INVESTIGATION OF THE ENVIRONMENTAL ACCEPTABILITY OF GEOTECHNICAL COMPOSITES, MADE FROM DIFFERENT RECYCLED MATERIALS

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Doctoral Dissertation
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RAZISKAVA OKOLJSKE SPREJEMLJIVOSTI GEOTEHNIČNIH KOMPOZITOV, PRIPRAVLJENIH IZ RAZLIČNIH RECIKLIRANIH MATERIALOV

Doktorska disertacija

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To my family.

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Abstract

Current and especially past industrial and mining activities, including underground and open pit mining, have often resulted in soil pollution that has become a global and alarming environmental problem. Among contaminants, heavy metals and metalloids are under environmental scrutiny due to their potential toxicity, persistence, and because they can be released from anthropogenic emissions into terrestrial environment as easily soluble, highly mobile, and highly bioavailable chemical species.

Significant efforts are being made to remediate contaminated soil areas and rehabilitate abandoned pits. The best available technique for the remediation of contaminated soils is the use of immobilizing agents that reduce the mobility of potentially toxic elements (PTEs), while for the reclamation of surface pits or quarries, appropriate solution is their filling using geotechnical composites made from recycled waste.

Among the various immobilizing agents, paper ash is a promising additive for the remediation of contaminated soils with PTEs. However, the long-term remediation efficiency has not yet been investigated. There is also no evidence of PTEs immobilization mechanisms after remediation.

To investigate the environmental acceptability of geotechnical composites made from recycled wastes for their use in the rehabilitation of surface pits and quarries, laboratory tests were mainly carried out. Only few studies report the results of field trials. There is also no data on the influence of preparation of geotechnical composites on the leaching of potentially hazardous substances (PHSs) and what are the long-term environmental impacts of geotechnical composites.

To gain insights into the mechanisms of cadmium (Cd), lead (Pb) and zinc (Zn) immobilization using paper ash for remediation, a laboratory study was conducted in uncontaminated, artificially contaminated and remediated soils. Long-term remediation efficiency and partitioning of Cd, Pb, and Zn was investigated over year applying the sequential extraction procedure and a complementary X-ray diffraction analysis. This methodological approach enabled tracking the temporal redistribution of Cd, Pb and Zn from easily to sparingly soluble soil fractions, evaluation of the efficiency of remediation and the stability of the newly formed mineral phases. After remediation, Cd, Pb and Zn were effectively immobilized by the precipitation of insoluble hydroxides and through the carbonization process in insoluble carbonate minerals.

The environmental acceptability of three geotechnical composites made from recycled wastes was investigated in the laboratory and field scale, using lysimeters. The results of laboratory leaching tests showed that two composites were in compliance with national legislation, while field investigation proved that optimally installed geotechnical composites are environmentally acceptable for the rehabilitation of mining sites. The laboratory leaching tests also showed that concentrations of several PHSs leached from one composite exceeded the legislative limit values. Nevertheless, this composite can be used for closing landfills for non-hazardous wastes. The procedures utilized in the PhD are promising ways to reduce waste disposal, to sustainably rehabilitate degraded areas, and to preserve natural resources.

Povzetek

Naraščajoče industrijske in rudarske dejavnosti, vključno s podzemnimi in odprtimi kopi, so povzročile onesnaženje tal, ki je postalo globalen in zaskrbljujoč okoljski problem. Med onesnažili, ki so pod okoljskim nadzorom, so tudi težke kovine in polkovine zaradi njihove potencialne toksičnosti, nerazgradljivosti ter ker se v kopensko okolje sproščajo iz antropogenih virov v obliki topnih, mobilnih in visoko biološko razpoložljivih kemijskih zvrsti.

Vloženi so znatni napori za remediacijo onesnaženih tal in odprtih kopov. Najboljša razpoložljiva tehnika za remediacijo onesnaženih tal je uporaba imobilizacijskih sredstev, ki zmanjšajo mobilnost potencialno toksičnih elementov (PTEs), medtem ko je za rekultivacijo površinskih kopov in kamnolomov ustrezna rešitev uporaba geotehničnih kompozitov, pripravljenih iz recikliranih odpadkov.

Med različnimi imobilizacijskimi sredstvi je papirniški pepel obetaven dodatek za remediacijo onesnaženih tal s PTEs. Dolgoročne učinkovitosti remediacije še niso raziskali. Prav tako ni podatkov o mehanizmih imobilizacije PTEs po remediaciji. Za raziskavo okoljske sprejemljivosti geotehničnih kompozitov, pripravljenih iz recikliranih odpadkov, za sanacijo površinskih kopov, so bile izvedene predvsem laboratorijske preiskave. Le nekaj študij poroča o rezultatih terenskih poskusov. Prav tako ni podatkov o vplivu priprave geotehničnih kompozitov na izluževanje potencialno nevarnih snovi (PHSs) in kakšni so dolgoročni vplivi geotehničnih kompozitov na okolje.

Da bi pridobili vpogled v mehanizme imobilizacije kadmija (Cd), svinca (Pb) in cinka (Zn) z uporabo papirniškega pepela za remediacijo, smo izvedli laboratorijsko študijo v neonesnaženih, umetno onesnaženih in remediiranih tleh. Dolgoročno učinkovitost remediacije in porazdelitev Cd, Pb in Zn smo raziskali v enem letu z uporabo sekvenčnih ekstrakcij in komplementarne X-žarkovne rentgenske difrakcijske analize. Tak metodološki pristop je omogočil sledenje časovni prerazporeditvi Cd, Pb in Zn iz lahko v težko topne frakcije tal, oceno učinkovitosti remediacije in stabilnosti novonastalih mineralnih faz. Cd, Pb in Zn so se učinkovito imobilizirali z obarjanjem netopnih hidroksidov in s postopkom karbonizacije v netopne karbonatne minerale.

Okoljsko sprejemljivost treh geotehničnih kompozitov iz recikliranih odpadkov smo raziskali v laboratorijskem in terenskem merilu z uporabo lizimetrov. Rezultati laboratorijskih izlužitvenih testov so pokazali, da sta dva kompozita skladna z nacionalno zakonodajo, terenska preiskava pa je pokazala, da so optimalno vgrajeni geotehnični kompoziti okoljsko sprejemljivi za sanacijo odprtih kopov. Laboratorijski izlužitveni testi so tudi pokazali, da so koncentracije več PHSs, izluženih iz enega kompozita, presegale zakonsko predpisane mejne vrednosti. Kljub temu se ta kompozit lahko uporablja za zapiranje odlagališč nenevarnih odpadkov. Postopka, uporabljena v doktorski disertaciji, predstavljata perspektiven način za zmanjšanje odlaganja odpadkov, trajnostno sanacijo degradiranih območij in ohranjanje naravnih virov.

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Abbreviations

BCR	...	European Community Bureau of Reference
BOD	...	biological oxygen demand
EDS	...	energy-dispersive X-ray spectroscopy
ESDAC	...	The European Soil Data Centre
EU	...	European Union
EWL	...	European Waste List
GC	...	gas chromatography
HPLC	...	high-performance liquid chromatography
IC	...	ion chromatography
ICP-MS	...	inductively coupled plasma mass spectrometry
IPS	...	International Postgraduate School
JSI	...	Jožef Stefan Institute
PHSs	...	potentially hazardous substances
PTEs	...	potentially toxic elements
SEM	...	scanning electron microscopy
TDS	...	total dissolved solids
US EPA	...	United States Environmental Protection Agency
WHO	...	World Health Organization
XRD	...	X-ray diffraction
ZAG	...	Zavod za gradbeništvo Slovenije

Chapter 1

Introduction

With all the environmental problems, people began to realize how important it is to preserve our ecosystem and that protecting it has become an important task for all individuals. Most of the damage caused by the human population is the result of the intensification of industrialization, mining and agricultural activities in recent decades. Great efforts are put into reduction of human activities impact on the ecosystem and rehabilitation of already degraded areas. To overcome these challenges, the European Union (EU) has adopted a set of policies and strategies under the European Green Deal (European Commission 2019a). The priorities of the European Green Deal include protecting the ecosystem, reducing air, water and soil pollution, moving towards a circular economy and improving waste management.

The doctoral dissertation is focused on research dealing with soil pollution, improving waste management by recycling waste materials for the construction sector, and evaluating the long-term environmental impacts of newly formed construction products.

1.1 Soil

Soil, water and air are all essential to human life and society. Among these components, soil is often overlooked. There is a need for greater awareness of healthy soil benefits and ensuring its quality and consequently its function. Soil quality and function depends on its physical, chemical and biological properties (Lambin et al., 2006). The most important are the regulating and productive functions, i.e. ecological soil functions. Other soil usages include raw material resources, land for building, areas for waste disposal etc. There are different definitions of soil. Generally, it is considered as the fine earth which covers land surfaces, generated in the process of the in situ weathering of rock materials or the accumulation of mineral matter transported by water, wind, or ice (Nortcliff et al., 2011). A soil on average contains approximately 45% solid material, 5% organic matter, and 50% pore space. The pore spaces are occupied with water and air. Soil is definitely a complex and dynamic system, which can be regarded as practically non-renewable, as soil formation is a remarkably slow process. It can take several hundred years for a centimetre of topsoil to form (Kalev & Toor, 2018). Alteration of soil processes leads to changes in the functioning of ecosystems, and many environmental problems (Lal, 2012).

Soil contaminants can be divided into two broad categories. The first one includes inorganic contaminants, which are further divided into metals/metalloids and non-metals, and the second category, which includes organic contaminants. The latter are further divided into halogenated and non-halogenated compounds (FAO and UNEP, 2021a). The heavy metal contamination is mostly instigated by anthropogenic activities, while natural processes like weathering and leaching spread pollution in other environmental

compartments (Wan et al., 2022). The most frequently occurring inorganic contaminants in soils are metals/metalloids such as arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), lead (Pb), and zinc (Zn) (FAO and UNEP, 2021a). In uncontaminated soils, heavy metals are mainly present in the sparingly soluble forms (e.g. oxides, hydroxides and silicates), while in contaminated soils, they occur also in mobile, bioavailable forms, which are of great environmental concern (Kumar et al., 2022).

According to the EU Commission, contaminated site is defined as an area, where the soil contamination presents a risk to human health, environment or other receptors (European Commission, 2006). Currently major soil problems in EU are loss of the resource due to erosion and flooding, local and diffuse soil contamination, especially in industrial and urban areas, and soil acidification, which can result in increased metal mobility (EEA, 2023). It was estimated that 2.8 million sites are potentially contaminated across the EU, of which 390 000 are expected to require remediation (FAO and UNEP, 2021b). Human activities contribute to soil contamination to a much greater extent, as natural pollution is recorded only in a few cases (e.g. accumulation of high levels of perchlorate in soil in the Atacama Desert in Chile) (Calderón et al., 2014). Two major activities that contribute to soil contamination are industrial and mine activities. Data reported by The European Soil Data Centre (ESDAC) (EU Soil Observatory, 2021) showed that waste disposal and treatment contribute to more than 37% of soil contamination, while different industrial activities up to 33.3%.

Legal requirements for soil protection at the European Union level have not been agreed, and currently Member States regulate soil protection at the national level through different policies and legislation. EU is developing the law that would regulate soil protection on the same level as air and water, and for all EU members. In 2021, the EU Commission adopted the EU Soil Strategy for 2030 (European Commission, 2021), which should contribute to the objectives of the EU Green Deal. The strategy aims to ensure that by 2025, all EU soils will be healthy and performing their basic function, additionally the restoration and sustainable use of soils will be normalised (European Commission, 2021). It is expected, that the law will take into account the differences between different soil types regarding biological, chemical, and physical composition and functional differences of soils (in terms of land use).

Currently, in Slovenia, soil protection is included in different legislative acts. The main documents concerning soil protection are the Environmental Protection Act (Official Gazette of RS, No. 158/20), and a Decree on Limit Values, Alert Thresholds and Critical Levels of Dangerous Substances into the Soil (Official Gazette of RS, No. 68/96). Other acts which affect the soil protection are the Decree on the Limit Input Concentration Values of Dangerous Substances and Fertilisers into Soil (Official Gazette of RS, No. 19/17), Decree on Burdening of Soil with Waste Spreading (Official Gazette of RS, No. 61/11), Decree on Waste Landfill (Official Gazette of RS, No. 13/21), and Decree on Waste (Official Gazette of RS, No. 77/22).

1.1.1 Methods for characterization of soil and limit values of contaminants

Analytical procedures for soil characterization are defined in Rules on Soil Status Monitoring (Official Gazette of RS, No. 44/22). When preparing soil samples for the analysis of metals, the SIST ISO 11466 (1996) or ISO 12914 (2012) standards must be followed. Both prescribe the extraction of metals using *aqua regia* (a mixture of nitric acid (HNO_3) and hydrochloric acid (HCl), in a molar ratio of 1:3). The determination of

extracted metals must be carried out according to the SIST EN ISO 17294-2 (2016) standard, which prescribes the use of the inductively coupled plasma mass spectrometry (ICP-MS) technique.

Limit values of contaminants, including metals, are defined in the Decree on Limit Values, Alert Thresholds and Critical Levels of Dangerous Substances into the Soil (Official Gazette of RS, No. 68/96). Limit and critical values for metals are given in Table 1.

Table 1: Limit and critical values of substances in the soil.

Dangerous substances	Limiting value (mg/kg dry matter)	Warning value (mg/kg dry matter)	Critical value (mg/kg dry matter)
Cadmium (Cd)	1	2	12
Copper (Cu)	60	100	300
Nickel (Ni)	50	70	210
Lead (Pb)	85	100	530
Zinc (Zn)	200	300	720
Mercury (Hg)	0.8	2	10
Cobalt (Co)	20	50	240
Molybdenum (Mo)	10	40	200
Arsenic (As)	20	30	55

1.1.1.1 Inductively coupled plasma mass spectrometry

ICP-MS is a highly sensitive analytical technique, which enables simultaneous determination of most of the elements in the periodic table, at very low concentration levels (below 0.01 µg L^{-1}). It couples inductively coupled plasma with mass spectrometer, which detects ions as mass to charge ratio (m/z) (Broekaert, 2006; Thomas, 2013).

Plasma is generated in a stream of argon (Ar) gas in a quartz torch. The torch is located in the centre of a cooled coil made of copper. A radio frequency generator (27 to 40 MHz) provides high-frequency high-power electric current that passes through the coil. The magnetic field which is generated by the electric current creates collisions between Ar atoms. As a consequence, ions and electrons are produced. The torch is made of three concentric tubes. Plasma gas (Ar) is introduced through the middle tube, sample aerosol is carried by Ar and is delivered through the inner tube, while Ar gas for cooling passes through the outer tube. Different nebulisers are used to aspirate the liquid sample into the plasma. Only fine aerosol passes into the plasma, while bigger droplets are settled. High plasma temperature (up to 10,000 K) dries aerosol droplets, which are dried, decomposed, vaporised, atomized and finally ionized, mainly as M^+ ions. The resulting positively charged ions are extracted into the vacuum system through a pair of interfaces (sampler and skimmer) cones. Electrostatic lenses keep the ions focused in a compact ion beam as they pass through the vacuum system to mass spectrometer. In ICP-MS, three types of mass analysers are used: magnetic sector field (high resolution), time-of-flight and the quadrupole analyser. The latter, being most commonly used, is made from four cylindrical rods, organised in a square. Quadrupole analyser uses a combination of direct (DC) and alternating (AC) current to separate ions based on the mass to charge ratio. The AC and DC provide a hyperbolic electric field. Only a narrow range of masses (m/z particles) can be transmitted. By altering the current, masses with selected (m/z) are passed to the detector (Broekaert, 2006; Thomas, 2013).

The main components of the ICP-MS instrument are shown in Figure 1.

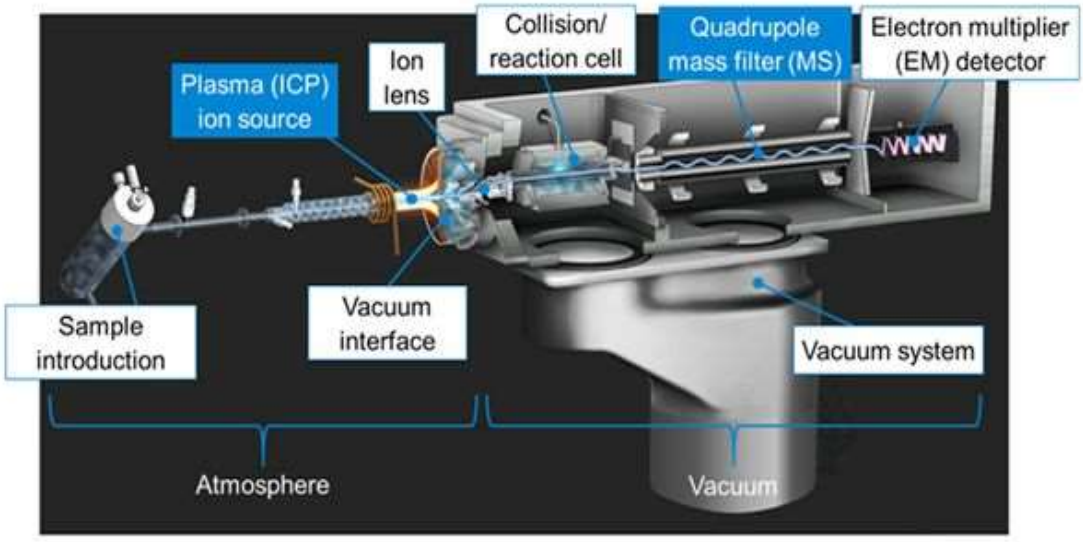


Figure 1: Main components of a single quadrupole ICP-MS instrument (Reproduced from Agilent Beginner's Guide to ICP-MS, with permission of Agilent Technologies).

ICP-MS can operate in pulse or analogue modes, which extend its linear dynamic range up to 9 orders of magnitude. The detector has high sensitivity and low background noise (Broekaert, 2006; Thomas, 2013).

ICP-MS can also be coupled to a chromatographic separation device, such as high-performance liquid chromatography (HPLC), ion chromatography (IC) and gas chromatography (GC).

1.2 Mining Activities and Waste Generation

Mining activities and waste generation significantly contribute to soil contamination (EU Soil Observatory, 2021).

1.2.1Mining activities and reclamation

Mining activities have been occurring for thousands of years. Mining is the main source of raw materials and therefore an important aspect of the development of today's society. On the other hand, mining is one of the largest sources of environmental pollution due to wastes and emissions during the processing of extracted materials, such as tailings or smelting operations (Rodríguez et al., 2014; Mwesigye et al., 2016; Izydorczyk et al., 2021).

Several studies suggest that the overall use of raw materials has increased in recent decades. For example, a report by the United Nations Environment Programme (UNEP) noted that the extraction of metals and minerals has increased by 2.7% annually over the past decade. Europe is currently heavily dependent on the import of raw materials, so alternatives are needed. The EU list of critical raw materials for 2020 (European Commission, 2020), compared to that of 2017, was expanded by four new ones (bauxite, lithium, titanium and strontium). The civil engineering sector is one of the most important consumers of raw materials in the world. For example, bauxite ore is a raw material for the extraction of aluminium (Al), hematite for iron (Fe), etc. It is necessary to find new possibilities to limit and prevent the large consumption of material resources in the civil engineering sector, since not all raw materials are renewable.

Large amounts of heavy metals e.g. Pb, Zn, Hg, and Cd have been released into the environment as results of mining and smelting activities, which have adversely affected the water and soil quality, plant growth, and food safety (Manhart et al., 2019; Xin et al., 2022). Giljum et al. (2022) reported that more than 3000 km^2 of forest was directly lost due to mining activities and that 80% of loss occurs in only four countries: Indonesia, Brazil, Ghana, and Suriname. Deforestation on the surrounding area, was also proved, in some cases up to 70 km^2 from mining site (Sonter et al., 2017). Water pollution is another aspect of mining activities impacting the environment (Hadži Jordanov et al., 2007; Casiot et al., 2007; Cairns et al., 2022). Study done by Okolo et al. (2018) has shown that open cast mining impacted on the water usage, thus leading to heavy metal contamination of Pb, As, Zn, Cu and Cd. The contaminated groundwater represents a health hazard for people who use this water for drinking (Diallo et al., 2022). It is known that exposure to heavy metals can cause different adverse health issues, among them gastrointestinal, respiratory, or neurological disorders (Balali-Mood et al., 2021; Witkowska et al., 2021). Preserving the quality of groundwater is thus highly important.

The final stage in the operation of mines is reclamation. It is of crucial importance that during the reclamation of a mine site restoration of surface, water quality, and waste disposal sites are carried out in such a way that long-term pollution does not occur (Hartman and Mutmansky, 2002). One of the possibilities of closing an open pit or quarry is to fill them to the original level with the aim of establishing the original morphology or establishing areas for urbanization; or installation of the highwall, i.e. embankment. That is usually done with extractive waste from the mine site. For the same purpose, the use of construction products made from recycled waste has been recognized as a promising alternative (Garbarino et al., 2018). The waste to be recycled is often combined with other waste or natural materials to produce recycled waste-based construction products with suitable mechano-physical characteristics, which also meet

environmental acceptability criteria, i.e. level of potentially hazardous substances (PHSs) are below the legislative limits.

1.2.2 Waste generation and use of waste materials

Waste disposal contributes to the general degradation of the environment. Although the prevention of waste generation is placed as a priority in the hierarchy of waste management in the EU (European Commission, 2019b), in many human activities the generation of waste cannot be avoided. Wastes are divided in two main categories, i.e. hazardous and non-hazardous waste. According to the Waste Framework Directive hazardous waste is waste that exhibits one or more hazardous properties. All others, i.e. those that do not have hazardous properties, are classified as non-hazardous waste (European Commission, 2008). In the EU, there is a standard coding system The European List of Wastes (EWL), which classifies and describes the type of waste with a six-digit code, according to the process in which it is created (European Commission, 2001).

In 2020, it was reported that 4.8 tonnes of waste was generated per capita in the EU and 39.2% of the waste was recycled, while 32.2% was landfilled (Eurostat, 2023). Landfilling is the least desirable practice in the waste management hierarchy as it takes land space and can cause air, water and soil pollution (European Commission, 2008).

In 2021, 9.4 million tonnes of all types of waste were generated in Slovenia, compared to the data for 2019, the number increased by 23%. Around 65% of the generated waste is construction and demolition waste, followed by municipal waste with 12% and waste from thermal processes with 8%. According to data, 8.1 million tonnes of waste was processed with the final treatment procedures and the amount of recycled waste increased by 5%. The most recycled waste was mineral waste (56%), followed by metals (21%), and paper and cardboard waste (6%) (SURS, 2022).

In Slovenia, regulations in the field of waste management are mostly based on the Environmental Protection Act (Official Gazette of RS, No. 158/20). The basic regulation governing waste is the Decree of Waste (Official Gazette of RS, No. 77/22), which is based on obligations to handle waste without negative impact on the environment or human health, and considering the hierarchy of waste management. Only treated waste for which an appropriate assessment has been made is permitted to be disposed of in landfills. Assessment should be conducted in accordance with the Decree on Waste Landfill (Official Gazette of RS, No. 13/21). From 2006, waste disposal in Slovenia has decreased by 89 % (SURS, 2022).

Problems that may occur with waste landfilling are complex chemical and microbiological reactions within the landfill that often lead to the formation of several gaseous pollutants, persistent organic pollutants, leachable heavy metals and solid particles (Calderón et al., 2014; Njoku et al., 2019; Siddiqua et al., 2022; Zari et al., 2022).

Leaching is one of the most important mechanisms of PHSs transfer to the environment, which directly affects the soil and consequently the groundwater. Contamination as a result of the leaching of PHSs from waste has been reported in many studies (Butera et al., 2014; Bandow et al., 2018; Diotti et al., 2020; Bridson et al., 2021). Rainfall and soil moisture play an important role in the formation of leachate in landfill areas. Precipitation passes through the waste and chemical and physical reactions occur that transport PHSs into the soil and further into the groundwater (Iravanian & Ravari, 2020). Groundwater is one of the most vulnerable water environments and is also one of the most important sources of drinking water. In the research done by Maqbool et al. (2011), it was shown that as a consequence of landfill leachates, a lot of parameters in

water streams exceed the limiting values set by the World Health Organization (WHO), including total dissolved solids (TDS), biochemical oxygen demand (BOD), total bacterial counts, heavy metals like Pb, Cd and Cu. Methane is also generated in landfills as waste decomposes, and by United State Environmental Protecting Agency (US EPA), landfills are the third-largest source of methane emissions in the United States (US EPA, 2022). Some of research shows that a landfill site affects people living and health condition in the surrounding area (Okeke & Armour, 2000; Palmiotto et al., 2014). The impact of odour can be significant for the windy area near the landfill, as there is a possibility of fine and coarse particles formation (Vrijheid, 2000; Brender et al., 2011). People with pre-existing lung and heart disease, the elderly and children are particularly sensitive to particulate air pollution (Bridges et al., 2000; Macklin et al., 2011).

The Member States, by the EU Landfill Directive, must reduce the amount of municipal waste disposed on landfill to 10% of the total amount of municipal waste generated by 2035 (EU, 2018). Recycling is one of the main ways to reduce the amount of landfilled waste, as it also reduces the consumption of raw materials by replacing them with secondary materials from the waste recycling process. The percentage of waste recycled (compared to waste generated) is generally increasing in the 27 countries of EU, indicating progress in the use of recycled waste, but the rate of progress is slowing. To be fully sustainable, progress should be accelerated, as still less than half of all generated waste is recycled (48 % in 2016) (MOP, 2022). A lot of effort is put into reducing and reusing waste before recycling, but the generation of waste is inevitable in many human activities, so learning to recycle waste in addition to reducing and reusing will help the environment by saving natural resources, energy and money.

In order to protect the environment, wastes need to go through different treatment processes before they can be reused and counted as secondary raw materials. By EU definition, secondary raw materials can be identified as materials that can be recycled and then injected back into the economy as new raw materials (European Commission, 2015).

Recycling is an effective means of conserving both renewable and non-renewable raw materials. It aligns with the principles of sustainable development and the circular economy, which are integral to the European Union's long-term strategy, known as The Green Deal (European Commission, 2019b). Directive 2008/98/EC specifies that waste ceases to be waste when it is processed, including recycling, and meets criteria, formulated in accordance with the following conditions:

- the material is commonly used for specific purposes,
- a market demand exists for such material,
- the material fulfils the technical requirements for a specific purpose and the, requirements of legislation and standards that apply to the product,
- the use of the substance or object will not cause a general adverse effect on the environment and human health (European Commission, 2008).

The construction industry presents a promising field for the utilization of recycled waste, given its high consumption of raw materials. In cases where the recycled waste is not environmentally inert, techniques such as immobilization of PHSs through the addition of various substances or processes can be employed. However, it is crucial to ensure that the utilization of new products derived from recycled materials does not pose risks to human health or the environment, including water, air, soil, plants, and animals. Furthermore, the construction products made from waste must not only meet environmental acceptability standards but also possess technical and economic properties that are comparable to commonly used materials. For the use in the construction sector, the product prepared from recycled waste has to comply with the Slovenian policy in the

field of waste, construction materials, and environment, namely the Construction Products Act (Official Gazette of RS, No. 82/13), the Construction Product Regulation 305/2011 (European Parliament, 2011), the Environmental Protection Act (Official Gazette of RS, No. 158/20), and the Decree on Waste (Official Gazette of RS, No. 77/22).

One of the possible applications of different types of recycled waste is preparation of geotechnical composites, which can be later used for fills or embankments (Ivannikov et al., 2019). A good example is construction and demolition waste , whose technical feasibility has been demonstrated and is often used in construction works such as road construction, or as fill material (Diotti et al., 2020). Due to their high binding capacity, whether pozzolanic or hydraulic, ashes obtained from various industrial processes are also very often used. Recycled material from the paper industry potential for use as fill material was reported in various studies (Bizjak et al., 2021). For replacement of conventional natural materials recycled glass, recycled plastic and tire-derived aggregates as alternatives were also investigated (Yaghoubi et al., 2022). Successfully remediated soil can be utilized as recycled material for the preparation of geotechnical composites (Oprčkal et al., 2020)..

1.2.3 Methods for the characterization of recycled waste products and limit values of contaminants

In many European countries, the environmental properties of waste-derived construction products are mostly evaluated with laboratory leaching tests, e.g. CEN/TS/14405, ISO/TS 21268, or DIN 38414-4 (Butera et al., 2012; Delay et al., 2007; Enell, 2012).

In Slovenia, the environmental acceptability of the recycled waste-based construction products (e.g. geotechnical composites, that will be used in the external environment (exposed to atmospheric influences) and have leaching properties are determined with standard leaching procedure SIST EN 1744-3 (2002). According to the procedure described in the standard SIST EN 1744-3 (2002), the leaching of the material is carried out, with the ratio of 1/10 between dry mass of a test sample and volume of leaching solution, i.e. demineralized water, for a period of 24 hours. The procedure, the set of PHSs and their permitted contents (see Table 2) in leachate are prescribed in the Decree on Waste (Official Gazette RS, No. 77/22). The exact list of PHSs to be monitored depends on the input materials used to make the product, while the limit values in the leachate depend on the intended use of the material.

Table 2: Permissible levels of pollutants in leachates of the processed substance or object at L/S = 10 l/kg in [mg/kg dry matter].

Parameter	Intended use of material		
	In an area without protection regimes according to water regulations	In an area without protection regimes according to water regulations if the average water permeability of processed substances or objects is $\leq 10^{-9}$ m/s	In water protection regimes areas
	mg/kg (dry matter)	mg/kg (dry matter)	mg/kg (dry matter)
Arsenic (As)	0.1	0.4	0.01
Barium (Ba)	20	20	1
Cadmium (Cd)	0.025	0.04	0.0025
Cobalt (Co)	0.03	0.5	0.003
Chromium (Cr)	0.5	0.6	0.05
Chromium VI (Cr^{6+})	0.1	0.15	0.005
Copper (Cu)	0.5	2	0.05
Mercury (Hg)	0.005	0.01	0.001
Molybdenum (Mo)	0.5	1	0.1
Nickel (Ni)	0.4	0.5	0.08
Lead (Pb)	0.5	0.6	0.035
Antimony (Sb)	0.3	0.5	0.03
Selenium (Se)	0.6	1	0.06
Zinc (Zn)	2	3.5	0.35
Fluoride (F^-)	10	10	1
Chloride (Cl^-)	800	1000	80
Sulphate (SO_4^2)	2500	5000	500

These tests are designed to simulate natural leaching behaviour of material under a short period of exposure to water-saturated conditions. These tests are conducted under laboratory conditions, but the behaviour of new products in the real environment is still unclear (Sormunen et al., 2018). In addition to the type and amount of PHSs, the behaviour of the newly formed product in the field also depends on the condition of the ground itself (mineralogical composition), as well as on the weather conditions.

Leaching tests are commonly used procedures for evaluation of the environmental impact of recycled waste materials on the land (van der Sloot et al., 2018). However, utilizing these materials for fill or embankment, weathering and leaching processes may result in groundwater contamination. Since groundwater is a vital source of drinking water, it is crucial to monitor PHSs in groundwater. Thus, there is a need to develop effective methods for monitoring groundwater contamination from construction products prepared from recycled waste. There are many studies that have utilized lysimeters to evaluate the leaching potential of waste materials (Mali, 2002; von Unold & Fank, 2008). Lysimeters are frequently employed in environmental research to evaluate the transport

of water through soil and waste materials, and to determine the risk of groundwater contamination by monitoring the mobility and fate of PHSs (von Unold & Fank, 2008). This process is dependent on factors such as mineralogical composition of soil, local weather conditions and the quality of the geotechnical composites installation (Hansen et al., 2000; Abdou and Flury, 2004). But currently, there is no legislation that would regulate the environmental acceptability of waste materials with the use of lysimetric tests, which are primarily employed for risk-assessment purposes. There are also no reports for leaching of chemical species of elements in percolated water from lysimeters.

1.2.3.1 Speciation analysis

For the evaluation of environmental hazards, total concentrations of elements are generally measured in waste and recycled materials as well as in their leachates (Tiruta-Barna & Barna, 2012). The role of trace elements and their impact on the environment and living organisms depends not only on their total concentrations but also on chemical forms in which they are actually present. For instance, Cr is highly toxic in the hexavalent oxidation state but far less toxic in the trivalent oxidation state (Marković et al., 2022). Individual chemical species of trace elements in different samples are quantitatively determined by speciation analysis. A fundamental tool for speciation analysis is the combination of separation technique, e.g. HPLC with element specific detector, e.g. ICP-MS (Milačič & Ščančar, 2020). In HPLC, the sample is injected onto the chromatographic column. The components of the sample travel through the mobile phase, and are selectively retained by the stationary phase. Chromatographic separation is based on differences in the travel speed of individual sample components in the mobile phase due to their selective retention on the stationary phase. The components in the sample are separated on the basis of differences in polarity, size or charge (Broekaert, 2006; Thomas, 2013).

In addition to the detection of individual elemental species, ICP-MS also enables multielemental detection of separated chemical species of elements. To successfully perform a multielemental speciation analysis, the chemical species of the elements must behave similarly and be efficiently separated on a chromatographic column using the same chromatographic conditions. Oxyanions of Cr(VI), As(V), Mo(VI) and V(V) are highly mobile in the form of alkali chromates, arsenates, molybdates and vanadates (CrO_4^{2-}, AsO_4^{3-}, MoO_4^{2-}, VO_4^{3-}). As negatively charged species they can be simultaneously separated on anion-exchange chromatographic columns. The main advantages of multielement speciation analysis over the commonly used single speciation procedures are speed and cost-effectiveness. Nevertheless, the multielemental speciation analysis was rarely applied (Marcinkowska & Barałkiewicz, 2016) although multielemental speciation analysis provides useful data in environmental studies. Drinčić et al. (2017a, 2017b) performed simultaneous speciation analysis of chromate, arsenate, molybdate and vanadate in leachates from building composites made of waste and recycled waste materials. Based on the results, the long-term environmental impacts of these composites were evaluated. These studies demonstrated the potential of multielemental speciation analysis in large series of samples, as is often the case in environmental studies.

1.3 Contamination of Soil and Remediation Approaches

The main goal of the remediation of contaminated soil is to reduce the risks that contaminants can pose to living organisms and the environment. Two types of remediation strategies are possible, elimination of contaminates or fixation in a chemically stable form (Nathanail and Bardos, 2005).

Soil remediation can be carried out in two different ways, namely in-situ or ex-situ. In-situ remediation means that the process is done directly on the contamination site, while ex-situ remediation begins with excavation of a contaminated soil. Regardless of whether after excavation the remediation takes place on the site or the soil is transferred away for the remediation, the excavation can represent a significant risk to the environment. The risk of spreading contamination also exists due to dislocating of contaminated soil for remediation. This is the reason why in-situ remediation is preferable, especially for heavily contaminated areas. Depending on the mechanisms that occur during the remediation process, the techniques can be divided into physical, chemical, and biological (Nathanail and Bardos, 2005). Different approaches have been studied, such as soil washing, electro-kinetic remediation, stabilization, bioremediation (Sivapullaiah et al., 2015; Venegas et al., 2015; Pande et al., 2022; X. Zhang et al., 2022).

1.3.1Heavy metals and metalloids as soil contaminants

More than 50% of contaminated soils are contaminated with heavy metals and/or metalloids (Gong et al., 2018). Heavy metals and metalloids are of great concern due to their potential toxicity, persistency and since they cannot be degraded. They are often released into the environment in the form of highly mobile chemical species that are bioavailable and can contaminate both surface and groundwater, and have irreversible consequences on living organisms (Violante et al., 2010; Zwolak et al., 2019). Humans are exposed to soil contamination in different routes, including ingestion, dermal contact, and inhalation (Witkowska et al., 2021).

Numerous studies have shown that heavy metals can affect human health. For example, the exposure to high concentration levels of heavy metal(oid)s, particularly Cd, As, Pb, and Cr, may cause a series of chronic diseases. They can damage the nervous and immune systems, induce cancer, and cause kidney and liver dysfunction (Balali-Mood et al., 2021; Kumar et al., 2022). Therefore, assessment of soil contamination with heavy metal(oid)s, possibilities for remediation and evaluation of effects on human health has attracted much scientific attention in recent years (Mohammadi et al., 2020; Ahmad et al., 2021; Karimian et al., 2021). Heavy metal(oid)s (e.g. As, Cd, Cr, Pb, Zn) are generally present in soils in low concentrations. In elevated concentrations, they appear mostly as a result of human activities and not as a result of natural processes.

The binding mechanisms of elements in different soil phases are complex and can vary depending on the soil's chemical and physical properties. The elements in the soil are distributed between different sparingly and easily soluble mineral phases. The most mobile forms of elements are released into the soil solution and are highly bioavailable to living organisms (Hooda, 2010).

Because Cd, Pb, and Zn occur frequently as contaminants in soil, they are under environmental scrutiny as they can pose major threats to both human health and the environment. In elevated concentrations, they are commonly present in soils near mining and industrial areas (X. Zhang et al., 2012; Duan et al., 2016; Antoniadis et al., 2019).

In soil, Cd is present exclusively in the Cd(II) oxidation state. The mobility of Cd depends strongly on the pH and the organic matter content in the soil. Low pH values, as well as the presence of chloride (saline soils), increases Cd solubility and with it mobility. On the other hand, soil organic matter, and/or Fe/Mn hydroxides and clay minerals are the main Cd adsorbents in soil, which decrease its mobility (Hooda, 2010). Nagajyoti et al., (2010) reported that plant growth in the presence of elevated Cd concentrations is inhibited mainly because Cd competes and prevents the absorption of calcium (Ca), magnesium (Mg), phosphorus (P), potassium (K), and alters water uptake by plants. Many studies have reported adverse effects on human health, such as the increased risk of

osteoporosis and fractures as well as cardiovascular disease and cancer (Godt et al., 2006; Järup & Åkesson, 2009; Genchi et al., 2020).

In the environment, Pb compounds tend to accumulate in soils and sediments. The behaviour of lead in soil depends on its chemical form and also on the characteristics of the soil. Compared to Cd and Zn, Pb is more strongly adsorbed on the sparingly soluble mineral phases. It was proven that only a small part of Pb total concentration in soils is bioavailable (Alloway, 2013; Steinnes, 2013). In soil, it occurs in the Pb(II) oxidation state and can replace Ca, strontium (Sr), barium (Ba), and K in different soil minerals (Bradl, 2004). It becomes less soluble with increasing pH in the soil due to complexation with organic matter, and sorption on oxides and encapsulation in a silicate lattice. On the other hand, in highly alkaline soils, solubility may also be increased as a consequence of the formation of soluble Pb-organic and Pb-hydroxy complexes (Adriano, 1986). It was also proven that the inorganic phase of soil is an important factor in Pb mobility even in soils dominated by organic matter (Bradl, 2004). Long-term exposure to Pb, leads to its accumulation in the human body, resulting in Pb poisoning. Elevated concentrations of Pb are found in the urine and blood of children living near Pb contaminated areas (Jez & Lestan, 2015; Chowdhury et al., 2021). Prolonged exposure to Pb causes severe effects on kidney and brain (Abadin et al., 2020). It can also affect the reproductive systems of both males and females (Flora et al., 2006).

Zinc is present in the Zn(II) oxidation state in soil. The solubility of Zn in soils is usually controlled by sorption reactions. Clays and organic matter reduce the mobility of Zn, especially at neutral and alkaline pH, while its release into the soil solution increases with decreasing pH (Kabata-Pendias & Mukherjee, 2007; Mertens & Smolders, 2013). A major fraction of Zn in the soil is also associated with Fe and Mn oxides, by adsorbing or coprecipitating on their surface (Vodyanitskii, 2010). Zn is considered an essential element, while a severe impact on human health by intoxication with Zn is relatively rare. High oversupply of Zn in human body causes nausea, dizziness, headaches, gastric distress, vomiting, and loss of appetite (Plum et al., 2010; Sangeetha et al., 2022).

1.3.2 Immobilization strategies for remediation of soils contaminated with heavy metals

Generally, for remediation of soil contaminated with heavy metals, the stabilization/solidification, i.e. immobilization method, is proven to be an effective and cost-effective remediation technique (Dai et al., 2018; Gong et al., 2018). Originally developed to convert toxic waste into a more stable form, this method has been extensively studied for soil remediation (Shen et al., 2019). With this remediation approach, the solubility and mobility of heavy metals are reduced by the addition of amendment (i.e. immobilization agent), which transform them into less soluble and less mobile forms, a process referred to as stabilization (Xu et al., 2021). Solidification, on the other hand, involves physically encapsulating the heavy metal in a material. In the construction sector, this encapsulation is used to enhance the immobilization process of heavy metals when preparing geotechnical composites in earthworks (Kogbara, 2017). To achieve effective immobilization of heavy metals, low water permeability and sufficient strength of composite, several geomechanical properties must be considered, including the addition of sufficient amounts of immobilization agent, optimal amount of water, and compaction of the material up to its maximum density (Dermatas & Meng, 2003; Kogbara et al., 2014).

The most commonly used additives for in situ immobilization include cement, clay minerals (Y. Xu et al., 2017), zeolites (Radziemska et al., 2019), biochar (M. Wang et al., 2018), phosphates (Zhao et al., 2014), humic substances (Kulikowska et al., 2015), and

various industrial by-products or waste like fly ash (Leelarungroj et al., 2018), paper-ash (Mavroulidou, 2018; Oprčkal et al., 2020) and red mud from alumina production (Oprčkal et al., 2020). Li et al. (2022) examined three industrial wastes including converter steel slag, carbide slag and phosphogypsum as an additive for the remediation of heavy metal-contaminated soil. The potential of different ashes, slags and red-mud was also investigated for remediation of soil contaminated with heavy metals (Voglar and Leštan, 2011; Serjun et al., 2015; Oprčkal et al., 2020; Banaszkiewicz et al., 2022).

Cement hydration in term of immobilization potential has been intensively studied, and it was found that the immobilization of heavy metals was successful due to the formation of new minerals and the hydration products (Chen et al., 2009). Considering that production of cement contributes about 8% of the total global CO_2 emissions, alternatives need to be sought in the construction sector and also for the soil remediation process. Pozzolanic materials are silica- or alumina-rich materials that in the presence of water react with $Ca(OH)_2$ forming cement hydration products (calcium silicate hydrates and calcium silicate aluminate hydrates) (Walker & Pavía, 2011; Onyelowe et al., 2021; Li et al., 2022). Many waste materials have pozzolanic characteristics and could serve as an excellent additives in soil remediation (Voglar & Leštan, 2011; Seco et al., 2012; Lasheen et al., 2013).

1.3.3 Methods for characterization of the mineral composition and partitioning of heavy metals in soils and waste products

Useful information about the stabilization of metals in different mineral phases after treatments with immobilizing agents can be obtained with scanning electron microscope (SEM), equipped with energy-dispersive spectroscopy (EDS) and powder X-ray diffraction (XRD) (Ashrafi et al., 2015; L. Wang et al., 2019). The SEM uses a focused beam of electrons to generate an image of the sample surface, while energy-dispersive X-ray spectroscopy (EDS) uses the same beam of electrons to excite the atoms in the sample and measure the elemental composition of different phases. With SEM-EDS, morphology, microstructure and a semi-quantitative chemical analysis of sample can be determined (Goldstein et al., 2003). The XRD is a technique for determination of the materials crystallographic structure. It is based on the diffraction of X-rays by the atoms in a sample, measuring the intensities as a function of the scattering angles (Pecharsky & Zavalij, 2009).

For the evaluation of heavy metal mobility and bioavailability, different extraction procedures have been carried out to identify and quantify the chemical forms in which heavy metals occur in soils. The partitioning of metals between different soil fractions was studied using single or sequential extraction procedures.

For single extraction procedures different extraction solutions like ammonium chloride, calcium chloride and ethylenediaminetetraacetic acid (EDTA) were used (Zhang et al., 2010; Kim et al., 2015). These procedures provide information on the presence of heavy metals in the mobile soil fractions. Sequential extraction procedures involve a number of extractions, which are sequentially applied to a solid sample. Each extractant is chemically more rigorous than the previous one (Zhang, 2020). In general, unbuffered salts and weak acids are first applied to extract the most mobile soil fractions, followed by reducing agents, oxidizing agents and strong acids to extract the sparingly soluble fractions (Hooda, 2010). The two most used sequential extraction procedures are the one proposed by Tessier et al. (1979) and a scheme proposed by European Community Bureau of Reference (BCR) (Ure et al., 1993). The BCR is a three-step sequential extraction procedure, based on acetic acid extraction in the first step, followed by hydroxylamine hydrochloride in the second step, and hydrogen peroxide/ammonium

acetate in the third step. Different modifications of the method were adopted in past years (Mossop & Davidson, 2003; Pueyo et al., 2008). Regardless of the modifications, in all procedures, acetic acid is used to extract the exchangeable fraction of soil. The use of acetic acid is not appropriate for highly alkaline sample matrices, since it reduces the pH of the sample, leading to apparently greater mobility of most metals, which does not reflect their actual mobility in the stabilized chemical forms under highly alkaline conditions (Ščančar et al., 2001).

The frequently used one was five-step Tessier's extraction procedure (Tessier et al., 1979) in which metals are partitioned between the following fractions: exchangeable, bound to carbonates, bound to Fe/Mn oxides and hydroxides, bound to organic matter and residual fraction, using the following extraction solutions: magnesium chloride ($MgCl_2$, pH 7.0) or sodium acetate solution (NaOAc, pH 8.2); NaOAc (pH 5.0); NH_2OH-HCl in 25% (v/v) HOAc; mixture of HNO_3 and H_2O_2 (pH 2); digestion with a mixture of acids including HF. With slight modifications, it was used in the evaluation of the environmental impacts of waste materials and contaminated sediments and soils (Milačič et al., 2012; Sakan et al., 2013).

1.4 Contaminated Areas and Excavated Pits in Slovenia

In Slovenia, several sites are heavily polluted with toxic metals. Due to the past mining activities and processing of the Pb and Zn ore (Finžgar & Leštan, 2008), the Mežica valley is still heavily contaminated with Cd, Pb and Zn. For the same reason, due to the long-term mining and processing of mercury (Hg) ore, the Idrija region is contaminated with Hg (Kocman et al., 2011). Past industrial activities also contributed to environmental pollution with Cd, Pb, Zn, and As in the Celje region (Žibret et al., 2018).

A large number of active or abandoned open-pit mines also exist in Slovenia from which different rocks, gravel or sand and other non-mineral raw materials have been extracted.

1.4.1 Old Zinc-Works area and remediation approaches

The largest area of contaminated soil in Slovenia (17 ha) is the Old Zinc-Works in Celje (Figure. 2).

Figure 2: The Old Zinc-Works area in Celje.

This area is a legacy of the past industrial activities (the last one in 1985), in which Cd, Pb, and Zn were the main pollutants. Next to that a poorly managed demolition of the old industrial infrastructure in 2002 caused additional contamination. In the following years, the place also became a location for illegal dumping of various wastes (Žibret, 2008; Žibret et al., 2018). Compared with other cities globally, some parts of Celje have one of the highest levels of Zn and Cd in the soil. Celje with around 40,000 inhabitants is among the largest cities in Slovenia. Due to the contaminated soil and the possibility of contamination spreading into water, air and food, there is a risk to human health. There are many reports that the highest exposure to Cd, Pb and Zn is when consuming plants grown in a polluted area (Eržen, 2003; Karo Bešter, 2013).

Many activities were carried out to rehabilitate the contaminated area, which was a difficult task due to the very high concentrations of contaminants and the non-homogeneity of the contaminated soil. Different methods, e.g. soil washing with EDTA (Joveska, 2018), or immobilization approaches using various remediation additives, e.g. cement (Voglar & Leštan, 2010), red mud, paper ash or combination of both (Oprčkal et al., 2020), were tested for the rehabilitation of the contaminated soil in the Old-Zinc Works. In geotechnical composites made from contaminated soil mixed with highly alkaline paper ash (pH 12) and with the addition of an optimal amount of water, Cd, Pb and Zn were successfully immobilized due to the formation of new hydration products. In addition to successful laboratory investigations, since 2014 tens of thousands of tons of contaminated soil have been processed in the field. However, there is a lack of data on the long-term stability of geotechnical composites, and a lack of knowledge about which soil phases the Cd, Pb, and Zn were transferred to after the remediation.

1.4.2TERMIT excavation pits and in reclamation approaches

TERMIT is a mining company for the production of quartz sand and the production of auxiliary foundry materials for foundries, ironworks and the building sector. The mining activity started in 1961. The company is obliged to regularly restore its excavated pits. The estimated quantity of material that TERMIT will need during the next 10 years for the reclamation of the degraded area is 1.5 M tonnes. The image of the area after the sand excavation is presented in Figure 3A, while the site after the reclamation in 2010 can be seen in Figure 3B.

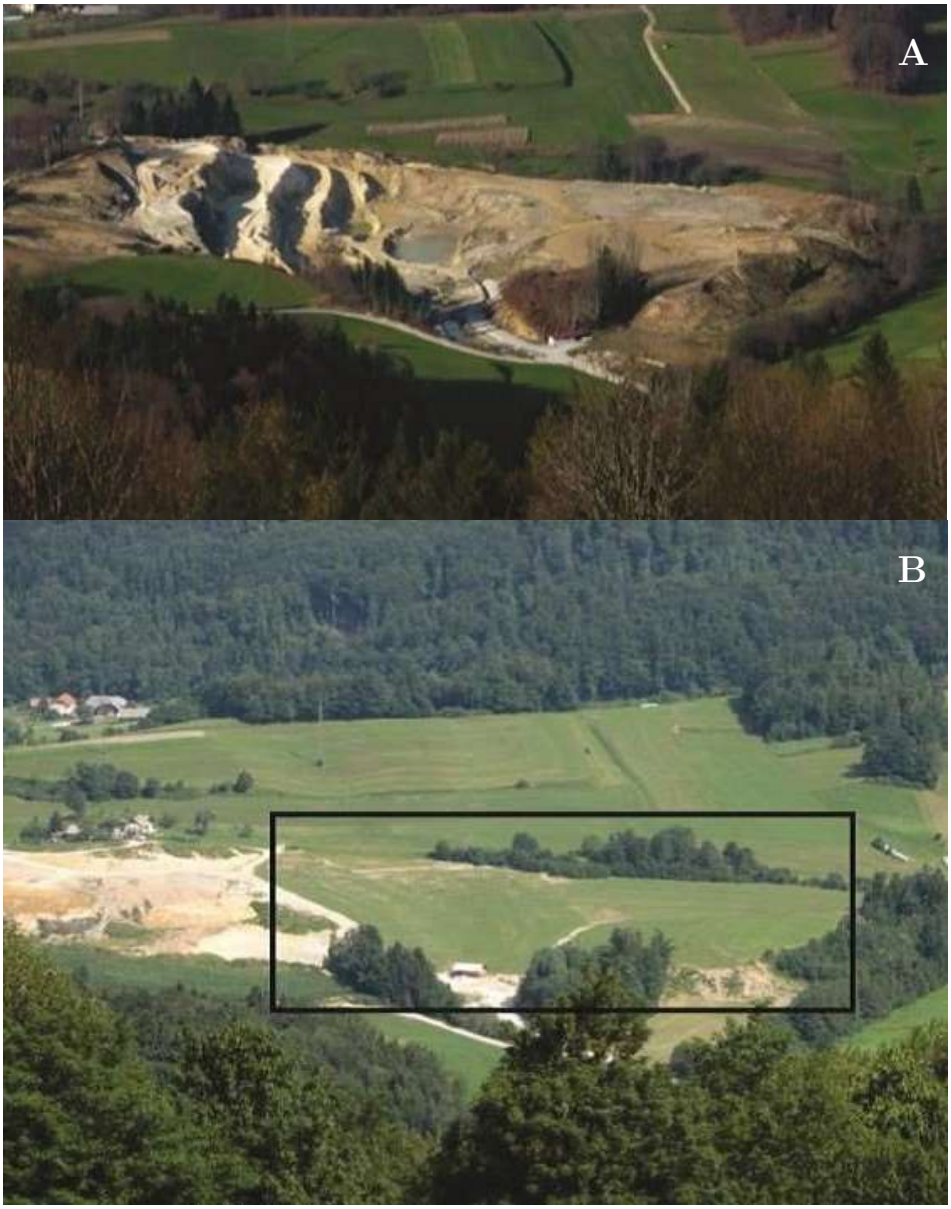


Figure 3: The excavated area before (A) and after the reclamation (B).

Since it is not possible to obtain such a large amount of raw material, the company has a license to collect various types of industrial waste and process them into geotechnical composites, which are then used as geotechnical fill in excavated sites.

When using waste materials for the preparation of recycled composites for the reclamation of open-pits or quarries, it is necessary to assess how the way of installing the composite influences its environmental acceptability regarding the release of the potentially hazardous substances. Such studies have mostly been conducted on a laboratory scale using standardized leaching tests, while reports of field studies are rare.

Chapter 2

Research Aims and Hypothesis

Although paper ash was found to be a promising additive for soil remediation, there is a lack of data on the long-term stability of geotechnical composites, and a lack of knowledge about which soil phases the Cd, Pb, and Zn were transferred to after the remediation. Therefore, research aims related to the use of paper ash are (i) to gain a deeper insight into the mechanisms of immobilization of Cd, Pb, and Zn after the remediation in different time intervals, using modified Tessier's sequential extraction procedure in combination with XRD analyses, (ii) to assess the long-term stability of newly formed mineral phases of Cd, Pb and Zn after remediation, and (iii) to evaluate the long-term environmental impacts of soil remediation.

It is hypothesized that the easily soluble fractions of the soil will be immobilized with paper ash into the sparingly soluble mineral phases of the soil, which after remediation will possess long-term stability and thus the environmental acceptability of the newly formed building composites.

When recycled waste materials are used for the preparation of composites used for earthworks, it is necessary to assess their environmental acceptability regarding the releases of potentially hazardous substances. Such investigations have been performed mainly on a laboratory scale applying standardized leaching tests, while there is a lack of data on the behaviour of these composites on field. Therefore, research aims related to the reclamation of open pits are to prepare geotechnical composites from different recycled waste materials and to follow the release of potentially hazardous substances from composites in the laboratory scale and in lysimeters installed on field using leachability tests and speciation analysis.

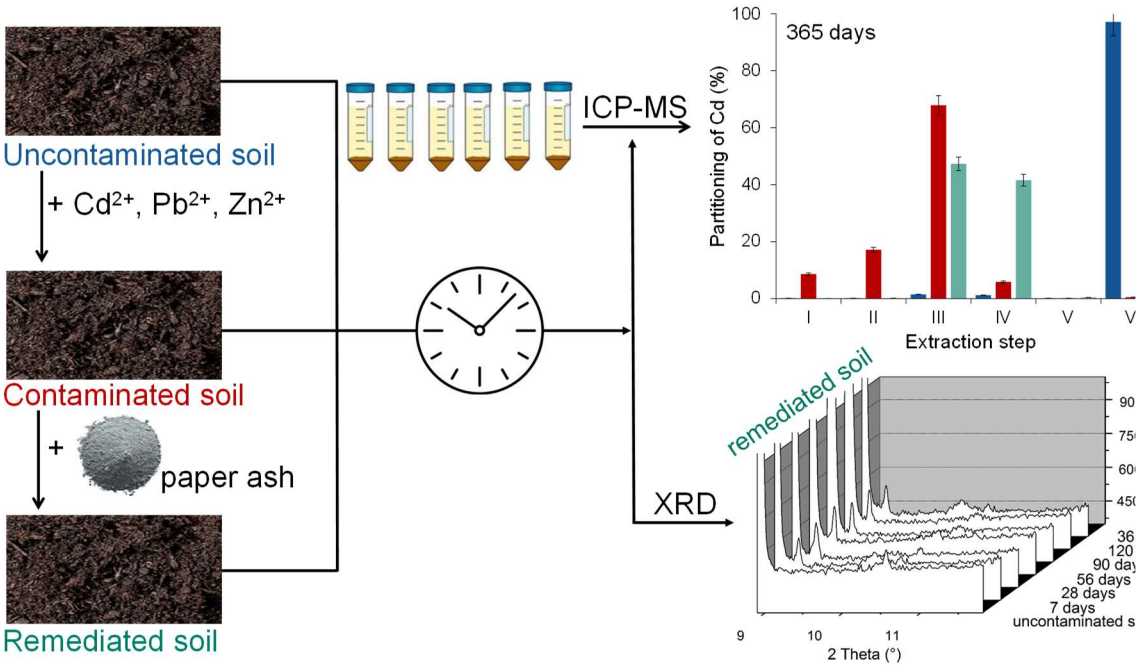
The hypothesis is that tailored mixing of waste materials in geotechnical composites and their proper installation on field will result in their environmental acceptability.

Chapter 3

Scientific Publications

Article 1: Environmental Impacts and Immobilization Mechanisms of Cadmium, Lead and Zinc in Geotechnical Composites Made from Contaminated Soil and Paper-Ash

ĐURIĆ, Marija, OPRČKAL, Primož, ZALAR SERJUN, Vesna, MAUKO PRANJIĆ, Alenka, ŠČANČAR, Janez, MILAČIČ, Radmila, MLADENOVIČ, Ana. (2021). Published in Applied Sciences, https://www.mdpi.com/2076-3417/11/24/11822/htm, DOI: 10.3390/app112411822.



Remediation of contaminated soils is one of top environmental priorities worldwide. Paper ash is a promising additive for remediation of heavily contaminated soils with metals, but no long-term remediation efficiency has been reported. To address this shortcoming, a comprehensive investigation was performed in building composites made from contaminated soil and paper ash over one year in seven time intervals after the

remediation, combining sequential extraction and XRD analyses. The mechanism of immobilization for the Cd, Pb and Zn with paper ash involved the formation of hydration products from the paper ash, which resulted in precipitation of insoluble Cd, Pb and Zn hydroxides, while through the carbonation process, Cd, Pb and Zn were stabilized in insoluble carbonates. After the remediation, concentrations of Cd, Pb and Zn in the water-soluble fraction were reduced far below the limit values for inert materials. A significant decrease in the Cd, Pb and Zn concentrations was also observed in the exchangeable fraction of the soil composite. Understanding the long-term immobilization mechanisms of Cd, Pb and Zn in building composites represents a basis for more sustainable management and use of waste materials generated by paper and pulp industry as well as those generated by the construction sector.

Data from our study revealed the long-term efficiency of the remediation with paper ash, which is related to the long-term stability of the hydroxide and carbonate mineral phases of Cd, Pb and Zn, formed after the remediation. Regarding the long-term environmental impacts of soil remediation with paper ash, it was demonstrated that the Cd, Pb and Zn in the remediated soil composites do not represent an environmental hazard.

The results provide novel findings and contribute important knowledge to strategies for effective remediation of soils contaminated with Cd, Pb and Zn by means of immobilization with paper ash. They can represent a basis for more sustainable management and use of the waste materials generated by paper and pulp industry as well as those generated by the construction sector, like for the rehabilitation of degraded sites, and can also initiate the industrial symbiosis in which the closed-loop system is established on a local level.

applied sciences

MDPI

Article

Environmental Impacts and Immobilization Mechanisms of Cadmium, Lead and Zinc in Geotechnical Composites Made from Contaminated Soil and Paper-Ash

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Abstract: Paper-ash is used for remediation of heavily contaminated soils with metals, but remediation efficiency after longer periods has not been reported. To gain insights into the mechanisms of immobilization of cadmium (Cd), lead (Pb), and znic (Zn), a study was performed in the laboratory experiment in uncontaminated, artificially contaminated, and remediated soils, and these soils treated with sulfate, to mimic conditions in contaminated soil from zinc smelter site. Remediation was performed by mixing contaminated soil with paper-ash to immobilize Cd, Pb, and Zn in the geotechnical composite. Partitioning of Cd, Pb, and Zn was studied over one year in seven-time intervals applying the sequential extraction procedure and complementary X-ray diffraction analyses. This methodological approach enabled us to follow the redistribution of Cd, Pb, and Zn over time, thus, to studying immobilization mechanisms and assessing the remediation efficiency and stability of newly formed mineral phases. Cd, Pb, and Zn were effectively immobilized by precipitation of insoluble hydroxides after the addition of paper-ash and by the carbonization process in insoluble carbonate minerals. After remediation, Cd, Pb, and Zn concentrations in the water-soluble fraction were well below the limiting values for inertness: Cd by 100 times, Pb by 125 times, and Zn by 10 times. Sulfate treatment did not influence the remediation efficiency. Experimental data confirmed the high remediation efficiency and stability of insoluble Cd, Pb, and Zn mineral phases in geotechnical composites.

Keywords: cadmium; lead; zinc; contaminated soil; paper ash; immobilization mechanisms

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1. Introduction

The growth of the human population and activities, like industrialization, mining, and the intensification of agriculture, have made soil pollution one of the world's most serious environmental problems. It could negatively influence agricultural production, threaten food safety, and endanger the health of natural ecosystems and lifeforms. There are over 10 million major soil-contaminated areas around the world, of which 50% are contaminated by heavy metals and metalloids [1,2]. The Food and Agriculture Organization of the United Nations (FAO) classified the prevention of soil pollution as a top priority worldwide [3].

Heavy metals and metalloids are of great concern due to their potential toxicity, persistency and since they cannot be degraded. These elements are frequently released into terrestrial environmental compartments with anthropogenic emissions in the form of easily soluble, highly mobile chemical species. These are bioavailable and can contaminate both surface and ground waters [4,5]. Significant efforts are being made to remediate

soil-contaminated sites in Europe [6] and around the world [1]. The crucial role of the remediation of contaminated soils is to reduce the mobility of metals and metalloids in the soil using different immobilizing agents. The process of immobilization occurs through adsorption, complexation, and precipitation reaction [7–9] and redistributes the heavy metals from the soil solution to the less-soluble soil fractions, while their total concentrations remain unchanged. The most commonly used amendments for in situ immobilization include cement [10], clay minerals [11], zeolites [12], biochar [13], phosphates [14], humic substances [15], and various industrial by-products like fly ash [16], paper-ash [17,18] and red mud from aluminum production [18]. Among the immobilization processes, a carbonation treatment under alkaline conditions (pH 10–10.5) was shown to effectively reduce the mobility of lead (Pb), zinc (Zn), chromium (Cr), copper (Cu), and molybdenum (Mo) in residues from the combustion of municipal solid waste [19]. When immobilization techniques are applied for remediation, the stability of the immobilized metals must be evaluated. For this purpose, it is necessary to know to which mineral phases the contaminants were redistributed after the remediation.

To evaluate the immobilization efficiency, leaching tests using demineralized water as the extracting solution (liquid-to-solid ratio of 10 L/kg) [20] or single-extraction procedures were often applied [21]. Sequential extraction procedures in combination with element-specific detectors, e.g., inductively coupled plasma mass spectrometry (ICP-MS), provide useful information about the partitioning of metals in soils, sediments, and waste materials [22,23]. They involve different extractants, which are applied successively to the solid material to selectively leach the particular chemical forms of the metals from the samples analyzed. Each extractant is chemically more rigorous than the previous one [21]. Many of these extraction procedures are based on the method developed by Tessier et al., which includes the five-step sequential extraction [24]. With slight modifications, Tessier's scheme was used in the evaluation of the environmental impacts of waste materials and contaminated sediments and soils [25,26]. In addition, frequently used were the BCR three-step sequential extraction procedures [27,28]. The BCR sequential extraction scheme, in which 0.11 M acetic acid is used to extract the exchangeable fraction, is not appropriate for highly alkaline sample matrices. After the addition of acetic acid, the pH of the sample is reduced, leading to apparently greater mobility of most metals, which does not reflect their mobility in stabilized chemical forms in highly alkaline conditions [29].

Sequential extraction procedures can also provide essential information on a metal's mobility after remediation. Janoš et al. [30] studied the leachability of Cd, Pb, Zn, and Cu from contaminated soils and soils amended with different additives. Three months after the soils' treatments, the BCR extraction procedure was applied to study the partitioning of the metals after the remediation. The results revealed that Cd and Pb mobility was effectively reduced after the addition of potassium humate, while Cu mobility was reduced after the addition of zeolite or fly ash. The addition of amendments did not influence the mobility of Zn. Ashrafi et al. [31] investigated the efficiency of the immobilization of Pb, Cd, and Zn in an artificially contaminated soil, using eggshell and banana-stem amendments. Three months after the soil amendments, Tessier's sequential extraction procedure was applied. The results showed that in eggshell-treated soil, Pb, Cd, and Zn were transferred from the easily mobile to sparingly soluble soil fractions, while the banana-stem amendment reduced the exchangeable Cd content and increased its residual form in the soil.

Useful information about the stabilization of metals in different mineral phases after treatments with immobilizing agents can be obtained with transmission electron microscopy (TEM), scanning electron microscope (SEM), and powder X-ray diffraction (XRD) [18,32,33]. XRD, SEM, and TEM, in combination with sequential extraction procedures, provide complementary data on the distribution of metals in different mineral phases of the contaminated soils, delivering valuable information about alternatives for the remediation of contaminated sites [34]. Nejad et al. [35] investigated the potential of biochars, red mud, and steel slag for the in situ stabilization of Cd, Cu, Pb, and Zn in soil. The results of the sequential extraction analysis demonstrated that the application

of biochars increases the metal fractions associated with carbonate and organic matter. The application of red mud and steel slag substantially increased the soil pH, leading to metal precipitation and their transfer from the easily soluble forms to the sparingly soluble fractions associated with Fe/Mn oxides and alumo-silicates. The latter findings were supported by the XRD analyses. By the above-reported approaches using sequential extraction procedures and/or their combination with XRD or microscopic techniques, it was possible only to evaluate the short-term efficiency of remediation (after three months). Since only one experiment was performed after three months, it was not possible to follow the mechanisms of immobilization of contaminants during the remediation process, nor to evaluate the efficiency of remediation and stability of the formed mineral phases after a longer period of time.

In Slovenia, the area around the abandoned zinc smelter "Old Zinc-works" site in the town Celje is heavily polluted with Cd, Pb, and Zn. Among the anions, sulfate is present as a contaminant. One of the promising methods for remediation is an in situ immobilization with paper-ash, which is locally available recycled material. The highly alkaline paper-ash (pH 12) is mixed with polluted soil, forming a geotechnical composite. The results reveal that the Cd, Pb, and Zn in a highly mobile water-soluble fraction are being significantly reduced after immobilization [18]. However, there is a lack of data on the stability of geotechnical composites and a lack of knowledge about which soil phases the Cd, Pb, and Zn were transferred to after the remediation.

In the present work, an investigation based on modified Tessier's sequential extraction procedure in combination with XRD analyses was performed (i) to gain a deeper insight into the mechanisms of immobilization by determining with which mineral phases Cd, Pb, and Zn are associated in different time intervals in the soil after the remediation with paper-ash, (ii) to assess the stability of newly formed mineral phases of Cd, Pb and Zn after remediation, and (iii) to evaluate the environmental impacts of soil remediation. For this purpose, natural soil with a grain size in the range of silt and clay and the same soil with the addition of sulfate was artificially contaminated with Cd, Pb, and Zn and remediated by the addition of paper-ash. Sulfate was added in a similar concentration as found at the "Old Zinc-woks" site to evaluate whether this contaminant has any influence on the mechanisms and efficiency of remediation by paper-ash. To achieve the above-mentioned objectives and to obtain data enabling the study of Cd, Pb, and Zn immobilization mechanisms, a sequential extraction procedure, and XRD analyses were performed over one year 7, 28, 56, 90, 120, and 365 days after the remediation.

2. Materials and Methods

2.1. Reagents and Materials

For the preparation of the samples and the standard solutions, Merck (Darmstadt, Germany) suprapure acids and Milli-Q water (18.2 MΩ cm) were obtained from Direct-Q 5 Ultrapure water system (Millipore, Watertown, MA, USA) were used. A stock IV CertiPUR ICP Multi Element Standard Solution containing 1000 mg/L ± 10 mg/L element concentrations in 1 M HNO3 (Merck, Darmstadt, Germany) was used for the preparation of working standard solutions for the ICP-MS determinations. All the other reagents were of analytical reagent grade.

Cadmium nitrate tetrahydrate ($(Cd(NO_3)_2\ 4H_2O)$, lead nitrate ($Pb(NO_3)_2$), zinc nitrate hexahydrate ($(Zn(NO_3)_2\ 6H_2O)$, calcium sulfate dehydrate ($CaSO_4\ 2H_2O$), magnesium chloride ($MgCl_2$), sodium acetate (CH_3COONa), hydroxylamine hydrochloride (NH_2OH), and hydrogen peroxide (H_2O_2) were purchased from Merck.

Samples were filtered using 0.45 µm Minisart cellulose nitrate membrane filters (Sartorius, Goettingen, Germany). To check the accuracy of the analytical procedures, the certified reference materials CRM 320R Trace Elements in River Sediment, Community Bureau of Reference (Geel, Belgium), and SPS-SW1 Quality Control Material for Surface Water Analysis obtained from SPS Spectrapure Standards AS (Oslo, Norway) were used.

2.2. Experimental Design

Natural, uncontaminated soil with a grain size in the range of clayey silt was dried at 40 °C and homogenized. Laboratory samples were obtained by the quartering procedure. After that, 0.5 kg of soil sample was treated with 10.3 g of gypsum ($CaSO_4$ $2H_2O$), thus that the leachable sulfate content was equivalent to that in the contaminated soil from "Old Zinc-works" site. To individual aliquots of 0.5 kg of untreated and sulfate-treated natural soils, an aqueous solution of a mixture of nitrate salts ($Cd(NO_3)_2$, $Pb(NO_3)_2$, and $Zn(NO_3)_2$) was added, thus that the contaminated soils contained approximately 10, 1000, and 10,000 mg/kg of Cd, Pb, and Zn, respectively. The contaminated soils were left for 48 h at 30 °C to allow equilibration of the added Cd, Pb, and Zn. Then, for the remediation, 0.25 kg aliquots of contaminated and sulfate-treated contaminated soils were amended with the paper-ash, thus that the soil-to-ash mass ratio was 75:25. This ratio was chosen based on the optimization of the paper ash remediation process from our previous research. After the addition of the paper-ash, water (wt. 30%) was added [18]. Samples were homogenized, transferred to plastic cylinders (diameter: 100 mm; height: 40 mm), and compacted manually with a rammer, simulating the field installation of geotechnical composites. The composites were then transferred to a climatic chamber at 20 ± 2 °C and 98% humidity and kept under constant temperature and humidity conditions until the end of the experiment. To follow the partitioning of the Cd, Pb, and Zn in the prepared uncontaminated, contaminated, and remediated soils, the modified Tessier's extraction procedure was applied in different time intervals over a time span of 365 days. Samples for the analysis were taken at 7, 28, 56, 90, 120, and 365 days after the remediation from the top and the bottom apertures of the cylinders. In uncontaminated, contaminated, and remediated soil, along with the Tessier extraction procedure, the XRD analyses were performed for each time interval. All the experiments were made using duplicate samples. A flow chart of the experimental design is presented in Figure 1.

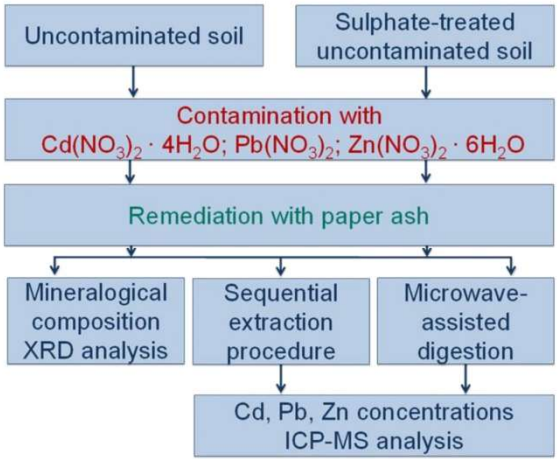

Figure 1. Flow chart of the experimental design.

2.3. Apparatus

Total concentrations Cd, Pb, and Zn in uncontaminated, contaminated, and remediated soil samples and their amounts in the individual phases of the sequential extraction procedures were determined by ICP-MS (7700x, Agilent Technologies, Tokyo, Japan). ICP-MS operating parameters are presented in Table S1 (Supplementary).

A CEM Corporation (Matthews, NC, USA) MARS 6 Microwave System was used for sample digestion.

Mineralogical composition of soil samples was determined by X-ray powder diffraction (XRD) on the Empyrean PANalytical diffractometer (PANalytical B.V., Almelo, The Netherlands) with Cu–Kα irradiation (λ = 1.54056 Å), at 45 kV and a current of 40 mA, over the 2θ angular range from 5° to 70°, using a step size of 0.01° and a measuring time per step of 100 s. The results were analyzed with the Highscore (PANalytical, Almelo, The Netherlands) diffraction software, using the Powder Diffraction File PDF-4+ (ICDD, Newtown Square, PA, USA) database as the reference source of data.

Scanning electron microscopy was performed by using a SEM 5500 LV (JEOL, Tokyo, Japan) microscope, equipped with energy dispersive spectroscopy (EDS, Oxford instruments, Abingdon, UK). During the analyses, low-vacuum mode (pressure of 20 Pa) and an accelerating voltage of 15 kV were used. A polished cross-section was prepared for SEM/EDS.

The specific surface area (BET) of paper ash was determined by nitrogen gas sorption (ASAP 2020, Micromeritics, Norcross, GA, USA). The sample was evacuated at 105 °C with an evacuation rate of 0.67 kPa/s until a final vacuum of 2 Pa was attained.

During the steps of the sequential extraction procedure, samples were mechanically shaken on a Vibromix 40 elliptical (Tehtnica, Železniki, Slovenia) orbital shaker. The Hettich Universal 320 Centrifuge (Hettich GmbH & Co. KG, Tuttlingen, Germany) was used to centrifuge the samples.

A WTW pH meter 3110 (Weilheim, Germany) pH meter was used to measure pH. An AE 163 analytical balance from Mettler (Zürich, Switzerland) was used for weighing.

2.4. Determination of the Total Metal Content in the Soil Samples

For digestion of soil samples, about 0.2 g of dry soil was weighed into a Teflon tube, and microwave-assisted digestion was applied using HNO_3, HF, and HCl acids [36]. The concentrations of Cd, Pb, and Zn in the digested samples were determined by ICP-MS.

2.5. Sequential Extraction Procedure

To Tessier's original partitioning scheme [24], water was added as the first extracting agent to leach Cd, Pb, and Zn from the most mobile soil fraction [25]. A total of 2.000 ± 0.001 g of soil sample were weighed in the centrifuge tube, and the sequential extraction procedure presented in Table 1 was applied. For mechanical shaking (steps I–III), an elliptical orbital shaker (300 rpm) was used. After shaking, centrifugation at 10,000 rpm (10 min) and filtration of the sample through 0.45 µm filter followed. Prior to the addition of the next extracting agent, the remaining solid residues were washed with 10 mL of water (shaken and centrifuged).

Table 1. The extraction procedure [25] used in the present study.

Step	Soil Fraction	Extracting Solution	Mode of Extraction
I	Water-soluble	Water (20 mL)	Shaking (16 h)
II	Exchangeable	1 M $NaCH_3COO$ (20 mL, pH 8.2)	Shaking (1 h)
III	Bound to carbonates	1 M $NaCH_3COO$ (20 mL, pH 5)	Shaking (5 h)
IV	Bound to Fe/Mn oxides and hydroxides	0.04 M NH_2OH HCl in 25% v/v CH_3COOH (20 mL, pH 2)	Extracted at 95 °C (6 h)
V	Bound to organic matter	156.25 mL of 30% H_2O_2 + 93.75 mL of 0.02 M HNO_3 (20 mL, pH 2)	Extracted at 85 °C (2 h)
VI	Bound to silicate lattice	0.2 g of dried residual sample	Microwave-assisted digestion

3. Results and Discussion

3.1. Quality Control of the Analytical Data

The accuracy of the analytical procedures for the determination of the Cd, Pb, and Zn concentrations in extracts from the sequential extraction procedure and the total element concentrations in the soil samples was checked by analyzing the SPS-SW1 Reference material for the measurements of elements in surface waters and certified reference materials CRM 320R Trace elements in river sediment. As evident from data given in Tables S2 and S3, the determined concentrations of the elements agreed well with the reported certified values (the agreement between the results was better than ±5%), which confirmed the accuracy of the analytical procedures. The expanded uncertainty of the analytical procedures applied was better than ±3% (k = 2).

3.2. Characteristics of the Soil and Paper-Ash

The mineralogical composition of the soil used is presented in the Supplementary Material (Figure S1). The results of the XRD analyses revealed that the soil is composed of quartz, dolomite, feldspar, calcite, illite/muscovite, clinochlore, and hornblende. The paper-ash is a fine-grade, highly alkaline (pH~12) hydraulically active material, with a specific surface area (BET) of 8.1 m^2/g, containing approximately 40% Ca, 6% Si, 5% Al, and 2% Mg. Ba, Fe, S, K, Zn, and Ni are present in lower concentrations and some other elements in trace amounts. Phase analyses revealed the presence of calcite, lime, portlandite, quartz, talc, gehlenite, anhydrite, and dolomite, together with an amorphous phase. SEM/EDS analysis results correlated with the XRD analysis (Figure 2A). The amorphous phase consists primarily of Si, Al, and Ca in different proportions (Figure 2B). Based on the leaching test, applying the standardized leaching procedure [37,38], it was found that the above-mentioned elements are present in paper-ash as low water-soluble species. Only the concentration of Ba exceeded the limiting value for inert materials, set by the current Slovenian landfilling legislation [37,38].

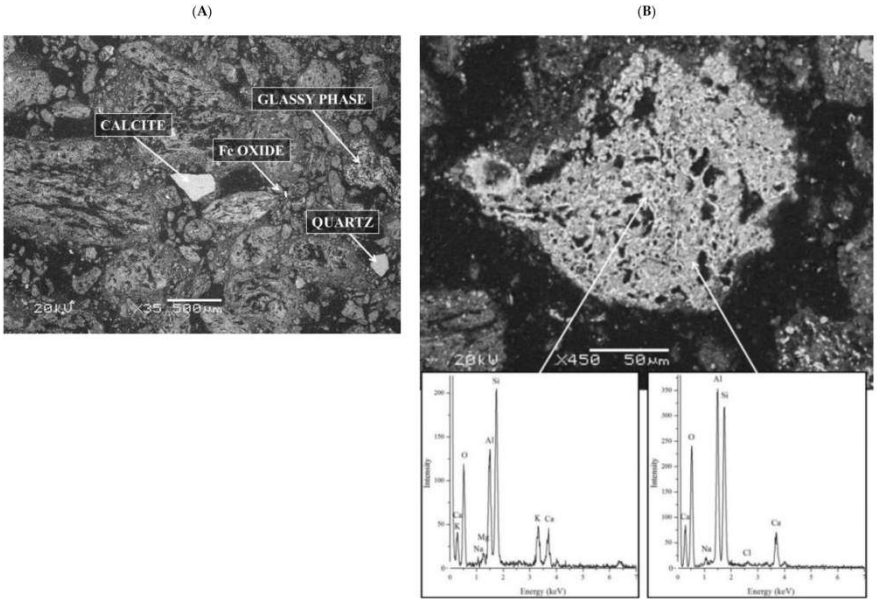

Figure 2. SEM micrographs of the paper ash; (**A**) showing the presence of different constituent phases; (**B**) the results of the semi-quantitative chemical analysis (EDS) of paper ash amorphous phase.

To separately follow the carbonation process for the paper-ash itself, a paste was prepared by mixing the paper-ash with an excess amount of demineralized water. The XRD analyses were performed at seven different time intervals to define the evolution of the calcite and portlandite mineral phases. The results in Figure S2 showed an increase in the relative quantity of calcite and a decrease in the relative quantity of portlandite.

3.3. Investigation of the Immobilization Mechanisms, Stability of the Mineral Phases of Cd, Pb, and Zn after the Remediation, and the Environmental Impacts of Soil Remediation

To study the mechanisms of immobilization and the stability of the mineral phases of Cd, Pb, and Zn after remediation, and to evaluate the environmental impacts of soil remediation, partitioning of Cd, Pb, and Zn were performed in uncontaminated, contaminated, and remediated soils over a period of one year in different time intervals by applying a sequential extraction procedure and the data were compared with complementary results from the XRD analyses.

3.4. Partitioning of Cd, Pb, and Zn in Uncontaminated, Contaminated, and Remediated Soils

Partitioning of Cd, Pb, and Zn was performed in uncontaminated, contaminated, and remediated soils by applying a modified Tessier's sequential extraction procedure [24] (see sequential extraction procedure in Materials and methods). To find out whether sulfate, as present in the soil from "Old Zinc-works" site, has any effect on the remediation, sulfate-treated uncontaminated, contaminated, and remediated soils were also investigated (see Experimental design). The results of the partitioning of the Cd, Pb, and Zn in the uncontaminated, contaminated, and remediated soils are presented in Figures 3–5, while in sulfate-treated uncontaminated, contaminated, and remediated soils in the Supplementary Material (Figures S3–S5). The related elemental concentrations in individual soil fractions of the extraction procedure related to data from Figures 3–5 and Figures S3–S5 are provided in the Supplementary Material (Tables S4–S9). The concentrations of Cd, Pb, and Zn in steps I to VI were summed and compared to the total Cd, Pb, and Zn concentrations obtained by microwave-assisted digestion. The mass balance was agreed to within ±5%, confirming the precision of the sequential extraction analysis.

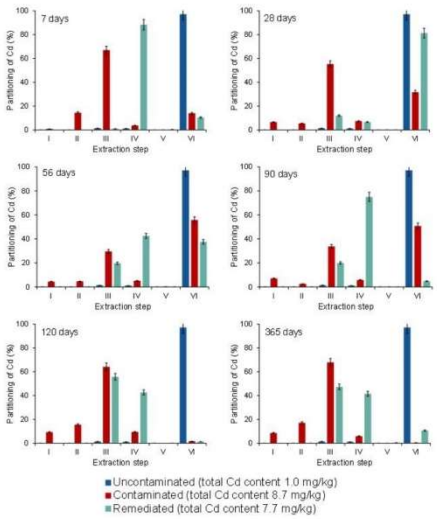

Figure 3. Partitioning of Cd in uncontaminated, contaminated, and remediated soil samples with time elapsed after the remediation. I water-soluble; II exchangeable; III bound to carbonates; IV bound to Fe/Mn oxides and hydroxides; V bound to organic matter; VI bound to silicate lattice.

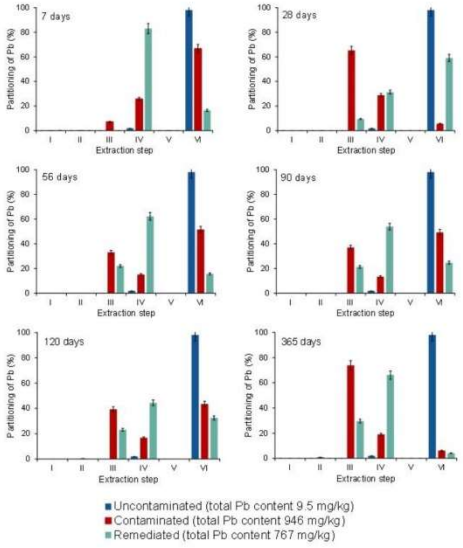

Figure 4. Partitioning of Pb in uncontaminated, contaminated, and remediated soil samples with time elapsed after the remediation. I water-soluble; II exchangeable; III bound to carbonates; IV bound to Fe/Mn oxides and hydroxides; V bound to organic matter; VI bound to silicate lattice.

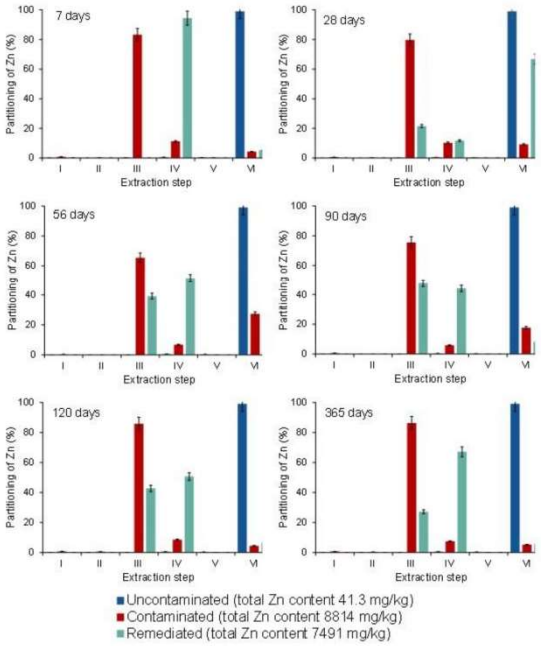

Figure 5. Partitioning of Zn in uncontaminated, contaminated, and remediated soil samples with time elapsed after the remediation. I water-soluble; II exchangeable; III bound to carbonates; IV bound to Fe/Mn oxides and hydroxides; V bound to organic matter; VI bound to silicate lattice.

In the uncontaminated soils, Cd, Pb, and Zn were associated almost exclusively with the insoluble residual fraction, bound to the silicate lattice. Their concentrations in the water-soluble and exchangeable fractions, which are mobile in the environment, were negligible, not exceeding 0.0007, 0.0003, and 0.0025 mg/kg for the Cd, Pb, and Zn, respectively (see the data from Tables S4–S9).

In the contaminated soils, the distribution of Cd, Pb, and Zn changed over time. After the contamination, the Cd was distributed mainly between the carbonate, exchangeable and residual fractions. In the water-soluble fraction, the Cd concentration exceeded the limiting value for inertness (0.04 mg/kg) [37,38]. During the experiment, the sum of the Cd concentrations in highly the mobile water-soluble and exchangeable fractions was around 2–3 mg/kg. The Pb in the contaminated soils was associated with carbonate, Fe/Mn oxides and hydroxides, and the residual fractions. After the soil contamination, the Pb concentration in the water-soluble fraction was close to the limit value for inert materials (0.5 mg/kg) [37,38], while its exchangeable concentrations were up to 30 times higher than in the water-soluble fraction (see data from Tables S4–S9). The Zn in the contaminated soils was distributed mainly in the carbonate fraction and, to a smaller extent, in the Fe/Mn oxides and hydroxides and residual fractions. In the water-soluble fraction of the contaminated soils, the Zn concentrations greatly exceeded (around 20 times) the criterion for inertness (4 mg/kg) [37,38], whereas the exchangeable Zn contents were approximately 2–4 times lower than the water-soluble concentrations.

In the remediated soils, the application of paper-ash substantially increased the soil's pH, which led to the precipitation of Cd, Pb, and Zn and their transfer from the easily soluble fractions to the sparingly soluble fraction associated with Fe/Mn oxides and hydroxides. In the early stage of remediation (Figures 3–5, soils that were not treated with sulfate), the Cd, Pb, and Zn were associated mainly with Fe/Mn oxides and hydroxides. After 28 days, Cd and Zn were redistributed to the residual fraction, while the Pb was between the residual and the fraction bound to Fe/Mn oxides and hydroxides. As the time elapsed, the CaO present in the paper-ash was hydrated, forming $Ca(OH)_2$ that, through the carbonation process, yielded $CaCO_3$. The newly formed carbonates, along with the hydroxides, bound the Cd, Pb, and Zn into insoluble compounds. The solubilities of the Cd, Pb, and Zn carbonates and hydroxides are presented in Table 2 (data from IUPAC-NIST Solubility Database [39].

Table 2. Solubility of $CdCO_3$, $PbCO_3$, and $ZnCO_3$, and $Cd(OH)_2$, $Pb(OH)_2$, and $Zn(OH)_2$ in water at 20 °C based on IUPAC Solubility Database (2012).

Compound	Solubility (g/100 mL)
$CdCO_3$	3.932×10^{-5}
$Cd(OH)_2$	2.697×10^{-4}
$PbCO_3$	7.269×10^{-5}
$Pb(OH)_2$	1.615×10^{-4}
$ZnCO_3$	4.692×10^{-5}
* $Zn(OH)_2$	1×10^{-4}

* Because of divergent results reported, provided value is approximate estimation, (IUPAC Solubility Database [39]).

After the stabilization in the mineral phases, until the end of the experiment, the Cd, Pb, and Zn remained associated mainly with the carbonate fraction and the fraction bound to the Fe/Mn oxides and hydroxides.

The data from Figures 3–5 and Figures S3–S5 further indicate that the addition of sulfate to soil samples had no effect on the remediation efficiency. The partitioning of Cd, Pb, and Zn in the remediated soil, which was not treated with sulfate (Figures 3–5), and in the sulfate-treated remediated soil (Figures S3–S5), was almost the same.

Due to the redistribution of Cd, Pb, and Zn from the water-soluble and the exchangeable fractions into the sparingly soluble fractions of soil composite (the formation of insoluble Cd, Pb, and Zn carbonates and hydroxides), the Cd, Pb, and Zn concentrations in

the easily soluble fractions significantly decreased, indicating the effective remediation of the contaminated soil by paper-ash.

The Cd concentration in the water-soluble fraction after the remediation was reduced from 0.8 to approximately 0.0005 mg/kg (Tables S4 and S7), which is 100 times lower than the limiting value for inert materials [37,38]. In the exchangeable fraction, this decrease was from 1.5 to 0.0005 mg/kg (3000 times), demonstrating the effective immobilization of Cd also from the exchangeable fraction. The Pb concentration, which during the course of the experiment in the water-soluble fraction of contaminated soils, in general, ranged from 0.2 to 0.8 mg/kg, was reduced by about 250 times after the remediation (Tables S5 and S8). The concentrations of Pb in the water-soluble fraction were about 125 times lower than the limit value for inert materials [37,38]. In the exchangeable fraction of soil that was not treated with sulfate, this decrease was from 8 to 0.1 mg/kg (80 times) after the remediation (Table S5), indicating the effective immobilization of Pb also in this easily soluble soil fraction. The effective immobilization of Pb from the exchangeable fraction was also observed in the sulfate-treated and remediated soil (Table S8). The Zn concentration in the water-soluble fraction was reduced from about 60 to 0.4 mg/kg (Table S6) after the remediation, which is 10 times lower than the limiting value for inert materials [37,38]. In the case of Zn, similar concentrations were found in the sulfate-treated remediated soils (Table S9). In the exchangeable fraction, the Zn concentrations in soil that were not treated with sulfate decreased after the remediation by about 50 times, and in the sulfate-treated soil by about 100 times (Tables S6 and S9). This shows that the immobilization of Zn was also effective in the exchangeable soil fraction.

It is important to stress that the Cd, Pb, and Zn were already effectively immobilized 28 days after the remediation and remained stabilized in the sparingly soluble soil composite fractions until the end of the experiment (1 year), demonstrating the remediation efficiency as well as the stability of the formed Cd, Pb, and Zn compounds. Since after the remediation the concentrations of Cd, Pb, and Zn in the water-soluble fraction were far below the limiting values for inertness [37,38] and thus were their concentrations in the exchangeable fraction, the Cd, Pb, and Zn in the remediated soil composites do not present an environmental hazard.

In an evaluation of the possible statistical significance of differences between the distribution of Cd, Pb, and Zn in contaminated and remediated soils, mean values ($n = 6$) from distribution of Cd, Pb, and Zn between the fractions of the Tessier's sequential extraction were compared by computing Student's t-test. In the water-soluble, exchangeable, bound to carbonates, and fraction bound to Fe/Mn oxides and hydroxides, there were statistically significant differences between the means of Cd, Pb, and Zn concentrations, when a probability of ≤ 0.05 was considered as significant. In the fraction bound to organic matter and sulfide, no statistically significant differences between the means of Cd, Pb, and Zn concentrations were observed when a probability of ≤ 0.05 was considered as significant (Table S10). This was expected since, in this fraction, very low elements concentrations were found in contaminated and remediated soils. In the residual fraction, it was not possible to apply Student's *t*-test due to large differences in Cd, Pb, and Zn concentrations determined at different time intervals in this fraction.

3.5. Investigation of the Mineralogical Composition of the Remediated Soils

To identify the mineral phases that were formed after the remediation, XRD analyses were performed in uncontaminated, contaminated, and remediated soils during each time interval as a sequential extraction procedure. In the case of contaminated soil without the addition of gypsum, there is no difference in XRD spectra in comparison to the uncontaminated soil, neither from the scope of analysis of crystalline phases nor from the scope of analyses for the potential presence of amorphous phases. In addition, there was no difference between the contaminated soil with the addition of gypsum in comparison to the uncontaminated soil with the addition of gypsum. The only difference between the

contaminated soil and contaminated soil with added gypsum was that the characteristic peaks of gypsum were detected in the XRD spectra of the latter, as can be seen in Figure S6.

The potential formation of secondary crystalline and amorphous phases of Cd, Pb, and Zn minerals was somehow expected after artificial contamination of soil. Therefore, special care was taken during the refinement of the XRD spectra to identify the potential presence of commonly occurring Cd, Pb, and Zn carbonate and sulfate minerals. However, no such phases were identified.

Since the data from the partitioning study revealed that the sulfate treatment does not influence the remediation efficiency, only the soils that were not treated with sulfate are presented. Sections of the XRD patterns of the contaminated and remediated soils, along with the XRD patterns of the uncontaminated soil, are presented in Figure 6.

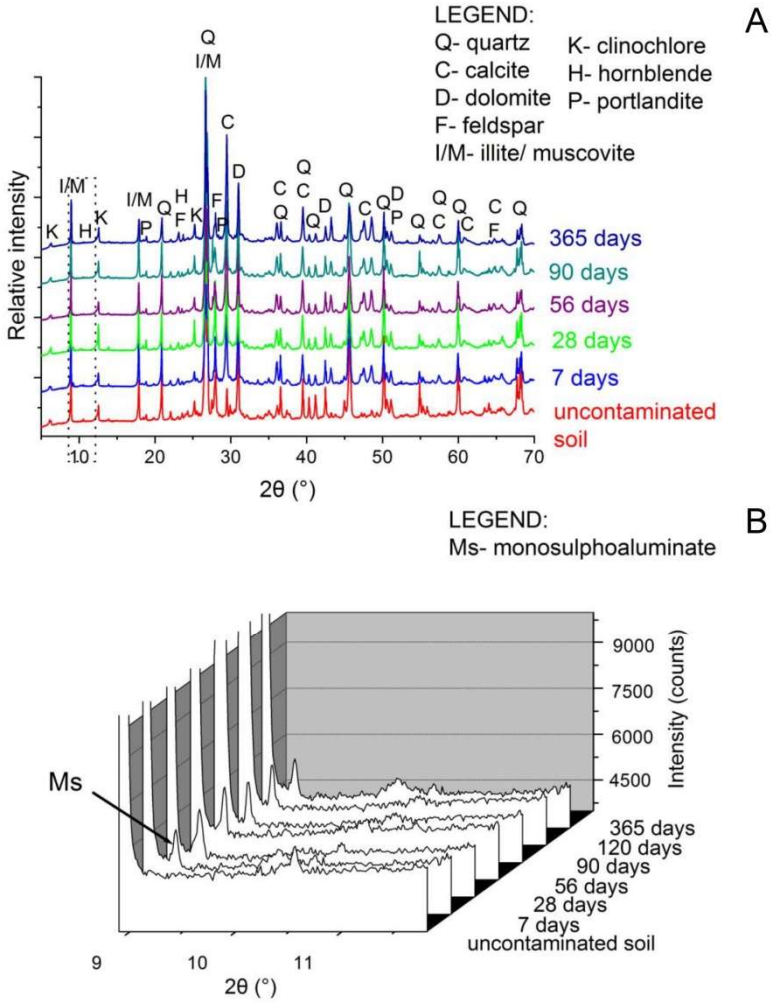

Figure 6. XRD patterns of (**A**) remediated soil and (**B**) corresponding section of the XRD patterns from 8.9°–11.8° 2θ with time elapsed after the remediation.

The results of the XRD analyses showed that a new mineral phase was formed due to the addition of paper-ash to the soil. A mono-sulpho-aluminate hydration product from the group of calcium aluminate hydrate minerals (CAH) was identified. Its relative quantity was not changed significantly during the experiment. The hydration product CAH, which was formed in the remediated soils, and the carbonation process, which was proven in the case of paper-ash, contribute to the effective immobilization of the Cd, Pb, and Zn. These XRD data supported the results obtained by the sequential extraction procedure.

In the reported literature, the BCR extraction scheme [30], the Tessier's sequential extraction procedure [31], and the use of sequential extraction procedures in combination with XRD analysis [34,35] were reported for the investigation of the immobilization of heavy metals in the soil after the remediation with different soil amendments. Since in these articles sequential extraction procedures were applied for only one-time interval after the remediation, by the reported approaches [30,31,34,35], it was only possible to estimate the efficiency of remediation by evaluating the redistribution of metals from the easily soluble to more sparingly soluble soil mineral phases. In the present investigation, the use of modified Tessier's sequential extraction procedure in combination with the complementary XRD analysis performed in time intervals of 7, 28, 56, 90, 120, and 365 days after the remediation, enabled us to follow the mechanisms of the remediation of Cd, Pb, and Zn with paper-ash, the study of the efficiency of the remediation and the stability of the newly formed insoluble mineral phases of Cd, Pb, and Zn. To the best of our knowledge, such a comprehensive methodological approach has not yet been reported.

4. Conclusions

Data from the present investigation based on a sequential extraction procedure and XRD analyses revealed that paper-ash is an effective additive for the immobilization process in remediation of Cd, Pb, and Zn in contaminated soils. Sulfate added to the soil did not affect the remediation efficiency. In the remediated soil composites, the Cd, Pb, and Zn were transferred from the easily soluble, highly mobile soil fractions to the sparingly soluble fractions of soil composite. Consequently, their concentrations in the water-soluble fraction were reduced far below the limit values for inert materials (Cd concentration was reduced from 0.8 to 0.0005 mg/kg, Pb concentration from 0.8 to 0.003 mg/kg, and Zn concentration from 60 to 0.4 mg/kg). A significant decrease in the Cd, Pb, and Zn concentrations was also observed in the exchangeable fraction of the soil composite (Cd concentration was reduced from 1.5 to 0.0005 mg/kg, Pb concentration from 8 to 0.1 mg/kg, and Zn concentration from 40 to 0.5 mg/kg).

The mechanism of immobilization for the Cd, Pb, and Zn with paper-ash involved the formation of hydration products from the paper-ash, which resulted in the precipitation of insoluble Cd, Pb, and Zn hydroxides, while through the carbonation process, Cd, Pb, and Zn were stabilized in insoluble carbonates.

The present study revealed the high efficiency of the remediation with paper-ash, which is related to the stability of the hydroxide and carbonate mineral phases of Cd, Pb, and Zn, formed after the remediation. Regarding the environmental impacts of soil remediation with paper-ash, it was demonstrated that the Cd, Pb, and Zn in the remediated soil composites do not present an environmental hazard.

To the best of our knowledge, such a comprehensive investigation using complementary analytical methodologies allowed us to understand the mechanisms of Cd, Pb, and Zn immobilization in geotechnical composites made from contaminated soil and paper-ash and their environmental impacts has not yet been performed.

The results of this study provide novel findings and contribute important knowledge to strategies for effective remediation of soils contaminated with Cd, Pb, and Zn by means of immobilization with paper-ash. The new findings can contribute to more sustainable management and use of waste materials generated in the paper and pulp industry for the remediation and rehabilitation of degraded areas. New knowledge can also initiate an industrial symbiosis of a closed-loop system that can be established locally.

From the scope of demands to achieve long-term efficiency of the soil remediation procedures with the immobilization approach, in addition to the laboratory experiments, there is a need for performing similar field tests, which will be a topic of our next investigations.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/app112411822/s1, Table S1: ICP-MS operating parameters for determination of element concentrations, Table S2: Concentrations of elements in standard reference material SPS-SW1 (Reference material for measurements of elements in surface waters) determined by ICP-MS, Table S3: Concentrations of elements in certified reference material CRM 320R (Trace Elements in River Sediment) determined by ICP-MS after microwave assisted digestion, Table S4: Concentrations of Cd in individual fractions of extraction procedure in uncontaminated, contaminated, and remediated soils during the course of the experiment, Table S5: Concentrations of Pb in individual fractions of extraction procedure in uncontaminated, contaminated, and remediated soils during the course of the experiment, Table S6: Concentrations of Zn in individual fractions of extraction procedure in in uncontaminated, contaminated, and remediated soils during the course of the experiment, Table S7: Concentrations of Cd in individual fractions of extraction procedure in uncontaminated soil treated with $CaSO_4$, contaminated and remediated soils during the course of the experiment, Table S8: Concentrations of Pb in individual fractions of extraction procedure in uncontaminated soil treated with $CaSO_4$, contaminated and remediated soils during the course of the experiment, Table S9: Concentrations of Zn in individual fractions of extraction procedure in uncontaminated soil treated with $CaSO_4$, contaminated and remediated soils during the course of the experiment, Table S10: Data on the statistical processing of the results, Figure S1: XRD pattern of uncontaminated soil, Figure S2: Sections of the XRD patterns of the paper ash paste, Figure S3: Partitioning of Cd in sulphate-treated uncontaminated, contaminated, and remediated soil samples with time elapsed after the remediation, Figure S4: Partitioning of Pb in sulphate-treated uncontaminated, contaminated, and remediated soil samples with time elapsed after the remediation, Figure S5: Partitioning of Zn in sulphate-treated uncontaminated, contaminated, and remediated soil samples with time elapsed after the remediation, Figure S6: XRD patterns of contaminated soil (A) and sulphate-treated contaminated soil (B) with time elapsed.

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Supplementary Materials: Environmental Impacts and Immobilization Mechanisms of Cadmium, Lead and Zinc in Geotechnical Composites Made from Contaminated Soil and Paper-Ash

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Table S1. ICP-MS operating parameters for determination of element concentrations.

Parameter	Type/Value	Helium mode	No gas mode
Sample introduction			
Nebuliser	Miramist		
Spray chamber	Scott		
Skimmer and sampler	Ni		
Plasma conditions			
Forward power	1550 W		
Plasma gas flow	15.0 L/min		
Carrier gas flow		1.05 L/min	0.75 L/min
Dilution gas flow		0.10 L/min	0.45 L/min
He gas flow		4.5 mL/min	
QP bias		-15 V	-3.6 V
Oct bias		-18 V	-8.0 V
Cell entrance		-40 V	-40 V
Cell exit		-60 V	-50 V
Deflect		-2.2 V	13.4 V
Plate bias		-60 V	-40 V
Sample uptake rate	0.3 mL/min		
Data acquisition parameters			
Isotopes monitored		^{66}Zn	^{111}Cd, ^{208}Pb
Isotopes of internal standards		^{72}Ge, ^{89}Y, ^{103}Rh, ^{115}In	^{72}Ge, ^{89}Y, ^{103}Rh, ^{115}In

Table S2. Concentrations of elements in standard reference material SPS-SW1 (Reference material for measurements of elements in surface waters) determined by ICP-MS. The results represent the mean concentration from three parallel samples. The uncertainty of ICP-MS determination was ± 2%.

Parameter	Certified concentration (µg/L)	Determined concentration (µg/L)
Cd	0.50±0.01	0.48±0.01
Pb	5.0±0.1	4.94±0.15
Zn	20[a]	19.7±0.6

[a]informative value

Table S3. Concentrations of elements in certified reference material CRM 320R (Trace Elements in River Sediment) determined by ICP-MS after microwave assisted digestion. The results represent the mean concentration from three parallel samples. The expanded uncertainty of analytical procedure was better than ± 3% (k = 2).

Element	Certified (mg/kg)	Determined (mg/kg)
Cd	2.64±0.18	2.52±0.07
Zn	319±20	308±9
Pb	85±5	87±2

Table S4. Concentrations of Cd in individual fractions of extraction procedure in uncontaminated, contaminated, and remediated soils during the course of the experiment. Concentrations of Cd were determined by ICP-MS. The results represent the mean concentration from two parallel samples. The expanded uncertainty of analytical procedure was better than ± 3% (k = 2).

Days after the start of the experiment	Extraction step	Uncontaminated soil Cd (mg/kg)	Contaminated soil Cd (mg/kg)	Remediated soil Cd (mg/kg)
7	I	0.0007	0.07	0.0007
	II	0.0007	1.30	0.0007
	III	0.015	5.90	0.07
	IV	0.012	0.32	6.80
	V	0.0007	0.01	0.03
	VI	1.01	1.20	0.80
	Total concentration	1.04	8.73	7.70
28	I	0.0007	0.57	0.0005
	II	0.0007	0.47	0.0007
	III	0.015	4.80	0.93
	IV	0.012	0.60	0.51
	V	0.0007	0.01	0.006
	VI	1.01	2.30	6.10
	Total concentration	1.04	8.73	7.70
56	I	0.0007	0.39	0.0005
	II	0.0007	0.41	0.0005
	III	0.015	2.60	1.50
	IV	0.012	0.45	3.30
	V	0.0007	0.01	0.002
	VI	1.01	4.90	2.90
	Total concentration	1.04	8.73	7.70
90	I	0.0007	0.62	0.0005
	II	0.0007	0.22	0.0005
	III	0.015	2.90	1.50
	IV	0.012	0.51	5.80
	V	0.0007	0.01	0.003
	VI	1.01	4.40	0.40
	Total concentration	1.04	8.73	7.70
120	I	0.0007	0.80	0.0008
	II	0.0007	1.40	0.006
	III	0.015	5.60	4.30
	IV	0.012	0.83	3.30
	V	0.0007	0.003	0.006
	VI	1.01	0.10	0.10
	Total concentration	1.04	8.73	7.70
365	I	0.0007	0.75	0.0005
	II	0.0007	1.50	0.007
	III	0.015	5.90	3.60
	IV	0.012	0.51	3.20
	V	0.0007	0.01	0.03
	VI	1.01	0.04	0.80
	Total concentration	1.04	8.73	7.70

Table S5. Concentrations of Pb in individual fractions of extraction procedure in uncontaminated, contaminated, and remediated soils during the course of the experiment. Concentrations of Pb were determined by ICP-MS. The results represent the mean concentration from two parallel samples. The expanded uncertainty of analytical procedure was better than ± 3% (k = 2).

Days after the start of the experiment	Extraction step	Uncontaminated soil Pb (mg/kg)	Contaminated soil Pb (mg/kg)	Remediated soil Pb (mg/kg)
7	I	0.0003	0.04	2.1
	II	0.0003	1.60	1.2
	III	0.0021	68.4	0.31
	IV	0.18	244	634
	V	0.0043	0.45	0.0003
	VI	9.3	631	127
	Total concentration	9.5	946	767
28	I	0.0003	0.41	0.13
	II	0.0003	2.03	0.32
	III	0.0021	617	72.6
	IV	0.18	273	240.8
	V	0.0043	0.17	0.001
	VI	9.3	53.3	453
	Total concentration	9.5	946	767
56	I	0.0003	0.19	0.001
	II	0.0003	1.4	0.005
	III	0.0021	313	169
	IV	0.18	143.2	478
	V	0.0043	0.49	0.0007
	VI	9.3	488	120
	Total concentration	9.5	946	767
90	I	0.0003	0.27	0.0002
	II	0.0003	1.24	0.014
	III	0.0021	350	163
	IV	0.18	127	414
	V	0.0043	0.29	0.0002
	VI	9.3	467	190
	Total concentration	9.5	946	767
120	I	0.0003	0.24	0.002
	II	0.0003	3.7	0.030
	III	0.0021	373	177
	IV	0.18	158	341
	V	0.0043	0.0001	0.0002
	VI	9.3	411	250
	Total concentration	9.5	946	767
365	I	0.0003	0.21	0.002
	II	0.0003	7.97	0.12
	III	0.0021	670	228
	IV	0.18	180	508
	V	0.0043	0.37	0.020
	VI	9.3	57.5	31.5
	Total concentration	9.5	946	767

Table S6. Concentrations of Zn in individual fractions of extraction procedure in in uncontaminated, contaminated, and remediated soils during the course of the experiment. Concentrations of Zn were determined by ICP-MS. The results represent the mean concentration from two parallel samples. The expanded uncertainty of analytical procedure was better than ± 3% (k = 2).

Days after the start of the experiment	Extraction step	Uncontaminated soil Zn (mg/kg)	Contaminated soil Zn (mg/kg)	Remediated soil Zn (mg/kg)
7	I	0.0025	69.0	7.6
	II	0.0025	15.1	6.4
	III	0.063	7338	5.6
	IV	0.22	993	7075
	V	0.14	15.2	1.9
	VI	40.9	384	395
	Total concentration	41.3	8814	7491
28	I	0.0025	50.7	0.6
	II	0.0025	15.4	1.4
	III	0.063	7022	1613
	IV	0.22	913	877
	V	0.14	5.4	1.7
	VI	40.9	808	4998
	Total concentration	41.3	8814	7491
56	I	0.0025	34.7	0.0012
	II	0.0025	10.4	0.015
	III	0.063	5763	2932
	IV	0.22	596	3861
	V	0.14	5.1	0.074
	VI	40.9	2405	698
	Total concentration	41.3	8814	7491
90	I	0.0025	58.3	0.1362
	II	0.0025	9.3	0.161
	III	0.063	6660	3568
	IV	0.22	525.3	3298
	V	0.14	3.4	0.191
	VI	40.9	1557	624
	Total concentration	41.3	8814	7491
120	I	0.0025	63.6	0.44
	II	0.0025	41.2	0.52
	III	0.063	7563	3198
	IV	0.22	753	3793
	V	0.14	0.10	0.55
	VI	40.9	393	498
	Total concentration	41.3	8814	7491
365	I	0.0025	55.3	0.41
	II	0.0025	36.8	0.65
	III	0.063	7606	2033
	IV	0.22	656	5024
	V	0.14	1.70	12.0
	VI	40.9	458	421
	Total concentration	41.3	8814	7491

Table S7. Concentrations of Cd in individual fractions of extraction procedure in uncontaminated soil treated with $CaSO_4$, contaminated and remediated soils during the course of the experiment. Concentrations of Cd were determined by ICP-MS. The results represent the mean concentration from two parallel samples. The expanded uncertainty of analytical procedure was better than ± 3% (k = 2).

Days after the start of the experiment	Extraction step	Uncontaminated soil Cd (mg/kg)	Contaminated soil Cd (mg/kg)	Remediated soil Cd (mg/kg)
7	I	0.0007	0.12	0.0007
	II	0.0007	2.00	0.0007
	III	0.015	4.70	0.072
	IV	0.009	0.23	6.40
	V	0.0007	0.01	0.01
	VI	0.97	1.90	1.30
	Total concentration	0.99	8.90	7.70
28	I	0.0007	1.5	0.0005
	II	0.0007	0.83	0.0005
	III	0.015	3.80	1.40
	IV	0.009	0.54	0.57
	V	0.0007	0.01	0.008
	VI	0.97	2.30	5.70
	Total concentration	0.99	8.90	7.70
56	I	0.0007	0.96	0.0004
	II	0.0007	0.93	0.0004
	III	0.015	3.40	1.10
	IV	0.009	0.46	2.80
	V	0.0007	0.009	0.0009
	VI	0.97	3.20	3.90
	Total concentration	0.99	8.90	7.70
90	I	0.0007	0.83	0.0005
	II	0.0007	0.22	0.0005
	III	0.015	3.40	1.30
	IV	0.009	0.51	5.30
	V	0.0007	0.007	0.002
	VI	0.97	4.00	1.20
	Total concentration	0.99	8.90	7.70
120	I	0.0007	1.00	0.002
	II	0.0007	1.60	0.006
	III	0.015	5.60	4.20
	IV	0.009	0.63	3.30
	V	0.0007	0.00	0.006
	VI	0.97	0.10	0.20
	Total concentration	0.99	8.90	7.70
365	I	0.0007	1.30	0.002
	II	0.0007	2.00	0.005
	III	0.015	5.10	3.80
	IV	0.009	0.50	3.30
	V	0.0007	0.01	0.023
	VI	0.97	0.10	0.90
	Total concentration	0.99	8.90	7.70

Table S8. Concentrations of Pb in individual fractions of extraction procedure in uncontaminated soil treated with $CaSO_4$, contaminated and remediated soils during the course of the experiment. Concentrations of Pb were determined by ICP-MS. The results represent the mean concentration from two parallel samples. The expanded uncertainty of analytical procedure was better than ± 3% (k = 2).

Days after the start of the experiment	Extraction step	Uncontaminated soil Pb (mg/kg)	Contaminated soil Pb (mg/kg)	Remediated soil Pb (mg/kg)
7	I	0.0003	0.0461	2.43
	II	0.0003	5.50	1.28
	III	0.0028	68.00	4.48
	IV	0.20	238	621
	V	0.0067	0.15	0.0003
	VI	8.50	659	44.5
	Total concentration	8.70	970	734
28	I	0.0003	0.77	0.022
	II	0.0003	5.50	0.064
	III	0.0028	713	103
	IV	0.20	228	259
	V	0.0067	0.13	0.002
	VI	8.50	22.3	311
	Total concentration	8.70	967	734
56	I	0.0003	0.35	0.0004
	II	0.0003	6.30	0.005
	III	0.0028	491	95.3
	IV	0.20	156	470
	V	0.0067	0.19	0.0001
	VI	8.50	316	168
	Total concentration	8.70	970	734
90	I	0.0003	0.32	0.0003
	II	0.0003	2.58	0.0078
	III	0.0028	515	122
	IV	0.20	139	325
	V	0.0067	0.28	0.0002
	VI	8.50	313	287
	Total concentration	8.70	970	734
120	I	0.0003	0.37	0.0014
	II	0.0003	2.5	0.029
	III	0.0028	374	194
	IV	0.20	157	328
	V	0.0067	0.001	0.0002
	VI	8.50	436	211
	Total concentration	8.70	970	734
365	I	0.0003	0.41	0.0037
	II	0.0003	17.5	0.07
	III	0.0028	753.3	205
	IV	0.20	171.2	501
	V	0.0067	1.23	0.0032
	VI	8.50	25.9	27.4
	Total concentration	8.70	970	734

Table S9. Concentrations of Zn in individual fractions of extraction procedure in uncontaminated soil treated with $CaSO_4$, contaminated and remediated soils during the course of the experiment. Concentrations of Zn were determined by ICP-MS. The results represent the mean concentration from two parallel samples. The expanded uncertainty of analytical procedure was better than ± 3% (k = 2).

Days after the start of the experiment	Extraction step	Uncontaminated soil Zn (mg/kg)	Contaminated soil Zn (mg/kg)	Remediated soil Zn (mg/kg)
7	I	0.0026	101.2	10.2
	II	0.0026	50.7	8.0
	III	0.047	7596	401
	IV	0.19	847	6511
	V	0.16	10.5	5.8
	VI	38.8	77.4	88.7
	Total concentration	39.2	8782	7024
28	I	0.0026	117	0.4
	II	0.0026	32.5	0.6
	III	0.047	7235	3022
	IV	0.19	376.1	421
	V	0.16	5.6	2.6
	VI	38.8	915	3578
	Total concentration	39.2	8782	7024
56	I	0.0026	82.8	0.0012
	II	0.0026	40.8	0.0073
	III	0.047	6278	3267
	IV	0.19	566	3097
	V	0.16	4.0	0.028
	VI	38.8	1711	660
	Total concentration	39.2	8782	7024
90	I	0.0026	76.8	0.13
	II	0.0026	19.7	0.023
	III	0.047	6350	3232
	IV	0.19	558	2451
	V	0.16	4.2	0.607
	VI	38.8	1672	1340
	Total concentration	39.2	8782	7024
120	I	0.0026	97.3	0.74
	II	0.0026	56.0	0.48
	III	0.047	7715	3247
	IV	0.19	749	3512
	V	0.16	0.1	1.02
	VI	38.8	64.9	264
	Total concentration	39.2	8782	7024
365	I	0.0026	93.9	1.31
	II	0.0026	68.5	0.44
	III	0.047	7894	2264
	IV	0.19	684	4668
	V	0.16	5.5	12.6
	VI	38.8	36.1	77.2
	Total concentration	39.2	8782	7024

Table S10. Data on the statistical processing of the results.

Data on the statistical processing of the results for Cd

t-Test: Two-Sample Assuming Unequal Variances	Step I		Step II		Step III		Step IV		Step V		Step VI	
	Variable 1	*Variable 2*	*Variable 1*	*Variable 2*	*Variable 1*	*Variable 2*	*Variable 1*	*Variable 2*	*Variable 1*	*Variable 2*	*Variable 1*	*Variable 2*
Mean	0.533333	0.000583	0.883333	0.002567	4.616667	1.983333	3.818333	0.536667	0.012833	0.008833	2.156667	1.85
Variance	0.072427	1.77E-08	0.331147	9.39E-06	2.261667	2.643627	4.936417	0.029187	0.000179	8.17E-06	4.440867	5.307
Observations	6	6	6	6	6	6	6	6	6	6	6	6
Hypothesized Mean Difference	0		0		0		0		0		0	
df	5		5		10		5		5		10	
t Stat	4.848973		3.749041		2.912386		3.607315		0.715478		0.240595	
P(T<=t) one-tail	0.002339		0.006653		0.007751		0.007712		0.253162		0.407365	
t Critical one-tail	2.015048		2.015048		1.812461		2.015048		2.015048		1.812461	
P(T<=t) two-tail	0.004678		0.013307		0.015501		0.015424		0.506324		0.814729	
t Critical two-tail	2.570582		2.570582		2.228139		2.570582		2.570582		2.228139	

Data on the statistical processing of the results for Pb

t-Test: Two-Sample Assuming Unequal Variances	Step I		Step II		Step III		Step IV		Step V		Step VI	
	Variable 1	*Variable 2*	*Variable 1*	*Variable 2*	*Variable 1*	*Variable 2*	*Variable 1*	*Variable 2*	*Variable 1*	*Variable 2*	*Variable 1*	*Variable 2*
Mean	0.372533	0.226667	2.99	0.2815	398.5667	134.985	435.9667	187.5333	0.295017	0.003733	351.3	195.25
Variance	0.718845	0.014427	6.74976	0.216494	48146.65	6877.631	18752.81	3410.347	0.034058	6.36E-05	57798.4	21318.98
Observations	6	6	6	6	6	6	6	6	6	6	6	6
Hypothesized Mean Difference	0		0		0		0		0		0	
df	5		5		6		7		5		8	
t Stat	0.417253		2.51365		2.752413		4.087612		3.86256		1.35895	
P(T<=t) one-tail	0.346902		0.026794		0.016593		0.002322		0.005925		0.105617	
t Critical one-tail	2.015048		2.015048		1.94318		1.894579		2.015048		1.859548	
P(T<=t) two-tail	0.693804		0.053589		0.033186		0.004645		0.011849		0.211233	
t Critical two-tail	2.570582		2.570582		2.446912		2.364624		2.570582		2.306004	

Data on the statistical processing of the results for Zn

t-Test: Two-Sample Assuming Unequal Variances	Step I		Step II		Step III		Step IV		Step V		Step VI	
	Variable 1	*Variable 2*	*Variable 1*	*Variable 2*	*Variable 1*	*Variable 2*	*Variable 1*	*Variable 2*	*Variable 1*	*Variable 2*	*Variable 1*	*Variable 2*
Mean	55.26667	1.531233	21.36667	1.524333	6992	2224.933	3988	739.3833	5.15	2.735833	1272.333	1000.833
Variance	142.2187	8.88644	194.4587	5.939499	488863.6	1717474	4162288	33598.56	28.307	21.18715	3344972	672560.6
Observations	6	6	6	6	6	6	6	6	6	6	6	6
Hypothesized Mean Difference	0		0		0		0		0		0	
df	6		5		8		5		10		7	
t Stat	10.70772		3.433377		7.861236		3.884742		0.840555		0.331792	
P(T<=t) one-tail	1.96E-05		0.009284		2.48E-05		0.005793		0.210121		0.37488	
t Critical one-tail	1.94318		2.015048		1.859548		2.015048		1.812461		1.894579	
P(T<=t) two-tail	3.92E-05		0.018568		4.95E-05		0.011586		0.420241		0.749759	
t Critical two-tail	2.446912		2.570582		2.306004		2.570582		2.228139		2.364624	

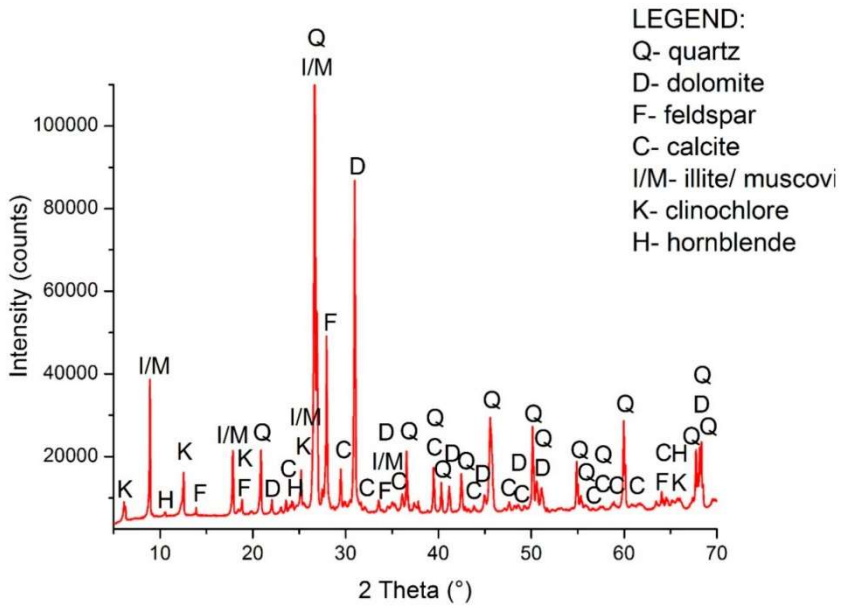
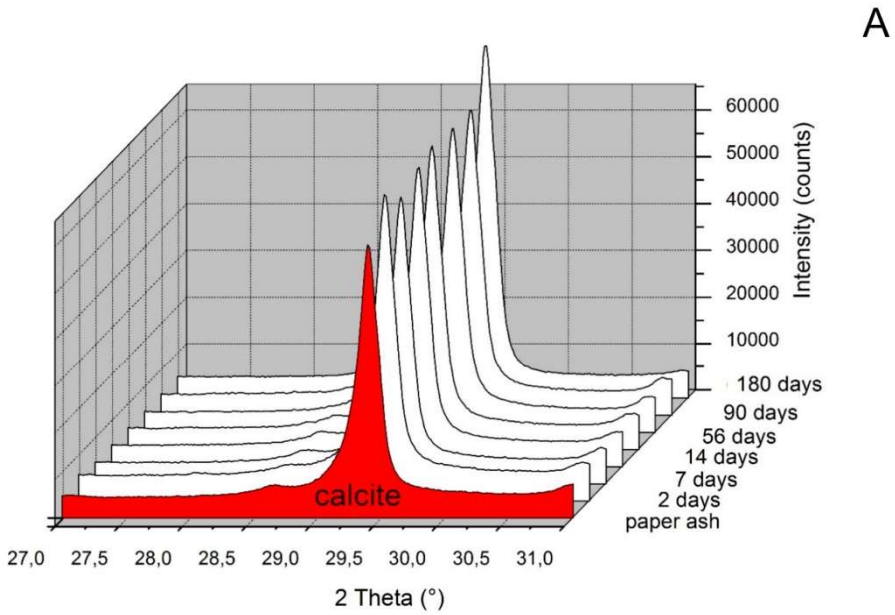


Figure S1. XRD pattern of uncontaminated soil.



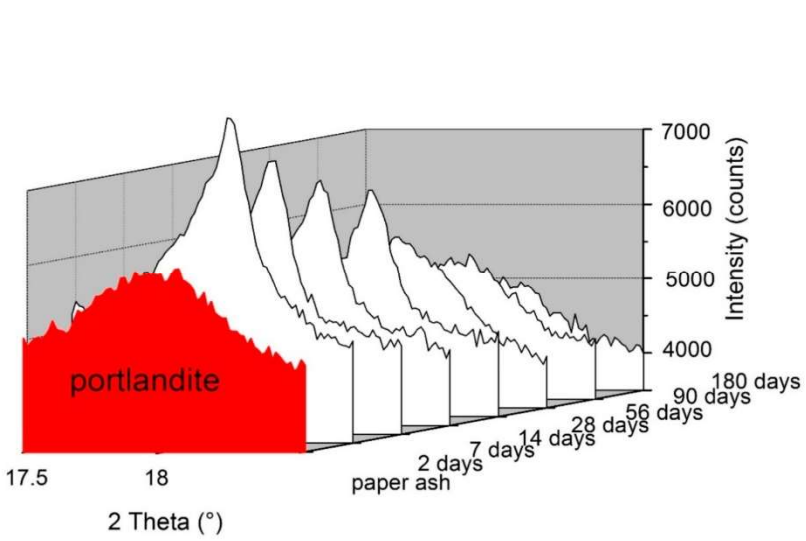


Figure S2. Sections of the XRD patterns of the paper ash paste.

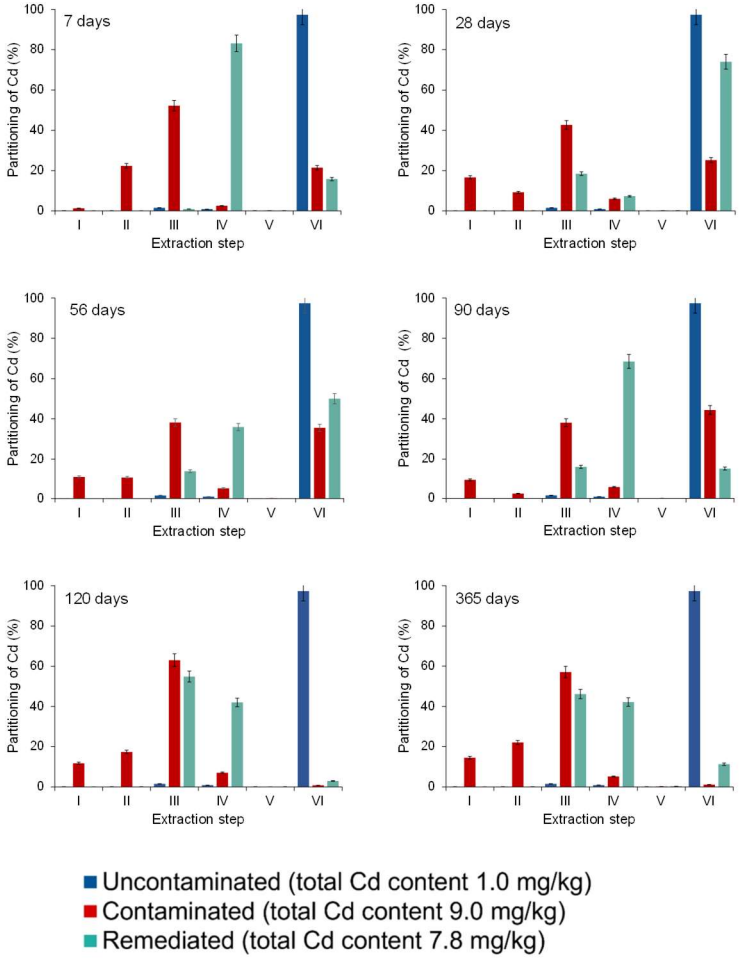


Figure S3. Partitioning of Cd in sulphate-treated uncontaminated, contaminated, and remediated soil samples with time elapsed after the remediation.

I water-soluble

II exchangeable

III bound to carbonates

IV bound to Fe/Mn oxides and hydroxides

V bound to organic matter

VI bound to silicate lattice

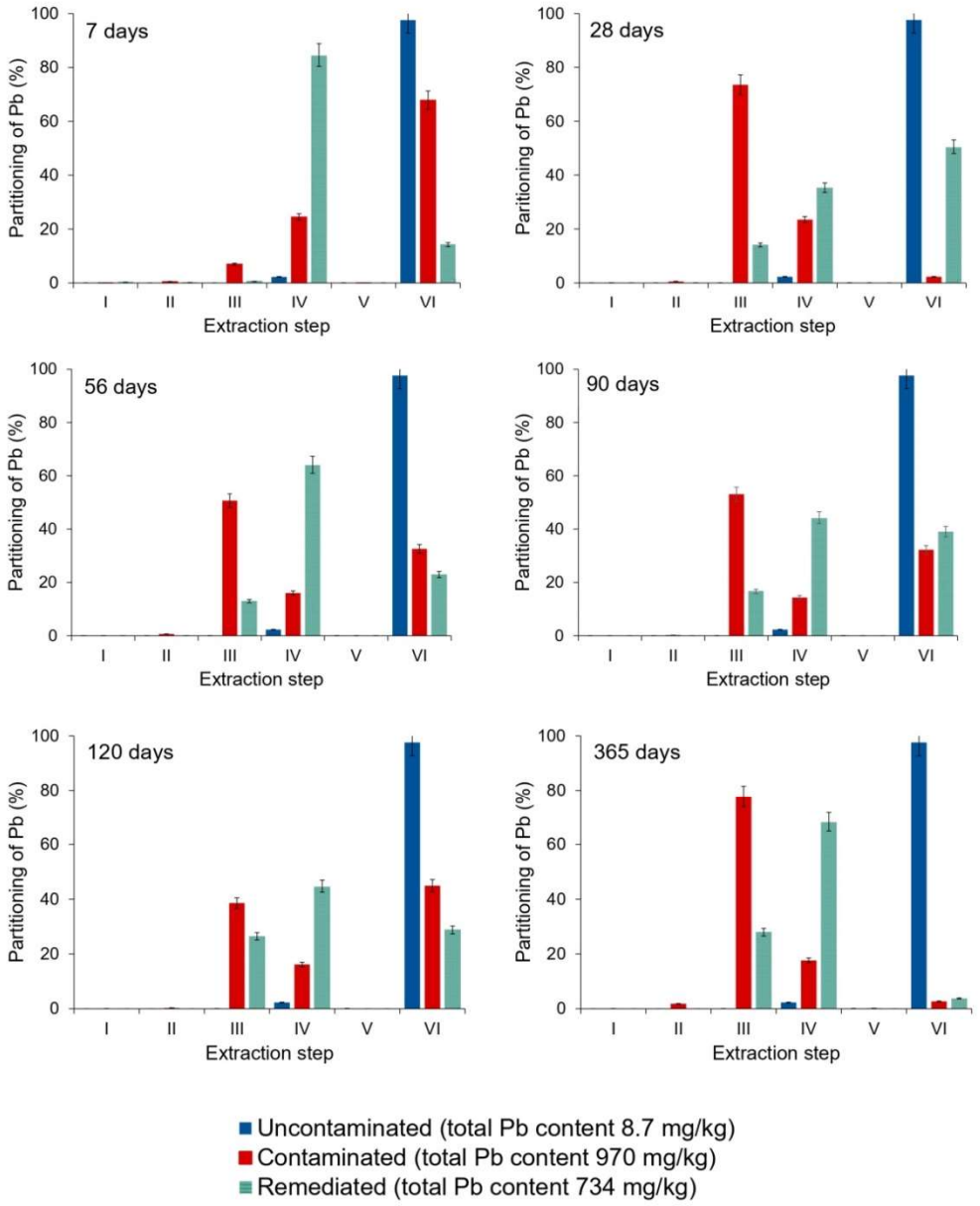


Figure S4. Partitioning of Pb in sulphate-treated uncontaminated, contaminated, and remediated soil samples with time elapsed after the remediation.

I water-soluble

II exchangeable

III bound to carbonates

IV bound to Fe/Mn oxides and hydroxides

V bound to organic matter

VI bound to silicate lattice

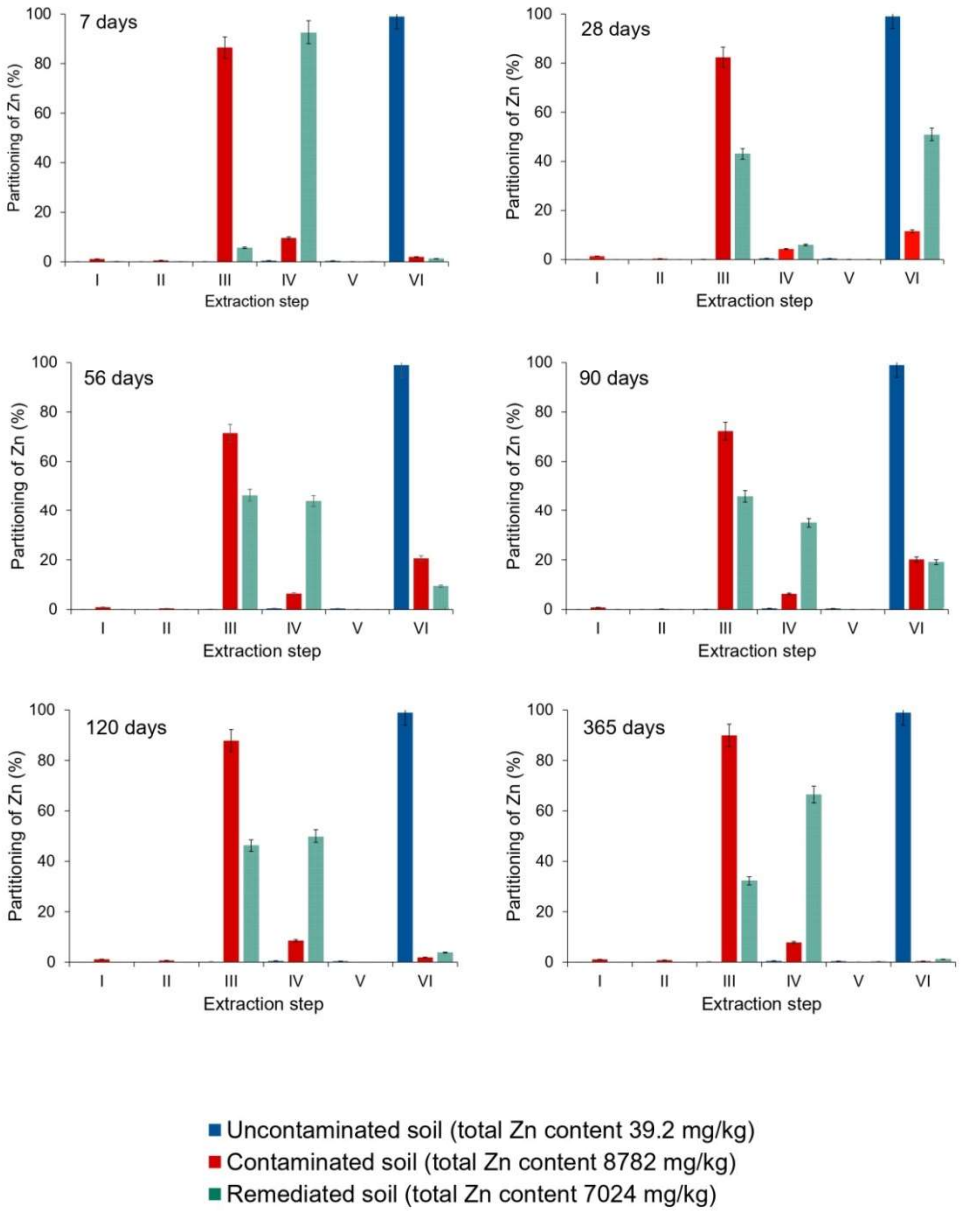


Figure S5. Partitioning of Zn in sulphate-treated uncontaminated, contaminated, and remediated soil samples with time elapsed after the remediation.

I water-soluble

II exchangeable

III bound to carbonates

IV bound to Fe/Mn oxides and hydroxides

V bound to organic matter

VI bound to silicate lattice

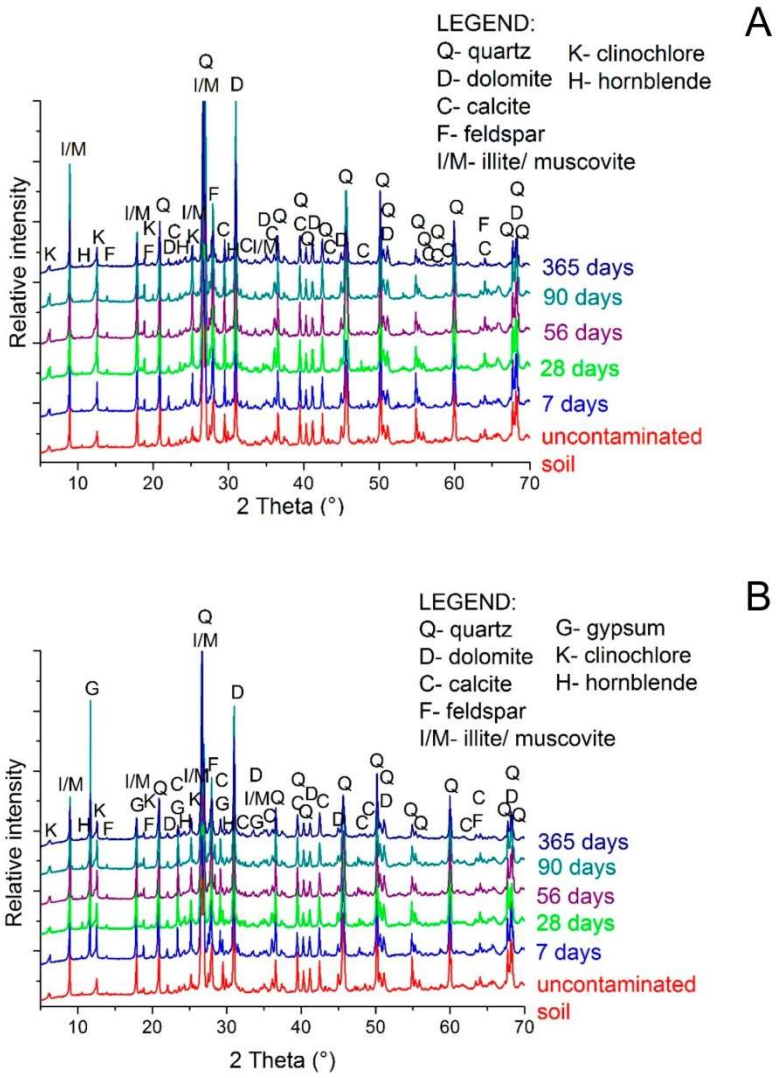


Figure S6. XRD patterns of contaminated soil (**A**) and sulphate-treated contaminated soil (**B**) with time elapsed.

Article 2: Environmental Acceptability of Geotechnical Composites from Recycled Materials: Comparative Study of Laboratory and Field Investigations

ĐURIĆ, Marija, ZALAR SERJUN, Vesna, MLADENOVIČ, Ana, MAUKO PRANJIĆ, Alenka, MILAČIČ, Radmila, ŠČANČAR, Janez, URBANC, Janko, MALI, Nina, SEŠEK PAVLIN, Alenka, TURK, Janez, OPRČKAL (2023). International Journal of Environmental Research and Public Health, https://www.mdpi.com/1660-4601/20/3/2014, DOI: 10.3390/ijerph20032014.

The environmental properties of three geotechnical composites from the recycling of selected waste were investigated on a laboratory scale and on field lysimeters in uncompacted and compacted form in order to investigate the influence of the installation process on the leaching of potentially hazardous substances. Field lysimeters were large enough to reflect conditions in earth structures intended for the revitalization of degraded mining areas. Composite 1 was prepared by mixing mine waste with paper mill sludge and foundry sand, Composite 2 was made from municipal waste digestate and paper ash, and Composite 3 from coal ash, foundry slag and waste incinerator bottom ash.

The results of standardized laboratory leaching tests proved that composites 1 and 3 are environmentally acceptable with national criteria for achieving end-of-waste status, as potentially hazardous substances were successfully immobilized. The leaching of potentially hazardous substances was also studied in percolated water from lysimeters. In field lysimeters, the lowest leaching rate was found for optimally designed Composites 1 and 3, while for Composite 2, leaching of potentially toxic elements was high, similarly as in the laboratory tests. A higher degree of compaction after installation had a beneficial effect on immobilization of hazardous substances in Composites 1 and 3, while this effect was not observed for Composite 2, which contained soluble organic matter that caused complexation of the Cu, Mo and Ni and their mobilization into the environment. The average concentrations of potentially hazardous substances in percolated water from lysimeters with compacted composites were lower in comparison to uncompacted. After one year of monitoring, a stable plateau was observed for Composite 3, which was assigned to effective long-term immobilization.

For Composite 1 and Composite 2, increasing trends of cumulative mass release of substances persisted, but decreased with time, which was assigned both to a progressing immobilization and wash-out of the potentially hazardous substances. Pozzolanic and hydration reactions that took place in Composite 2 and Composite 3, due to the addition of ashes, resulted in higher immobilization efficiency due to the formation of larger quantity of newly formed mineral phases that incorporate the potentially hazardous substances into their stable crystalline structure.

Our study proved that optimally installed Composites 1 and 3 are environmentally acceptable to be used in construction as an alternative to raw materials for revitalization of degraded mining sites or, along with Composite 2, for closure operations at landfills. By this way, locally available waste streams are valorised and channelized into beneficial and sustainable recycling practice.

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Article

Environmental Acceptability of Geotechnical Composites from Recycled Materials: Comparative Study of Laboratory and Field Investigations

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Abstract: The environmental properties of three geotechnical composites made by recycling wastes were investigated on a laboratory scale and in the field with the use of lysimeters designated for the revitalization of degraded mining sites. Composites were prepared by combining the mine waste with paper-mill sludge and foundry sand (Composite 1), with digestate from municipal waste and paper ash (Composite 2), and with coal ash, foundry slag and waste incineration bottom ash (Composite 3). The results of laboratory leaching tests proved that Composites 1 and 3 are environmentally acceptable, according to the legislative limits, as the potentially hazardous substances were immobilized, while in Composite 2, the legislative limits were exceeded. In the field lysimeters, the lowest rate of leaching was determined for optimally compacted Composites 1 and 3, while for Composite 2 the leaching of Cu was high. This study proved that optimally installed Composites 1 and 3 are environmentally acceptable for use in construction as an alternative to virgin materials, for the revitalization of degraded mining sites or, along with Composite 2, for closure operations with landfills. In this way, locally available waste streams are valorised and channelized into a beneficial and sustainable recycling practice.

Keywords: waste; recycling; lysimeter; potentially hazardous substances; immobilization; revitalisation

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1. Introduction

Although waste prevention has been set as a priority in the EU's waste-management hierarchy [1], the generation of waste cannot be avoided in many human activities. Fortunately, different forms of waste could be used as secondary resources. This is in line with the concepts of sustainable development and the circular economy that are embedded in the long-term strategy of the EU [2]. Establishing a circular economy based on the responsible use of materials, water, and energy was recognized as an opportunity for resource-insufficient Europe to maintain access to vital resources, maintain its global competitiveness, and ensure a high-quality environment [3]. However, the quantity of materials from waste steams is not sufficient to support a circular economy [4] and the mining of natural resources is still of vital importance, even though it has many adverse impacts on the environment, causing deforestation, erosion, contamination and the alteration of soil, local water bodies and wetlands, dust emissions, and land degradation [5]. Consequently, mining activities have a negative social perception, especially in the case of open-pit mining, which results in up to ten times more land degradation than underground mining [6].

Reclamation activities are emphatically enforced by the regulations in most countries. According to EU law [7], Member States are obliged to demand that mining operators

include site-rehabilitation measures in their projects. The most frequent approach to the rehabilitation of open pits is backfilling with extractive waste or the installation of construction products made from recycled waste in earth structures in order to restore the original morphology or to establish areas for urbanization [8]. In the latter case, the waste to be recycled is often combined with other waste or natural materials to produce geotechnical composites with suitable mechano-physical characteristics and to reduce the level of potentially hazardous substances (PHSs) below the legislative limits, all in order to comply with the legal, environmental, and technical demands [9–11].

In many Member States, the environmental acceptability of recycled waste-based construction products is determined based on laboratory leaching procedures, which gives information about whether the material is compliant with the arbitrary legislative limits. These standardised tests might not reflect exactly the behaviour of the investigated material in natural conditions [12]. Field experiments using lysimeters are designed to provide the most straightforward information about the potential environmental impacts of investigated materials in the natural environment by monitoring the fate and mobility of PHSs, depending on the geographical weather conditions and the quality of the installation. At present, there is no legislation that would regulate the environmental acceptability of materials with the use of such tests, which are currently used mostly for risk-assessment studies. [12,13].

Due to the general increase in the volume of waste production, attention is paid to the issues of waste management. The circular economy and resource efficiency imply the minimization of material losses and the maximization of material circulation. When waste generation cannot be prevented, it should be used as a resource [14]. Based on a review done by Mohammad A. Al-Ghout et. all [15], in terms of the technical advantages and disadvantages, the incineration of municipal solid waste (MSW) appears to be the best choice compared to other management solutions (e.g., digestion, composting, landfilling). Nevertheless, landfilling is still one of the most common methods of municipal waste management. As for the incineration procedure, dealing with incinerated municipal waste, i.e., bottom and fly ash, has become one of the biggest challenges. The physical and chemical characteristics of these ashes are not easy to generalize, and their uses are different. With a different pre-treatment, ashes can be used as alternatives for the production of lightweight aggregate in the construction field [16] or as recycled aggregate in road construction [17]. The use of incinerated MSW (bottom and fly ash) for the preparation of geopolymers has also been reported in recent years [18–20]. For industrial waste recycling, treatment, incineration, and landfill are the current practices used in waste management. Recycling and treatment of solid or liquid industrial wastes usually produces non-hazardous residues and they are generally used on site. Industrial waste is also used, as is incinerated MSW, in the civil construction sector. [21]

Three construction products, referred to here as geotechnical composites, were developed through the use of recycled waste materials. Industrial and municipal wastes, i.e., paper-mill sludge and paper ash, coal ash, solid-waste incineration bottom ash, foundry slag and sand, digestate from the mechanical and biological treatment of municipal waste, were used in combination with Termit's mine waste. They were designated for the rehabilitation of abandoned open-pit mining sites, for the company Termit d.d., which is one of the largest Slovenian mining companies dealing with the extraction and processing of silica sand and the production of auxiliary casting materials for foundries and ironworks.

The aim of this study was to investigate the environmental acceptability of three construction products based on recycled waste for final use as geotechnical composites, designated for the rehabilitation of abandoned open-pit mining sites at Termit d.d. Both laboratory and field investigations large enough to reliably reflect the conditions of earth structures on a large scale were made using lysimeters. Percolated water from the lysimeters was periodically collected over one year and analysed to evaluate the release of PHSs into the environment. The experimental field data were supported and compared with the data from the laboratory leaching tests.

The optimal installation of the geotechnical composites made from recycled materials is of vital importance to ensure their environmental acceptability [22]. Therefore, the influence of installation, i.e., the compaction efficiency, on the release of PHSs from the composites was also investigated.

2. Materials and Methods

2.1. Raw Materials

Selected non-hazardous wastes were used as raw materials for the experiments in this study:

Paper-mill sludge (PMS) is composed of 95% dewatered residues, made up of rejected cellulose fibres and mineral fillers from the chemical–mechanical processes in paper production, and 5% dewatered sludge from a biological treatment plant for purification of industrial wastewater from the paper mill.

Paper ash (PA) was also obtained from the paper mill, where it was formed in a steam boiler, in which the de-inking sludge from the paper recycling process and the sludge from the treatment of paper-mill wastewater were incinerated. This ash was a mixture of 90% bottom ash and 10% fly ash.

Coal fly ash (CA) was formed in a heating plant during co-combustion of coal (76%), biomass (21%) and paper sludge (up to 3%). The CA sample was collected in filters for air-pollution control.

Solid-waste incineration bottom ash (SWIA) is a coarse-grained material that consist of larger particles of burnt and charred waste metals and glass. It was formed in an incinerator for industrial and mixed-municipal solid wastes.

Foundry slag (FSL) was obtained from cast-iron production after being formed in a cupola furnace. The FSL was a coarse-grained material with some grains up to 100 mm in size.

Foundry sand (FS) was obtained from disintegrated moulds and cores used in the production of ferrous metal castings. The moulds and cores consisted of quartz sand with organic and inorganic binders.

Digestate (DI) from mechanical-biological anaerobic treatment of mixed municipal solid waste was used. The digestate sample was a coarse-grained material, consisting of a heterogeneous mixture of organic (29%) and inorganic (71%) components.

Mine waste (MW) was generated during the processing of quartz sand at Termit. It was clayey sandy silt that was separated from the quartz sand in a washing process and later dewatered in a filter press.

Detailed information about the source and EWL (European Union's List of Wastes) classification of the raw materials is given in Table S1.

A flow chart of the experimental set-up is given in Figure S1.

2.2. Geotechnical Composites

Three geotechnical composites were prepared by mixing the raw materials in ratios based on the dry-mass content, as presented in Table 1.

The composition of the geotechnical composites was carefully tailored by taking into account the waste properties, the technical requirements for geotechnical reclamation fill, as well as the type and quantities of waste for which Termit has permission to collect and recycle.

2.2.1. Preparation of Laboratory Samples

First, the maximum reference dry density and the optimal water content in the composites according to the Proctor compaction test were determined [23]. These are the basic geotechnical parameters required to ensure the optimal installation of the composites by compaction, so that the mechanical stability and immobilization of the potentially toxic substances (PTS) are achieved. The maximum dry density and optimal water content, i.e.,

a gravimetric water content, which is the ratio between the masses of water and dry matter in composite, are given in Table S2 for each composite.

Table 1. Composition of the geotechnical composites.

Raw Material	Composite 1 (wt.%)	Composite 2 (wt.%)	Composite 3 (wt.%)
Paper-mill sludge (PMS)	20	/	/
Foundry sand (FS)	30	/	/
Mine waste (MW)	50	20	50
Paper ash (PA)	/	40	/
Digestate (DI)	/	40	/
Solid-waste incineration bottom ash (SWIA)	/	/	5
Foundry slag (FSL)	/	/	5
Coal ash (CA)	/	/	40

To conduct a laboratory investigation of the environmental acceptability of composites, all the composites were prepared in the laboratory in the form of monolithic cylindrical test samples of 10 cm in diameter and 12 cm in height (Figure 1).

Figure 1. An example of laboratory sample of the geotechnical Composite 2.

The laboratory samples were then cured in a climatic chamber under constant temperature and humidity conditions (22 ± 2 °C and 98% humidity) for 28 days. After curing, the samples were subjected to a tank leaching test, according to procedure SIST EN 1744-3:2002 [24] (liquid-to-solid ratio (L/S) = 10:1). Demineralised water was used as the leaching agent.

2.2.2. Field Installation of Geotechnical Composites into Lysimeters

Six box-shaped lysimeters were constructed in the field. The lysimeters were positioned at the facilities of Termit in Moravce, central Slovenia (GK coordinates Y: 482,072.37 X: 110,160.84). A schematic of the structure of an individual lysimeter is shown in Figure 2, while the construction process is presented in Figure S2. Composites with the composition in Table 1 were prepared in the field, with the utilization of an industrial-scale

waste-processing technology and construction procedures. The stages of the preparation procedure are presented in Figure S3. Each composite was installed in parallel in two lysimeters in different ways. In the first case it was gradually backfilled into the box structure of the lysimeter and each embankment was levelled with the bucket of an excavator. Thickness of obtained uncompacted layers was around 20 cm, while in the second case, the composite was installed in layers, which were compacted with a vibrating plate. After compaction, each compacted layer was around 10-cm-thick. Each lysimeter was covered with a 15-cm-thick layer of quartz aggregate 4/16, placed on top to prevent surface runoff and evaporation of the precipitation [25].

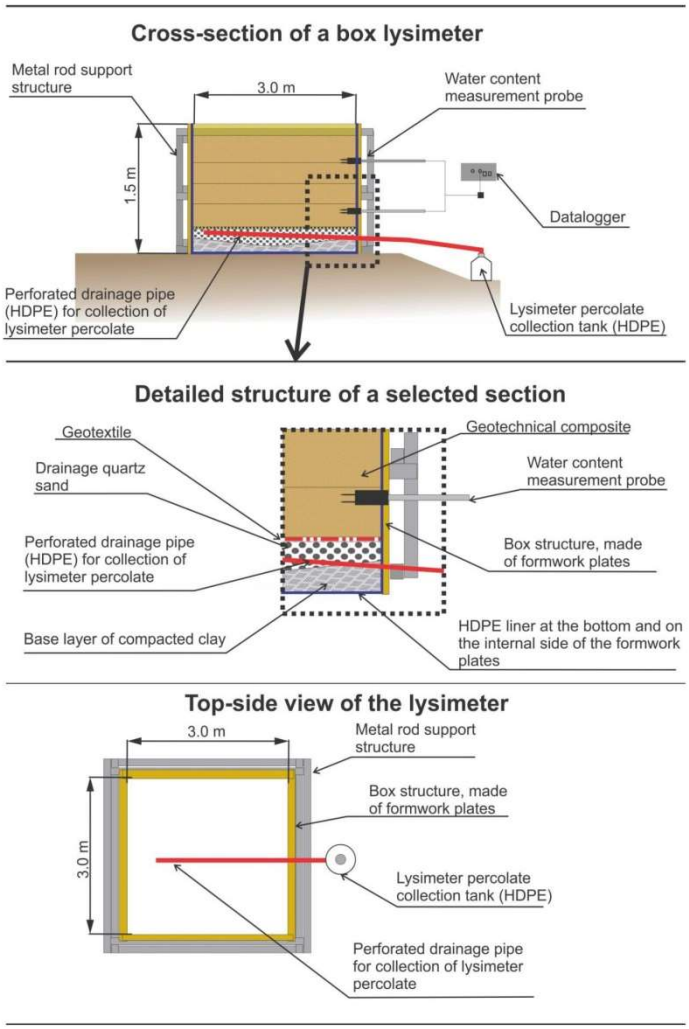

Figure 2. Schematically presented structure of individual lysimeter.

Uncompacted composites represent an installation that is extremely non-compliant with construction requirements and daily practice. The characteristics of such composites are reflected in a low mechanical stability, a high porosity, and a low leaching resistance. Therefore, a greater infiltration of rainwater and, consequently, more leaching was expected. The installation of the geotechnical composites using compaction was the correct procedure in the earth structures.

The degree of compaction was determined using a nuclear density probe (Troxler 3400, Research Triangle Park, NC). For composites 1 and 2, this parameter was lower than for the laboratory samples, which had at least 98% of the reference dry density. It was not possible to achieve such a high degree of compaction in the lysimeters because only light compaction equipment could be used, due to the limited amount of access.

The dimensions, masses, degree of compaction and permeability of uncompacted and compacted composites installed in the lysimeters are presented in Table 2.

Table 2. Selected geometrical and technical parameters geotechnical composites installed in the lysimeters and their permeability expressed using the infiltration coefficient.

Parameter	Composite 1		Composite 2		Composite 3	
	Uncompacted	Compacted	Uncompacted	Compacted	Uncompacted	Compacted
Surface area exposed to precipitation (m^2)	9	9	9	9	9	9
Height of a geotechnical fill in lysimeter (m)	1.15	1.15	1.35	1.20	1.20	1.25
Degree of compaction (%) *	n.a.	94	n.a.	92	n.a.	99
Dry mass of installed composite (Mg)	13.45	18.32	9.16	11.52	13.41	15.85
Infiltration coefficient (m/s) **	7.5×10^{-4}	2.1×10^{-7}	1.7×10^{-4}	5.6×10^{-5}	6.3×10^{-6}	6.3×10^{-7}

* Ratio between maximum reference dry density and dry density of installed composite. ** Measured according to the ISO/DIS 22282-5:2007 [26].

A weather station with a rain gauge, an air-temperature and a humidity probe were installed next to the lysimeters to gather the meteorological data needed to assess the water balance in the lysimeters. Additionally, two sensors for measurements of water content and temperature inside the composites were horizontally installed in each lysimeter, gathering the data every hour.

Percolated water from each lysimeter was collected in a plastic tank of 1000 litres, from which the percolates were taken twice per month, on average, depending on the amount and frequency of precipitation events. The entire volume of collected percolates was measured and poured out from the collector tank at each sampling interval. The data provided in the Supplementary Materials show the amount of precipitation and the volume of percolated water collected between samplings (Table S3a–c), while the fluctuations of the temperature and the moisture content in the composites (upper and lower sensors) are presented in Figure S4a–c. The data points in Figure S4a–c are presented as the average values, which were calculated from the data collected by the temperature and humidity probes between two sampling intervals. As expected, changes in temperature and precipitation reflected seasonal variations. Composites 1 and 3 had better water-retention capacities than Composite 2, in which lower average moisture contents were determined due to the more rapid percolation of water. There were no significant trends in moisture content for the uncompacted and compacted composite 2; the uncompacted composite 1 had a higher moisture content, indicating a higher retention capacity, in comparison to its compacted form; while for composite 3 the situation was the opposite (Figure S4a–c).

2.3. Analytical Methods

2.3.1. Determination of Total Element Concentrations of Potentially Toxic Elements in Raw Materials and Composites

To determine the total element concentrations in the raw materials and the laboratory samples of the composites, 0.25 g of lyophilised sample was subjected to microwave-assisted digestion (MARS 6 Microwave System, NC, USA), using a mixture of nitric, hydrochloric and hydrofluoric acids [27], and concentrations of potentially toxic elements (PTEs): cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), chromium (Cr), nickel (Ni), arsenic (As), selenium (Se), antimony (Sb), molybdenum (Mo), mercury (Hg) and barium (Ba) were determined by means of inductively coupled plasma mass spectrometry (ICP-MS, 7700x, Agilent Technologies, Tokyo, Japan).

2.3.2. Determination of the Mineralogical Composition of the Raw Materials and Composites

The mineralogical compositions of the raw materials and the laboratory samples of the composites were determined by X-ray powder diffraction (XRD), using a PAN analytical diffractometer, with Cu–Kα irradiation (λ = 1.54056 Å), at 45 kV and a current of 40 mA, over the 2θ angular range from 5° to 70°, using a step size of 0.01° and a measuring time per step of 100 s. The patterns were analysed with PAN analytical X'Pert High Score Plus software.

2.3.3. Determination of the Chemical Composition of the Aqueous Leachates and Percolated Water from the Lysimeters

Samples of aqueous leachates from the laboratory tests were filtered through 0.45-µm membrane filters and the total concentrations of PTEs were determined by ICP-MS, according to the procedure EN ISO 17294-2:2016 [28] under the optimal measurement conditions listed in Table S4. The concentrations of chloride (Cl^-), fluoride (F^-) and sulphate (SO_4^{2-}), were determined by spectrophotometry (HACH DR/2010, CO, USA), the Cl^- and SO_4^{2-} according to the procedure ISO 15923-1:2013 [29], while F^- was determined with the SPADNS method [30]. The phenolic index was determined according to the ISO 14402:1999(E)-point 4 procedure [31]. In each sample, the pH and conductivity were measured (SevenCompact pH/Cond S213, Mettler-Toledo, Columbus, OH, USA). The accuracies of the analyses are listed in Tables S4–S8.

In the laboratory investigations, leaching of the PHSs, given as the concentration (c) of each parameter from the dry mass unit of a certain composite, were calculated by multiplying the measured concentration of each individual parameter in the leachate (a) by the volume of the leaching solution (V), divided by the dry mass (m_d) of a sample of composite, using Equation (1).

$$c(mg/kg) = \frac{a\ (mg/L)\ *\ V\ (L)}{m_d\ (kg)} \quad (1)$$

In the case of lysimeter experiments the samples of percolated water were, upon collection, prepared and analysed according to the same protocol as described for the case of the laboratory leachates. Afterwards, the leaching of the PHSs was first calculated for all the sampling intervals. The measured concentration of each individual parameter in the percolated water (a_i) was multiplied by the volume of water percolated in each interval (V_i) and divided by the dry mass of a composite installed in the lysimeter (m_{dl}), to calculate the concentrations of each parameter (c_i) in each interval. Then the average concentrations of the parameters for all 17 sampling intervals were calculated. The cumulative mass-release concentrations (C_i) of the selected PHSs were calculated for each of 17 successive sampling intervals (i) using Equation (2).

$$C_i\ (mg/kg) = \sum_{i=1}^{17} \left(\left(\frac{a_1 * V_1}{m_{dl}} \right) + \ldots + \frac{a_i * V_i}{m_{dl}} \right) \quad (2)$$

The trends for the cumulative mass release of selected PHSs were plotted as a function of the cumulative mass-release concentration against the L/S, which increased with time as the cumulative amount of percolated rainwater was also increasing.

3. Results and Discussion

3.1. Mineralogical Characterization

The mineralogical compositions of the raw materials are shown in Figure S5. The raw materials are composed of crystalline mineral phases. In PMS, PA, CA and FSL amorphous phases are also present, represented in the XRD spectrum as a hump. The elevated background in the XRD spectrum of PMS reflected the presence of an organic component, in which cellulose (partially in crystalline form) predominated (Figure S5). The amorphous humps in the XRD spectres of PA, CA and FSL were assigned to the inorganic glassy phase.

The mineralogical compositions of the composites are presented in Figure 3.

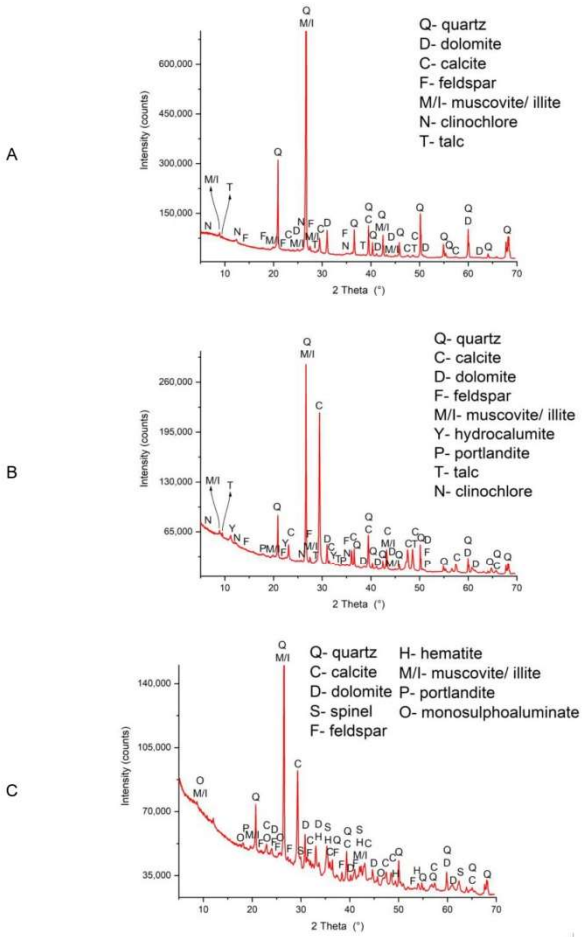

Figure 3. XRD patterns of: (**A**) composite 1; (**B**) composite 2; and (**C**) composite 3.

As is evident from Figure 3, the prevailing mineral phase in composite 1 was quartz, which was also the major crystalline phase of its two constituents: FS and MW (Figure S5). Calcite, kaolinite, talc, and dolomite, which are present as minor phases, originated from the PMS (Figure S5).

In composite 2, quartz and calcite were predominant phases (Figure 3), originating from all three raw materials of the composite (Figure S5). Among the minor phases, dolomite, feldspar, muscovite/illite, talc and clinochlore were introduced into the composite with the addition of DI and MW, while portlandite originated from the PA (Figure S5). The newly formed mineral phase in composite 2 was identified in the XRD spectra as hydrocalumite (Figure 3). It is a result of the pozzolanic and hydration reactions, which are characteristic for PA [9,22].

In composite 3, quartz was the predominating crystalline constituent, which originated from the CA, SWIA and FSL (Figure S5). Other mineral phases were present in a minority, for example, hematite and spinel (from SWIA) (Figure S5). In composite 3, a newly formed mineral phase, i.e., mosoluphoaluminate, was identified, which was the hydration and pozzolanic product from the use of CA (Figure 3).

3.2. Total Concentrations of PTEs in the Raw Materials and Composites

The total concentrations of PTEs in the raw materials and composites after microwave-assisted digestion determined by ICP-MS are presented in Tables S9 and S10, respectively.

As evident from Table S9, the total concentrations of PTEs in the raw materials were the highest in bottom ash from the solid-waste incineration and in the foundry sand. The comparison of the total concentrations and the concentrations of these elements in aqueous leachates (Table S11) showed that their mobility was very low, although some values exceeded the national limits for end-of-waste criteria [32].

3.3. Environmental Impacts of Geotechnical Composites

To evaluate the environmental acceptability of the geotechnical composites, laboratory and field experiments were performed, as described in the experimental set-up (2.4).

3.3.1. Leaching of Potentially Hazardous Substances from the Raw Materials and Laboratory Samples of Geotechnical Composites

Aqueous leachates from the raw materials and the laboratory samples of composites are presented in Figures 4 and 5, respectively, while the pH values, conductivity as well as the individual concentrations of the elements and anions related to the data from Figures 4 and 5, are provided in Tables S11 and S12.

The data presented in Figure 4 show that in all the raw materials, the limits were exceeded for at least one parameter, when considering the Slovenian end-of-waste criteria [32]. The exception was MW, in the leachates of PMS and FS, where the concentrations of F^- were around twice the limit. In addition, As in the leachate of FS was nearly twice the limit. In PA, Ba greatly exceeded the limit (by a factor of 12), while Cu and Mo exceeded this value by 1.5 times. In the leachate from DI, concentrations of most parameters (i.e., As, Cu, Hg, Mo, Ni, Pb, Sb, Zn and all anions) exceeded the limits. Cu and Sb exceeded the limits by a factor of 16, and Zn and Cl^- by a factor of 5. In the leachate of SWIA, the concentrations of Cr, Hg, Mo, Sb and all anions exceeded the limits, Cr and Mo by 16 times and Cl^- by 7 times. In FSL, only SO_4^{2-} exceeded the limit, by 2 times, while in CA, the Ba in the leachate exceeded the limit by a factor of 10.

The results of the leaching tests from Composites 1, 2 and 3 are presented in Figure 5, while the support data are summarized in Table S12.

Composite 1 (Figure 5A) fulfilled the environmental acceptability criteria in both the uncompacted and compacted forms. Composite 1 produced a slightly alkaline leachate (pH 8). PMS and MW are considered as immobilization additives due to the constituents having a high sorption capacity (clay minerals) [33]. Despite the presence of phenolic

polymer resins in the FS, the values of the phenolic index in the leachate were below the determination limit.

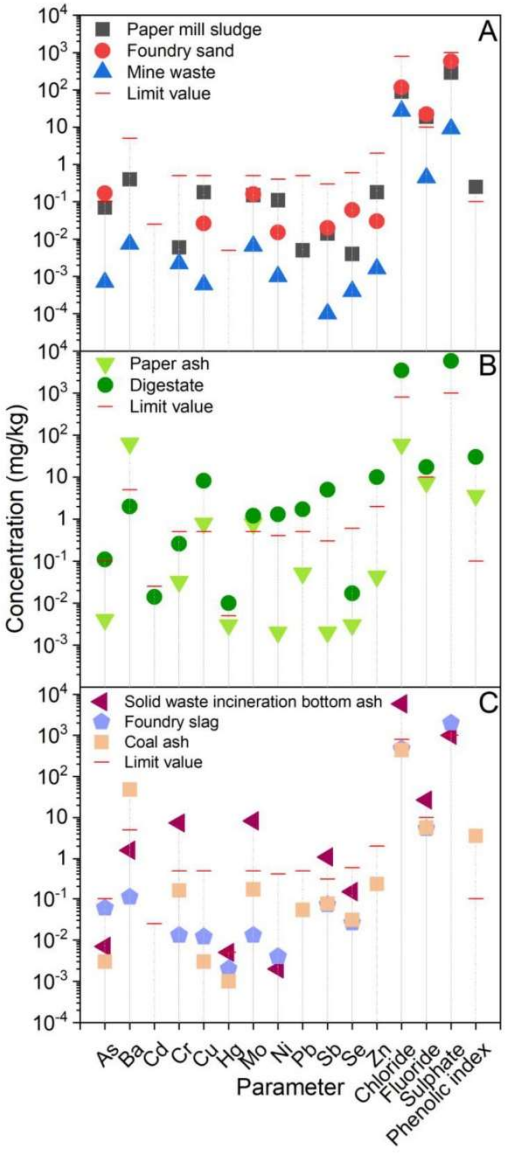

Figure 4. Concentrations of potentially hazardous substances in aqueous leachates from raw materials: (**A**) paper-mill sludge, foundry sand and mine waste; (**B**) paper ash and digestate; and (**C**) slag from waste incineration, foundry slag and coal combustion ash, used for the preparation of geotechnical composites. Limit values (from the Decree on waste; Official Gazette of Republic of Slovenia, 2020) are also given.

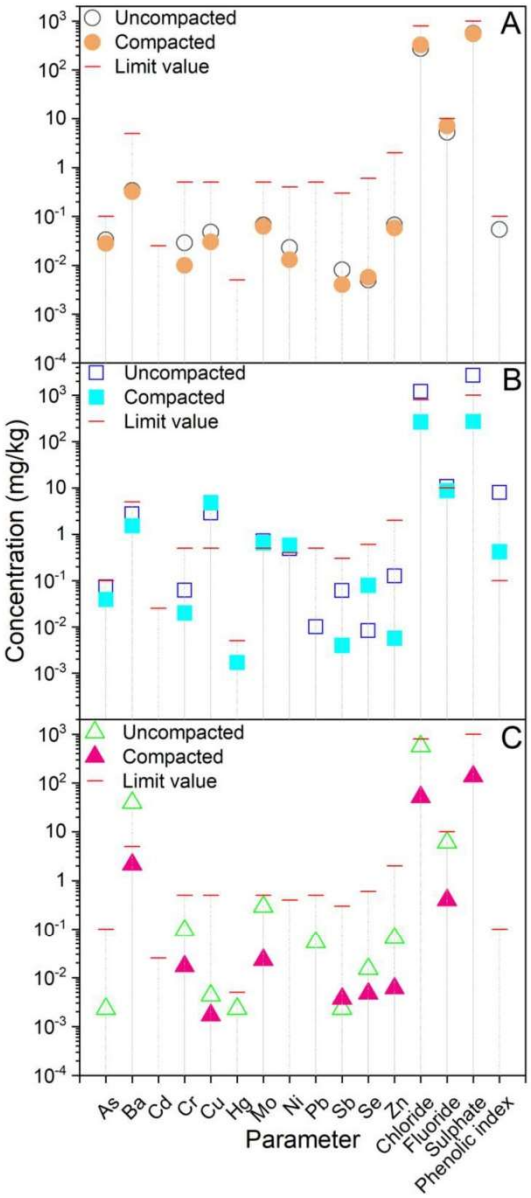

Figure 5. Concentrations of potentially hazardous substances in aqueous leachates from uncompacted and compacted geotechnical composites: (**A**) composite 1; (**B**) composite 2; and (**C**) composite 3. Limit values from the Decree on waste; Official Gazette of Republic of Slovenia, 2020 are also given.

Legislative criteria were also met for composite 3 (Figure 5C) in the compacted form. In composite 3, the CA was used as a pozzolanic and hydraulically active alternative binder.

The binding ability of the CA was evident from the formation of a new phase from the group of CAH minerals (i.e., monosulfoaluminate—$Ca_4Al_2SO_{10}$ $16H_2O$) (Figure 3), which is also known to be able to incorporate soluble ions of PTEs in its crystalline lattice and chemically immobilize them [34]. Lime and portlandite are the constituents of the CA that produced an alkaline pH of the pore solution in composite 3, which favoured the formation of insoluble or low-soluble metal hydroxides.

In the uncompacted composite 3, only Ba did not meet the legislative criterion. The reason is that in alkaline conditions, the highly soluble Ba hydroxide was formed, and not enough soluble sulphate was available in the pore solutions to lower its solubility through the formation of the low-solubility Ba-sulphate [35]. On the other hand, in the compacted composite the Ba ions were chemically immobilized because of the effective diffusion of the ions to the surface adsorption sites of the clay minerals from MW. Compacted composite 3 had a low water permeability, also enabling the effective physical immobilization of Ba [9,22].

In composite 2 (Figure 5B) the environmental limits were exceeded for parameters Cu, Mo, and Ni, as well as for the phenolic index in both the uncompacted and compacted forms, and additionally for SO_4^{2-}, Cl^- and F^- in the uncompacted form. High values of the phenolic index indicated the presence of polyphenolic compounds, which were evolving either from the humic and fulvic substances, or due to their formation during the microbiological decay of the plastic waste in the mechanical-biological treatment, in which the DI was generated [36]. In this composite, PA had the role of an alternative binder and the main immobilization additive because of its pozzolanic and hydraulic activity [37]. By mixing humid DI with dry PA, instant hydration of the CaO (lime) present in the PA occurred, resulting in the formation of portlandite ($Ca(OH)_2$) and a pore solution saturated with Ca^{2+} and OH^- (Figure 3). High pH values of the pore solutions in the composite had perturbing effects on the microbial community [38,39]. In this way, pathogenic organisms potentially present in the DI after the microbiological treatment of this waste were destroyed (see pH and electrical conductivity in leachate from composite 2, Table S12). The binding characteristics of the PA were reflected in the formation of the hydration product, i.e., calcium aluminate hydrate (CAH), more specifically hydrocalumite ($Ca_4Al_2(OH)_{12}(Cl,CO_3,OH)_2$ $4H_2O$). The CAH present in composite 2 chemically immobilized the PTEs by incorporating them into its stable crystalline lattice [39]. However, Cu and Ni were already strongly complexed with soluble organic matter (e.g., humic and fulvic acids, and low-molecular-mass organic acids) [40,41], and therefore remained mobile. The leaching of Cu was much higher than that of Ni, because Cu formed stronger complexes with the organic matter and its total content in the composite was 10 times higher [40,42]. In the uncompacted composite, the conditions were aerobic, which resulted in a lower pH (due to carbonation reactions) and therefore the mobility of the dissolved organic matter was lower than for the anaerobic conditions in the compacted composite [43]. Accordingly, the pH of the leachate from the uncompacted composite 2 was lower (pH 10.8) than in the compacted sample (pH 11.6) (Table S12). Due to the smaller amount of dissolved organic matter, the extent of the Cu and Ni complexation and thus the Cu and Ni release from the uncompacted composite 2 was smaller than from the compacted sample (Table S12) [44]. The release of Mo from composite 2 was related to the negative charge of the molybdate oxyanion (MoO_4^{2-}), which was not effectively immobilised by the constituents of composite 2 at the highly alkaline pH. The slightly lower leaching of Mo from the compacted composite was due to physical immobilization. Similarly, negatively charged SO_4^{2-}, Cl^- and to a lesser extent F^-, were not effectively immobilized under the highly alkaline conditions in the uncompacted composite 2. However, in the compacted form, the leaching of these anions was significantly reduced below the legislative limits due to physical immobilization.

3.3.2. Results from the Field Lysimetric Experiments

The mobility of PHSs from the geotechnical composites installed in the lysimeters was followed from 10th June 2020 to 3rd June 2021.

The difference in the results between the laboratory leaching tests and the results from the lysimeter tests was expected, and they were in line with the literature reports [12,13]. In laboratory, under such water-saturated conditions, the chemical equilibria were achieved during leaching due to a surface dissolution and diffusion of the PHSs [44]. In the lysimetric tests, rainwater was the leaching solution, which was infiltrated and gradually percolated through the geotechnical composites under sub-saturated conditions [13,44]. The cumulative L/S ratio in the lysimeters was more than 10-times lower than for the laboratory test, only from 0.6 to 1.1 for the uncompacted composites, and 0.4 to 0.9 for the compacted composites. The lower L/S ratio for the compacted composites was due to the lesser infiltration of rainwater due to their lower porosity.

The pH and the conductivity of the laboratory leachates from composites 1 and 2 were higher than the average values determined in the percolates. Lower pH values in the percolates were due to the more intensive carbonation but can also be attributed to the hydrodynamics of the rainwater infiltration, which can cause the localized wash-out of alkalis, among other ions, when probably preferential leaching routes were formed. Slightly lower pH values and the higher conductivity of the laboratory leachates in comparison to lysimeter percolates were determined for composite 3. This can be attributed to the slower carbonation and the diffusion of alkalis from this composite at lower L/S ratios in comparison to the laboratory tests [12].

Time-dependent changes in the conductivity and the pH values of the percolates are presented in Figures S6 and S7. The pH values of the percolates from composite 1 remained relatively constant during the field experiment, while a slight decrease was observed in composites 2 and 3, which is related to the carbonization. Due to a more intensive wash-out in composite 3 the pH values were higher in the uncompacted composite. This is also indicative of the high concentration of alkalis in the CA. The conductivity of the percolates gradually decreased with time due to the continuous leaching and the wash-out of ions, and due to the gradual time-dependent increase in their immobilization and the formation of new mineral phases, especially in composites 2 and 3, in which pozzolanic and hydraulically active ashes were used [22].

The results for the different parameters, given as an average value for all the concentrations determined in the percolates from all the sampling intervals, are presented in Figure S8, while the support data are given in Table S3a–c.

The lowest average concentrations of PHSs for all the sampling intervals were determined in percolates from the compacted composites 1 and 3. In composite 2, very low average concentrations of PHS were also determined in the percolates, with the exception of Cu, where the concentration was about 4500 times higher than in Composites 1 and 3, similar to the laboratory experiments.

The average leaching of PHSs from the geotechnical composites in the field was significantly lower (generally 25 to 150 times), compared to the leaching from the composites in the laboratory tests. This difference cannot be solely attributed to the difference in L/S, but also indicates that the same immobilization mechanisms of PHSs, as discussed in Section 3.3.1, took place in composites in the lysimeters, but were more effective under natural conditions and over a longer time period, in the case of the field experiment, in comparison to the short-term laboratory experiments [45].

Figures 6–8 show a comparison between the trends in cumulative time-dependent mass releases of selected PHSs in relation to the L/S value. A larger amount of rainwater percolated through the uncompacted composites 1 and 3 compared to their compacted forms. Consequently, a higher cumulative mass release of PHS came from the uncompacted composites. This proved that when the composites were compacted up to the maximum dry density the effective physical immobilization of the PHSs can be achieved [14]. The only exceptions, with a slightly higher concentration in the compacted form, were Cl^- and Cr in composite 1. The infiltration and percolation of the water in composite 2 were very similar for the compacted and uncompacted forms. This was also reflected in the mass release of the PHSs, which was almost the same in both cases. The exception was Zn, which

showed more intensive leaching from the compacted composite. This can be attributed to the fact that higher dissociation and crushing of the grains occurred during the installation of the composite by compaction, which led to the release of Zn [46]. The results from the lysimeter were not fully comparable with the observations from the laboratory experiments, in which more intensive leachings of the elements (Mo, Cu, and Ni) were determined in the compacted composite, which was probably due to the heterogenetic composition of DI or due to the more intensive crushing of contaminated grains during the compaction in the laboratory [46].

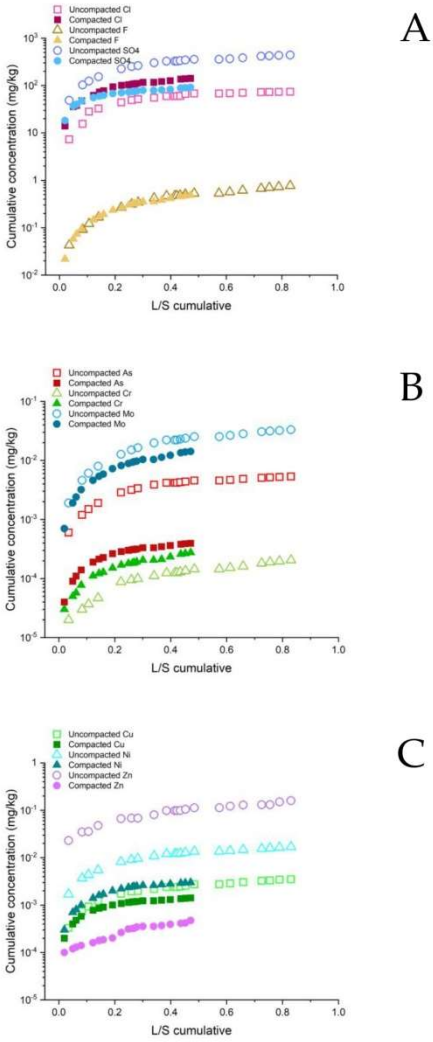

Figure 6. Cumulative concentrations of: (**A**) Cl^-, F^-, SO_4^{2-} (mg/kg); (**B**) As, Cr, Mo (mg/kg); and (**C**) Cu, Ni, Zn (mg/kg) as a function of cumulative liquid to solid ratio (L/kg) in field lysimetric experiments in uncompacted and compacted composite 1.

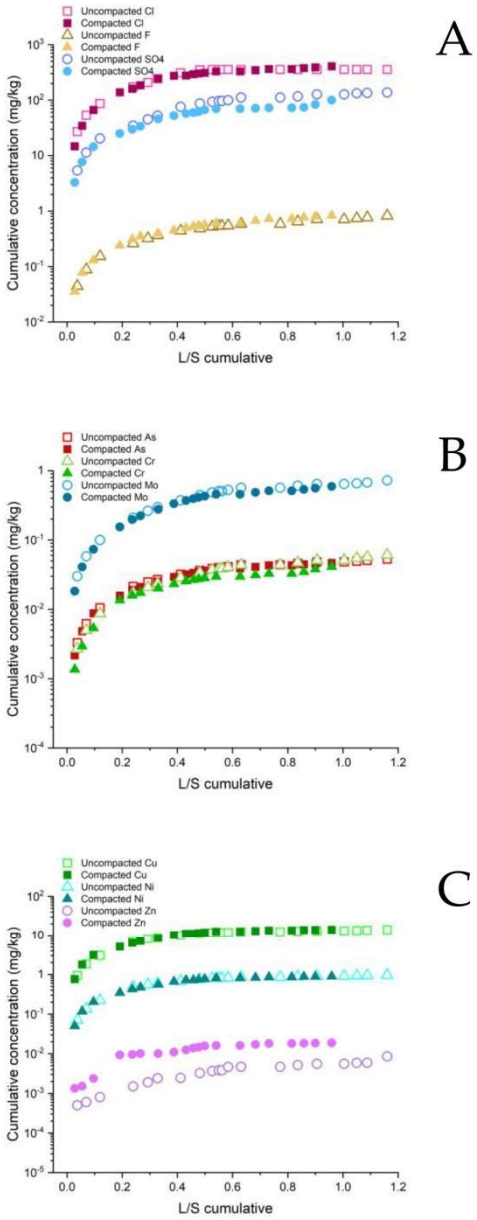

Figure 7. Cumulative concentrations of: **(A)** Cl^-, F^-, SO_4^{2-} (mg/kg); (**B**) As, Cr, Mo (mg/kg); and (**C**) Cu, Ni, Zn (mg/kg) as a function of cumulative liquid to solid ratio (L/kg) in field lysimetric experiments in uncompacted and compacted composite 2.

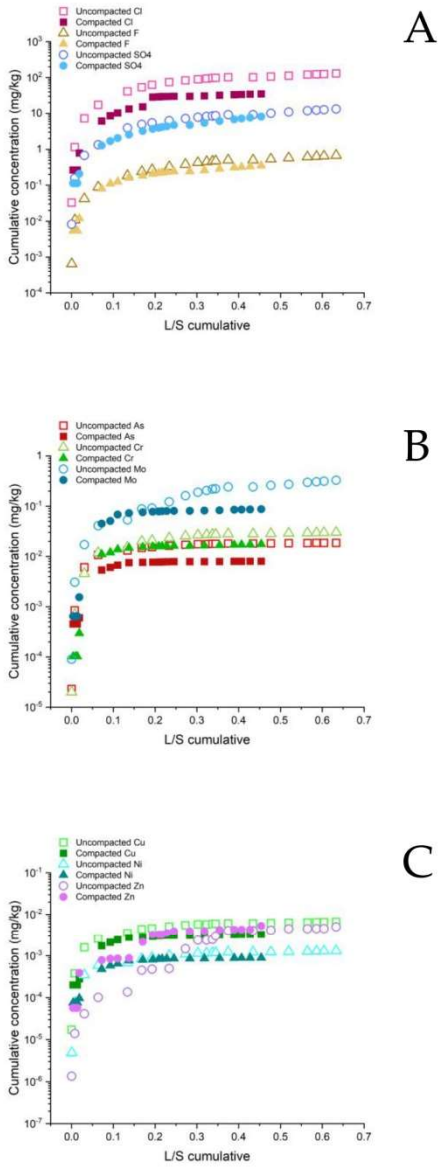

Figure 8. Cumulative concentrations of: (**A**) Cl^-, F^-, $SO_4{}^{2-}$ (mg/kg); (**B**) As, Cr, Mo (mg/kg); and (**C**) Cu, Ni, Zn (mg/kg) as a function of cumulative liquid to solid ratio (L/kg) in field lysimetric experiments in uncompacted and compacted Composite 3.

Higher values of the cumulative mass releases of As, Cr, and Mo were determined for composites 2 and 3, even though the total content of these elements was much lower in comparison to composite 1. This might be related to the lower immobilization of these oxyanion metals due to alkaline pore solutions in both composites or due to complexation

with soluble organic matter in composite 2 [44,47]. The immobilization of Cu, Ni, and Zn appeared to be the highest in composite 3 due to the formation of low-solubility hydroxides and incorporation in the newly formed mineral phases [48], followed by composite 1, while the least effective was in composite 2, in which the leaching of these metals was increased due to the complexation with dissolved organic matter that has increased mobility under alkaline conditions in this composite [42,48,49].

The trends in the cumulative mass release of the PHSs, as seen in the logarithmic scale graphs, indicated a sharp increase in the initial time intervals after the installation, followed by a steady decrease in the intensity of the leaching in the later time intervals. Cumulative values for composite 3 appeared to stabilize due to effective the immobilization. The intensity of the long-term release of the PHSs is relatively low and stable. Exceptions are SO_4^{2-}, F^- (uncompacted and compacted composite 3) and Mo (uncompacted composite 3), in which the intensity of long-term release is relatively higher compared to other PHSs. In contrast, for composite 1, the slightly increasing trends in cumulative mass release can be observed for all the parameters in Figure 6, indicating that a certain mass flow of PHSs can be expected in the future, but it appears that the immobilization is effective. Similar trends were observed for composite 2 (Figure 7); however, the immobilization in this composite was far less effective, and therefore the cumulative mass release of PHSs was more intensive in comparison to composites 1 and 3.

4. Conclusions

The environmental properties of three geotechnical composites, made of various voluminous waste materials, were studied on the basis of laboratory and field investigations. The wastes used had concentrations of PHS in aqueous leachates that exceeded the threshold values set by the national legislation.

After being processed into composites, immobilization of the PHSs occurred. The results obtained in the standardised laboratory leaching tests showed that composite 1 and composite 3 complied with the Slovenian limits for end-of-waste status. Meanwhile, in the leachate from composite 2 the parameters of Cu, Mo and Ni exceeded the limits.

The composites were installed in lysimeters in uncompacted and compacted forms to investigate the influence of the installation process on the environmental properties. The leaching of the PHSs was studied. More effective immobilization of the PHSs was observed in the field lysimeters than in the laboratory experiments. This was attributed to the longer period of exposure to natural conditions. The average concentrations of PHSs in the percolated water from compacted composites were lower in comparison to the uncompacted ones. After one year of monitoring, the trends in the cumulative mass release of the PHSs decreased in the intensity of leaching observed for composite 3, which was considered to have achieved an effective long-term immobilization. For composite 1 and composite 2, increasing trends of the cumulative mass release of the substances persisted, but decreased with time; the composites were considered to have achieved both a progressive immobilization and the wash-out of the PHSs. After a longer time, the PHSs also slowly diffused through the composites and bonded to the surface adsorption sites on the clay minerals from the MW. Pozzolanic and hydration reactions that took place in composite 2 and composite 3, due to the addition of ashes, resulted in higher immobilization efficiency due to the formation of larger quantities of newly formed mineral phases that incorporated the PHS into their stable crystalline structure. The lowering trend of the pH values of the percolate from uncompacted composite 2 indicated that a process of carbonation took place in the composites in which the ashes were used. The drop in the pH values that was observed for composite 3 was only minor, due to a high buffer capacity.

Based on the results of this study it can be concluded that composite 1 and composite 3 do not represent an environmental hazard, over the long term and under natural conditions. Therefore, they can be used for the rehabilitation of abandoned open-pit mines, while the use of composite 2 is limited, for example, to closure operations at a landfill for non-

hazardous wastes, where potential leaching of the PHSs into the environment can be prevented.

This study confirmed the need for a holistic approach to studying the environmental properties of recycled materials from construction products. Such an approach can be a basis for the successful transfer of recycling solutions that are developed in the laboratory to the field.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ijerph20032014/s1, Figure S1: A flow chart of the experimental set-up; Figure S2: Different stages of a field construction of lysimeters: Metal rod support structure (A) and the same structure placed at the final location of lysimeters (B), installation of an internal box structure, made from water resistant formwork plates (C), and the bottom-up view on the finalized structure of the box lysimeters, with a lysimeter percolate collection tank placed in front (D); Figure S3: Different stages of a field preparation of geotechnical composites for the lysimeter experiments: Preparation of a composite, according to predetermined dry mass ratios and with addition of optimal amount of water, by the use of excavator mixing bucket (A), filling of the lysimeter with a layer of a composite (B), spreading of a composite in a layer of uniform thickness of 30 cm (C), and the final installation of the layer of a composite by a vibration compactor in box lysimeters (D); Figure S4a: Temperature (A) and moisture (B) of uncompacted and compacted Composite 1 (measurements from upper and lower sensor); Figure S4b: Temperature (A) and moisture (B) of un-compacted and compacted Composite 2 (measurements from upper and lower sensor); Figure S4c: Temperature (A) and moisture (B) of un-compacted and compacted Composite 3 (measurements from upper and lower sensor); Figure S5: XRD patterns of raw materials (A) Paper mill sludge, (B) Foundry sand, (C) Mine waste, (D) Paper ash, (E) Digestate, (F) Bottom ash from incineration of waste, (G) Foundry slag and (H) Coal ash; Figure S6: pH values of percolates from (A) Composite 1, (B) Composite 2 and (C) Composite 3 as function of different sampling period. Results represent values obtained from samplings in a period from June 2020 to June 2021; Figure S7: Conductivity values (mS/m) of percolates from (A) Composite 1, (B) Composite 2 and (C) Composite 3 as function of different sampling period. Results represent values obtained from samplings in a period from June 2020 to June 2021; Figure S8: Concentrations of potentially hazardous substances in percolated water from lysimeters installed below uncompacted and compacted geotechnical composites (A) Composite 1, (B) Composite 2 and (C) Composite 3. Results represent average concentrations of elements and anions obtained from 18 (Composites 1 and 3) or 17 (Composite 2) samplings in a period from June 2020 to June 2021; Table S1: Basic information about the input raw materials used in the experiments; Table S2: Maximum reference dry density and optimal moisture content of geotechnical composites; Table S3a: Precipitation, volume of collected lysimetric water of PTEs and anions (dry mass basis), pH and conductivity in lysimetric water from uncompacted Composite 1; Table S3b: Precipitation, volume of collected lysimetric water of PTEs and anions (dry mass basis), pH and conductivity in lysimetric water from uncompacted Composite 2; Table S3c: Precipitation, volume of collected lysimetric water of PTEs and anions (dry mass basis), pH and conductivity in lysimetric water from uncompacted Composite 3; Table S4: ICP-MS (Agilent 7900) operating parameters for the determination of element concentrations in aqueous leachates; Table S5: Certified and determined concentrations of PTEs in the standard reference material SPS-SW1 (Reference material for measurements of elements in surface waters) determined by ICP-MS. The results represent the mean concentration obtained from four parallel samples; Table S6: Concentrations of chlorides, fluorides and sulphates in the standard reference material Anions—While Volume obtained from Merck KGaA (Darmstadt, Germany) determined by spectrophotometry. The results represent the mean concentration obtained from four parallel samples; Table S7: Concentrations of elements in certified reference material CRM 320R (Trace Elements in River Sediment) determined by ICP-MS after microwave-assisted digestion. The results represent the mean concentration from three parallel samples; Table S8: LODs for the determination of element concentrations aqueous leachates and lysimetric waters by ICP-MS and anions by spectrophotometry, and determination of the total element concentrations in composite samples by ICP-MS; Table S9: Total concentrations of PTEs in raw materials after microwave-assisted digestion determined by ICP-MS. The expanded uncertainty of the analytical procedure was better than $\pm$ 3% (k = 2); Table S10: Total concentrations of PTEs in composites after microwave-assisted digestion determined by ICP-MS. The results represent the mean concentration obtained from three

parallel samples; Table S11: Concentrations of PTEs and anions in aqueous leachates from raw materials applying the SIST EN 1744-3:2002 leaching test. Limits for inertness, set by the current Slovenian legislation, are also given. Values highlighted with red exceed the threshold values for inertness. pH and electrical conductivity of aqueous leachates are also given. The expanded uncertainty of analytical procedure was better than ± 3% (k = 2); Table S12: Concentrations of PTEs and anions in aqueous leachates from three uncompacted and compacted Composites 1, 2 and 3, applying SIST EN 1744-3:2002 leaching test. Results represent average concentrations of elements and anions obtained from three analysed samples for each composite. Limits for inertness, set by the current Slovenian legislation, are also provided. Values highlighted with red exceed the threshold values for inertness. pH and electrical conductivity of aqueous leachates are also given. The expanded uncertainty of analytical procedure was better than ± 3% (k = 2).

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Conflicts of Interest: Author Alenka Paviln is employed by the company Termit d.d. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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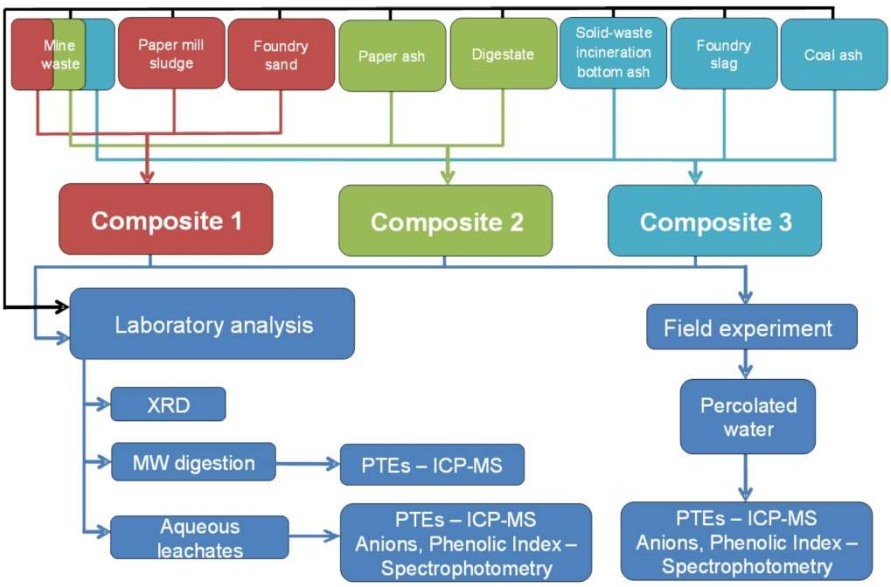

Figure S1 A flow chart of the experimental set-up.

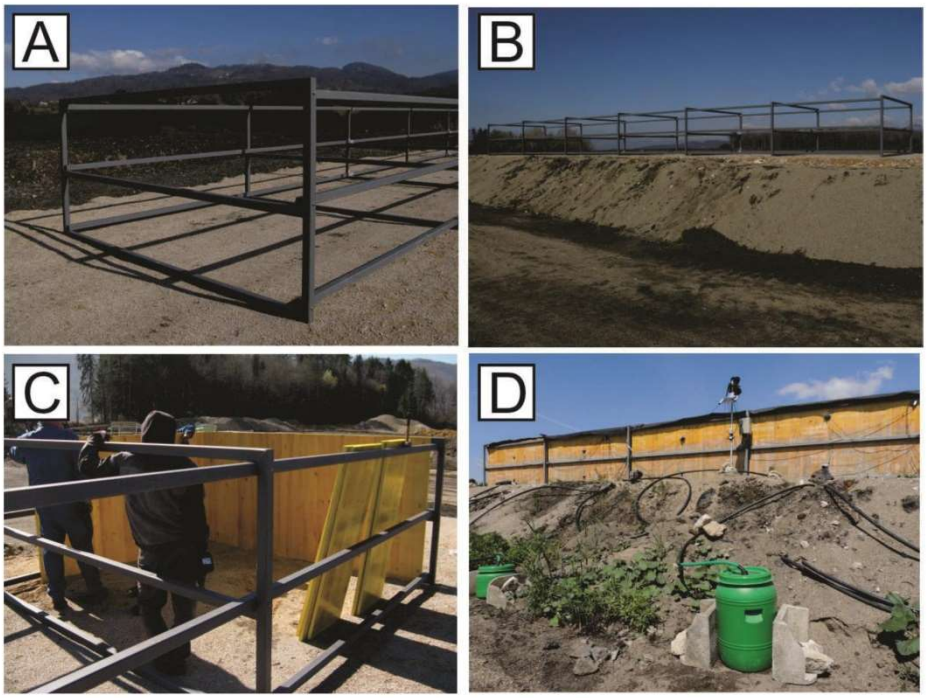

Figure S2 Different stages of a field construction of lysimeters: Metal rod support structure (A) and the same structure placed at the final location of lysimeters (B), installation of an internal box structure, made from water resistant formwork plates (C), and the bottom-up view on the finalized structure of the box lysimeters, with a lysimeter percolate collection tank placed in front (D).

Figure s3 Different stages of a field preparation of geotechnical composites for the lysimeter experiments: Preparation of a composite, according to predetermined dry mass ratios and with addition of optimal amount of water, by the use of excavator mixing bucket (A), filling of the lysimeter with a layer of a composite (B), spreading of a composite in a layer of uniform thickness of 30 cm (C), and the final installation of the layer of a composite by a vibration compactor in box lysimeters (D).

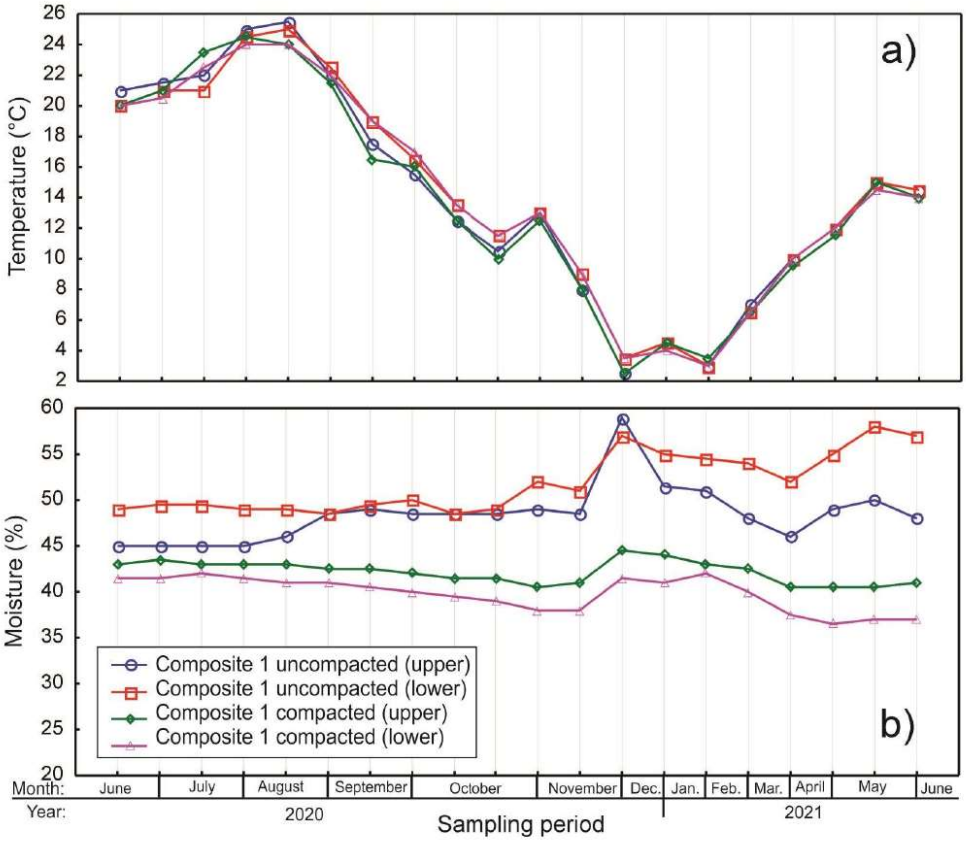

Figure S4a Temperature (A) and moisture (B) of uncompacted and compacted Composite 1 (measurements from upper and lower sensor).

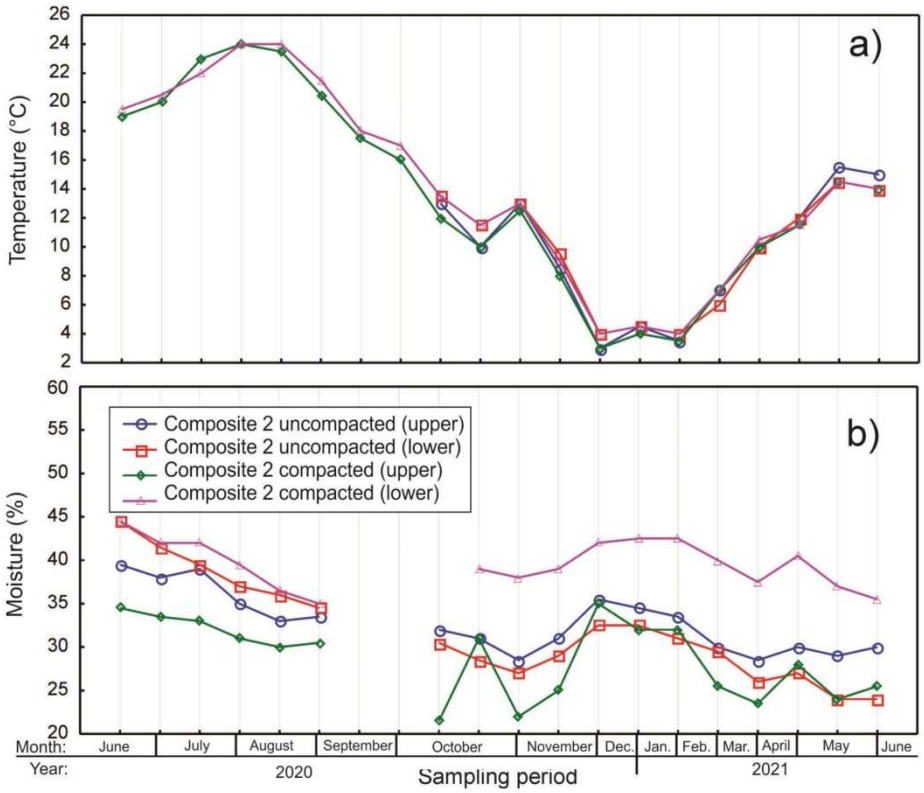

Figure S4b Temperature (A) and moisture (B) of un-compacted and compacted Composite 2 (measurements from upper and lower sensor).

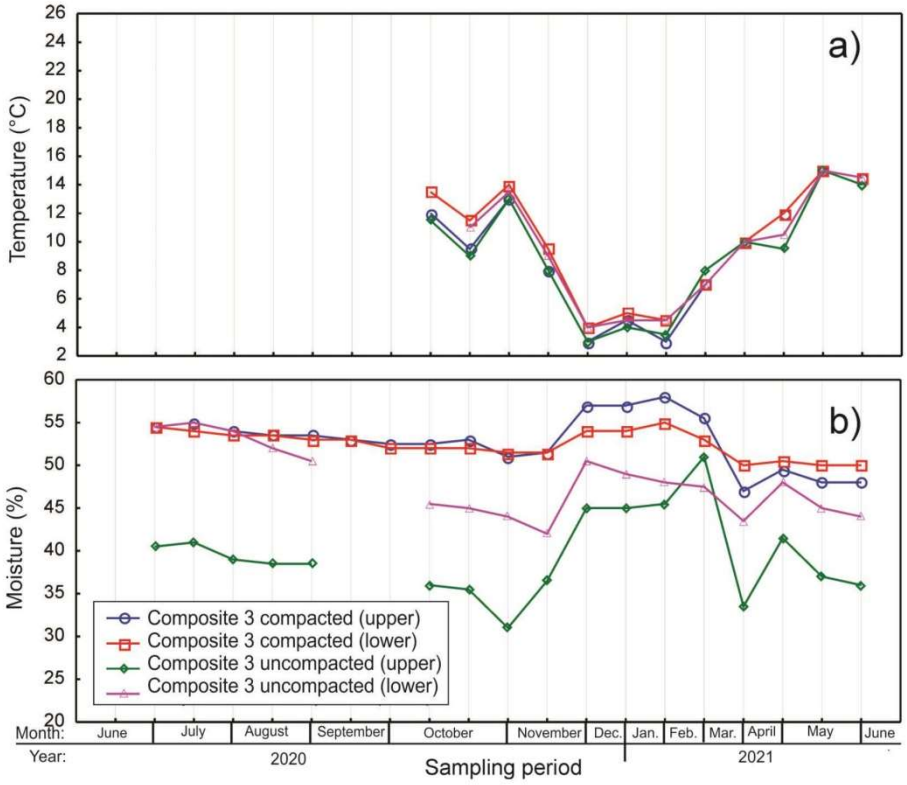

Figure S4c Temperature (A) and moisture (B) of un-compacted and compacted Composite 3 (measurements from upper and lower sensor).

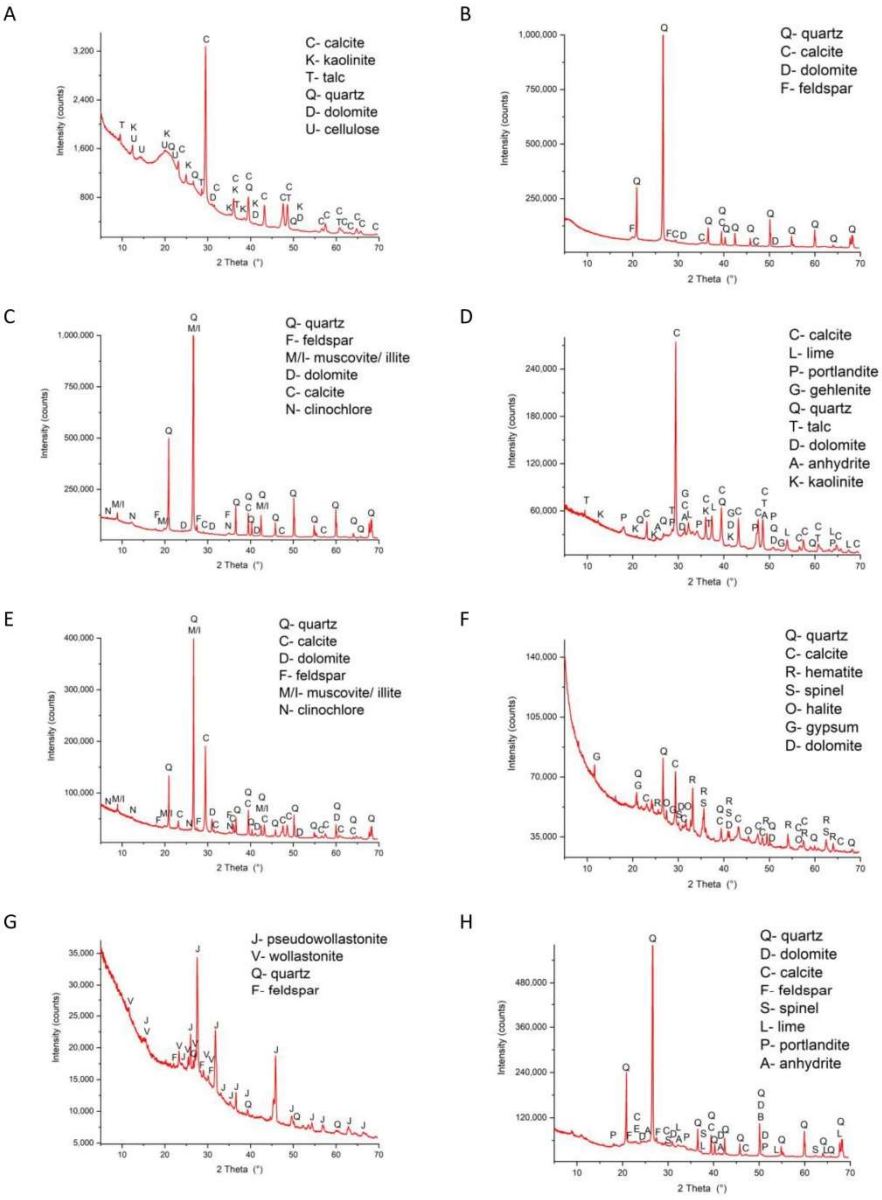

Figure S5. XRD patterns of raw materials (A) Paper mill sludge, (B) Foundry sand, (C) Mine waste, (D) Paper ash, (E) Digestate, (F) Bottom ash from incineration of waste, (G) Foundry slag and (H) Coal ash.

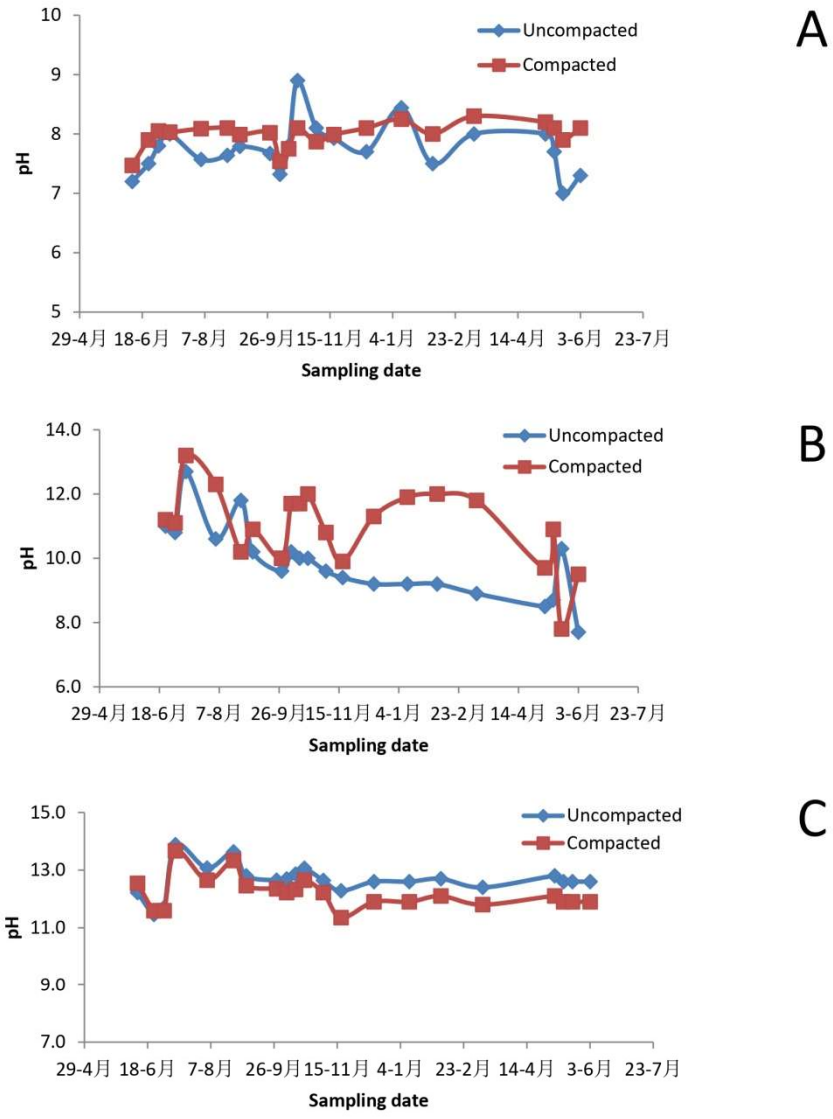

Figure S6 pH values of percolates from (A) Composite 1, (B) Composite 2 and (C) Composite 3 as function of different sampling period. Results represent values obtained from samplings in a period from June 2020 to June 2021.

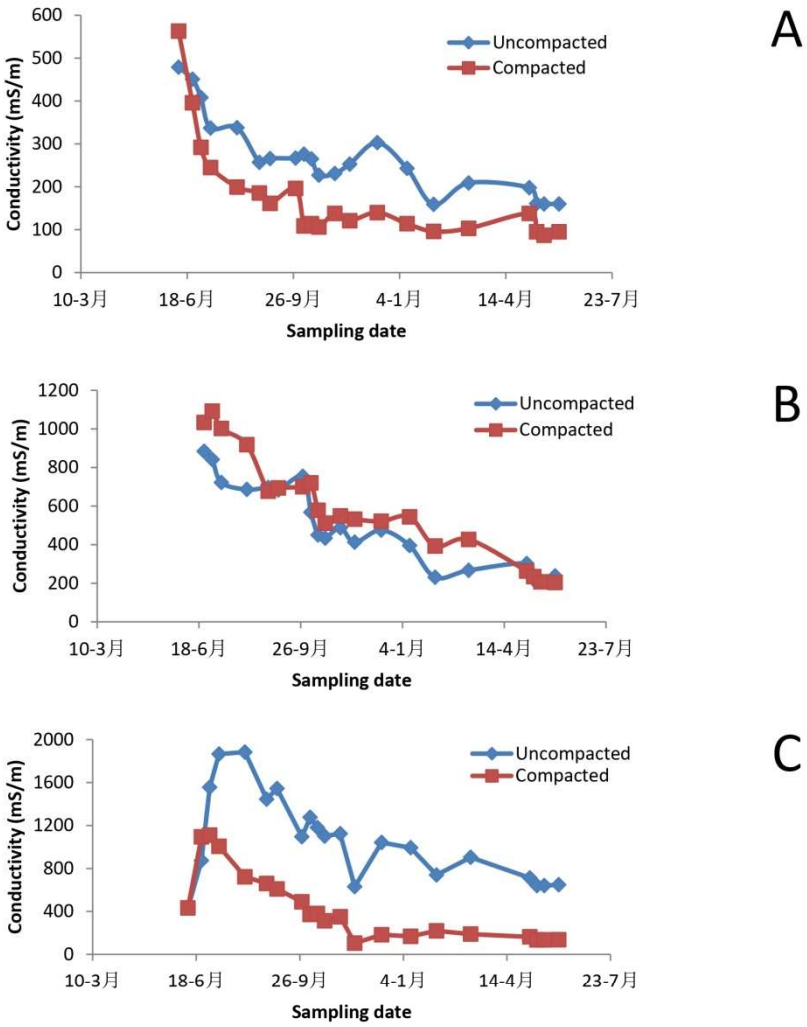

Figure S7 Conductivity values (mS/m) of percolates from (A) Composite 1, (B) Composite 2 and (C) Composite 3 as function of different sampling period. Results represent values obtained from samplings in a period from June 2020 to June 2021.

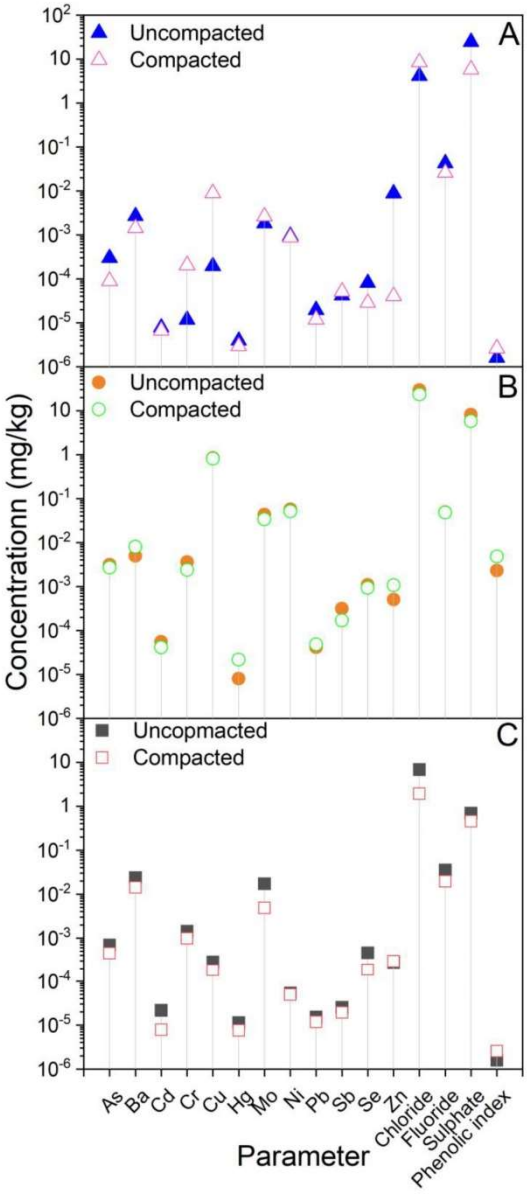

Figure S8. Concentrations of potentially hazardous substances in percolated water from lysimeters installed below uncompacted and compacted geotechnical composites (A) Composite 1, (B) Composite 2 and (C) Composite 3. Results represent average concentrations of elements and anions obtained from 18 (Composites 1 and 3) or 17 (Composite 2) samplings in a period from June 2020 to June 2021.

Table S1
Basic information about the input raw materials used in the experiments.

Type of input raw material	Abbreviation used in the text	European waste code*	Source of a raw material	Contact information of the source company
Paper-mill sludge	PMS	03 03 10	Paper mill for production of label and packaging paper	Brigl & Bergmeister GmbH –Vevče, Papirniška pot 25, 1261 Ljubljana, Slovenia
Paper ash	PA	10 01 01	Paper mill for production of newsprint and packaging paper	VIPAP Videm Krško d.d., Tovarniška ulica 18, Krško, 8270 Krško
Coal fly ash	CA	10 01 02		
Solid-waste incineration bottom ash	SWIA	19 01 12	Chemical products factory and incineration of waste	Albaugh TKI d.o.o. (Formerly PINUS TKI), Grajski trg 21, Rače, 2327 Rače, Slovenia
Foundry slag	FSL	10 09 03	Foundry for production and mechanical processing of metal castings	Livar d.d., Ljubljanska cesta 43, 1295 Ivančna Gorica, Slovenia
Foundry sand	FS	10 09 08		
Digestate from the mechanical-biological anaerobic treatment of municipal solid waste	DI	19 06 04	Public utility company – Regional Waste Management Centre – RCERO	JP VOKA SNAGA d.o.o., Vodovodna cesta 90, 1000 Ljubljana, Slovenia
Mining waste	MW	01 04 09	Mining company for the production and processing of silica sands	Termit d.d., Drtija 51, 1251 Moravče, Slovenia

* European Union's List of Wastes (European Commission, 2000)

Table S2
Maximum reference dry density and optimal moisture content of geotechnical composites

Parameter	Composite 1	Composite 2	Composite 3
Maximum reference dry density (Mg/m^3)	1.83	1.12	1.48
Optimal water content (%)	13.8	34.0	22.6

Table S3a

Precipitation, volume of collected lysimetric water, concentrations of PTEs and anions (dry mass basis), pH and conductivity in lysimetic water from uncompacted Composite 1.

	Sampling period (2020)													
Parameter	**4.6.-10.6.**	**10.6.-23.6.**	**23.6.-1.7.**	**1.7.-10.7.**	**10.7.-4.8.**	**4.8.-25.8.**	**25.8.-4.9.**	**4.9.-28.9.**	**28.9.-6.10.**	**6.10.-13.10.**	**13.10.-20.10.**	**20.10.-4.11.**	**4.11.-18.11.**	**18.11.-14.12.**
Precipitation (mm)	76	86	48	63	182	66	51	120	79	61	28	22	44	45
Volume of collected water (L)	470	650	310	460	1100	500	310	780	600	400	100	160	250	430
As (mg/kg)	0,0006	0,0006	0,0003	0,0004	0,0010	0,0003	0,0002	0,0005	0,0003			0,00009	0,0001	0,0002
Ba (mg/kg)	0,0052	0,0033	0,0012	0,0025	0,0053	0,0031	0,0018	0,0058	0,0049			0,0005	0,0013	0,0022
Cd (mg/kg)	0,000007	0,00001	0,000005	0,000007	0,00002	0,000007	0,000005	0,00001	0,000009			0,000002	0,000004	0,000006
Cr total (mg/kg)	0,00002	0,00001	0,000007	0,00001	0,00004	0,000007	0,000005	0,00001	0,00001			0,000005	0,000006	0,000010
Cu (mg/kg)	0,00033	0,0004	0,0002	0,0003	0,0005	0,0002	0,00006	0,0002	0,0002			0,00007	0,00009	0,0002
Hg (mg/kg)	0,000003	0,000005	0,000002	0,000003	0,000008	0,000004	0,000002	0,000006	0,000004			0,000001	0,000002	0,000003
Mo (mg/kg)	0,0019	0,0027	0,0015	0,0019	0,0047	0,0024	0,0013	0,0034	0,0024			0,0007	0,0008	0,0016
Ni (mg/kg)	0,0017	0,002	0,0007	0,0011	0,0027	0,0009	0,0005	0,0013	0,0012	Technical problem	Technical problem	0,0003	0,0004	0,0008
Pb (mg/kg)	0,00002	0,00002	0,00001	0,00002	0,00004	0,00002	0,00001	0,00003	0,00002			0,000006	0,000009	0,00002
Sb (mg/kg)	0,00005	0,00007	0,00003	0,00004	0,0001	0,00003	0,00002	0,00006	0,00005			0,00001	0,00001	0,00003
Se (mg/kg)	0,00023	0,0002	0,00006	0,0001	0,0003	0,00008	0,00003	0,0001	0,00006			0,00002	0,00001	0,00004
Zn (mg/kg)	0,023	0,012	0,0006	0,012	0,019	0,0019	0,00004	0,012	0,018			0,0003	0,0061	0,0077
Chloride (mg/kg)	7,3	8,2	12,7	4,4	11,4	5,2	2,3	4,1	3,8			1,1	6,0	1,3
Fluoride (mg/kg)	0,043	0,049	0,030	0,044	0,10	0,046	0,031	0,08	0,05			0,01	0,02	0,03
Sulfate (mg/kg)	48,6	54,1	22,1	28,4	71,9	25,8	12,9	38,0	25,6			6,9	10,9	12,1
Phenolic index (mg/kg)						0,0004								0,0001
pH	7,2	7,5	7,8	8,0	7,6	7,6	7,8	7,7	7,3	7,8	8,9	8,1	7,9	7,7
Conductivity (mS/m)	479	451	408	337	338	257	266	267	276	265	227	231	253	303
L/S	0,035	0,048	0,023	0,034	0,082	0,037	0,023	0,058	0,045	0,030	0,007	0,012	0,019	0,032
L/S (cumulative)	0,035	0,083	0,106	0,141	0,222	0,259	0,283	0,341	0,385	0,415	0,422	0,434	0,453	0,485

	Sampling period (2021)								
Parameter	**14.12.-11.1.**	**11.1.-5.2.**	**5.2.-10.3.**	**10.3.-6.5.**	**6.5.-13.5.**	**13.5.-20.5.**	**20.5.-3.6.**	Average value	Standard deviation of results
Precipitation (mm)	165	66	45	150	47	75	77	76	43
Volume of collected water (L)	1200	520	625	890	400	460	550	526	230
As (mg/kg)		0,0001	0,0002	0,0002	0,00009	0,00008	0,0001	0,0003	0,0002
Ba (mg/kg)		0,0018	0,0024	0,0015	0,0004	0,0025	0,0025	0,0027	0,0017
Cd (mg/kg)		0,000008	0,000009	0,00001	0,000006	0,000007	0,00001	0,000008	0,000003
Cr total (mg/kg)		0,000008	0,000009	0,00002	0,000009	0,000007	0,0000	0,00001	0,000009
Cu (mg/kg)		0,00009	0,0002	0,0002	0,00008	0,0001	0,00	0,0002	0,0001
Hg (mg/kg)		0,000004	0,000005	0,000007	0,000003	0,000003	0,000004	0,000004	0,000002
Mo (mg/kg)		0,0012	0,0017	0,0025	0,0007	0,0007	0,001	0,0018	0,0011
Ni (mg/kg)	Technical problem	0,0005	0,0007	0,0007	0,0004	0,0005	0,0006	0,0009	0,0006
Pb (mg/kg)		0,00002	0,00002	0,00003	0,00001	0,00002	0,00002	0,00002	0,000009
Sb (mg/kg)		0,00003	0,00005	0,00007	0,00003	0,00003	0,0000	0,00004	0,00002
Se (mg/kg)		0,00003	0,00004	0,00010	0,00001	0,00002	0,0000	0,00008	0,00008
Zn (mg/kg)		0,0097	0,0074	0,0012	0,0002	0,019	0,0094	0,0088	0,0074
Chloride (mg/kg)		0,77	1,5	2,3	0,51	0,44	0,7	4,1	3,7
Fluoride (mg/kg)		0,036	0,047	0,058	0,031	0,026	0,042	0,043	0,021
Sulfate (mg/kg)		10,2	17,9	29,8	8,6	7,9	8,6	24,5	18,4
Phenolic index (mg/kg)						0,0002	0,0003	0,0002	0,0001
pH	8,4	7,5	8,0	8,0	7,7	7,0	7,3	7,8	0,42
Conductivity (mS/m)	243	159	209	198	161	160	160	268,9	91,5
L/S	0,089	0,039	0,046	0,066	0,030	0,034	0,041		
L/S (cumulative)	0,574	0,613	0,659	0,725	0,755	0,789	0,830		

Table S3a (continued)

Precipitation, volume of collected lysimetric water, concentrations of PTEs and anions (dry mass basis), pH and conductivity in lysimetic water from compacted Composite 1.

	Sampling period (2020)													
Parameter	**4.6.-10.6.**	**10.6.-23.6.**	**23.6.-1.7.**	**1.7.-10.7.**	**10.7.-4.8.**	**4.8.-25.8.**	**25.8.-4.9.**	**4.9.-28.9.**	**28.9.-6.10.**	**6.10.-13.10.**	**13.10.-20.10.**	**20.10.-4.11.**	**4.11.-18.11.**	**18.11.-14.12.**
Precipitation (mm)	76	86	48	63	182	66	51	120	79	61	28	22	44	45
Volume of collected water (L)	360	550	220	340	770	390	280	610	570	470	270	100	170	410
As (mg/kg)	0,00004	0,00005	0,00002	0,00003	0,00005	0,00002	0,00001	0,00004	0,00002	0,00002	0,000007	0,00000	0,000005	0,00002
Ba (mg/kg)	0,0019	0,0008	0,0006	0,0013	0,0031	0,0018	0,0012	0,0025	0,0025	0,002	0,0006	0,0004	0,0005	0,0013
Cd (mg/kg)	0,000004	0,00001	0,000002	0,000004	0,00001	0,000004	0,000003	0,00001	0,000006	0,000005	0,000003	0,000001	0,000002	0,000004
Cr total (mg/kg)	0,00003	0,00002	0,000007	0,00002	0,00003	0,00001	0,000006	0,00002	0,00002	0,00001	0,000003	0,000003	0,000006	0,000013
Cu (mg/kg)	0,0002	0,0002	0,00008	0,0001	0,0002	0,00008	0,00005	0,0001	0,00007	0,00006	0,00003	0,00001	0,00002	0,00003
Hg (mg/kg)	0,000002	0,000003	0,000001	0,000002	0,000004	0,000002	0,000002	0,000003	0,000003	0,000003	0,000001	0,000001	0,000001	0,000002
Mo (mg/kg)	0,0007	0,0012	0,0005	0,0008	0,0014	0,0008	0,00046	0,0014	0,0009	0,0007	0,0004	0,0002	0,0002	0,0007
Ni (mg/kg)	0,0003	0,0004	0,0001	0,0002	0,0004	0,0002	0,0001	0,0003	0,0002	0,0002	0,00008	0,00003	0,00004	0,0001
Pb (mg/kg)	0,00001	0,00002	0,00001	0,00001	0,00002	0,00001	0,00001	0,00002	0,00002	0,00001	0,000007	0,000003	0,000005	0,00001
Sb (mg/kg)	0,00002	0,00004	0,00001	0,00002	0,00005	0,00002	0,00001	0,00002	0,00002	0,00001	0,000006	0,000003	0,000003	0,00001
Se (mg/kg)	0,00004	0,00003	0,00001	0,00001	0,00004	0,00001	0,00001	0,00001	0,00001	0,000008	0,000004	0,000002	0,000002	0,00001
Zn (mg/kg)	0,0001	0,00002	0,00001	0,00001	0,00002	0,0000	0,00001	0,00002	0,00006	0,00005	0,000007	0,000003	0,00002	0,00001
Chloride (mg/kg)	14,0	21,9	2,3	9,5	14,3	11,0	4,9	16,1	6,8	3,6	2,9	1,4	2,2	5,6
Fluoride (mg/kg)	0,022	0,036	0,016	0,022	0,05	0,029	0,016	0,04	0,03	0,036	0,017	0,01	0,01	0,02
Sulfate (mg/kg)	18,3	18,6	3,4	7,3	8,0	4,2	2,3	5,6	3,0	2,6	1,3	0,7	1,6	2,6
Phenolic index (mg/kg)					0,0002					0,0001			0,00005	
pH	7,5	7,9	8,1	8,0	8,1	8,1	8,0	8,0	7,5	7,8	8,1	7,9	8,0	8,1
Conductivity (mS/m)	563	396	292	245	199,4	185,6	161,3	196,1	108,6	114	106,1	138	120,8	140
L/S	0,020	0,030	0,012	0,019	0,042	0,021	0,015	0,033	0,031	0,026	0,015	0,005	0,009	0,022
L/S (cumulative)	0,020	0,050	0,062	0,080	0,122	0,144	0,159	0,192	0,223	0,249	0,264	0,269	0,278	0,301

	Sampling period (2021)								
Parameter	**14.12.-11.1.**	**11.1.-5.2.**	**5.2.-10.3.**	**10.3.-6.5.**	**6.5.-13.5.**	**13.5.-20.5.**	**20.5.-3.6.**	Average value	Standard deviation of results
Precipitation (mm)	165	66	45	150	47	75	77	76	45
Volume of collected water (L)	1000	640	565	950	510	480	680	553	248
As (mg/kg)		0,0022	0,0022		0,0015	0,0008	0,0012	0,0027	0,0015
Ba (mg/kg)		0,0078	0,0098		0,0008	0,0015	0,0035	0,0080	0,0063
Cd (mg/kg)		0,00005	0,00004		0,00003	0,00003	0,00004	0,00004	0,00002
Cr total (mg/kg)		0,0015	0,0015		0,0020	0,0031	0,0034	0,0024	0,0017
Cu (mg/kg)		0,41	0,44		0,31	0,12	0,16	0,81	0,57
Hg (mg/kg)		0,000006	0,00001		0,00002	0,000008	0,000006	0,000022	0,000064
Mo (mg/kg)		0,030	0,026		0,026	0,021	0,034	0,034	0,017
Ni (mg/kg)	Technical problems	0,023	0,024	Technical problems	0,018	0,0083	0,013	0,051	0,038
Pb (mg/kg)		0,00003	0,0001		0,00002	0,00003	0,00002	0,00005	0,00006
Sb (mg/kg)		0,00006	0,00007		0,00010	0,0004	0,0006	0,0002	0,0002
Se (mg/kg)		0,00024	0,0003		0,0002	0,0003	0,0003	0,0009	0,0022
Zn (mg/kg)		0,0011	0,0009		0,0001	0,0002	0,0003	0,0011	0,0016
Chloride (mg/kg)		16,1	17,2		15,3	12,1	17,1	23,4	17,2
Fluoride (mg/kg)		0,062	0,055		0,043	0,032	0,034	0,048	0,020
Sulfate (mg/kg)		1,3	1,6		1,5	9,2	16,6	5,8	4,2
Phenolic index (mg/kg)						0,006		0,66	0,78
pH	11,9	12	11,8	9,7	10,9	7,8	9,5	11,0	1,2
Conductivity (mS/m)	544	393	427	263	234	207	204	590	270
L/S	0,087	0,056	0,049	0,082	0,044	0,042	0,059		
L/S (cumulative)	0,627	0,683	0,732	0,814	0,859	0,900	0,959		

Table S3b

Precipitation, volume of collected lysimetric water, concentrations of PTEs and anions (dry mass basis), pH and conductivity in lysimetic water from uncompacted Composite 2.

	Sampling period (2020)												
Parameter	**10.6.-23.6.**	**23.6.-1.7.**	**1.7.-10.7.**	**10.7.-4.8.**	**4.8.-25.8.**	**25.8.-4.9.**	**4.9.-28.9.**	**28.9.-6.10.**	**6.10.-13.10.**	**13.10.-20.10.**	**20.10.-4.11.**	**4.11.-18.11.**	**18.11.-14.12.**
Precipitation (mm)	86	48	63	182	66	51	120	79	61	28	22	44	45
Volume of collected water (L)	340	300	455	1100	490	325	760	640	410	225	100	205	430
As (mg/kg)	0,0033	0,0029	0,0043	0,011	0,0034	0,0020	0,0051	0,0045	0,0024	0,0011		0,0013	0,0025
Ba (mg/kg)	0,0082	0,0036	0,0055	0,042	0,0075	0,0004	0,0002	0,0029	0,0037	0,0017		0,0020	0,00009
Cd (mg/kg)	0,00003	0,00003	0,00005	0,0001	0,00006	0,00006	0,0001	0,0001	0,00005	0,00004		0,00003	0,00004
Cr total (mg/kg)	0,0027	0,0023	0,0037	0,0086	0,0036	0,0026	0,0051	0,0052	0,0033	0,0015		0,0019	0,0034
Cu (mg/kg)	0,95	0,9	1,2	4,1	1,0	0,57	1,2	1,2	0,58	0,018		0,26	0,57
Hg (mg/kg)	0,000004	0,000003	0,000005	0,00001	0,000005	0,000004	0,000008	0,000007	0,000004	0,000002		0,000002	0,000005
Mo (mg/kg)	0,03	0,028	0,042	0,11	0,053	0,034	0,077	0,071	0,041	0,021	Technical problems	0,020	0,041
Ni (mg/kg)	0,071	0,066	0,089	0,26	0,071	0,043	0,083	0,084	0,04	0,0037		0,016	0,038
Pb (mg/kg)	0,00001	0,00001	0,00002	0,00006	0,00007	0,00006	0,00004	0,00004	0,00007	0,0001		0,00002	0,00002
Sb (mg/kg)	0,00007	0,0001	0,0002	0,0004	0,0003	0,0002	0,0007	0,0005	0,0004	0,0002		0,0002	0,0004
Se (mg/kg)	0,0004	0,0004	0,0012	0,011	0,0016	0,0006	0,0009	0,0008	0,00001	0,000007		0,0002	0,00001
Zn (mg/kg)	0,0005	0,0001	0,0002	0,0007	0,0004	0,0005	0,00004	0,0008	0,0004	0,0002		0,0008	0,00002
Chloride (mg/kg)	27,1	26,2	33,3	85,3	35,3	36,6	65,6	41,9	3,1	12,7		11,2	22,8
Fluoride (mg/kg)	0,04	0,04	0,06	0,11	0,06	0,04	0,08	0,04	0,04	0,02		0,010	0,038
Sulfate (mg/kg)	5,38	5,93	9,04	14,4	10,2	7,5	23,7	10,8	6,5	3,2		3,4	11,7
Phenolic index (mg/kg)			1,30						0,6			0,3	
pH	11,0	10,8	12,7	10,6	11,8	10,2	9,6	10,2	10,0	10,0	9,6	9,4	9,2
Conductivity (mS/m)	884	841	722	686	696	683	754	568	450	434	487	413	475
L/S	0,037	0,033	0,050	0,120	0,053	0,035	0,083	0,070	0,045	0,025	0,011	0,022	0,047
L/S (cumulative)	0,037	0,070	0,120	0,240	0,293	0,329	0,412	0,481	0,526	0,551	0,562	0,584	0,631

	Sampling period (2021)								
Parameter	**14.12.-11.1.**	**11.1.-5.2.**	**5.2.-10.3.**	**10.3.-6.5.**	**6.5.-13.5.**	**13.5.-20.5.**	**20.5.-3.6.**	Average value	Standard deviation of results
Precipitation (mm)	165	66	45	150	47	75	77	76	45
Volume of collected water (L)	1300	580	640	900	420	350	660	532	303
As (mg/kg)		0,002200	0,0023		0,0012	0,0012	0,0021	0,0031	0,0024
Ba (mg/kg)		0,000900	0,0015		0,0005	0,0014	0,0021	0,0049	0,0099
Cd (mg/kg)		0,00006	0,00006		0,00003	0,00003	0,00005	0,00005	0,00002
Cr total (mg/kg)		0,0034	0,0038		0,0037	0,0021	0,0044	0,0036	0,0017
Cu (mg/kg)		0,34	0,35		0,20	0,24	0,43	0,83	0,93
Hg (mg/kg)		0,00002	0,00001		0,00002	0,000008	0,00001	0,000008	0,000006
Mo (mg/kg)		0,039	0,038		0,011	0,019	0,052	0,043	0,025
Ni (mg/kg)	Technical problems	0,023	0,024	Technical problems	0,014	0,013	0,025	0,057	0,059
Pb (mg/kg)		0,00004	0,00004		0,00002	0,00001	0,00002	0,00004	0,00003
Sb (mg/kg)		0,0004	0,0005		0,0004	0,0001	0,0002	0,0003	0,0002
Se (mg/kg)		0,0003	0,0004		0,0002	0,0002	0,0003	0,0011	0,0026
Zn (mg/kg)		0,0005	0,0004		0,0003	0,00007	0,0026	0,0005	0,0006
Chloride (mg/kg)		17,7	23,4		12,4	15,7	25,9	29,2	20,5
Fluoride (mg/kg)		0,06	0,06		0,03	0,03	0,06	0,049	0,023
Sulfate (mg/kg)		4,9	10,4		5,5	1,8	3,3	8,1	5,3
Phenolic index (mg/kg)						0,1		0,58	0,51
pH	9,2	9,2	8,9	8,5	8,7	10,3	7,7	9,9	1,2
Conductivity (mS/m)	395	231	267	302	219	212	238	498	219
L/S	0,142	0,063	0,070	0,098	0,046	0,038	0,072		
L/S (cumulative)	0,773	0,836	0,906	1,004	1,050	1,088	1,160		

Table S3b (continued)

Precipitation, volume of collected lysimetric water, concentrations of PTEs and anions (dry mass basis), pH and conductivity in lysimetic water from compacted Composite 2.

	Sampling period (2020)												
Parameter	**10.6.-23.6.**	**23.6.-1.7.**	**1.7.-10.7.**	**10.7.-4.8.**	**4.8.-25.8.**	**25.8.-4.9.**	**4.9.-28.9.**	**28.9.-6.10.**	**6.10.-13.10.**	**13.10.-20.10.**	**20.10.-4.11.**	**4.11.-18.11.**	**18.11.-14.12.**
Precipitation (mm)	86	48	63	182	66	51	120	79	61	28	22	44	45
Volume of collected water (L)	320	310	475	1100	520	340	740	660	500	310	220	250	480
As (mg/kg)	0,0022	0,0027	0,0039	0,0071	0,0033	0,0019	0,0040	0,0043	0,0027	0,0015	0,0012	0,0014	0,0026
Ba (mg/kg)	0,0083	0,0086	0,015	0,0019	0,019	0,0015	0,0001	0,018	0,015	0,0073	0,0012	0,013	0,0036
Cd (mg/kg)	0,00002	0,00002	0,00004	0,00007	0,00005	0,00003	0,00008	0,00008	0,00005	0,00004	0,00002	0,00002	0,00001
Cr total (mg/kg)	0,0014	0,0016	0,0024	0,0082	0,0023	0,0015	0,0028	0,0030	0,0023	0,0012	0,0007	0,0008	0,0015
Cu (mg/kg)	0,76	1,0	1,3	2,0	1,3	0,74	1,4	1,6	0,92	0,028	0,38	0,40	0,72
Hg (mg/kg)	0,000003	0,000003	0,000004	0,00001	0,0003	0,000006	0,000006	0,000006	0,000004	0,000003	0,000002	0,000002	0,000004
Mo (mg/kg)	0,018	0,023	0,032	0,081	0,043	0,027	0,053	0,058	0,037	0,022	0,017	0,018	0,028
Ni (mg/kg)	0,050	0,067	0,087	0,14	0,080	0,047	0,084	0,10	0,056	0,0051	0,023	0,023	0,043
Pb (mg/kg)	0,000008	0,000008	0,00002	0,00005	0,00002	0,0002	0,00003	0,00003	0,00002	0,0002	0,00002	0,00001	0,00002
Sb (mg/kg)	0,00003	0,00005	0,0001	0,0004	0,0002	0,0001	0,0003	0,0002	0,0001	0,00007	0,00006	0,00007	0,00005
Se (mg/kg)	0,0003	0,0003	0,0010	0,0095	0,0013	0,0005	0,0006	0,0007	0,00001	0,000008	0,000006	0,0002	0,00001
Zn (mg/kg)	0,0013	0,0002	0,0009	0,0070	0,0002	0,0005	0,00003	0,0008	0,0015	0,0015	0,0006	0,0012	0,00027
Chloride (mg/kg)	14,7	19,6	32,2	71,6	22,1	24,8	57,2	32,1	3,5	15,3	9,07	8,7	18,5
Fluoride (mg/kg)	0,04	0,04	0,05	0,11	0,07	0,04	0,04	0,05	0,05	0,03	0,02	0,02	0,04
Sulfate (mg/kg)	3,3	4,4	6,8	10,5	4,7	4,0	12,1	6,9	4,3	2,7	1,9	5,4	2,8
Phenolic index (mg/kg)				1,7					0,8			0,1	
pH	11,2	11,1	13,2	12,3	10,2	10,9	10	11,7	11,7	12	10,8	9,9	11,3
Conductivity (mS/m)	1033	1092	1002	918	677	694	700	720	578	511	549	532	521
L/S	0,028	0,027	0,041	0,095	0,045	0,030	0,064	0,057	0,043	0,027	0,019	0,022	0,042
L/S (cumulative)	0,028	0,055	0,096	0,191	0,237	0,266	0,330	0,388	0,431	0,458	0,477	0,499	0,540

	Sampling period (2021)								
Parameter	**14.12.-11.1.**	**11.1.-5.2.**	**5.2.-10.3.**	**10.3.-6.5.**	**6.5.-13.5.**	**13.5.-20.5.**	**20.5.-3.6.**	Average value	Standard deviation of results
Precipitation (mm)	165	66	45	150	47	75	77	76	45
Volume of collected water (L)	1000	640	565	950	510	480	680	553	248
As (mg/kg)		0,0022	0,0022		0,0015	0,0008	0,0012	0,0027	0,0015
Ba (mg/kg)		0,0078	0,0098		0,0008	0,0015	0,0035	0,0080	0,0063
Cd (mg/kg)		0,00005	0,00004		0,00003	0,00003	0,00004	0,00004	0,00002
Cr total (mg/kg)		0,0015	0,0015		0,0020	0,0031	0,0034	0,0024	0,0017
Cu (mg/kg)		0,41	0,44		0,31	0,12	0,16	0,81	0,57
Hg (mg/kg)		0,000006	0,00001		0,00002	0,000008	0,000006	0,000022	0,000064
Mo (mg/kg)	Technical problems	0,030	0,026	Technical problems	0,026	0,021	0,034	0,034	0,017
Ni (mg/kg)		0,023	0,024		0,018	0,0083	0,013	0,051	0,038
Pb (mg/kg)		0,00003	0,0001		0,00002	0,00003	0,00002	0,00005	0,00006
Sb (mg/kg)		0,00006	0,00007		0,00010	0,0004	0,0006	0,0002	0,0002
Se (mg/kg)		0,00024	0,0003		0,0002	0,0003	0,0003	0,0009	0,0022
Zn (mg/kg)		0,0011	0,0009		0,0001	0,0002	0,0003	0,0011	0,0016
Chloride (mg/kg)		16,1	17,2		15,3	12,1	17,1	23,4	17,2
Fluoride (mg/kg)		0,062	0,055		0,043	0,032	0,034	0,048	0,020
Sulfate (mg/kg)		1,3	1,6		1,5	9,2	16,6	5,8	4,2
Phenolic index (mg/kg)						0,006		0,66	0,78
pH	11,9	12	11,8	9,7	10,9	7,8	9,5	11,0	1,2
Conductivity (mS/m)	544	393	427	263	234	207	204	590	270
L/S	0,087	0,056	0,049	0,082	0,044	0,042	0,059		
L/S (cumulative)	0,627	0,683	0,732	0,814	0,859	0,900	0,959		

Table S3c

Precipitation, volume of collected lysimetric water, concentrations of PTEs and anions (dry mass basis), pH and conductivity in lysimetic water from uncompacted Composite 3.

	Sampling period (2020)													
Parameter	**10.6.-17.6.**	**17.6.-23.6.**	**23.6.-1.7.**	**1.7.-10.7.**	**10.7.-4.8.**	**4.8.-25.8.**	**25.8.-4.9.**	**4.9.-28.9.**	**28.9.-6.10.**	**6.10.-13.10.**	**13.10.-20.10.**	**20.10.-4.11.**	**4.11.-18.11.**	**18.11.-14.12**
Precipitation (mm)	40	86	48	63	182	66	51	120	79	61	28	22	44	45
Volume of collected water (L)	5,5	100	305	445	940	460	330	550	520	400	280	190	100	400
As (mg/kg)	0,00002	0,0008	0,0052	0,0046	0,0025	0,0016	0,0006	0,0009	0,0008	0,0004	0,0001	0,00024	0,00009	0,0002
Ba (mg/kg)	0,00007	0,0021	0,0045	0,032	0,039	0,0089	0,032	0,026	0,042	0,033	0,023	0,0069	0,0040	0,011
Cd (mg/kg)	0,0000001	0,000003	0,00002	0,00003	0,00001	0,00004	0,000005	0,00004	0,00005	0,00004	0,00002	0,00002	0,000004	0,00003
Cr total (mg/kg)	0,00002	0,0007	0,0039	0,0073	0,0034	0,0048	0,00081	0,0025	0,0021	0,0011	0,0005	0,0004	0,0001	0,0005
Cu (mg/kg)	0,00002	0,0004	0,0012	0,0010	0,0010	0,0009	0,0002	0,0005	0,0004	0,0002	0,00003	0,0002	0,00005	0,0001
Hg (mg/kg)	0,0000001	0,000006	0,00002	0,00002	0,00004	0,00003	0,000002	0,00004	0,000004	0,000003	0,000004	0,000008	0,000001	0,000006
Mo (mg/kg)	0,00009	0,0030	0,014	0,024	0,013	0,035	0,0037	0,030	0,040	0,027	0,016	0,013	0,0035	0,020
Ni (mg/kg)	0,000005	0,00007	0,0003	0,0002	0,00009	0,0002	0,00006	0,0001	0,00009	0,00004	0,000007	0,00003	0,000007	0,00003
Pb (mg/kg)	0,0000002	0,000004	0,00001	0,00002	0,00004	0,00002	0,00001	0,00002	0,00002	0,00001	0,00001	0,000007	0,000004	0,00001
Sb (mg/kg)	0,000001	0,00001	0,00007	0,00007	0,00008	0,00007	0,00002	0,00005	0,00004	0,00002	0,000004	0,00002	0,000004	0,00001
Se (mg/kg)	0,000003	0,00008	0,0004	0,0009	0,0013	0,0008	0,0002	0,0008	0,0007	0,0006	0,0003	0,0002	0,00007	0,0004
Zn (mg/kg)	0,000001	0,00001	0,00003	0,00006	0,00004	0,0003	0,00002	0,00002	0,0010	0,0009	0,00001	0,00009	0,0006	0,0011
Chloride (mg/kg)	0,03	1,1	6,1	10,0	23,8	12,3	9,3	11,7	8,7	6,0	4,6	3,5	1,0	3,1
Fluoride (mg/kg)	0,00	0,01	0,03	0,05	0,10	0,05	0,03	0,06	0,05	0,05	0,03	0,01	0,01	0,03
Sulfate (mg/kg)	0,01	0,15	0,52	0,66	2,6	1,03	0,49	0,82	0,93	0,60	0,42	0,28	0,15	0,60
Phenolic index (mg/kg)	0,0005													
pH	12,2	11,5	11,7	13,9	13,1	13,6	12,8	12,7	12,7	12,9	13,1	12,6	12,3	12,6
Conductivity (mS/m)	430	874	1556	1865	1884	1445	1544	1095	1276	1181	1101	1123	630	1042
L/S	0,0004	0,007	0,023	0,033	0,070	0,034	0,025	0,041	0,039	0,030	0,021	0,014	0,007	0,030
L/S (cumulative)	0,0004	0,008	0,031	0,064	0,134	0,168	0,193	0,234	0,273	0,302	0,323	0,337	0,345	0,375

	Sampling period (2021)								
Parameter	**14.12.-11.1.**	**11.1.-5.2.**	**5.2.-10.3.**	**10.3.-6.5.**	**6.5.-13.5.**	**13.5.-20.5.**	**20.5.-3.6.**	Average value	Standard deviation of results
Precipitation (mm)	165	66	45	150	47	75	77	74	44
Volume of collected water (L)	800	570	575	600	290	240	390	404	228
As (mg/kg)		0,00007	0,00008	0,0002	0,00003	0,00003	0,00003	0,0007	0,0012
Ba (mg/kg)		0,053	0,073	0,0003	0,0019	0,029	0,015	0,024	0,020
Cd (mg/kg)		0,00003	0,00003	0,00003	0,00001	0,000009	0,00001	0,00002	0,00001
Cr total (mg/kg)		0,0004	0,0004	0,0004	0,0002	0,0002	0,0004	0,0014	0,0020
Cu (mg/kg)		0,00009	0,0001	0,0002	0,00005	0,00005	0,00009	0,0003	0,0003
Hg (mg/kg)		0,000004	0,000004	0,00004	0,000009	0,000002	0,000003	0,00001	0,00001
Mo (mg/kg)	Technical problems	0,017	0,012	0,026	0,0091	0,0070	0,015	0,017	0,011
Ni (mg/kg)		0,00001	0,00003	0,00001	0,00001	0,00001	0,00002	0,00005	0,00006
Pb (mg/kg)		0,00002	0,00002	0,00002	0,00001	0,00001	0,00001	0,000015	0,000008
Sb (mg/kg)		0,000004	0,000004	0,00003	0,000002	0,000007	0,00001	0,00003	0,00003
Se (mg/kg)		0,0003	0,0004	0,0008	0,0002	0,0001	0,0002	0,0005	0,0004
Zn (mg/kg)		0,00008	0,0004	0,00002	0,00002	0,000009	0,0005	0,0003	0,0004
Chloride (mg/kg)		5,1	6,0	8,1	2,7	2,3	4,2	6,8	5,5
Fluoride (mg/kg)		0,03	0,04	0,04	0,02	0,02	0,03	0,035	0,022
Sulfate (mg/kg)		0,85	0,86	0,89	0,43	0,36	0,58	0,70	0,55
Phenolic index (mg/kg)							0,0003	0,0004	0,0002
pH	12,6	12,7	12,4	12,8	12,6	12,6	12,6	12,7	0,5
Conductivity (mS/m)	993	739	904	712	640	640	649	1063	413
L/S	0,060	0,043	0,043	0,045	0,022	0,018	0,029		
L/S (cumulative)	0,434	0,477	0,520	0,565	0,586	0,604	0,633		

Table S3c (continued)

Precipitation, volume of collected lysimetric water, concentrations of PTEs and anions (dry mass basis), pH and conductivity in lysimetic water from compacted Composite 3.

	Sampling period (2020)													
Parameter	**10.6.-17.6.**	**17.6.-23.6.**	**23.6.-1.7.**	**1.7.-10.7.**	**10.7.-4.8.**	**4.8.-25.8.**	**25.8.-4.9.**	**4.9.-28.9.**	**28.9.-6.10.**	**6.10.-13.10.**	**13.10.-20.10.**	**20.10.-4.11.**	**4.11.-18.11.**	**18.11.-14.12**
Precipitation (mm)	40	86	48	63	182	66	51	120	79	61	28	22	44	45
Volume of collected water (L)	60	100	60	75	850	325	280	430	520	380	230	125	180	270
As (mg/kg)	0,0005			0,0001	0,0048	0,0007	0,0007	0,0008	0,0001	0,00006	0,00003	0,00005	0,00006	0,00004
Ba (mg/kg)	0,0011			0,0057	0,048	0,0084	0,018	0,0090	0,032	0,031	0,014	0,0015	0,0036	0,0031
Cd (mg/kg)	0,000001			0,000001	0,00005	0,000006	0,00002	0,000005	0,000007	0,000005	0,000003	0,000002	0,000002	0,000003
Cr total (mg/kg)	0,0001			0,0002	0,011	0,0010	0,0018	0,0010	0,0005	0,0003	0,0001	0,0001	0,0001	0,0001
Cu (mg/kg)	0,0002			0,00008	0,0014	0,0004	0,0003	0,0004	0,0001	0,00004	0,0001	0,00003	0,00003	0,00001
Hg (mg/kg)	0,000002			0,000001	0,00004	0,00002	0,000004	0,00002	0,00001	0,000002	0,000001	0,000004	0,000002	0,000002
Mo (mg/kg)	0,0006	Technical problems	Technical problems	0,0009	0,043	0,0059	0,017	0,0043	0,0031	0,0021	0,0011	0,0008	0,0003	0,0006
Ni (mg/kg)	0,00008			0,00002	0,0004	0,0001	0,00007	0,0001	0,00003	0,00001	0,00003	0,000007	0,000007	0,000009
Pb (mg/kg)	0,00001			0,000002	0,00003	0,00001	0,000009	0,00001	0,00002	0,00001	0,000007	0,000004	0,000006	0,000009
Sb (mg/kg)	0,000006			0,000005	0,0001	0,00004	0,00003	0,00003	0,00002	0,00001	0,000006	0,000005	0,000006	0,000007
Se (mg/kg)	0,00004			0,00006	0,0019	0,0002	0,0004	0,0002	0,00009	0,00006	0,00005	0,00003	0,00003	0,00004
Zn (mg/kg)	0,00006			0,0003	0,0004	0,00006	0,00002	0,00001	0,0013	0,0011	0,000007	0,000004	0,0003	0,0004
Chloride (mg/kg)	0,26			0,52	5,4	2,5	1,7	3,0	2,0	13,2	0,65	0,47	0,17	0,26
Fluoride (mg/kg)	0,01			0,01	0,07	0,03	0,02	0,03	0,02	0,02	0,01	0,01	0,01	0,01
Sulfate (mg/kg)	0,11			0,09	1,1	0,41	0,35	0,54	0,66	0,48	0,29	0,16	0,23	0,34
Phenolic index (mg/kg)	0,0008													
pH	12,5	11,6	11,6	13,7	12,7	13,3	12,5	12,4	12,2	12,3	12,7	12,2	11,4	11,9
Conductivity (mS/m)	432	1094	1110	1006	722	660	609	489	371	380	312	350	104,5	183
L/S	0,0038	0,0063	0,004	0,005	0,054	0,021	0,018	0,027	0,033	0,024	0,015	0,008	0,011	0,017
L/S (cumulative)	0,0038	0,0101	0,014	0,019	0,072	0,093	0,110	0,138	0,170	0,194	0,209	0,217	0,228	0,245

	Sampling period (2021)								
Parameter	**14.12.-11.1.**	**11.1.-5.2.**	**5.2.-10.3.**	**10.3.-6.5.**	**6.5.-13.5.**	**13.5.-20.5.**	**20.5.-3.6.**	Average value	Standard deviation of results
Precipitation (mm)	165	66	45	150	47	75	77	74	44
Volume of collected water (L)	600	555	575	555	280	325	420	343	213
As (mg/kg)		0,00001	0,00003	0,00006	0,000005	0,00002	0,000005	0,0004	0,0011
Ba (mg/kg)		0,031	0,018	0,0004	0,0026	0,018	0,011	0,014	0,014
Cd (mg/kg)		0,000007	0,000007	0,000007	0,000004	0,000004	0,000005	0,00001	0,00001
Cr total (mg/kg)		0,0003	0,0003	0,0003	0,0001	0,0002	0,0002	0,0010	0,0025
Cu (mg/kg)		0,00002	0,00006	0,00005	0,00001	0,00002	0,00002	0,0002	0,0003
Hg (mg/kg)		0,000004	0,000004	0,000004	0,000002	0,000002	0,000003	0,00001	0,00001
Mo (mg/kg)	Technical problems	0,0011	0,0012	0,0019	0,0007	0,0007	0,0013	0,005	0,010
Ni (mg/kg)		0,000007	0,00001	0,000007	0,000004	0,000006	0,000005	0,00005	0,00009
Pb (mg/kg)		0,00002	0,00002	0,00002	0,000009	0,00001	0,00001	0,000012	0,000006
Sb (mg/kg)		0,000007	0,00001	0,00001	0,000007	0,00001	0,00001	0,00002	0,00003
Se (mg/kg)		0,00001	0,00005	0,0001	0,00002	0,00002	0,00003	0,0002	0,0004
Zn (mg/kg)		0,00006	0,0003	0,00002	0,00001	0,00001	0,0010	0,0003	0,0004
Chloride (mg/kg)		0,88	1,2	1,3	0,39	0,57	0,66	1,9	3,1
Fluoride (mg/kg)		0,02	0,03	0,022	0,013	0,013	0,017	0,019	0,015
Sulfate (mg/kg)		0,70	0,73	0,70	0,35	0,41	0,53	0,45	0,25
Phenolic index (mg/kg)							0,0002	0,0005	0,0005
pH	11,9	12,1	11,8	12,1	11,9	11,9	11,9	12,2	0,6
Conductivity (mS/m)	168	219	189	163	135	135	136	427	324
L/S	0,038	0,035	0,036	0,035	0,018	0,021	0,026		
L/S (cumulative)	0,283	0,318	0,354	0,389	0,407	0,427	0,454		

Table S4
ICP-MS (Agilent 7900) operating parameters for the determination of element concentrations in aqueous leachates.

Parameter	Type/Value	Helium mode	HECM mode	No gas mode
Sample introduction				
Nebuliser	Micromist			
Spray chamber	Scott			
Skimmer and sampler	Ni			
Plasma conditions				
Forward power	1550 W			
Plasma gas flow	15.0 L min^{-1}			
Carrier gas flow		1.05 L min^{-1}	1.05 L min^{-1}	1.05 L min^{-1}
Makeup gas flow		0.10 L min^{-1}	0.10 L min^{-1}	0.10 L min^{-1}
He gas flow		4.5 mL min^{-1}	10 mL min^{-1}	
QP bias		-13.0 V	-93 V	-3.0 V
OctP bias		-18.0 V	-100 V	-8.0 V
Cell entrance		-40 V	-100 V	-30 V
Cell exit		-60 V	-150 V	-50 V
Deflect		1.6 V	-74 V	11.4 V
Plate bias		-60 V	-150 V	-35 V
Sample uptake rate	0.3 mL min^{-1}			
Data acquisition parameters				
Isotopes monitored		^{52}Cr, ^{55}Mn, ^{56}Fe, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{75}As, ^{95}Mo,	^{78}Se	^{111}Cd, ^{123}Sb, ^{137}Ba, ^{201}Hg, ^{208}Pb
Isotopes of internal standards		^{72}Ge, ^{89}Y, ^{103}Rh, ^{115}In	^{72}Ge, ^{89}Y, ^{103}Rh, ^{115}In	^{72}Ge, ^{89}Y, ^{103}Rh, ^{115}In

Quality of analytical data and limits of detection

The quality of the analytical measurements of the PHSs in aqueous leachates and the samples of percolated water from the lysimeters by ICP-MS was checked with an analysis of the standard reference material SPS-SW1 (Reference material for measurements of elements in surface waters) obtained from Spectrapure Standards (Oslo, Norway) and measurements of Cl^-, F^- and SO_4^{2-} by spectrophotometry, by analysing reference material Anions – While Volume, Merck KGaA (Darmstadt, Germany). The results are provided in Tables 5S–6S.

To check the quality of the determination of total element concentrations in the composite sample by ICP-MS after microwave-assisted digestion, certified reference material CRM 320R Trace Elements in River Sediment (Community Bureau of Reference, Geel, Belgium) was analysed. The results provided in Tables 7S.

The results provided in Tables 5S–7S indicate that the determined concentrations of the elements showed a good correlation with the reported certified values (the agreement between the results was better than ± 5%), thereby confirming the accuracy of the analytical procedures applied. The expanded uncertainty for the ICP-MS determinations was better than ± 3% (k = 2) and for spectrophotometry it was better than ± 5% (k = 2).

The limits of detection (LODs) for the determination of elements by ICP-MS and anions by spectrophotometry in aqueous leachates and samples of percolated water from lysimeters as well as the total elemental concentrations by ICP-MS in the composite samples are provided in Table 8S.

Table S5
Certified and determined concentrations of PTEs in the standard reference material SPS-SW1 (Reference material for measurements of elements in surface waters) determined by ICP-MS. The results represent the mean concentration obtained from four parallel samples.

Parameter	Certified value (µg/L)	Determined (µg/L)
As	10.0±0.1	9.9±0.3
Ba	50±1	49±1
Cd	0.50±0.01	0.49±0.01
Total Cr	2.00±0.02	1.99±0.06
Cu	20±1	19.6±0.6
Hg	/	/
Mo	10.0±0.1	10.1±0.6
Ni	10.0±0.1	10.0±0.1
Pb	5.0±0.1	4.8±0.1
Sb	/	/
Se	2.00±0.02	2.02±0.06
Zn	20[b]	19.1±0.6

[b]informative value/not certified

Table S6
Concentrations of chlorides, fluorides and sulphates in the standard reference material Anions – While Volume obtained from Merck KGaA (Darmstadt, Germany) determined by spectrophotometry. The results represent the mean concentration obtained from four parallel samples.

Parameter	Certified (mg/L)	Determined (mg/L)
chlorides	95.0 ± 9.50	93.5 ± 5.0
fluorides	1.17 ± 0.117	1.10 ± 0.06
sulphates	44.3 ± 4.43	42.5 ± 2.0

Table S7
Concentrations of elements in certified reference material CRM 320R (Trace Elements in River Sediment) determined by ICP-MS after microwave-assisted digestion. The results represent the mean concentration from three parallel samples.

Parameter	Certified (mg/kg)	Determined (mg/kg)
As	21.7±2.0	20.4±0.6
Ba	/	/
Cd	2.64±0.18	2.52±0.07
Cr	59±4	62.7±1.3
Cu	46.3±2.9	44.2 ±0.9
Hg	/	/
Mo	/	/
Ni	27.1±2.2	26.6±0.6
Pb	85±5	81±3
Sb	/	/
Se	/	/
Zn	319±20	311±7

Table S8
LODs for the determination of element concentrations aqueous leachates and lysimetric waters by ICP-MS and anions by spectrophotometry, and determination of the total element concentrations in composite samples by ICP-MS.

Parameter	Aqueous leachates, lysimetric water samples (mg/kg)	Composite samples (mg/kg)
As	0.001	1.5
Ba	0.02	30
Cd	0.002	3
Total Cr	0.002	3
Cu	0.001	1.5
Hg	0.001	1.5
Mo	0.002	3
Ni	0.002	3
Pb	0.005	7.5
Sb	0.001	1.5
Se	0.003	4.5
Zn	0.005	1.5
Cl^-	2	/
F^-	1	/
SO_4^{2-}	10	/

Table S9
Total concentrations of PTEs in raw materials after microwave-assisted digestion determined by ICP-MS. The expanded uncertainty of the analytical procedure was better than ± 3% (k = 2).

Parameter (mg/kg)	Paper-mill sludge	Foundry sand	Paper ash	Coal ash	Solid-waste incineration bottom ash	Foundry slag	Digestate	Mine waste
As	0.39	5.8	1.3	3.0	11	8.37	17	4.1
Ba	17	268	65	332	2708	246	600	157
Cd	0.31	0.45	0.14	0.50	44	1.5	1.3	0.27
Cr	28	70	55	2	600	234	350	42
Cu	7.2	31	88	352	1500	35	600	10
Hg	0.31	1.1	0.2	0.2	12	1.2	/	0.6
Mo	2.7	4.0	3.4	3.0	160	7.2	19	7.9
Ni	6.4	23	9.4	12	113	32	130	15
Pb	12	32	17	76	1115	47	390	17
Sb	0.20	2.6	0.63	1.4	120	4.9	9.5	0.71
Se	20	9.3	3.9	4.0	8.0	8.0	1.3	18
Zn	20	3680	48	100	14734	2646	680	47

Table S10
Total concentrations of PTEs in composites after microwave-assisted digestion determined by ICP-MS. The results represent the mean concentration obtained from three parallel samples.

Element	Composite 1 (mg/kg)	Composite 2 (mg/kg)	Composite 3 (mg/kg)
As	10.8	3.90	3.10
Ba	911	431	138
Cd	2.03	0.5	0.10
Cr	150	125	76.2
Cu	171	334	20.4
Hg	0.69	0.22	0.02
Mo	18.8	5.63	3.62
Ni	85.3	36.7	20.3
Pb	123	356	15.4
Sb	6.44	10	0.88
Se	1.95	0.906	0.823
Zn	1140	313	510

Table S11
Concentrations of PTEs and anions in aqueous leachates from raw materials applying the SIST EN 1744-3:2002 leaching test. Limits for inertness, set by the current Slovenian legislation, are also given. Values highlighted with red exceed the threshold values for inertness. pH and electrical conductivity of aqueous leachates are also given. The expanded uncertainty of analytical procedure was better than ± 3% (k = 2).

Sample/ Parameter	Paper-mill sludge	Foundry sand	Paper ash	Digestate	Solid-waste incineration bottom ash	Foundry slag	Coal ash	Mine waste	Limit value*
As (mg/kg)	0.07	0.17	0.004	0.11	0.007	0.06	0.003	0.0007	0.1
Ba (mg/kg)	0.4	<0.02	63	2	1.6	0.11	48	0.0073	5
Cd (mg/kg)	<0.002	<0.002	<0.002	0.014	<0.002	<0.002	<0.002	<0.002	0.025
Cr (mg/kg)	0.006	<0.002	0.032	0.26	7.4	0.013	0.16	0.0022	0.5
Cu (mg/kg)	0.18	0.026	0.79	8.2	<0.001	0.012	0.003	0.0006	0.5
Hg (mg/kg)	<0.001	<0.001	0.003	0.0099	0.005	0.002	0.001	<0.0001	0.005
Mo (mg/kg)	0.15	0.16	0.77	1.2	8.3	0.013	0.17	0.0065	0.5
Ni (mg/kg)	0.11	0.015	0.002	1.3	0.002	0.004	<0.002	0.0010	0.4
Pb (mg/kg)	0.005	<0.005	0.051	1.7	<0.005	<0.005	0.054	<0.0005	0.5
Sb (mg/kg)	0.014	0.02	0.002	5	1.1	0.073	0.077	0.0001	0.3
Se (mg/kg)	0.004	0.06	0.003	0.017	0.15	0.026	0.031	0.0004	0.6
Zn (mg/kg)	0.18	0.03	0.043	10	<0.005	<0.005	0.23	0.0016	2
Cl^- (mg/kg)	89	116	59.8	3440	5830	473	438	27	800
F^- (mg/kg)	19	22	7.44	17.2	26.8	5.39	5.69	0.44	10
SO_4^{2-} (mg/kg)	290	580	<10	5860	1000	2000	<10	9	1000
Phenolic index (mg/kg)	0.25	<0.05	3.6	30	<0.20	<0.05	3.6	<0.05	0.1
pH	7.3	10.0	12.5	9.2	11.1	9.4	12.3	8.6	/
Conductivity (mS/m)	62	55	988	293	522	56	1164	16	/

* Decree on waste (Official Gazette of the Republic of Slovenia, nos. 37/15, 69/15 and 129/20)

Table S12
Concentrations of PTEs and anions in aqueous leachates from three uncompacted and compacted Composites 1, 2 and 3, applying SIST EN 1744-3:2002 leaching test. Results represent average concentrations of elements and anions obtained from three analysed samples for each composite. Limits for inertness, set by the current Slovenian legislation, are also provided. Values highlighted with red exceed the threshold values for inertness. pH and electrical conductivity of aqueous leachates are also given. The expanded uncertainty of analytical procedure was better than ± 3% (k = 2).

Sample/	Composite 1		Composite 2		Composite 3		Limit
Parameter	Uncompacted	Compacted	Uncompacted	Compacted	Uncompacted	Compacted	value*
As (mg/kg)	0.033	0.028	0.072	0.039	0.0023	<0.001	0.1
Ba (mg/kg)	0.337	0.32	2.74	1.52	39.3	2.15	5
Cd (mg/kg)	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.025
Cr (mg/kg)	0.029	0.01	0.062	0.02	0.095	0.017	0.5
Cu (mg/kg)	0.048	0.03	2.85	4.8	0.0043	0.0017	0.5
Hg (mg/kg)	<0.001	<0.001	0.0017	0.0017	0.0023	<0.001	0.005
Mo (mg/kg)	0.0667	0.062		0.65	0.293	0.023	0.5
Ni (mg/kg)	0.023	0.013	0.49	0.58	<0.002	<0.002	0.4
Pb (mg/kg)	<0.005	<0.005	0.01	<0.005	0.053	<0.005	0.5
Sb (mg/kg)	0.0080	0.004	0.061	0.004	0.0023	0.0037	0.3
Se (mg/kg)	0.0050	0.0057	0.0083	0.079	0.015	0.0047	0.6
Zn (mg/kg)	0.067	0.058	0.125	0.0057	0.0650	0.0060	2
Cl^- (mg/kg)	274	323	1210	267	568	51.8	800
F^- (mg/kg)	5.3	7.1	10.6	8.7	6	0.7	10
SO_4^{2-} (mg/kg)	563	543	2667	273	137	137	1000
Phenolic index (mg/kg)	0.054	<0.01	7.9	0.42	<0.01	<0.01	0.1
pH	8.0	8.3	10.8	11.6	12.4	11.6	/
Conductivity (mS/m)	292	193	562	681	1158	495	/

* Decree on waste (Official Gazette of the Republic of Slovenia, nos. 37/15, 69/15 and 129/20)

Article 3: Simultaneous Speciation of Chromium, Molybdenum and Arsenic in Lysimetric Water from Geotechnical Composites Installed in Field Lysimeters

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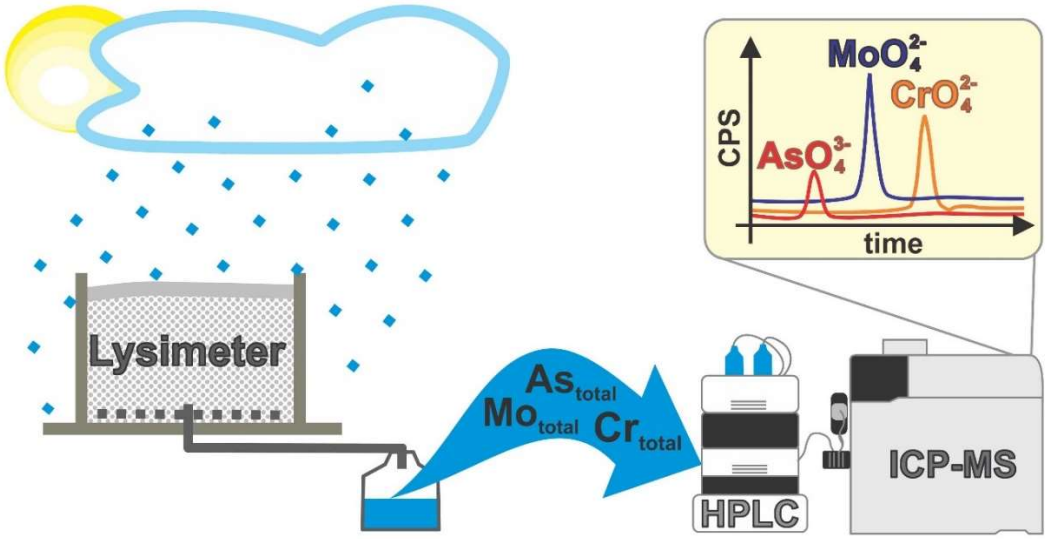

The role of trace elements and their impact on the environment and living organisms depends not only on their total concentrations but also on the chemical species in which they are actually present. In order to prevent environmental hazards and to evaluate the efficiency of the remediation of contaminated sites, and environmental impacts of recycled materials, it is necessary to follow the release of the most mobile, toxic chemical species of elements into the target environmental compartments. In such studies, speciation analysis is an indispensable analytical tool. For speciation analysis, the most frequently used is HPLC coupled to ICP-MS, which is a sensitive and versatile element-specific detector. Despite its multielemental capability, ICP-MS was rarely used as a detector in simultaneous, multielemental speciation analysis since simultaneous speciation of elements is possible only if the chemical species of elements behave similarly and are effectively separated on a chromatographic column under the same chromatographic conditions.

The potential of simultaneous speciation analysis was investigated in studies of the environmental impacts of Cr, Mo and As in geotechnical composites installed in field lysimeters. The anion-exchange HPLC-ICP-MS procedure was used for simultaneous speciation of negatively charged oxyanions of chromate (CrO_4^{2-}), molybdate (MoO_4^{2-}) and arsenate (AsO^{3-}). Results showed that the release of toxic chemical species of elements into lysimetric waters depends on the compaction process. Speciation analysis provided data on the presence of toxic elemental species, and also made an important contribution to understanding the physicochemical processes that govern their toxicity and to assessing their environmental impacts. The main advantages of multielemental speciation

analysis over the commonly used single speciation procedures are speed and cost-effectiveness.

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Simultaneous speciation of chromate, molybdate and arsenate in lysimetric water from geotechnical composites installed in field lysimeters

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Anion-exchange high performance liquid chromatography inductively coupled plasma mass spectrometry (HPLC-ICP-MS) was used for simultaneous speciation of chromate, molybdate and arsenate. The repeatability of measurement tested for multielemental standard solution of chromate, molybdate and arsenate (50 ng mL^{-1} of Cr, Mo and As, pH 12) was ± 0.9%, ± 4.9% and ± 4.1%, respectively. Limits of quantification (LOQs) were low (0.53 ng mL^{-1} for chromate and arsenate and 1.03 ng mL^{-1} for molybdate, expressed as elemental concentrations). A wide linear concentration range (from LOQs to 500 ng mL^{-1}) was obtained. The performances of this method enabled simultaneous speciation analysis in samples of water from lysimeters, in which three geotechnical composites, made of recycled waste, were installed in parallel in compacted and uncompacted, 20 times less dense form. The release of toxic chemical species of elements into lysimetric waters from each composite was studied. The results revealed that the degree of compaction and the composition of composites both have a significant influence on leaching of chromate, molybdate and arsenate. The study proved that multielemental speciation analysis is fast and cost-effective method for investigations of environmental impacts of materials, made from recycled waste, and can be used in other similar applications.

Trace elements undergo biogeochemical cycling on the Earth. They are also significantly involved in various biological processes. The role of trace elements and their impact on the environment and living organisms depends not only on their total concentrations but also on the chemical species in which they are actually present. The individual chemical forms of elements determine their toxicity, mobility and bioavailability[1,2]. Management of waste substances is an emerging problem and depends on the characteristics and the content of pollutants in the waste. In order to save natural resources, growing attention is being paid to the efficient reuse and recycling of waste[3–7], which are the main challenges of the circular economy[8]. When waste cannot be reused or recycled, efforts are focused on adequate treatment for ensuring its safe disposal[9]. To prevent environmental hazards of recycled materials, it is necessary to follow the release of the most mobile, toxic chemical species of elements into the target environmental compartments[3,10–18]. For such studies, speciation analysis has become an indispensable tool[19,20] as it enables quantitative determination of individual chemical species of trace elements in different sample matrices. The basic analytical tool for the speciation analysis is a combination of a separation technique with element specific detector. Frequently used is high performance liquid chromatography (HPLC) coupled with inductively coupled plasma mass spectrometry (ICP-MS), which is a sensitive, robust and versatile element specific detector. HPLC-ICP-MS was mostly used for speciation of a single element in a given sample[21]. In the environmental studies, when the effects of potentially toxic elements on the environment are investigated, it is necessary to determine the chemical species of multiple elements in the same sample. In this case, the use of single speciation analysis is time-consuming, expensive, and therefore not efficient. Multielemental speciation analysis on the other hand offers the possibility of reducing analyses time and costs, especially in cases, when

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large numbers of samples need to be analyzed. Despite its multielemental capability, ICP-MS was rarely used as a detector in simultaneous multielemental speciation analysis. This is due to the fact that simultaneous speciation of elements is possible only if the chemical species of elements behave similarly, and are effectively separated on a chromatographic column under the same chromatographic conditions. Marcinkowska et al.[22] overviewed the applications of multielemental speciation analysis by HPLC hyphenated with ICP-MS. Chemical species of two, three or four elements: arsenic (As), selenium (Se), chromium (Cr), cadmium (Cd), antimony (Sb) and tellurium (Te) were simultaneously determined. These studies were mostly related to environmental water samples. For each set of elements, the chromatographic conditions were optimized and the polyatomic interferences in the ICP-MS determination were eliminated using ammonia or oxygen as the reaction gases, or helium as the collision gas in the dynamic reaction or collision cells[23–28]. Simultaneous speciation analysis was also used to assess the impact of potentially toxic elements on the terrestrial and aquatic environment. To this end, Wolf et al.[29] studied the influence of forest fires on the mobility and transformation of chemical species of As, Se and Cr in soil. Soil and wildfire ashes leachates were analyzed by applying reversed phase ion-pairing HPLC-ICP-MS procedure for simultaneous speciation of As(III), As(V), Se(IV), Se(VI), Cr(III) and Cr(VI). In our group, a novel analytical procedure was developed for the simultaneous speciation of chromate, molybdate, tungstate and vanadate in alkaline extracts of manual metal arc (MMA) welding fumes loaded on filters[30]. Negatively charged oxyanions were separated on the anion-exchange chromatographic column and detected on-line by ICP-MS. The procedure was further optimized for the simultaneous determination of chromate, molybdate and vanadate in highly alkaline leachates of construction composites prepared from fly ash and cement with the addition of electric arc furnace dust[31]. The obtained results provided complementary information on the release and immobilization of toxic chemical species of elements from construction composites. Drinčić et al.[31] also developed HPLC-ICP-MS procedure for simultaneous speciation of chromate, arsenate, molybdate and vanadate at alkaline pHs. The separated elemental species were detected by ICP-MS recording masses at the most abundant isotopes at *m/z* 52, 75, 95 and 51, respectively. The advantage of the method is that enables also simultaneous determination of vanadium (V) species in considerably higher concentrations than those of Cr, molybdenum (Mo) and As, using low abundance (0.250%) ^{50}V isotope.

To further demonstrate the advantages in using multielemental speciation analysis in environmental studies, the aim of this investigation was to perform simultaneous speciation analysis of chromate (CrO_4^{2-}), molybdate (MoO_4^{2-}) and arsenate (AsO_4^{3-}) in lysimetric water by HPLC-ICP-MS to assess the environmental impacts of geotechnical composites made of different recycled materials installed in field lysimeters.

Materials and methods

Instrumentation. Total concentrations of Cr, Mo and As in lysimetric water were determined by ICP-MS, using instrument Agilent 7900 (Tokyo, Japan). Chromate, molybdate and arsenate were separated on an Agilent series 1200 quaternary pump. 7725i Rheodyne injection valve (Cotati, Ca, USA) equipped with a 0.1 mL injection loop was used for sample injection. Separation of elemental species was performed on a strong anion-exchange fast protein liquid chromatography (FPLC) column of Mono Q 5/50 GL (Sigma-Aldrich, St. Luis, MO, USA). To control the stability of the mass spectrometer, the eluent was spiked with internal standards containing 100 ng mL^{-1} of scandium (Sc), germanium (Ge), rhodium (Rh) and indium (In). In speciation analysis, data processing was based on peak area and was processed with Agilent MassHunter software. The ICP-MS operating parameters were optimized for plasma robustness and for the introduction of the minimum amounts of salts used in the separation process using the High Matrix Introduction (HMI) system. To eliminate the polyatomic inferences of chlorine on *m/z* 52 and 75, and carbon on *m/z* 52, the high energy collision mode (HECM) was applied, using helium as a collision gas. ICP-MS operating parameters for total element concentrations and speciation analysis are summarized in Table 1.

The pH was measured with WTW 330 pH meter (WTW GmbH, Weilheim, Germany).

A Mettler AE 163 (Mettler Toledo, Zürich, Switzerland) analytical balance was used for weighing.

Reagents and materials. Ultrapure 18.2 MΩ cm water (MilliQ) obtained from a Direct-Q 5 Ultrapure water system (Millipore Watertown, MA, USA) was used for the preparation of all solutions. Merck (Darmstadt, Germany) suprapur sodium hydroxide monohydrate ($NaOH \cdot H_2O$) and suprapur sodium carbonate (Na_2CO_3) were used to prepare alkaline buffer solutions (0.2% NaOH + 0.3% sodium carbonate Na_2CO_3). Stock standard solutions of Cr, As, Sc, Ge, Rh and In (1000 ± 2 mg L^{-1} in 2–3% HNO_3) were purchased from Merck. Chromate was prepared from stock solution K_2CrO_4 in water (Merck), containing 1000 ± 2 mg L^{-1} of Cr and molybdate from stock solution $(NH_4)_6Mo_7O_{24}$ in water (Merck), containing 1000 ± 2 mg L^{-1} of Mo. Arsenate stock solution (1000 ± 2 mg L^{-1} As) was made by dissolving 0.4170 g of $Na_2HAsO_4{\cdot}7H_2O$ salt (Sigma-Aldrich, St. Luis, MO, USA) in 100 mL of water. Sodium chloride (suprapur) used in HPLC separations was purchased from Merck. Samples were filtered using 0.45 µm Minisart cellulose nitrate membrane filters (Sartorius, Goettingen, Germany). SPS-SW1 Quality Control Material for Surface Water Analysis purchased from SPS Spectrapure Standards AS (Oslo, Norway), was used to check the accuracy of the total Cr, Mo and As determination in lysimetric water. The determined values for Cr, Mo and As (1.99 ± 0.05 ng mL^{-1}, 10.1 ± 0.6 ng mL^{-1} and 9.9 ± 0.2 ng mL^{-1}, respectively) agreed well with the certified values (2.00 ± 0.02 ng mL^{-1}, 10.0 ± 0.1 ng mL^{-1} and 10.0 ± 0.1 ng mL^{-1}). For verifying the accuracy of the determination of Cr(VI) by the HPLC-ICP-MS procedure, Certified Reference Material (Chromium Standard Solution 0.050 mg L^{-1} Cr(VI) ± 0.002 mg L^{-1} Cr(VI) K_2CrO_4 in H_2O) (Merck) was used. A good agreement was obtained between the determined Cr(VI) (46 ± 1 ng mL^{-1}) and the certified value (47 ± 2 ng mL^{-1}), which confirms the accuracy of the analytical procedure used.

Parameter	Type/value Speciation analysis	Type/Value Total element concentration analysis
Sample introduction		
Nebuliser	Miramist	Miramist
Spray chamber	Scott	Scott
Skimmer and sampler	Ni	Ni
Plasma conditions		
Forward power	1550 W	1550 W
Plasma gas flow	15.0 L min^{-1}	15.0 L min^{-1}
Carrier gas flow	0.75 L min^{-1}	1.05 L min^{-1}
Dilution gas flow	0.45 L min^{-1}	0.00 L min^{-1}
He gas flow	10 mL min^{-1}	4.5 mL min^{-1}
QP bias	− 120 V	− 100 V
Oct bias	− 100 V	− 18 V
Cell entrance	− 150 V	− 38 V
Cell exit	− 150 V	− 62 V
Deflect	− 75 V	− 2.6 V
Plate bias	− 150 V	− 60 V
Sample uptake rate	1.5 mL min^{-1}	0.3 mL min^{-1}
Data acquisition parameters		
m/z of isotopes monitored	^{52}Cr, ^{75}As, ^{95}Mo	^{52}Cr, ^{75}As, ^{95}Mo
m/z of internal standards	^{45}Sc, ^{72}Ge, ^{103}Rh, ^{115}In	^{45}Sc, ^{72}Ge, ^{103}Rh, ^{115}In
Total acquisition time	600 s	

Table 1. ICP-MS operating parameters.

	Eluent				
Time (min)	A (%)	B (%)	C (%)	Flow rate (mL min^{-1})	Steps in the chromatographic procedure
0.0	100	0	0	1.5	Separation
10.0	0	100	0	1.5	
10.1	0	0	100	1.5	Regeneration
13.0	0	0	100	1.5	
13.1	100	0	0	1.5	Equilibration
20.0	100	0	0	1.5	

Table 2. Chromatographic program for separation of chromate, molybdate and arsenate on the anion-exchange HPLC Mono Q column. Eluent A: MilliQ water. Eluent B: 0.7 mol L^{-1} NaCl. Eluent C: 2 mol L^{-1} NaCl.

Preparation of working standard solutions. Multielemental working standard solutions of chromate, molybdate and arsenate used for the speciation analysis were prepared from stock single standard solutions (containing 1000 ± 2 mg L^{-1} of element). First, 0.5 mL of stock standards were pipetted into 10 mL volumetric flasks and filled with MilliQ water to prepare a multielemental standard of chromate, molybdate and arsenate, containing 50.0 ± 0.1 mg L^{-1} of element. Aqueous multielemental standard solutions with concentrations 25.00 ± 0.05 mg L^{-1}, 10.00 ± 0.02 mg L^{-1} and 5.00 ± 0.01 mg L^{-1} were prepared from 50.0 ± 0.1 mg L^{-1} standard with appropriate dilution with water. Working standards in an alkaline buffer (0.2% NaOH + 0.3% Na_2CO_3, pH 12) in concentrations 50.0 ± 0.5 ng mL^{-1}, 100 ± 1 ng mL^{-1}, 250 ± 2 ng mL^{-1} and 500 ± 5 ng mL^{-1} were prepared by pipetting 0.1 mL of the appropriate aqueous multielemental standards added to 9.9 mL of an alkaline buffer.

Analytical procedure for simultaneous speciation of chromate, molybdate and arsenate. The procedure previously developed and validated in our group for simultaneous speciation of oxyanions chromate, arsenate, molybdate and vanadate in water leachates from recycled materials was used[31]. Briefly, 0.1 mL of sample was injected onto the column and linear gradient elution from water to 0.7 M NaCl (0 to 100%) applied for 10 min at a flow rate of 1.5 mL min^{-1}. The outlet of the chromatographic column was connected on-line with ICP-MS. After separation, the column was regenerated with 2 mol L^{-1} NaCl for 3 min and equilibrated with water for 7 min. The eluate from the regeneration step was directed to waste through a software controlled six-port valve. Chromatographic program for separation of chromate, molybdate and arsenate on the anion-exchange HPLC Mono Q column is given in Table 2.

If not stated otherwise, all the analyses were done at least in three replicates.

Lysimetric water. Three geotechnical composites, with commercial names Tersan, Tersan-P and Digeterm, which were composed of recycled waste materials, have been prepared in cooperation with Slovenian mining and waste recycling company Termit d.d. Later on, each of the composites was installed in the field in parallel in two zero-tension box-shaped lysimeters (dimension of each lysimeter was 3 m × 3 m, × 1.2 m), one in uncompacted and the other in compacted form. The lysimeters represented the proxy of an earth structures—geotechnical fills, which are commonly built-in civil engineering with the use of recycled materials. Simulation of a proper installation process, according to geotechnical principles, was performed by compacting each composite in separate lysimeter in 3 layers up to at least 92% of maximum dry density with a handheld vibrating plate compactor. The composites in uncompacted form, were on the other hand filled in the lysimeters without proper compaction process. Therefore, they had approximately 20% lower density. Uncompacted Tersan, Tersan-P and Digeterm also had 1000 times, 100 times and 10 times higher water permeability, respectively, due to higher porosity comparing to their compacted forms. With this experimental approach it was intended to simulate a scenario of what the potential environmental impacts would be if the composites were not installed properly (in line with basic geotechnical demands). The Tersan composite consisted of mining waste (50%), foundry sand (30%) and paper mill sludge (20%), and had a pH of around 8, the Tersan-P composite consisted of mining waste (50%), coal ash (40%), foundry slag (5%) and bottom ash from waste incineration (5%) and had a pH of around 12.5, and the Digeterm composite consisted of digestate from mechanic-biological treatment of municipal waste (40%), paper ash (40%) and mining waste (30%) and had a pH of around 11. For the preparation of geotechnical composites, materials were used as gathered from the industrial processes. Lysimetric water was collected in 1000 L reservoirs after rainfall events. Before analysis, samples were filtered through 0.45 µm filters. Total concentrations of Cr, Mo and As and speciation analysis of chromate, molybdate and asenate in lysimetric waters from uncompacted and compacted Tersan and Tersan-P composites were performed without sample dilution. Since the Digeterm lysimetric water from uncompacted and compacted composites contained high concentrations of dissolved substances, the samples were diluted 5 times before the determinations of the total element concentrations and speciation analysis.

Results and discussion

Capability of the HPLC-ICP-MS method for the simultaneous speciation analysis of chromate, molybdate and arsenate. To demonstrate the capability of the HPLC-ICP-MS analytical procedure for simultaneous speciation analysis of oxyanions CrO_4^{2-}, MoO_4^{2-} and AsO_4^{3-}, multielemental working standard solution of oxyanions containing 50 ng mL^{-1} Cr, Mo and As was prepared in alkaline buffer (pH 12) and injected onto the column. The pH of 12 was chosen because these oxyanions are the most stable under highly alkaline conditions. The chromatographic column used enabled the separation at high alkaline conditions[19,30,31]. Separated species were detected simultaneously by ICP-MS recording *m/z* 52, 95 and 75, respectively. Typical chromatograms of multielemental standard solution and blank sample (buffer) are presented in Fig. 1.

As can be seen, arsenate is eluted from 3.8 to 4.3 min, molybdate from 5.4 to 6.6 min and chromate from 6.4 to 7.5 min. Since elution profiles were recorded at different *m/z* by ICP-MS, simultaneous speciation analysis of molybdate and chromate is possible although their peaks are slightly overlapped. The peak areas of the separated oxyanions species (expressed as arbitrary units of counts per second, cps) are 75,800, 61,700 and 10,795 for chromate, molybdate, and arsenate, respectively. This is in agreement with their ionization energies, which are 6.7665 eV, 7.09243 eV and 9.7886 eV for Cr^+, Mo^+, As^+, respectively[32]. Accordingly, the peak area of the eluted As species is the smallest because As^+ has the highest ionization energy and is less efficiently ionized in plasma than Cr. Blank for Mo originates from metal parts of the pump and represents approximately 9% of the signal of the molybdate standard (50 ng mL^{-1} Mo). In the calculations, the blank for Mo was subtracted from the Mo signal.

The repeatability of measurement was tested for six consecutive simultaneous speciation analyses of a multielemental standard solution of chromate, molybdate and arsenate (50 ng mL^{-1} of element) in alkaline buffer solution (pH 12). The relative standard deviation was found to be ± 0.9%, ± 4.9%, and ± 4.1% for chromate, molybdate, and arsenate, respectively.

Limits of detection (LODs) and limits of quantification (LOQs) were calculated as the concentration that provides a signal (peak area) equal to 3 *s* or 10 *s* of the blank sample in the chromatogram. To calculate LODs and LOQs, 6 blank samples of the alkaline buffer solution were injected onto the column. LODs for chromate, molybdate and arsenate were found to be 0.16, 0.31 and 0.16 ng mL^{-1}, respectively, while LOQs were 0.53, 1.03 and 0.53, respectively. The linearity of measurement for chromate, molybdate and arsenate was obtained over the concentration range from LOQs to 500 ng mL^{-1} with the correlation coefficients better than 0.998.

As no certified reference material is available for the simultaneous determination of chromate, arsenate and molybdate, the accuracy of the analytical procedure was verified by the spike recovery test. For this purpose, multielemental standard solution of chromate, molybdate and arsenate (pH 12), containing 50 ng mL^{-1} of each element, was added to lysimetric water from Tersan-P compacted geotechnical composite. The recoveries were calculated as a ratio between found and added elemental concentration. The results are presented in Table 3.

Data from Table 3 indicate that recoveries for chromate, arsenate and molybdate of spiked leachate sample lied between 100 and 103%, which confirmed the accuracy of the analytical procedure.

Based on the above described analytical performances, the method was confirmed to be of adequate sensitivity for the simultaneous speciation analysis of oxyanions in lysimetric water.

Simultaneous speciation analysis of chromate, molybdate and arsenate in lysimetric water. The simultaneous speciation procedure was used to determine chromate, molybdate and arsenate in lysimetric water from geotechnical composites installed in field lysimeters. Total concentrations of Cr, Mo and

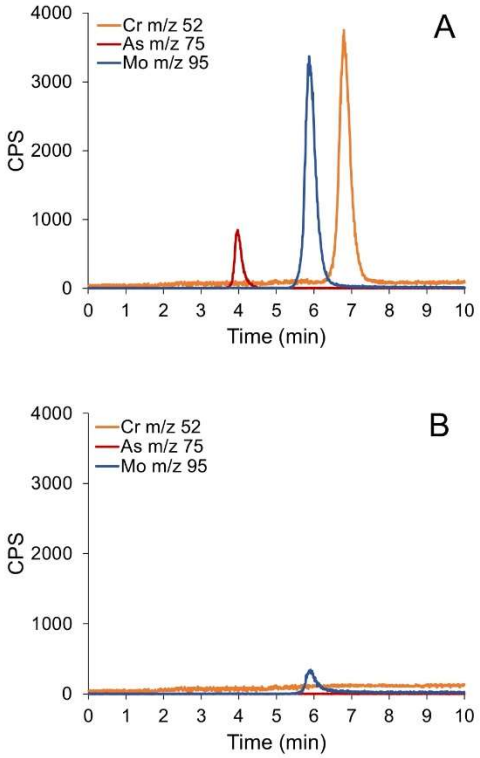

Figure 1. Simultaneous separation of chromate, molybdate and arsenate in 0.2% NaOH + 0.3% Na_2CO_3 buffer (pH 12) on the HPLC Mono Q column followed by ICP-MS detection at *m/z* 52, 95 and 75, respectively. (**A**) chromate, molybdate and arsenate (50 ng mL^{-1} of element), (**B**) blank.

Species	Elemental concentration in lysimetric water (ng mL^{-1})	Elemental concentration added (ng mL^{-1})	Elemental concentration in lysimetric water found (ng mL^{-1})	Recovery (%)
CrO_4^{2-} *m/z* 52	8.9 ± 0.1	50.0 ± 0.5	58.6 ± 0.6	100
MoO_4^{2-} *m/z* 95	55.4 ± 2.7	50.0 ± 0.5	109 ± 5	103
AsO_4^{3-} *m/z* 75	< 0.160	50.0 ± 0.5	50.7 ± 2.1	102

Table 3. Spike recovery test of chromate, molybdate and arsenate for lysimetric water from Tersan-P compacted geotechnical composite spiked with multielemental standard solution of oxyanions containing 50 ng mL^{-1} Cr, Mo and As. Concentrations in the unspiked and spiked samples were determined by simultaneous HPLC-ICP-MS speciation analysis. The results represent the average of three determinations of chromate, molybdate and arsenate with standard deviation of measurements.

As and chromate, molybdate and arsenate in lysimetric waters are presented in Table 4, while the corresponding chromatograms of elemental species in Fig. 2.

From data in Table 4 it can be seen that the total As concentrations in lysimetric water from Tersan and Tersan-P composites are low. Lysimetric water from uncompaced Tersan and Tersan-P composites contained 3.9 and 1.9 ng mL^{-1} of total As, respectively, while in lysimetric water from compacted composites, total As concentrations were about 0.5 ng mL^{-1}. The data in Table 4 also show that the water percolated from the Digeterm composite contains As in concentration of about 35 ng mL^{-1}, from both, the uncompaced and compacted composites. In the environment, inorganic As is present in its trivalent (As(III)) and pentavalent (As(V)) forms. Both, As(III) and As(V) species are toxic, but As(III) is more toxic than As(V)[33]. Speciation analysis (Table 4 and Fig. 2) indicates that arsenate (elution time from 3.8 to 4.3 min) was not detected in any of the analyzed

Sample	Total Cr (ng mL^{-1})	CrO_4^{2-} (expressed as Cr) (ng mL^{-1})	Total Mo (ng mL^{-1})	MoO_4^{2-} (expressed as Mo) (ng mL^{-1})	Total As (ng mL^{-1})	AsO_4^{3-} (expressed as As) (ng mL^{-1})
Tersan uncompacted	0.402	< 0.160	56.1	54.8	3.85	< 0.160
Tersan compacted	0.205	< 0.160	38.5	37.5	0.557	< 0.160
Tersan-P uncompacted	10.6	10.3	590	581	1.89	< 0.160
Tersan-P compacted	10.2	8.9	56.8	55.4	0.474	< 0.160
Digeterm uncompacted	80.8	3.33	653	537	36.8	< 0.800
Digeterm compacted	37.7	36.9	627	525	34.6	< 0.800

Table 4. Total concentrations of Cr, Mo and As in lysimetric water from uncompacted and compacted Tersan, Tersan-P and Digeterm geotechnical composites determined by ICP-MS, and concentrations of chromate, molybdate and arsenate determined by HPLC-ICP-MS. The results represent the average of three determinations of total Cr, Mo and As concentrations and concentrations of chromate, molybdate and arsenate. Measurement uncertainty for ICP-MS is better than ± 1.5%, while for the HPLC-ICP-MS better than ± 5%.

lysimetric water samples from uncompacted and compacted composites. Its concentrations were below LOD, 0.160 ng mL^{-1} in lysimetric water from Tersan and Tersan-P composites, and 0.800 ng mL^{-1} in lysimetric water from Digeterm composites. The higher LOD for Digeterm composites was due to 5 times dilution of samples. The data in Fig. 2 show a small peak of As eluted from 2.4 to 2.7 min in Digeterm lysimetric water from compacted composite, and two small peaks from 2.0 to 2.4 and 2.4 to 2.7 min from uncompacted composite. These As peaks most likely correspond to As complexed by soluble organic matter, which derived from the digestate, one of the main constituents of the Digeterm composite. Currently, there is no legislation regulating on the limit values of contaminants in lysimetric waters. Since the total As concentrations in Tersan and Tersan-P lysimetric water are much lower than those regulated by EU legislation for water intended for human consumption (10 ng mL^{-1} As)[34], it can be concluded that As in these geotechnical composites was effectively immobilized in compacted and uncompacted form, while in the Digeterm composite, As immobilization was not as effective. However, the risk of groundwater contamination is low.

The data in Fig. 2 and Table 4 further indicate that Mo is eluted as the molybdate anion at concentrations close to the total Mo content in the individual lysimetric waters studied. In the environment, Mo is commonly present in the hexavalent oxidation state (in the form of MoO_3 and molybdates) and as tetravalent Mo (mainly in the form of molybdenite (MoS_2)). Mo is an essential micronutrient for plants, animals and humans, while exposure to excessive levels of molybdate is associated with adverse health effects (mostly towards respiratory and renal functions). Mo is widely used in metallurgical applications and is frequently found as environmental pollutant. In the aquatic environment, under physiological conditions (pH > 6.5), Mo compounds are rapidly transformed to MoO_4^{2-}. In low redox environments, molybdate can be reduced to MoS_2. Mo is more mobile under alkaline conditions, while adsorption increases with decreasing pH. The primary route of human exposure to Mo is food intake and, to a lesser extent, consumption of drinking water[35]. Mo concentration is not regulated in lysimetric water or public drinking water supplies. In line with the need to re-evaluate the latest World Health Organization (WHO) guidelines for drinking water quality, a health-based Mo level of 70 ng mL^{-1} was proposed[36]. As can be seen from the data in Table 4, Mo concentrations in the Tersan lysimetric water with a pH close to 8 are below 70 ng mL^{-1}, in the uncompacted composite 54.8 ng mL^{-1} and in the compacted 37.5 ng mL^{-1}. The higher Mo content in the lysimetric water from uncompacted composite is due to its less effective physical immobilization associated with a 1000 times higher water permeability compared to the compacted composite. In the Tersan-P lysimetric water with a pH of about 12.5, Mo is highly mobile in uncompacted composite, while in the compacted composite it is effectively immobilized (by physical mechanisms related to 100 times lower water permeability compared to uncompacted composite). In lysimetric water from uncompacted composite, Mo concentrations are 10 times higher than those in water from compacted composite. The behavior of Mo in Tersan-P and Tersan lysimetric water (pH 12.5 and 8, respectively) is consistent with the fact that Mo is more mobile under alkaline conditions, while it is more efficiently adsorbed on the surface of Fe oxyhydroxides at lower pHs[35]. Consequently, its concentration in lysimetric water from uncompacted Tersan composite is significantly lower than in water from uncompacted Tersan-P composite. In Digeterm lysimetric water with high pH (pH around 11), physical immobilization of Mo is not effective. Approximately 530 ng mL^{-1} is leached into lysimetric water from uncompacted and compacted Digeterm composites. Physical immobilization is impaired due to the presence of significant amounts of organic matter derived from the digestate, which is a constituent in the Digeterm composite (40%), making it more porous in both, compacted and uncompacted forms. The concentrations of molybdate in lysimetric water from uncompacted and compacted Tersan (54.8 and 37.5 ng mL^{-1} Mo, respectively), and compacted Tersan-P (55.4 ng mL^{-1} Mo) composites do not represent an environmental hazard. On the other hand, lysimetric water from uncompacted Tersan-P (581 ng mL^{-1} Mo) and uncompacted and compacted Digeterm composites 537 and 525 ng mL^{-1} Mo, respectively) may pose an environmental threat, especially in terms of groundwater contamination with molybdate.

The data in Table 4 and Fig. 2 also show that the total concentration of Cr in the lysimetric water from the uncompacted and compacted Tersan composite was below 0.4 ng mL^{-1} Cr, while no chromate was detected (values were below 0.160 ng mL^{-1} Cr). In lysimetric water from uncompacted and compacted Tersan-P composite, total Cr and chromate concentrations were similar (approximately 10 ng mL^{-1} Cr). In the lysimetric water from

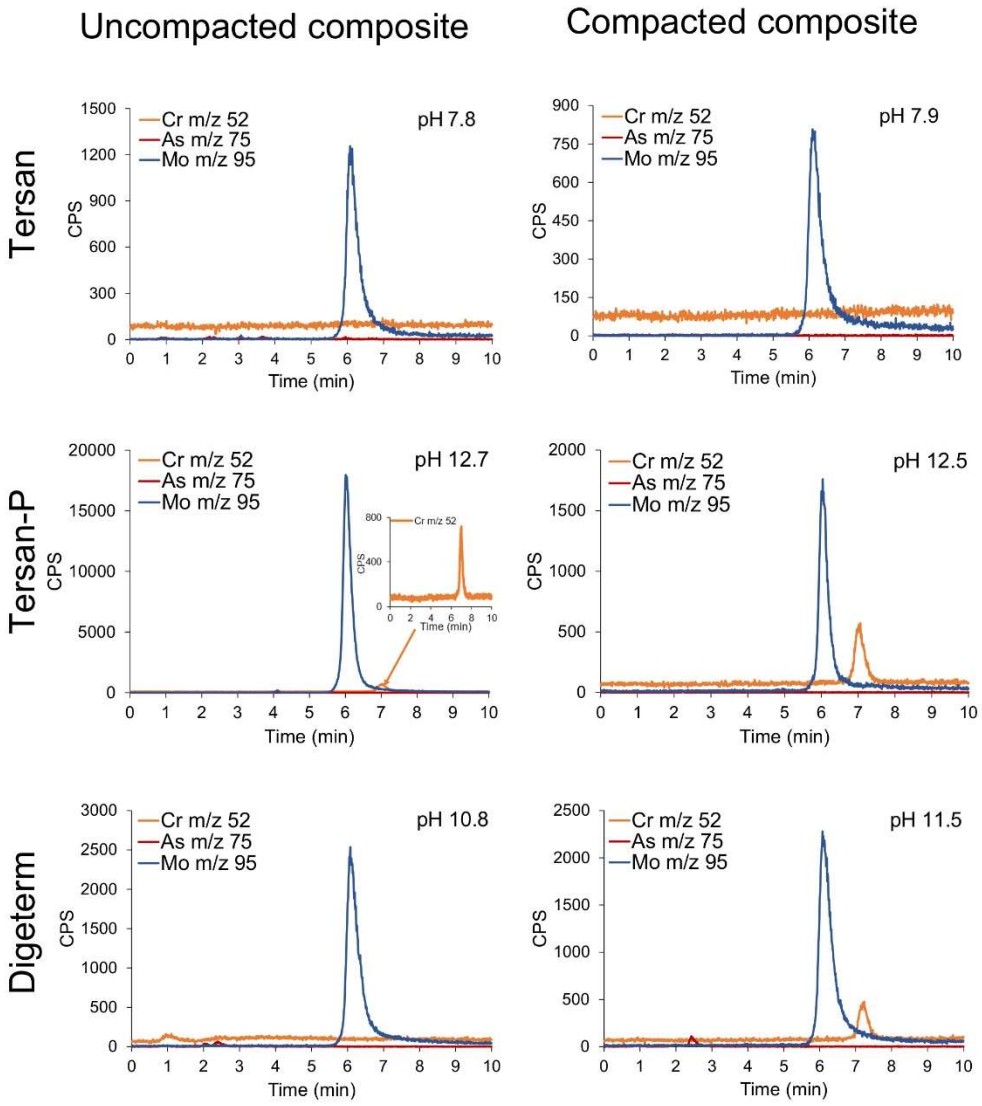

Figure 2. Simultaneous speciation of chromate, molybdate and arsenate in lysimetric water from uncompacted and compacted geotechnical composites, using the HPLC Mono Q column for separation and ICP-MS for detection of separated species at *m/z* 52, 95 and 75, respectively. In Digeterm composites, sample was diluted 5 times before speciation analysis. Total element concentrations and concentrations of chromate, molybdate and arsenate are provided in Table 4.

compacted Digeterm composite, the content of total Cr and chromate was about 37 ng mL^{-1} Cr. In the water from uncompacted Digeterm composite the total Cr content was significantly higher (81 ng mL^{-1}) than the chromate content (3.3 ng mL^{-1} Cr). In the environment, the most stable are trivalent and hexavalent Cr compounds. The latter is highly toxic, carcinogenic and mutagenic[37]. Due to intensive use in different industrial applications, Cr often pollutes the environment. Cr(VI) compounds are highly mobile in environmental compartments and are more stable at alkaline pHs. Cr(VI) is readily reduced by natural reducing agents such as Fe(II), S^{2-} and organic

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Author contributions

M.Dj.: Planning and performance of experiments, ICP-MS measurements, writing of the draft manuscript; L.L.: Performance of speciation analysis; P.O.: Design of experiments, samplings, review and editing; A.M.: Design of experiments, review and editing, supervision; A.M.P.: review, J.Š.: Design of experiments, review and editing, supervision. R.M.: Design of experiments, review and editing. All authors have read and agreed to the submitted version of the manuscript.

matter. Humans can be exposed to toxic Cr(VI) by consuming contaminated drinking water[21]. Current legislation does not regulate Cr concentrations in lysimetric waters. The total concentrations of Cr in Tersan and Tersan-P lysimetric water are much lower than those regulated by EU legislation for water intended for human consumption (50 ng mL^{-1} Cr)[34], and WHO guidelines for drinking water quality (50 ng mL^{-1} Cr)[38]. The data in Fig. 2 and Table 4 show that the chromate is effectively immobilized in the compacted Digeterm composite. Concentrations of total Cr and chromate in Digeterm lysimetric waters (approximately 37 ng mL^{-1}) are lower than those in the legal requirements for drinking water. In the uncompacted Digeterm composite, the higher porosity of the material (10 times higher water permeability that in the compacted composite) allows the release of soluble organic matter deriving from the decaying organic compounds of the digestate. The released organic matter lowers the pH by almost one unit (pH of lysimetric water in the compacted Digeterm composite was 11.5, while in the uncompacted 10.8). Lower pH and the more efficient contact of Cr(VI) with the organic matter have a favorable effect on its reduction to Cr(III). Of the total Cr concentration 81 ng mL^{-1}, only 3.3 ng mL^{-1} remained in its hexavalent form in lysimetric water from the uncompacted Digeterm composite. With regard to toxic chromate concentrations, the investigated lysimetric waters do not represent environmental hazard.

Conclusions

The potential of simultaneous speciation analysis in studies of the environmental impacts of Cr, Mo and As in geotechnical composites made of different recycled materials installed in field lysimeters was presented.

The results revealed that speciation analysis provides complementary information on the immobilization of Cr, Mo and As and their chemical species in various geotechnical composites, and allows tracking their release in lysimetric water. Arsenate was not present in lysimetric water from uncompacted and compacted Tersan and Tersan-P composites. In Digeterm lysimetric waters, As was most likely complexed by organic matter, while its concentrations (around 37 ng mL^{-1} As) do not represent environmental hazard. Molybdate was detected in all the analyzed samples at concentrations close to the total Mo content. In Tersan (uncompacted and compacted) and Tersan-P compacted composites Mo was leached into lysimetric water in concentrations lower than 56 ng mL^{-1}, which are not hazardous to the environment. In Tersan-P (uncompacted) and Digeterm (uncompacted and compacted) composites, Mo was not effectively immobilized and its release into lysimetric water as molybdate in concentrations 525 to 580 ng mL^{-1} Mo, posed an environmental risk for groundwater pollution. Hexavalent Cr was effectively immobilized in all the studied geotechnical composites. Due to the more intensive release of soluble organic matter from the uncompacted Digeterm composite, chromate reduction was very effective in uncompacted composite (total Cr 81 ng mL^{-1}, chromate 3.3 ng mL^{-1} Cr), while in the compacted composite the hindered contact with organic matter prevented chromate reduction (total Cr 37.7 ng mL^{-1}, chromate 36.9 ng mL^{-1} Cr). However, chromate concentrations released into the lysimetric water from compacted Digiterm composite did not represent environmental hazard. Speciation analysis not only provided data on the presence of toxic elemental species, but also made an important contribution to understanding the physicochemical processes that govern their toxicity. It should be emphasized that simultaneous speciation analysis is a cost-effective analytical tool and allows for rapid analysis of toxic elemental species. Such an analytical approach can be used in many other environmental studies, where a relatively large number of samples need to be analyzed, and for environmental monitoring purposes.

Data availability

Data of the current study are available from the corresponding author on reasonable request.

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Competing interests
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Chapter 4

Conclusions

Remediation of contaminated soils is one of top environmental priorities worldwide. Paper ash is a promising additive for remediation of heavily contaminated soils with metals, but no long-term remediation efficiency has been reported. There is also no evidence on the immobilization mechanisms of metals after the remediation.

Data from our investigation based on a sequential extraction procedure and XRD analyses revealed that paper ash is an effective additive for the immobilization process in remediation of Cd, Pb, and Zn in contaminated soils. In the remediated soil composites, the Cd, Pb, and Zn were transferred from the easily soluble, highly mobile soil fractions to the sparingly soluble fractions of soil composites. Consequently, their concentrations in the water-soluble and exchangeable soil fractions were reduced far below the limit values set by national legislation. The mechanism of immobilization for the Cd, Pb, and Zn with paper-ash involved the formation of hydration products from the paper-ash, which resulted in the precipitation of insoluble Cd, Pb, and Zn hydroxides, while through the carbonation process, Cd, Pb, and Zn were stabilized in insoluble carbonates. The experimental data further confirmed the long-term efficiency of the soil remediation with paper ash and proved that the remediated soil composites do not present an environmental hazard.

The outcomes from this part of research contribute to sustainable remediation of highly contaminated soils with Cd, Pb and Zn using waste materials generated in the paper and pulp industry. It confirmed the hypothesis that the easily soluble fractions of the soil can be immobilized with paper ash into the sparingly soluble mineral phases of the soil, which after remediation possess long-term stability and thus the environmental acceptability of the newly formed building composites.

Open pits can cause environmental problems and also have a negative social perception, so in most countries is mandatory to reclaim them. One of the most sustainable ways of reclamation is installation of geotechnical fill made of different recycled waste. Such geotechnical composites have appropriate mechano-physical characteristics and are also environmentally acceptable.

In this research, environmental impacts of three geotechnical composites made from different waste materials installed in field lysimeters, and in the laboratory scale were investigated. The results showed that although the concentrations of PHSs in the aqueous leachate of waste materials used for the preparation of composites exceeded the limit values set by national legislation, the immobilization processes that occurred after processing the waste in composites significantly reduced the leaching of PHSs from the composites. The extent of PHSs release from the composites depended on the composition and degree of compaction during installation of the geotechnical composites. The data obtained in the standardized laboratory leaching tests showed that Composite 1 made

from mine waste (50 wt. %), foundry sand (30 wt. %) and paper-mill sludge (20 wt. %), and Composite 3 made from mine waste (50 wt. %), coal ash (40 wt. %), solid-waste incineration bottom ash (5 wt. %) and foundry slag (5 wt. %) complied with the Slovenian limits for end-of-waste status, while in the leachate from Composite 2 made from digestate (40 wt. %), paper ash (40 wt. %) and mine waste (20 wt. %), Cu, Mo and Ni exceeded these limits. The results of the analysis of percolated water leached from the field lysimeters in uncompacted and compacted form, supported by data from multielemental speciation analysis of chromate, molybdate and arsenate, showed that immobilization of the PHSs was more effective in the lysimeters in compacted form, with the exception of chromate that was more effectively reduced in uncompacted Composite 2 due to more efficient leaching of reducing substances released from the organic matter (digestate) present in the composite. After one year of field monitoring, the trends in the cumulative mass release of the PHSs in percolated water decreased for Composite 3, which achieved an effective long-term immobilization. For Composite 1 and Composite 2, increasing cumulative mass release trends persisted but decreased over time. In Composite 2 and Composite 3, due to the addition of ashes, pozzolanic and hydration reactions took place, resulting in the formation of new mineral phases that incorporated PHSs into their stable crystal structures. Consequently, higher immobilization efficiency was achieved. The results also revealed that Composite 1 and Composite 3 exhibit long-term environmental acceptability and can be used for the rehabilitation of abandoned open pit mines, while Composite 2 can be used for closure operations at non-hazardous waste landfills. In such a way, locally available waste materials are valorised and transformed into valuable and sustainable recycled materials.

The results of this part of study confirmed the hypothesis that tailored mixing of waste materials in geotechnical composites and their optimal installation on field can result in environmental acceptability of geotechnical composites and highlighted the potential for sustainable waste management in the construction sector.

Chapter 5

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Publications Related to the Thesis

Journal Articles

Đurić, M., Zalar Serjun, V., Mladenovič A., Mauko Pranjić, A., Milačič, R., Ščančar, J., Urbanc, J., Mali, N., Pavilin, A., Turk, J., Oprčkal, P. (2023). Environmental acceptability of geotechnical composites from recycled materials: comparative study of laboratory and field investigations. *International Journal of Environmental Research and Public Health, 20(3).* DOI: 10.3390/ijerph20032014.

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Biography

Author of this thesis Marija Đurić started her higher education at the Faculty of Chemistry, University of Belgrade, studying Environmental Chemistry, where she finished her bachelor and master studies. In 2018, she finished her master's degree with a thesis entitled "Investigation of the effect of high density polyethylene on the yield and composition of pyrolysis products of bar lithotype lignite" under the supervision of Prof. Dr. Ksenija A. Stojanović. For her master thesis she received the best master's thesis award from the "Professor Mirjana Šaban" Fund.

In October 2018, she started working at the Slovenian National Building and Civil Engineering Institute as a Young Researcher under the supervision of Dr. Ana Mladenović, and enrolled in the doctoral study at the Jožef Stefan International Postgraduate School, Ecotechnologies programme under the supervision of Prof. Dr. Janez Ščančar.