Journal of Environmental Management 308 (2022) 114580

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

The environmental impact of historical Pb-Zn mining waste deposits in Slovenia

Miloš Miler *, Špela Bavec, Mateja Gosar

Geological Survey of Slovenia, Dimičeva ulica 14, SI-1000 Ljubljana, Slovenia

ARTICLE INFO

Keywords:
Metals
Stream sediment
Stream water
Characterisation
Mineral solubility

ABSTRACT

Mining waste deposits (MWDs) represent significant and constant pollution source for the environment worldwide, thus it is very important to identify and diminish their environmental impacts. The aim of this study was to determine long-term environmental impacts and their temporal variations of MWDs in Pb–Zn mining districts in Slovenia and assess stability of potentially harmful element (PHE)-bearing phases in stream water. The results showed that investigated MWDs are important source of PHEs in stream sediments and that PHEs mostly occur as fine-grained and liberated PHE-bearing ore minerals. MWDs have generally stronger impact on sediments of smaller streams draining MWDs and main streams close to their confluences, however, fine-grained PHE-bearing material is transported along major watercourses over long distances causing regional pollution. Main ore minerals are mostly soluble in stream water. However, measured PHE leaching potential of MWDs is negligible. PHE levels in stream waters are thus low, demonstrating that drainage of MWDs predominantly contributes to PHE pollution in solid particulate form. Possible long-term remediation solution that would reduce environmental impact is recovery of metals from fine grain size fractions of MWDs, which could become an effective practice in sustainable management of historical MWDs. However, further studies of MWDs' secondary resource potential, processing technology and evaluation of environmental aspects of extraction are needed.

1. Introduction

Mining and milling operations and smelting-refining processes are important anthropogenic sources of potentially harmful elements (PHE) in the environment (Dudka and Adriano, 1997; Jordan et al., 2009). Mining itself affects relatively small areas, however, ore processing and tailings/mining waste deposits (MWD hereafter) near the mining areas have more significant impact (Hoskin et al., 2000; Jerzykowska et al., 2014; Shu et al., 2018). The issues associated with mining wastes are of global importance as almost every country has or has had a mining industry and thus related mining waste issues. Studies on pre-mining characteristics and on post-mining practises are necessary to understand the sources and mechanisms of contaminant behaviour and to enable sustainable rehabilitation of mining waste (Anawar, 2015). Behaviour of PHEs and environmental impacts are unique to each specific mining waste environment. Physico-chemical properties of the tailings may lead to leaching of PHEs that can be transported by acid mine drainage to the MWD surroundings including surface soils overlying mining waste (Rodríguez et al., 2009). Although the mature systems of old MWDs relatively strongly bind PHEs from primary sulphides, there is still some release of PHEs, which are mobile in soils and can potentially cause local environmental problems (Jerzykowska et al., 2014). Fresh and weathered tailings may contain similar PHE contents, however they commonly occur in different mineral forms (Shu et al., 2018). Apart from pH, mineralogy and liquid/solid ratio also significantly affect leaching and in-vitro bioaccessibility of PHEs from historic MWDs (Helser and Cappuyns, 2021). Despite their negative environmental impacts, historical Pb–Zn MWDs have been recognised as possible secondary resources of valuable metals that remained in the waste (Dino et al., 2018; Helser and Cappuyns, 2021).

To understand the mechanisms of formation, transport and fate of waste derived PHEs, geochemical and mineralogical characterisation of the waste material is crucial, especially of waste deposited under subaerial conditions where it is exposed to precipitation leaching and oxidation processes (Lindsay et al., 2015 and references therein; Jamieson et al., 2015 and references therein; Anawar, 2015 and references therein). Oxidation of sulphides, particularly pyrite, leads to acidification, which is generally associated with decrease in pH, release

* Corresponding author.
E-mail addresses: milos.miler@geo-zs.si (M. Miler), spela.bavec@geo-zs.si (Š. Bavec), mateja.gosar@geo-zs.si (M. Gosar).

https://doi.org/10.1016/j.jenvman.2022.114580
Received 7 October 2021; Received in revised form 4 January 2022; Accepted 19 January 2022
Available online 3 February 2022

of PHEs and precipitation of Fe (III)-(oxy)hydroxides and Fe (III)-hydroxy sulphates. In contrast, dissolution of carbonate, (oxy)hydroxide, and silicate minerals in mining waste has an important neutralising effect (Jurjovec et al., 2002). When present in abundant concentrations, these minerals control PHE mobility and oxidation rates. In addition, secondary precipitates may form cemented layers within the oxidation zone, limiting pore water migration and oxygen ingress, thus inhibiting sulphide mineral oxidation, but also their further neutralization (Salomons, 1995). Reactivity of the material is also navigated by chemical composition, grain size, crystallinity, texture, encapsulation, and grain-scale heterogeneity (Jamieson et al., 2015). Metal contents in the environment surrounding MWDs increase in prevailing wind directions and suggest that wind transport of dust is an important factor affecting the spread of pollution (Rodríguez et al., 2009). Dust emissions from MWDs are strongly influenced by land use and climate change (Tegen et al., 2004), which has already been observed in some regions (Zhang et al., 2003; Prospero and Lamb, 2003). Due to the presence of PHEs in mining waste material, increased dust mobility is of particular concern, as it contributes to the transport and accumulation of contaminants in water, sediments, soil, and biota. Nevertheless, the main source of pollution to aquatic ecosystems in mining districts is still mining wastewater discharged to surface waters (Kříbek et al., 2014 and references therein).

In Slovenia, there are 33 metal mines, which have all been closed in the past century, and 156 related MWDs have been registered in total (Gosar et al., 2020). Among these, 61 were classified as waste with low to critical environmental impact, based on the deposit size, stability, erosion and PHE content (Gosar et al., 2014, 2017). Of these, 41 are Pb–Zn MWDs located in three different mining districts in north-northeastern (NNE) (Mežica area) and central part of Slovenia (Litija and Pleše areas). The environment in the Mežica area is heavily polluted with PHEs, particularly soils (Šajn, 2006; Zupan et al., 2008; Finžgar et al., 2014) and Meža River sediments (Svete et al., 2001; Fux et al., 2007; Gosar and Miler, 2011; Žibret et al., 2018), which was partly attributed to washing out of MWD material (Miler and Gosar, 2012). Also in Litija area, the PHE pollution of soils and attic dust was partly ascribed to mining and smelting activities (Jemec and Šajn, 2007; Šajn and Gosar, 2007, 2014), while the erosion of contaminated soil affected Sava River sediments (Žibret and Gosar, 2017). In the Pleše area, environmental impacts of mining and ore processing have not been studied yet, despite several events that caused erosion of barite-rich mining waste into the valley below the mine, which covered and contaminated most of the area.

Based on previous findings, the present study systematically addresses Pb and Zn mining waste deposits, stream sediments and surface stream water in the three Slovenian study areas by employing multimethod approach in order to achieve a comprehensive assessment of environmental impact of mining waste and propose effective MWD management practices. The aims of the study were to (a) estimate contribution of MWDs to sediment and water pollution, assess distribution of PHEs and their temporal variations, (b) identify PHE-bearing phases and assess their stability in stream water and their impact on water pollution and (c) determine origin of Pb-bearing phases and their fate in the environment.

2. Study areas

The largest Pb–Zn mine in Slovenia, located in Mežica area (about 60 km NNE of Ljubljana), is an epigenetic, Mississippi Valley-type (MVT) ore deposit where mineralization occurs in Middle to Upper Triassic dolomites and limestones (Drovenik et al., 1980; Štrucl, 1984; Zeeh et al., 1998; Spangenberg et al., 2001). The main exploited ore minerals were galena, sphalerite, wurtzite, cerussite, smithsonite, wulfenite, descloizite, hemimorphite and anglesite, associated with pyrite, marcasite and limonite (Drovenik et al., 1980; Štrucl, 1984). Mining of Pb–Zn ore and primary Pb smelting in the Mežica area ceased in 1995 and the smelter was transformed into a Pb-based waste and used Pb-acid battery recycling (secondary Pb processing) plant. There are 32 critical MWDs in Mežica area (Fig. 1), with a total volume of approximately 7,400,000 m^3 (Gosar et al., 2020), where waste material was deposited as spoil heaps in nearby narrow valleys and on steep slopes of small streams. They mostly consist of carbonate gangue material, which hosted the Pb–Zn ore deposits (Gosar and Miler, 2011; Miler and Gosar, 2012; Gosar et al., 2013 and references therein), but also of low-grade ore and separation tailings or slag.

In Litija area (about 25 km east of Ljubljana), a polymetallic hydrothermal vein mineral deposit is situated, which was developed in Carboniferous-Permian mudstones, shales, siltstones, quartz sandstones and conglomerates. Most important ore minerals were cerussite, barite, cinnabar, galena, sphalerite, chalcopyrite and limonite, which were mined and processed until 1965. The 7 critical MWDs in Litija (Fig. 2), with a total volume of about 130,000 m^3 (Gosar et al., 2020), are composed of quartz sandstone and shale as gangue material and low-grade ore.

One of the oldest mines in Slovenia, located in Pleše area, 10 km southeast of Ljubljana, is a polymetallic hydrothermal syngenetic to epigenetic ore deposit with mineralised lenses within Carboniferous-Permian clastic rocks and partly in overlying Lower Triassic dolomites (Drovenik et al., 1980; Mlakar, 2003). Main ore minerals galena, barite and sphalerite, associated with minor chalcopyrite, pyrite, tetrahedrite, cinnabar, metallic mercury and myargirite (Sedlar, 1950; Drovenik et al., 1980), were exploited and processed (galena) until 1963 (Mlakar, 2003 and references therein). The 2 critical MWDs in Pleše area (Fig. 3), which have a total volume of 110,000 m^3 (Gosar et al., 2020), are composed of gangue quartz sandstone and conglomerate, micaceous shale, claystone and dolomite, as well as low-grade ore.

All study areas have relatively similar meteorological conditions, which contribute to behaviour of MWDs. The Mežica area has prevailing mean annual temperature of 9 °C, relative humidity of 79% and precipitation rate of 1400 mm, while Litija and Pleše areas have mean annual temperature of 11 °C, relative humidity of 75% and precipitation rate of 1300 mm (Slovenian Environment Agency, 2021a).

3. Materials and methods

3.1. Sampling and sample preparation

Sampling campaigns were carried out in 2013 (late autumn) and 2017 (early summer) in the Mežica, Litija and Pleše areas.

Mining waste material was sampled in 2013 at 7 MWDs (4 in Mežica, 2 in Litija and 1 in Pleše area). The collected samples comprised 3 kg composites of 5 subsamples taken at different locations on the surface of each MWD, including upper 20 cm of material, which is most likely to be transported by surface runoff or wind resuspension.

Sediments of 1st, 2nd and 3rd order streams (relative to MWD locations and modified after Horton (1945)) were sampled in 2013 at 22 locations in Mežica (Fig. 1; Supplementary Table S1), 7 in Litija (Fig. 2; Supplementary Table S1) and 5 in Pleše area (Fig. 3; Supplementary Table S1). In 2017 sampling was repeated at selected locations (13 in Mežica, 7 in Litija and 1 in Pleše area) to observe changes in PHE distribution and mineral composition over a 3-year period. Each 1–2 kg sample consisted of 5 subsamples acquired over a distance of 20–40 m.

Mining waste and stream sediment samples were air dried at between 25 and 30 °C for 14 days and sieved to fraction <0.125 mm for chemical analysis. Nine of the sieved 1st order stream sediment samples (6 from Mežica, 2 from Litija and 1 from Pleše area), taken below each MWD, and 7 of the sieved mining waste samples (4 from Mežica, 2 from Litija and 1 from Pleše area) were analysed with scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS). For determination of water leachable fraction, air-dried mining waste samples were sieved to a fraction <4 mm.

Stream waters were sampled only in 2017 at the same sampling

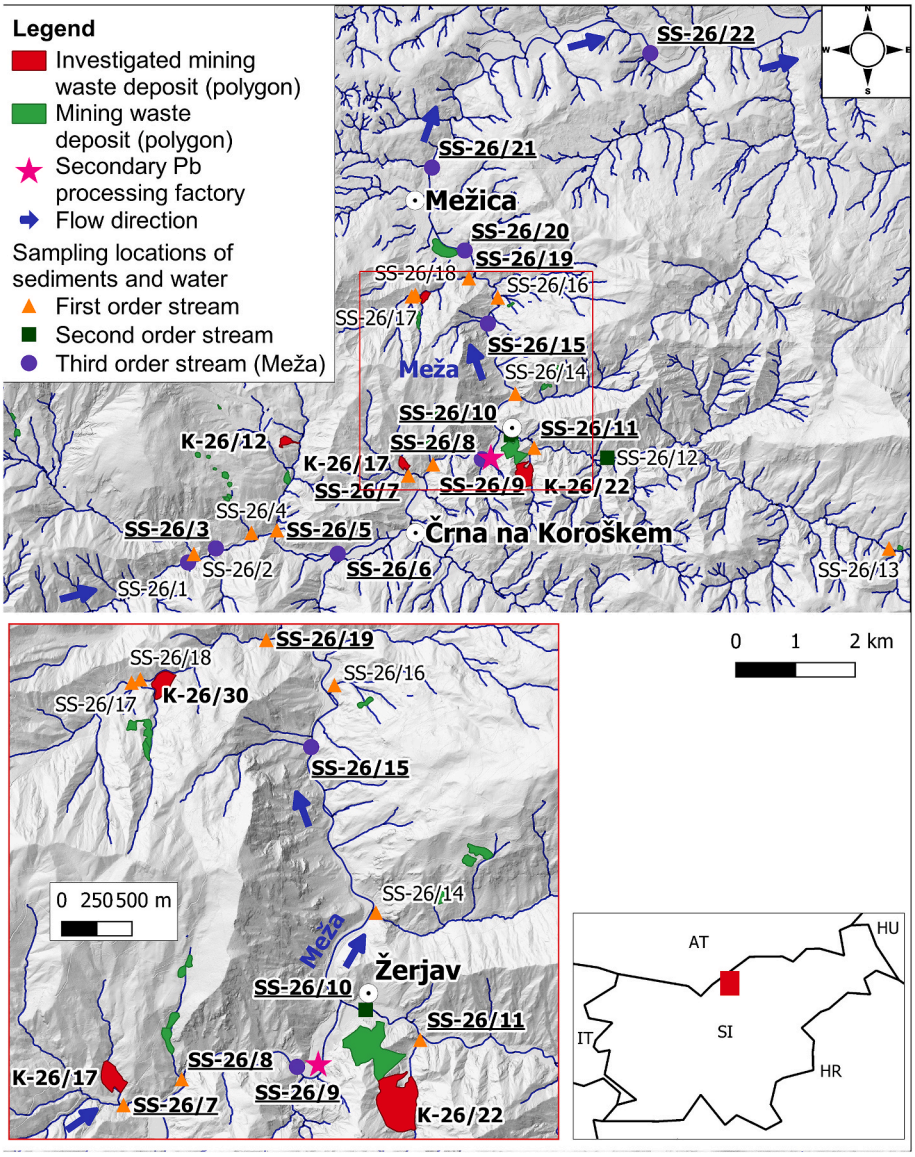

Fig. 1. QGIS map of MWDs and sampling locations in Mežica mining area. Investigated MWDs are marked in bold. At underlined and bolded sediment and water sampling locations, samples were taken in 2013 and 2017, at others only in 2013. Detail of the central part of study area (red square) is shown in figure at the bottom left. Lidar hillshade and hydrography layers were taken from Slovenian Water Agency (2018). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

locations as stream sediments. Water samples were filtered through <0.45 μm sterile surfactant-free cellulose acetate (SFCA) filters using sterile PP syringes, stored in rinsed 60 ml HDPE bottles at temperature between 8 and 10 °C and transported to the laboratory.

3.2. Chemical analyses of mining waste material and stream sediments

Chemical analyses of mining waste material and sediments were performed in Bureau Veritas Mineral Laboratories in Vancouver, Canada. Contents of 15 chemical elements (As, Ba, Cd, Ce, Co, Cr, Cu, Hg, La, Mo, Ni, Pb, Sb, Y and Zn) were measured by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) after the aqua regia (AR) digestion of 15 g sample ($HCl:HNO_3:H_2O$ at a ratio of 1:1:1 at 95 °C). Additionally, Pb isotopes were measured in sediments from 2017 and mining waste material using quadrupole-based ICP-MS after AR digestion, according to established protocols used at Bureau Veritas Mineral Laboratories. The mass bias was corrected by using NIST-981-1Y standard, produced by the National Institute of Standards and Technology and provided by the laboratory, between sample measurements. Accuracies of analytical methods in 2013, estimated by calculation of the relative systematic error between the measured and recommended values of reference materials (OREAS 45P and OREAS 133B produced by Ore Research & Exploration Pty Ltd, and DS10 and GC-7 produced by Bureau Veritas Mineral Laboratories) were in the range of 2.4–26.7% with a median of 6.2% for ICP-MS and 0.9–2.6% with a median of 1.8% for ICP-ES. The precision was estimated from relative differences between duplicate measurements by calculation of relative percentage difference (%RPD). The calculated precision was in the range of 1–14.4% with a median of 6.3%. Accuracy of ICP-MS analysis in 2017 varied from 0.3 to 11.1% with a median of 3.0%, based on reference materials OREAS 151b produced by Ore Research & Exploration Pty Ltd and DS10, while the precision ranged between 1.6 and 15.3% with a median of 4.9%. Accuracy of quadrupole-based ICP-MS Pb isotope analysis in 2017 was in the range of 1.3–11.6% with a median of 5.5%, based on reference material NIST-983-1Y produced by the National Institute of Standards and Technology and provided by the laboratory, while the precision was 3.4% (0–7.1%). Water leaching tests of mining waste material were conducted in ERICo (Velenje, Slovenia) according to standard SIST EN 12457–2: 2004. Concentrations of As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb and Zn in water leachates of mining waste were determined using ICP-MS according to standard SIST EN ISO 17294–2: 2005. The results of chemical analyses of stream sediments and mining waste material were statistically treated by calculating mean, median, 25th and 75th percentile, minimum and maximum

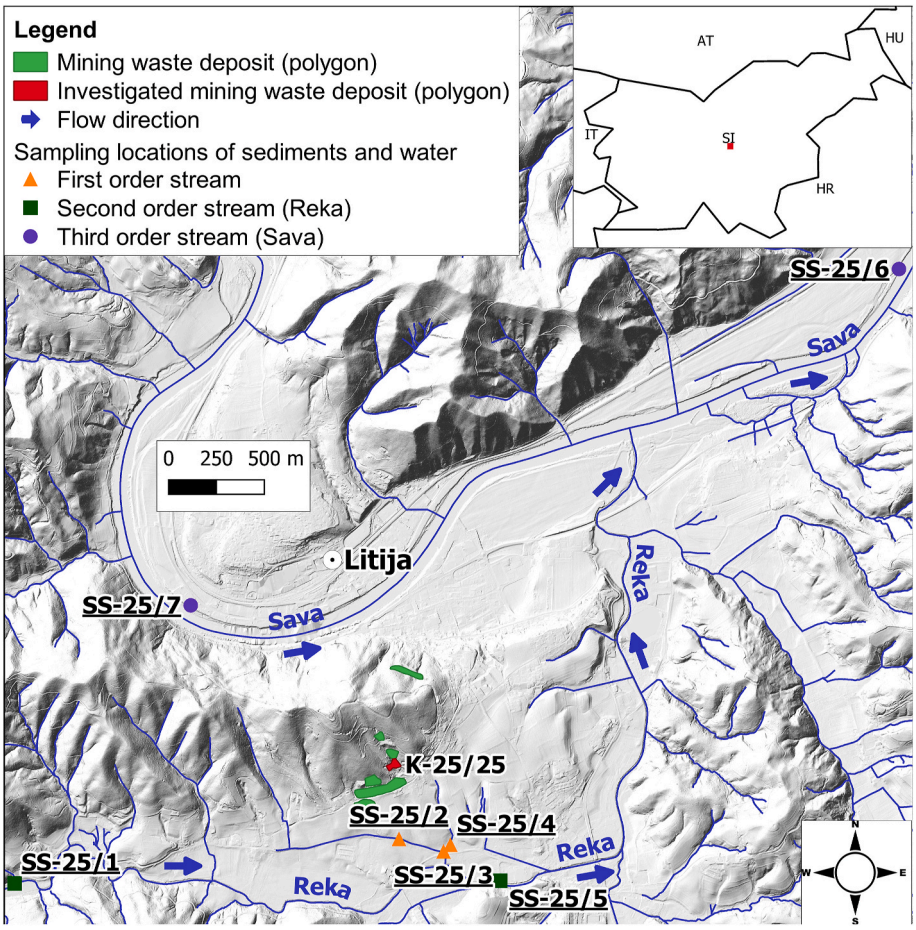

Fig. 2. QGIS map of MWDs and sampling locations in Litija mining area. Investigated MWDs are marked in bold. At underlined and bolded sediment and water sampling locations, samples were taken in 2013 and 2017. Lidar hillshade and hydrography layers were taken from Slovenian Water Agency (2018).

values.

3.3. Chemical analysis of stream water

Chemical analysis of As, Ba, Cd, Ce, Co, Cr, Cu, Hg, La, Mo, Ni, Pb, Sb, Y and Zn in stream water was performed in Activation Laboratories Ltd. (Actlabs), Canada using ICP-MS. Prior to chemical analysis, samples were acidified with ultra-pure nitric acid to dissolve potentially precipitated elements. The accuracy of analytical method ranged from 0.6 to 16.6% with a median of 5.2%, based on reference material IV-STOCK-1643 provided by the laboratory, while precision ranged between 0 and 50%, with a median of 1.8%. The results of chemical analyses of stream water were statistically treated by calculating mean, median, 25th and 75th percentile, minimum and maximum values.

3.4. Physico-chemical properties of surface stream water

At each sampling location, pH, temperature (T), oxidation-reduction potential (Eh), electrical conductivity (EC) and concentration of dissolved oxygen (DO) in surface water were measured in the field, simultaneously with sampling of water, by using a portable multimeter (Thermo Scientific Orion Star A329). The results of measurements of physico-chemical properties of stream water were statistically treated by calculating mean, median, 25th and 75th percentile, minimum and maximum values.

3.5. SEM/EDS analysis

Selected sediments of 1st order streams draining MWDs and mining waste material samples were analysed with SEM/EDS to determine chemical and mineral composition of PHE-bearing phases, their size and quantity and relative mineral abundances in samples. Each sample was homogenized, mounted on carbon tape, coated with carbon and inspected at magnification of 100 × (sediments) and 200 × (mining waste material) in the backscattered electron (BSE) mode using a JEOL JSM 6490LV SEM, coupled with an Oxford INCA Energy 350 EDS system at 20 kV accelerating voltage, spot size 50, 10 mm working distance and acquisition time of 30 s. Grain size was measured using a measuring tool included in the JEOL SEM software (JEOL, 2007). Relative mineral abundances in investigated samples were estimated from distribution of constituent elements, obtained by EDS elemental mapping of evenly distributed fields-of-view at the same magnifications with acquisition time of 700 s, in accordance with established procedure (Miler and Gosar, 2012, 2019), and by comparison with mineral grain percentage composition charts for sediments (Compton, 1962). Mineral composition of PHE-bearing phases was assessed from atomic ratios of constituent chemical elements detected in grains and comparison with data from mineral databases (Anthony et al., 2009; Barthelmy, 2012). The software was calibrated for quantification using premeasured universal standards included in the EDS software, according to fitted standards procedure (Goldstein et al., 2003), referenced to a cobalt optimization standard. The correction of EDS data was performed by standard ZAF-correction procedure included in the INCA Energy software (Oxford Instruments, 2006). SEM/EDS analysis was performed at Geological Survey of Slovenia.

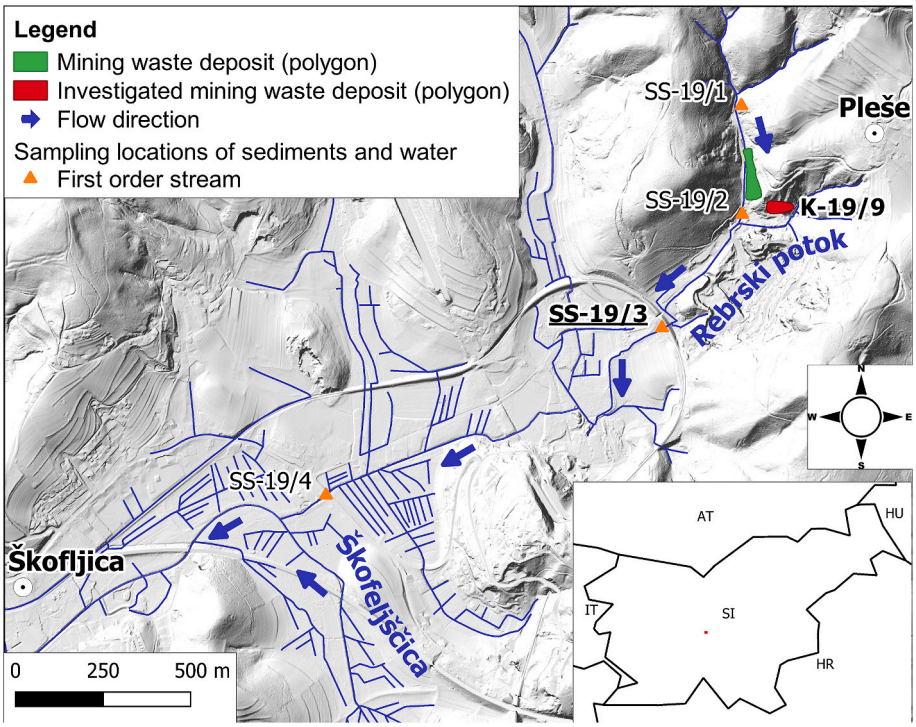

Fig. 3. QGIS map of MWDs and sampling locations in Pleše mining area. Investigated MWDs are marked in bold. At underlined and bolded sediment and water sampling locations, samples were taken in 2013 and 2017, at others only in 2013. Lidar hillshade and hydrography layers were taken from Slovenian Water Agency (2018).

3.6. Environmental indices and impact assessment

As a criterion for evaluating the influence of MWDs on pollution of the main 2nd or 3rd order watercourse sediments, the Geoaccumulation Index (Igeo) modified after Müller (1979) and Förstner and Müller (1973) was calculated using Equation (1):

$$Igeo = log2[\frac{C_n}{1.5 \times B_n}], \quad \text{Eq. 1}$$

where C_n is the content of an element in stream sediment of the main 2nd or 3rd order watercourse downstream of a confluence with 1st order stream draining the MWDs in its catchment area and B_n is the content of an element in stream sediment of the main 2nd or 3rd order watercourse upstream of the confluence with the same 1st order stream.

3.7. Solubility of PHE-bearing minerals in simulated surface water

The solubility of most important ore minerals in studied MWDs and PHE-bearing secondary products of ore mineral weathering in surface water was assessed by calculating amount of phases released into solution after simulated dissolution of equal amounts of minerals in aqueous solution under conditions identical to those in studied surface waters (at T = 4 and 19 °C; pH = 7 and 9; Eh = 140 and 600 mV; and mean element concentrations characteristic of waters in each study area). These calculations were carried out using PHREEQC program (version 2.14.3; Parkhurst and Appelo, 1999) and a thermodynamic database LLNL.DAT.

3.8. Assessment of entrainment of PHE-bearing phases in 2nd and 3rd order streams

The possibility of entrainment of PHE-bearing phases in 2nd and 3rd order streams was estimated from the Sundborg diagram (Sundborg, 1956) by considering basic archival hydrological data on major 2nd and 3rd order streams obtained from archive of hydrological data (Slovenian Environment Agency, 2021b) and mean grain size of PHE-bearing phases.

4. Results

4.1. Chemical composition of MWDs

Mežica MWDs (Fig. 1, Table 1) contain extremely high levels of Cd, Pb and Zn, ranging between 51 and 317 mg/kg, 10,300–51,100 mg/kg and 5128–22,600 mg/kg, respectively. MWDs K-26/12 and K26/30 additionally contain significant levels of As (93 and 159 mg/kg, respectively) and K-26/30 of Mo (412 mg/kg). Critical values for soils (Supplementary Table S2) are exceeded by up to 26 times for Cd, up to 43 times for Pb and up to 71 times for Zn. Water leach Pb concentrations (Table 1) exceed limit values for inert waste (Supplementary Table S2) in all Mežica MWDs, while they are exceeded for Cd and Zn in K-26/12 and K-26/30. None of water leach PHE concentrations exceed limit values for stabilised and non-reactive waste.

Two largest MWDs in Litija area (Fig. 2, Table 1) are particularly enriched in Pb, Sb and Hg, reaching up to 14,500 mg/kg, 76 mg/kg and 44 mg/kg, respectively. They exceed critical values for soils (Supplementary Table S2) by up to 27 times for Pb, 5 times for Sb and 4 times for Hg. Water leach Pb concentration in MWD K-25/25 (Table 1) significantly exceeds limit values for dangerous wastes (Supplementary Table S2).

The Pleše MWD (Fig. 3, Table 1) has high contents of Zn (1395 mg/kg), Ba (689 mg/kg) and Pb (528 mg/kg). Contents of Zn and Ba exceed critical values for soils (Supplementary Table S2) by 2 and 1.1 times, respectively. The water leach concentrations of all PHEs (Table 1) are below the limit values for inert, stable and non-reactive, as well as dangerous waste (Supplementary Table S2).

Contents of Y (2.4–5.8 mg/kg), La (1.9–9.4 mg/kg) and Ce (3.9–23 mg/kg) (Table 1) in MWDs from all studied areas are below the Slovenian soil (Y = 11 mg/kg; La = 17 mg/kg; Ce = 38 mg/kg) (Gosar et al., 2019) and European grazing soil (Y = 6.4 mg/kg; La = 13.6 mg/kg; Ce = 27.1 mg/kg) medians (Sadeghi et al., 2013).

Table 1
PHE contents after aqua regia digestion (mg/kg), PHE concentrations in water leachates (mg/kg) and Pb isotope ratios in mining waste material.

Area	Sample	Method	As	Ba	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Zn	Sb	Y	La	Ce	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
Mežica	K-26/12	aqua regia	93	199	317	7.1	33	41	1.3	99	24	21,200	51,100	2.8	5.1	5.8	14	18.8	15.8	38.7
		water leach	<0.01	2.39	0.061		<0.05	0.03		0.058	<0.01	0.864	1.79	0.002						
	K-26/17	aqua regia	65	223	51	6.3	18	22	0.6	122	18	18,400	10,300	8.6	4.5	6.3	14.5	18.3[a]	15.4[a]	37.5[a]
		water leach	0.02	0.952	0.037		<0.05	0.061		0.042	<0.01	0.647	1.82	0.023						
	K-26/22	aqua regia	42	319	146	2.2	15	18	0.2	53	11	5128	26,100	2.2	2.4	1.9	3.9			
		water leach	<0.01	0.708	0.0205		<0.05	0.0155		0.108	<0.01	1.659	2.125	0.0055						
	K-26/30	aqua regia	159	119	180	4.8	21.2	19.58	0.7	412.1	17.1	22,600	44,000	3.8	4.7	3.8	9.5	18.5	15.8	38.7
		water leach	0.011	2.08	0.1		<0.05	0.065		0.018	<0.01	0.761	5.11	0.003						
	Galena																	18.4[a]	15.7[a]	38.5[a]
Litija	K-25/23	aqua regia	89	189	0.2	3.3	4.5	257.2	44	0.5	6.9	14,500	780	76	2.5	5.2	15.4			
		water leach	<0.01	0.412	0.019		<0.05	0.356		<0.05	0.017	1.55	1.16	0.006						
	K-25/25	aqua regia	28	317	1.2	6.2	7.9	194	30	0.48	11	14,000	796	20	4.6	9.4	23.0	17.5	15.1	37.5
		water leach	<0.01	1.77	0.021		<0.05	0.123		<0.05	0.014	139.8	3.0	<0.002						
Plešе	K-19/9	aqua regia	32	689	3.0	14.6	5.7	39	4.6	0.9	24	528	1395	6.1	5.8	3.5	7.5	17.4	15.0	36.2
		water leach	<0.01	1.68	<0.005		<0.05	0.044		<0.05	<0.01	0.08	0.148	0.002						
	Galena																	18.2[b]	15.6[b]	38.6[b]

[a] Data from Miler and Gosar (2019).
[b] Data from Mlakar (2003).

4.2. Chemical composition of stream sediments

Sediments of 1st and 2nd order streams draining MWDs in the Mežica area (Figs. 1 and 4, Supplementary Table S3) have very high Pb contents exceeding critical level for soils (Supplementary Table S2) in most of the sediments by up to 87 times in 2013 and up to 10 times in 2017. Critical soil Zn and Cd levels are exceeded in sediments from locations SS-26/5, SS-26/8, SS-26/11 and SS-26/19 by up to 25 times for Zn and 10 times for Cd in both years. Critical soil Mo level is exceeded only in sediment from location SS-26/8 by up to 10 times in 2013 and 1.5 times in 2017, while As critical level is only slightly exceeded in 2013. In most of 3rd order stream (Meža River) sediments (Figs. 1 and 4, Supplementary Table S3), Pb and Zn critical levels are highly exceeded, except in sediments upstream of confluences with 1st order streams that drain largest MWDs. Critical soil Cd and Sb levels are exceeded in sediments from locations SS-26/15, SS-26/20 (except Cd in 2013), SS-26/21 in 2013 and SS-26/22, downstream of secondary Pb processing plant by more than 2 times for Cd and about 5 times for Sb in both years.

In sediments of 1st order streams draining most of MWDs in the Litija area (Figs. 2 and 5a, b, Supplementary Table S3), critical soil Pb level (Supplementary Table S2) is exceeded in sediments from all locations by up to 23 times in 2013 and 3 times in 2017 (except SS-25/2). Critical soil Ba level is exceeded in all samples by up to 2 times in 2013 and 3 times in 2017 (except SS-25/3). Critical values for Hg and Zn are exceeded in most 1st order stream sediments sampled in 2013 by up to 8 times for Hg and 3 times for Zn, but only in SS-25/3 sampled in 2017 Zn level was exceeded by up to 2 times. Contents of PHEs in 2nd (stream Reka) and 3rd (Sava River) order sediments do not exceed soil critical values, except for Ba in SS-25/5 sampled in 2017.

In the Pleše area stream sediments (Figs. 3 and 5c, Supplementary Table S3), critical soil Ba level (Supplementary Table S2) is exceeded by up to 4 times in 2013 in all 1st order stream sediments, collected downstream of the Pleše MWDs. Critical soil Pb level is exceeded at the same locations (except SS-19/4) by up to 4 times in 2013. In 2017, the Ba content was somewhat higher and Pb content lower than in 2013, but still exceeding critical values.

In stream sediments from all areas, REE contents are generally low; Y (0.6–9.6 mg/kg), La (0.9–16.2 mg/kg) and Ce (2–39.8 mg/kg) (Figs. 4 and 5, Supplementary Table S3). They are mostly below Slovenian (Gosar et al., 2019) and European grazing soil (Sadeghi et al., 2013) medians.

4.3. Chemical composition of surface stream water

In the Mežica area (Figs. 1 and 6a, Supplementary Table S4), Pb, Zn and Cd concentrations exceed regulation values for surface waters (Supplementary Table S2) in water of 1st order streams that drain largest MWDs (K-26/12, K-26/22, K-26/30) by up to 3 times for Pb, and 4 times for Zn and 12 times for Cd (both only in stream draining K-26/22). In 3rd order stream, only Cd slightly exceeds regulation values at locations SS-26/15 and SS-26/20. Values of physico-chemical parameters (pH, EC and DO) in the 3rd order stream are generally a bit lower than in 1st and 2nd order streams, while the Eh values are slightly higher (Fig. 6a, Supplementary Table S4). According to the measured parameters (pH, Eh and DO), waters in inspected areas are classified as slightly alkaline and relatively well aerated.

In Litija area, the concentrations of PHEs in stream waters (Fig. 6b, Supplementary Table S4) are below the regulation values (Supplementary Table S2). Physico-chemical parameters (Fig. 6b, Supplementary Table S4) show that pH, Eh and DO values are higher, and EC values are lower in 2nd and 3rd order streams than in 1st order streams draining MWDs.

In stream water of the Pleše area, concentrations of PHEs (Fig. 6b, Supplementary Table S4) are below the regulation values (Supplementary Table S2). Basic water physico-chemical parameters are similar to those in the Mežica area, but water is slightly less aerated and has

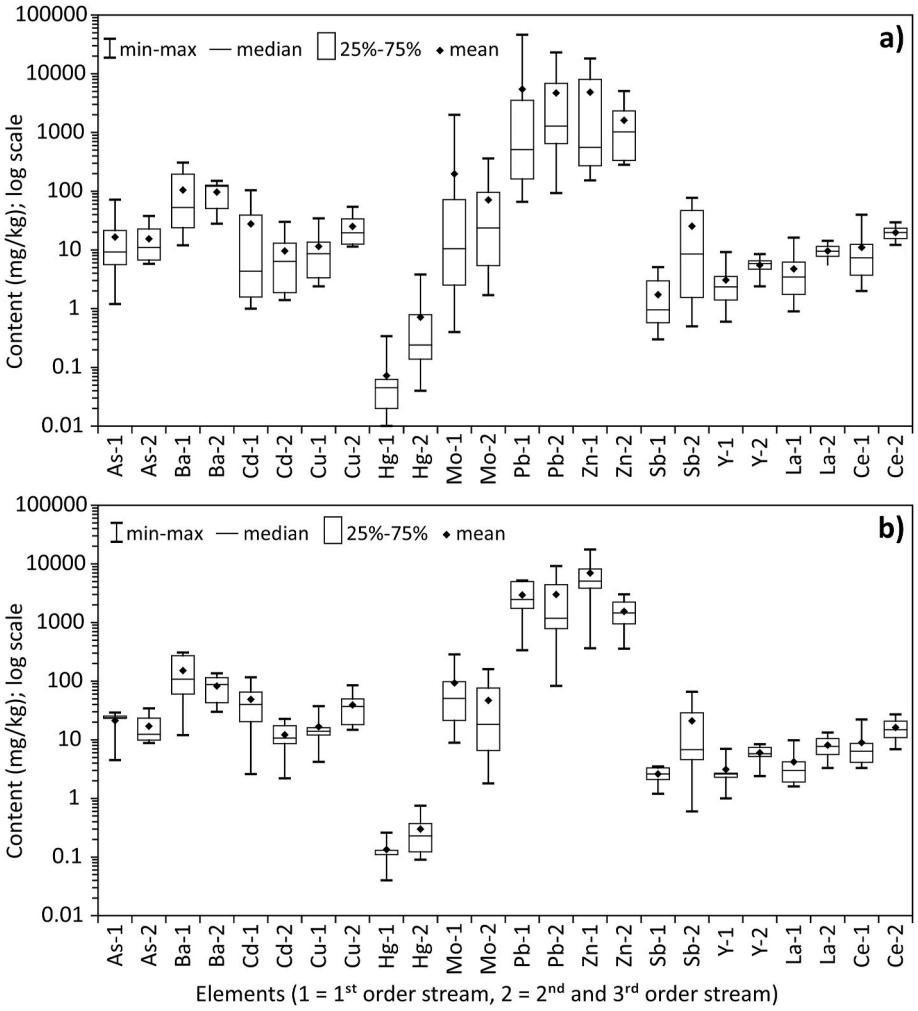

Fig. 4. Box and whiskers plot for PHEs and REEs in stream sediments of Mežica area from (a) 2013 and (b) 2017.

somewhat higher EC.

4.4. Relative mineral abundances in MWDs

MWDs from the Mežica area are predominantly composed of carbonates (59%), mostly dolomite, and silicates (33%), while average quantity of metal-bearing grains, which are all PHE-bearing phases, is 8%. PHE-bearing phases are most abundant in K-26/22, followed by K-26/30, K-26/12 and K-26/17 (Fig. 7a, Supplementary Table S5). Ore minerals (5%), such as cerussite, smithsonite, sphalerite, barite and also wulfenite and descloizite, strongly predominate among PHE-bearing phases. Smithsonite and sphalerite prevail in MWD K-26/22, while cerussite is prevalent in K-26/12. PHE-bearing secondary products of ore mineral weathering, such as Fe-oxyhydroxides and Fe-oxyhydroxy sulphates with minor Pb and Zn and Mn-oxides with Pb represent 3%. Number of major REE-bearing minerals (monazite) is negligible. The average size of PHE-bearing phases is 11 μm.

In Litija area, investigated MWDs are predominantly composed of silicates (68%) and about 31% of metal-bearing grains, of which 26% are PHE-bearing phases. PHE-bearing phases are abundant in both MWDs (Fig. 7a, Supplementary Table S5). Ore minerals, such as barite, Pb-sulphate with Ba (baritoanglesite), cerussite and also cinnabar and sphalerite, represent 23% of all PHE-bearing phases. Baritoanglesite prevails in K-25/23 and cerussite in K-25/25. PHE-bearing secondary products of ore mineral weathering represent 3%, of which Fe-oxyhydroxy sulphates and Fe-oxyhydroxides with minor Pb, Zn and Cu are most abundant and Mn-oxides with Pb least abundant. The average size of PHE-bearing phases in MWDs is 12 μm.

The MWD from Pleše area is composed of 68% silicates, 10% carbonates (dolomite and calcite) and 22% of metal-bearing grains. PHE-bearing phases represent 17% of metal-bearing grains (Fig. 7a, Supplementary Table S5). Ore minerals are represented by barite and sphalerite, which amount to 11% of all PHE-bearing phases. PHE-bearing secondary products of ore mineral weathering represent 6%, of which Fe-oxyhydroxides with minor Pb and Zn are most abundant. Among REE-bearing minerals, monazite and florencite are present. The average size of PHE-bearing phases is 15 μm.

4.5. Relative mineral abundances in sediments of 1st order streams draining MWDs

Sediments of 1st order streams from Mežica area are predominantly composed of carbonates (66–70%) and about 25% of silicates, while average quantity of metal-bearing grains ranges between 5 and 9% of all grains in samples from 2013 to 2017, respectively. PHE-bearing phases represent 4 and 8% of all metal-bearing grains in 2013 and 2017, respectively. Ore minerals (3–5%), such as cerussite, sphalerite, smithsonite, barite, wulfenite and descloizite, strongly predominate among PHE-bearing phases (Fig. 7b and c, Supplementary Table S6). Abundant (1–3%) are also PHE-bearing secondary products of ore mineral weathering, such as Fe-oxyhydroxides and Fe-oxyhydroxy sulphates with minor Pb and Zn and Mn-oxides with Pb. REE-bearing minerals are represented by scarce monazite and xenotime, which do not contribute to REE mineral enrichment further downstream in larger Drava River

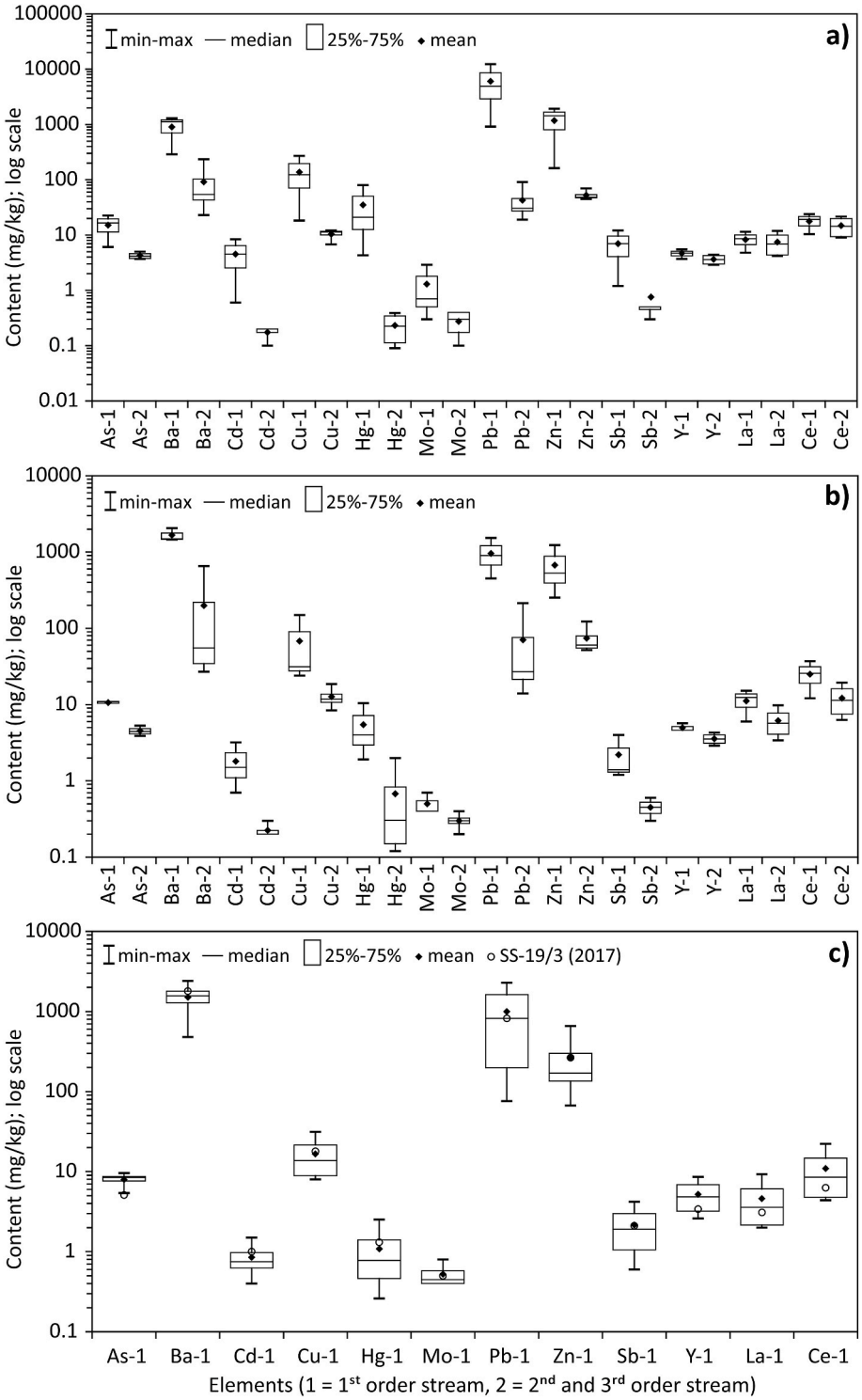

Fig. 5. Box and whiskers plot for PHEs and REEs in stream sediments of Litija area from (a) 2013 and (b) 2017 and (c) stream sediment of Pleše area from 2013 to 2017.

(Šoster et al., 2017). The greatest number of PHE-bearing phases was found in sediments of streams that drain largest MWDs (SS-26/11, SS-26/8, SS-26/19 and SS-26/5). PHE-bearing phases were more abundant in 2017 than in 2013 and their mean grain sizes were close to 17 μm in 2017 and 30 μm in 2013, which is larger than those in MWDs.

In Litija area, 1st order stream sediments are predominantly composed of silicates (66–92%), mostly K-feldspars, 5–23% carbonates and between 3 and 12% metal-bearing grains in samples from 2013 to 2017, respectively. Of these metal-bearing grains, PHE-bearing phases represent 3% in 2013 and 8% in 2017. PHE-bearing phases are represented predominantly by ore minerals (2–6%), such as barite, cerussite and also pyromorphite (Fig. 7b and c, Supplementary Table S6). PHE-bearing secondary products of ore mineral weathering Fe-oxyhydroxides and Fe-oxyhydroxy sulphates with minor Pb and Zn and Mn-oxides with Pb represent 0.2–1.4% of all PHE-bearing phases. REE-bearing minerals are represented by monazite, xenotime and

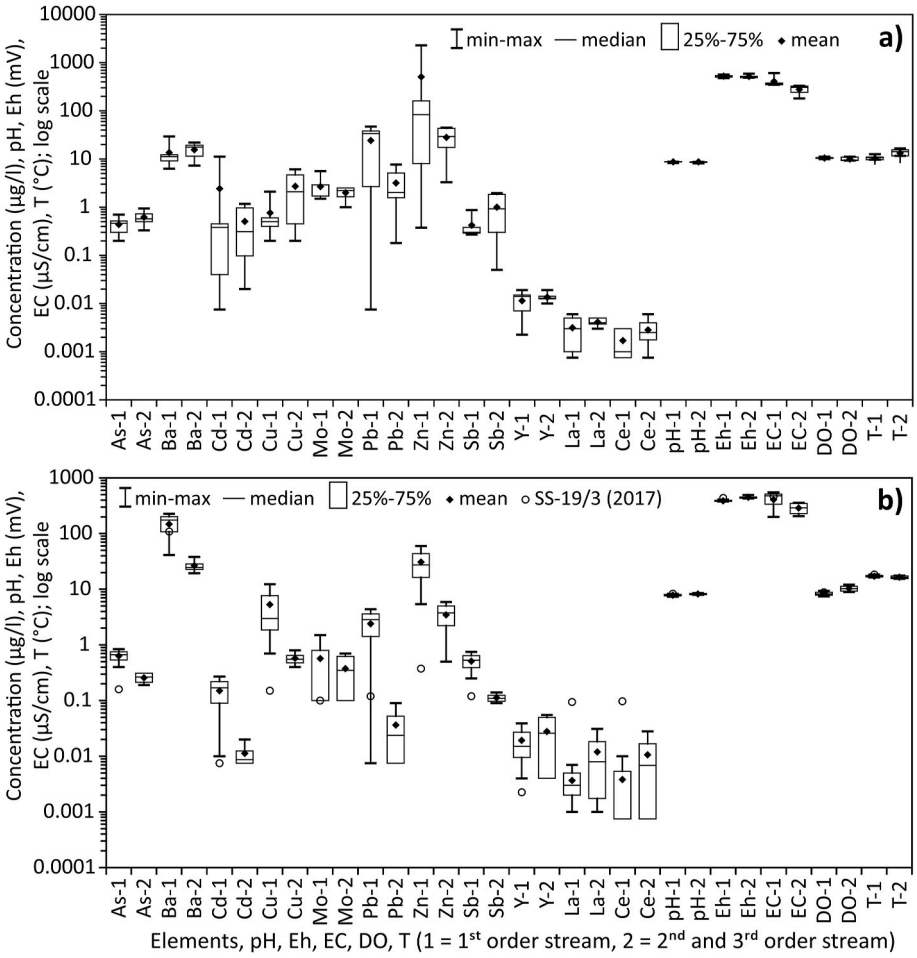

Fig. 6. Box and whiskers plot for PHEs, REEs and basic physico-chemical parameters (pH, Eh, EC, DO, T) in surface stream water of (a) Mežica area and (b) Litija and Pleše areas.

allanite. PHE-bearing phases were slightly more abundant in 2013 and their average grain-sizes were about 26 µm in 2013 and 11 µm in 2017, which is somewhat larger or similar to those in MWDs.

Sediments of 1st order stream draining MWDs in Pleše area are characterised by 46–50% carbonates (mostly dolomite) about 30% silicates and 20% metal-bearing grains, of which 19% are PHE-bearing phases. PHE-bearing phases are predominated by ore minerals (18–19%), mostly barite and cerussite, while PHE-bearing secondary products of ore mineral weathering (Fe-oxyhydroxides with minor Pb and Zn and Mn-oxides with Pb) represent 0.4–1.4% of all PHE-bearing phases (Fig. 7b and c, Supplementary Table S6). The PHE-bearing phases are more abundant in sample from 2017 as compared to 2013. The average grain-sizes are about 36 µm in 2013 and 21 µm in 2017, which is larger than those in MWDs.

4.6. Modes of occurrence of PHE- and REE-bearing minerals and phases

Major PHE-bearing phases occur in similar forms in all MWDs and sediments from investigated areas. Ore minerals sphalerite (Fig. 8a), smithsonite and pyromorphite occur as very porous and strongly corroded fragments and massive grains. In addition to Zn, sphalerite contains minor levels of Cd. Pyromorphite is most likely authigenic and also occurs as coatings on grains of non-metallic minerals. Cerussite and barite (Fig. 8b) form pitted, cracked polycrystalline and massive grains and fragments. Hemimorphite, pyrite, galena, anglesite, wulfenite (Fig. 8c), descloizite (Fig. 8d) and chalcopyrite occur as massive grains with sometimes preserved crystal surfaces. Cinnabar (Fig. 8e), which was found only in Litija MWDs, forms porous aggregates composed of minute crystals and massive grains, but also occurs as coatings on surfaces of some Fe-oxyhydroxides and Fe-oxyhydroxy sulphates. Baritoanglesite (Fig. 8f) occurs as pitted and partly corroded idiomorphic crystals.

Secondary products of ore mineral weathering Fe-oxyhydroxides with minor Pb and Zn (Fig. 8g), and also minor Cu in Litija MWDs, occur as fragments and crystals, and as porous aggregates composed of minute crystals. Fe-oxyhydroxy sulphates with minor Pb and Zn (Fig. 8h), and Cu in the case of Litija MWDs, form massive grains with pronounced shrinkage cracks due to oxidation of original sulphides from which they formed. Mn-oxides with Pb (Fig. 8i) and psilomelane with Pb form porous aggregates of authigenic minute crystals.

Geogenic REE-bearing minerals monazite (Fig. 8j), xenotime, allanite and florencite occur mainly as massive fragments or as well-defined crystals, as well as inclusions in non-metallic minerals.

4.7. Grain size distribution of PHE-bearing phases

In Mežica MWDs (Fig. 9a), grain sizes of ore minerals and secondary products of ore mineral weathering are well sorted. About 64% of ore mineral grains are smaller than 10 µm, while 26% grains have sizes between 10 and 20 µm. Secondary minerals have 55% grains below 10 µm and 30% grains are in the size range of 10–20 µm. In MWDs from Litija (Fig. 9b) and Pleše (Fig. 9c) areas, ore minerals and secondary products of ore mineral weathering are poorly sorted. Grains of ore minerals are mostly smaller than 10 µm (about 45%) and about 31% are between 10 and 20 µm. Sizes of secondary minerals are mostly between 10 and 20 µm (42%) and below 10 µm (30%).

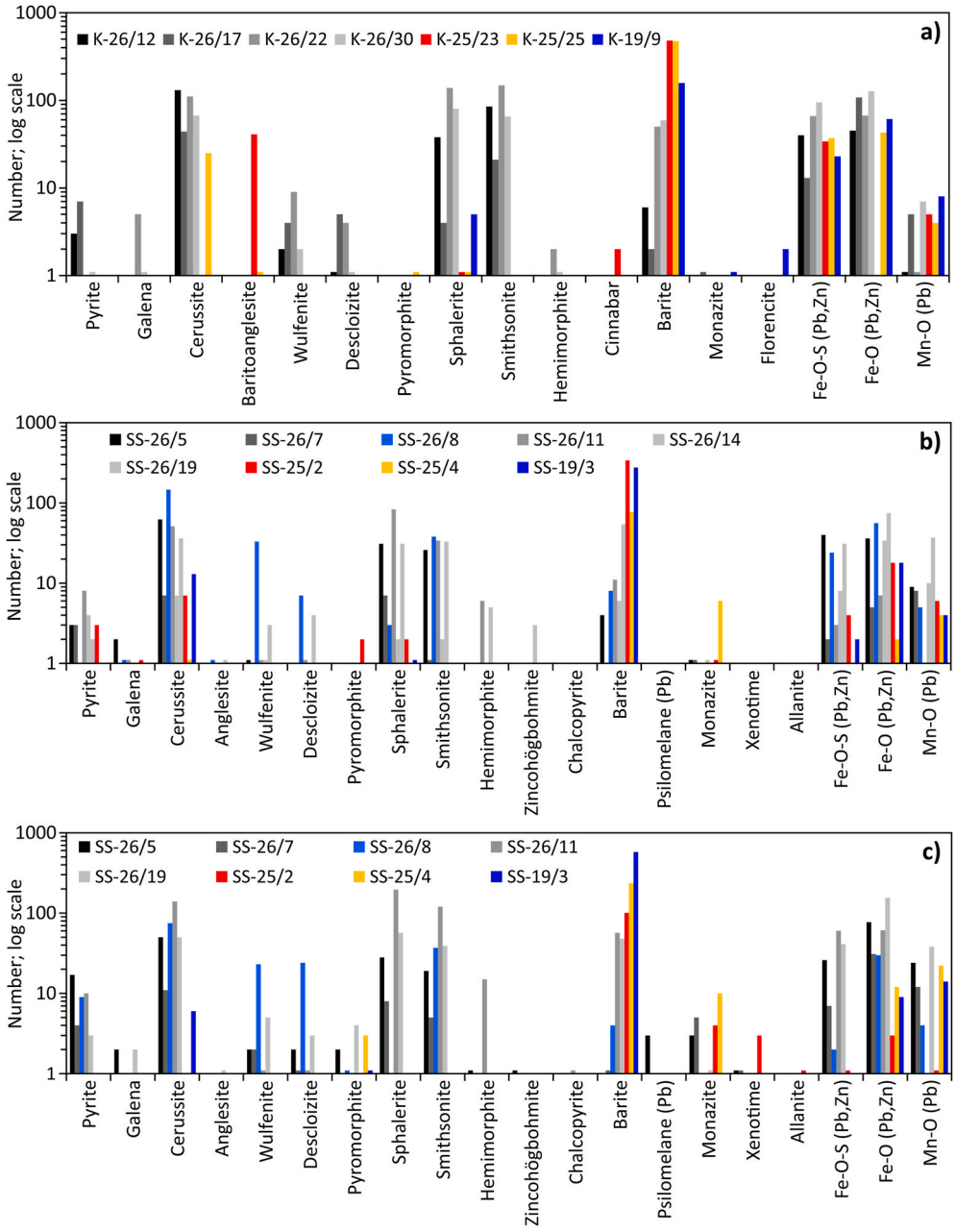

Fig. 7. Number of PHE- and REE-bearing phases in (a) MWDs and in 1st order stream sediments of Mežica, Litija and Pleše areas from (b) 2013 and (c) 2017.

In Mežica area stream sediments (Fig. 9d), ore minerals and secondary products of ore mineral weathering are poorly sorted. Their grain sizes are mostly between 10 and 30 μm (about 50% grains). About 16% of ore mineral grains have sizes between 30 and 40 μm, while 18% of secondary mineral grains are smaller than 10 μm. In areas of Litija (Fig. 9e) and Pleše (Fig. 9f), ore minerals and secondary products of ore mineral weathering in stream sediments are poorly sorted. Sizes of ore minerals in Litija area sediments are mostly in the range 10–30 μm (63%), while those of secondary minerals are in the ranges 10–20 μm (35%), 20–30 μm (21%) and also 40–50 μm (18%). In Pleše area sediments, ore mineral grains have similar size distribution as in Mežica, although they have somewhat more grains in the size range 60–70 μm. Secondary minerals have grain sizes mostly between 20 and 40 μm (42%) and between 40 and 50 μm (25%).

4.8. Entrainment of PHE-bearing phases in 2nd and 3rd order streams

Assessment of entrainment of PHE-bearing phases showed that in the 3rd order stream in Mežica area, the conditions required for entrainment of PHE-bearing phases were achieved for 30% of all measured hydrological data obtained from Slovenian Environment Agency (2021b) for the period between both sampling campaigns. In Litija area, these conditions were achieved for 16% of all data in 2nd order stream and 100% of data in 3rd order stream, while in Pleše area the PHE-bearing phases could have been entrained only in 1% of the time.

4.9. Solubility of PHE-bearing phases assessed by PHREEQC

Simultaneous dissolution of most important ore minerals (galena-PbS, cerussite-$PbCO_3$, anglesite-$PbSO_4$, sphalerite-ZnS, smithsonite-$ZnCO_3$, barite-$BaSO_4$, cinnabar-HgS, pyrite-FeS_2) and PHE-bearing secondary products of ore mineral weathering or their possible mineral

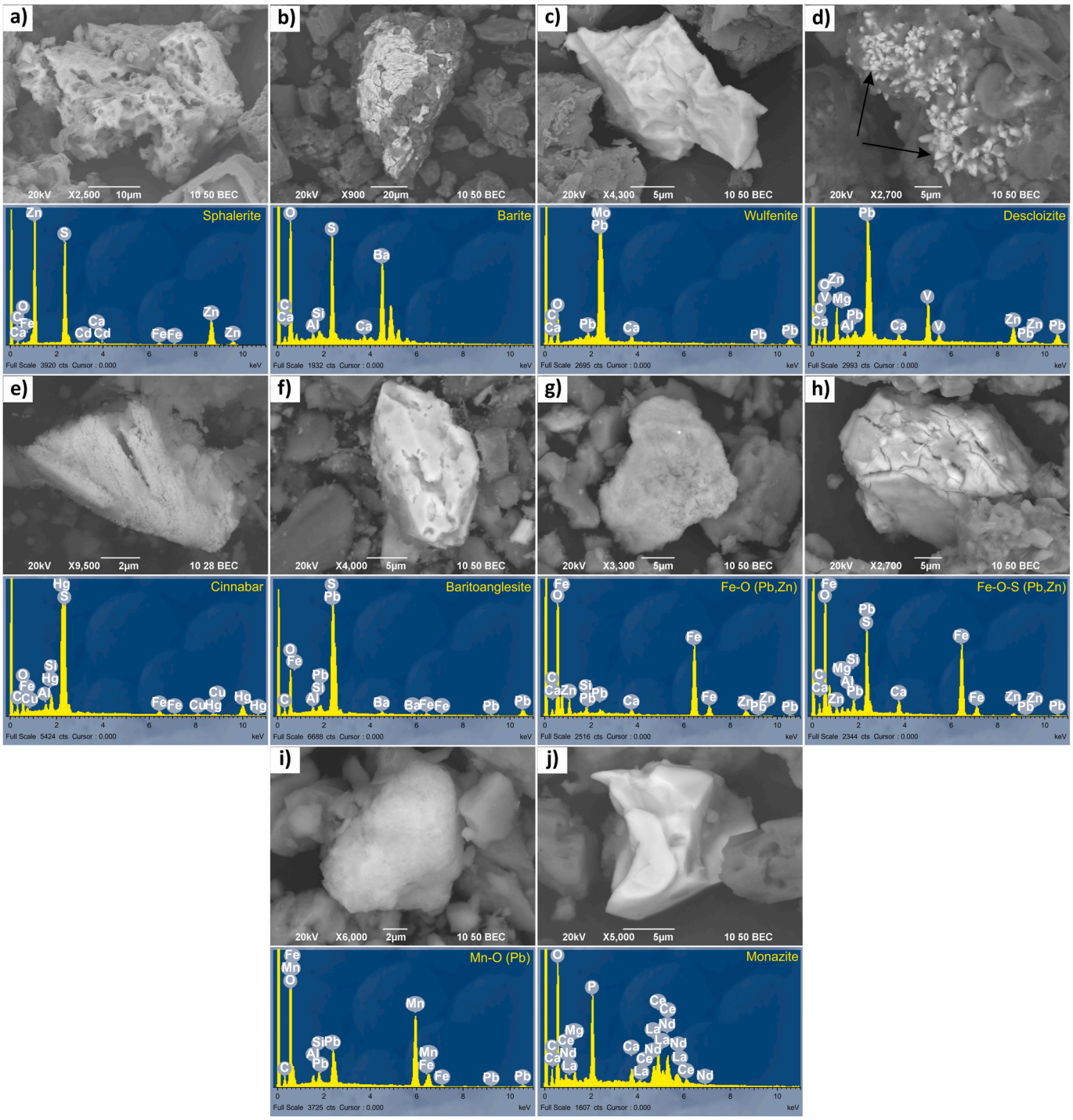

Fig. 8. SEM (BSE) images and EDS spectra of PHE- and REE-bearing phases in MWDs and 1st order stream sediments: (a) Sphalerite with Cd; (b) Barite; (c) Wulfenite; (d) Descloizite (arrows); (e) Cinnabar; (f) Baritoanglesite; (g) Fe-oxyhydroxides with minor Pb and Zn; (h) Fe-oxyhydroxy sulphates with minor Pb and Zn; (i) Mn-oxides with Pb; (j) Monazite.

equivalents (melanterite-$FeSO_4$, goethite-FeOOH, pyrolusite-MnO_2, pyromorphite-$Pb_5(PO_4)_3Cl$), found in studied MWDs, was predicted. Although modelling approach using PHREEQC code is simplified as it does not consider physical properties of PHE-bearing phases and organic phases, and could underestimate their solubilities, it provides approximation of their solubility, which is very important in view of ever-increasing climate changes. The results of PHREEQC calculations are provided as the amounts of PHE-bearing phases in simulated stream water solution from all three studied areas (Fig. 10a–c).

4.10. Stable Pb isotopes in MWDs and stream sediments

In order to assess the origin of Pb-bearing phases and their fate in the environment, Pb isotope composition was determined. The analysis of Pb isotopes in stream sediments from the Mežica area (Fig. 11a and b, Table 1, Supplementary Table S3) showed two distinct clusters of Pb isotope ratios ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$). The one with higher ratios includes 3rd order stream sediments SS-26/3, SS-26/15, SS-26/20 and 1st order stream sediments SS-26/5, SS-26/8, which are isotopically very close to galena from Mežica ore deposit and K-26/17, K-26/12 and

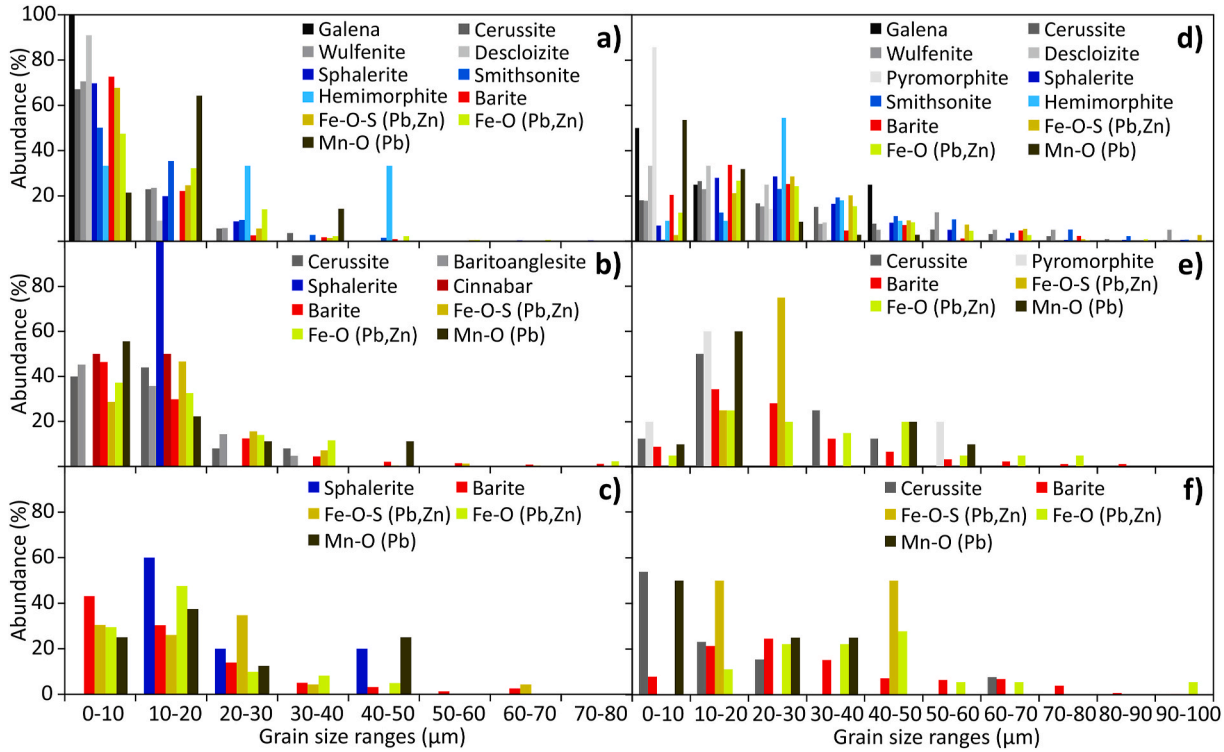

Fig. 9. Grain-size distribution of PHE-bearing phases in MWDs from (a) Mežica, (b) Litija and (c) Pleše areas and 1st order stream sediments from (d) Mežica, (e) Litija and (f) Pleše areas.

K-26/30 MWD material. Other sediments have lower $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios and form the second cluster.

Also in the Litija area, Pb isotope ratios (Fig. 11c and d, Table 1, Supplementary Table S3) in 2nd order stream sediment taken upstream of MWDs and in 3rd order stream sediments are very similar to ratios in galena from Pleše, which has identical Pb isotopic composition as galena from Litija ore deposit. They are higher than ratios in K-25/25 MWD material, and much higher than ratios in sediments of 1st and 2nd order streams taken downstream of MWDs.

In Pleše area, Pb isotope ratios (Fig. 11c and d, Table 1, Supplementary Tables S3) in stream sediment are much lower than the ratios in galena from Pleše ore deposit and K-19/9 MWD material.

5. Discussion

5.1. Environmental impact

The results indicate that stream sediments, particularly sediments in 1st order streams draining MWDs, are significantly contaminated with PHE. Thus, investigated MWDs represent a major source of PHE in sediments of study areas. In general, determined mineral composition of MWDs and quantities of PHE-bearing phases in MWDs match well with those in sediments of 1st order streams.

Contents of PHE are high in MWDs and in 1st order stream sediments. In some of these stream sediments, contents of PHE are higher than in MWDs they are draining. In the Mežica area, about 2 times higher contents of Mo and Ba were found in streams draining K-26/12 and K-26/30, respectively. Similarly, contents of Ba and Zn in sediments of 1st order streams in Litija area are up to 6 and 2 times, respectively, higher than those in MWDs, while 1st order stream sediment from Pleše area has about 2 and 3 times higher contents of Ba and Pb, respectively, than MWDs. All these high PHE contents agree well with quantities of PHE-bearing phases in sediments from streams draining MWDs and most probably result from other smaller MWDs and accumulation of fine-grained PHE-bearing material from MWDs and weathering of ore outcrops in the catchment areas. Namely, the grain size distribution of PHE-bearing ore minerals and secondary products of ore weathering in MWDs from all locations and areas showed that their sizes are mostly 10 μm or less (Mežica area) and close to 20 μm (Litija and Pleše areas), which makes them prone to wind erosion and surface water runoff. In 1st order stream sediments, the mean grain sizes of ore minerals and secondary products of ore mineral weathering mostly peak at around 30 μm and 50 μm. This demonstrates that relatively large PHE-bearing phases, eroded from MWDs, are transported over short distances and deposited on streambed until next high-water event, thus contributing to high PHE contents. PHE-bearing phases smaller than 10 μm remain suspended in water and are being transported over very long distances. Fast-flowing streams erode their own stream beds at higher water levels, particularly streams in Mežica area (Fux and Gosar, 2007; Gosar and Miler, 2011), as also indicated by estimated possibility of entrainment of PHE-bearing phases. Thus, the mineral abundances, grain sizes of PHE-bearing phases in sediments and PHE contents, depend on hydrological conditions during the high-water events, which could be different at different times of sampling.

In order to estimate contribution of MWDs to the main watercourse sediment PHE load, Geoaccumulation indices (Igeo) (Table 2) were calculated. According to calculated Igeo values, most of the investigated MWDs contributed to moderate contamination of sediments in main watercourses in 2013. In the Mežica area, the MWD K-26/12 and 12 smaller MWDs K-26/1–11 and K-26/13 (not analysed) caused a moderate to strong contamination of 3rd order stream (Meža River) sediments with Mo and Pb, and moderate contamination with Cd and Hg. In 2017, the contribution of these MWDs to the Mo, Pb and Cd load was similar, while the contribution to Zn load slightly increased and there was no contribution to Hg load. The K-26/17 and 4 smaller MWDs K-26/18–21 (not analysed) gave rise to moderate contamination with Ba, Hg and Sb in 2013, while in 2017 the contamination with Sb was moderate to strong. Hg content is relatively low in K-26/17, therefore it either originates from other 4 smaller MWDs or anthropogenic activities, mostly industry, located in a town upstream of K-26/17. In 2013,

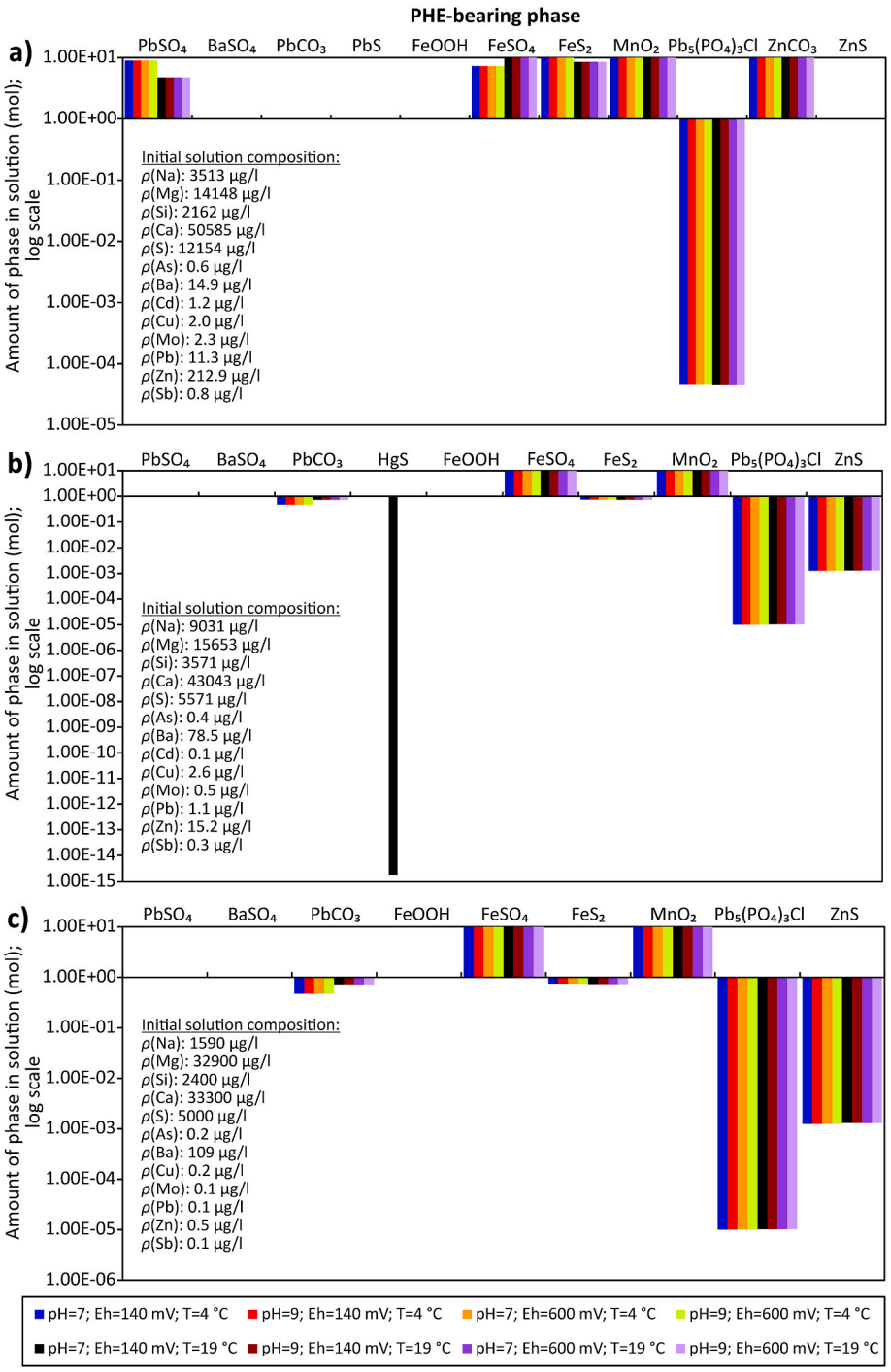

Fig. 10. Amounts of PHE-bearing phases in solution released after simulated simultaneous dissolution of equal amounts of PHE-bearing phases in aqueous solution simulating stream water (T = 4 and 19 °C; pH = 7 and 9; Eh = 140 and 600 mV; mean element concentrations characteristic of waters in each study area) in (a) Mežica area; (b) Litija area and (c) Pleše area, obtained by PHREEQC calculations.

seemingly significant influence of K-26/22 and 4 smaller MWDs K-26/23–26 (not analysed) on strong contamination with Sb and moderate contamination with Mo and Pb was observed. In 2017, situation was similar, except the Sb and Cu loads were somewhat lower and higher, respectively. However, Sb, Mo, Cu and Pb contents in 3rd order stream sediment at location SS-26/15 (Supplementary Table S3) are significantly higher than those in K-26/22 MWD (Table 1) and sediments of 1st and 2nd order streams (SS-26/10, SS-26/14) that drain K-26/22–26 (Supplementary Table S3). Sb content observed in SS-26/15 is even higher than that reported in sediments of streams draining an antimony mine MWDs (e.g. Teršič et al., 2018). In addition, there was no contribution of K-26/22 to PHE load in 2nd order stream sediment (Table 2). The most probable source of PHE load in 3rd order stream sediment at location SS-26/15 was secondary Pb processing plant located in close vicinity of the MWDs, which has already been confirmed as the major active source of recent pollution with Sb, Pb and Cu in the area (Miler and Gosar, 2013, 2019). This is also in agreement with other studies (Svete et al., 2001; Fux and Gosar, 2007; Gosar and Miler, 2011; Gošar et al., 2015) that suggested Pb recycling industry as the source of pollution in river sediments and water downstream of the plant. The

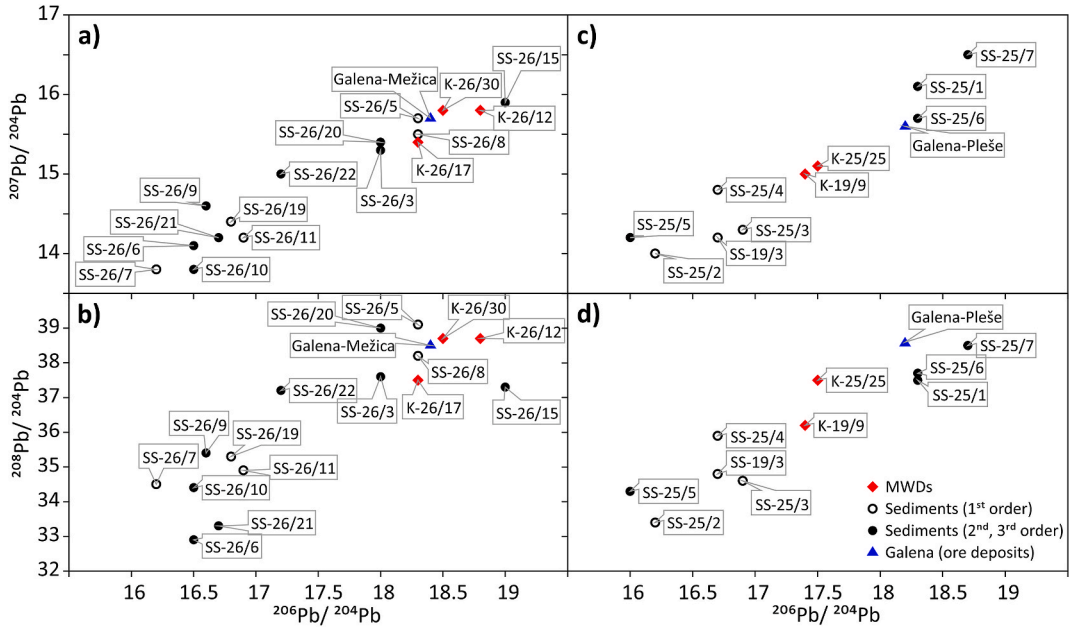

Fig. 11. Pb isotope ratios in MWD material, stream sediments and galena from ore deposits in studied areas of (a, b) Mežica and (c, d) Litija and Pleše. Pb isotope data for Mežica galena are from Miler and Gosar (2019) and data for Pleše galena from Mlakar (2003).

Table 2
Sediment Geoaccumulation index (Igeo) in main 2nd or 3rd order watercourse upstream and downstream of confluence with 1st order stream that is draining MWDs in its catchment area.

Sediment samples		Stream	MWDs	Igeo-2013											
Upstream	Downstream			As	Ba	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Zn	Sb
SS-26/3	SS-26/6	3rd order	K-26/1-13	-0.3	-0.3	1.4	-0.7	-0.4	-0.5	1.4	2.5	-0.7	2.7	0.9	0.1
SS-26/6	SS-26/9	3rd order	K-26/17-21	0.2	1.6	-0.2	0.2	-0.1	0.4	1.8	0.7	0.0	0.3	0.0	1.7
SS-26/9	SS-26/15	3rd order	K-26/22-26	0.5	-0.9	0.4	-0.9	-0.7	0.2	-2.7	1.1	-0.6	1.6	0.5	**3.6**
SS-26/12	SS-26/10	2nd order	K-26/22	-0.5	-1.0	-0.4	-0.7	-0.7	-0.4	-4.3	-0.8	-0.8	-0.7	-0.8	-1.0
SS-26/15	SS-26/20	3rd order	K-26/27-30	-1.3	-0.6	-1.5	-0.6	-0.8	-1.1	1.5	-1.2	-0.6	-1.3	-1.6	-1.6
SS-26/18	SS-26/19	1st order	K-26/30	2.6	**4.0**	**3.2**	0.7	0.5	1.2	0.4	**4.0**	0.2	**4.9**	**3.8**	2.1
SS-26/20	SS-26/21	3rd order	K-26/31	-0.1	-0.4	0.9	-0.7	-0.5	-0.4	-3.2	0.1	-0.8	0.2	0.9	0.0
SS-25/1	SS-25/5	2nd order	K-25/22-27	-0.5	1.4	-0.6	-0.4	-0.3	0.2	1.3	0.4	-0.3	1.0	0.0	0.2
SS-25/7	SS-25/6	3rd order	K-25/22-28	-0.7	0.5	0.4	-0.9	-0.5	-0.5	1.1	-0.6	-0.8	0.1	-0.7	-0.6
SS-19/1	SS-19/3	1st order	K-19/9, 10	-1.2	1.1	0.2	-2.2	-1.2	-0.8	1.4	-0.6	-1.4	**3.6**	0.8	1.5
SS-19/1	SS-19/4	1st order	K-19/9, 10	-0.4	1.1	0.4	-0.3	0.8	0.4	0.4	-0.3	0.1	1.1	0.7	0.4
Sediment samples		**Stream**	**MWDs**	**Igeo-2017**											
Upstream	**Downstream**			**As**	**Ba**	**Cd**	**Co**	**Cr**	**Cu**	**Hg**	**Mo**	**Ni**	**Pb**	**Zn**	**Sb**
SS-26/3	SS-26/6	3rd order	K-26/1-13	-0.2	-0.2	1.8	-0.5	-0.5	-0.5	-0.4	2.8	-0.5	2.9	1.5	0.0
SS-26/6	SS-26/9	3rd order	K-26/17-21	-0.3	1.1	-0.8	-0.2	-0.1	0.2	1.0	-0.6	-0.4	0.0	-0.8	2.5
SS-26/9	SS-26/15	3rd order	K-26/22-26	0.4	-1.1	0.4	-1.3	-0.4	1.0	0.7	1.7	0.0	1.8	0.1	2.6
SS-26/12	SS-26/10	2nd order	K-26/22	/	/	/	/	/	/	/	/	/	/	/	/
SS-26/15	SS-26/20	3rd order	K-26/27-30	-0.3	-0.3	-0.3	-0.2	-0.3	-1.2	-1.0	0.2	-0.7	-0.3	-0.1	-0.6
SS-26/18	SS-26/19	1st order	K-26/30	/	/	/	/	/	/	/	/	/	/	/	/
SS-26/20	SS-26/21	3rd order	K-26/31	-2.5	-0.9	-1.8	-0.7	-1.1	-0.9	-1.8	-5.2	-0.9	-4.1	-2.1	-3.9
SS-25/1	SS-25/5	2nd order	K-25/22-27	-0.5	2.6	0.0	-0.8	0.1	0.6	**3.5**	0.0	-0.6	2.2	0.3	0.4
SS-25/7	SS-25/6	3rd order	K-25/22-28	-0.8	-0.1	-0.6	-0.6	-0.7	-0.5	0.9	-1.0	-0.6	0.2	-0.7	-0.3
SS-19/1	SS-19/3	1st order	K-19/9, 10	/	/	/	/	/	/	/	/	/	/	/	/
SS-19/1	SS-19/4	1st order	K-19/9, 10	/	/	/	/	/	/	/	/	/	/	/	/

<0	UNCONTAMINATED
0-1	UNCONTAMINATED TO MODERATELY CONTAMINATED
1-2	MODERATELY CONTAMINATED
2-3	MODERATELY TO STRONGLY CONTAMINATED
3-4	STRONGLY CONTAMINATED
4-5	STRONGLY TO VERY STRONGLY CONTAMINATED
>5	VERY STRONGLY CONTAMINATED

2013 Igeo values showed that K-26/30 MWD had significant impact on 1st order stream sediment (Table 2), which is strongly to very strongly contaminated with Pb, Mo and Ba, strongly with Zn and Cd, moderately to strongly with As and Sb, and moderately with Cu. However, the combined contribution of K-26/30 and 3 smaller MWDs K-26/27–29 (not analysed) to 3rd order stream sediment PHE load was moderate only with respect to Hg. Since the MWDs and adjacent 1st order stream sediment contain much lower Hg level than sediment in 3rd order stream, Hg enrichment was attributed to other unidentified sources. In 2017, no significant contribution was observed. Also, no contribution of

K-26/31 to PHE load in 3rd order stream sediment was observed in 2013 and 2017 (Table 2). In general, the impact of investigated MWDs on 3rd order stream sediment pollution is much more apparent upstream of secondary Pb processing area (Fig. 1). Downstream, the impact of MWDs is suppressed due to strong contribution of secondary Pb processing industry. Additionally, it could partly be a result of resuspension and remobilisation of polluted river sediments in upper parts of the stream, which is consistent with small grain sizes (10 μm or less) of PHE-bearing ore minerals and secondary products of ore mineral weathering in MWDs that are easily resuspended and transported by wind and surface water runoff. This was also confirmed by estimated possibility of entrainment of PHE-bearing phases.

In Litija area, MWDs K-25/22, K-25/25 and 4 smaller MWDs K-25/23–24, K-25/26–27 (not analysed) caused moderate contamination of sediment of 2nd order stream with Ba, Hg and Pb in 2013, while in 2017 the contamination significantly increased to strong for Hg and moderate to strong for Ba and Pb (Table 2). Further downstream, the MWDs K-25/22–28 contributed to moderate contamination of 3rd order stream (Sava River) sediments with Hg only in 2013. Temporal variations in contribution of Litija MWDs are most probably related with increased erosion of the fine-grained MWD material and re-sedimentation of sediments due to variations in stream flow regime at various times of sampling, which is also consistent with estimated entrainment of PHE-bearing phases. The effect of MWDs on PHE load in 3rd order stream is generally strongly diluted due to greater river size, its discharge and much greater ability to entrain PHE-bearing phases.

In Pleše area, the K-19/9–10 MWDs contributed significantly to strong contamination of sediments of local 1st order stream about 500 m below MWDs with Pb and moderate contamination with Sb, Hg and Ba in 2013 (Table 2). Further downstream, about 1500 m below MWDs, they still contributed to moderate contamination with Ba and Pb, but there was no influence on Hg content. Barium and Pb enrichment in 1st order stream sediments indicates that solid Ba- and Pb-bearing phases, occur in intermediate mobile grain size fraction, which is being resuspended and transported in the upper, higher flow velocity part, but deposited in the lower, low flow velocity part of the stream. This agrees with grain size distribution of PHE-bearing phases in sediments (Fig. 9f) and also with limited ability of the streams to entrain PHE-bearing phases.

In all investigated areas, the impacts of MWDs on PHE loads in sediments depend on distance from the MWDs, which is a function of grain size distribution of PHE-bearing phases in MWDs and MWD lithology, as well as hydrological conditions (e.g. high-water events) that affect the washing out and re-sedimentation of stream sediments. Furthermore, dilution effect due to stream order is also very important. In general, annual variations in river regime and extreme weather events cause rapid erosion of MWD material, resuspension and transport of PHE loaded sediment along smaller and larger streams over long distances and thus dispersion of pollution. There, fine-grained PHE-bearing phases as well as PHEs dissolved in stream water can affect groundwater and aquifers during high-water events (e.g. Brenčič and Keršmanc, 2016).

5.2. Solubility of PHE-bearing phases in stream water and impact on water pollution

Calculated solubilities of ore minerals and PHE-bearing secondary products of ore mineral weathering by PHREEQC code showed that the same species of ore minerals and secondary products of ore mineral weathering behave similarly in streams draining MWDs in areas of Litija and Pleše, with silicate-rich lithology, but differently in streams of the Mežica area, where carbonate bedrock prevails. Smithsonite, pyrolusite, pyrite, melanterite and anglesite should be the most soluble minerals in streams of the Mežica area, while pyromorphite should be much more stable (Fig. 10a). Cerussite, galena, sphalerite, barite and goethite are supposed to be stable and rather precipitate from solutions. There are no thermodynamic data for wulfenite, descloizite and hemimorphite, therefore their stability and solubility could not be assessed by using PHREEQC calculations. According to some studies, wulfenite is insoluble and rather precipitates at neutral pH (e.g. Conlan et al., 2012), solubility of descloizite is also low at pH above 8 (e.g. Sracek et al., 2014), while hemimorphite is generally soluble at pH above 7 in carbonate rich and silicate poor environment (e.g. McPhail et al., 2003; McPhail et al., 2006; Medas et al., 2017). In streams draining MWDs in areas of Litija and Pleše, anglesite (baritoanglesite), barite and goethite appear to be insoluble, while pyromorphite, sphalerite, cerussite, pyrite and particularly melanterite and pyrolusite are most soluble (Fig. 10b and c). Cinnabar in Litija area is slightly soluble only at lower pH and Eh and higher temperature. Solubility of all minerals in simulated stream waters in all areas varies somewhat with changes in water temperature, while variations in pH and Eh have no effect. Thus, anglesite and pyrite are less soluble at higher temperature, while melanterite, cerussite and sphalerite are slightly more soluble.

In Mežica area, morphologies of ore minerals (smithsonite, pyromorphite, cerussite, barite and galena) agree well with their calculated solubilities, while heavily corroded grains of sphalerite and uncorroded massive grains of pyrite and anglesite show that they behave differently as predicted by calculations. Massive wulfenite, descloizite and hemimorphite grains confirm that they are stable under given conditions. In Litija and Pleše areas, rather porous and pitted cerussite, pyromorphite and partly sphalerite grains agree with simulations. Occurrence and morphology of cinnabar grains show that it can be dissolved but can also precipitate when conditions change, which corresponds to solubility calculations. Partly corroded grains of baritoanglesite, insoluble according to calculations, indicate that they were exposed to dissolution. In all studied areas, morphologies of Fe-oxyhydroxides with minor Pb and Zn (and Cu) show they are insoluble or even precipitate as authigenic phases, while occurrence of Fe-oxyhydroxy sulphates with minor Pb and Zn (and Cu) is consistent with their unstable nature. Fe-oxyhydroxides and Fe-oxyhydroxy sulphates act as sinks for PHEs (Piantone et al., 2004), including Pb, Zn and Cu. However, they represent an exchangeable fraction and PHEs can thus be released back into aqueous solution when the natural conditions change. Observed grains of Mn-oxides with Pb and psilomelane with Pb are authigenic precipitates, which is not consistent with their calculated solubilities. Possible causes of inconsistencies between observed dissolution effects and calculated solubilities could be different local micro-conditions in MWDs and stream sediments, but also modes of occurrence and size of individual grains, as these are not accounted for in simulations. Particularly mineral porosity, cracks and small grain size (around 10 μm and 30 μm) increase specific surface areas of insoluble minerals, which can thus be subjected to dissolution when the conditions at microlevel change.

The results of MWD material leaching behaviour tests and their comparison with quantities of PHE-bearing phases in MWDs showed relatively good agreement between leachable Zn and Fe-oxyhydroxy sulphates with Pb and Zn, particularly in Mežica area. In Litija MWDs, higher Cu and Zn leachability could be related with presence of Fe-oxyhydroxy sulphates with minor Pb, Zn and Cu, and exceptionally high Pb leachability with presence of baritoanglesite, which is supported by observed grain morphology, but not by calculations.

Good agreement was also observed between concentrations of Pb, Zn and Cd in stream water and abundance of Pb-, Zn- and Cd-bearing phases in 1st order stream sediments from all areas. At locations with highest Pb stream water concentration, 1st order stream sediments had the highest quantities of Fe-oxyhydroxy sulphates with Pb and Zn (and Cu), while highest Zn and Cd water concentrations corresponded to highest quantities of sphalerite and smithsonite in stream sediments. The latter is consistent with observed dissolution effects but not entirely with calculated solubility.

According to calculated solubilities and observed morphologies of PHE-bearing phases, smithsonite, sphalerite, Fe-oxyhydroxy sulphates with minor Pb and Zn contribute the most to PHE pollution of stream

water under current environmental conditions in Mežica area. In Litija and Pleše areas, the greatest impact has dissolution of cerussite, sphalerite and Fe-oxyhydroxy sulphates with minor Pb and Zn (and Cu).

5.3. Origin and fate of Pb-bearing phases in the environment

Significant variations in Pb isotopic composition of sediments from all areas were determined. These variations do not seem to be connected with locations of stream sediments relative to MWDs (upstream or downstream of MWDs), which is not consistent with observations in some other mining regions (e.g. Potra et al., 2018). The variations observed in our case imply several possible explanations. The most plausible cause could be mixing of different sources of Pb-bearing phases. Stream sediment samples SS-26/3, SS-26/5, SS-26/8, SS-26/15 and SS-26/20 in Mežica area and SS-25/1, SS-25/6–7 in Litija area with higher isotopic ratios most probably reflect isotopic composition of primary Pb-bearing ore minerals and their secondary weathering products. Other sediments could be affected by fractionated Pb species emitted from current Pb recycling processes or by variations in isotopic composition of secondary raw materials, which is also common in smelting and refining processes (e.g. Shiel et al., 2010). Another possibility are differences in composition of local bedrock lithology and its presence in stream sediments, which can have different isotopic composition than ore minerals, particularly K-feldspars (e.g. Tyrrell et al., 2012; Johnson et al., 2018) and carbonate rocks (e.g. Kesler et al., 1994; Schroll et al., 2006). Very good agreement was observed between pseudo-total (AR) Pb sediment contents and Pb isotope ratios only in sediments of 1st order streams draining MWDs and not upstream of MWDs or in large 3rd order streams. This shows prevalent influence of Pb pollution on Pb isotope composition and also that higher Pb content and Pb isotope ratios should correspond to larger quantity of Pb-bearing ore minerals. However, there was no agreement between Pb isotope ratios and either contents of K, quantities of Pb-bearing phases or relative mineral abundances in investigated stream sediments. Since stream sediments contain certain amounts of organic matter and microorganisms (e.g. Logue et al., 2004), biologically induced isotopic fractionation and fractionation through preferential leaching of certain minerals and formation of secondary minerals with different isotopic composition (e.g. Reimann et al., 2008), cannot be ruled out, although some other authors argue against this (e.g. Le Roux et al., 2008). Fractionation induced by weathering of primary Pb-bearing ore minerals in streams was also considered as a possible cause of variations. However, Pb isotopes have been reported to be immune to fractionation via weathering of primary sulphides (e.g. Gulson et al., 2018). Variations due to chosen analytical procedure (quadrupole ICP-MS) could not be ruled out (e.g. Gulson et al., 2018), particularly interferences with Hg in Hg-bearing samples from Litija. In order to provide more accurate explanation on Pb isotope variations, further detailed studies are foreseen.

5.4. Mitigation of environmental impacts of MWDs

Several different measures can be undertaken to mitigate environmental impacts of MWDs. One of the medium-term solutions that includes immobilisation of fine-grained PHE-bearing material is improving geotechnical characteristics, particularly stability and erodibility of MWDs, by establishing surface drainage and proper anti-erosion control using nets and biological recultivation. A more efficient long-term solution is reuse of mining waste, which would remove the source of contaminants and improve the quality of local environment. However, the reuse of MWD material as construction aggregates has already proven controversial from the environmental point of view, since its improper use contributes to regional dispersion of hazardous material and increases pollution and health risk as in the case of kindergarten sandboxes where aggregates from Mežica MWDs were used as sandbox sand (Zupančič et al., 2021). The more acceptable way includes extraction of remaining metals from fine-grained fractions, followed by reuse of PHE-free gangue materials for construction. Further detailed studies of MWDs' secondary resource potential, processing technology and evaluation of environmental, legislative and social aspects of extraction are foreseen.

6. Conclusions

The results of the study showed that MWDs and stream sediments in all investigated areas contain very high levels of PHEs, particularly Pb, Zn, Cd, As, Ba and Hg, which mostly occur as PHE-bearing ore minerals (cerussite, sphalerite, smithsonite, barite, cinnabar), but also as secondary products of ore mineral weathering (Fe-oxyhydroxides and Fe-oxyhydroxy sulphates with Pb and Zn, and Mn-oxides with Pb). Water leaching potential of PHEs in MWDs is generally negligible and levels of PHEs in surface waters are decreasing with increasing stream order, which demonstrates that water drainage of MWDs predominantly contributes to pollution in solid particulate form rather than in dissolved form. Fine-grained solid pollutants mostly burden sediments of 1st order steams draining MWDs, while 3rd order stream (river) sediments are additionally affected by other local sources, such as Pb recycling plant in Mežica area. Most of the PHE-bearing ore minerals are soluble either in surface water under given conditions or under variable micro-conditions in stream sediment. However, released PHEs are partly removed by precipitation or coprecipitation of mostly stable secondary weathering products. Nevertheless, the fine-grained PHE-bearing material is being transported along rivers over long distances, thus causing regional dispersion of pollution. Since the investigated MWDs are a constant pollution source for local environment as well as regionally, it is very important to diminish their environmental impacts. One of the efficient solutions for the future is recycling of mining waste, which includes the extraction of remaining metals, followed by reuse of PHE-free gangue materials for construction.

Credit author statement

Miloš Miler: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft preparation, Writing-Reviewing and Editing, **Špela Bavec:** Conceptualization, Methodology, Investigation, Writing – original draft preparation, Writing-Reviewing and Editing, **Mateja Gosar:** Conceptualization, Methodology, Investigation, Writing – original draft preparation, Writing-Reviewing and Editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors acknowledge financial support from the state budget by the Ministry of the Environment and Spatial planning, obtained through the projects Inventory of closed facilities for management of waste derived from mining and other raw material extractive industries (contract No. 2330-13-000128) and Monitoring of closed facilities for management of waste derived from extractive industries (contract No. 2550-17-340000), which were performed by Geological survey of Slovenia in the scope of the national implementation tasks of the Directive 2006/21/EC. The study was also partly financed by the Slovenian Research Agency through the research programmes Groundwater and Geochemistry (P1-0020) and Mineral Resources (P1-0025), and research projects Source identification of solid pollutants in the environment on the basis of mineralogical, morphological and geochemical properties of particles (Z1-7187) and Dynamics and matter flow of potentially toxic elements (PTEs) in urban environment (J1-

1713). Financial assistance was provided also by Slovenian National Commission for UNESCO, National Committee of the International Geosciences and Geoparks Programme.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2022.114580.

References

Anawar, M.H., 2015. Sustainable rehabilitation of mining waste and acid mine drainage using geochemistry, mine type, mineralogy, texture, ore extraction and climate knowledge. J. Environ. Manag. 158, 111–121. https://doi.org/10.1016/j.jenvman.2015.04.045.

Anthony, J.W., Bideaux, R.A., Bladh, K.W., Nichols, M.C., 2009. The Handbook of Mineralogy. Mineralogical Society of America, Chantilly, VA. http://www.handbookofmineralogy.org/ (accessed 3 May 2021).

Barthelmy, D., 2012. The mineralogy database. http://webmineral.com/. (Accessed 3 May 2021).

Brenčič, M., Keršmanc, T., 2016. Groundwater under strong influence of surface water – case study from Črneče (Northern Slovenia). Geologija 59 (1), 85–98. https://doi.org/10.5474/geologija.2016.006.

Compton, R.R., 1962. Manual of Field Geology, fourth ed. Wiley, New York.

Conlan, M.J.W., Mayer, K.U., Blaskovich, R., Beckie, R.D., 2012. Solubility controls for molybdenum in neutral rock drainage. Geochem. Explor. Environ. Anal. 12, 21–32. https://doi.org/10.1144/1467-7873/10-RA-043.

Dino, G.A., Rossetti, P., Perotti, L., Alberto, W., Sarkka, H., Coulon, F., Wagland, S., Griffiths, Z., Rodeghiero, F., 2018. Landfill mining from extractive waste facilities: the importance of a correct site characterisation and evaluation of the potentialities. A case study from Italy. Res. Pol. 59, 50–61. https://doi.org/10.1016/j.resourpol.2018.04.012.

Dudka, S., Adriano, D.C., 1997. Environmental impacts of metal ore mining and processing: a review. J. Environ. Qual. 2, 590–602. https://doi.org/10.2134/jeq1997.00472425002600030003x.

Drovenik, M., Pleničar, M., Drovenik, F., 1980. The origin of Slovenian ore deposits (in Slovene). Geologija 23 (1), 1–137.

Finžgar, N., Jež, E., Voglar, D., Leštan, D., 2014. Spatial distribution of metal contamination before and after remediation in the Meza Valley, Slovenia. Geoderma 217–218, 135–143. https://doi.org/10.1016/j.geoderma.2013.11.011.

Förstner, U., Müller, G., 1973. Heavy metal accumulation in river sediments: a response to environmental pollution. Geoforum 4/2, 53–61. https://doi.org/10.1016/0016-7185(73)90006-7.

Fux, J., Gosar, M., 2007. Lead and other heavy metals in stream sediments in the area of Meža Valley (in Slovene). Geologija 50/2, 347–360. https://doi.org/10.5474/geologija.2007.025.

Goldstein, J., Newbury, D., Joy, D., Lyman, C., Echlin, P., Lifshin, E., Sawyer, L., Michael, J.R., 2003. Scanning Electron Microscopy and X-Ray Microanalysis, third ed. Kluwer Academic/Plenum Publishers, New York.

Gosar, M., Miler, M., 2011. Anthropogenic metal loads and their sources in stream sediments of the Meža River catchment area (NE Slovenia). Appl. Geochem. 26/11, 1855–1866. https://doi.org/10.1016/j.apgeochem.2011.06.009.

Gosar, M., Šajn, R., Miler, M., Markič, M., Čarman, M., 2014. Preparation of Inventory of Closed Facilities for Management of Waste Derived from Extractive Industries: Report of the 3rd Phase of the Project (In Slovene). Geological Survey of Slovenia, Ljubljana. http://www.arso.gov.si/varstvo%20okolja/odpadki/poro%C4%8Dila%20in%20publikacije/PORO%C4%8CILO%203%20FAZE_21022014.pdf. (Accessed 31 January 2017).

Gosar, M., Miler, M., Bavec, Š., 2017. Monitoring of Closed Facilities for Management of Waste Derived from Extractive Industries: Report on Performed Work for the Ministry of the Environment and Spatial Planning (RS) (In Slovene). Geological Survey of Slovenia, Ljubljana. http://www.arso.gov.si/varstvo%20okolja/odpadki/poro%C4%8Dila%20in%20publikacije/OdpadkiRudarji.pdf. (Accessed 21 August 2018).

Gosar, M., Šajn, R., Bavec, Š., Gaberšek, M., Pezdir, V., Miler, M., 2019. Geochemical background and threshold for 47 chemical elements in Slovenian topsoil. Geologija 62/1, 5–57. https://doi.org/10.5474/geologija.2019.001.

Gosar, M., Šajn, R., Miler, M., Burger, A., Bavec, Š., 2020. Overview of existing information on important closed (or in closing phase) and abandoned mining waste sites and related mines in Slovenia. Geologija 63/2, 221–250. https://doi.org/10.5474/geologija.2020.018.

Gošar, D., Costa, M.R., Ferreira, A., Štrucl, S.F., 2015. Assessment of past and present water quality in closed Mežica Pb-Zn Mine (Slovenia). Comunicações Geológicas 102/1, 65–69.

Gulson, B., Kamenov, G.D., Manton, W., Rabinowitz, M., 2018. Concerns about quadrupole ICP-MS lead isotopic data and interpretations in the environment and health fields. Int. J. Environ. Res. Publ. Health 15, 723. https://doi.org/10.3390/ijerph15040723.

Helser, J., Cappuyns, V., 2021. Trace elements leaching from Pb–Zn mine waste (Plombières, Belgium) and environmental implications. J. Geochem. Explor. 220, 106659. https://doi.org/10.1016/j.gexplo.2020.106659.

Hoskin, W., Bird, G., Stanley, T., 2000. Mining - facts, figures and environment. Ind. Environ. 23, 4–8.

Jamieson, H.E., Walker, S.R., Parsons, M.B., 2015. Mineralogical characterization of mine waste. Appl. Geochem. 57, 85–105. https://doi.org/10.1016/j.apgeochem.2014.12.014.

Jemec, M., Šajn, R., 2007. Geochemical research of soil and attic dust in Litija area, Slovenia (in Slovene). Geologija 50 (2), 497–505. https://doi.org/10.5474/geologija.2007.035.

JEOL, 2007. JSM-6490LV Scanning Electron Microscope, Instruction Manual. JEOL Ltd., Tokyo.

Jerzykowska, I., Majzlan, J., Michalik, M., Göttlicher, J., Steininger, R., Błachowski, A., Ruebenbauer, K., 2014. Mineralogy and speciation of Zn and as in Fe-oxide-clay aggregates in the mining waste at the MVT Zn–Pb deposits near Olkusz, Poland. Chem. Erde 74, 393–406. https://doi.org/10.1016/j.chemer.2014.03.003.

Johnson, S.P., Kirkland, C.L., Evans, N.J., McDonald, B.J., Cutten, H.N., 2018. The complexity of sediment recycling as revealed by common Pb isotopes in K-feldspar. Geosci. Front. 9, 1515–1527. https://doi.org/10.1016/j.gsf.2018.03.009.

Jordan, G., Bidoglio, G., DÀlessandro, M., Sommer, S., Hamor, T., Panagos, P., Van Liedekerke, M., Vijdea, A., 2009. Sustainable mineral resources management: from regional mineral resources exploration to spatial contamination risk assessment of mining. Environ. Geol. 58 (1), 153–169. https://doi.org/10.1007/s00254-008-1502-y.

Jurjovec, J., Ptacek, C.J., Blowes, D.W., 2002. Acid neutralization mechanisms and metal release in mine tailings: a laboratory column experiment. Geochem. Cosmochim. Acta 66, 1511–1523. https://doi.org/10.1016/S0016-7037(01)00874-2.

Kesler, S.E., Krstic, D., Appold, M.S., 1994. Lead isotope geochemistry of Mississippi Valley-type deposits of the southern appalachians. Econ. Geol. 89, 307–321. https://doi.org/10.2113/gsecongeo.89.2.307.

Kříbek, B., Majer, V., Pasava, J., Kamona, F., Mapani, B., Keder, J., Ettler, V., 2014. Contamination of soils with dust fallout from the tailings at the Rosh Pinah area, Namibia: regional assessment, dust dispersion modeling and environmental consequences. J. Geochem. Explor. 144, 391–408. https://doi.org/10.1016/j.gexplo.2014.01.010.

Lindsay, M.B.J., Moncur, M.C., Bain, J.G., Jambor, J.L., Ptacek, C.J., Blowes, D.W., 2015. Geochemical and mineralogical aspects of sulfide mine tailings. Appl. Geochem. 57, 157–177. https://doi.org/10.1016/j.apgeochem.2015.01.009.

Le Roux, G., Sonke, J.E., Cloquet, C., Aubert, D., de Vleeschouwer, F., 2008. Comment on "The biosphere: a homogeniser of Pb isotope signals". In: Reimann, C., Flem, B., Arnoldussen, A., Englmaier, P., Finne, T.E., Koller, F., Nordgulen, Ø. (Eds.), Appl. Geochem, vol. 23, pp. 2789–2792. https://doi.org/10.1016/j.apgeochem.2008.05.017.

Logue, J.B., Robinson, C.T., Meier, C., Van der Meer, J.R., 2004. Relationship between sediment organic matter, bacteria composition, and the ecosystem metabolism of alpine streams. Limnol. Oceanogr. 49 (6), 2001–2010. https://doi.org/10.4319/lo.2004.49.6.2001.

McPhail, D.C., Summerhayes, E., Welch, S., Brugger, J., 2003. The geochemistry of zinc in the regolith. In: Roach, I.C. (Ed.), Advances in Regolith. CRC for Landscape Environments and Mineral Exploration, pp. 287–291.

McPhail, D.C., Summerhayes, E., Jayaratne, V., Christy, A., 2006. Hemimorphite solubility and stability of low-T zinc minerals. Geochem. Cosmochim. Acta 70, A414. https://doi.org/10.1016/j.gca.2006.06.1582.

Medas, D., Podda, F., Meneghini, C., De Giudici, G., 2017. Stability of biological and inorganic hemimorphite: implications for hemimorphite precipitation in non-sulfide Zn deposits. Ore Geol. Rev. 89, 808–821. https://doi.org/10.1016/j.oregeorev.2017.07.015.

Miler, M., Gosar, M., 2012. Characteristics and potential environmental influences of mine waste in the area of the closed Mežica Pb-Zn mine (Slovenia). J. Geochem. Explor. 112, 152–160. https://doi.org/10.1016/j.gexplo.2011.08.012.

Miler, M., Gosar, M., 2013. Assessment of metal pollution sources by SEM/EDS analysis of solid particles in snow: a case study of Žerjav, Slovenia. Microsc. Microanal. 19/6, 1606–1619. https://doi.org/10.1017/S1431927613013202.

Miler, M., Gosar, M., 2019. Assessment of contribution of metal pollution sources to attic and household dust in Pb-polluted area. Indoor Air 29, 487–498. https://doi.org/10.1111/ina.12548.

Mlakar, I., 2003. On the problems of Ba, Pb, Zn Pleše ore deposit (Slovenia) (in Slovene). Geologija 46/2, 185–224. https://doi.org/10.5474/geologija.2003.018.

Müller, G., 1979. Index of geoaccumulation in sediments of the rhine river. J. Geol. 2/3, 108–118.

Oxford Instruments, 2006. INCA Energy Operator Manual. Oxford Instruments Analytical Ltd, High Wycombe.

Parkhurst, D.L., Appelo, C.A.J., 1999. Users' Guide to PHREEQC (Version 2)—a Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. U.S. Geological Survey, Denver.

Piantone, P., Bodénan, F., Chatelet-Snidaro, L., 2004. Mineralogical study of secondary mineral phases from weathered MSWI bottom ash: implications for the modelling and trapping of heavy metals. Appl. Geochem. 19, 1891–1904. https://doi.org/10.1016/j.apgeochem.2004.05.006.

Potra, A., Ruhl, L.S., Samuelsen, J.R., 2018. Legacy lead from past mining activity and gasoline additives: evidence from lead isotopes and trace element geochemical studies in the white river basin, southern ozark region. USA. Geosciences 8, 189. https://doi.org/10.3390/geosciences8060189.

Prospero, J.M., Lamb, P., 2003. African droughts and dust transport to the caribbean: climate change implications. Science 302/5647, 1024–1027. https://doi.org/10.1126/science.1089915.

Reimann, C., Flem, B., Arnoldussen, A., Englmaier, P., Finne, T.E., Koller, F., Nordgulen, O., 2008. The biosphere: a homogeniser of Pb isotope signals. Appl. Geochem. 23, 705–722. https://doi.org/10.1016/j.apgeochem.2007.12.002.

Rodríguez, L., Ruiz, E., Alonso-Azcárate, J., Rincón, J., 2009. Heavy metal distribution and chemical speciation in tailings and soils around a Pb–Zn mine in Spain. J. Environ. Manag. 90, 1106–1116. https://doi.org/10.1016/j.jenvman.2008.04.007.

Sadeghi, M., Petrosino, P., Ladenberger, A., Albanese, S., Andersson, A., Morris, G., Lima, A., De Vivo, B., The GEMAS Project Team, 2013. Ce, La and Y concentrations in agricultural and grazing-land soils of Europe. J. Geochem. Explor. 133, 202–213. https://doi.org/10.1016/j.gexplo.2012.12.007.

Salomons, W., 1995. Environmental impact of metals derived from mining activities: processes, predictions, prevention. J. Geochem. Explor. 52, 5–23. https://doi.org/10.1016/0375-6742(94)00039-E.

Schroll, E., Köppel, V., Cerny, I., 2006. Pb and Sr isotope and geochemical data from the Pb–Zn deposit Bleiberg (Austria): constraints on the age of mineralization. Mineral. Petrol. 86, 129–156. https://doi.org/10.1007/s00710-005-0107-3.

Sedlar, J., 1950. The Possibility of Development of Mines in the Sava Folds with Special Regard to Litija. Diploma thesis. University of Ljubljana, Faculty of Natural Sciences and Engineering, department of Geology, Ljubljana.

Shiel, A.E., Weis, D., Orians, K.J., 2010. Evaluation of zinc, cadmium and lead isotope fractionation during smelting and refining. Sci. Total Environ. 408, 2357–2368. https://doi.org/10.1016/j.scitotenv.2010.02.016.

Shu, X.-H., Zhang, Q., Lu, G.-N., Yi, X.-Y., Dang, Z., 2018. Pollution characteristics and assessment of sulfide tailings from the Dabaoshan Mine, China. Int. Biodeterior. Biodegrad. 128, 122–128. https://doi.org/10.1016/j.ibiod.2017.01.012.

Slovenian Environment Agency, 2021a. Archive - Observed and Measured Meteorological Data in Slovenia. Ministry of the Environment and Spatial Planning, Slovenian Environment Agency, Ljubljana. http://meteo.arso.gov.si/met/sl/archive/. (Accessed 5 July 2021).

Slovenian Environment Agency, 2021b. Hydrological Data - Archive Hydrological Data. Ministry of the Environment and Spatial Planning, Slovenian Environment Agency, Ljubljana. https://www.arso.gov.si/en/water/data/. (Accessed 20 December 2021).

Slovenian Water Agency, 2018. eVode. http://www.evode.gov.si/sl/vodni-kataster/zbirka-vode/zbirka-podatkov-o-povrsinskih-vodah/hidrografija/#collapse-237. (Accessed 3 May 2021) (in Slovene).

Spangenberg, J.E., Lavrič, J.V., Herlec, U., 2001. Sulfur-isotope study of the Mežica Mississippy Valley-type lead-zinc ore deposits, Slovenia. In: Piestrzynski, A. (Ed.), Mineral Deposits at the Beginning of the 21st Century. Proc. 6th Bienn. SGA Meeting, Kraków (Poland), 26-29 August 2001. Balkema, Lisse, pp. 181–184.

Sracek, O., Mihaljevič, M., Kříbek, B., Majer, V., Filip, J., Vaněk, A., Penížek, V., Ettler, V., Mapani, B., 2014. Geochemistry and mineralogy of vanadium in mine tailings at Berg Aukas, northeastern Namibia. J. Afr. Earth Sci. 96, 180–189. https://doi.org/10.1016/j.jafrearsci.2014.04.003.

Sundborg, A., 1956. The River Klarålven: chapter 2. The morphological activity of flowing water—erosion of the stream bed. Geogr. Ann. 38, 165–221.

Svete, P., Milačič, R., Pihlar, B., 2001. Partitioning of Zn, Pb and Cd in river sediments from a lead and zinc mining area using the BCR three-step sequential extraction procedure. J. Environ. Monit. 3, 586–590. https://doi.org/10.1039/b106311c.

Šajn, R., 2006. Factor Analysis of soil and attic-dust to separate mining and metallurgy influence, Meža valley, Slovenia. Math. Geol. 38 (6), 735–747. https://doi.org/10.1007/s11004-006-9039-7.

Šajn, R., Gosar, M., 2007. Soil pollution in surroundings of Litija as a reflection of mining, metallurgy and natural conditions. Geologija 50 (1), 131–145. https://doi.org/10.5474/geologija.2007.011.

Šajn, R., Gosar, M., 2014. Multivariate statistical approach to identify metal sources in Litija area (Slovenia). J. Geochem. Explor. 138, 8–21. https://doi.org/10.1016/j.gexplo.2013.12.007.

Šoster, A., Zavašnik, J., Ravnjak, M., Herlec, U., 2017. REE-bearing minerals in Drava river sediments, Slovenia, and their potential origin. Geologija 60 (2), 257–266. https://doi.org/10.5474/geologija.2017.018.

Štrucl, I., 1984. Geological and geochemical characteristics of ore and host rock of lead-zinc ores of the Mežica ore deposit. Geologija 27, 215–327.

Tegen, I., Werner, M., Harrison, S.P., Kohfeld, K.E., 2004. Relative importance of climate and land use in determining present and future global soil dust emission. Geophys. Res. Lett. 31, L05105. https://doi.org/10.1029/2003GL019216.

Teršič, T., Miler, M., Gaberšek, M., Gosar, M., 2018. Contents of arsenic and some other elements in stream sediments and waters of the Medija drainage basin, central Slovenia (in Slovene). Geologija 61/1, 5–24. https://doi.org/10.5474/geologija.2018.001.

Tyrrell, S., Haughton, P.D.W., Daly, J.S., Shannon, P.M., 2012. The Pb isotopic composition of detrital K-feldspar: a tool for constraining provenance, sedimentary processes and paleodrainage. In: Sylvester, P. (Ed.), Quantitative Mineralogy and Microanalysis of Sediments and Sedimentary Rocks, Mineralogical Association of Canada Short Course Series 42. Mineralogical Association of Canada, Québec, pp. 203–217.

Zeeh, H., Kuhlemann, J., Bechstdädt, T., 1998. The classical Pb-Zn deposits of the Eastern Alps (Austria/Slovenia) revisited: MVT deposits resulting from gravity driven fluid flow in the Alpine realm. Geologija 41, 257–273. https://doi.org/10.5474/geologija.1998.014.

Zhang, X.Y., Gong, S.L., Zhao, T.L., Arimoto, R., Wang, Y.Q., Zhou, Z.J., 2003. Sources of Asian dust and role of climate change versus desertification in Asian dust emission. Geophys. Res. Lett. 30/24, 2272–2276. https://doi.org/10.1029/2003GL018206.

Zupan, M., Grčman, H., Lobnik, F., 2008. Research of Soil Pollution in Slovenia (In Slovene). Slovenian Environment Agency, Ljubljana.

Zupančič, N., Miler, M., Ašler, A., Pompe, N., Jarc, S., 2021. Contamination of children's sandboxes with potentially toxic elements in historically polluted industrial city. J. Hazard Mater. 412, 125275. https://doi.org/10.1016/j.jhazmat.2021.125275.

Žibret, G., Gosar, M., 2017. Multi-elemental composition of the Sava River sediments (Slovenia, EU). Environ. Earth Sci. 76, 501. https://doi.org/10.1007/s12665-017-6835-y.

Žibret, G., Gosar, M., Miler, M., Alijagić, J., 2018. Impacts of mining and smelting activities on environment and landscape degradation—Slovenian case studies. Land Degrad. Dev. 29, 4457–4470. https://doi.org/10.1002/ldr.3198.