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EVENT POSTPONMENT ANNOUNCEMENT

Scientific Committee and Organizing Committee announce that the 2020 edition of the Slovak Environment Agency's flagship event in the field of contaminated sites

the International Conference CONTAMINATED SITES 2020
will be rescheduled to Spring or early Summer, 2021.

Due to growing concerns over the coronavirus (COVID-19), and with the well-being of attendees, partners and staff as the number one priority, the Committees have decided that rescheduling the event is the only responsible course of action at this time. This decision was made after consulting with the SEA's management, the Ministry of Environment of the Slovak Republic, partners, and staff, to whom committees would like to express gratitude for their understanding, patience, and continued support.

The Scientific and Organizing Committee of the Conference

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CONTENTS

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].

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.

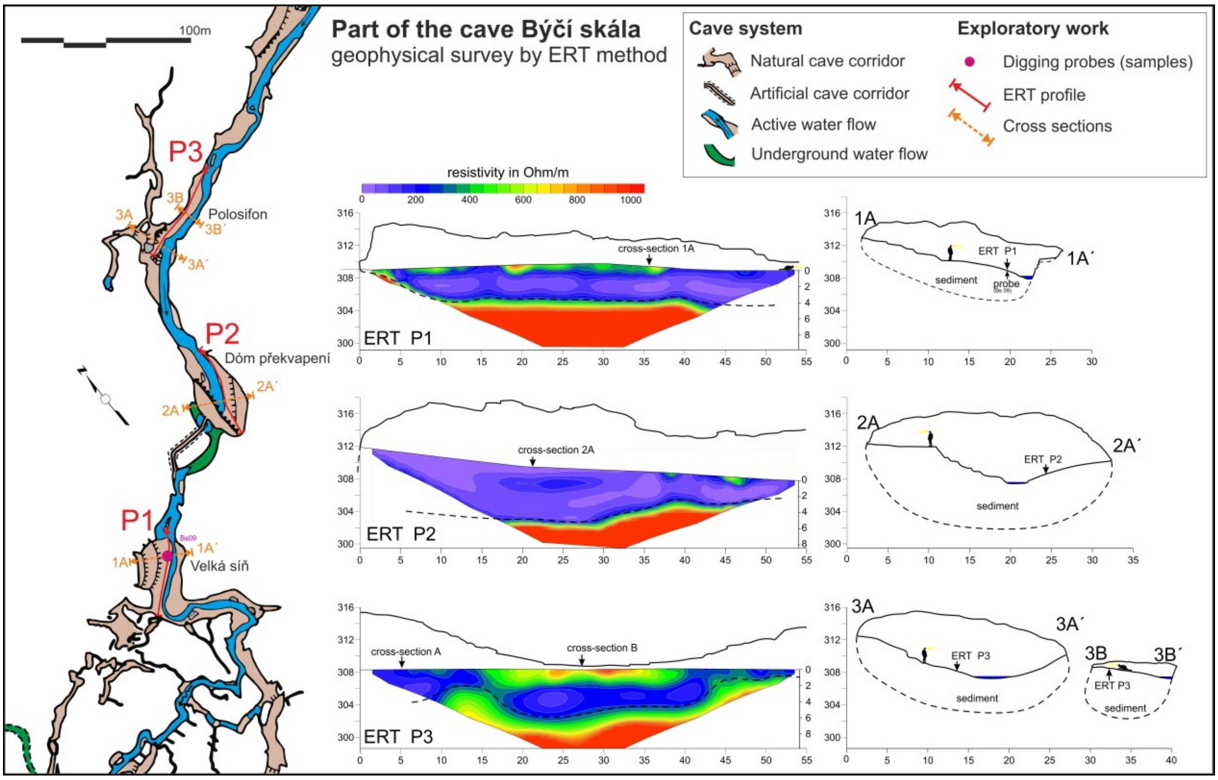

Fig. 1 Interpretation of ERT method to determine the thickness of the sedimentary fill in the CS

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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ELIMINATION OF THE INFLUENCE OF GROUNDWATER INFLOW INTO THE DUMP BODY CONTAINING HCH BALLAST ISOMERS

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KEYWORDS

Dump, contaminated site, groundwater, HCH, remediation, inflows

ABSTRACT

The dump was built at the end of the 1960s, in a former surface uranium mine. Simultaneously with the subsequent mining of kaolin, the pits were loaded with tailings from the surroundings and over 5,000 tons of pure ballast isomers of HCH (hexachlorocyclohexane) were transported. Due to their deep placement (approx. 30 to 40 m below the current surface of the dump body), it was decided to passive drainage in such a way as to eliminate leaches of contaminants, which would reach further into the recipient.

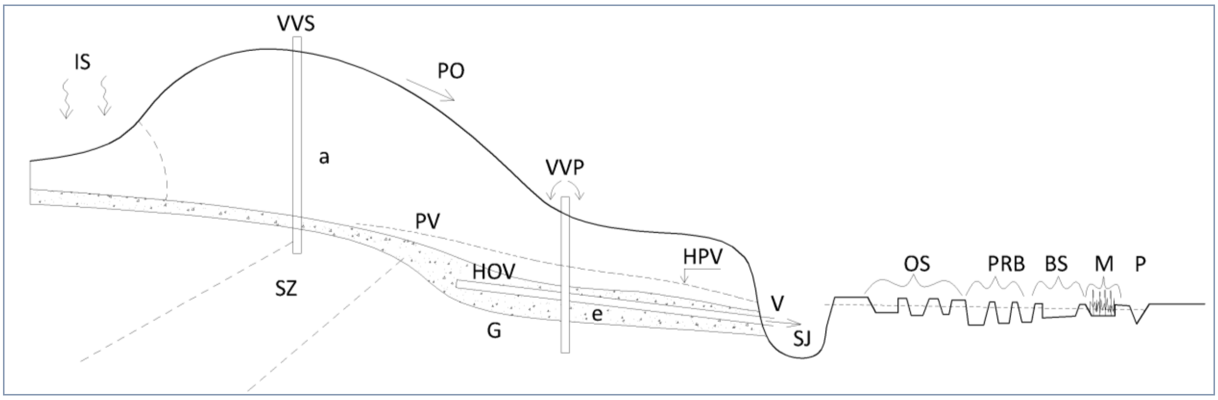

Fig. 1 Schematic section of the old dump Hájek

IS – precipitation infiltration into the dump body; a – dump body; e – eluvium (sand and clay, especially kaolin); G – granite massif (fractured media); SZ – fracture system; VVS – dry vertical well (rapid infiltration only); VVP – vertical artesian well (overflow after about 2 weeks after heavy precipitation); PO – surface runoff (limited infiltration into dump body); PV – original spring groundwater inflow into dump body); HPV – groundwater level (confined aquifer); HOV – sub-horizontal drainage well; V – discharge from the sub-horizontal well; SJ – starting pit (shaft); OS – oxidation and sedimentation; PRB – permeable reaction barrier (iron chips); BS – biosorption (peat, activated carbon); M – wetland (wetland plants, pine bark); P – stream

DRAINAGE OF THE DUMP BODY

Main idea of the drainage is based on preventing the inflow of clean water (groundwater and precipitation) into the dump body by draining them out of the dump body. Drainage of clean groundwater should be decreased amount of contaminated water, which flows from the dump body.

Reducing the inflow of groundwater into the dump body was performed by draining through a perforated sub-horizontal well, which was drilled into the area, where was spring in 1960s and now is located in depth app. 30–40 m under the dump body level.

The water is further cleaned by a system of wetlands, which consist of few sub-basins for oxidation and sedimentation processes, permeable reaction barrier with iron chips, biosorption with peat and activated carbon and wetland with plants and pine bark.

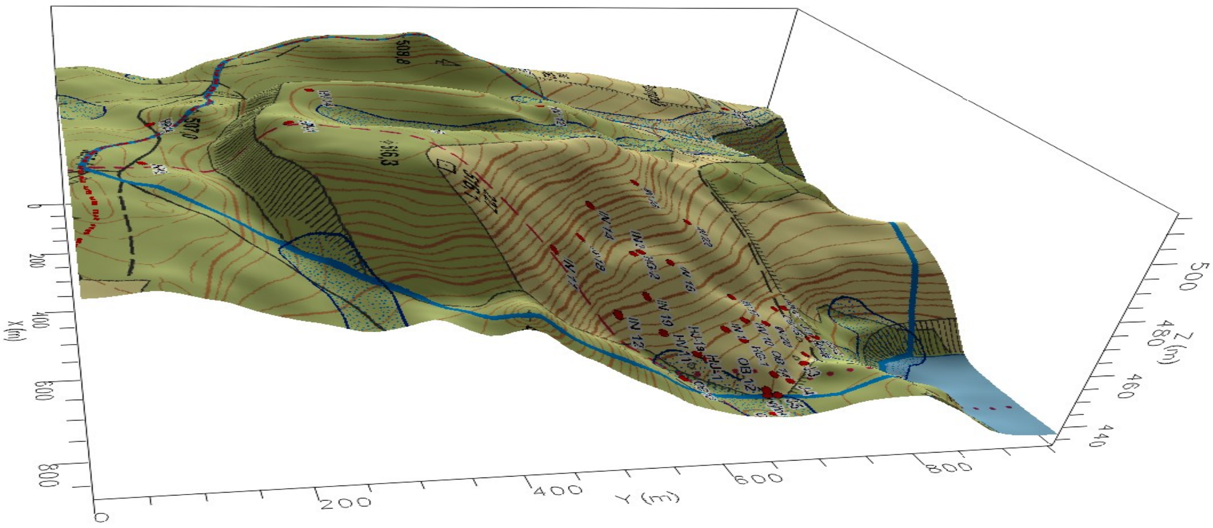

Fig. 2 Model of the old dump Hájek

RESULTS

The dump body was drained by sub-horizontal well, so all clean groundwater which inflows into the dump body from the original spring flows out of the dump body and their saturated by HCH isomers and other contaminants is limited. Final cleaning takes place thanks to a system of wetlands, from which water flows into the stream, where it must meet strict environmental limits.

Fig. 3 Aerobic wetland under the dump Hájek

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POLLUTION EMISSIONS AND AIR CLEANING MEASURES IN THE REPUBLIC OF NORTH MACEDONIA

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KEYWORDS

Air quality, sources of pollution, measures

ABSTRACT

Quality and healthy living environment is one of the basic preconditions for a quality life for all citizens in the Republic of North Macedonia. Air pollution can cause deterioration in human health, including premature death, as well as ecosystem disturbances. This is causing enormous economic damage to the state, expressed through reduced labor productivity and deterioration of the environment.

The emission of air pollutants originates from almost all economic and social human activities: traffic, industry, combustion and power plants, households, construction activities, landfills (especially wild) for waste and agricultural activities. Analysis of emissions data in the Republic of North Macedonia will be presented in tabular and graphical form.

In order to improve air quality, the Republic of North Macedonia has approximated European legislation with the adoption of air quality standards. These measures outline ways to reduce enormous air pollution and make recommendations to citizens on how to protect themselves.

EMISSRIONS OF AIR POLLUTION

Emissions of air pollutants come from almost all economic and social human activities: traffic, industry, combustion and energy plants, households, construction activities, landfills (especially illegal) waste and agricultural activities. Combustion of biomass by households, i. e. the burning of solid fuels such as wood and coal, is an important source of directly emitted solid particles and polycyclic aromatic hydrocarbons (PAHs), which belong to the class of carcinogens. Agriculture is a major responsible activity for ammonia (NH_3) emissions, which has an impact on both human health and ecosystems.

The amounts of pollutant emissions emitted by the above sectors affect their concentrations in the air. In order to take measures to reduce them and to achieve better air quality, there is a need to monitor the state of air quality, i.e. monitor pollutants for their qualitative and quantitative identification.

The collection and processing of data on air emissions is carried out continuously throughout the year within the work of the sector Macedonian Environmental Information Center (MICS) in the MoEPP. Relevant data for ambient air quality monitoring during 2008 to 2017 are given in the charts below.
In the Republic of North Macedonia, in the period from 2008 to 2017, twofold trend was recorded for SO_2 – sulphur dioxide, NO_x – nitrogen oxides, CO – carbon monoxide and TSP – total suspended particulates.

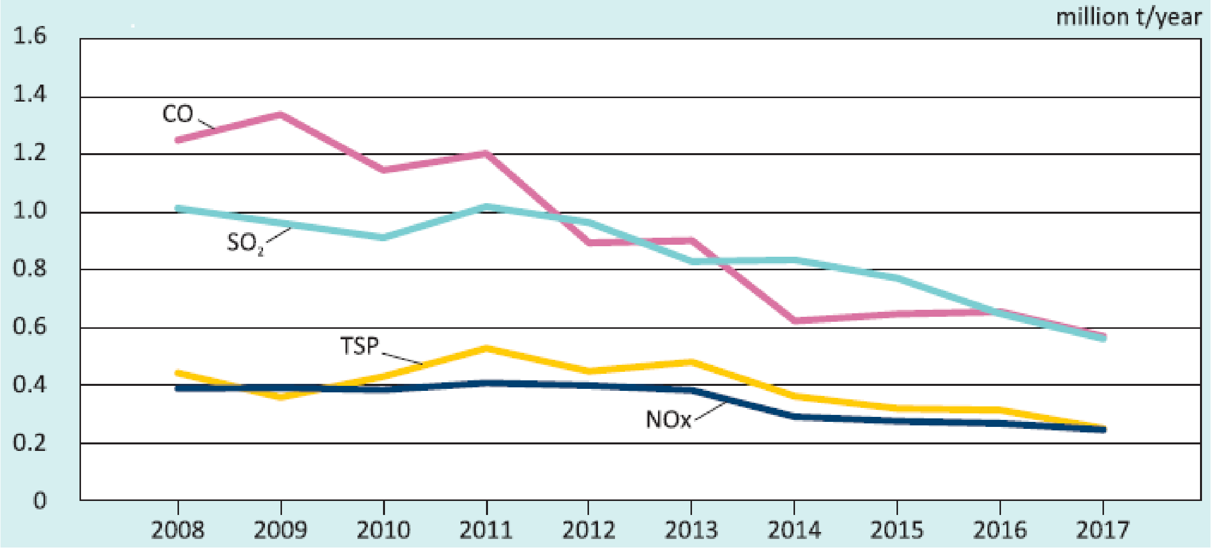

Fig. 1 Total annual emission of air pollutants

In the period from 2008 to 2011 variable trend was recorded in all abovementioned pollutants, while from 2011 to 2017 downward trend was recorded mainly, and in certain years, non variability in emission of certain substances was generally recorded.

During the recent years such a trend is due to implementation of measures at the national level, measures by the operators from their ISKZ licenses, closing of certain installations, as well as reducing of the quantity of fossil fuels in the combustion processes (coal, wood etc.) and other.
The total emission of air pollutants presented is shown in chart 1 by sectors of activities under the SNAP Nomenclature which are grouped in four areas such as combustion processes, production processes, transport and other.

Fig. 2 Total annual emission of air pollutants presented by sectors under the SNAP Nomenclature

Chart 2 shows the trend described in 1 for the total emissions of pollutants. At the same time, biggest emission of air pollutants is found in the sector of Combustion processes, in the magnitude of around 78 %. Emissions from the Transport sector during the last years have share of around 12–13%, and emissions from Production processes amount to around 7 % Emissions of pollutants from other sectors like waste, agriculture and fugitive emissions contribute around 3 %.

MEASURES FOR REDUCTION OF AIR POLLUTION EMISSIONS

Effective implementation of air quality improvement measures is crucial for air quality. Measures to improve air quality are divided into separate sectors.

In the field of electricity generation, reduction of emissions of pollutants is achieved by increasing the share of renewable sources in total energy consumption, reducing fuel consumption of existing thermal power plants.

Expanding the district heating network can effectively reduce the use of wood for heating in households, thereby affecting air quality in urban areas caused by households.

In addition to household heating, an important sector of emissions is road traffic, which mainly contributes to NO_2 concentrations but also to PM_{10} and $PM_{2.5}$ concentrations. Improving public transport in larger urban areas, promoting the use of low-emission vehicles and cycling, as well as creating pedestrian and low-emission zones are effective measures to control pollution in urban areas. The impact of road dust can be reduced by improving street cleaning, especially in dry periods.

CONCLUSION

The trend analysis contains information on emissions from all sectors of pollution, as well as case studies prepared to analyze the share of different sources in air pollution. Trend analysis covers the main pollutants that are measured continuously (suspended particles, NO_x, SO_2, and CO).

According to the analysis, there was a significant downward trend in sulfur dioxide concentrations over the period. This is due to the change in fuel used in some heating plants and the use of low sulfur fuels. Such a similar trend cannot be seen in other pollutants. Concentrations of suspended particles are at the same level during the period, i.e. significantly exceed the limit values in all urban areas in the country. High concentrations of suspended particles pose a serious risk to public health. Therefore, measures to improve air quality should be implemented urgently, which will apply to the main sectors of emissions, i.e. heating in households, road traffic and industry.

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DETOXIFICATION AND PURIFICATION OF ARSENIC-CONTAMINATED SITE BY SILICON-BASED APPROACH

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KEYWORDS

Arsenic, barley, silicon, rice

ABSTRACT

Arsenic (As) is a toxic metalloid of high concern from both the environmental and human health points of view. Mining and ore processing are the most widespread sources of As pollution. Over the last decade soluble silicon (Si) or solid Si-rich substances were reported to be effective for detoxification of contaminated sites and controlling the mobility and translocation of As in the soil-plant system. However, the mechanisms of Si–As interactions are not clear because both elements are metalloids. To reveal Si-related mechanisms responsible for the As behavior, the impact of potassium silicate on As mobility in soil and uptake by and translocation within rice plants were studied at two As-polluted sites near the Shimen realgar mine (China). In greenhouse experiment, application of Si substances significantly increased the underground and aboveground biomass of As-stressed plants. Mobile forms of As in Si-added soil reduced by 20 to 45 %. Silicon assisted the retention of As in the roots, resulting in reduction of total As and its soluble forms in the leaves by 35 to 70%. Application of Si fertilizer had a higher effect on As(III) than As(V) or organic As forms. The following mechanisms of Si–As interaction in the soil-plant system were determined: a) As adsorption by Si minerals; b) reduced As bioavailability by altering As speciation in the soil; c) decreased As uptake by and translocation within plants; d) mitigation of biotoxicity through transformation of highly toxic As(III) into less toxic organic As.

Arsenic (As) is classified as a Group I human carcinogen. Among the main anthorogenic sources of As in the soil are coal combustion, As-based pesticides and herbicides, chromated copper arsenate for wood preservation, and mining [1]. Mining and ore processing are the most widespread sources of As pollution.

Silicon is the second most abundant element in soil. Soil solution contains monomers and polymers of silicic acid at concentrations ranging between 0.1 and 2.0 mM. Unlike polysilicic acid, monosilicic acid (MSi) is recognized as chemically and biochemically active. It is absorbed by plants and microorganisms and reacts with numerous inorganic and organic compounds. Over the last decade, some investigations reported that soluble forms of Si or solid Si-rich materials can be used for detoxification of contaminated sites and controlling the mobility and translocation of As in the soil-plant system [2, 3]. The soil solution Si was reported to correlate negatively with the As accumulation by straw and grain of rice [4]. However, the mechanisms of Si–As interactions are not clear because both elements are metalloids. The main aim of this investigation was to determine the effect of soil-applied potassium silicate (K_2SiO_3) on the As mobility in soil and translocation to rice (field test) and barley (greenhouse test).

Shimen realgar mine is the biggest realgar deposit in Asia, located in the Hunan Province, China. Long-term intensive mining led to severe soil and water pollution in the surrounding areas. The average As concentrations in local agricultural soils reach up 100 mg kg^{-1}, posing a serious threat to human health [5].

Two paddy soils near the mining area were used for field test with rice (*Oryza sativa* L. cv. Yuzhenxiang) and greenhouse test with barley (*Hordeum vulgare L,* cv Zelenogradec 770). Selected chemical soil properties are presented in Table 1. In both tests, soil was fertilized with N as urea at 200 mg kg^{-1}, P as CaH_2PO_4 at 150 mg kg^{-1}, and K as KCl at 200 mg kg^{-1} before planting; K_2SiO_3 was applied at rates of 150 and 300 mg kg^{-1}. In greenhouse, the temperature regime was 26 ± 2 °C during the day and 24±2 °C at night. The light and night periods were each 12 h, with a light intensity of 950 mmol photons m^{-2} s^{-1}. The air humidity was 75 ± 5 % during the day and 70 ± 5 % at night. Field test was conducted under natural conditions at day temperatures 25–28 ^{o}C and night temperatures 22–25 ^{o}C and 93–98 % humidity.

Rice was harvested at maturity (105 days after transplanting), and the biomass of roots, shoots, and grains was measured. Barley was harvested 30 days after seeding and the biomass of roots and shoots was measured. Collected plant tissues were dried at +65 °C for 24 h and weighed. Soils were sampled after harvesting.

Tab. 1 Selected chemical properties of the soils used in field and greenhouse tests

Paddy soil	pH	C_{org} g kg^{-1}	Alkali-hydrolyzed N	Na_2HCO_3 - extractable P	Water-soluble K	Total Fe	Total As	Total Ca
			----------------------- mg kg^{-1} -------------------------					%
Medium contaminated	5.43	30.4	206.6	3.44	96.8	23.1	30.6	0.106
Highly contaminated	5.46	29.4	152.5	0.41	106.3	23.3	66.9	0.121

Total As in plant samples was analyzed after microwave digestion with concentrated nitric acid using an Atomic Fluorescence Spectrometry (AFS-7300). Total Si in roots and shoots was tested using H_2O_2 and NaOH microwawe digestion followed by Mullin and Riley colorimetric method [6, 7]. The plant-available Si in soil samples was analyzed in HCl extracts [8]. The H_2SO_4-extractable As in soil was determined as well [9]. Each treatment and analysis were conducted in triplicate. The obtained data was processed using Excel 2010.

Total As The plant biomass was less by 9.7–37.5 % on highly contaminated soil than that on medium contaminated soil (Table 2). The Si addition provided significant increases in the biomass, by 26–38.4 % and 14.8–50.0 %, accordingly for rice and barley.

Tab. 2 Dry weight of plants (g plant^{-1})

Paddy soil	Si treatment, mg kg^{-1}	Roots	Shoots	Grain
		-----------------------g plant^{-1} ------------------------		
Rice, field test				
Medium contaminated	0	7.76±0.18	33.93±0.99	25.63±0.83
	150	9.18±2.15	38.13±1.05	30.77±1.86
	300	10.00±0.14	46.97±1.12	34.97±0.47
Highly contaminated	0	4.85±0.22	30.63±0.76	20.80±1.48
	150	5.67±0.33	34.50±1.15	23.87±0.47
	300	6.38±0.09	38.60±1.08	27.90±1.90
Barley, greenhouse test				
Medium contaminated	0	1.21±0.03	1.03±0.03	-
	150	1.39±0.04	1.22±0.02	-
	300	1.56±0.03	1.43±0.03	-
Highly contaminated	0	1.02±0.03	0.82±0.03	-
	150	1.22±0.03	1.04±0.04	-
	300	1.38±0.0.4	1.23±0.02	-

Total As and Si in plant tissues are presented in Table 3. The plant accumulation of both As and Si was dependent on the level of soil contamination. An increase in the total Si in plant at higher contamination could be related to the role of Si in mitigating biotic and abiotic stresses. Stress-exposed plants were shown to enhance the Si uptake [10]. The Si application significantly reduced the total As in the roots and shoots of rice and barley as well as rice grain. This data is consistent with other reports [11, 12].

Mobile forms of Si and As in soil are presented in Table 4. Generally the data from field and greenhouse tests were similar. With addition of K_2SiO_3, the plant-available Si increased, while acid-extractable As decreased.

Tab. 3 The total content of Si and As in plants

Paddy soil	Si treatment, mg kg^{-1}	Roots		Shoots		Grain
		Si, %	As, mg kg^{-1}	Si, %	As, mg kg^{-1}	As, mg kg^{-1}
Rice, field test						
Medium contaminated	0	0.81±0.14	81.19±0.29	1.68±0.21	8.51±0.48	0.46±0.05
	150	0.91±0.09	75.98±3.05	2.24±0.19	6.66±0.03	0.34±0.04
	300	0.97±0.05	46.00±2.85	1.78±0.08	6.28±2.26	0.31±0.02
Highly contaminated	0	0.56±0.36	90.37±0.40	1.16±0.43	16.02±0.19	0.81±0.02
	150	0.52±0.06	66.84±1.37	1.49±0.10	14.99±0.83	0.70±0.03
	300	0.50±0.05	61.30±3.10	1.24±0.07	9.54±2.33	0.69±0.05
Barley, greenhouse test						
Medium contaminated	0	0.83±0.05	92.3±3.5	0.85±0.06	4.53±0.05	-
	150	0.87±0.04	73.4±3.3	0.94±0.08	4.22±0.04	-
	300	0.96±0.05	42.3±3.2	1.04±0.07	4.10±0.04	-
Highly contaminated	0	0.92±0.07	96.7±4.6	0.94±0.05	10.52±0.06	-
	150	0.95±0.04	74.5±3.6	0.96±0.05	7.43±0.05	-
	300	0.98±0.05	56.4±4.6	1.17±0.06	6.21±0.05	-

Tab. 4 Acid-extractable Si and As in tested paddy soils (mg kg^{-1})

Paddy soil	Si treatment, mg kg^{-1}	Si	As
		--------------mg kg^{-1} ----------------	
Rice, field test			
Medium contaminated	0	42.3±2.0	1.31±0.07
	150	61.2±7.2	1.19±0.09
	300	73.4±15.2	1.22±0.18
Highly contaminated	0	41.0±2.3	2.84±0.34
	150	64.2±7.3	3.21±0.44
	300	71.2±15.1	3.17±0.16
Barley, greenhouse test			
Medium contaminated	0	43.5±1.6	1.42±0.06
	150	62.3±4.5	1.24±0.08
	300	74.5±10.2	1.26±0.09
Highly contaminated	0	42.3±2.1	2.87±0.12
	150	67.4±5.4	2.30±0.07
	300	71.6±8.5	2.19±0.09

Thus, the application of K_2SiO_3 promoted decreasing the mobile forms of As in the soil and its accumulation by rice and barley. Several mechanisms can be supposed to explain the Si impact on the As behavior in the soil-plant system. Applied Si mineral substances increase the soil adsorption properties [13]. Potassium silicate dissolves to form monosilicic acid, which in turn contributes to the As adsorption by soil minerals. Additional Si nutrition inhibits the As uptake by and translocation within plants due to competition between Si and As(III), the predominant form of As in paddy soil, for transport system. Our study also showed that the plant supplementation with Si mitigates the As biotoxicity through the transformation of highly toxic As(III) into less toxic organic As [14].

ACKNOWLEDGMENTS

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APPLICATION OF WASTE FROM THERMAL POWER PLANTS FOR THE SYNTHESIS OF NANOPOROUS MATERIAL ZEOLITE 4A

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KEYWORDS

Fly ash, synthesis, nanoporous material, structural methods

ABSTRACT

Removal of fly ash waste is a worldwide problem precisely that is why our studies will be focused on the synthesis of nanoporous material from this material that will contribute to the reduction of waste generated by industry. Fly ash by physical properties is a solid powder material whose color varies but is usually gray due to present impurities. In terms of chemical composition, due to the high content of SiO_2 and Al_2O_3 components, it is a suitable raw material for the synthesis of zeolite 4A which has been further tested as a heavy metal wastewater and polluted soil. The chemical composition of the fly ash is shown in tabular form, and the tests of the obtained zeolite 4A were investigated by structural methods (x – ray and IR method). 90 – 100 °C low temperature synthesis has been applied.

The problem which is solved is the utilization of industry waste material (floating ash) in obtaining a pure product labeled as zeolite 4A. The resulting product possesses the excellent qualities characteristic of zeolites that have contributed in recent decades to a wide range of applications worldwide in various fields, replacing conventional methods with new technological processes.

CHARACTERISTICS OF FLY ASH

Disposal of fly ash is a global problem, which is why our research will focus on the synthesis of nanoporous material from this material, which will help reduce the waste generated by industry. The characteristics of fly ash depend on the type of coal and the way the ash is collected with electrostatic precipitators. Fly ash according to its physical properties is a fine, very fine-grained, powdery material (Figure 1). The color of the ash can vary from dark gray to black, depending on the amount of carbon

Fe_2O_3 in the ash. The lighter the color, the lower the carbon content. In terms of chemical composition, due to the high content of SiO_2 and Al_2O_3 components it is a suitable raw material for the synthesis of zeolite 4A which is further tested as an adsorbent of heavy metals from wastewater and contaminated soils. The chemical composition of the floating ash is shown in Table 1.

Fig. 1 Appearance of fly ash

SYNTHESIS OF ZEOLITE 4A

For the synthesis of the nanoporous material, the following molar ratio of oxides is chosen: $SiO_2/Al_2O_3 = 1.3$; $Na_2O/SiO_2 = 3$; $H_2O/Na_2O = 50$. The chemical composition of $NaAlO_2$ is $Na_2O = 30\ \%$, $Al_2O_3 = 40\ \%$ and $H_2O = 30\ \%$. The chemical composition of the substrate is $3.9\ Na_2O \times SiO_2 \times Al_2O_3 \times 195\ H_2O$.

Tab. 1 Chemical composition of fly ash

Substance	Percent (%)
SiO_2	52,36
Al_2O_3	23,92
Fe_2O_3	7,91
CaO	7,52
MgO	2,32
Na_2O	0,90
K_2O	1,80
SO_3	1,20
Loss on ignition	1,90
Total	99,88

The synthesis consists of five phases in the first phase there is dosing and mixing of the components according to the given molar ratio, second phase gel formation, third phase crystallization, fourth phase filtration, fifth phase drying in a dryer at a temperature of 120 °C. The components are dosed in a reactor supplied with a mixer, a return cooler is attached whose function is to condense the evaporated water and return it back so as not to disturb the ratio of the components. The contents of the reactor are heated to a temperature of 90–100 °C during continuous stirring with a magnetic mixer for 2, 4 and 6 hours. After heating the gel from the reactor is filtered through filter paper and washed with distilled water to pH 7, the resulting product is dried in a dryer at a temperature of 120 °C. Complete crystallization is completed within 6 hours. A thermostat is used as a heating element. Low temperature synthesis is applied.

The obtained nanoporous material was examined by structural methods x-ray and IR-method and the diffractogram and infrared spectrum are shown in Figure 2 and Figure 3. The chemical composition of the nanoporous material is given in Table 2.

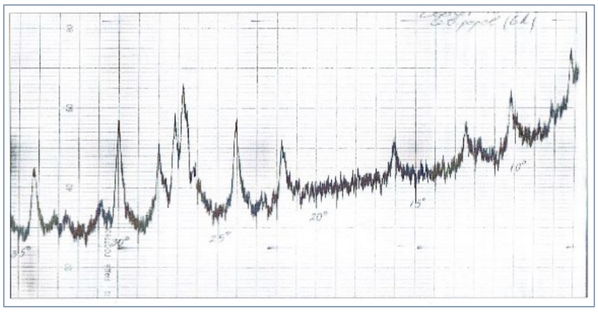

Fig. 2 IR-spectrum of nanoporous fly ash material

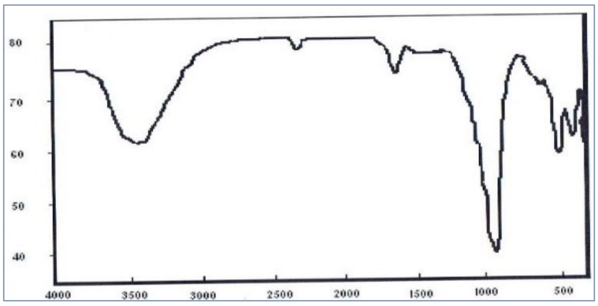

Fig. 3 Diffractogram of nanoporous fly ash material

Tab. 2 Chemical composition of the nanoporous material

Substance	Participation in (mol%)
SiO_2	35,45
Al_2O_3	27,96
Fe_2O_3	5,52
Na_2O	11,00
Loss on ignition	20,07
Total	100

The problem to be solved is the use of industrial waste material (fly ash) in obtaining a pure product marked as zeolite 4A. The resulting product possesses excellent qualities characteristic of zeolites that contribute in recent decades to have a wide range of application in the world in various fields, substituting conventional methods with new technological procedures. Zeolite 4A is characterized especially by its specific crystal lattice which as a magnet attracts and binds to itself many toxic substances and compounds in terms of size and their active surface they are a very useful material with a wide range of their application, as ion exchanger, molecular sieve, adsorbent of various gases and application as a catalyst. Zeolite also finds a place in the purification of waste in eco-agriculture for the production of healthy ecological food, in medicine, in industry and in other spheres of everyday life.

CONCLUSION

From our tests we can conclude that fly ash is a suitable raw material for nanoporous material. Its use uses waste material in obtaining useful material on the one hand and on the other hand reduces the waste generated by thermal power plants that use solid fuels. The use of fly ash also reduces soil and water pollution in the vicinity of thermal power plants. It is necessary to perform remediation of the soil and it should be useful for growing crops. Further research will be focused on testing the obtained nanoporous material as an adsorbent of heavy soil and contaminated wastewater. This fly ash is also used in the cement industry.

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SEQUENTIAL NANO-BIO-REMEDIATION USING „GREEN“ BIONANOPARTICLES AND BACTERIA

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KEYWORDS

Bionanoparticles, bacteria, dechlorination, degradation, flavonoids, green synthesis, nZVI, plant, PCBs, polyphenols

INTRODUCTION

Plant bio nanoparticles (the so-called green nanoparticles) represent a biological alternative to synthetic nanoparticles utilized in nanoremediation of organic chlorinated contaminants. Bionanoparticles are at the forefront of research for their great potential in the degradation of persistent organic pollutants (POPs) from the environment and for their plant origin, which predetermine their low toxic side effects. The origin of plant iron bionanoparticles depends on the type and kind of plants used, which must contain secondary metabolites such as phenols, polyphenols, flavonoids, terpenoids or other bioactive substances in their structure. Polyphenols in plant material play a key role in the formation of bionanoparticles, so it is necessary that the plant parts used have a high content of these substances in their structure (1–8).

The aim of the research was to test various plants (rosemary, grape peel, pine needles, lemon balm, ivy, banana peel, green tea, dill and magnolia leaves) for the presence and number of polyphenols and flavonoids, which are the basic phytochemicals for the formation of metal plant bionanoparticles using extracted phytochemicals by the addition of ferrous salts (10–13). In the next step, the bionanoparticles are used for nano-biodegradation of polychlorinated biphenyls (PCBs). Nanoparticles dechlorinate higher chlorinated PCB congeners to lower chlorinated, which are more readily degraded by specialized bacteria with degradation capacity. The type of plant with the greatest potential for bionanoparticle formation, nanoparticle activity, means the efficiency of dehalogenation and subsequent biodegradation using the addition of suitable bacteria are some parameters that need to be verified in relation to the possibility of using this hybrid decontamination approach.

MATERIALS AND METHODS

Determination of polyphenols spectrophotometrically

Determination of total polyphenols was performed using Folin-Ciocalteu reagent (FC). For analysis, a 0.1 ml sample of the plant ethanol extract was pipetted, 0.5 ml of FC reagent was added and after exactly 3 minutes 1.5 ml of 20 % sodium carbonate was added. The final volume was made up to 10 ml with distilled water. After 2 hours the absorbance at 765 nm was measured. The number of polyphenols in the sample was calculated using a calibration line constructed by adding 0.1 ml of ethanolic gallic acid standard solution at various concentrations.

Determination of flavonoids spectrophotometrically

The content of total flavonoids was determined by the $AlCl_3$ method. To a 2 ml sample of the plant ethanol extract was added 200 µl of a 5 % ethanolic solution of $AlCl_3$. After 30 minutes, the absorbance at 420 nm was measured. The number of flavonoids in the sample was calculated using a calibration line constructed by adding a 1 mg.ml^{-1} solution of the rutin standard at various concentrations.

Preparation of green bionanoparticles

0.1390 g of $FeSO_4 .7H_2O$ was added to each 50 ml flask to the prepared herbal aqueous extracts of green tea and lemon balm and the pH was adjusted between 7–8 with 0.05 M NaOH (9). The flasks were placed on a shaker in a dark box for 48 hours at 20 °C and a rotation speed of 100 rpm. After incubation, the mixture was centrifuged to separate precipitated nanoparticles at 4500 rpm for 10 minutes.

Degradation of PCBs using bionanoparticles

100 ml reagent bottles were prepared in duplicate. To each of them were added 100 ml of minimal mineral medium, 185 µl of the solution Delor 103 with a concentration of 54 g.l^{-1} and 3 ml of prepared nanoparticles. In all flasks, the pH was adjusted between 7–8 with 0.05 M NaOH solution and placed on a shaker for 7 days at 20 °C and 100 rpm in the dark.

Degradation of PCBs by nanoparticles and sequential application of bacterial strains

100 ml of minimal mineral medium, 185 µl of Delor 103 solution with a concentration of 54 g.l^{-1} and 3 ml of prepared nanoparticles were added to a 100 ml reagent bottle. In all flasks, the pH was adjusted between 7–8 and placed on a shaker for 7 days at 20 °C and 100 rpm in the dark. After 7 days, the mixture was poured into a cultivation flask and the biomass of the bacterial strain *Stenotrophomonas maltophilia* or *Ochrobactrum anthropi* both at a final concentration of 1 g.l^{-1} were

added to the cultivation flask. Cultures of bacteria isolated from sediments contaminated with PCBs were centrifuged for 20 minutes at a rotation speed of 3600 rpm before application. The culture flasks were placed on a rotary shaker where they were incubated for 14 days at 27 °C and 180 rpm.

Analysis of indicator PCB congeners by gas chromatography

In the samples extracted with n-hexane, the non-degraded amount of indicator PCB congeners was determined by gas chromatography with a GC HP5890 instrument. The conditions for the analysis are as follows: gas chromatograph with electron capture detector (ECD, 280 °C), N_2 gas (40 $ml.min^{-1}$), H_2 carrier gas (85 kPa), with silicate capillary column (30 mx 0.25 mm ID) and with a non-polar stationary phase HP-5MS (thickness 0.25 µm). Temperature mode setting: injector 250 °C, detector 280 °C and furnace 50 °C. The Instrument Offline program was used for peak identification and analysis, where the following 7 indicator PCB congeners were determined (Fig. 1 and 2): PCB 8 (2,4´ -), PCB 28 (2,4,4´-), PCB 52 (2.2´, 5.5´-), PCB 101 (2.2´, 4.5.5´-), PCB 118 (2.3´, 4.4´, 5-), PCB 138 (2 , 2´, 3,4,4´, 5-), PCB 153 (2,2´, 4,4´, 5,5´-). From equation (4), the amount of degraded PCB was evaluated:

$$P = \frac{Y - X}{Y} . 100\ \% \qquad (1)$$

P is the percentage degradation of the PCB congener, Y is the concentration of the PCB congener in the analytical control, and X represents the residual concentration of the PCB congener in the sample.

RESULTS

The intention of the presented work was to test selected plants and fruits for the presence of polyphenols and flavonoids to precipitate from their extracts by adding $FeSO_4$. 7 H_2O zero-valent iron bionanoparticles and apply them to polychlorinated biphenyls (PCBs) and determine the effectiveness of their dechlorination. Bacteria with PCB degradation ability, namely *Stenotrophomonas maltophilia* and *Ochrobactrum anthropi* isolated in our previous works from PCB contaminated river sediments, have been used for nano-bio sequentional degradation of PCBs. To determine polyphenols and flavonoids, 9 species of plants (salvia, rosemary, green tea, pine, ivy, nettle, magnolia, and dill) and 4 species of fruit (banana, mandarin, grape, and orange) were tested. The highest concentration of the monitored polyphenols and flavonoids was from salvia (0.73 $g.l^{-1}$ and 0.4639 $g.l^{-1}$) and rosemary (0.38 $g.l^{-1}$ and 0.293 $g.l^{-1}$) (Tab. 1). Extracts from lemon balm and green tea were used for the synthesis of bionanoparticles and nanoemediation of selected PCB congeners. Evidence of the presence of the formed nanoparticles was a visually detectable color change of the extracts after the addition of $FeSO_4.7H_2O$ to the aqueous extract to a dark purple to black color formed by precipitated bionanoparticles. By the addition of bionanoparticles alone, the degradation efficiency of PCBs was 46 % for nZVI from green tea and 31 % for nZVI from lemon balm (Fig. 1).

Tab. 1 Concentration of polyphenols and flavonoids determined in the plant extracts

PLANT/FRUIT TYPE	Used plant parts	polyfenols (mg.ml^{-1})	flavonoids (mg.ml^{-1})
IVY CLIMBING *(HEDERA HELIX)*	Leaves	0.14	0.2878
ROSEMARY MEDICALL *(SALVIA ROSMARINUM)*	Leaves	0.38	0.293
PINE FOREST *(PINUS SYLVESTRIS)*	Needles	0.16	0.108
SALVIA MEDICALL *(SALVIA OFFICINALLIS)*	Leaves	0.73	0.464
MANDARIN *(CITRUS RETICULATA)*	Peel	0.39	0.185
BANANA *(MUSA ACUMINATA)*	Peel	0.22	0.0101
LEMON BALM *(MELLISA OFFICINALLIS)*	Leaves	0.34	0.244
NETTLE HETROTHALLIC *(URTICA DIOICA)*	Leaves	0.039	0.289
ORANGE (*CITRUS SINEUSIS)*	Peel	0.18	0.0844
GRAPE *(VITIS VINIFERA)*	Peel	0.05	0.0374
MAGNOLIA *(MAGNOLIA GRANDIFLORA)*	Leaves	0.131	0.0923
DILL *(ANETHEUM GRAVEOLEUS)*	Leaves	0.135	0.658
GREEN TEA *(CAMELLIA SINENSIS)*	Leaves	0.38	0.0817

Nanobioremediation of PCB congeners with nZVI from lemon balm and the addition of the *O. anthropi* strain was the most efficient, with the level of degradation reaching 58 %. Nanobioremediation with nZVI obtained from green tea and *O. anthropi* was less efficient than the nanoparticles alone and reached 21 %. The combination of nZVI synthetized from lemon balm and the *S. maltophilia* strain achieved PCB degradation of 52 %, and the combination of nZVI obtained from green tea and the *S. maltophilia* strain achieved degradation efficiency of 40 % (Fig. 2 and Fig. 3).

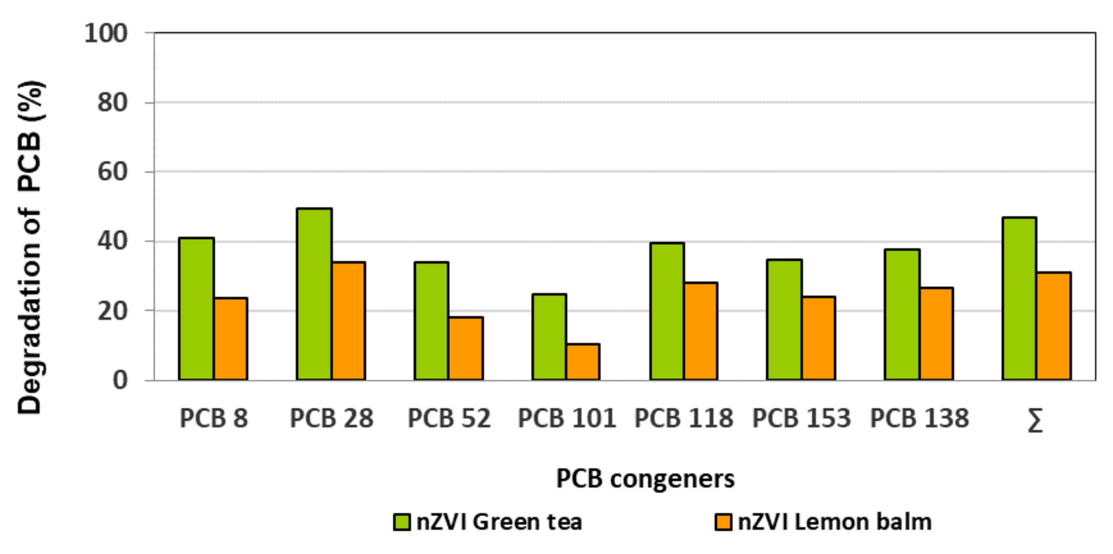

Fig. 1 Degradation of 7 indicator PCB congeners in PCB commercial mixture Delor 103 in the minimal mineral medium by bionanoparticles of nZVI obtained from the green tea and lemon balm

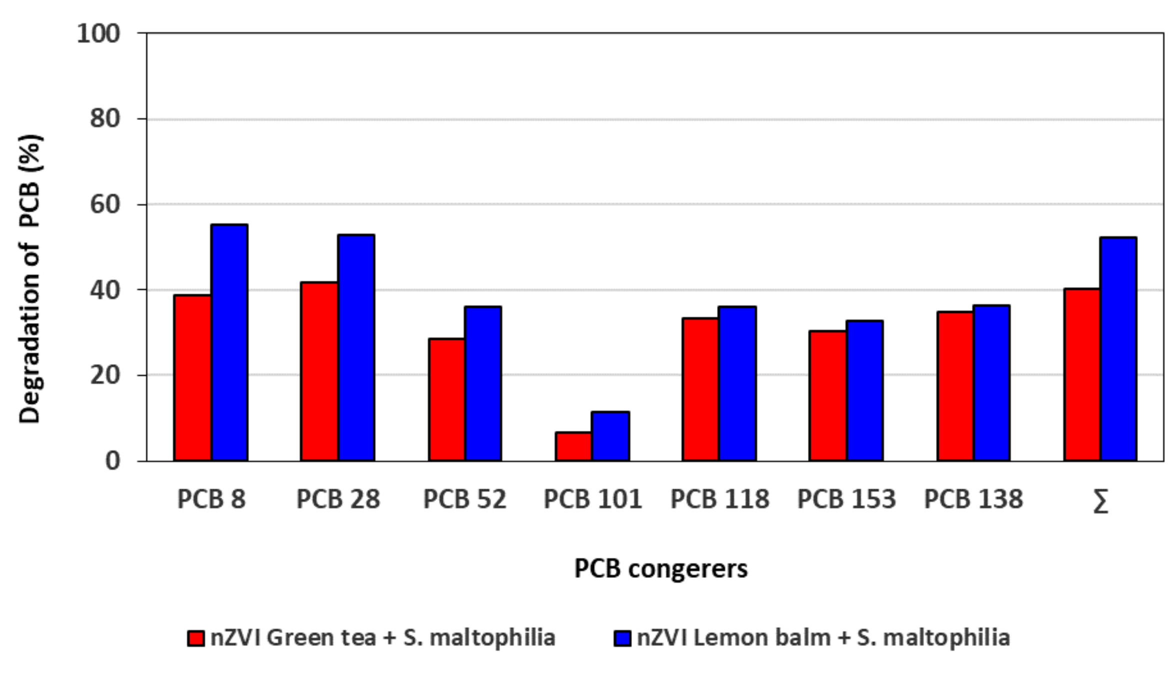

Fig. 2 Sequential degradation of 7 indicator PCB congeners in PCB commercial mixture Delor 103 in the minimal mineral medium by bionanoparticles of nZVI obtained from the green tea and lemon balm and addition of bacteria S. maltophilia

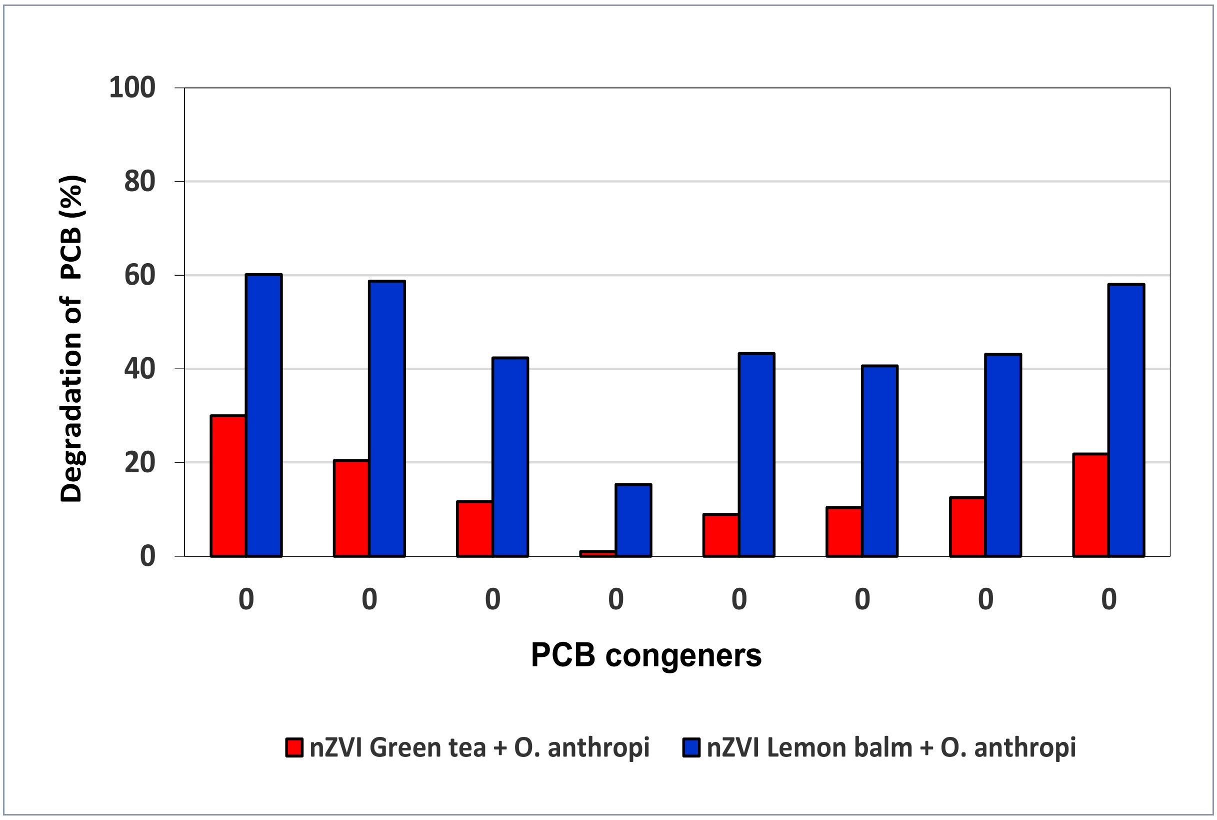

Fig. 3 Sequential degradation of 7 indicator PCB congeners in PCB commercial mixture Delor 103 in the minimal mineral medium by bionanoparticles of nZVI obtained from the green tea and lemon balm and addition of bacteria O. anthropi

CONCLUSION

The used sequential nano-bio-remediation - dechlorination of PCBs with plant nano-zero-valent iron particles and subsequent biodegradation by bacteria with the PCB degradation ability appears based on the data we have obtained to be an effective decontamination technology.

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CURRENT STATUS OF SOIL CONTAMINATION WITH HEAVY METALS IN POLAND

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KEYWORDS

Chemical degradation, heavy metals, soils, remediation, Poland

ABSTRACT

Heavy metal pollution is a sign of chemical degradation of the environment. Currently, there are many sources, mainly of anthropogenic origin, from which metals can enter to the environment. Accordingly, this paper presents the current state of soil pollution with heavy metals in Poland. This situation was referred and compared to other EU countries. In this context, particular attention was paid to agricultural soils. Possible reasons for heavy metal contamination and the potential for its reduction were underlined. In addition, the work reviews remediation methods proposed for practical use. Based on recent data on arable soil contamination with heavy metals, first of all Cd, Cu, Ni, Pb and Zn is low. The vast majority of soils show natural contents of heavy metals. The problem of chemical soil degradation expressed by heavy metal pollution is local and concerns highly industrialized and mining areas connected with metal deposits. Such a situation may be observed mainly in the south of Poland and it presently accounts for approximately 3 % of the county's area.

INTRODUCTION

Chemical degradation of soils, similarly as other types of degradation, is the result of harmful human activity. In practice, the results of anthropogenic impact may include acidification, salinity, reduction of organic matter content and microbial activity or heavy metal contamination. Globally there are over 20 million ha of land contaminated by the heavy metal(loid)s As, Cd, Cr, Hg, Pb, Co, Cu, Ni, Zn, and Se, with the present soil concentrations higher than the geo-baseline or regulatory levels (Liu et al. 2018). For the EU-28 around it is estimated that 2.8 million sites have been polluted/are being polluted with heavy metals (Pérez and Eugenio 2018). Tòth et al. (2016) showed that although most of the examined elements remain under the corresponding threshold values, still one or more of the metals exceed the adopted threshold, which was 28.3 % total surface area of Europe. According to this Thematic Strategy for Soil Protection (UE Com 2012/46), these phenomena are distinguished and emphasised as particularly dangerous and threatening soil health. While the effect of soil acidification, a decrease in organic matter content or reduction of biodiversity and biological activity of soil may be compensated for by proper agrotechnics, an effective heavy metal reduction is difficult to perform. Despite differences in phyto – and ecotoxicity of heavy metals, their excessive amounts in the environment should always be considered as highly unfavourable, because these elements are easily incorporated into the food chain, constituting a serious health hazard to living organisms. Therefore, there is a need for constant control and monitoring of heavy metals in the environment, with particular emphasis on agricultural soils. This is particularly so because the chemical forms, in which metals from anthropogenic sources are introduced into the environment, show much greater solubility than metals of lithogenic origin. Thus they can change the natural balance of the soil environment by chemical, biological and physical properties modification.

GENERAL RULES RELATED TO HEAVY METAL CONTAMINATION IN POLAND

Currently in Poland the following legal regulations related to EU standards are binding, such as Directive 2004/35/EC of the European Parliament and the Council of 21 April 2004 on environmental liability with regard to the prevention and remedying of environmental damage, the so-called directive ELD and Directive 2010/75/EU of the European Parliament and the Council of 24 November 2010 on industrial emissions, the so-called IED directive. In Poland, similarly as in most European countries, the adopted national regulations include both procedures to avoid new contaminations and to repair those date back 30 years, the so-called historical contaminations. In view of the above, Polish legislation on soil protection and contamination as well as remediation is based first of all on the National Regulations – Environmental Protection Law, referred to as the Environmental Protection Act (Journal of Law 2019, item 1396), Ordinance of the Ministry of the Environment of 1 September 2016 on the method of conducting the assessment of ground surface pollution (Journal of Law 2016, item 1395), National Regulations – Prevention of environmental damage and repair (Journal of Law 2019, item 1395). Comprehensive monitoring of heavy metal soil pollution is mainly carried out by the Environmental Protection Inspection.

Additionally, research is carried out as part of the State Monitoring of the Environment, conducted by the State Geological Institute and individual scientific institutions and universities. Research data are available in reports and are also included in the annual elaborations of the Central Statistical Office (CSO) on environmental protection. The permissible contents of noxious substances in terms of land groups distinguished on the basis of their use and land subgroups are given in the Ordinance of the Ministry of the Environment of 1 September 2016 on the method of conducting the assessment of ground surface pollution (Journal of Law 2016, item 1395).

CONTAMINATED SITES AND THEIR REMEDIATION TECHNIQUES

Topsoil heavy metal contents are characterised by significant variability caused by such natural factors as geological formation and background levels as well as anthropogenic factors: industrial and mining activities, waste and landfill, urbanisation and transport. Regardless of these aspects the average heavy metal amounts in Polish arable soils are concurrent with data presented by Tȯth et al. (2016) for European soils. Thus most Polish soils contain amounts of metals within acceptable concentrations and thus they may be classified as soils of high agricultural value. Arable soils contaminated with heavy metals occur locally in Poland, mainly in industrialised areas, which account for less than 3 % of the country's area. In this aspect the lands are located in the areas of mining and processing of metal ores, both current and historical, the vicinity of metallurgical plants as well as municipal and industrial landfills, while urban and post-industrial areas also need to be calculated. The atmosphere, and specifically particulate matter, is an abundant metal source for plants grown in the vicinity of metallurgical plants. A similar tendency for European soils was underlined by Tȯth et al. (2016), who occasionally found polluted sites in any regions of the continent, but they were mainly connected with historical and recent industrial and mining areas. Currently among various anthropogenic factors, metallurgical dusts should be taken under consideration as a heavy metal source, because they are gradually redistributed and easily transported in the soil, water and air. Industry was the dominant source of cadmium emissions in 2017 (75 %), which included emissions from combustion processes and emissions from production processes. The main sources of Pb, Zn and Cr emissions in 2017 were connected with production processes, especially iron and steel metallurgy and amounted to 58 %, 45 % and 47 % respectively, of total emitted amounts. In the case of Ni in 2017 the main combustion processes were related with the energy production and transformation sector such as coal and fuel oil, as well as combustion processes both in industry and outside it (households). Road transport (34%) was the dominant source of Cu emissions in 2017, with pollution originating primarily from abrasion of tires and brakes. The dominant source of Cd emissions in 2017 was industry (75 %), which included both emissions from combustion processes and emissions from production processes. However, due to the increased ecological awareness expressed in reducing industrial emissions and waste landfill use, increasing purity of various agrochemicals, eliminating the presence of heavy metals in different products of general use, the amounts of heavy metals introduced into the environment, including soils, have been sharply decreased. This tendency was confirmed by data of the Central Statistical Office (CSO 2019). In 2017, compared to 2000, a reduction was recorded in atmospheric emissions of chromium, zinc, cadmium and nickel. Only in the case of copper and lead, the emission levels in 2017 were higher compared to those of 2000 by 25 % and 0.2 %, respectively (Figure 1) (CSO 2019).

Contaminated sites need to undergo remediation and/or reclamation processes. There are two main types of remediation: *ex-situ* (soil is excavated and remediation is carried out in another location) and *in-situ* (soil undergoes remediation processes on-site). Remediation techniques utilise physical/ chemical, biological and thermal technologies such as capping, encapsulation, landfilling, soil flushing, soil washing, electrokinetic extraction, stabilisation, solidification, vitrification, phytoremediation and bioremediation. Liu et al. (2018) indicated that chemical stabilisation serves as a temporary soil remediation technique, phytoremediation needs improvement in efficiency, surface capping and landfilling are applicable to small, seriously contamination sites, while solidification and vitrification are the last remediation options.

Land reclamation is a much broader concept of contaminated sites repair and is addressed to degraded or devastated lands. Rosada and Przewocka (2017) divided methods used in the reclamation of soils contaminated with heavy metals into three groups: immobilisation of metals, their removal from soil and changes in land use. For this purpose, the most popular technics such as liming, utilisation of minerals containing phosphates or sulfates, the application of substances with a large amount of organic matter or additives rich in clay minerals (Jakubus et al. 2019). The main aim of application of various substances is to form stable complexes with heavy metals, which make the metals sparsely available for plants and in such a form reduce ecological risk posed by heavy metals.

The second group includes processes leading to the partial removal of heavy metals from the soil. These methods, apart from biological techiques (phytoremediation), are very expensive and controversial because they lead to degradation of the soil environment. Especially the use of invasive techniques such as soil extraction and rinsing, electrochemical methods and removal of soil layers lead to heavy soil degradation. Unfortunately, such a non-invasive method as phytoremediation is characterised by low efficiency and a long duration. A considerable role is also associated with the utilisation of natural or synthetic heavy metal absorbents in the soil, but due to their costs they may be applied on a small scale.

The third group of methods is based on changing land use by planting woody and shrubby vegetation. This method is most often adopted around protection zones of industrial plants on soils contaminated with heavy metals and the zones are planted with fast-growing poplar.

The cost and duration of soil remediation are technique-dependent and site-specific, up to \$500 ton^{-1} soil (or \$1500 m^{-3} soil or \$100 m^{-2} land) and lasting approximately 15 years (Liu et al. 2018). Pérez and Eugenio (2018) for European countries documented that the median cost of remediation per site varies from country to country, representing a cost of 124 000 EUR per site. Additionally the average investment for investigation and remediation of contaminated sites was calculated as 618 EUR per capita.

CONCLUSIONS

Heavy metal emissions in Poland have remained at a similar level since 2000, showing a downward trend. In 2017, the dominant source of metal emissions included combustion processes in industry, coal combustion in households, production processes in iron and steel industries. Soils in Poland contaminated with metals constitute a small percentage and are mainly located in the industrial and mining areas located in southern and south-western Poland. Polish arable soils represent average contents of heavy metals and thus they may be classified as sites non-contaminated with heavy metals.

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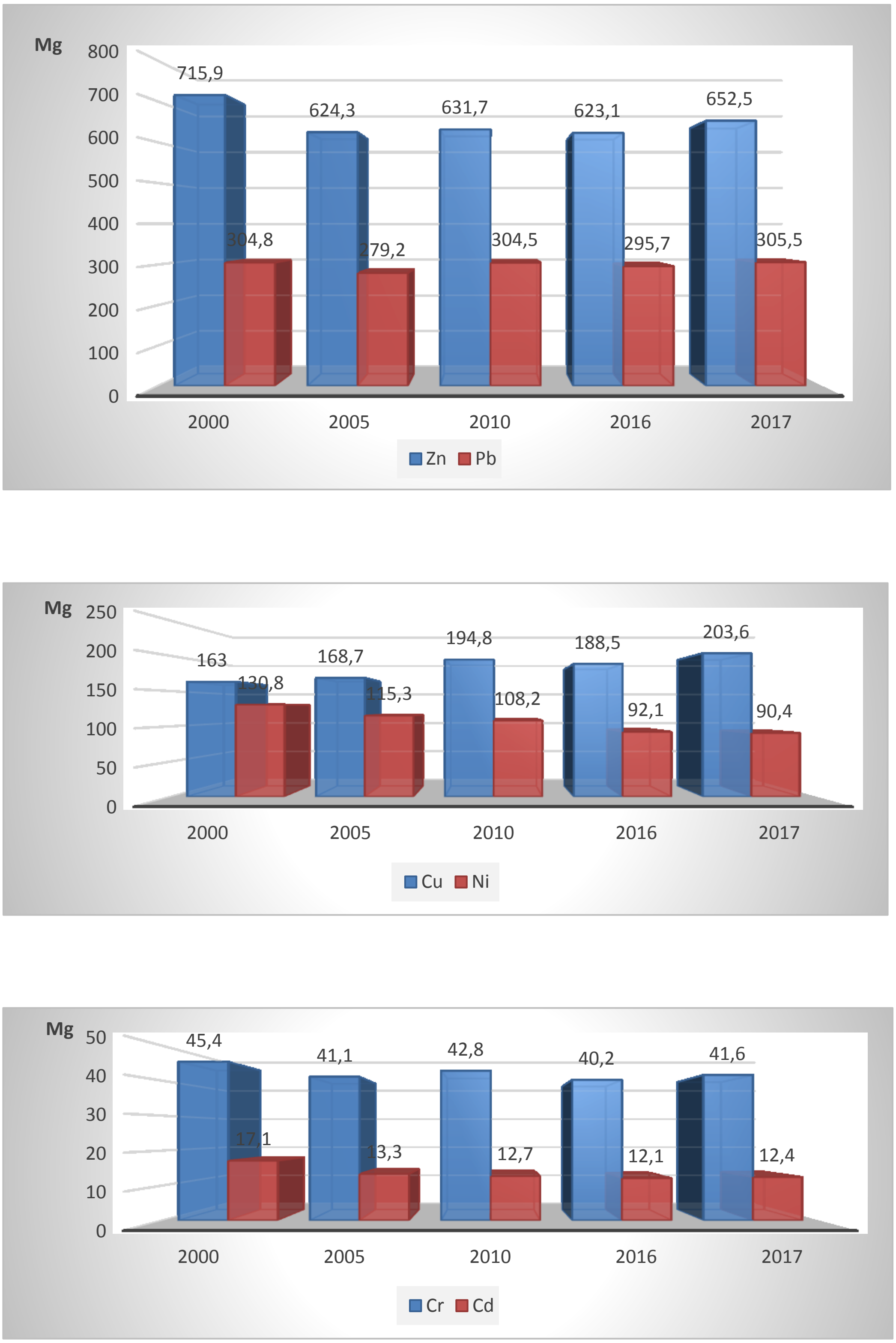

Fig. 1 The changes of heavy metal total emission in Poland in 2017 (CSO 2019)

CONTAMINATED SITES ASSESSMENT BY SELECTED MULTIVARIATE STATISTICAL METHODS

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KEYWORDS

Groundwater pollution assessment, Contaminated Site, Multivariate Statistics, Bratislava, Slovakia

INTRODUCTION

Groundwater pollution by anthropogenic activity is currently a significant problem threatening drinking water resources and endangering the environment (Liu and Lipták 2000; Rapant and Kordík 2003). Multivariate statistical analyses were performed in this study to assess the groundwater pollution by contaminated sites in former industrial zone in Bratislava, Slovakia. In Slovakia, such procedure does not reflect assessment of contaminated sites. Multivariate statistical methods offer a precise insight in the issue of contaminated sites.

MATERIAL AND METHODS

The area of interest is located in the former industrial complex in Bratislava, Slovakia, where the Apollo Refinery was operating until 1944 (Fig. 1). The Apollo refinery was destroyed by allied forces and since then a large volume of oil has leaked to the rock environment. In addition to the Refinery in the industrial area, the factories Gumon and Chemika (and many more) operated in the recent past as well. From the site of the former Apollo Refinery, pollutants, especially oil substances, BTEX and polycyclic aromatic hydrocarbons (PAHs), have extended. The Gumon Chemical Plant was put into operation in 1911 and oil, BTEX and aliphatic chlorinated hydrocarbons (CAHs) have spread from the area of factory (Auxt et al., 2002 in Kordík et al., 2015). The Chemika Plant was a factory that concentrated on paints and varnish production. High oil substances content, such as gasoline, oil, diesel or kerosene, have also been observed within the site (Kordík et al., 2015; Jantáková et al., 2018).

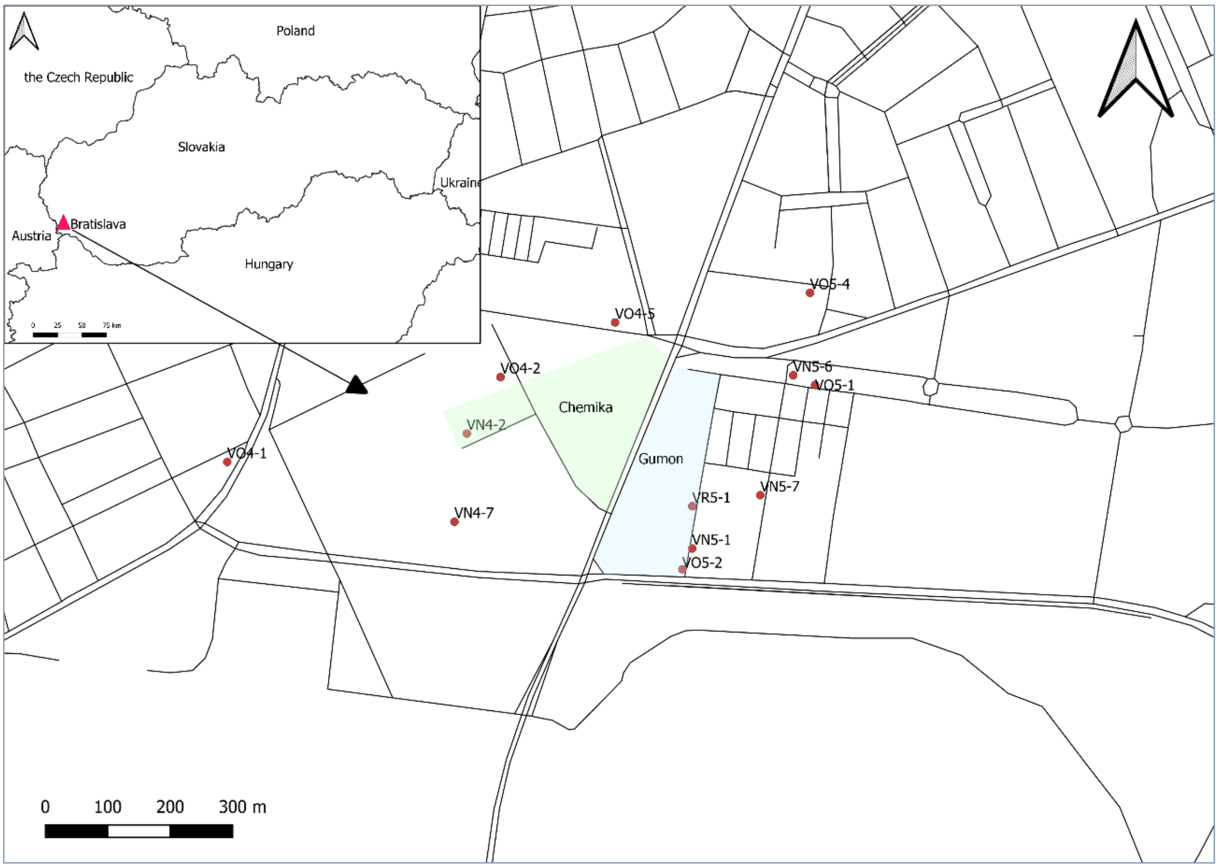

Fig. 1 Map of the studied locality

Multivariate statistical analyses represented by Spearman’s rank correlation analysis and hierarchical cluster analysis (HCA) were performed to interpret hydrogeochemical data in order to get a picture of contaminated sites of Chemika and Gumon. Shapiro-Wilk test was performed to recognize the normality of data. Considering the non-normal distribution, nonparametric methods were used. To examine the degree of association, the Spearman's rank correlation coefficient (ρ) was used. The coefficient acquires the values 〈-1.1〉 , where ρ = 1 indicates a perfect positive association, while perfect negative if ρ = -1. The significance of the correlation was tested by a two-tailed significance test at the significance level α < 0.05 (Helsel & Hirsch, 1992). Q-mode and R-mode HCA were used to classify boreholes and hydrogeochemical parameters into groups with a maximum degree of association between objects in the same group and a minimum degree of association between objects in different groups (Kráľ et al. 2009). Dendrograms (a binary tree) were produced to illustrate the relationships revealed by HCA (Banoeng-Yakubo et al., 2009).

RESULTS

The Spearman’s rank correlation results are presented in Table 1. The highest correlation between EC and Cl^- and Na^+ ($\rho = 0.99$) reflects impact of Cl^- and Na^+ ions on the EC value. Negative strong correlations among pH and selected parameters (EC, HCO_3^-, Cl^-, Mg^{2+}, Na^+) suggest an opposite development of pH considering the increase/decrees of those parameters. Strong positive correlation was observed between COD and NES ($\rho = 0.92$) and COD and TOC ($\rho = 0.92$) reflecting the presence of organic pollution in groundwater.

Tab. 1 Spearman’s correlation matrix

	pH	EC	HCO_3^-	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	NH_4^+	NES	PAU	Nap	TOC	COD	Surf
pH														
EC	**-0,97**													
HCO_3^-	**-0,93**	**0,92**												
Cl^-	**-0,95**	**0,99**	**0,87**											
Ca^{2+}	-0,56	0,47	0,59	0,51										
Mg^{2+}	**-0,92**	**0,90**	**0,88**	**0,91**	**0,75**									
Na^+	**-0,94**	**0,99**	0,90	**0,98**	0,44	**0,89**								
NH_4^+	-0,51	0,46	0,66	0,32	0,19	0,38	0,44							
NES	-0,47	0,38	0,65	0,33	0,38	0,35	0,33	0,62						
PAU	-0,38	0,31	0,42	0,26	0,01	0,22	0,31	0,53	0,55					
Nap	0,10	-0,05	0,05	-0,10	-0,34	-0,29	-0,05	0,31	0,34	0,60				
TOC	-0,49	0,44	0,70	0,35	0,29	0,34	0,42	**0,80**	0,91	0,66	0,50			
COD	-0,32	0,26	0,55	0,20	0,39	0,25	0,22	0,65	**0,92**	0,51	0,40	**0,92**		
Surf	0,01	0,02	0,20	-0,02	0,19	0,02	0,01	0,37	0,64	0,41	0,51	0,64	0,75	

Note: Bolds indicate correlations at the significance level $\alpha < 0.05$.

(Nap – naphthalene, Surf – surfactants, NES – nonpolar extractable substances)

Two-step groups have been recognized in dendrogram at Fig 2a. The first group is composed of fundamental chemical parameters present in groundwater. The second group represents the organic pollution at the sites. Dendrogram at Fig 2b consists of three main clusters. Median of chemical parameters represented in the observed boreholes in selected clusters is shown in Table 2. The most polluted boreholes are grouped in cluster 1 (VO5-2, VN4-7). The least affected boreholes by pollution (even the contamination is still present) are grouped in cluster 3 (VN4-2, VO4-1, VO4-5).

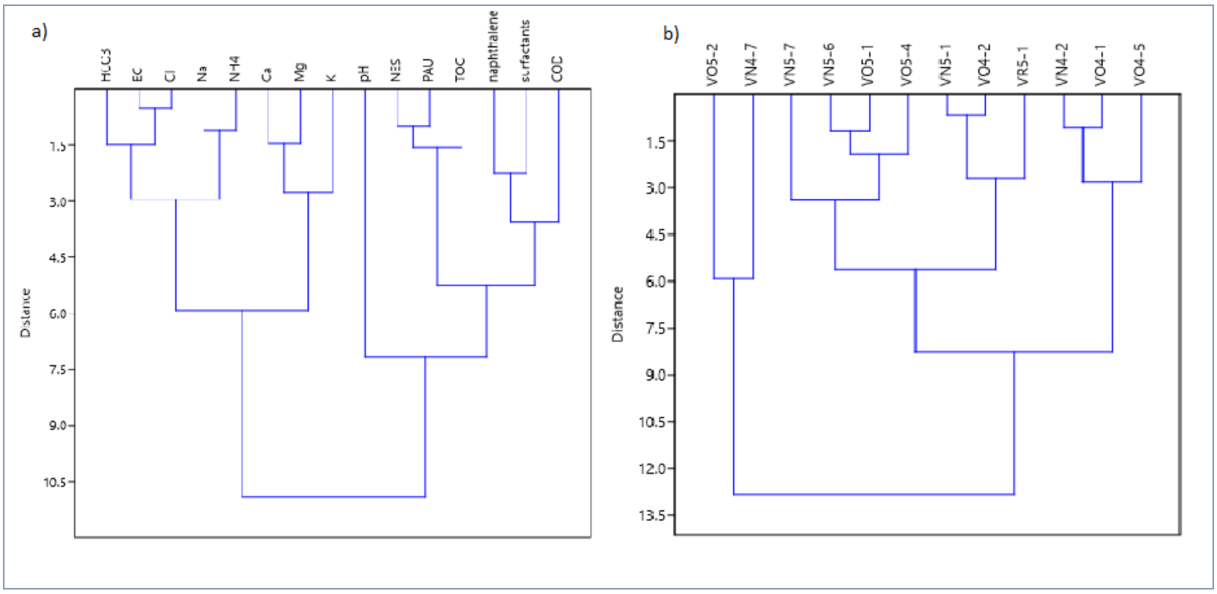

Fig. 2 Hierarchical dendrogram of chemical parameters (a) and boreholes (b)

Tab. 2 Median of the parameters of the three main clusters (dendrogram Fig2b) determined by HCA

Cluster	pH	EC	HCO_3^-	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	K^-
1	7,03	161,50	619,00	140,00	99,90	30,60	169,60	11,05
2	7,42	69,70	375,00	32,00	94,40	19,00	26,80	7,07
3	7,27	107,00	402,00	75,40	113,00	26,10	61,60	15,60
Cluster	NH_4^+	COD	TOC	PAL	NES	Nap	PAU	
1	4,23	7,44	10,35	0,33	0,47	0,03	0,21	
2	0,36	2,91	5,00	0,67	0,03	0,02	0,00	
3	0,03	1,28	1,30	0,09	0,01	0,02	0,03	

CONCLUSION

The use of a combination of the aforementioned methods represents a promising tool for risk assessment, for the evaluation of geological survey on contaminated sites and for the process of environmental burden assessment itself.

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CURRENT HYGIENIC CONDITION OF AGRICULTURAL SOILS IN KROMPACHY-RUDŇANY AREA

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ABSTRACT

Krompachy-Rudňany area 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 area were determined. The most risk elements on agricultural soils of Krompachy-Rudňany area 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.

KEYWORDS

Soil monitoring, soil contamination, risk elements, Krompachy-Rudňany area, Slovakia

INTRODUCTION

The contaminated area 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 area was characteristic since 1899 year. Later, after 1991 year the mining activities have been slowly finished. In comparison with Rudňany, in Krompachy area 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., 2019). 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 area 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 area

Elements Statistics	**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

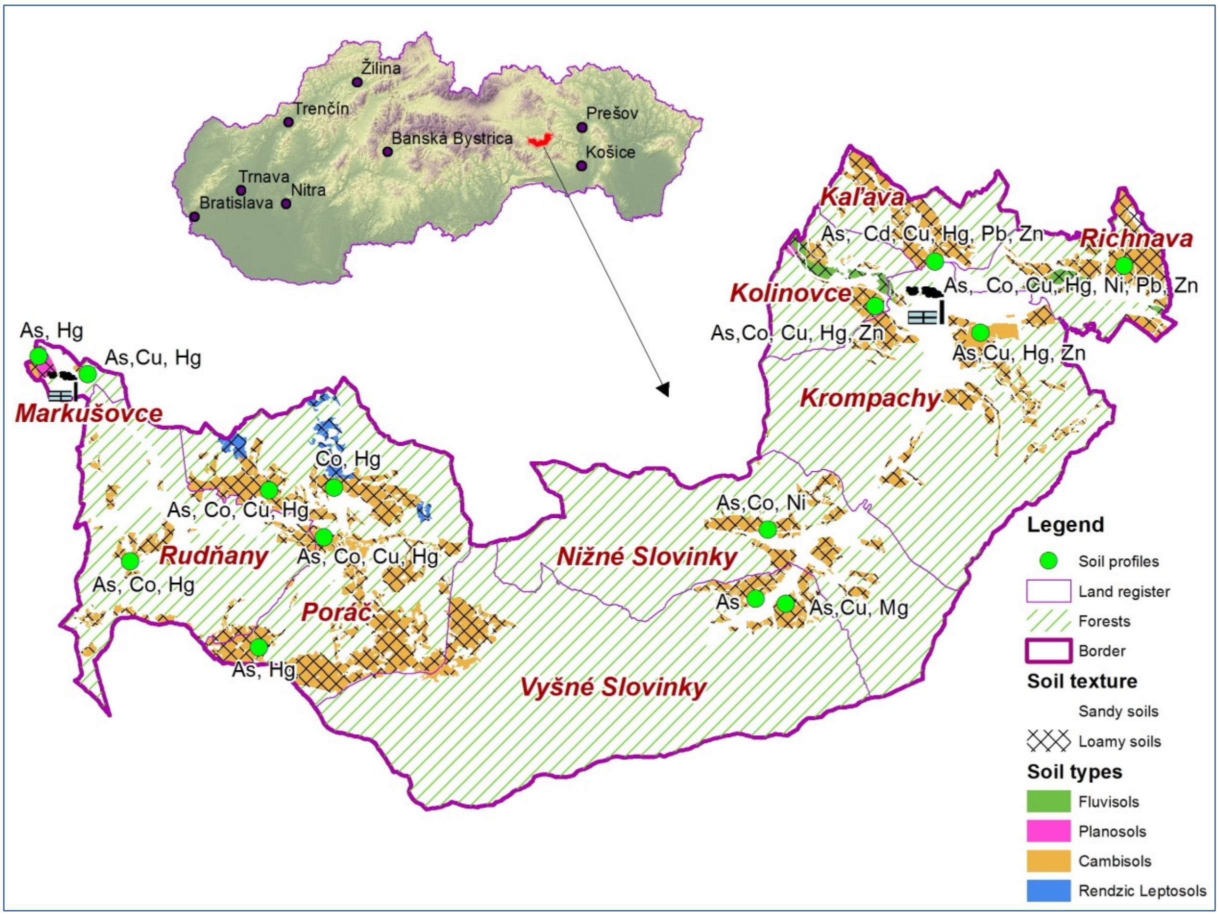
Table 2. Content of risk elements (mg.kg^{-1}) extracted with aqua regia in subsoil of agricultural soils (30–40 cm) in Krompachy-Rudňany area

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

Explanations: see Table 1

Location of Krompachy-Rudňany area 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 Maps 1 and 2.

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 (Table 1 and 2). It is an important risk element practically in all evaluated monitoring sites (Map 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 position.



Maps 1 and 2 Krompachy-Rudňany area and distribution of above-limit values of risk elements on agricultural

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 (Map 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., 2019).

Average content of cobalt in topsoil and subsoil slightly exceed the hygienic value (MPRV SR, 2013) – (Table 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 exceed 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 nickel 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 (Map 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 (Map 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 (Table 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., 2019).

Average content of Hg in agricultural soils of Krompachy-Rudňany area 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 %) (Table 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 area 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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WILL NATURAL SORBENTS IMPROVE SOIL HEALTH IN CONTAMINATED MINING SITES?

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KEYWORDS

Technosol, sorbent, potentially toxic elements, chicken manure, bentonite, biochar, organo-zeolitic substrate

INTRODUCTION

Mining activities produce a special type of soil referred to as technosols, which are concentrated on mining heaps. They contain increased content of potentially toxic elements (PTEs) in the soil, which leads to the degradation of vegetation (Slukovskaya et al., 2019). One way to contribute to the improvement of the properties of technosol is adding sorbents, which are characterized as solid substances capable of absorbing or adsorbing other substances. They can be of inorganic or organic origin, natural or artificially prepared (Fingas, 2002). They also has an effect on the pH change. It is known that the acid soils affecting the release and mobility of some PTEs (Kabata-Pendias and Pendias, 1999).

In our paper we evaluate the effect of natural organic and inorganic sorbents added to technosol taken from two historically significant mining areas: abandoned Cu-mining spoil heaps Maximilian near Špania Dolina village (Central Slovakia) and abandoned Fe–Cu sulphide mine Libiola (Sestri Levante, Eastern Liguria, Italy) to improve soil properties (pH and change the contents of the selected PTE).

MATERIAL AND METHODS

During the vegetation season of 2019, a pot experiment was carried out in the greenhouse of the Faculty of Natural Sciences of Matej Bel University in Banská Bystrica. Stratified sampling of technosol was collected by from 0–20 cm depth from both of the heaps, Maximilian and Libiola. We used natural sorbents which were mixed with technosol in quantities I. Bentonite 10 %, II. chicken manure 1 %, III. biochar 20 %, IV. organo-zeolitic substrate (prepared by mixing perlite, chicken manure and $CaCO_3$) 9 %. The mixture of technosol and sorbents was put into self-watering pots. Each variant was realized in three replications. Due to the smaller amount of technosol from Libola, we did not use chicken manure as a sorbent. To the each pot 7 g of the grass mixture prepared by mixing of species colonial bentgrass (*Agrostis capillaris* L.), creeping bentgrass (*A. stolonifera* L.), red fescue (*Festuca rubra* L.) and kentucky bluegrass (*Poa pratensis* L.) in a ratio of 2 : 2 : 1 : 1 were seeded. There was a regular watering. After three months, the aboveground biomass of the plants was cut off and representative soil samples were taken from each pot. The content of PTEs in the soil samples was determined using the method multi-acid ICP-ES in an accredited laboratory at the Mineral Laboratories of Bureau Veritas (Vancouver, Canada). pH of soil samples was determined according to Sobek et al. (1978).

Tab. 1 Values of the monitored indicators of the natural sorbents influence on the change of soil properties

Locality	**Substrate**	**Average pH$_{H2O}$ b. s.**	**Average pH$_{H2O}$ a. c.**	**Average amount of Cu a. c.** ($mg \cdot kg^{-1}$)	**Average amount of Cn a. c.** ($mg \cdot kg^{-1}$)	**Average amount of Cr a. c.** ($mg \cdot kg^{-1}$)	**Average amount of Mn a. c.** ($mg \cdot kg^{-1}$)
Libiola	heap	3.42	3.43	2639	367	583	785
	BE	3.90	3.68	2156	300	457	799
	BCH	6.21	5.41	1590	246	327	612
	OZ	6.46	6.81	1838	276	393	675
Špania Dolina	heap	5.17	5.87	1153	37	17	249
	BE	6.72	6.73	889	41	14	370
	BCH	6.51	6.62	780	25	15	325
	OZ	6.91	7.22	900	40	17	245
	CHM	7.06	7.57	1145	39	18	215

Explanations: b. s. – before sowing, a. c. – after cutting, heap – technosol from the heap without added sorbent; BE – variant with bentonite; BCH – variant with biochar; OZ – variant with organo-zeolitic substrate; CHM – variant with chicken manure

RESULTS

The effect of used natural sorbents was not the same for each of the selected PTEs and to change of the pH. Libiola heap is more acidic (pH ≐ 3.42) compared to Maximilian heap (pH ≐ 5.17). Table 1 shows that the addition of sorbents to technosols at the beginning of the experiment contributed to an increase pH compared to control samples for Libiola in order BE < BCH < OZ and for the heap Maximilian BCH < BE < OZ < CHM. At the end of the experiment, the pH was higher than the previous measurements, except for the variant with bentonite and biochar in technosol from Libiola.

The analysis of control samples from the examined localities shows that they have a different content of selected PTEs. Technosol from the Maximilan heap contains several times lower amounts of Cu, Zn, Cr, Mn than technosol from Libiola. For the technosol from Libiola, biochard proved to be an effective sorbent for reducing the amount of Cu, Zn Cr, Mn and for the heap Maximilian Cu, Zn. Chicken manure was effective for Mn and bentonite for Cr. The different effectiveness of sorbents in reducing the amount of PTEs may be related to the change in pH, that affects their mobility and release.

CONCLUSION

The addition of natural sorbents (bentonite, biochar, chicken manure, organo-zeolitic substrate) contributes to the improvement of the soil properties of the technosol (change of pH and content of PTEs), which is documented in our study.

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AN INNOVATIVE HOLISTIC DPSIR-BASED APPROACH FOR THE REMEDIATION OF CONTAMINATED SITES

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KEYWORDS

Contaminant, DPSIR, impact, risk, stakeholders, Taranto

ABSTRACT

The DPSIR model is an useful guidance to decision-makers and it considers a chain of causal links starting from "Driving forces" (economic, environmental, human activities) through "Pressures" (emissions, waste, discharges etc.) to "States" (physical, chemical and biological situation of environment) and "Impacts" on targets such as human beings, eventually leading to political or technical "Responses". Despite its advantages, DPSIR does not explicitly state any direct cause-and-effect relationship and it is difficult to link the quality/quantity of certain pressures to the status indicators, as well as to establish a direct correspondence between a response and mitigation of impacts. In this context, this study aimed to develop and apply an innovative holistic approach based on an implemented version of DPSIR to the case study of Mar Piccolo in Taranto (Southern Italy), one of the most contaminated areas in Europe. For this purpose, three toolboxes were developed.

1. Toolbox 1 connects driving forces to pressures, identifying what is the current state of the system (D-P-S),
2. Toolbox 2 recognizes and categorizes different types of impacts (S-I),
3. Toolbox 3 gauges the effectiveness of responses to put into place to control the system states and impacts (I-R).

Given the complexity of the relationships involved, this work was focused on toolbox 1. Its main objective is to provide spatial extent and magnitude of the contamination in a certain area, also identifying all possible "hot-spots". The Italian Decree of the Ministry of Environment n. 173/2016 defined criteria and methodological procedures for classifying dredging sediments and their appropriate management, according to the pollution level and the eco-toxicological effects. Chemical data were integrated following the Weight-Of-Evidence (WOE) criteria (Sediqualsoft software), based on the number of parameters exceeding threshold limits, the magnitude of such exceedances and type of contaminant (Priority or Priority Hazardous substances, according to the Annex II of the Directive 2008/105/EC). The threshold values considered for the Ratio-to-Reference (RTR) calculations were the site-specific values of intervention for marine sediments (ICRAM, 2004).The Hazard Quotient for chemistry (HQC) is calculated according to Eq. 1, where an average RTR_W is obtained for all of the parameters with RTR ≤ 1 (i.e. below the normative limit), while the RTR_W was individually added into the summation Σ for those with RTR > 1 (Piva et al., 2011):

$$\mathrm{HQc} = \frac{\sum_{f=1}^{N} \mathrm{RTR_w(j)_{RTR(f)\leq 1}}}{N} + \sum_{k=1}^{M} \mathrm{RTR_w(k)_{RTR(k)>1}} \qquad \text{(Eq. 1)}$$

with N and M as the number of parameters with RTR respectively ≤ or > 1, while j and k are indices allowing to repeat the calculation for N or M times. The values of HQC are assigned to one of six classes of chemical hazard.

The Mar Piccolo of Taranto is a semi-enclosed marine basin in Apulia, Italy, and has a surface area of about 21 km^2 divided in two inlets. For several decades this area has been subjected to chemical pollution originating from different industrial activities, such as the steel plant ex-ILVA, the concrete factory Cementir, the Eni refinery station, and the Military Arsenal (Labianca et al., 2018) (Fig. 1a), but also human activities, such as wastewater discharge and mussel farming. The chemical data from the ISPRA coring campaign in the period 2005–2010 (ISPRA, 2010) were employed in this analysis. The pollutants considered were metals and organic compounds. The sample points and the coring depths at 0–10 cm, 10–30 cm, 30–50 cm, 100–120 cm are shown in Figures 1b, c, d, e.

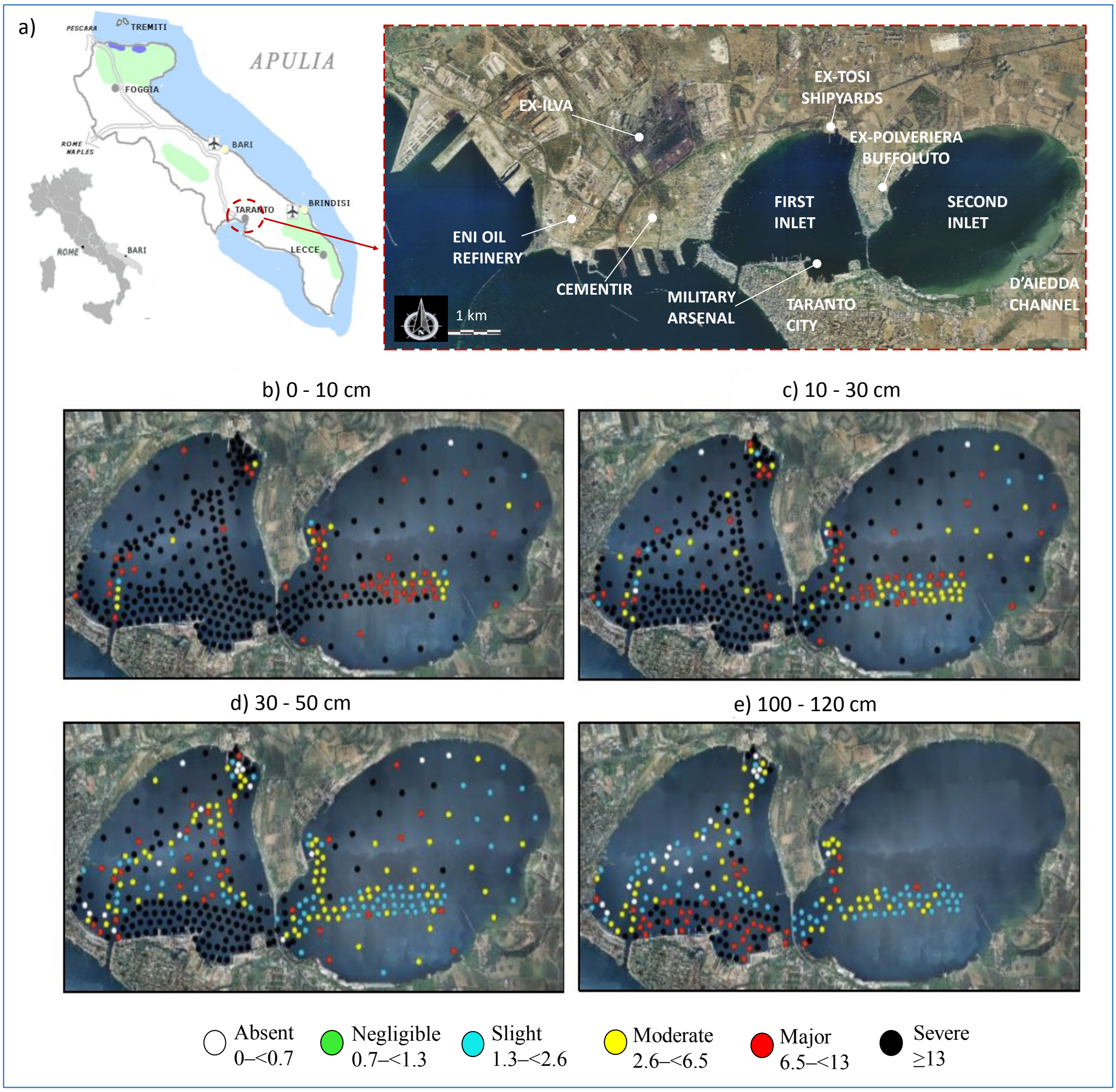

Fig. 1. (a) Localization of the Mar Piccolo of Taranto; HQc chromatic maps showing sediment chemical hazard at different depth (b) 0–10 cm, (c) 10–30 cm, (d) 30–50 cm, (e) 100–120 cm.

It is evident that the sediment quality increases with the depth. It is notable that the first layers of the sea bottom are the most polluted (0–10 cm, 10–30 cm, 30–50 cm), showing a spread contamination in both inlets of the Mar Piccolo. The area of the Marine Arsenal appears to be the most critical of the Mar Piccolo, since even deep layers (100–120 cm) record high values of the HQc index. A difference between the two inlets is also evident, highlighting a more severe, spread and deeper contamination in the First Seno. The obtained results made possible the identification of spatial extent of the contamination as well as possible "hot spots". This first toolbox is preparatory for the development of second and third toolboxes, with as final objective the identification of the best remediation technology. Of great importance was the use of a WOE approach, useful for summarizing large complex data sets into supplementary indices.

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THE BASIS FOR THE PREPARTION OF THE FIRST INVENTORY OF POTENTIALLY CONTAMINATED SITES (PCSs) IN SLOVENIA

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ABSTRACT

Slovenia does not have a register of potentially contaminated sites (PCSs) or a system of their comprehensive management. Therefore, based on the existing national spatial database of functionally degraded areas (FDAs), which includes abandoned areas of past human activities, we identified those areas, that depending on the previous activity and the current state, can be included in the PCSs database. We identified 411 areas as PCSs, which represents more than a third of all FDAs in Slovenia. Looking at the type of activity, PCSs of mineral extraction, industrial activities and infrastructure (landfills/waste disposal sites included) prevail. This is the first proposal of a database and of spatially displaying PCSs in Slovenia. We estimate that this is an appropriate basis for further supplementation, research, and in the future also for the preparation of appropriate measures. We plan to submit the first data to the European Environmental Agency at the beginning of 2021, which will enable the inclusion of the Slovenian data in the indicator for monitoring contaminated sites on the level of European Union.

KEY WORDS

first inventory of PCSs, functionally degraded areas (FDAs), old environmental burdens, waste disposal sites, soil, groundwater, online application for monitoring PCSs, Slovenia

INTRODUCTION AND PROBLEMS

Slovenia does not have a system of managing contaminated sites, i.e. sites identification, preliminary survey, main site investigation and implementation of risk reduction measures. The Ministry of the Environment and Spatial Planning is responsible for establishing a database of potentially contaminated sites (PCSs) due to binding regulations on waste and water protection (especially drinking water sources). The obligation to remediate in the past contaminated areas is carried out on the basis of the valid Environmental Protection Act (2004), but in reality, it is carried out unplanned, with a very limited extent, without defined goals or monitoring the implementation of remediation. In the case of the old environmental burdens, it is most often a matter of remediation of the contaminated soils or land. Abandoned landfills – municipal or waste disposals, abandoned areas of industrial and mining activity (i. e. brownfields) and polluted underground pits predominate. Despite remediation falls under the authority of the Ministry of the Environment and Spatial Planning, the municipality of the contaminated sites is also financially involved. Currently, the state has no plans and specific priorities for the implementation of remediation, and in 2020 we began activities to establish the first inventory of PCSs.

PRELIMINARY RESULTS ON POTENTIALLY CONTAMINATED SITES IN SLOVENIA IN 2020

Due to the absence of a systemic approach, the preparation of the first inventory was based on the national records of so-called functionally degraded areas (FDAs), i.e. underutilized or abandoned areas with a visible impact of the previous use and reduced use value. The FDA spatial data layer was established in 2017 (for the needs of the Ministry of Economic Development and Technology), and the data was updated in 2019 and 2020 (Lampič, Kušar, Zavodnik Lamovšek, 2017; Internal data, 2020). Thus, in Slovenia we can monitor spatial processes on completely or partially abandoned areas and identify areas in which there is a greater interest of investors and areas which remain abandoned for a longer period. According to the latest data (September 2020), we have 1167 FDAs in Slovenia. For the purpose of establishing the PCSs database, we focused on those FDAs where activities that cause soil and groundwater pollution were carried out (in some places they are still carried out) (a) industrial and commercial activities – e. g. industrial and commercial services, mining, b) military, c) storage – e. g. oil storage, chemical storage, storage of manure, d) agricultural sites, e) waste water treatment facilities etc. From the mentioned data we identified 411 areas as PCSs, which represents more than a third of all FDAs in Slovenia.

We obtained a series of data on individual locations from field visits, interviews and from other sources, that indicate the presence of various types of pollution as well as other forms of environmental degradation and environmental threats (e. g. extreme spread of non-native invasive plant species, presence of asbestos (in construction material – asbestos roofing), asbestos waste, poor physical conditions of buildings (dangerous sites) …). We note that the share of PCSs among abandoned areas of agricultural, industrial, infrastructural (including landfills) and mining activities is significantly higher compared to other FDAs.

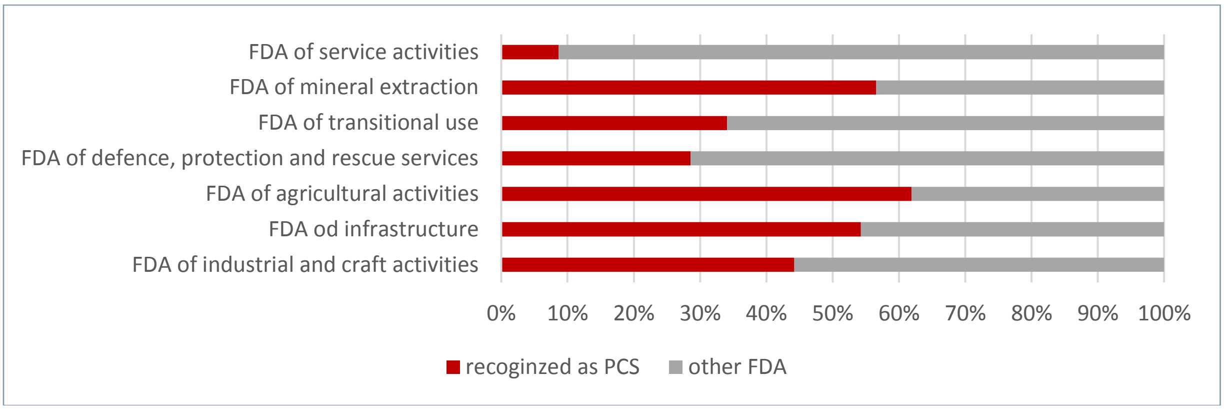
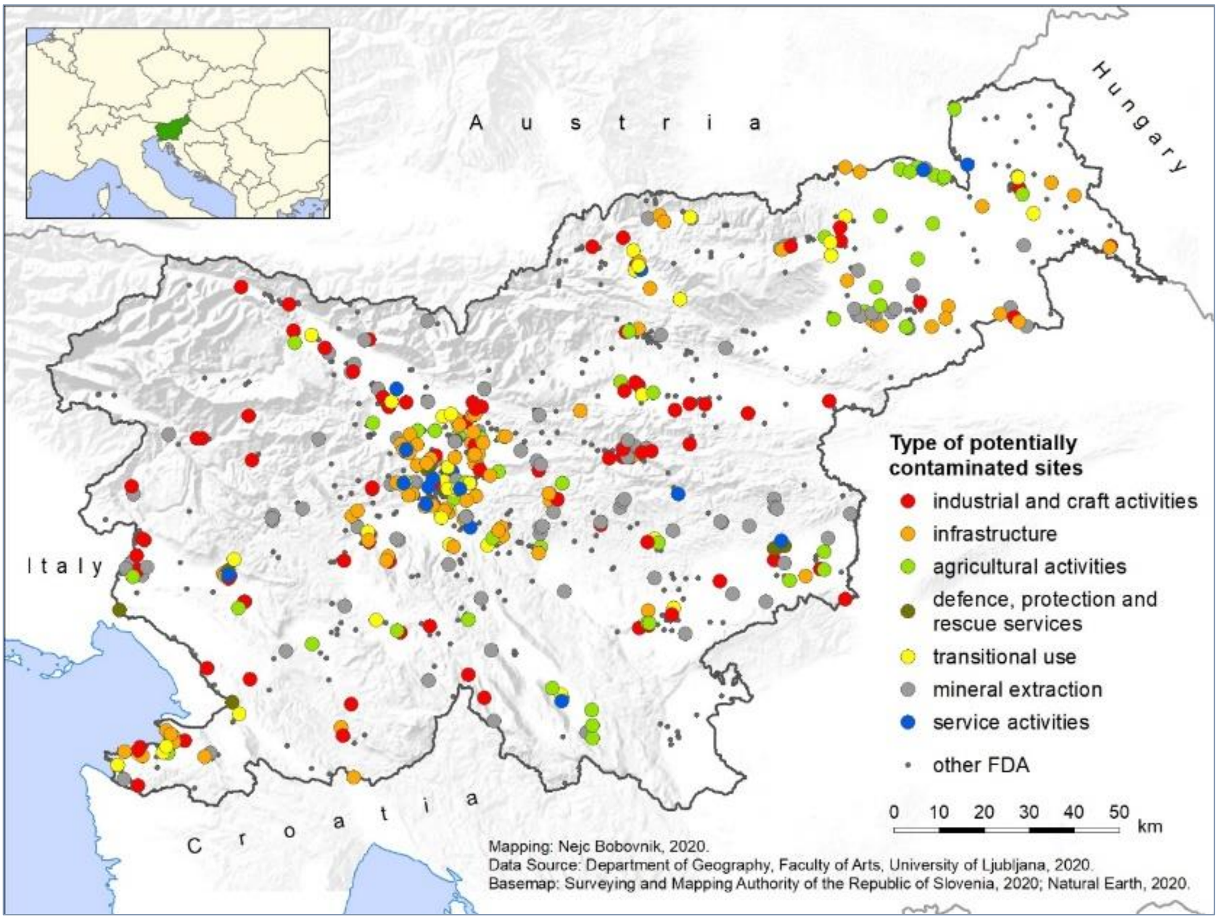


Fig 1. Share of recognized potentially contaminated sites (PCSs) in the functionally degraded areas (FDAs) database for each FDAs type.

The spatial representation of PCSs in Slovenia indicates that contaminated areas are present in both urbanized and rural areas. The differences are greater in the types of activities, as in the rural areas, predominant types are areas of agricultural activity, military and mining, while in urban areas PCSs of industrial activities, service activities and transitional use prevail.



Mapping: Nejc Bobovnik, 2020.
Data Source: Department of Geography, Faculty of Arts, University of Ljubljana, 2020.
Basemap: Surveying and Mapping Authority of the Republic of Slovenia, 2020; Natural Earth, 2020.

Fig 2. Spatial distribution of potentially contaminated sites (PCSs) in Slovenia by the type of activity.

The presentation of currently identified types of activities on PCSs in Slovenia does not fully correspond to the structure for monitoring contaminated areas according to the source of pollution (van Liedekerke et al., 2014). But we can clearly understand that the greatest threat of pollution (soil and groundwater) are represented by industrial activities, by infrastructural activities (with landfills) and the extraction of mineral resources, in some regions also by agricultural activity.

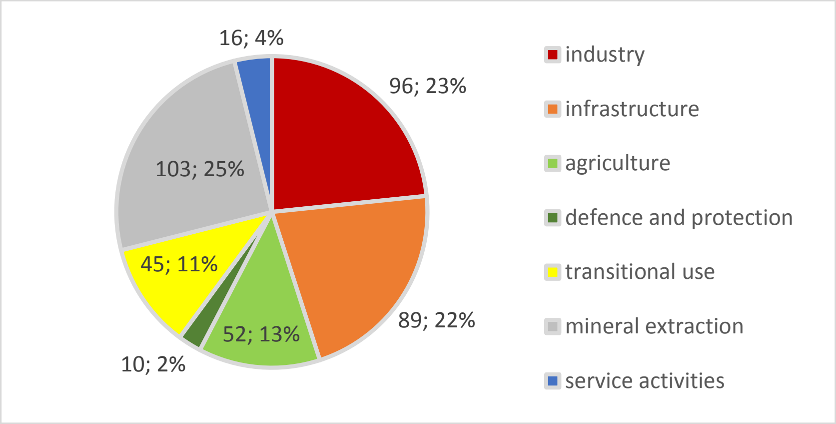


Fig 3. The structure of potentially contaminated sites (PCSs) in Slovenia by the type of activity (number and share of PCSs).

Information on spatial and development plans of municipalities for FDAs in Slovenia indicates the possibilities of remediation of identified PCSs. Among the 411 areas the municipalities do not see a real possibility of development and remediation for as many as 188 PCSs (46 %). They often point out old environmental burdens as one of the key obstacles to development, which reaffirms the need for prior remediation for successful land recycling. Only 75 areas (18 % of PCSs) have spatial plans in place, but often in many places the environmental remediation is not planned.

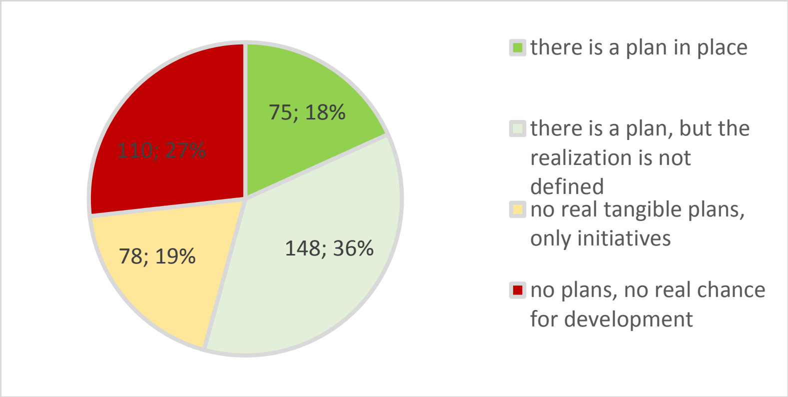


Fig 4. Spatial and development plans for potentially contaminated sites (PCSs) in Slovenia (number and share of PCSs).

From responsibility for remediation of PCSs point of view, the problem of ownership must be mentioned. In the revival of FDAs in Slovenia, we are already facing problems connected to ownership (many private owners, rapid changes of owners, etc.) and it will be similar with identified PCSs. Only 55 areas are publicly owned, and all others are either privately owned or have mixed ownership (public-private). Most PCSs have changed owners recently, so enforcing the “polluter pays” principle will be even more challenging.

CONCLUSION

Empirical studies of all 1167 FDAs in Slovenia, which are the result of one of the most detailed (and systematic) approaches on the national level, have highlighted that many aspects of spatial and environmental degradation require urgent consideration. In 2020, Slovenia does not yet have data on estimated PCSs, much less by pollution sources and by the type of pollutants. By analysing the national records of FDAs in Slovenia, we have excluded those areas where, due to the past activity, soil pollution can be expected with great certainty, and in some places also groundwater pollution. Depending on past and current activity, the level of threat can vary. From the available data and extensive fieldwork, we found that, in addition to the old environmental burdens, new environmental threats are appearing spontaneously and to a large extent – illegal dumping of large quantities (including hazardous) of waste (systematic dumping on private land by companies or private individuals), dumping of various soil residues and construction waste. These are numerous and scattered activities, but the environmental inspection in Slovenia is still unresponsive in this field. We would like to point out that due to the lack of data and spatial information on potentially contaminated sites in Slovenia, monitoring of soil and groundwater pollution is less effective, and mostly we lag behind in the preparation and implementation of appropriate measures.

Fig 5. An example of an illegal landfill – disposal of hazardous waste in the immediate hinterland of the Slovenian capital Ljubljana (a). In August 2020, there were two major fires in the landfill area (b).

Fig 6. Several industrial sites in Slovenia remain untouched due to ownership issues and presence of old environmental burdens.

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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.

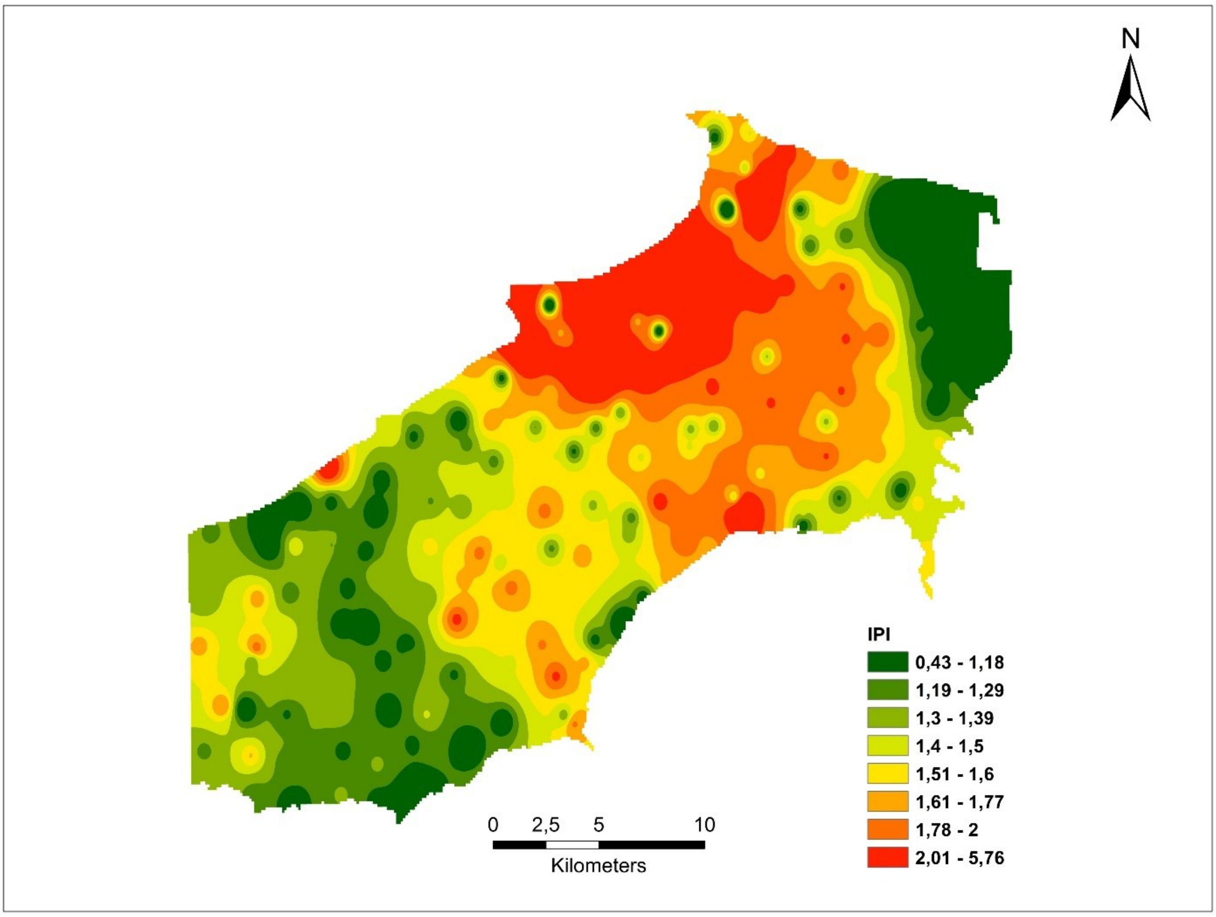

Fig. 1 Spatial distribution of integrated pollution index of metals in soils of the Mitidja plain.

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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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.

The contaminated superficial aquifer consists of a coarse sand with permeability between 3.6×10^{-4} and 1×10^{-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).

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

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

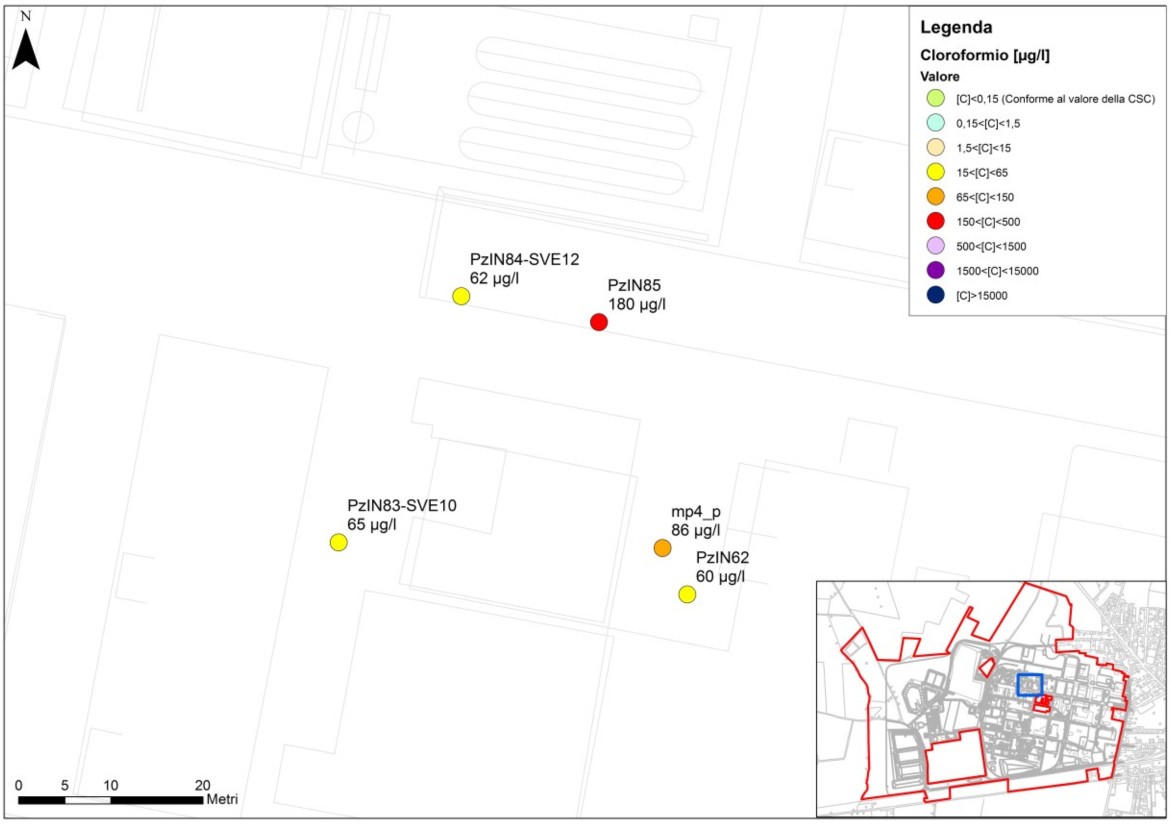


Fig. 2 Pre-treatment CF concentration in the source zone (September 2017)

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.

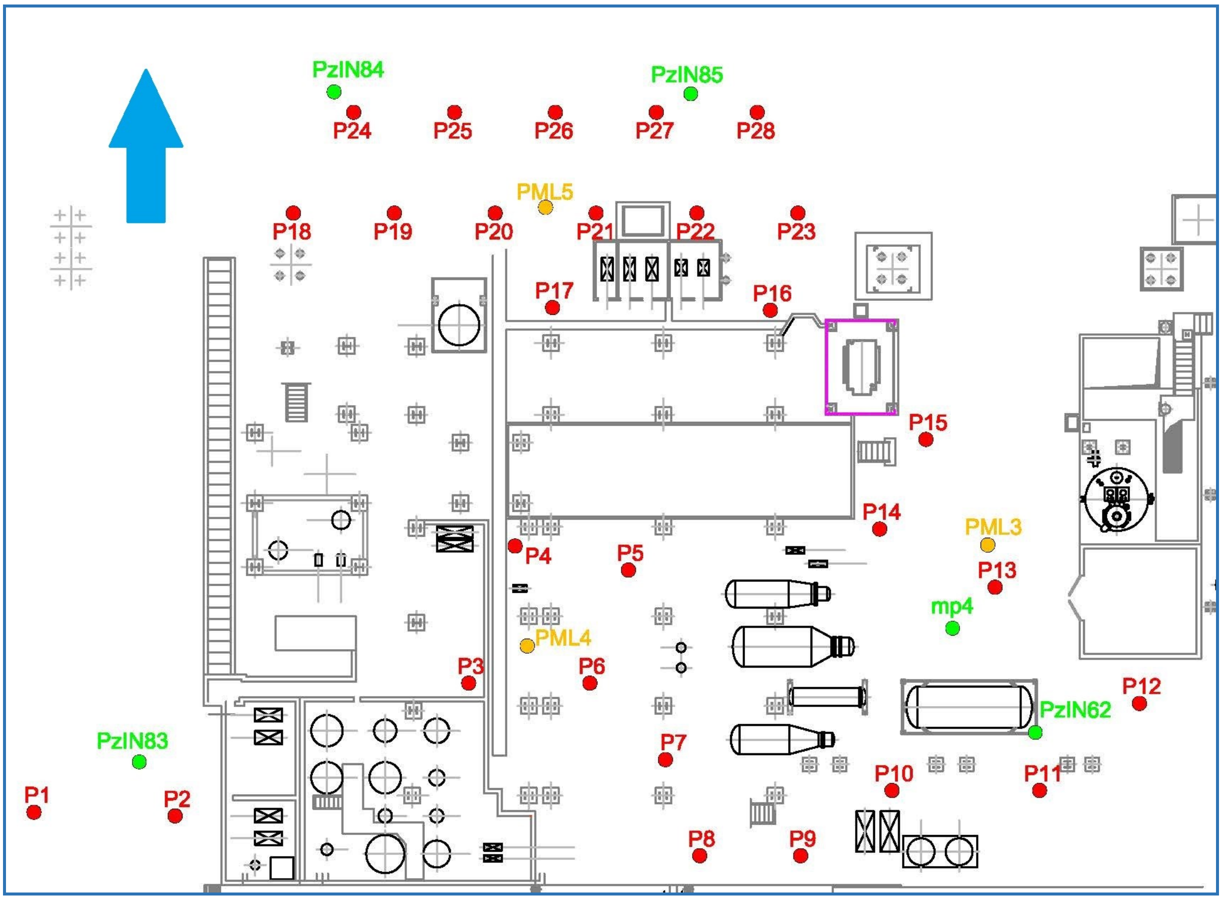
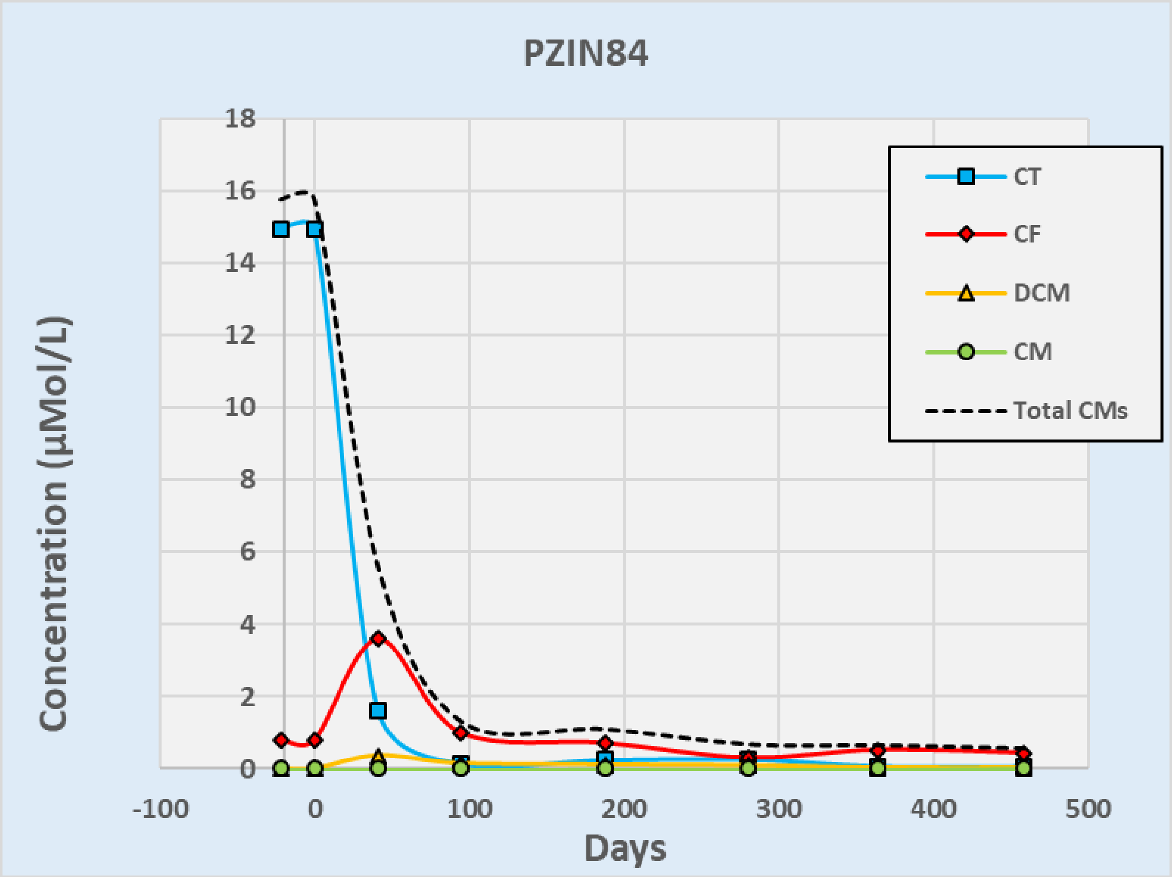


Fig. 3 Grid of the injection points (in red) and monitoring points (in green and orange) together with the stratum-direction

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.


PZIN84
Concentration (µMol/L)
18
16
14
12
10
8
6
4
2
0
-100
0
100
200
300
400
500
Days
CT
CF
DCM
CM
Total CMs

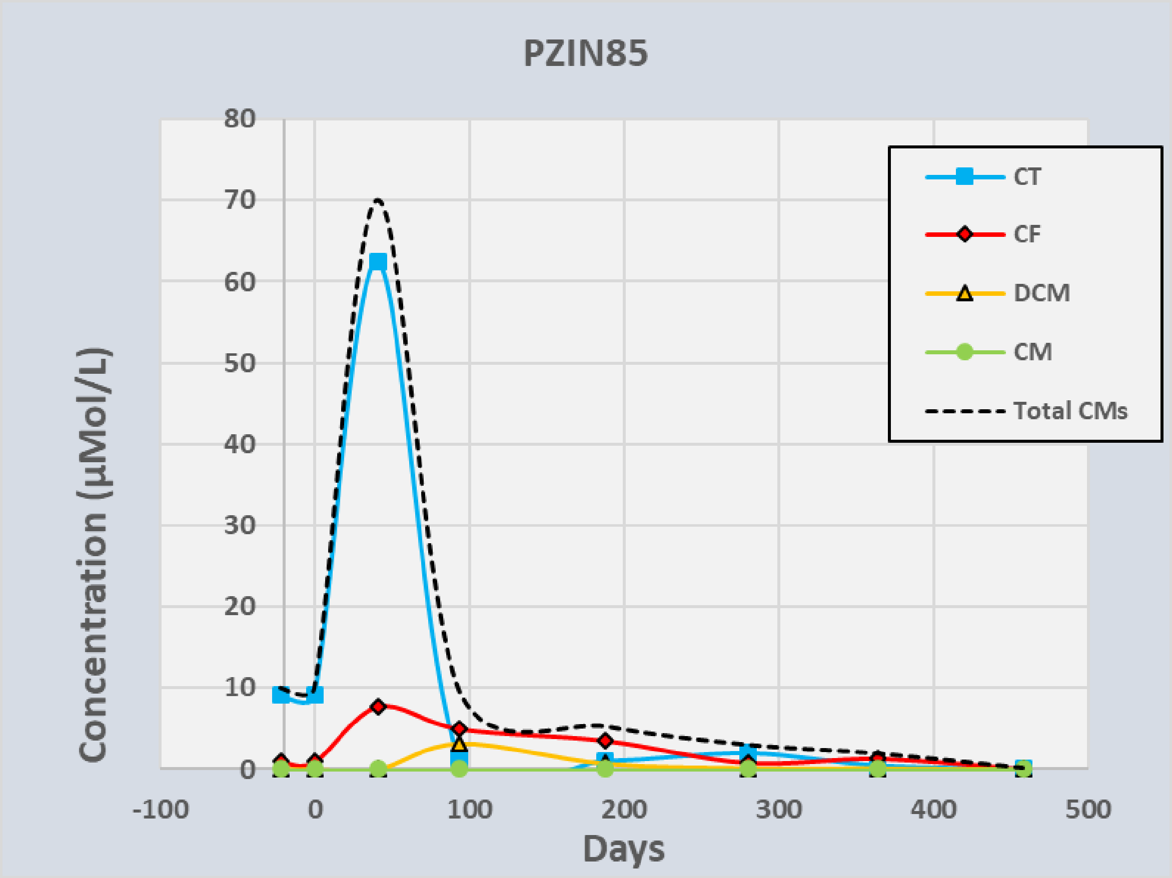

PZIN85
Concentration (µMol/L)
80
70
60
50
40
30
20
10
0
-100
0
100
200
300
400
500
Days
CT
CF
DCM
CM
Total CMs

Fig. 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).

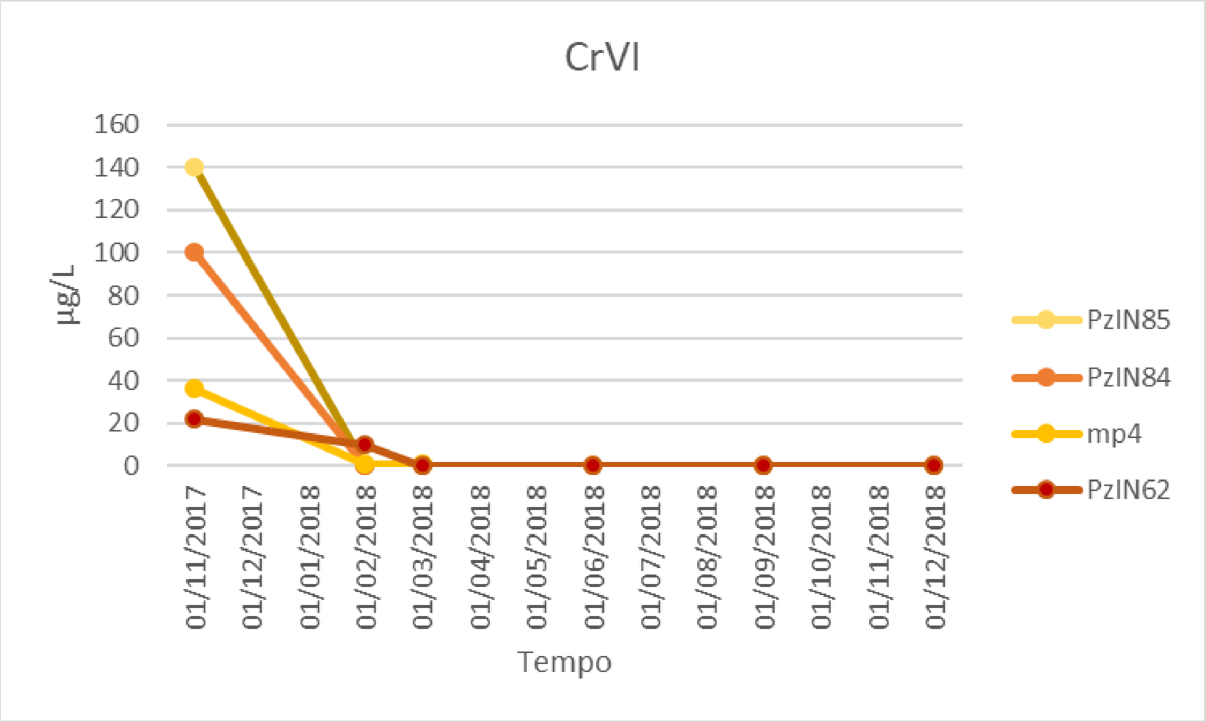


Fig. 5 Evolution of hexavalent chromium concentrations in groundwater at the main monitoring points in the treatment area before and after the EHC Liquid injection performed in December 2017

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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USING SILICON-RICH INDUSTRIAL BY-PRODUCTS FOR PURIFICATION OF WASTE-WATER AND CONTAMINATED SITES: THEORY AND TECHNOLOGY

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KEYWORDS

Heavy metals, mine tailings, purification, silicon, waste water

ABSTRACT

Many modern technologies aimed at resolving environmental problems have limited application because of high cost or/and low efficiency. As evident from recent reports, silicon (Si)-rich substances are a promising agent in technologies of detoxification of waste waters and contaminated sites and regulation of heavy metal behavior in the environment. Metallurgical and chemical industries produce a lot of Si-rich by-products, which often don't contain hazardous elements and could be used for purification of industrial waste water and remediation of contaminated sites. Considering that some by-products had insufficiently high content of active Si, technology for Si activation was used. Filtration tests have shown the ability of initial and treated industrial by-products to reduce the concentration of As, Cd, Cr, Hg, and Ni in waste water by 95 to 99 %. Greenhouse test with soils from contaminated sites (China and Russia) has demonstrated that application of Si-rich products provided reductions in the mobility of pollutants by 60 to 98 % and protected cultivated plants against toxicity. The efficiency of Si-rich products directly depends on the content of water- and acid-soluble Si. Several Si-mediated mechanisms, that impact the pollutant behavior, were determined:

1) interaction between monosilicic acid and heavy metal with the formation of insoluble silicates;
2) adsorption of pollutants on the surface of Si-rich materials;
3) capsulation of pollutants by polymers of silicic acid.

Mine and industrial waste waters and leaching of pollutants from contaminated sites (landfills, mine tailings and ex-industrial areas) are the largest sources of pollutants that cause the environmental and human health problems [1]. Elaboration of cost-effective technologies for the waste water detoxification and the pollutant immobilization is critically important. Conventional techniques for purification of the waste water and recovering of contaminated sites can be prohibitively expensive and low effective [2]. One of the most prospective ways to reduce the remediation cost is related to involving local by-products, for example slags. Some types of slags are recommended to use for landfill formation [3]. However, slags are generally low efficient for reduction of heavy metal (HM) bioavailability, moreover, some slags contain potentially toxic elements and can be a source of additional environmental contamination.

As evident from recent reports, silicon (Si)-rich substances could be a promising agent in technologies for detoxification of waste waters and contaminated sites and regulation of heavy metal behavior in the environment [4]. Our preliminary research showed that monosilicic acid can be used for enhancing the efficiency of mineral substances as an adsorbent [5, 6]. The aim of this investigation was to demonstrate the impact of Si-treatment on the efficiency of metallurgical slag to adsorb heavy metals from mine tailings and mine waste-water.

Calcium-Si slag (Novokuzneck metallurgical enterprise, Russia) and zeolite (Orlov region, Russia) were treated with concentrated monosilicic acid (MSi). The activation process included mixing of a material with monosilicic acid solution contained 1.2 g L^{-1} of Si at a proportion of 4:1 followed by drying under normal conditions.

Treated slag and zeolite were tested for:

(a) filtration of contaminated water and

(b) growing barley plants on contaminated soil.

Filtration test was conducted in plastic columns with diameter 5 cm and length 20 cm. Untreated and MSi-treated slag and zeolite were mixed with quartz sand at a proportion of 1:1 to enhance water penetration. Water was contaminated with As – 10 ppm; Cd – 10 ppm; Cr – 10 ppm, Hg – 10 ppm; Ni – 10 ppm; and Pb – 10 ppm. The contaminated water was added to the column at 100 mL h^{-1} using a peristaltic pump. The percolates were collected in fractions at 1 hour intervals. A total of 1L of water was applied to each column. Percolated solutions were analyzed for As, Se, Cd, Pb, Ni, Cr, and Hg by ICP OES spectrometer Perkin Elmer Optima 5300 DV. Each treatment had 3 replications.

Greenhouse test was performed in a climatic chamber at 24 ^{o}C and day/night regime 12/12 hours. Barley (*Hordeum vulgare* L.) was grown in plastic pots filled with 200 g of ground from cromium mine tailings („Chrompik“ enterprise, Russia). The treated and untreated slag and zeolite were added at a rate of 5 g pot^{-1}. After 3 week-growth, barley was harvested and biomass of roots and shoots was measured. The total leaf contents of As, Se, Cd, Pb, Ni, Cr and Hg were determined by ICP OES spectrometer Perkin Elmer Optima 5300 DV after microwave digestion in a HNO_3-H_2O_2 mixture. Each treatment had 3 replications.

Waste water filtration test demonstrated reductions in As, Cd, Cr, Hg, Ni and Pb to the levels that meet the requirements of Integrated Wastewater Discharge Standard GB 8978б, whereas untreated zeolite and Ca-Si slag adsorbed only small portion of pollutants (Fig. 1). The treatment with MSi changes remarkably the surface of both slag and zeolite, as was shown in our previous study [6]. Soil-applied MSi-treated materials contribute to the monosilicic acid release to the soil solution. Monosilicic acid can react with HM with the formation of slightly soluble silicates, thus providing HM immobilization.

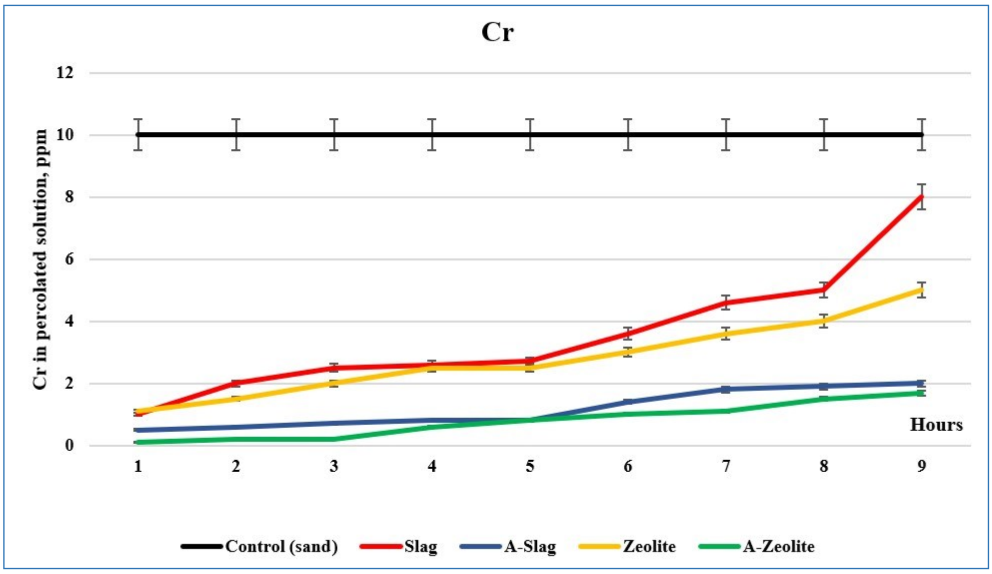
In the pots without slag or zeolite addition, barley plants did not germinate. Untreated and MSi-treated slag or zeolite mitigated the pollutant biotoxicity (Fig. 2). The treatment with MSi promoted an additional increase in the root and shoot biomass.

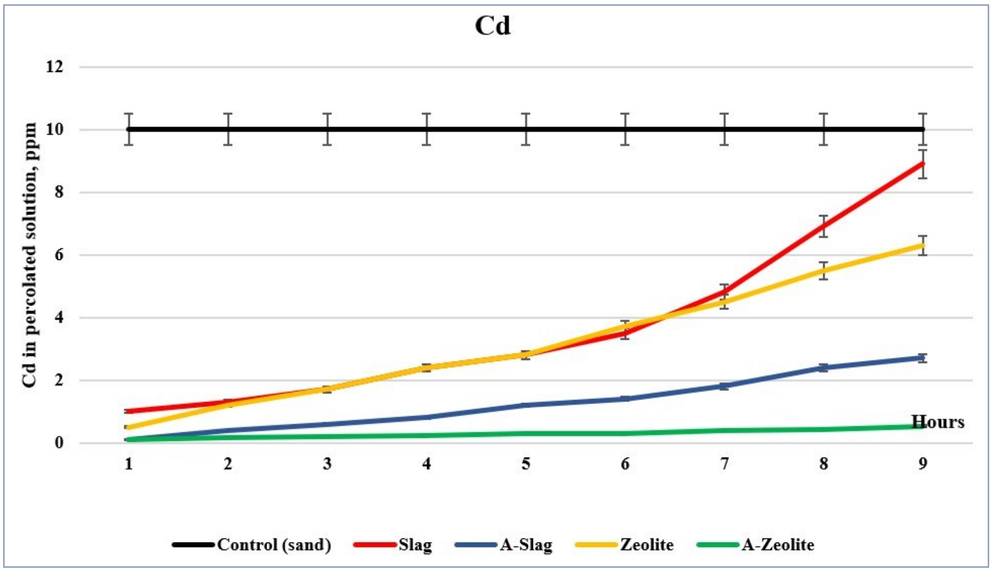
The accumulation of tested pollutants in the roots and shoots also was much lower in the plants grown under application of MSi-treated slag or zeolite (Table 1).

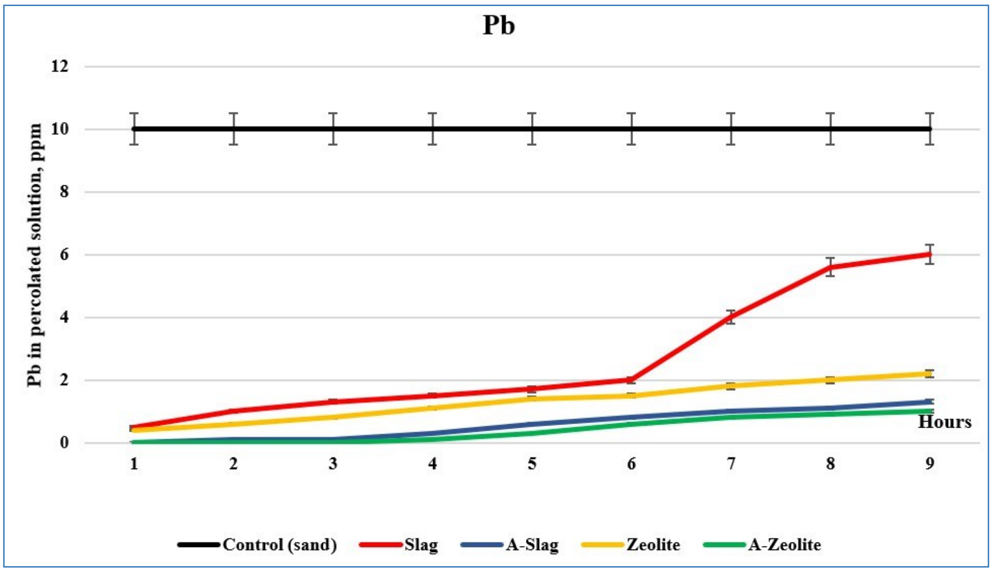
As evident from our results, local materials such as natural Si-rich minerals and some types of industrial ecologically safe by-products can be used for detoxification of contaminated sites (mine tailings, landfills, and others) and purification of industrial waste-waters. The efficiency of Si-rich substances as detoxification agent directly depends on the concentration of water- and acid-soluble Si in the system. Several mechanisms can be supposed to be responsible for Si action.

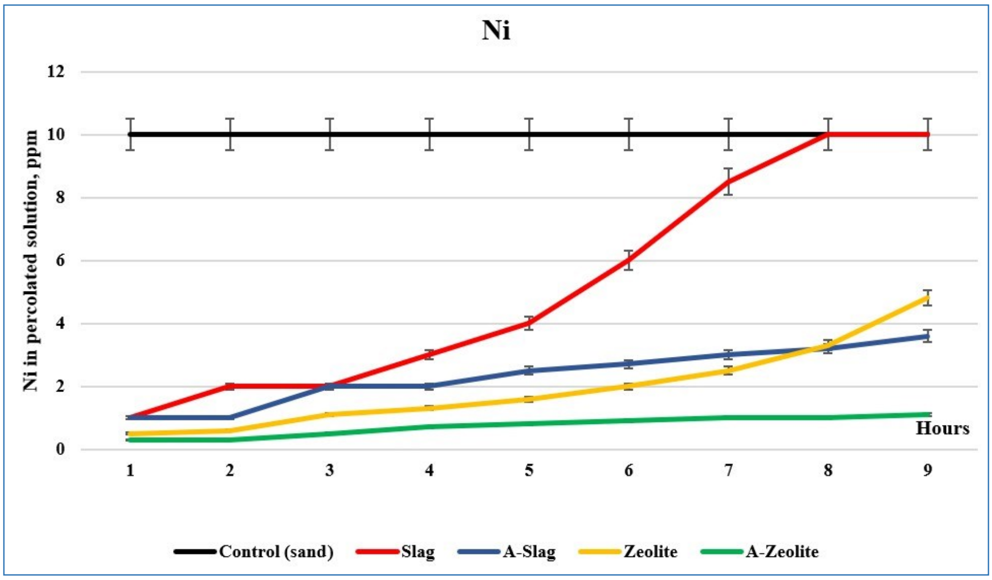
1) Chemical reaction between monosilicic acid and heavy metal with the formation of slightly soluble or insoluble silicates.
2) Chemical or physicochemical adsorption of As, Cd, Cr, Hg, Ni and Pb on the surface of Si-rich materials.
3) Adsorbed metal and non-metal pollutants can be capsulated by polymers of silicic acid.

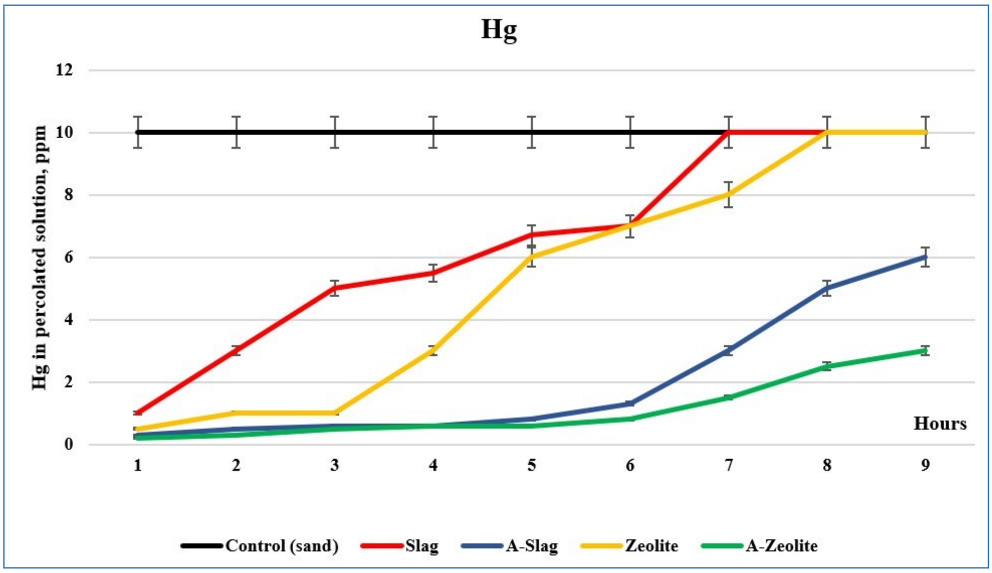
Using local Si-rich by-products contributes to decreasing remediation cost.


Cr
Cr in percolated solution, ppm
12
10
8
6
4
2
0
1
2
3
4
5
6
7
8
9
Hours
Control (sand)
Slag
A-Slag
Zeolite
A-Zeolite


Cd
Cd in percolated solution, ppm
12
10
8
6
4
2
0
1
2
3
4
5
6
7
8
9
Hours
Control (sand)
Slag
A-Slag
Zeolite
A-Zeolite


Pb
Pb in percolated solution, ppm
12
10
8
6
4
2
0
1
2
3
4
5
6
7
8
9
Hours
Control (sand)
Slag
A-Slag
Zeolite
A-Zeolite


Ni
Ni in percolated solution, ppm
12
10
8
6
4
2
0
Hours
1
2
3
4
5
6
7
8
9
Control (sand)
Slag
A-Slag
Zeolite
A-Zeolite


Hg
Hg in percolated solution, ppm
12
10
8
6
4
2
0
Hours
1
2
3
4
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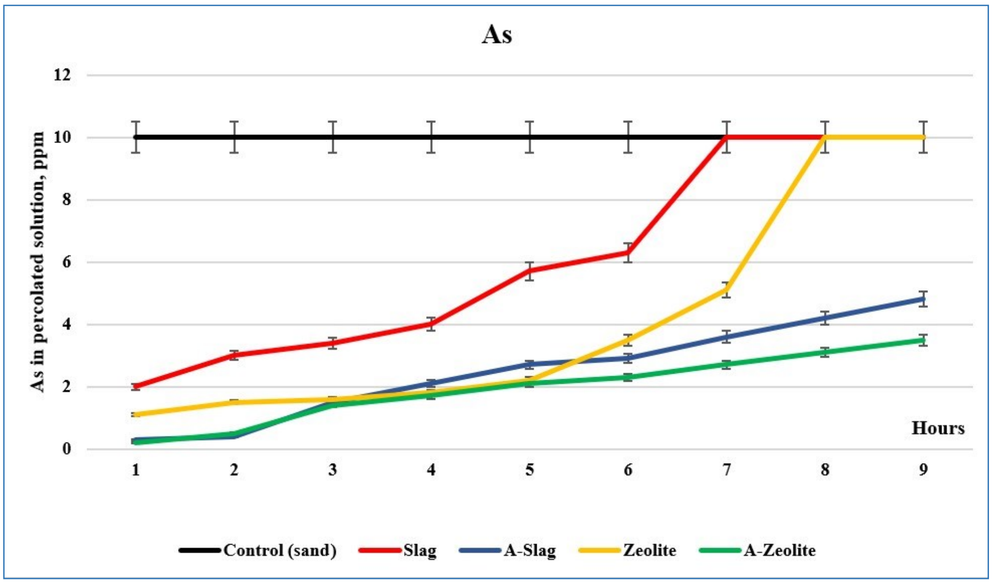
6
7
8
9
Control (sand)
Slag
A-Slag
Zeolite
A-Zeolite


As
As in percolated solution, ppm
12
10
8
6
4
2
0
Hours
1
2
3
4
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8
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Control (sand)
Slag
A-Slag
Zeolite
A-Zeolite

Fig. 1 Dynamic of pollutants in waste-water filtration test

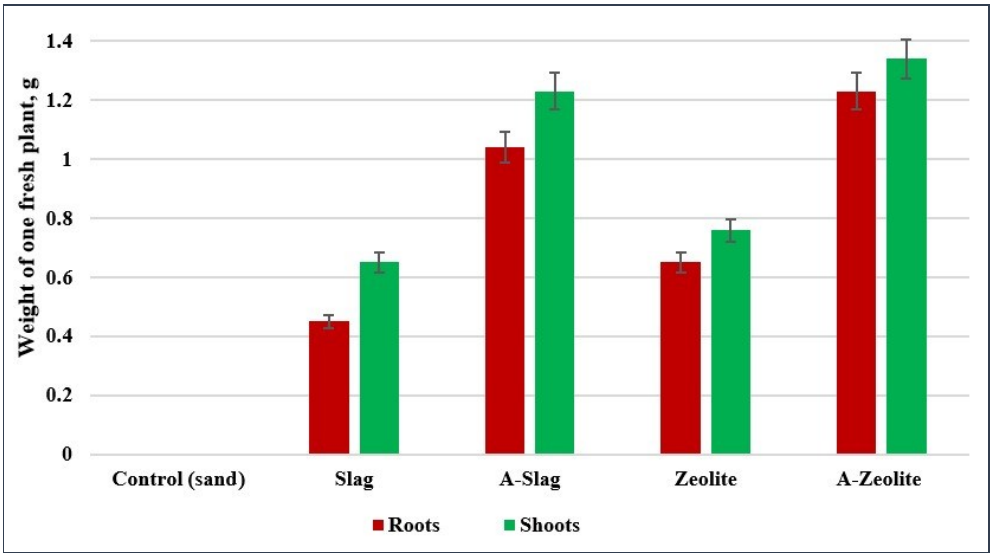

Fig. 2 Fresh weight of barley roots and shoots in greenhouse test, g.

Tab. 1 Total content of tested pollutants in the roots and shoots of barley, mg kg^{-1}

	Slag		A-Slag		Zeolite		A-Zeolite	
	Roots	Shoots	Roots	Shoots	Roots	Shoots	Roots	Shoots
As	1.42±0.03	0.54±0.06	0.72±0.06	0.23±0.02	1.33±0.02	0.34±0.03	0.65±0.04	0.21±0.01
Cd	0.63±0.02	0.32±0.02	0.23±0.03	0.12±0.02	0.75±0.06	0.31±0.02	0.43±0.04	0.12±0.01
Cr	0.33±0.02	0.23±0.02	0.14±0.02	0.05±0.01	0.32±0.04	0.20±0.01	0.23±0.02	0.05±0.01
Hg	0.24±0.02	0.12±0.01	0.14±0.01	0.05±0.01	0.21±0.02	0.15±0.01	0.15±0.01	0.04±0.01
Ni	0.55±0.05	0.23±0.04	0.23±0.02	0.11±0.01	0.59±0.05	0.33±0.03	0.34±0.03	0.11±0.01
Pb	0.86±0.06	0.45±0.04	0.45±0.03	0.18±0.02	0.85±0.07	0.42±0.03	0.44±0.03	0.21±0.02

ACKNOWLEDGMENTS

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WATER AND SOIL ENVIRONMENTAL RISK ASSESSMENT IN LITHUANIA

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KEYWORDS

Quality, contaminated sites, water, environmental impact assessment, soil, Lithuania

ABSTRACT

The quality of water and soil are conditioned not only by the natural phenomena, but also by the economic activity on the surface of land, especially the existence of pollution sources. The inventory of sources of pollution started in Lithuania back in 1990–1995. At that time, the main focus was on the inventory and examination of landfill sites and former Soviet Union military bases, and former warehouses of pesticides.

Law on Environmental Monitoring was adopted in 1997. It 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. 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 280 m^2, or 0.43 % territories of the country. However, in contaminated sites the allowable limits are not exceeded (Bukantis *et al.*, 2013).

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. Dangerous chemical substances, found when examining the soil and the underground water of contaminated sites are petroleum products, heavy metals, miscellaneous pesticides and other less common dangerous chemical substances used in specific industry branches and others (Vasarevicius *et al.*, 2015). The diffusive pollution sources are distinguished into two main groups: pollution conditioned by agricultural activity and pollution conditioned by residents discharging waste water,

which is not collected and treated. In agriculture, the diffusive pollution is formed due to fertilisation of crops by using livestock manure and mineral fertilisers (Bukantis *et al*., 2013).

In Lithuania, artificial drainage is a common agricultural practice. The country remains one of the most extensively drained in the world. The total drained land area occupies 47 % of the country’s land area and 86%of the agricultural land area, of which 87 % is tile-drained (Povilaitis *et al*., 2015) and 80% of total nitrogen and 53 % of total phosphorus that enters streams originates from agricultural areas (Povilaitis *et al*., 2014).

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. However, eutrophication of surface freshwater remains problematic, with a slight increase (European Commission, 2019), and is obligated to reduce the amounts of total N and total P entering the Baltic sea by 11,800 and 880 metric tons (26 % and 66 %), respectively by 2021 (Povilaitis et al., 2018).

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. Originally, more than 800 storage depots with pesticides stored in them have been identified in Lithuania on 2006. The assessment of depots location in regard of the sensitive environment shows that the majority of depots (516 objects) are located in the sensitive environment – agricultural areas, recreational zones – and only 111 objects are located in the insensitive environment (Kadunas *et al*., 2006).

Contamination can severely reduce soil quality and threaten human health or the environment 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. This serves as the basis for remediating these contaminated sites under the national environment protection strategy (2015) and management plan of contaminated sites for 2013–2023, approved by the Minister of Environment (European Commission, 2019).

Lithuania has provided a rough estimate about the overall contaminated sites management cost at high and very high risk, which account to circa EUR 1 300 million. EUR 19 million from the EU CF has been designated for the treatment of the 36 historically contaminated sites on state land for the period 2013–2020. Information about contribution of private and public sector is not available (Perez, Eugenio, 2018).

The need for the management of a chemical contaminated site is determined after a detailed ecogeological research of the contaminated site and an evaluation of the results obtained. Contaminated site management plan preparation area organized by the owner or the manager or the user, according to environmental recovery measures for selection.

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SYNTHESIS OF ORGANOCLAYS AND STUDY OF THEIR SORPTION PROPERTIES IN RELATION TO INORGANIC AND ORGANIC POLLUTANTS

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KEYWORDS

Clay minerals, organic substances, clay modification, adsorption, heavy metals, humic substances

ABSTRACT

The review on the synthesis and use of a new class of sorbents based on clay minerals and organic substances – organoclays is given. The mechanisms of interaction between minerals with an expanding and non-expanding structural cell and organic substances are shown. Data on the effective adsorption of organic and inorganic pollutants by organoclays are presented. An adsorption of heavy metals by kaolinite in the presence of fulvic acids has been studied.

Adsorption is one of the most effective processes used for wastewater treatment and the immobilization of pollutants in soils and grounds. The main adsorbents that have shown satisfactory results in the immobilization of inorganic and organic toxicants include: zeolites (activated and natural) (Syafalni et al., 2014), natural clay minerals (Singh et al., 2018), modified clay minerals (Yadav et al., 2019; Han et al., 2019), activated carbons (Singh et al., 2018; Mirmohseni, 2012), agricultural waste (Anastopoulos and Kyzas, 2018; Ahmad and Danish, 2018), biochar (Gorovtsov et al., 2020; Premarathna et al., 2019), industrial waste and sludge materials (Zhao et al., 2016; Anastopoulos et al., 2017), polymer resins (Singh et al., 2018; Rivas and Muñoz, 2009). To increase the efficiency and selectivity of mineral sorbents, they are modified by inorganic (Perelomov et al., 2016) and organic (Sarkar et al., 2019, etc.) substances.

The interaction of organic substances with clay minerals is a complex process, depending on the chemical nature of the surface and structural parameters of the minerals, physical and chemical properties of organic substances and environmental conditions. Organic substances have a significant effect on minerals, modifying their surface due to the formation of both chemical compounds and intermolecular agglomerates built by hydrogen bonds and other long-range forces, as well as coagulation contacts. As a result, the physical, chemical, and physico-chemical properties of organo-mineral systems that include organic substances and clay minerals differ markedly from the properties of individual components both in terms of the electrical properties of the double electric layer of colloidal particles and the number of functional groups available for interaction with inorganic and organic pollutants.

Organoclays, which are the product of the interaction of clays and organic substances, combine the useful characteristics of clay minerals and organic substances in one adsorbent. Organo-clay composite materials based on layered silicates can be divided into three large groups: (i) microcomposites, phase separated, (ii) intercalated nanocomposites, and (iii) exfoliated nanocomposites (Mukhopadhyay and De, 2014). Organoclays are understood as clays modified with organic substances, while modification does not lead to exfoliation of silicates, i.e. the filler is organic matter, and the surface structures of the clay mineral acts as a matrix.

The ability of clay minerals to modify is due to the fact that the outer and inner surfaces of the layered silicates are hydrophilic and polar. This facilitates the wetting and penetration of both low- and high-molecular compounds containing polar groups, such as acetone and its derivatives (Sohn and Kim, 2000), methyl methacrylate, proteins and amino acids (Ding and Henrichs, 2002), and other compounds with hydroxyl (Yu et al., 2003) and nitrile groups (Farkas and Dekany, 2003) into the interlayer space of the layered silicates. The minerals of the montmorillonite group are also intercalated by substances containing ester groups due to their specific interaction with cations and hydroxyl groups on the surface of silicate plates (Park et al., 2002). At the same time, the polarity of the silicate surface hinders the interaction of montmorillonite with non-polar and weakly polar polymers (Rashid et al., 1972).

Among the known methods for modifying clays by organic substances (according to Gerasin et al., 2013) are:

1) Ion exchange of clay cations to organic cations;
2) Adsorption of polyvinyl alcohol, polyacrylamide, alkyl ketones, acrylonitrile and other compounds that form complexes with the clay surface or exchangeable cations;

3) Adsorption of anions, in particular polyacrylates, on the side faces of silicate plates at pH <5 as a result of protonation of hydroxyl groups;
4) Inoculation of organosilanes onto the clay surface;
5) Introduction of organic molecules capable to Van der Waals or ion-dipole interaction with the clay surface, for example, alkyl ammonium cations, for which the affinity for clay decreases in the series $RNH^+ > RNH_2^+ > RNH_3^+$ and increases with increasing length of the aliphatic ion chain.

The simplest alkyl ammonium cations Me_4N^+ and alkyl amines $MeNH_2$, Me_2NH and Me_3N effectively displace Na^+ ions from montmorillonite, making the surface of the clay mineral organophilic, which ensures its compatibility with macromolecules (Snircova et al., 2009).

The geometry of the interaction of organic substances with clay minerals may be showed by the example of structures formed during the modification of clays with an expanding structural cell by surface-active substances. It is known that surfactants, including one aliphatic chain or having a plane molecular structure, are absorbed by clay, forming one or two adsorption layers with parallel orientation of the chains relative to the plane of the silicate plates and increasing the interlayer distance. With a large cation exchange capacity of clay material, molecules of primary amines with an aliphatic chain exceeding a certain length form “pseudo-triple” layers. Quaternary ammonium salts molecules containing two long aliphatic chains can form “paraffin” mono- and bilayers, which are located in the interplanar space of montmorillonite at a certain angle to the surface of the layered silicate and are attached to one or different plates (Gerasin et al., 2013).

However, apparently, intercalation of organic matter in clay minerals in vivo occurs in rare cases. Probably, the sizes of a significant part of macromolecules, such as humic or fulvic acids, are larger than the interlayer spaces in clays. Therefore, for this type of interaction, the properties of the outer surface are much more important for the binding of organic matter than the internal crystalline structure of clays (Kayugin and Zhuravsky, 2009). In this regard, it is logical to assume that intercalation of humic acids will be more effective when their concentration in solution is significantly lower than the critical micelle concentration.

Currently, various polymers are used to synthesize organoclays based on layered silicates, such as polyvinyl chloride, epoxies, polyurethanes, polyesters, polypropylene, polystyrene, chitosan, etc. Recently, the ability of organoclays to immobilize inorganic and organic pollutants in the environment has been widely studied. So, Sarkar et al. (2010) investigated the detoxification of hexavalent chromium by adsorbing it with the organoclay composed of bentonite and commercial alkyl ammonium surfactant Arquad®. The synthesized organoclay effectively adsorbed the toxicant from the solution, and the amount of adsorbed chromium increased with an increase in the amount of modifier. The introduction of this organoclay into the soil also reduced the bioavailability of arsenic (Sarkar et al., 2012). Jin et al. (2016) studied the simultaneous sorption of 2,4-dichlorophenol and Cu (II) ions from a mixture by organoclay based on bentonite and humic acids. The experiment showed the non-competitive nature of the adsorption of inorganic and organic pollutants. The composite based on montmorillonite and acrylamide, synthesized by treatment with an aryldiazonium salt and photopolymerization, selectively removed lead from the solution (Msaadi et al., 2017). Modification of montmorillonite with poly-4-vinylpyridine copolymerized with styrene was effective for removing atrazine (Zadaka et al., 2009). Xu et al. (2018) synthesized the organoclay based on chitin, which removed up to 99.99 % of methylene blue from the solution.

However, some quaternary ammonium salts are toxic to soil microorganisms (Sarkar et al., 2013). These compounds showed toxicity to anaerobic bacteria, and the toxic effect increased with decreasing alkyl chain length (Tezel et al., 2006). The LD50 values of the hexadecyltrimethylammonium cation in an aqueous solution for heterotrophic soil bacteria vary from 1.14 to 146.26 mg/L, and Gram negative bacteria are more sensitive to this compound compared to Gram positive bacteria (Nye et al., 1994). Quaternary ammonium salts exhibit both acute and chronic toxicity, and DNA damage and a mutagenic effect can be considered (Ferk et al., 2007). Thus, the use of synthetic quaternary ammonium salts for the synthesis of organoclays can cause significant harm to biota, therefore, additional studies of their toxic properties are necessary.

Within the frame of the project for study the effect of natural and modified humic substances on the adsorption of heavy metals by clay minerals we have studied the adsorption of Zn by a mineral with non-expanding structural cell – kaolinite, modified with natural fulvic acids isolated from lowland peat. The experiment was carried out under the following conditions: mass of the mineral – 0.2 g, the concentration of fulvic acid – 0.2 g/l, the range of metal concentrations – 0.05 – 0.8 mmol/l (3.27 – 52.08 g/l) , electrolyte – 20 mmol KNO_3, pHin – 5, the ratio of solid and liquid phases – 0.2 g : 25 ml. The experiment was carried out for 4 hours with constant stirring on a magnetic stirrer (500 rpm). After reaching equilibrium, the solutions were centrifuged for 15 min at 8,000 rpm and then filtered through a syringe filter with a pore size of 45 µm. The experiment was carried out in triplicate. To study the effect of pH on the adsorption process, experiments were carried out with the pH of the initial solution 3, 4 and 5 at a constant zinc concentration of 52.08 g/l. We also studied the effect of the sequence of fulvic acids and Zn addition on the adsorption process at the maximum concentration of the element.

The adsorption of Zn by kaolinite and kaolinite in the presence of natural fulvic acids is satisfactorily approximated by the Langmuir equation. Under the conditions of our experiment, fulvic acids enhanced the adsorption of zinc ions. Our results show that there is a tendency towards an increase in the adsorption of zinc ions by kaolinite with an increase in pH under acidic conditions. Modification of kaolinite with fulvic acids forms new sites with different functional groups for the sorption of microelements.

Thus, the synthesis of organoclays based on clay minerals and natural organic substances, including humic substances, can be a promising direction in the development of effective and cheap sorbents for inorganic and organic pollutants.

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TRACE ELEMENTS IN THE ALLUVIAL SOILS NEAR INDUSTRIAL CITY

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KEYWORDS

Heavy metals, urban soils, floodplain, soil pollution

ABSTRACT

Concentrations and profile distribution of a total content and forms of heavy metals in the alluvial soils near Tula city were studied. In the soils near the industrial center the concentrations of heavy metals may not exceed hygiene standards due to intensive removal and accumulation in immobile forms. Agricultural use can cause uniform distribution of total and mobile forms of heavy metals. A content, distribution and speciation of heavy metals in the fluvisols depend not only on industrial load value, but also on the soil properties and the ratio of the processes of metal input to and removal from the soils.

Alluvial soils, as a rule, have higher fertility compared to zonal soils due to the better supply of moisture, nutrients and good structure; therefore they are intensively used in agriculture, primarily for growing vegetable crops that are most demanding on nutrition and moisturizing conditions. Fluvisols occupy 590 million hectares on Earth and provide food for about 25 % of the world's population (Kellogg and Orvedal, 1969). Heavy metals (HM) are well-known environmental pollutants. HM come into alluvial soils by agricultural, urban and industrial sources and by mining and smelting activities (Cappuyns and Swennen, 2007). The specifics of accumulation and transformation of HM in fluvisols are determined by soil genesis, including location in a subordinate landscape, the effects of the alluvial process, and bedding with carbonate rocks. In arable soils, these processes are affected by watering, the application of high doses of mineral and organic fertilizers and chemical plant protection products. Due to the significant technogenic emission of harmful substances, suburban and urban alluvial agricultural soils should be subject to continuous environmental monitoring (Mensik et al. 2020).

In the study concentrations and profile distribution of the total content of heavy metals and their forms in alluvial meadow soils of Upa river near Tula city (Central Russia) and assessment of they use for safe agricultural products were investigated. The study 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`). One site is occupied by natural meadow vegetation. Another site is represented by agricultural soil used to grow row crops. The plots are located in close proximity to each other, at a distance of about 3 km from the metallurgical plant.

The total Mn concentration in the soil under the meadow is slightly higher than its content in arable soils for all the studied depths (Table). This may be due to both technogenic deposition and active participation in the biological cycle in natural ecosystems. In arable soil, both total and mobile forms of Mn are more evenly distributed in depth. A decrease in the concentration of mobile Mn in the upper layer of agricultural soil can be due to migration to deeper horizons, lateral removal or removal with a crop.

Tab. 1 Heavy metal concentrations in studied alluvial soils

Site	**Depth cm**	**Concentration of heavy metals, mg/kg**											
		Mn total	**Mn mobile**	**Fe total**	**Fe mobile**	**Pb total**	**Pb mobile**	**Zn total**	**Zn mobile**	**Cd total**	**Cd mobile**	**Ni total**	**Ni mobile**
Upa floodplain, meadow	0–20	760	128.3	33,000	81.8	15.0	0.8	100	12.2	0.35	0.16	24.5	0.60
	0–40	600	14.1	22,500	18.2	15.0	0.4	120	5.1	0.30	0.06	28.5	0.10
	0–60	700	9.9	25,000	10.2	17.5	0.1	125	2.3	0.25	0.05	25.5	0.05
Upa floodplain, arable	0–20	580	22.3	31,500	21.9	15.0	0.5	225	13.2	0.40	0.13	27.5	0.05
	20–40	560	18.1	27,000	30.1	15.5	0.5	115	10.9	0.35	0.11	22.5	0.05
	40–60	540	19.8	23,500	43.7	15.0	0.5	95	23.1	0.25	0.08	21.0	0.30
Approximate permissible concentrations (2009)						**130**		**220**		**2**		**80**	
Maximum permissible concentrations (2006)		**1500**	**100–140**	**22,300**		**32**	**6**	**100**	**23**				**4**

The total Fe content in the 0–60 cm layer in natural and arable soils is comparable and exceeds clark value for soils (Alekseenko and Alekseenko, 2013) in the 0–20 cm layer (Table). The maximum accumulation of Fe in the upper layer of these soils does not relate either with the content of humus, or with the fraction of physical clay, or with acidity and may be due to aerotechnogenic input from the metallurgical plant. In the arable soil in a layer of 0–40 cm, total Fe is distributed more evenly. The concentration of mobile forms of Fe is maximal in the upper layer of natural soil and decreases with depth; in arable soil, on the contrary, it increases with depth.

The total Pb concentrations are same in both arable soil and soil under the meadow at different depths (Table). One of the main sources of Pb in urban soils, away from the point sources of its emission, is motor vehicles. The studied sites are located at a considerable distance from the major highways of the city. The total stock of mobile forms of Pb in the layer of 0–60 cm in both soils is comparable. In arable fluvisol the element is distributed more evenly. In the natural soil, its concentration is maximal in the upper layer and decreases with depth.

The concentration of Zn both in natural soil under the meadow and in arable soil, in general, is within the limits of the existing hygiene standards (Approximate… 2009; Maximum… 2006), but exceeds the more strong standards that were existed in the USSR (Maximum… 1990) (Table). Its maximum concentration is noted in arable soil in a layer of 0–20 cm and slightly exceeds the approximate permissible concentrations in the Russia. This occurs despite the heavier particle size and higher soil humus content under the meadow and similar acidity. The source of Zn can be organic fertilizers, aerotechnogenic fallout, as well as fluff brought during floods. It is logical to assume that during floods in arable soil, due to their better water permeability, a higher amount of the element is retained. In the soil under the meadow, the element concentrations slightly increase with depth, while on the arable soil they decrease. The distribution of mobile forms is the opposite and in the layer of 40–60 cm in arable soil reaches a value of estimated permissible concentrations. Since high concentrations of Zn cause the greatest concern, its forms associated with various soil components were studied for upper horizons of natural soil and arable alluvial soil according to Tessier method (Tessier et al. 1979) (Figure). The element concentrations in the exchangeable fraction were lower than the sensitivity level of the device. The largest amount of Zn in the upper layer of the soils is in the residual fraction and the fraction associated with oxides and hydroxides of Fe and Mn (Figure). Karathanasis and Pils (2005) also note that residual forms were most important for the retention of Zn in alluvial soils. The retention of Zn in the Fe-Mn oxide fraction is explained by the high stability constants of Zn oxides and the ability of Zn to replace Mn in the oxide surface (Ma and Rao 1997). In fractions strongly bound to organic matter and extracted with sodium acetate (bound to carbonates), approximately the same amount of element is present, regardless of the nature of soil use. The increase in Zn concentration in the upper horizon of arable soil is due to a significant increase in its content in the residual fraction. The metals that make up this fraction are represented by inert compounds in the primary and clay minerals and are not able to pass into the soil solution and be uptake by plants.

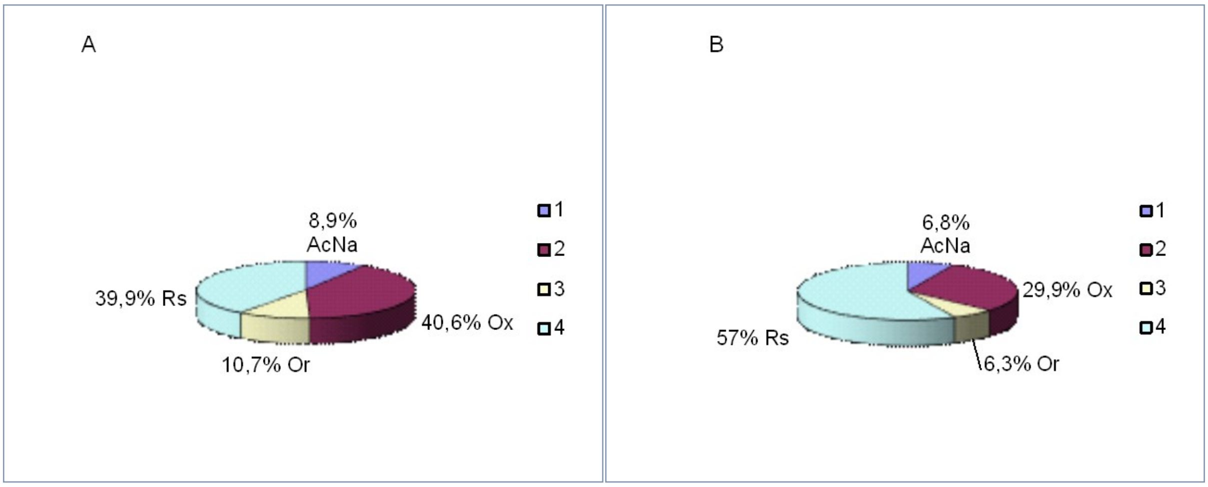

Fig. Zn speciation in natural under meadow (A) and arable (B) alluvial soils (% from total). AcNa – carbonate-bound fraction, Org – organic-bound fraction, Ox – Fe-Mn oxide-bound fraction, Res – residual fraction

There were no essential differences in the contents of total Cd and total Ni between arable and natural soils; their concentrations are within the established standards (Table). In both soils, the maximum concentrations of total and mobile Cd are characteristic of the upper layer and decrease with depth. The greatest number of mobile Cd and Ni is observed in the soil samples with highest humus concentration and content of physical clay. In arable soils in the layer of 0-40 cm the concentrations of mobile Ni are minimal and aligned in depth.

So, despite being on the outskirts of the industrial city, concentrations of most HM, with the exception of Zn and Fe, in the natural and arable alluvial meadow soils of Upa river is within the established standards and clark values, which may be due to the predominance of the removal of these elements over the input. In the fluvisol under meadow, the maximum amount of total Fe and Mn is observed in comparison with arable soil. The maximum concentrations of HM mobile form (with the exception of Zn) 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 heavy metals, which is often expressed in their most uniform distribution. The increase in Zn concentrations in agricultural soils 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.

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.

Tab. 1 Basic fertility parameters

Nº	**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

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

Nº	**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

Tab. 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	GI
118–140	12.1	26.5	25.9	35.5	38.6	61.4	GI

Soil textural class – acording ISSS, [2]

Tab. 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

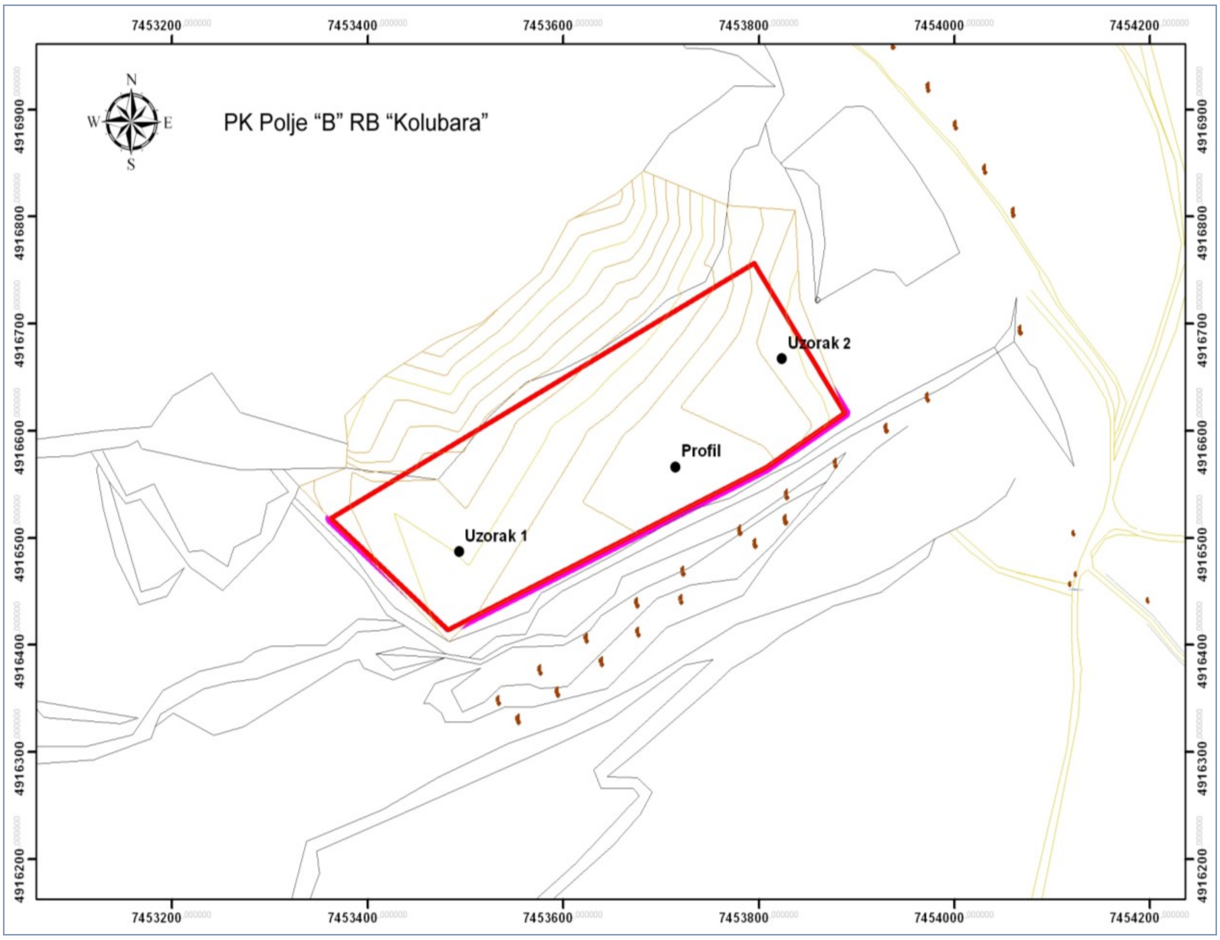
7453200
7453400
7453600
7453800
7454000
7454200
4916900
4916800
4916700
4916600
4916500
4916400
4916300
4916200
N
W
E
S
PK Polje “B” RB “Kolubara”
Uzorak 2
Profil
Uzorak 1

Fig. 1 a 2 Location of studied area

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 (Gl), 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 (Gl). Unstructured, non-carbonate, water appears at 140 cm.

Fig. 3 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).

ACKNOWLEDGMENT

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CONTAMINATED HETEROGENEOUS AQUIFERS: HOW TO ACCELERATE MICROBIOLOGICAL REMEDIATION WITH GROUNDWATER CIRCULATION WELL (GCW) TECHNOLOGY

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KEYWORDS

Aquifer pollution, in situ, microbiological remediation, nutrients, groundwater circulation

HYDRAULIC BASICS ABOUT VERTICAL GROUNDWATER CIRCULATION AND RELATED REMEDIATION ASPECTS

Heterogenous sand and gravel aquifers represent the main challenge for groundwater remediation at the majority of contaminated sites. The site geology of sandy aquifers is often characterized by alternating silty or clayey strata or intercalated lenses. These strata are less permeable than the other aquifer material by a factor of >100. Very low permeability silty and clayey strata in the aquifer will be a reservoir for contaminants. The total porosity and sorption capacity for contaminants per unit volume of these layers are often much higher than the adjacent aquifer material. Through sedimentation processes, heterogeneities also appear on micro-scale dimensions (cm–mm range). In many aquifers*,* these numerous thin beds of micro-scale silty and clayey layers are more or less horizontally arranged and cause preferred horizontal flow and show a higher flow resistance in a vertical direction. This anisotropy impact, therefore, always the vertical migration of contaminants and has a definite influence on vertical groundwater movement. Residual saturation pools, ganglia, or dead-end pores in layered fine sands or silts are hard to access for horizontal flow. Extracted groundwater from a fully screened or screened only in permeable zones mainly remove only contaminants from the higher permeable zones (Fig. 1). Although the concentrations decrease, they remain at a stable, low level due to back diffusion.

Pump-and-treat (P&T) is the most popular remediation technique; however, as described above, it is limited by the removal of contaminants from dead-end pores in better permeable zones and low permeable strata. Even in situ solutions like bioremediation depend on the delivery of the remediation agents throughout the aquifer. Furthermore, microbial degradation is naturally limited through unfavorable geochemical conditions or a lack of microbes or nutrients. Also, direct injections of amendments into a contaminated aquifer tend to suffer from restricted distribution in heterogeneous, anisotropic, and low permeable systems. The standard injection technique frequently leads to preferential transport pathways within the slightly higher permeability zones bypassing the lesser, often highly contaminated, silty and clayey zones. The injection methods are not appropriate for contaminated sites, which are horizontally extended or expand into great depth because of their insufficient amendment distribution and very high costs.

IEG-GCW® as an efficient remediation technology can be used along with in situ chemical and physical treatment processes (surfactants, nanoparticles, zero-valent iron, ion exchange, and oxidation) to speed up remediation processes. For microbiological groundwater remediation, a GCW system will be combined with biological degradation. A GCW system is constructed with 2 or more screen sections, adapted to the geological and hydrogeological situations to create strong vertical downward or upward gradients to achieve a 3D groundwater circulation cell around the well. The high potentiometric head differences establish and maintain the circulation flow. The forced flow will circumvent the low conductivity regions and subsequently penetrate the lower permeable zones, bringing simultaneously together contaminants, nutrients, amendments, and microbes. The 3D hydraulic cells will act as an in situ bioreactors where circulation flow directions can easily be changed. Dissolvable additives, reactants, etc. can directly be added via the circulating water, or added directly via multilevel injection wells (MIWs) into the GCW radius of influence or combined with an on-site reactor.

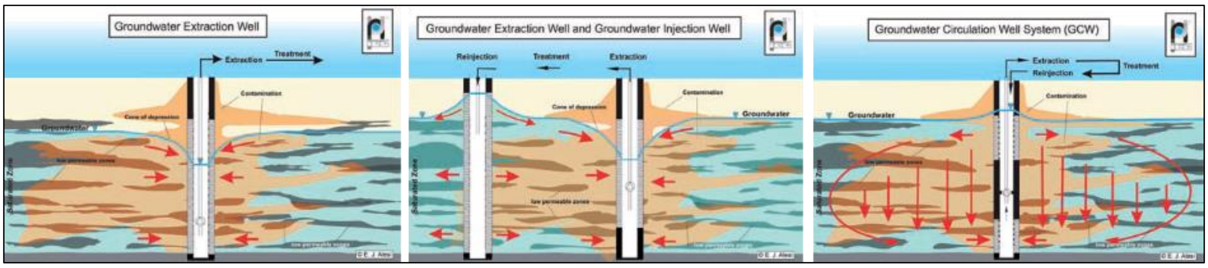

Figure 1 Heterogeneous aquifer with low permeable zones. Remediation flow dynamics:

The general flow of a standard extraction well (left); horizontal circulation wells, the combination of a standard extraction and a reinjection well, (middle); vertical groundwater circulation well (GCW) (extraction and infiltration screens in a vertical axis (right)

A combination of an extraction and a reinjection well (Fig. 1, middle) does not create relevant vertical hydraulic gradients. In contrast, the vertical circulation induces a flow perpendicular to lower permeable layers and improves contaminant mobilization and nutrients delivery (Fig. 1, right). No groundwater will be removed from the aquifer, hydraulic balances are not disturbed.

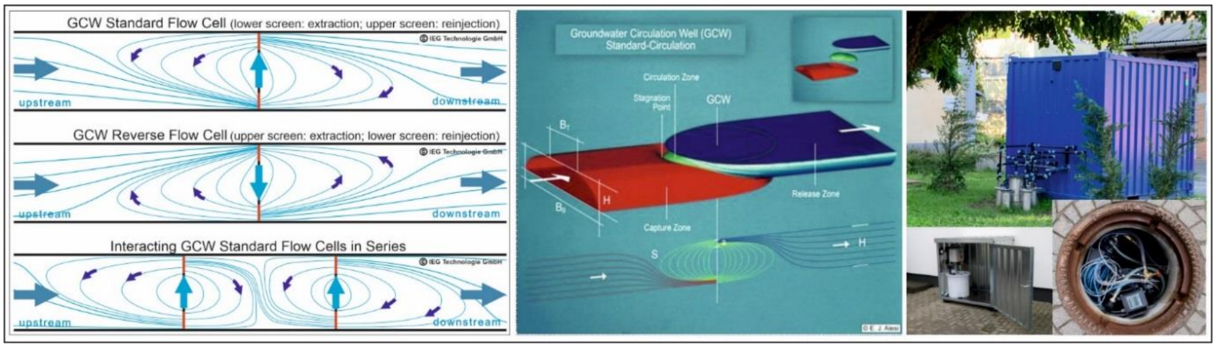

Figure 2 Flow Principle of IEG-GCW®: Standard and Reverse Flow Cells (left); capture zone, circulation cell and release zone (middle); system installations below ground and with on-site liquid amendment system in a container (right)

The option for several screen sections allows the adaption of the GCW flow to the contamination pattern and redirect the circulation directions (Fig. 2, left), depending on geological structures, the kind of pollutants, and their distribution in the aquifer. The hydraulic GCW-terms for numerical calculation and modeling is demonstrated in Fig. 2 (middle).

An IEG-GCW® system for enhanced microbiological degradation does not need a physical treatment of groundwater. Sometimes it makes sense to include in the beginning a treatment system to eliminate high contaminant concentration through direct removal because of the high toxicity to microbes. To a later stage, only microbial degradation can establish. The GCW system can be used and maintained in aerobic and anaerobic settings. An arrangement of multilevel monitoring wells (MLSW) around the GCW allows getting specific detailed information about the trends of hydrogeochemical and groundwater parameters, contaminants, metabolites, nutrient concentrations, flow rates.

REMEDIATION CASE: POLLUTED SITE IN NORTHERN ITALY

A large operational industrial site in Northern Italy is heavily contaminated by different CAHs, due to past uncontrolled degreasing activities. A hydraulic extraction and barrier system of 30 – 50 wells have been working over a decade long. After a decade of pumping in low permeable layers CAH concentrations up to 100 mg/L have been still detected. Around one of the source areas, despite pumping, concentrations > 1000 µg/l are prevailing. The contamination reaches a depth of 26 m below ground.

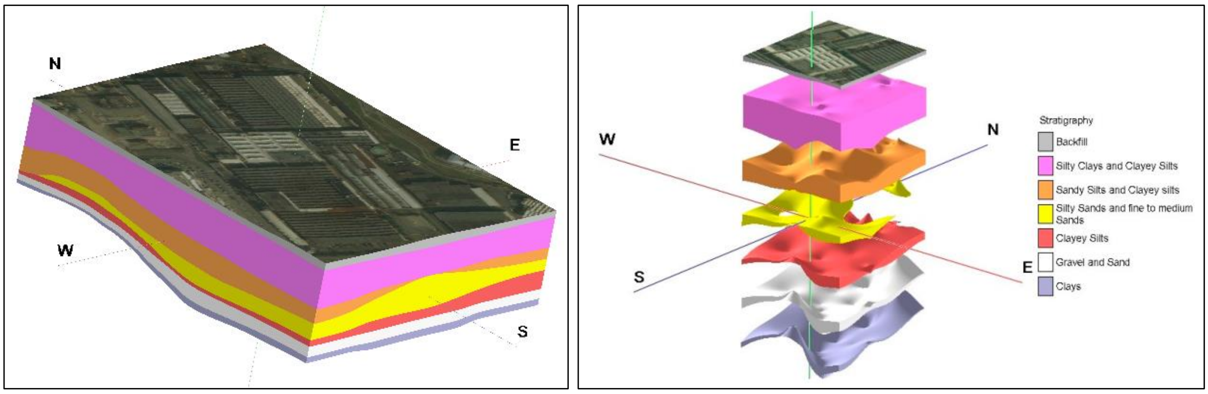

Figure 3: 3D geological model and "exploded" lithostratigraphic model

The aquifer is represented by fine to middle sands with intercalated layers of less permeable sandy silts to clayey silts. The highest contaminations were found in the low permeable strata. Fig. 3 shows a geological model of the site. It is based on 87 drillings with stratigraphically logs and numberless particle-size analyses, pumping tests, and some additional triaxial cell permeability tests and assessments of water content. This data allowed an analytical evaluation of the textural and permeability characteristics. A preliminary site evaluation suggested that an active dechlorinating microbial community has been established, the lack of electron donor being the limiting factor for the complete conversion to non-chlorinated final compounds (ethene and ethane).

The clayey silts in the middle of the aquifer with a hydraulic conductivity up to 10^{-7} m/s act as a persistent slow-releasing secondary contamination source, kinetically controlled by slow back-diffusion mechanisms. Major contaminants are cis-dichloroethene (cDCE) and vinyl chloride (VC) up to 100 mg/l. To enhance the existing passive P&T containment to an active remediation scenario the selected system has to fulfill several requirements. Strong vertical gradients for forced fluid flow through lower permeable layers must be created, and an appropriate amendment for stimulating microbial degradation has to be selected.

In microcosm studies, PHB (Poly-3-hydroxy-butyrate), a new electron donor for in situ biological reductive dechlorination was tested. PHB has strict and defined degradation pathways. The fermentation rate can be easily controlled by its shape and size (powder, granules, or pellets) and by the operating conditions (temperature, residence time). The lab tests demonstrated the effectiveness of PHB as a suitable electron donor source for enhanced reductive dechlorination processes up to non-toxic ethene. In a pilot field test, IEG has drilled and installed a modified IEG-GCW® system with 3 screen sections and peripheral screen access close to the source area. Figure 4 (left) demonstrates the location in the aquifer. The groundwater was extracted from the lower and intermediate screens and reinjected into the upper screen. The external treatment unit was composed of a sand vessel for suspended solids filtration, a zero-valent iron (ZVI) vessel for reductive dechlorination, and a PHB reactor for electron donor supply. The reinjected water showed after operation time high levels of dissolved organic carbon (DOC) and volatile fatty acids (VFA) and a CAH reduction of ca. 50 % in the effluent of the ZVI/PHB reactor.

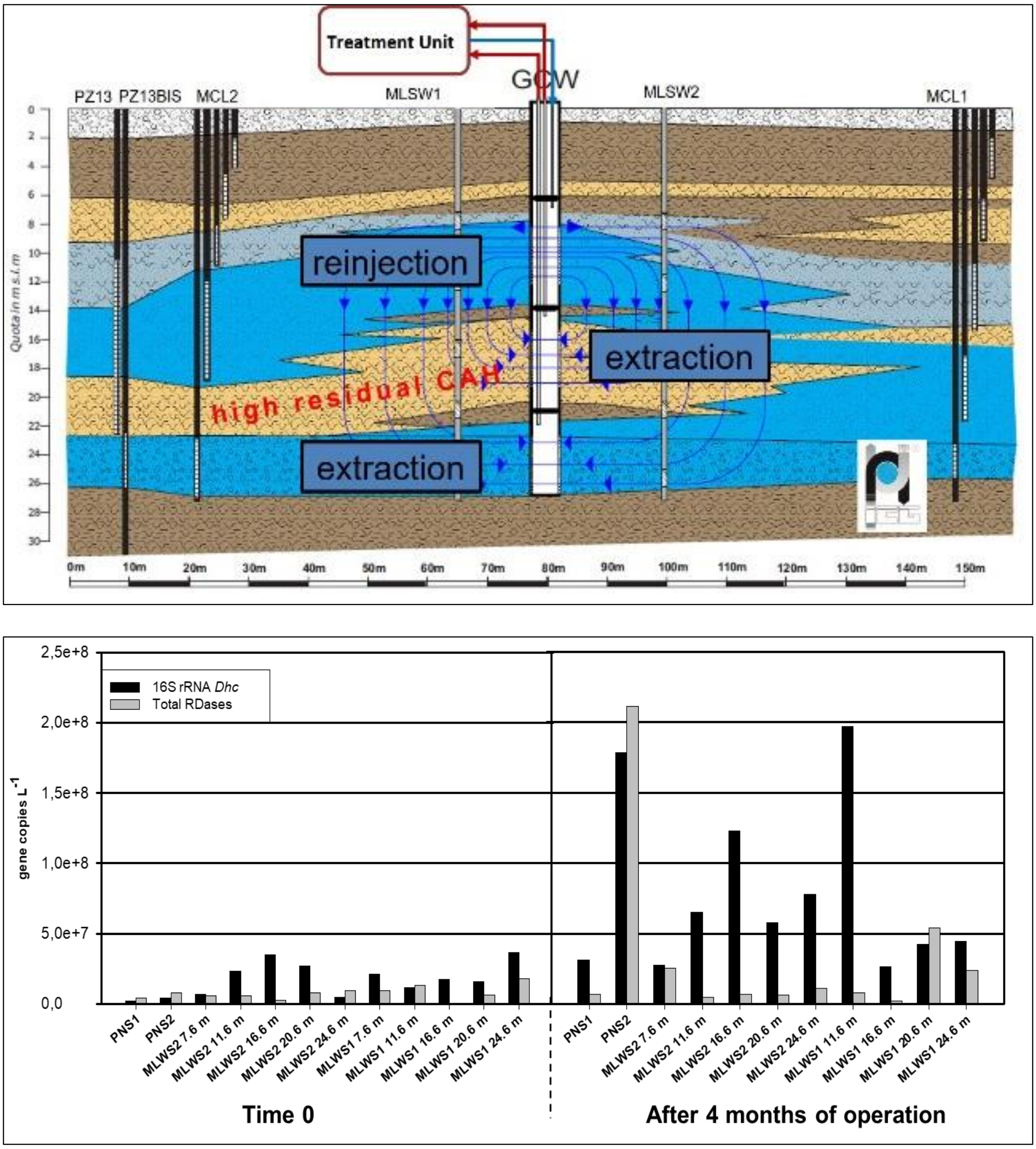

Figure 4: Schematic geological profile with the location of the pilot IEG-GCW® 1 (left) and the development of gene copies in different depths after 4 months of operation (right)

After four months of running the system, the gene copies of Dehalococcoides (Dhc) show a tremendous increase in different aquifer depths (Fig. 4, right). Due to strong vertical flow gradients, the contaminants in the highly contaminated low permeable layers are mobilized, the original composition of contaminants decreases, and metabolites increase through more favorable conditions for microbial degradation. Figure 5 (left) shows the decreasing CAH concentrations around the pilot IEG-GCW® 1.

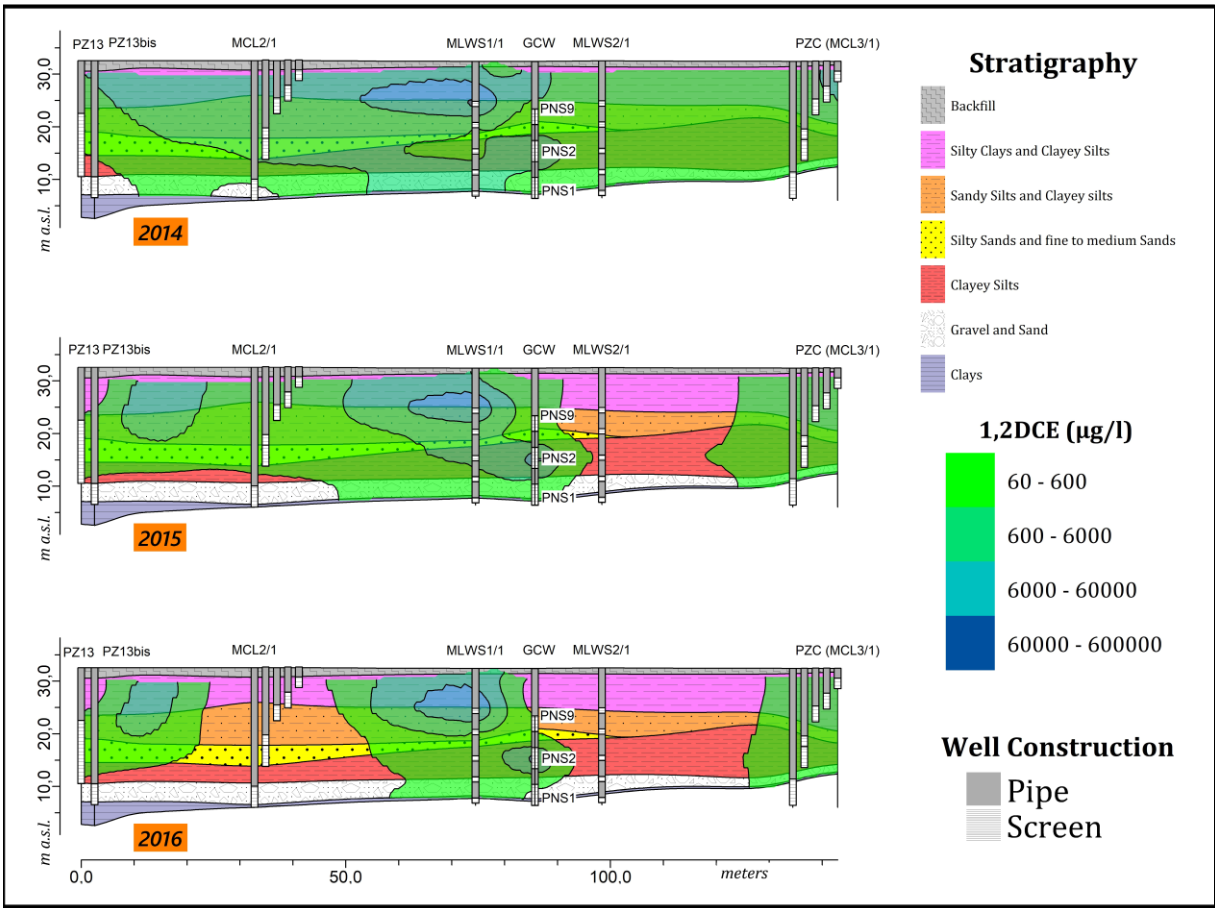

Figure 5: Concentrations of CAH in the progress of the pilot test

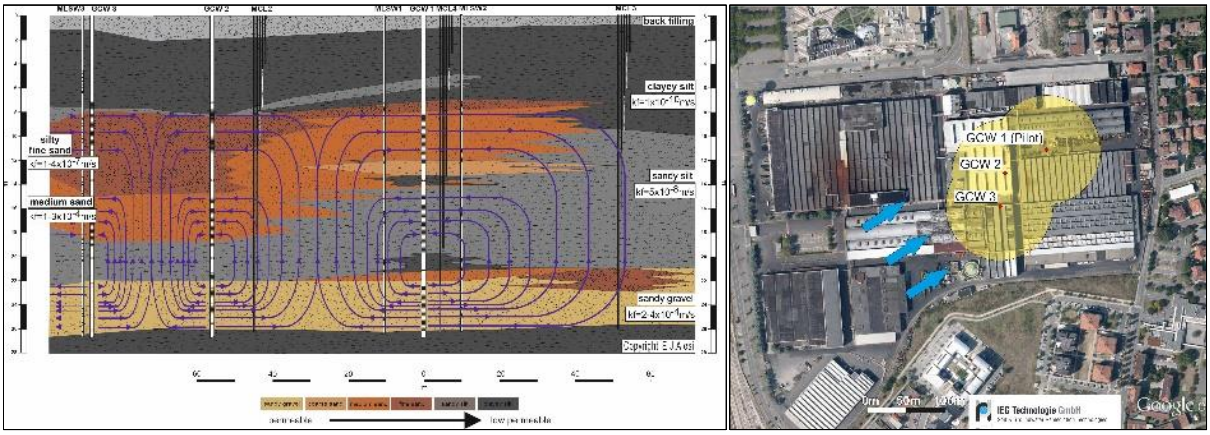

Figure 6 Schematic geological profile with the flow regime of IEG-GCW® (left), location of the new wells (right)

Two further IEG-GCW® wells and treatment systems were installed and go into operation in July 2019 to cover the contaminated area outside the radius of influence (ROI) of the GCW 1 (Fig. 5, right). The locations of the new GCWs were numerically calculated that the vertical flow lines of each GCW touch and create a strong vertical flow field (Fig. 5, middle). The GCW layout based on the drilling of 4 multilevel wells in the surrounding and the geological drilling profiles on the proposed GCW locations.

CONCLUSIONS

Comparable to other remediation technologies the implementation of IEG-GCW®-systems establishes favorable conditions for microbiological groundwater remediation. Extraction and recharge are balanced. Therefore, the technology inherently resources conservatively. Using the combination of effective hydraulic flow cells and continuous delivery of amendments into the aquifer the system provides reliable degradation milieu and adaptable flow dynamics towards changing remediation requirements. In the case of heterogeneous aquifers, compared to P&T or injection techniques, GCWs accelerate remediation. The special well hydraulics create a flow perpendicular through less permeable layers and amendments/chemicals can be distributed therein. The system is characterized by low operational costs, small space requirements, and can be easily installed without interfering residential areas or operational industrial sites (Fig. 2, right).

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) was to determine the trace elements contents in medicinal plants and in soils of their wild habitats.

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 type, under all plant species sampled, were Calcic Gleysol (Obrenovac) and Humogley (Pančevo). 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.

Fig. 1 Serbian Republic, 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)

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).

Tab. 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
Mn	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.

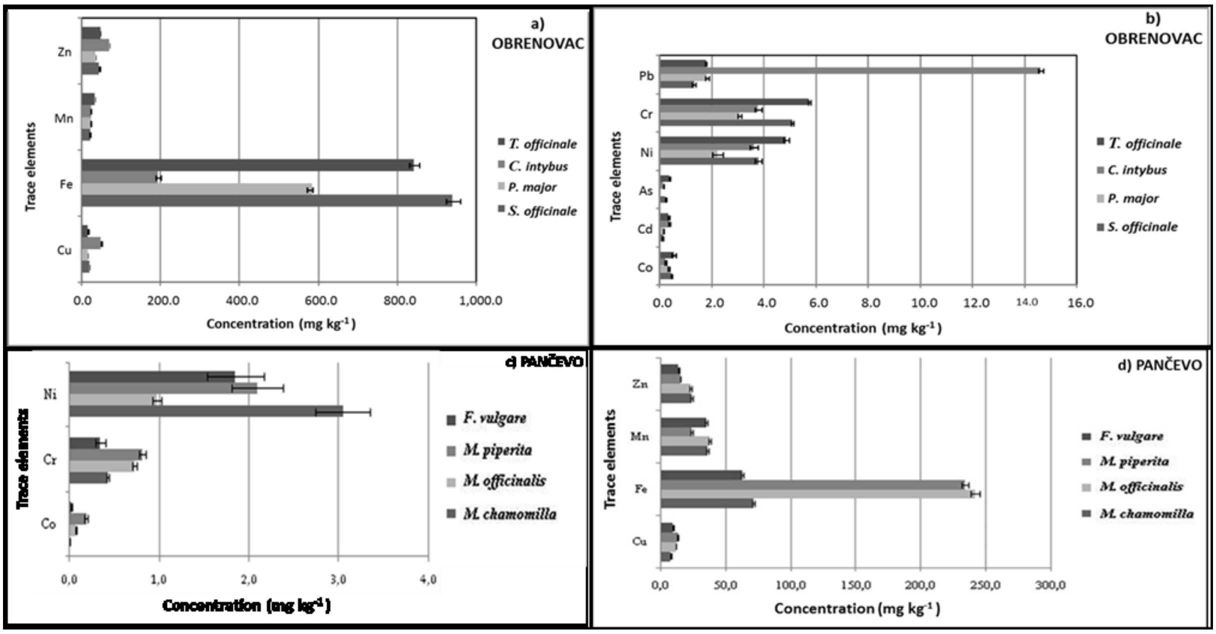

Fig. 1 Trace elements content in plants collected from the area of Obrenovac (a, b) and Pančevo (c, d)

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, 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.

NATIONAL INVENTORY OF CONTAMINATED SITES IN PROGRESS – THE STATE AND OUTLOOK

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KEYWORDS

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

ABSTRACT

The first year and a half of the field work on the National Contaminated Sites Inventory (NIKM), running over the whole territory of Czechia (2018–2021), brought us a lot of knowledge, enabling us to refine the activities, time schedule and to make more precise, the methodical procedures of the inventory. Ongoing monitoring and control of the "yield" of individual data sources (old SEKM records, clues from remote sensing, new contaminated sites), led to some methodical modifications and to detailed instructions offered for inventory teams via control days, training and consultations. According to the actual data, the project target value and objectives are expected to be fulfilled.

INTRODUCTION

The NIKM project [1], managed by CENIA, is focussed on the inventory and evaluation of information of contaminated sites (CS) throughout the Czech Republic. The existing records of CS include clues of CS, obtained from the remote sensing project task, are gathered in the SEKM database. All records together with the records of newly discovered CS collected in the running field campaign of the inventory, are filled in with detailed information about the CS and concluded with CS prioritization (risk ranking). The approval process includes several steps of records control, verification, and validation. In October–November 2019, after six months of the filling in of the database SEKM 2, a transition to working in the new inventory module and in the upgraded SEKM 3 database was successfully managed.

In February 2019, the existing database SEKM was amended with the data from a separate register of CS used in spatial planning (so-called territorial analytical data), forming the initial inventory datastore of 13233 records. In another separate SEKM database (17011 records) were stored the clues of CS gathered with the help of remote sensing (RS) methodology [2][3] in the initial phase of the NIKM project. In fig. 1 you can see a composition of the data input.

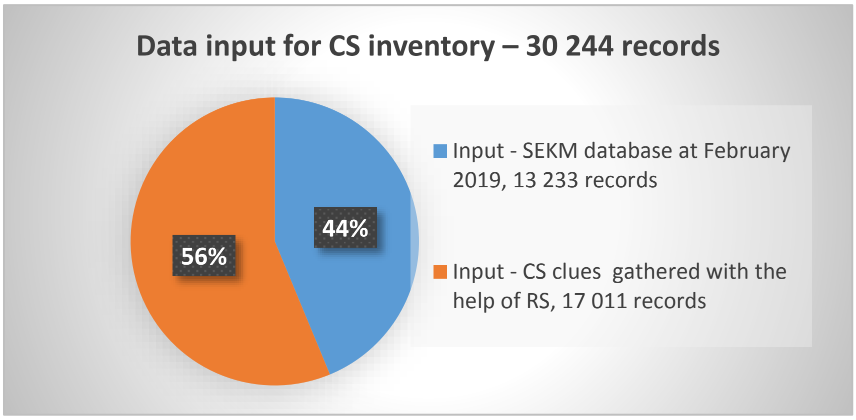

Fig. 1 Data input for CS inventory (the state in February 2019)

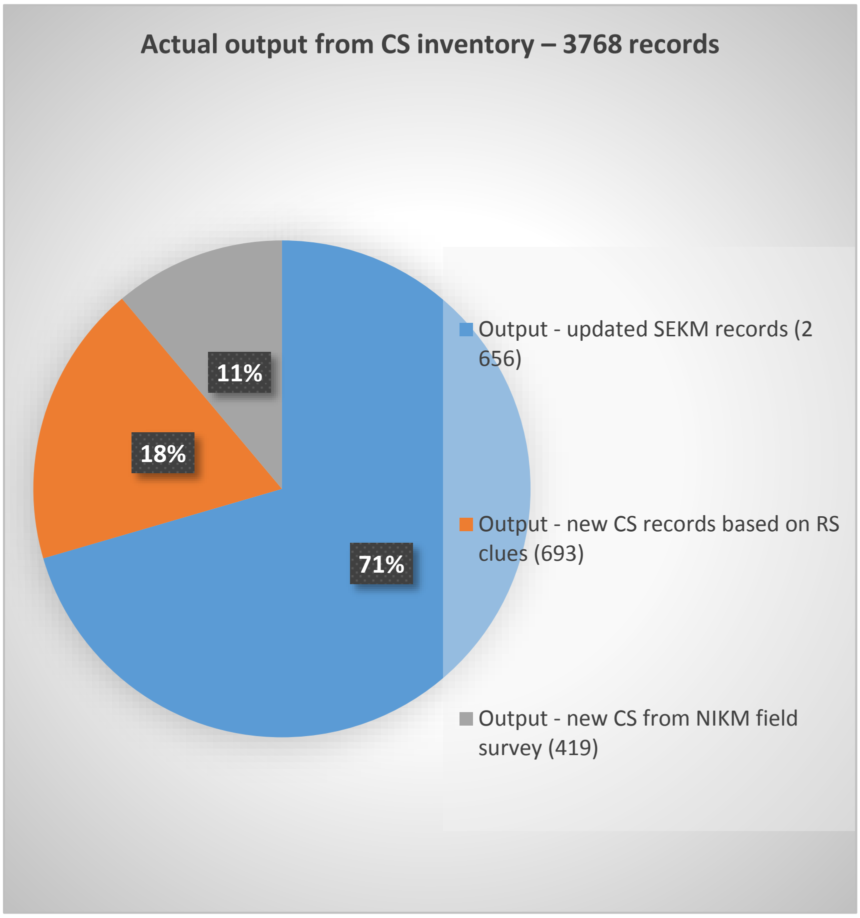

Fig. 2 Data output from CS inventory (the state on 31st August 2020, 32 districts – 42.2 % of Czechia)

The actual output of the inventory (after 32 districts being evaluated) is composed by the updated SEKM records, by new CS records based on RS clues and by new CS registered within the NIKM field survey (information from public administration, environmental inspection and also from the public) – see fig. 2.

THE TIMESCHEDULE AND THE STATE OF THE INVENTORY WORKS BY THE END OF AUGUST 2020

Field inventory work started in March 2019. Then a preparatory 2-month phase took place, including training and piloting activities. We use districts as a mapping unit – there are 77 (incl. Prague) in Czechia. Their areas differ in size (the smallest is 230.1 km^2, while the largest is 1945.5 km^2), the average district area is 1024.3 km^2. Twelve inventory teams are continuously and simultaneously working in assigned districts according to the approved time schedule. The inventory in individual regions (14 in Czechia) will be finished in form of regional reports, the first is to be ready in October 2020.

The inventory works within Czechia's territory are divided up among three members of the NIKM inventory consortium (see fig. 3) – DEKONTA (blue districts in the map), GEOtest (pink districts) and VZ Ekomonitor (green districts). Intensively coloured districts shown in fig. 3 are already completed. The map also serves as a visualization of district inventory management and control.
(T = planned term; D = delivery term; A = acceptance term; timeliness in days; timeliness verbally).

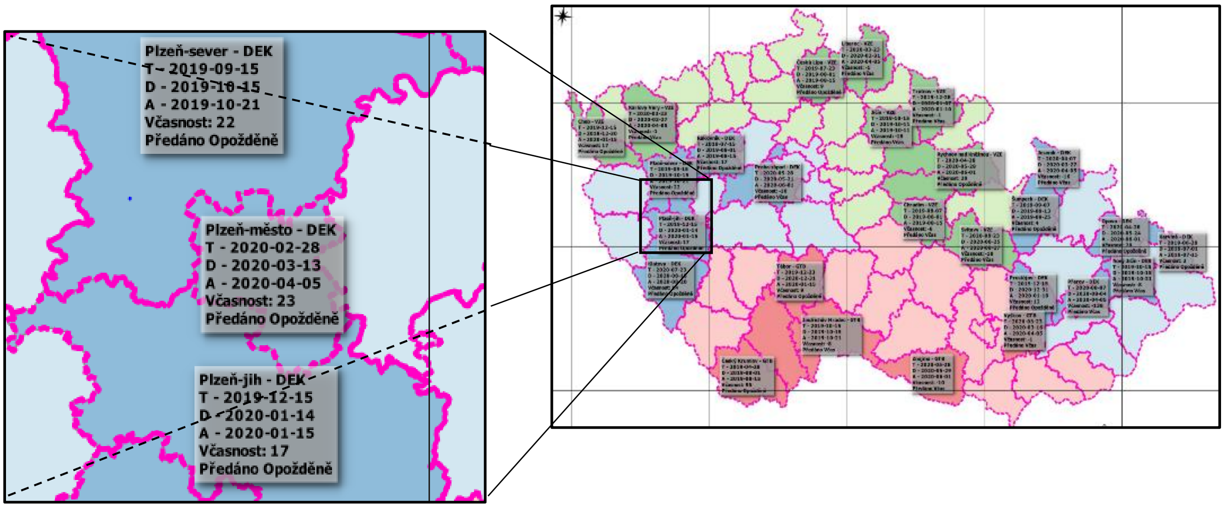

Fig. 3 Coverage of Czechia territory with completed CS inventory in 32 districts

Operational monitoring and management include the ongoing recording of input / output data for each finished district and the analyses of old data records and contaminated sites clues and yields (percentage portion of finally registered sites counted from inventory input). Based on these data (see tab. 1 and [4]), we projected the expected number of records by the end of the inventory (31. 12. 2021), i. e. the linear prediction from the number of current day approved SEKM records. This allows us to assess the probability of fulfilment of the prescribed target value of 9053 contaminated sites. It also allows us to prepare tools and actions to improve a yield of input records and/or to intensify the search and collection of new, hitherto unknown contaminated sites.

On the 31. 8. 2020, based on data from 42.2 % of the Czechia territory, the linear projection (average 118 records × 77 districts) of the final inventory output is 9067 records, i. e. 100.2 % of the project target value (see fig. 4). Background data can be found in the summary of the corresponding poster [4]. Otherwise, we can calculate a prognosis for new records (average 13 per district, i. e. 13 × 77 = 1008) and for the SEKM + RS data source (average 365 per district, i. e. 365 × 77 = 28 086) – in total 29094 with the average yield of 28.7 %, so we can estimate 9686 records, i. e. 107 % of the projected target.

Tab. 1 Summary of basic data from CS inventory in 32 districts (the state of play by 31. 8. 2020)

	SEKM records			**Remote sensing clues and records**			**New CS records**	**Input records in total**	**Output – CS records in total**	**Excluded records in total**
	Input SEKM	registered	excluded	Input RS	registered	excluded				
Records – input on 02/2019	13233			17011				30244		
Records – output by 31/08/2020		2656			693		419		3768	
Excluded records by 31/08/2020			1779			6218				8017
Processed data by 31/08/2020	4761	2656	1799	6911	693	6218	419	12091	3768	8017
An average per district	149	118	56	216	22	194	13	378	118	251

Some of the impressionable factors resulting in higher yields of records are: effective utilisation of information collected e. g. in the Geofond, duly observation on the location of CS clues (gathered with the help of RS) and in making the appropriate forms of photo documentation (see chapter 3 below). The average yield of CS clues (RS) in 32 districts is 10.0 % (min. 1.5 %, max. 56.6 %).

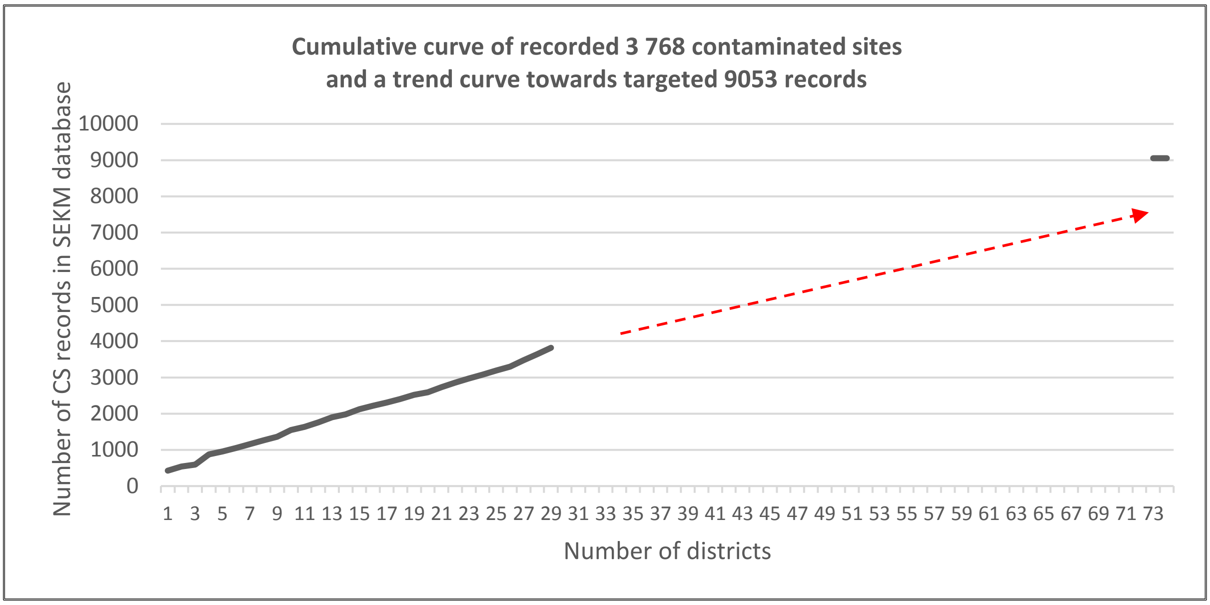

Fig. 4 Cumulative curve of recorded CS after 32 districts finished (42.2 % of Czechia territory)

METHODOLOGICAL SUPPORT AND CONTROL OF INVENTORY WORKS

From the beginning of inventory works we focus on the efficiency of the project methodology, namely in view of strengthening the quality of CS records and aiming not to miss any potential CS. Based on gathered experience from the first phase of field work, we completed the methodology with some methodical handbooks and detailed instructions. The inventory teams were additionally instructed and trained in the frame of field control days and training meetings.

The Series of Handbooks for field mappers consist of:

- Interpretation key for searching for clues in aerial photomaps and other cartographic documents. October 2019, 90 pages.
- Evaluation of contaminated sites clue interpretations (summary). October 2019, 29 pages.
- Possibilities of geographical support of field inventory incl. processing of additional assessments and analyses by remote sensing methods. October 2019, 7 pages.
- Possibilities of using a remotely piloted aircraft (RPA) in a field survey in the NIKM 2 project. November 2019, 11 pages.
- Validation / approval of the exclusion of the remote sensing clues or how to correctly document and justify the irrelevance of the contaminated site clue. March 2020, 8 pages.
- Photo documentation of the locality or how to correctly and legally, unassailably make photo documentation of a RS clue or contaminated site (with a record in SEKM). April 2020, 26 pages.

STANDARDIZATION OF THE METHODOLOGY FOR CONTAMINATED SITES CLUES INTERPRETATION

Based on the authors' experience in the implementation of the NIKM project task *Support for the inventory of contaminated sites by remote sensing methods,* two methodologies were prepared and submitted for certification.

- **Methodology of thematic mapping of environmental phenomena by RS methods** [5]

The purpose of this methodology is to contribute to the standardization of procedures for ensuring the quality and effectiveness of mapping the clues of contaminated sites and the performance of similar tasks in the institution of the Ministry of the Environment or in other ministries and institutions.

- **Methodical procedure of mapping clues of contaminated sites by RS methods** [6]

The methodology summarizes the procedures and process elements tested in the NIKM project. It can be applied selectively or be supplemented for the given new mapping project by other specific steps. The technical mapping procedure respects the purpose and scope of work focussed on the identification of clues of CS. Mapping consists of the examination of one or more source map layers in a GIS environment and capturing mapped phenomena in a newly created map layer. It consists of the so-called first-phase mapping and the second-phase, i. e. the revision evaluation.

CONCLUSIONS

According to the actual state, we believe ourselves to be on a good path in being able to achieve the project objectives. The linear prediction from the number of current day approved SEKM records for the end of the inventory (31. 12. 2021) allows us to expect, with a slight optimism, fulfilment of the prescribed target value (indicator) of 9053 contaminated sites, each with an evaluated priority. The inventory activities including field surveys are run according to the project methodology, which is continuously completed with some methodical handbooks and detailed instructions offered for inventory teams via control days, training, and ongoing consultations.

ACKNOWLEDGEMENT

Project NIKM – 2nd stage (National Inventory of Contaminated Sites) is co-financed from European Union Funds – the Cohesion Fund – in the frame of the Operational Programme of the Environment 2014–2020, the area of intervention 4.2. – The Rehabilitation of Old Environmental Burdens.

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THE STATE OF THE IMPLEMENTATION OF THE PROJECT NATIONAL INVENTORY OF CONTAMINATED SITES IN NUMBERS, PICTURES AND GRAPHS

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KEYWORDS

Inventory, CS – contaminated sites, RS –remote sensing, SEKM – System for registration of CS

ABSTRACT

The poster presents some maps, tables, graphs, and comments to illustrate the current state of play, of the National Inventory of Contaminated Sites (NIKM) project. It also presents the relation between the improvements of the methodology and the changes in efficiency of the inventory process. The trends from observed data in the first group of 32 districts (from 77 in total) are illustrated in graphs (linear and 3rd grade polynomic projection).

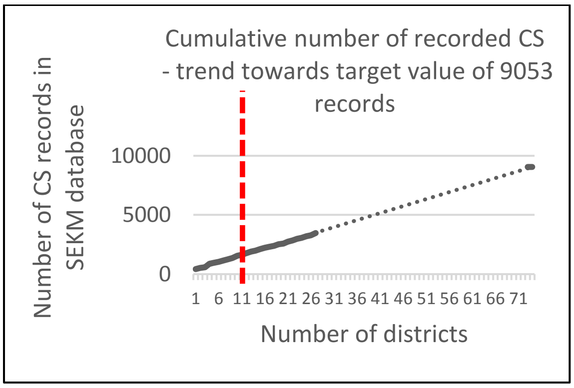
INTRODUCTION

The NIKM project [1] is focussed on the inventory and evaluation of information on CS throughout Czechia. The existing records of CS include clues of CS obtained from the remote sensing partial project task, are gathered in the SEKM database. All records together with the records of newly discovered CS collected in the running field campaign of the inventory are inputted into SEKM. Field inventory work started in March 2019. As a mapping unit we designated districts – there are 77 (incl. Prague). Twelve inventory teams are working in assigned districts according to the time schedule. The tasks are divided up among three members of the NIKM inventory consortium (see [1]). Based on data from the inventory in districts (see tab. 1), we projected the expected number of records, expected by the end of the inventory.

Tab. 1 Basic data from CS inventory in 32 districts (state by 31.8.2020)

	SEKM			Remote sensing			New CS records	Input in total	Output – CS records in total
	Input SEKM	registered	exluded	Input RS	registered	exluded			
District	13233			17011				30244	3485
Česká Lípa	166	85	81	163	38	125	14	343	**137**
Český Krumlov	92	44	48	157	8	149	4	253	**56**
Chrudim	200	82	118	155	20	135	12	367	**114**
Karviná	89	67	22	125	3	122	17	231	**87**
Rakovník	171	107	64	173	5	168	1	345	**113**
České Budějovice	160	74	86	340	5	335	8	508	**87**
Šumperk	282	224	58	110	34	76	23	415	**281**
Beroun	150	96	54	272	4	268	2	424	**102**
Jablonec n./Nisou	115	84	31	137	11	126	10	262	**105**
Jičín	101	62	39	206	10	196	7	314	**79**
Jindřichův Hradec	177	87	90	326	7	319	6	509	**100**
Nový Jičín	110	77	33	183	4	179	26	319	**107**
Plzeň – sever	148	104	44	234	58	176	17	399	**179**
Cheb	131	77	54	181	4	177	0	312	**81**
Plzeň – jih	94	58	36	287	73	214	13	394	**144**
Tábor	151	116	35	408	18	390	8	567	**142**
Prostějov	68	50	18	186	70	116	9	263	**129**
Trutnov	134	76	58	106	10	96	2	242	**88**
Plzeň-město	73	50	23	128	11	117	4	205	**65**
Karlovy Vary	306	72	234	158	18	140	2	466	**92**
Vyškov	115	73	42	121	10	111	7	243	**90**
Jeseník	91	81	10	24	4	20	8	123	**93**
Pardubice	149	96	53	412	41	371	8	569	**145**
Liberec	208	104	104	348	14	334	2	558	**120**
Praha – západ	104	68	36	365	35	330	14	483	**117**
Znojmo	143	82	61	413	26	387	18	574	**126**
Rychnov n./K.	108	80	28	151	17	134	6	265	**103**
Opava	152	98	36	229	3	226	15	396	**116**
Hradec Králové	149	43	45	220	21	199	40	409	**104**
Přerov	215	105	32	76	43	33	35	326	**183**
Klatovy	243	80	75	247	48	199	40	530	168
Svitavy	166	115	51	270	20	250	41	477	115
32 districts in total	**4761**	**2656**	**1673**	**6394**	**625**	**5769**	**338**	**11084**	**3485**

The linear prediction from the number of current day approved SEKM records allows us to assess the probable fulfilment of the prescribed target value of 9053 contaminated sites. It also allows us to prepare additional tools and actions to improve a yield of input records and/or to intensify the search and collection of new, hitherto unknown contaminated sites. On 31.8.2020, based on data from 42.2 % of Czechia territory, the predicted number of final inventory output is 9067 records, i.e. 100.2 % of the project target value (see fig. 1). Some trends of the selected parameters of CS records set within the group of 32 districts are shown in fig. 2.



The dashed red line in tab. 1 and in the following figures is dividing the group of 32 districts into the first group of 14 districts (filling in SEKM2) and the second group of 18 districts (filling in SEKM3 after training, accepted improvements in methodology). Dotted black line in the graphs always shows the linear trend and the dashed black line the 3rd grade polynomic projection.

Fig. 1 Cumulative numbers of recorded CS (32 districts – 42.2 % of Czechia territory)

We have evaluated some factors influencing a higher yield of records: improved CS administration in a new SEKM3 system, proper observation on the location of CS clues and making appropriate forms of photo documentation. E.g. the average yield of CS clues (RS) in 32 districts is 10 % (min. 1.5 %, max. 56.6 %).

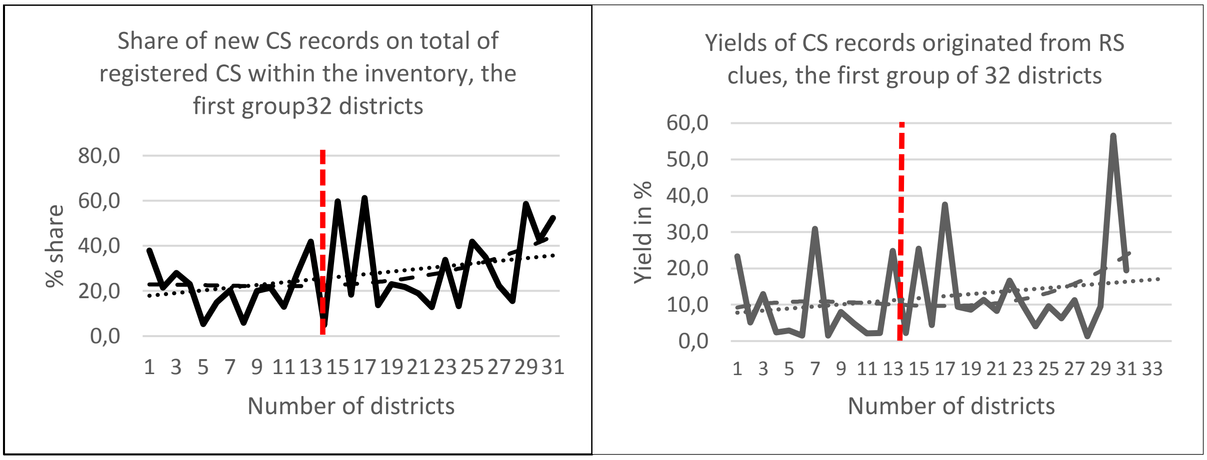


Fig. 2 The analysis of trends of selected parameters of CS records set within the group of 32 districts

THE METHODOLOGICAL SUPPORT AND CONTROL OF INVENTORY WORKS

Based on gathered experience from the first phase of field works (14 districts), we completed the methodology with some handbooks and detailed instructions. A series of handbooks for field mappers consists of six brochures totalling 171 pages [3]. The inventory teams were instructed and trained in the frame of field control days and training meetings. The transition from the SEKM2 to SEKM3 database in November 2019, involving an intensive training period of filling in the new database, also helped to improve the inventory process.

CONCLUSIONS

The linear trend from today's data towards the end of the inventory period (31.12.2021), shows a probable fulfilment of the prescribed target value (indicator) of 9053 CS. The inventory activities in line with the project methodology were supported with some methodical handbooks and detailed instructions. This support together with the transition from the SEKM2 to SEKM3 database seems to be, according to the analyses of trends of some CS district parameters, a turning point towards a higher efficiency of inventory.

ACKNOWLEDGEMENT: Project NIKM – 2nd stage (National Inventory of Contaminated Sites) is co-financed from European Union Funds – the Cohesion Fund – in the frame of the Operational Programme of the Environment 2014–2020, the area of intervention 4.2. – The Rehabilitation of Old Environmental Burdens.

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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, inovations, 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]

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.

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

Fig. 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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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, 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, and 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 $4.489*10^{-5}$ 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.

1. 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. Waters contaminated with organic pollutants, heavy metals and pathogenic microorganisms pose a serious risk to public health and important issue of environmental protection. 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 [1]. Therefore toxicity of pesticides and their degradation products is making these chemical substances a potential hazard by contamination of the environment.

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. The fly and bottom ash could be used as a constructive material, specifically as a substitute for the sand and gravel in structures, and as a binding component in certain types of cement [2], mostly concrete and masonry. The utilization of TTP solid wastes lead to the decrease disposal of these compounds to the landfills, and thus allows an improved natural resource conservation. The use of fly and bottom ash, however, still poses a great challenge as the only 30% of the total ash produced in the world is currently reused [3]. As an additional benefit to their potential (re)use, the U.S. Environmental Protection Agency (EPA) in 2014. has reclassified fly and bottom ash as non-hazardous materials [3].

Fly and bottom ash present the most abundant waste material occurred from the coal combustion, but also an effective adsorbent for different pollutants removal from the wastewaters [6]. TPP solid waste has a significant potential in wastewater treatment stemming from the properties of the major chemical components: alumina, silica, ferric oxide, calcium oxide, magnesium oxide, and carbon, glassy phase, as well as from its physical properties, such as porosity, particle size distribution, and surface area [3, 4]. This research is focused on the utilization of fly ash, as a waste product from the TPP, in order to develop novel and low cost adsorbents, reducing the amount of waste and encouraging energy savings and reuse of the materials.

2. EXPERIMENTAL PART

2.1. Materials and methods

Material activation

The FA used in this study was obtained from waste product from the Termal Power Plants (TPP) Morava, Serbia. According to the ASTM standards (eng. American Society for Testing and Materials), fly ash is classified into the different types, which are based on the content of silica, aluminium, and iron oxides ($SiO_2 + Al_2O_3 + Fe_2O_3$) [3]. The Serbian fly ash is classified as type F [3]; with the content of $SiO_2 + Al_2O_3 + Fe_2O_3$ oxides higher than 70 %, wherein the CaO content is less than 10 % of the total. The chemical activation of FA (the addition of lime), is performed in order to provides better adsorption and mechanical properties of the modified samples (MFA) used in production of construction materials.

Optimization of adsorbent activation

Optimization of the adsorption synthesis was performed by the surface response methodology (RSM), based on two factors of the D-optimal design. The operational values of the selected variables in the experimental plan obtained through the software, includes 18 experimental papers with five point replicates. The output variable was the adsorption capacity (fig. 1a). The data obtained in these experiments were fitted with a second-order polynomial equation and the coefficients of the response function and their statistical significance were evaluated by the least square method, using commercial software Design-Expert, Software Version 9 (Stat-Ease, Inc. 2021 E. Hennepin Ave. Suite 480 Minneapolis, USA).

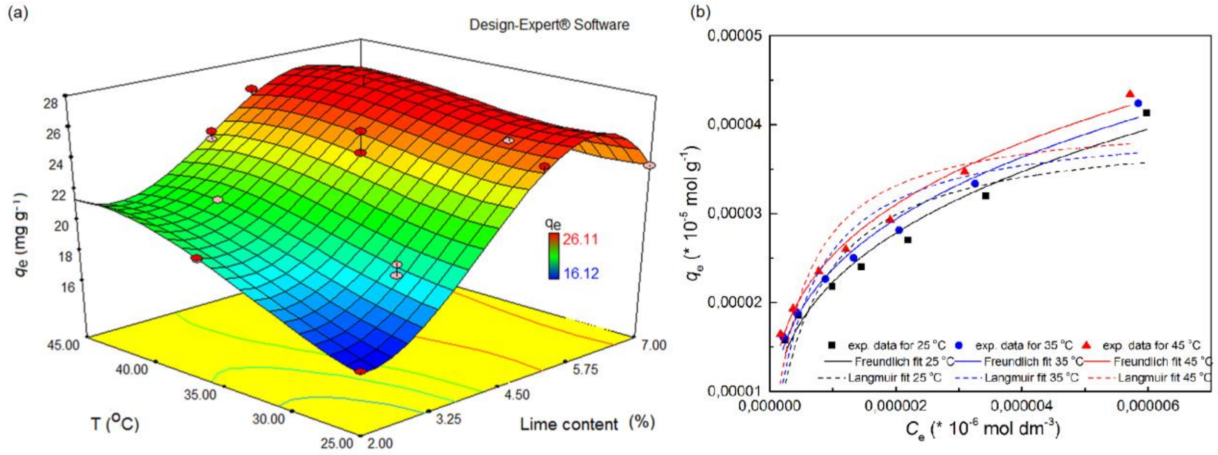

Fig. 1 Contour diagram representing relation between capacity vs T and lime content (%) for MFA (a) and experimental plan and fitting of adsorption experimental data with Freundlich and Langmuir isotherm model adsorption of DDT on MFA

2.2. Conditions and procedure for adsorption DDT on the MFA

Adsorption experiments were carried out in batch conditions, with the initial concentration of DDT solutions (C_0 = 2.23*10^{-5} mol L^{-1}) and dose adsorbent of 250 to 1250 mg L^{-1}. Thermodynamic adsorption experiments were performed at 25, 35 and 45 °C. The effect of contact time on the adsorption of DDT was monitored over a period of 10–90 minutes. The amount of adsorbed ions is calculated from the difference between the initial and the equilibrium concentration.

All experiments were repeated three times, and only their mean values are given. The maximum deviation is < 3 % (experimental error). All calculated standard errors for isotherm parameters, kinetic and thermodynamic parameters were determined using Microsoft Excel solver using nonlinear regression. The concentration of Dichlorodiphenyltrichloroethane (DDT) was analyzed using UV-VIS spectrophotometry and high-performance liquid chromatography (HPLC)).

3. RESULTS AND DISCUSSION

3.1. The effect of the contact time on the adsorption of DDT

The effect of time on the adsorption of DDT was analyzed in the range from 10 to 90 minutes.

The kinetic results demonstrate that process was fast in the first 60 minutes for DDT (81.8 %), and adsorption rate substantially decrease in the period from 60 to 90 minutes. Percent of DDT removal increase to 90.4 %. Equilibrium was established for 150 and 180 minutes of DDT adsorption.

3.2. Adsorption kinetics

In order to study the adsorption kinetics, the pseudo-first, pseudo-second-order and second order kinetic models were used [4–7]. According to the regression coefficient (r), as well as the Δq values and calculated standard error for all model parameters, the experimental kinetic data are better described using the pseudo-second order (PSO) kinetic models (Table 1).

Tab. 1 Kinetic parameters for DDT adsorption onto MFA

Adsorbate/order of kinetic law		Pseudo-first	Pseudo-second	Second order
DDT	q_e (mol g^{-1})	7.25*10^{-6}	1.75*10^{-5}	1.75*10^{-5}
	k (k_1, k_2)	0.0313	0.0196	0.0117
	R^2	0.903	0.992	0.892

3.3. Adsorption isotherm

The state of interaction/bonding on the solutes/adsorbent surface can be recorded by fitting experimental data with various adsorption isotherms. The experimental data were compared to the models of the Langmuir and Freundlich isotherms utilized elsewhere in previous research within the literature [5–7], whose parameters are provided in Tab. 2. Analysis of the experimental data of DDT adsorption on the adsorbent MFA indicate that the best fit of the data for an adsorbent according to the correlation coefficient is of a Freundlich-isotherm model (Figure 1b).

Tab. 2 Adsorption isotherm parameters for DDT adsorption on the MFA

Isotherm model and model parameters		Temperature		
		25 °C	35 °C	45 °C
Langmuir isotherm	q_m (mol g^{-1})	4.49*10^{-5}	4.57*10^{-5}	4.65*10^{-5}
	K_L (L mol^{-1})	1034205	1178934	1361805
	R^2	0.958	0.966	0.973
Freundlich isotherm	K_F (mg g^{-1}) (dm^3 mg^{-1})$^{1/n}$	10.85	11.43	102.011
	1/*n*	0.289	0.282	0.273
	R^2	**0.980**	**0.983**	**0.990**

According to the Freundlich isotherm, the mechanism of DDT adsorption onto MFA could be described by heterogeneous adsorption, where the adsorbed ions/molecules had different enthalpies and adsorption activation energies. The n value from the Freundlich isotherm is a measure of the adsorption intensity or surface heterogeneity. Values of n close to zero indicate a highly heterogeneous surface. Value obtained of n < 1 implies chemisorption process, the higher value (table of fig. 2) is an indication of cooperative adsorption, i.e., physisorption and chemisorption, with different contribution at different steps of the equilibration of the system [6, 7]. Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were calculated using Van't Hoff thermodynamic equations [5–7]. The calculated thermodynamic parameters (Table 3) may cast light on the adsorption mechanisms of the studied pollutions on MFA.

Tab. 3 Calculated Gibbs free energy of adsorption, enthalpy and entropy
for DDT adsorption on MFA

Adsorbate	ΔG° (kJ mol^{-1})			ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	R^2
	25 °C	35 °C	45 °C			
DDT	-44.29	-46.11	-47.98	10.85	184.88	0.997

The negative adsorption standard free energy changes (ΔG^0) and positive standard entropy changes (ΔS^0) at all temperatures indicates that the adsorption reactions are spontaneous (Table 3). The decrease of Gibbs free energy (ΔG^0) with increasing temperature indicates that spontaneity of the reaction increases. The positive values of ΔS^0 indicates a higher disorder tendency at the interface between MFA surface and DDT solutions. This is presumably due to the increase of released solvent molecules when solvated solute distributes on the solid phase from the aqueous solution and the number of molecules increases at the solid-liquid interface. Generally, the change of free energy in the case of physisorption was recorded to be between -20 and 0 kJ mol^{-1}, for both physisorption and chemisorption between -20 and -80 kJ mol^{-1}. Therein, the interaction between DDT and MFA of the physisorption processes.

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: 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. Adsorption data were modeled by using Langmuir and Freundlich isotherm, while kinetic data was successfully fitted by using pseudo-second-order equation.

Desorption experiments indicated low recovery which open the question of valuable methodology for waste management. 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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IMPROVED MANAGEMENT OF CONTAMINATED SITES IN SERBIA

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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 with the Regulation on Reporting on contaminated sites and the List of polluting activities. In the past years, UNEP and other UN agencies provided project support with a strong capacity-building component for managing contaminated sites. By strengthening of administrative capacities, facilitating exchange of experiences and field investigation, these projects contributed to enhanced cooperation between institutions dealing with land management issues, but also to the increased share of sites where detailed surveys and remediation were carried out in comparison to the 2007.

INTRODUCTION

In the territory of the Republic of Serbia there are 709 sites identified as either potentially contaminated or contaminated, 557 of which belong in the first and 152 in the latter category. Divided according to the main types of localized sources of soil contamination, municipal waste landfills have the largest share of 31.17 % in the total number of sites, as is shown by 2016 data which is the same as in previous years. Out of 709 sites, 478 are either in need of or have undergone investigation and 103 are currently under investigation. There are 93 sites in need of remediation and 564 sites that may require one. In the period 2008–2015, the Ministry of Environmental

Protection issued approvals for 91 projects for rehabilitation and remediation.

In order to improve the management of contaminated sites in Serbia, the Ministry of Environmental Protection and Serbian Environmental Protection Agency (SEPA) cooperate with UN Agencies in a variety of projects.

RESULTS AND DISCUSSION

Investigation of industrial sites suspected to be contaminated was a part of the GEF-funded project *Enhanced Cross-sectoral Land Management through Land Use Pressure Reduction and Planning* which is implemented by United Nations Environment Programme (UNEP) in close cooperation with the Ministry of Environmental Protection and SEPA in the period 2015–2019 (Vidojevic et al, 2016, 2017). The Project aims at providing the lacking methodologies, knowledge and coordination mechanisms for sustainable and integrated management of soil as a natural resource. It supports the establishment of state, provincial and local networks for land use and soil quality monitoring, strengthening of administrative capacities and contributes to enhanced cooperation among institutions dealing with land degradation issues. The Project further on supports the development of a Cadastre of contaminated sites managed by SEPA and a policy framework for integrated land use management and its implementation at local level. The data and information for the selected 32 potentially contaminated sites collected from previous studies and through numerous consultations included: previous land use, type of industry, surface area, type and quantity of hazardous substances found at the location and in the surrounding area, soil and groundwater quality, as well as geological, pedological and hydrological features. The collected data are sorted and transferred to digital format in order to complete a database of contaminated sites. Field missions to the identified sites were conducted in the period September – December 2016 with the purpose to identify receptors of pollution and potential exposure routes, and to prepare and elaborate sampling programs, whereas the soil sampling itself took place in 2017 when 264 soil samples were analysed. The conducted research was the basis for creating a list of prioritized sites for remediation and a preliminary assessment of the risks that the selected sites pose to human health and the environment. For this purpose, the project team applied the Preliminary Risk Assessment Model for the identification and assessment of problem areas for Soil contamination in Europe – PRA.MS. The Project also received a contribution from the Italian Ministry of Environment, Land and Sea that enabled the development of Site Characterization Plans for two priority sites, in addition to the procurement of the laboratory analytical equipment, personal protective equipment and data storage server for SEPA as well as numerous study visits and opportunities for experience sharing with Italian expert institutions ISPRA, ENEA, ISS and INAIL (Falconi et al, 2018).

Additional investigation of sites contaminated with PCB is a part of another GEF-funded project *Environmentally sound management and final disposal of PCBs in Serbia* implemented by UNIDO in close cooperation with the Ministry of Environmental Protection and SEPA. Namely, in 2018, this project envisages further investigation of three sites where PCB contamination was previously confirmed through UNEP/GEF project, while a pilot remediation will be conducted at the most heavily polluted site.

Furthermore, through the WHO project funded by UN Environment's SAICM Quick Start Programme Trust Fund titled *Strengthening Serbian national capacities and inter-sectorial synergies for safe management of contaminated sites and related hazardous substances to prevent negative impact on human health and the environment* the methodology for the analysis of major health outcomes of residents living close to contaminated sites has been developed in 2018.

CADASTRE OF CONTAMINATED SITES

According to the Law on Soil Protection, the Cadastre of Contaminated Sites is a set of relevant data on endangered, polluted and degraded soil. Serbian Environmental Protection Agency (SEPA) has been constantly working to improve the methodology of data collection, quality and the way of systematization and presentation of data. The last updated database of the Cadastre shows that 709 potentially contaminated and contaminated sites have been identified and recorded on the territory of the Republic of Serbia.

The main purpose of the Cadastre is to provide systematic data on sources of pollution such as the type, quantities, methods and location of discharges of pollutants into the soil, in order to implement preventive or remediation measures. Data collection is defined in more detail in the Rulebook on the content and manner of keeping the cadastre of contaminated sites, type, content, forms, manner and deadlines for data submission. The Rulebook contains six forms that create the basis for data collection and are baseline for operating the Cadastre.

The content of the forms is given according to the phases of site research and phases of remediation implementation:

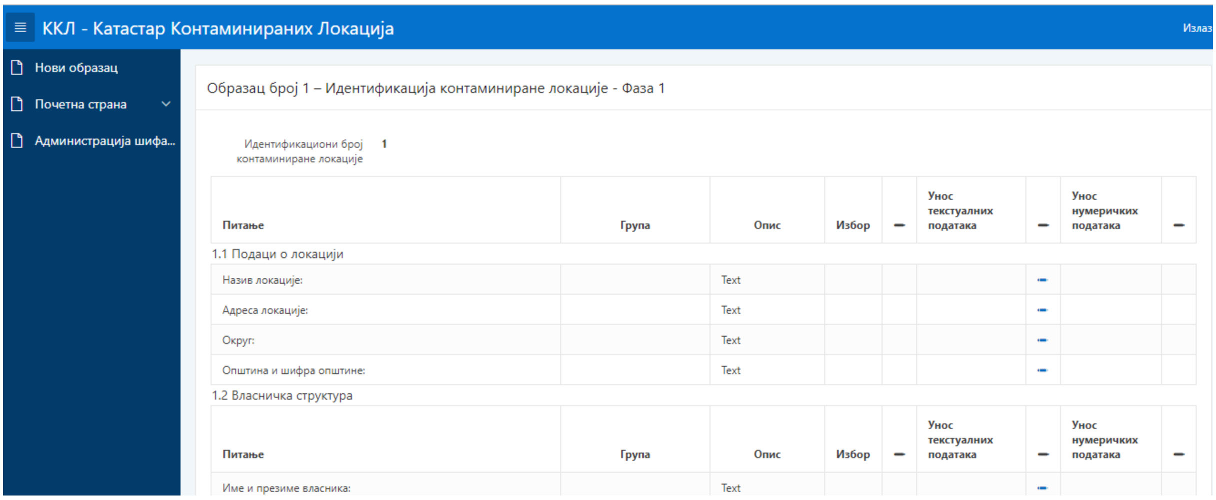
1. Form No. 1 – Identification of the contaminated site – Phase 1. This Form provides basic information about the site such as: name of the site, municipality/city where site location is, coordinates, ownership structure and what type of land use is at the location (Fig. 1);
2. Form No. 2 – Preliminary investigations of the contaminated site – Phase 2. This Form provides various information that may be relevant and determined by preliminary surveys such as: contaminated site and its area, depth of contaminated soil, groundwater pollution, proximity to sensitive areas (settlements, rivers, agricultural areas), type of land, etc;

3. Form No. 3 – Detailed research of the contaminated site – Phase 3. This Form provides detailed responses to the following questions: contaminated soil and its area, depth of contaminated soil, groundwater pollution, proximity to sensitive areas (settlements, rivers, agricultural areas), type of soil, etc;
4. Form No. 4 – Planned remediation – Phase 4. This Form provides information related to planned remediation techniques and costs, as well as planned remediation techniques to specific sources of pollution (if there are more than one);
5. Form No. 5 – Implemented remediation – Phase 5. This Form provides information related to the implemented remediation techniques and realized costs, as well as the application of remediation techniques to special sources of pollution (if there are more than one);
6. Form No. 6 – Monitoring after remediation – Phase 6. This Form provides information on monitoring state of the environment at a specific location after the applied remediation techniques.

   At the end of each phase, before submiting forms you need to answer folowing questions: Who is the Client of the phase, who verifies that specific phase, prices and costs for the specific phase and whether it is necessary to work on the next phase. Forms shall be completed sequentially to the extent which the contaminated site has been investigated and/or if remediation is planned or is already carried out.

   Reporting to SEPA is conducted once a year, by logging in to the application. All those who apply for request from SEPA or the person in charge of keeping the cadastre, have access to the application. There are two types of accounts for logging in after getting Administrator's approval and creation of account:

1. Logging as *Public user* – Logging this way there is just option to see and download all available data without any possibility of changing it and
2. Logging as *Legal entity* – This type of account is for all those who need to submit new data every year. They can manage its own data, get access to see and download data of another Legal entities but without possibility of changing it.



Образац број 1 – Идентификација контаминиране локације - Фаза 1

Идентификациони број контаминиране локације 1

Питање	Група	Опис	Избор	−	Унос текстуалних података	−	Унос нумеричких података	−
1.1 Подаци о локацији								
Назив локације:		Text				−		
Адреса локације:		Text				−		
Округ:		Text				−		
Општина и шифра општине:		Text				−		
1.2 Власничка структура								

Питање	Група	Опис	Избор	−	Унос текстуалних података	−	Унос нумеричких података	−
Име и презиме власника:		Text				−		

Fig. 1 Form 1 (Phase 1)

All questions could be answer by marking checkbox or or typing alphanumeric signs.

In the period October – December 2018, 8 regional workshops were held where representatives of local self-governments were trained to use and enter data into this application. As part of the previous project activities, on the first page after logging in, a map of the Republic of Serbia is provided with data from 32 locations where preliminary research on contaminated sites has been conducted (Fig. 2).

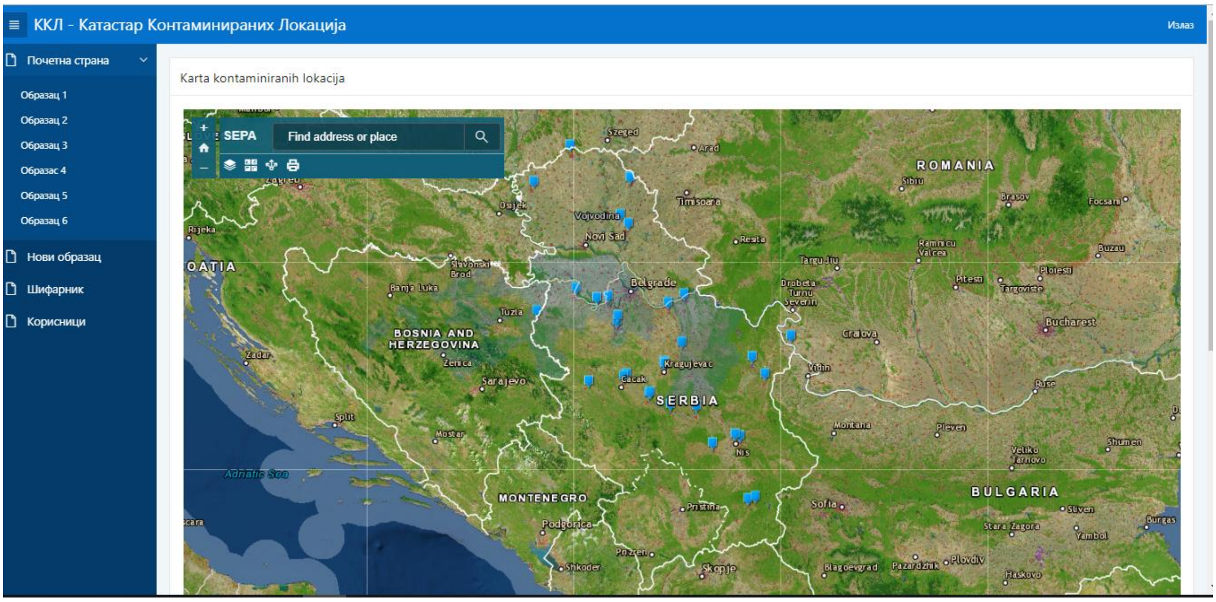


Fig. 2 Map of the Republic of Serbia with 32 preliminary investigated location

CONCLUSION

The results of 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 reporting system for the national Cadastre of Contaminated Sites, developed capacity for the investigation and improved overall management of contaminated sites.

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The activity has been implemented within the framework of the national project
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OP KŽP

European Union
Cohesion Fund

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AGENCY