying the adsorption processes of fulvic acids on clay minerals, studied by the measurement of optical density changes, allow us to draw the following conclusions: The adsorption of peat`s FA on the surface of bentonite (Fig. 1a) at the studied concentrations proceeds according to the polymolecular mechanism and has a stepwise character. The isotherm can be classified as L3 type according to Giles. The stepwise adsorption can be explained by the formation of new sorption sites upon modification of the bentonite surface by FA and an increase in the interlayer space due to the partial intercalation of organic molecules. The adsorption of FA by kaolinite (Fig. 1b) can be described by the mechanism of monomolecular adsorption and is the L2 isotherm in accordance with Giles.

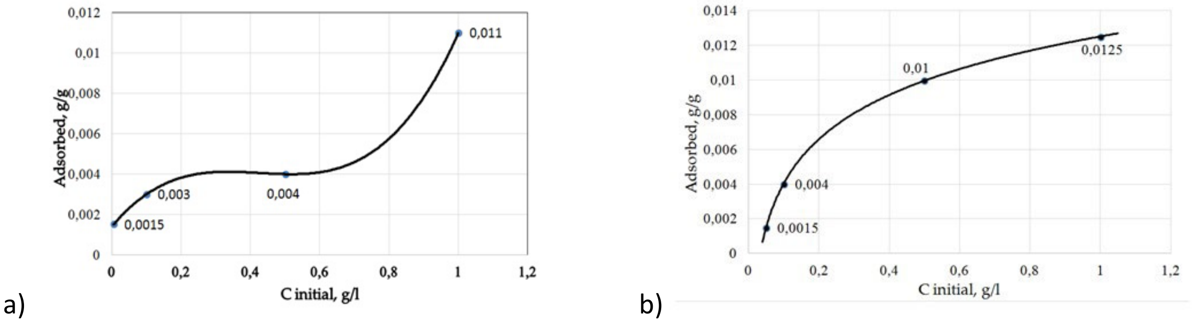
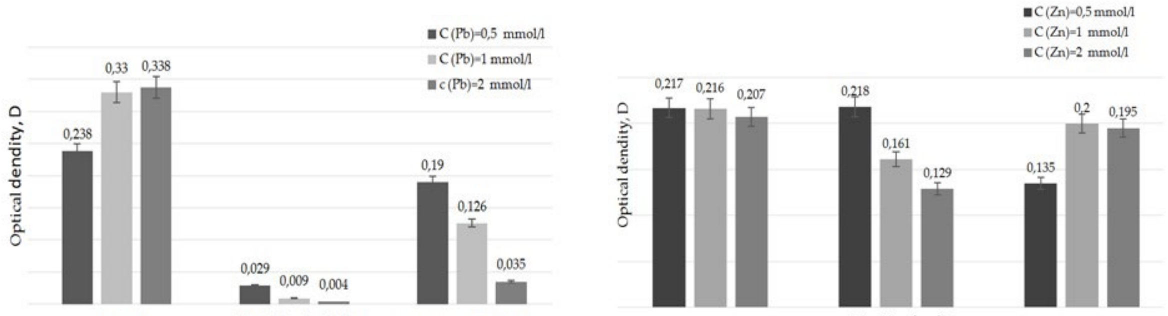


Figure 1. Isotherm of FA adsorption on bentonite (a) and kaolinite (b)

Adsorption processes in the systems: FA – Pb – kaolinite and FA – Pb – bentonite

Our data of IR spectrometry and ^{13}C NMR spectroscopy indicate a significant number of functional groups in the composition of the used FA, which can be involved to the formation of complex compounds and salts with Pb. Our results demonstrate that an optical density of the FA and Pb solution increases at an increase of the concentration of Pb ions up to the metal concentration of 1 mmol and then practically does not change (Fig. 2a). This behavior of the system may be due to the formation of colored complex compounds of the metal with FA. Pb ability to interact with wide range of organic ligands are closely associated with its heavy atom effect, inert lone pair effect, large ionic radius, and its borderline position on the hard – soft acid – base scale (Chu et al., 2013). Complexes of Pb with organic ligands exhibit frequently unique optical (including luminescent) properties which are seldom realized in other metal-organic complexes (Wang et al., 2021). In the FA - Pb^{2+} - kaolinite and FA - Pb^{2+} - bentonite systems the optical density decreases with an increase of the Pb concentration (Fig. 2a), that indicates the active adsorption of FA and metal-FA complexes by the clay minerals. Adsorption processes occur more efficiently on kaolinite at all used Pb concentration, despite its lower adsorption capacity.



a) b)

Figure 2. Dependence of the optical density of the studied systems on the Pb^{2+} (a) and Zn^{2+} (b) concentration.

Adsorption processes in the systems: FA – Zn – kaolinite and FA – Zn – bentonite

Results of study by soil column-Donnan membrane technique of metals speciation in eighteen soil solutions, covering a wide range of metal sources and concentrations show that in soil solution Zn mainly exist as free ions (Ren et al., 2015). Zn is not sensitive to dissolved organic matter reactivity due to low affinity for FA (Vega and Weng, 2013). Perhaps this explains the absence of optical density change in FA-Zn^{2+} system at all used Zn concentrations (Fig. 2b). Based on the data of optical density of solutions changes, the adsorption of complex compounds of Zn^{2+} with FA on kaolinite increases with increasing concentrations of the metal, that demonstrates the importance of trace element cations in the interaction between soil organic matter and the clay mineral. However, in the presence of Pb, absorption by kaolinite proceeds more efficiently than in the presence of Zn.

In the case of bentonite, the low concentration of Zn^{2+} leads to a decrease in optical density compared to the FA-Zn^{2+} system, and at a concentration of 1 and 2 mmol / l, the optical density practically does not decrease (Fig. 2b). Thus, it can be assumed that Zn promotes the adsorption of fulvic acids by bentonite only at certain low concentrations. It is possible that at the lowest the metal concentration used, Zn promotes the adsorption of FA-Zn^{2+} complexes through the formation of cation bridges with the mineral surface (Elliot and Huang, 1981). At higher concentrations, a more complex behavior of complexes of Zn and FA is observed, which, based on the absence of a change in optical density, can formally be interpreted as the absence of adsorption.

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PHYSICOCHEMICAL CHARACTERIZATION OF DIFFERENTLY SOURCED BIOCHARS AND THEIR POTENTIAL USE FOR THE PHYTOSTABILISATION OF SOILS POLLUTED BY TRACE ELEMENTS

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KEYWORDS
Mine, Metal(loid)s, Biochar, Physicochemical properties, Sorption analysis

ABSTRACT

Mining activity in the Touissit area of Eastern Morocco has resulted in an environmentally hazardous accumulation of heavy metals (HMs) specifically lead (Pb) and zinc (Zn) in tailing residues [1]. Pb-Zn contamination of tailings exhibits a huge threat to human health and sustainable land use [2]. Therefore, it is mandatory to remediate the HM contaminated soil. In this regard, many eco-friendly techniques have attracted attention worldwide, such as minimizing the bioavailability of HMs in soil by using stabilizing agents is a cost-effective and reliable method to manage HM pollution [3]. Among several stabilizers, biochar has been widely known due to its tremendous affinity for HMs, low cost, and eco-friendliness [4]. However, the sorption capacities of biochars considerably depend on their properties and the nature of the target metals [5]. Biochars with high pH tend to have high metal binding and stabilization ability [6]. Thus, the current study is aimed to mitigate the tailing residues impacts by a phytomanagement approach using a combination of differently sourced biochar and local plants in order to immobilize metals in these polluted soils. In this context, differently sourced biochars were physiochemically characterized and their sorption capacities towards Pb and Zn were analyzed. Further, polluted technosol was amended with different biochars to evaluate their ability to mitigate the metal pollutants and improve plant growth.

Before defining the field-implementation strategy, we investigated the physicochemical properties and metals content of two mining technosols, muddy waste (Mw) and sandy waste (Sw). Physicochemical properties such as pH and electrical conductivity (EC) were measured using the soil pore water (SPW) of two wastes. Pseudo-total and bioavailable concentrations of metals were determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) followed by digesting samples using Hydrochloride (HCl) and Nitric acid (HNO_3) for pseudo-total concentration, while bioavailability has been assessed by a simple extraction using $CaCl_2$ and NH_4NO_3 (only $CaCl_2$ extraction results will be discussed here). Furthermore, five differently sourced (Palm fronds (Pf), Eucalyptus wood (Ew), Eucalyptus chips (Ec), Citrus wood (Cw), and Argan nuts (An)) biochars were characterized for physicochemical properties and metals sorption capacities, notably for lead (Pb) and Zinc (Zn), at different $Pb(NO_3)$ and $Zn(SO_4)$ concentrations ranging from 0.1 to 2.5 $g.L^{-1}$. The percentage of metal ions removal by studied biochars was calculated by the following equation $100*[(C_0\_C_e/C_0)]$, with C_0 and C_e are the initial and equilibrium concentration (mg/L) of Pb and Zn ions. Furthermore, biochar samples were observed by scanning electronic microscopy (SEM) equipped with an energy dispersive spectroscopy (EDS) before and after sorption analysis. Ultimately, the two technosols were amended with 2% (w:w) of the studied biochars and vegetated with bean seedlings (Phaseolus vulgaris) to perform a phytotoxicity test.

Table 1 presents the physicochemical properties of mining technosol which revealed the alkalinity nature of Sw and Mw with pH 9.45 and 8.38, respectively. Indeed, the EC was too low in Sw than Mw. Pb and Zn pseudo total and bioavailable concentrations were almost higher in Mw than Sw, except for the bioavailable concentration of Pb which was higher in Sw (8.15 mg.kg^{-1}) than in Mw (5.85 mg.kg^{-1}). The pseudo total content of contaminants recorded for Mw was 12.5 and 5.3 g/kg respectively for Pb and Zn.

Table 1. Touissit physico-chemical properties

Soils	pH	EC (µs.cm^{-1})	Total metal conc. (mg.kg^{-1})		Bioavailable metal conc. (mg.kg^{-1})	
			Pb	Zn	Pb	Zn
Sw	9.45 ± 0.015 a	73.2 ± 0.2 a	5546.33 ± 172.71 a	3512.14 ± 122.44 a	8.15 ± 0.51 a	2.91 ± 0.297 a
Mw	8.38 ± 0.013 b	173.18 ± 1.2 b	12493.09 ± 155.14 b	5344.87 ± 45.98 b	5.88 ± 0.23 b	1.46 ± 0.094 b

Differently sourced biochars presented various Pb and Zn sorption capacities as Pf, Ec, and Cw were among the top 3 with the highest sorption capacity for both Pb and Zn. In fact, at the highest dose of Pb (2.5 g.L^{-1}), the maximum removal was recorded by Pf and Ec with a percentage of 74.5% and 70%, respectively. However, The maximum of Zn removal at 2.5 g.L^{-1} was recorded by Ec (23%) and Cw (11%). On the other hand, the sorption curves always tend to decrease with the increase of the concentration of HMs which is a proportional factor to the pH variation (Figure 1).

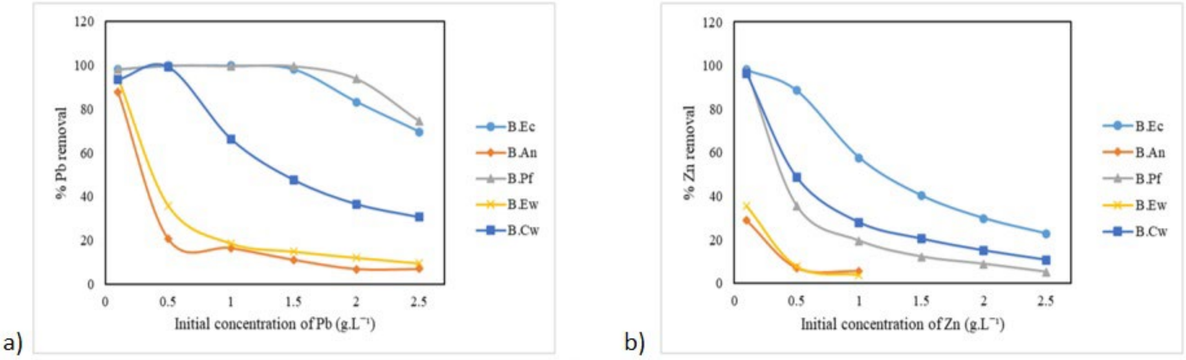

Figure 1. Effect of concentrations on the sorption of Pb (a) and Zn (b) ions by different biochars

To this end, biochars subjected to SEM study coupled with EDS, showed Pb and Zn deposits, related to the presence of Ca^{2+} (present in biochars particles as a cuboid mineral) (Figure 2). Moreover, Phytotoxicity test that was carried out using *Phaseolus vulgaris*, did not show any significant differences in terms of metals concentration in SPW and in the different plant organs after 12 days of growth in technosols (Mw and Sw) amended and non-amended with 2% (w/w) of the of different biochars.

In conclusion; Pf, Ec, and Cw derived biochars are the most competent in terms of sorption, however, their application as an amendment was not different from the rest of the biochars regarding contaminants mitigation in technosol. Thus, the use of other amendments in combination with the different biochars and plants that are able to fix HMs should be planned in order to assess plant growth and metal immobilization.

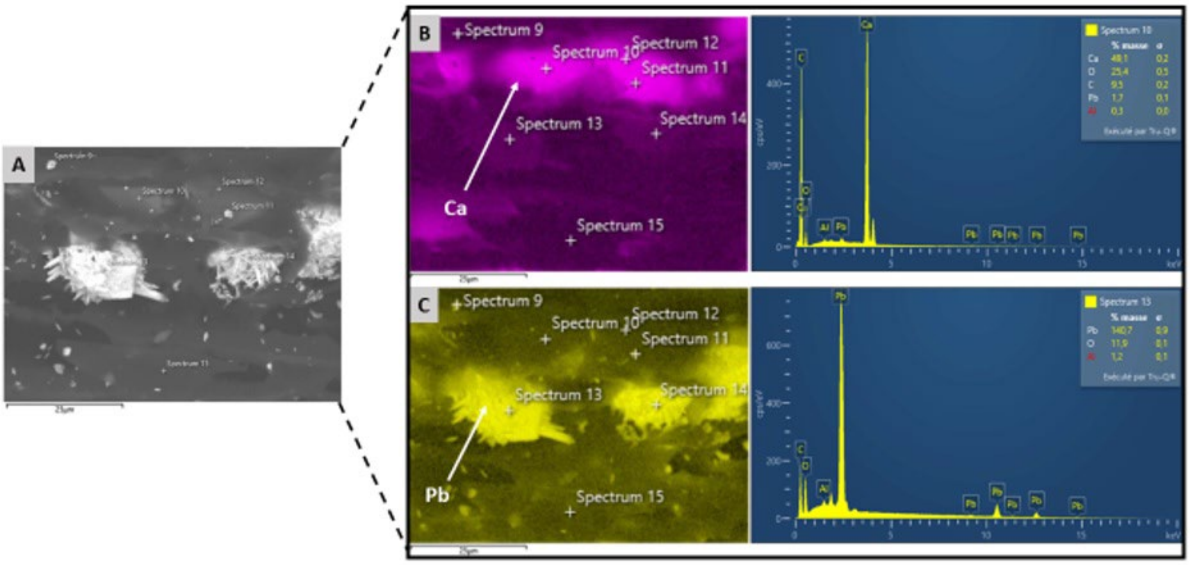

Figure 2. Example of SEM image (A) and EDS-mapping and spectrum of Ca (B) and Pb (C) present on the surface of Cw-derived biochar particles after the sorption experiment

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