Environmental risk related to presence and mobility of As, Cd and Tl in soils in the vicinity of a metallurgical plant — Long-term observations

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HIGHLIGHTS

- The contents of As, Cd and Tl in soil are considerably higher than 20 years earlier.
- An increase in the share of organic and residual fractions in soils was measured.
- The quantity of phytoavailable As, Cd and Tl has increased over the last two decades.
- Nowadays the main source of pollution is erosion and deflation processes.

ARTICLE INFO

ABSTRACT

Analysis of the content of As, Cd and Tl accompanying Zn—Pb ores was performed using soil material sampled around the zinc-works in Miasteczko Śląskie. It was found that the total content of As, Cd and Tl was considerably higher than the values recorded at the same sites 20 years earlier. This clearly confirms considerable pollution of the environment which continues despite pro-ecological actions taken by the zinc-works. The analysis of the spatial distribution of pollution revealed that the zinc-works itself is no longer the main source of contamination as was the case in 1998. Instead, in 2018 the main sources of As, Cd and Tl emissions were the erosion and deflation processes in old, unprotected mining and industrial waste dumps located near the zinc-works. The most polluted soil layers are the top layers in the soil profile. The content of As, Cd and Tl determined in them was 10 times greater than in the deep layers. There was also a positive change in environmental conditions, which occurred over the preceding 20 years, namely an increase in the content of sparingly soluble fractions, fractions bound with organic matter, and residual fractions. It was also found that depending on the geochemical background and readily mobile fraction values used in the calculations, there is still very high contamination and very high ecological risk with respect to As, Cd and Tl after 20 years. However, when using the quantity of phytoavailable elements as well as the quantity of cations on ion exchange positions and bound to carbonates to calculate the risk assessment code, the analysis showed that environmental conditions improved.

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1. Introduction

The condition of the environment is the sum of gradual changes which have occurred in it over hundreds of millions of years as well as sudden ones recorded in numerous research papers, especially in the recent century. Changes occurring in the chemical composition of surface water, atmosphere and pedosphere affect the biosphere's chemistry (Bączek-Kwinta et al., 2018; De Miguel et al., 2007; Kicińska, 2019; Liu et al., 2018a, 2018b). They result not only in entire species or individuals dying out, but also in the refinement of adaptation processes in environments which were strongly transformed by human activity. This adaptation mostly involves the improvement of organisms' tolerance following repeated contact with growing quantities of toxic substances (Kicińska and Jelonek-Waliszewska, 2017; Pietrzykowski et al., 2018).

Technological progress is the cause of increased exploitation of mineral resources (Data on Poland, 2019; Shen et al., 2017), but at the same time makes humanity turn towards more sustainable

management of such resources. High-tech processing of metal ores and closed circulation of waste in the economy are undoubtedly crucial tasks that must be tackled to further civilizational development. Unfortunately, the ever-increasing consumption of natural resources causes further and more in-depth transformation of primeval ecosystems (Ghayoraneh and Qishlaqi, 2017). It occurs by introducing increasingly transformed and hazardous chemical compounds into the environment, which aggressively affect the natural biochemical and geochemical processes causing their acyclicity and incompleteness (Cortada et al., 2018; Kabata-Pendias and Pendias, 2000; Hansen et al., 2001). Soil is the main food chain link in the biosphere. It provides plants with the minerals they require and allows for the development of life, especially in land ecosystems. Apart from substances that are needed to support life, soil also contains those that are highly toxic (pollutants). These undoubtedly include As, Cd and Tl in the amounts exceeding their natural content of 0.1−30, 0.01−2.5 and 0.01−2.8 (mg·kg^{-1}), respectively (Kabata-Pendias and Szteke, 2012). The elements listed are frequently used in industrial production but are highly toxic for living organisms. As, Cd and Tl are introduced to the environment as a by-product of e.g. Zn, Pb or Cu ore processing and as a result of combustion of solid fuels which may contain considerable amounts of these elements (Piekut et al., 2019; Antonkiewicz et al., 2018; Kosa and Kicińska, 2016; Kicińska, 2017; Kicińska, 2017; Kicińska and Mamak, 2017; Liu et al., 2016). These elements are considered very harmful and very hazardous to human health (De Miguel et al., 2016; Kicińska, 2017; IARC, 1987; IARC, 1990).

Despite introducing limitations in the use of As, Cd and Tl in production processes, their concentrations in soil remain to exceed the natural levels (Akopyan et al., 2018; Kicińska and Bożęcki, 2017; Piekut et al., 2019). Considering the readily soluble character and ease of migration of As and Cd compounds (Kabata-Pendias and Mukherjee, 2007) as well as their considerable dissipation in the environment, we decided to conduct a study based on 20-year observations of areas in the vicinity of a plant processing Zn−Pb ores with the purpose of: (i) establishing changes in the total content of As, Cd and Tl and their ability to migrate in top soil layers and within soil profiles; (ii) identifying fractions that bind these elements based on a phase composition analysis and multi-step chemical extraction; and (iii) determining the availability of As, Cd and Tl to living organisms by means of extracting phytoavailable forms of the metals from various soils. Based on these calculations, the final aim of the study was to (iv) determine the environmental risk related to the presence of readily mobile forms of As, Cd and Tl based on the following geochemical indices and factors: contamination factor (*CF*), pollution load index (*PLI*), geoaccumulation index (I_{geo}), total degree of contamination (C_d), ecological risk factor (E_f), potential ecological risk index (*RI*) and risk assessment code (*RAC*).

2. Study area

The "Miasteczko Śląskie" zinc-works is located in Miasteczko Śląskie in Śląskie Province in southern Poland. The plant is located about 1 km N of the city centre next to province road 908 and about 11 km NE of the town of Tarnowskie Góry. The zinc-works was established in 1967 and currently employs 700 people and conducts multiple types of operations including production of lead, zinc, tin and copper as well as production of other non-ferrous metals, inorganic chemicals and noble metals. Additionally, it produces and supplies steam, hot water and air for air conditioning systems and collects hazardous waste. The production of zinc and lead in the "Miasteczko Śląskie" zinc-works is conducted in a pyrometallurgical process. Zinc is manufactured using the Imperial

Smelting Process (ICP) and then rectified. Lead and cadmium are refined. The zinc-works produces 80 000 tons of zinc per year, which amounts to 40% of Poland's national output and 50% of the national output of lead and its alloys. In the 1980s, this plant was considered one of the biggest polluters in Europe.

3. Materials and methods

3.1. Materials and location of sampling sites

The research material comprised top layer soil samples (collection depth of 0−20 cm below ground level) and soil profiles (samples collected at 10 cm intervals from ground level to the depth of 50 cm) collected in the years 1998 and 2018 in the vicinity of Miasteczko Śląskie zinc-works. Samples from soil profiles (subsoil) were taken separately from top-layer samples. A total of 10 independent top layer soil samples were collected in each of the 4 sites (habitats) differing in distance and location in relation to the zinc-works (depending on the prevailing wind direction) (Fig. 1). The total number of top layer soil samples in each of the sampling campaigns amounted to 40 and the weight of each independent sample was at least 0.5 kg. The soil samples were dried in room temperature (22 °C), sieved using a sieve with 2 mm mesh, averaged, reduced and dehumidified (at 105 °C).

3.2. Analytical methods

The samples were used to establish the pH and quantity of As, Cd and Tl cations leached by an aqueous solution (1:10 ratio between the solid phase and the solution) and to perform BCR sequential extraction (European Commission's Community Bureau of Reference, EC 1881/2006, Davidson et al., 1998, Quevauviller, 2003). The extraction allowed for establishing the percentage share of the following forms (fractions):

I. exchangeable − easily soluble in the acid environment. Provides the metals contained at the exchangeable positions as well as those bound by carbonates; extraction with 0.1 M CH$_3$COOH;

II. reducible − susceptible to reduction. Provides the metals bound by amorphous oxides/oxyhydroxides of Fe and Mn; extraction with 0.1 M NH$_2$OH·HCl;

III. oxidisable − susceptible to oxidation. Provides the metals contained within the organic, metalorganic and sulphidic components; extraction with 30% H$_2$O$_2$ and 1 M CH$_3$COONH$_4$;

IV. residual − extraction with HCl:HNO$_3$ (mixed at the ratio 3:1).

Single extraction procedure was applied to evaluate the mobility of As, Cd and Tl in soils. It involved using aqueous solutions of increasing acidity (i.e. decreasing pH) obtained by adding 7 different doses of acid (from 0 to 120 mmol HNO$_3$ per dm^{-3}).

The pseudo-total content of the elements analysed in the soil samples was determined by extraction in *aqua regia* (HCl + HNO$_3$, at the ratio 3:1) in a SCP SCIENCE microwave oven, type DigiPREP HT, at 130 °C.

The determinations of the bioavailable (e.g. for plants and soil organism) quantities of metals were conducted after a 2.5-h extraction of the analytical samples with 0.11 M solution of EDTA (solid to liquid ratio 1:10). EDTA is used extensively in soil sciences to determine the bioavailability of trace elements (including metals) and possible decontamination methods of polluted soils (Lo and Yang, 1999; Manouchehri et al., 2006; Karczewska et al., 2009).

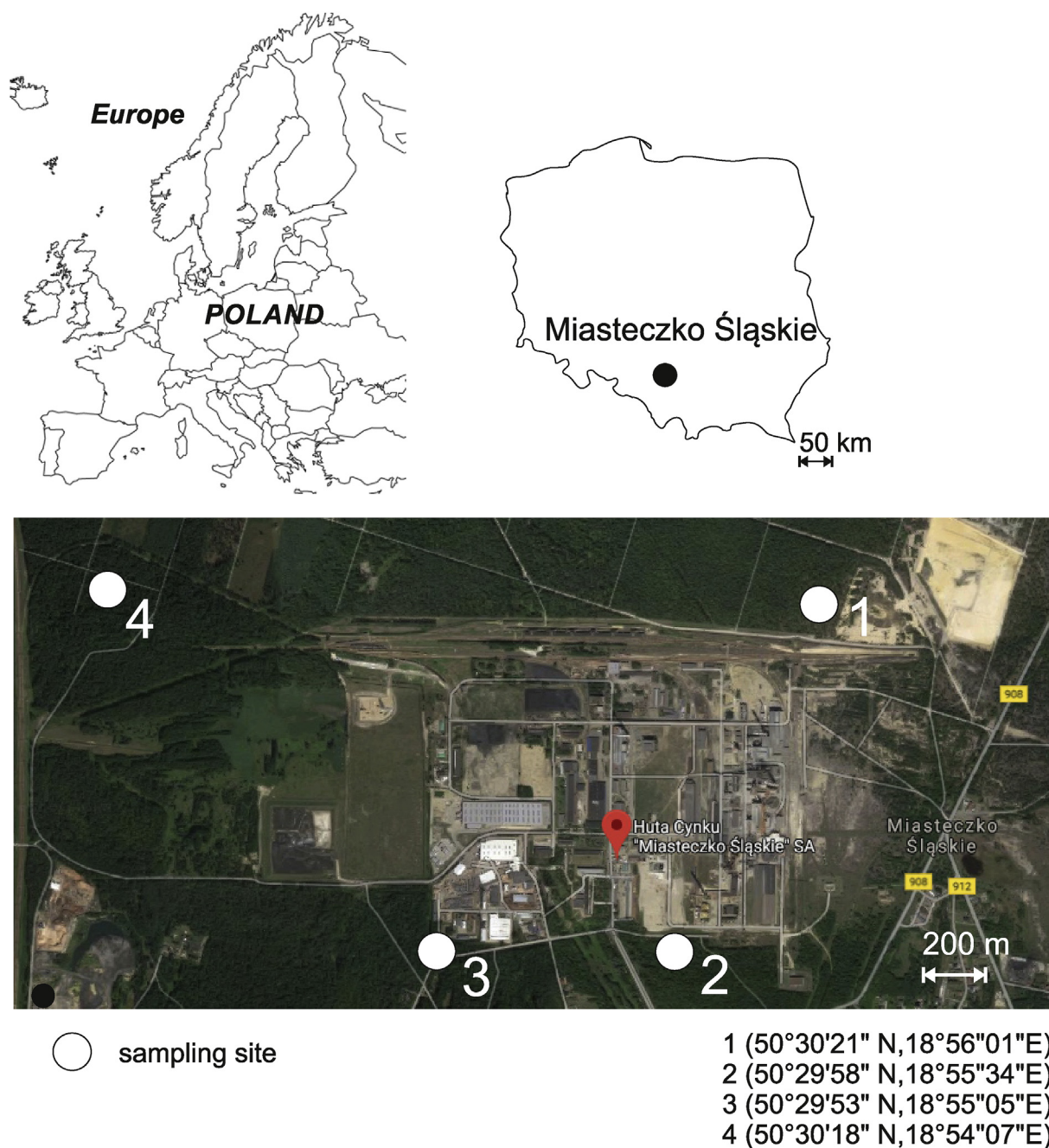X-ray fluorescence method (Rigaku WD-XRF ZSX Primus II

Fig. 1. Sampling sites (based on google maps).

spectrometer, X-ray tube) was used to determine the chemical (total content) and phase composition of the material collected for elemental analysis of the fragmented material by identifying spectral lines and detecting any coincidence of these lines. The analysis was conducted within the fluorine-uranium range (F−U) using SQX Calculation software (fundamental parameters method). Sample compositions were normalized to 100%. The phase composition of crystalline components was carried out using a Rigaku MiniFlex 600 XRD diffractometer. The interplanar distances obtained from the X-rays patterns were used for identifying crystalline phases based on the data of the International Centre for Diffraction Data catalogue and the XRAYAN software. Soil chemical composition was analysed with the XRF method only for samples from year 2018.

The chemical composition was determined using the method of induced coupled plasma mass emission spectroscopy (ICP-MS) at the certified geochemical laboratory (certificate no. AB1050) of the AGH University of Science and Technology in Krakow. The Certipur Certified Reference Material (CRM048, Lot LRAB1604) was used as a standard. The precision of the determining As, Cd and Tl was 10%, while the accuracies (AO) ranged between 90 and 98%. The limits of detection (LOD) and quantification (LOQ) parameters were calculated from the following equations:

$$LOD = X_b + 3SD_b \qquad (1)$$

$$LOQ = X_b + 10SD_b \qquad (2)$$

where:

X_b — mean concentration of the blank (zero concentration) sample;

SD_b — the standard deviation of the blank; and their values are presented in Table 2.

3.3. Risk assessment indicators

Environmental risk assessment was calculated according to risk assessment code (RAC), dividing the element's concentration in exchangeable fraction (i.e. EDTA-extractable phase) by the total concentration of this element. When the ratio in less than 1%, it means the element has no adverse impact on the environment. If the ratio is between 1 and 10%, a low risk is defined, 11−30% is medium risk, and 31−50% indicates a high risk. The values above 50% indicate a very high risk to the environment (Pan et al., 2013).

To evaluate the degree of soil contamination with As, Cd and Tl, the following indices were used: Geoaccumulation Index (I_{geo}), Contamination Factor (CF) and Pollution Load Index (PLI). I_{geo} (Eq. (3)) allows for evaluating the soil contamination by a comparison of the concentration of the analysed element with the geochemical background value (Müller, 1981):

$$I_{geo} = \log_2 \frac{Cn}{1.5Bn} \qquad (3)$$

where:

C_n — content of the analysed element in a soil sample ($mg \cdot kg^{-1}$),

B_n — geochemical background for the analysed element ($mg \cdot kg^{-1}$),

1.5 — natural fluctuation of the given element content in the natural environment, with a slight anthropogenic effect.

I_{geo} classifies soils in a 7-stage scale, where class 0 denotes non-polluted soils, and class 6 — extremely polluted soils.

As the second indicator for evaluation of the condition of soil contamination, contamination factor (CF) was used, calculated

based on the following equation:

$$CF = \frac{Cn}{Bn} \qquad (4)$$

where:

C_n — content of the element in a soil sample ($mg \cdot kg^{-1}$),

B_n — geochemical background of the analysed element ($mg \cdot kg^{-1}$).

Håkanson (1980) classified soils using a four-stage scale based on the contamination factor, where CF values lower than 1 mean low contamination, 1 to 3 — moderate contamination, 3 to 6 — heavy contamination, and values higher than 6 — very heavy contamination.

The Pollution Load Index (PLI) represents the total pollution calculated for all elements analysed. This index was calculated using the formula below:

$$PLI = \sqrt[n]{ConcF1 ConcF2 \ldots ConcFn} \qquad (5)$$

where:

$ConcFn$ — denotes the content of the element in the sample in relation to its geochemical background.

If PLI<1, there is no pollution. If PLI>1, the environmental matrix studied is polluted.

Based on the work of Håkanson (1980), C_d — degree of contamination, E_f — potential ecological risk factor and RI — potential ecological risk index were calculated. The values of 10, 30 and 30 respectively were used as the toxic response factor for As, Cd and Tl.

Statistical calculations and data presentations were conducted with the Statistica ver. 13.1 and Excel applications. The differences between means were detected by the Tukey's HSD test at a significance level of 0.05. Based on the statistical evaluation of the uncertainty of the analysed parameters, the quantity and type of the analysed material can be considered sufficient for a proper geochemical reasoning, although the obtained research results are of exploratory character.

Table 1
Chemical total content (mass %) of top layer soils samples from zinc-works surrounding measured by XRF diffraction in 2018.

Sample site	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	ZnO	PbO	CaO	K$_2$O	SO$_3$	MgO	TiO$_2$	P$_2$O$_5$	Na$_2$O	CuO	MnO	CdO	Σ	Others < 0.1
	[% mass]																
1[a]	71.17	7.78	4.95	4.74	4.08	1.70	1.69	1.49	0.65	0.40	0.30	0.20	0.15	0.14	<0.1	99.44	BaO, Cl, Cr$_2$O$_3$, NiO, As$_2$O$_3$, SeO$_2$, Rb$_2$O, SrO, ZrO$_2$, SnO$_2$, Bi$_2$O$_3$
2[a]	69.06	7.70	6.07	1.09	1.14	9.36	1.97	0.63	1.26	0.46	0.14	0.5	<0.1	0.20	<0.1	99.58	Cl, Cr$_2$O$_3$, NiO, CuO, As$_2$O$_3$, Rb$_2$O, SrO, ZrO$_2$, BaO,
3[a]	80.56	6.48	3.75	0.61	0.49	3.63	1.68	0.40	0.77	0.41	0.23	0.46	<0.1	0.15	0.1	99.62	Cl, V$_2$O$_5$, Cr$_2$O$_3$,NiO, CuO, As$_2$O$_3$, Rb$_2$O, SrO, ZrO$_2$, BaO,
4[a]	73.18	5.22	3.27	3.96	2.39	6.51	1.32	1.36	0.61	0.39	0.33	0.31	<0.1	<0.1	0.36	99.21	Cl, Cr$_2$O$_3$, NiO, CuO, As$_2$O$_3$, SeO$_2$, Rb$_2$O, SrO, Y$_2$O$_3$, ZrO$_2$, SnO$_2$, BaO, Tl$_2$O$_3$
For all samples ($n = 40$)																	
Min	69.06	5.22	3.27	0.61	0.49	1.70	1.32	0.40	0.61	0.39	0.14	0.20	0.02	0.06	0.03	83.52	Cl, Cr$_2$O$_3$, NiO, As$_2$O$_3$, SeO$_2$, Rb$_2$O, SrO, Bi$_2$O$_3$
Max	80.56	7.78	6.07	4.74	4.08	9.36	1.97	1.49	1.26	0.46	0.33	0.50	0.38	0.20	0.36	119.54	Y$_2$O$_3$, ZrO$_2$, SnO$_2$, BaO, Tl$_2$O$_3$, V$_2$O$_5$,
Av	73.49	6.80	4.51	2.60	2.03	5.30	1.67	0.97	0.82	0.42	0.25	0.37	0.15	0.14	0.16	99.68	
Me	72.18	7.09	4.35	2.53	1.77	5.07	1.69	1.00	0.71	0.41	0.27	0.39	0.10	0.15	0.04	97.75	
SD	4.33	1.05	1.09	1.78	1.37	2.90	0.23	0.46	0.26	0.03	0.07	0.12	0.07	0.05	0.02	13.83	
V	6	15	24	68	67	55	14	47	32	7	28	32	47	36	13		

Min − minimum, Max − maximum, Av − arithmetic average, Me − median, SD − standard deviation, V − coefficient of variation.
[a] Average for 10 samples from each site.

Table 2
The content of As, Cd and Tl in top layer soils samples from the close surrounding of zinc-works.

Parameters		As		Cd		Tl	
		$(mg \cdot kg^{-1})$					
CRM	reference values	123 ± 1.90		224 ± 3.64		52.0 ± 1.68	
	measure values	115 ± 2.60		203 ± 0.34		50.9 ± 0.20	
	(AO%)	(93.5)		(90.5)		(97.9)	
LOD		0.0014		0.0013		0.0077	
LOQ		0.0034		0.0029		0.0220	
Sample sites							
year		1998[b]	2018[a]	1998	2018	1998	2018
1		34	262	24	739	24	74
2		195	237	188	168	47	5
3		13	113	9	47	17	5
4		61	689	22	3056	37	143
For all samples ($n = 40$)							
Av ± SD		76 ± 14	326 ± 128	61 ± 17	1003 ± 303	31 ± 3	55 ± 15
Me		48	250	23	454	31	40
V		18	39	28	30	10	27
Upper limit determined for soil belong to:							
II category *(% of samples upper this limit)*[c]		10 *(100%)*		2 *(100%)*		−	
IV category *(% of samples upper this limit)*[c]		100 *(100%)*		15 *(100%)*		−	
Natural content [d] *(% of samples upper this limit)*[d]		<0.9−3.4 *(100%)*		1.1−0.8 *(100%)*		0.014−2.8 *(100%)*	

CRM − certified research material, LOD - limit of detection, LOQ − limit of quantification, AO − analysis trueness.
- not specified.
Av − arithmetic average, Me − median, SD − standard deviation, V − coefficient of variation.
   [a] For 2018 (this study).
   [b] For 1998 (Kicińska-Świderska, 1999).
   [c] According to Minister of the Environment (2016) for 2018 year sampling only: II category - arable land, orchards, pastures, permanent meadows, IV category - industrial areas, mining areas, communication areas.
   [d] According to Kabata-Pendias and Szteke (2012) for the appropriate type of soil.

4. Results

4.1. Chemical and phase composition of soil samples

4.1.1. Total chemical composition (XRF) and phase composition (XRD) of soil

The dominant chemical component in soils is silica (SiO_2), whose content ranges from 69 to over 80% mass (Table 1). The content of oxides is much smaller (in % mass): Al_2O_3 (5−8), Fe_2O_3 (3−6), CaO (2−9), K_2O (1−2), MgO (0.6−1.3) and P_2O_5 (0.1−0.3). The substances and elements listed above are commonly found in soils. Their content does not differ significantly from chemical composition of unpolluted soils found in this region. However, when it comes to the quantities of Zn, Pb and Cd compounds, the differences are significant: oxide forms of these elements found in soil samples collected in the vicinity of Miasteczko Śląskie amounted to: 0.6−4.7%, 0.5−4.1% and 0.03−0.4% respectively, while their natural content in soils amounts to (in $mg \cdot kg^{-1}$): 35−80, 13−25 and 0.05−0.5 respectively (Kabata-Pendias and Pendias, 2000).

Also, sulphur compounds (<1% mass) and Ti, Na, Cu and Mn oxides (<0.5% mass) were found in the samples tested. Finally, trace quantities (<0.1% mass) of As, Ba, Bi, Cl, Cr, Ni, Rb, Se, Sn, Sr, Tl, Y and Zr were also found.

Zn and Pb ($V \geq 67$) displayed the greatest variability in soils (expressed by the variability index − V), which points to a varying level of soil contamination with these metals. Slightly lower variability was found in the case of Ca, S and Cu compounds ($V \geq 47$), considerably lower variability in the case of Mn, Na, Mg, P and Fe compounds ($V \geq 24$), while the lowest variability was observed for Ti and the major component − silica ($V \geq 6$). In 1998, soil chemical composition was not analysed with the method described.

The phase composition of the soil comprised mostly silicates (quartz), aluminosilicates (albite and sanidine), carbonates (dolomite and calcite) and silty minerals (illite and kaolinite) (Fig. 2).

4.1.2. Pseudo-total content of As, Cd and Tl in soil samples

The content of As, Cd and Tl in top layer soil samples collected in 2018 varies between 113 and 689, 47−3056 and 5−143 ($mg \cdot kg^{-1}$), respectively (Table 2). Having compared these values with those listed in the Regulation of the Minister of the Environment (2016) on the assessment of ground pollution as limits for As and Cd for category II soils (arable land, orchards and pastures) amounting to 10 and 2 $mg\,kg^{-1}$ respectively, and for category IV soils (industrial areas, mining areas and communication areas) amounting to 100 and 15 $mg\,kg^{-1}$ respectively, we concluded that the limits were exceeded in all samples tested. This should be considered a distressing situation. In samples taken in 1998 the contents of elements discussed ranged from 13 to 195 $mg\,kg^{-1}$ in the case of As, from 9 to 188 $mg\,kg^{-1}$ in the case of Cd, and from 17 to 47 $mg\,kg^{-1}$ in the case of Tl, which means the values were considerably lower. The analysis of the soil environment in close vicinity of the zinc-works in 2018, based on mean contents of As, Cd and Tl, demonstrated that its quality deteriorated. After 20 years, the content of As is now 5 times higher, the content of Cd is 20 times higher, and the content of Tl is on average 30% times higher than in 1998. Also, the variability of As, Cd and Ti content in soil samples collected in 2018 was higher than 20 years earlier. The content of all three elements determined in the years 2018 and 1998 was analysed with regard to their spatial distribution (Fig. 3). It was observed that the location of the site most polluted with As, Cd and Tl changed over the two decades. In 2018, the most polluted soils were found in site no. 4 (Fig. 1), while in 1998 the highest pollution levels were recorded in site no. 2. In 1998, the most polluted soils were found near the entry gate to the zinc-works. This site is located 50 m SE from the main furnaces. The biggest immission of dust emitted by the smoke
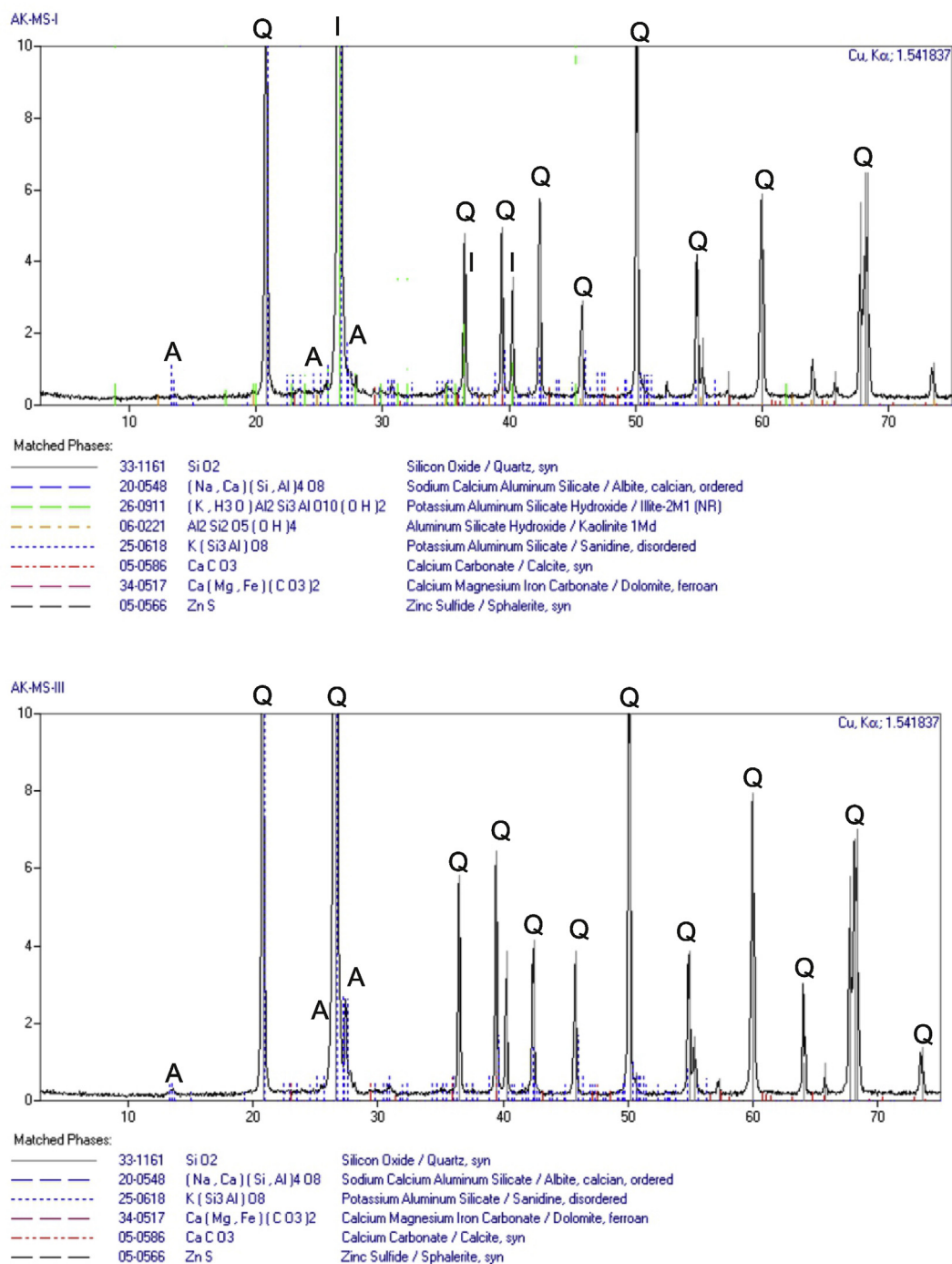
Fig. 2. XRD patterns of soil samples (1 and 3, see Fig. 1).

stacks of the zinc-works occurred there. After twenty years, the most polluted site is located further away from the zinc-works (about 2 km) and in a different direction (NW). This shows that there is no relation between pollution and the prevailing winds (NW and W winds), and demonstrates the effectiveness of actions taken by the zinc-works to protect the environment, e.g. the reduction of pollutant emissions to the atmosphere. At the site closest to the zinc-works (site no. 2, Fig. 1) the contents of Cd and Tl decreased, while the content of As increased slightly (by about 20%). When analysing the spatial development of areas around the zinc-works, we found that without any doubt the present source of

emissions is unrestored former industrial waste dumps, which release new loads of hazardous/toxic substances due to weathering processes. The increase in the content of As, Cd, and Tl in soils collected in site no. 4 is undoubtedly due to the fact that the site is closest to landfills and old heaps.

When analysing the vertical distribution of As, Cd and Tl concentrations in soil profiles, we observed that the highest concentration values were found in soil layers closest to the ground surface (Fig. 4), i.e. they were 10 times higher than the values measured in layers located directly below them. The contents of As and Cd measured in soil profiles in 2018 were considerably higher than
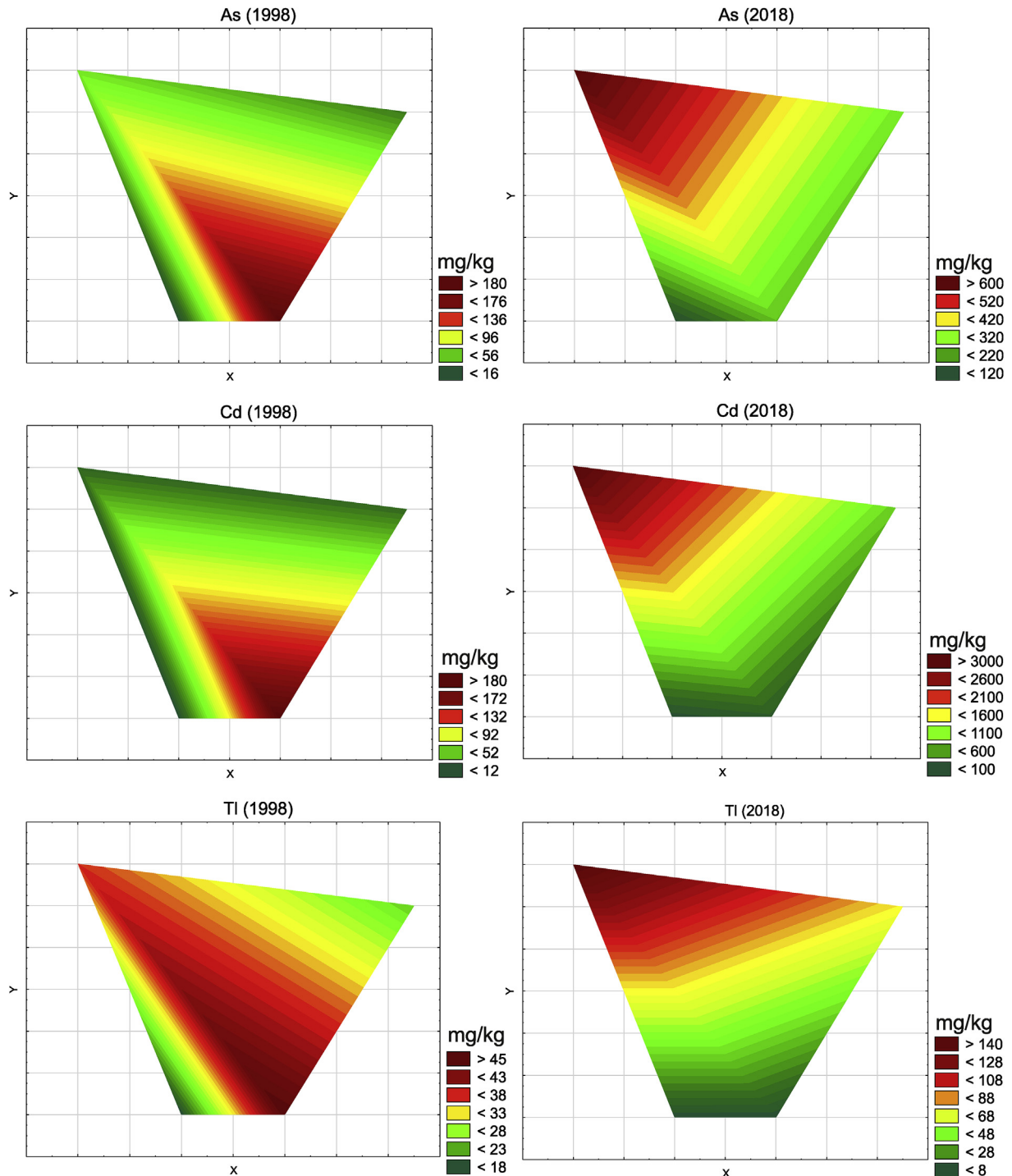
Fig. 3. Spatial distribution of As, Cd and Tl content in top layer soils samples.

those recorded 20 years earlier. The only exception is the profile from site no. 2 in which Cd and Tl contents were significantly lower in 2018 compared to 1998, but only to a depth of 20 cm. Below this depth, the contents of the elements analysed were comparable to those dating 20 years back. The reason for this is undoubtedly the long-lasting and direct fall of industrial dust created in the processing of Zn−Pb ores (currently − concentrates) as well as pollutants (also in the form of finest fractions), whose presence is related to low-height emissions and burning of solid fuel in household furnaces. Despite considerable differences in element concentrations in the top layer and in the subsoil, the concentrations recorded did not represent values that may be considered natural at any of the levels. This confirms that for many years, if not for many centuries, the soil has been subject to pollution and to prolonged migration of toxic compounds into the soil profile, resulting in a probability of ground water contamination.

4.2. Fractions binding As, Cd and Tl in soils
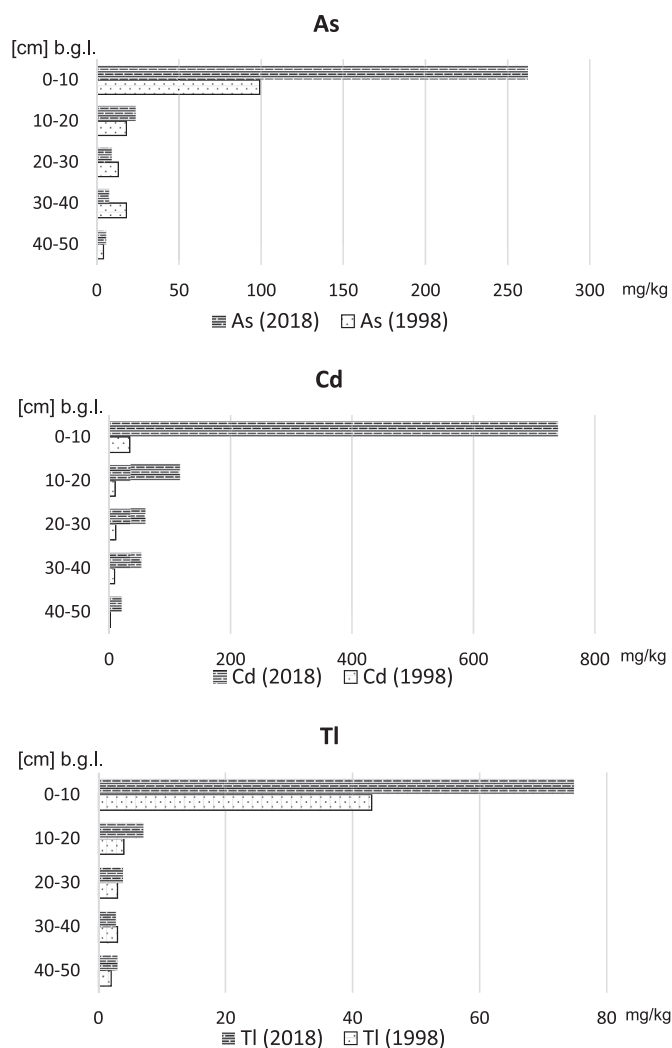
Over-normative total content of an element in the soil

Fig. 4. Vertical distribution of As, Cd and Tl in soil profile (site 1, see Fig. 1).

Fig. 5. Share (%) of As, Cd and Tl-binding fractions in top layer soil samples.

environment does not mean that there exists a severe hazard to crops or soil organisms caused by its presence. It is the form of the element that is important. Therefore, the next step of the study involved performing (BCR) multi-step extraction to establish the percentage of cations bound to individual fractions (see chapter 2) and compare changes in this respect which occurred over the last 20 years. The percentage of As, Cd and Tl cations bound on ion exchange positions and bound to carbonates, as well as to oxidisable, organic and residual fractions in the years 1998 and 2018 is presented in Fig. 5. In the case of all three elements analysed, the following changes were found.

In 1998, the largest quantity of As was found in the residual fraction (over 77% of the *pseudo*-total content), a considerably smaller quantity was found in reducible forms (14%), while cations bound to the oxidisable fraction and organic forms amounted to 7%. The smallest quantity of As (about 2%) was found on ion exchange position or was bound to carbonates. In 2018, the order of fractions in the *pseudo*-total amount of As was the same (IV > II > III > I), but the percentages were different. In general, the quantity of As in residual fractions increased (to 87%), while the quantity of As on ion exchange positions or bound to carbonates (1%), in reducible forms (9%) and in oxidisable and organic fractions (3%) decreased. The

direction of these changes is desirable and highly beneficial from the environmental standpoint.

In the case of Cd, the greatest change was recorded in the percentage of cations on ion exchange positions and cations bound to carbonates. In 1998, it amounted to 66%, while in 2018 — it was only 9%. The quantity of Cd extracted in step IV of extraction (residual fraction) increased from 4% recorded in 1998 to 88% recorded in

2018. In 1998, 18% and 12% of *pseudo*-total Cd content respectively was bound in reducible and oxidisable fractions, while in 2018 these values decreased to 2% and 1%, respectively.

Also in the case of Tl, the final element studied, positive changes were recorded. In samples collected in 2018, 13% more Tl was found in the residual fraction, while 10% more was found in the oxidisable fraction compared to 1998. On the other hand, there was a slight decrease (by 1%) in the quantity of this metal in reducible forms and a decrease by 22% in the quantity of cations on ion exchange positions and bound to carbonates.

In general, all these changes are positive. The increase in the quantity of As, Cd and Tl bound to organic matter and remaining in the residual fraction confirms that they are more strongly bound than 20 years earlier, which translates into lower environmental risk.

4.3. Mobility of As, Cd and Tl

4.3.1. Water leaching

Ions of elements (particularly metals) extracted using an aqueous solution are the most mobile and most readily leachable part of their total content found in the soil. The quantity of As extracted using an aqueous solution from top layer soil samples collected around the zinc-works in 1998 varied from 0.11 to 0.15 mg dm^{-3} (0.13–2.78% of the total content). After 20 years, these quantities were considerably smaller, ranging from 0.003 to 0.023 mg dm^{-3} (0.01–0.20% of the total content) (Table 3). In the case of Cd, the trend was slightly different. The mean quantity of Cd extracted using an aqueous solution from top layer soil samples collected in the vicinity of Miasteczko Śląskie increased almost 10 times. In 1998, it ranged from 0.01 to 0.05 mg dm^{-3} (0.02–1.44% of the total content), whereas in 2018 – from 0.01 to 0.15 mg dm^{-3} (0.08–0.31% of the total content). The largest percentage of the total content was extracted in the case of Tl. In 1998, it amounted to 0.31–1.89% (mean 0.89%), while in 2018 it was 0.88–3.33% (mean 2.30%). The content of Tl in the aqueous solution ranged from 0.03 to 0.19 mg dm^{-3} in top layer soil samples collected in 1998 and from 0.004 to 0.479 mg dm^{-3} in samples collected in 2018.

For the entire 20-year period and in the case of all 3 elements analysed, the greatest percentage of mobile and readily leachable forms was found in site no. 3 (Fig. 1).

When comparing the quantities determined in the study with the limits listed in the Regulation of the Minister of the Environment (2014) on the conditions to be met when discharging sewage to water or soil, and on substances particularly harmful to the aquatic environment, we found that in 2018 the upper limits of As, Cd and Tl content amounting to 0.1, 0.4, 1.0 mg dm^{-3} respectively were not exceeded in any of the samples tested.

4.3.2. EDTA leaching

The purpose of the 0.11 M extraction using EDTA solution was to determine the hazard related to the availability of As, Cd and Tl to plants in the area. The absolute quantities of phytoavailable As, Cd and Tl are considerably higher than the values presented in the preceding chapter. For top layer soil samples collected in 1998, these values ranged from: 0.61–5.85, 7.76–71.82, 7.21–16.08 (mg·kg^{-1}), respectively (Table 4). After 20 years, the values were slightly higher: 1.5–55.7, 9–2484, 1.08–19.88 (mg·kg^{-1}), respectively. When converted to percentage of *pseudo*-total content, the share of phytoavailable forms decreased in the case of Cd (on average by 22%) and Tl (on average by about 3%), while in the case of As the percentage share remained almost the same. In 1998, the largest share of phytoavailable elements was found in site no. 2, while in 2018 the most phytoavailable forms of As, Cd and Tl were found in site no. 4.

4.3.3. Acid leaching

In areas under severe influence of the metallurgical industry, soil acidity is a considerable environmental problem. It is related to the emissions of sulphur oxides and their transformations occurring e.g. in the air (mainly hydration). This results in a decrease of soil pH leading to changes in adsorption and mobility of elements, especially those found in top layers of soil profiles.

The samples collected in 1998 and 2018 presented a tendency for an increase in the quantity of released As, Cd and Tl with simultaneous decrease of pH (Fig. 6). The first portion of acid (20 mmol HNO$_3$) caused a considerable decrease of pH (by 2.5 units), while the quantities of As, Cd and Tl extracted using this solution were 2.3, 1.7 and 5.6 mg kg^{-1}, respectively (mean value for all samples). Consecutive applications of acid resulted in further decrease of pH by 1–2 units (to a value of 4). Further applications of acid did not result in pH decrease greater than 0.5. The quantities of As, Cd and Tl cations released into the solution increased gradually by 10–15% until reaching their maximum values of 9.8, 16.0 and 9.3 (mg·kg^{-1}) respectively, recorded at 120 mmol of acid. This experiment confirmed the existence of a considerable risk related to the

Table 3
Concentrations of As, Cd and Tl extracted by water solution from soil samples.

| Sample sites	Water solution					
	As		Cd		Tl	
	1998	2018	1998	2018	1998	2018
	mg/dm^3					
1	0.15	0.003	0.04	0.15	0.03	0.120
2	0.11	0.023	0.01	0.03	0.09	0.004
3	0.15	0.022	0.05	0.01	0.12	0.015
4	0.12	0.006	0.04	0.23	0.19	0.479
Upper limit[a]	–	0.100	–	0.40	–	1.000
mg/kg (%)						
1	0.38 (1.12)	0.03 (0.01)	0.08 (0.33)	1.55 (0.21)	0.07 (0.31)	1.20 (1.61)
2	0.26 (0.13)	0.23 (0.10)	0.03 (0.02)	0.28 (0.17)	0.23 (0.48)	0.05 (0.88)
3	0.36 (2.78)	0.22 (0.20)	0.13 (1.44)	0.14 (0.31)	0.32 (1.89)	0.16 (2.99)
4	0.30 (0.49)	0.06 (0.01)	0.09 (0.41)	2.34 (0.08)	0.48 (1.30)	4.79 (3.33)
for all samples ($n = 40$)						
Me	0.33 (0.80)	0.14 (0.05)	0.09 (0.37)	0.91 (0.19)	0.27 (0.89)	0.68 (2.30)

"-" no data.
In bracket % of total concentration.
 [a] According to Regulation of the Minister of Environment (2014).

Table 4
Concentrations of As, Cd and Tl extracted by 0.11 M EDTA solution from top layer soil samples.

Sampling sites	As		Cd		Tl	
	1998	2018	1998	2018	1998	2018
	mg·kg^{-1} (% of total concentration)					
1	1.22 (3.6)	8.7 (3.3)	16.62 (69.2)	248 (33.6)	16.08 (67.0)	13.23 (17.7)
2	5.85 (3.0)	1.5 (0.6)	71.82 (38.2)	94 (55.7)	7.66 (16.3)	4.32 (83.8)
3	0.61 (4.7)	6.1 (5.4)	7.76 (86.2)	9 (18.0)	4.21 (24.8)	1.08 (20.8)
4	3.45 (5.7)	55.7 (8.1)	14.38 (65.4)	2484 (81.3)	7.21 (19.5)	19.88 (13.8)
for all samples (n = 40)						
Me	2.34 (4.14)	7.39 (4.34)	15.50 (67.31)	171 (44.67)	7.44 (22.15)	8.78 (19.25)
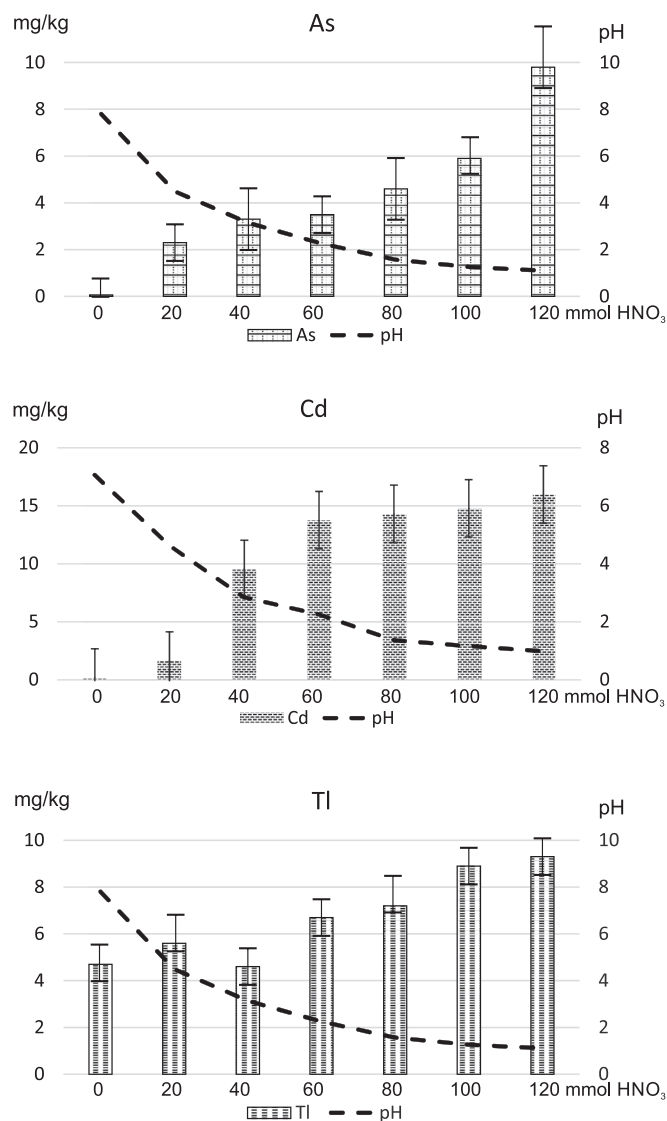
Fig. 6. Leaching of As, Cd and Tl from soil samples (1998) as a result of acidification.

release of "new" doses of toxic elements occurring with even the slightest decrease in soil pH.

4.4. Environmental risk (RAC)

The following geochemical factors and indices were calculated

Table 5
Contamination Factor (CF) and geo-accumulation index (I$_{geo}$) calculated for As, Cd and Tl content in 1998 and 2018 year in soils collected next to zinc-works.

parameter	1998			2018		
	As	Cd	Tl	As	Cd	Tl
CF[a]	VH	VH	VH	VH	VH	VH
CF[b]	C	VH	M	M	VH	VH
I$_{geo}$[a]	VI	VI	VI	VI	VI	VI
I$_{geo}$[b]	IV	V	II	II	VI	VI

CF classification.
L − low degree of contamination (CF < 1).
M − moderate degree of contamination (1 ≤ CF < 3).
C − considerable degree of contamination (3 ≤ CF < 6).
VH − very high degree of contamination (CF ≥ 6).
I$_{geo}$ classification.
0 − unpolluted (I$_{geo}$≤0).
I − form unpolluted to moderately polluted (0<I$_{geo}$≤1).
II − moderately polluted (1<I$_{geo}$≤2).
III − form moderately polluted to strongly polluted (2<I$_{geo}$≤3).
IV − strongly polluted (3<I$_{geo}$≤4).
V − form strongly polluted to extremely polluted (4<I$_{geo}$≤5).
VI − extremely polluted (I$_{geo}$>5).
  [a] GB according Kabata-Pendias and Pendias (2000).
  [b] GB based as mean concentration for the least polluted place in this study area.

in accordance with the adopted methodology and based on the determined quantities of elements analysed for the years 1998 and 2018: CF, C$_d$, I$_{geo}$, E$_f$, RI, PLI and RAC.

4.4.1. CF

The contamination factor represents the relation between the current quantity of a given element and its natural content. It was calculated based on 4 different geochemical background values (Table 5). The first reference value was the "natural content in Polish soils" based on the work by Kabata-Pendias and Pendias (2000). The values for As, Cd and Tl were 3.0, 0.05 and 0.4 mg kg^{-1}, respectively. Mean concentrations of As, Cd and Tl in soils near Miasteczko Śląskie calculated for all samples collected (n = 40) were divided by the values mentioned above. In the case of all elements analysed (both for the year 1998 and 2018), a very high degree of contamination was found.

The second reference value was element content calculated for the least polluted site in the vicinity of the zinc-works (for n = 10). In the case of both sampling campaigns and all three elements, site no. 3 was the least polluted (Fig. 1). Mean values calculated for the years 1998 and 2018 were used as reference levels (Table 2). The final CF calculations for the year 1998 yielded the following values: CF = 2, denoting a moderate degree of contamination in the case of Tl, CF = 5, denoting a considerable degree of contamination in the case of As, and CF = 7, denoting a very high degree of contamination in the case of Cd. The CF values for the year 2018 for As, Cd and Tl were 3, 21 and 11 respectively, denoting a moderate degree of contamination in the case of As and a very high degree of

contamination in the case of Cd and Tl.

4.4.2. C_d, E_f and RI

The calculated degree of contamination (C_d) for all elements analysed in the case of the first reference value (i.e. natural content) was $C_d > 32$ for both sampling campaigns, denoting a very high degree of contamination indicating serious anthropogenic pollution. The risk related to the presence of Cd is the most serious, that resulting from the presence of Tl is smaller and that resulting from the presence of As is the smallest. The potential ecological risk factors (E_f) calculated for As, Cd and Tl amounted to 250, 36 450 and 2340 respectively in the case of samples collected in 1998. In the case of samples collected in 2018, the E_f values were 1090, 601 620 and 4290 respectively. In the case of both sampling campaigns, the calculated $E_f \geq 320$, which denotes a very high ecological risk resulting from the presence of As, Cd and Tl in the soil environment.

The potential ecological risk index for all the elements analysed (*RI*) calculated based on element contents in the samples from 1998 was 39 040, while for the year 2018 it was 15 times higher and amounted to 607 000. As values of $RI \geq 600$ were obtained, the area directly adjacent to the zinc-works presents a very high ecological risk.

4.4.3. I_{geo} and PLI

The second index used to evaluate the environmental risk was I_{geo} (Table 5). Similarly to *CF*, 4 values were used as reference levels. Following mathematical modelling, a result of "extremely polluted soil quality" was obtained in the case of both sampling campaigns for all elements tested when using natural quantities as reference values. When using the 2nd reference value i.e. contents determined in site no. 3, moderate pollution of soil was found in the case of As, and extreme pollution of soil in the case of Cd and Tl. Also, the pollution level increased for Cd and Tl as compared to results from 1998.

Because the indices and factors analysed provided varying partial pollution levels with As, Cd and Tl, we decided to calculate an aggregate index i.e. the pollution load index (*PLI*). Regardless of the selected reference level, the *PLI* values calculated with formula no. 5 (Materials and Methods) ranged from 1 to 89 for the year 1998 and from 6 to 452 for the year 2018. Since in all cases *PLI*>1, the area analysed is considered polluted.

4.4.4. RAC

While the calculations of indices and factors mentioned above were based on the total content of elements in soil, the next geochemical indicator − RAC, denotes the environmental risk and takes into consideration the form of a given element as well as its potential availability to living organisms. The following fraction was used as readily mobile and phytoavailable: 1) As, Cd and Tl cations extracted using 0.11 M EDTA and 2) cations on ion exchange positions and bound to carbonates (Table 6).

In the first case, the results for the 1998 samples were: low risk in the case of As in all sites studied, very high risk in the case of Cd and mixed risk in the case of Tl (sites no. 1, 3 and 4 were characterised by medium risk, while site no. 2 was characterised by very high risk). The mean values for the samples collected denoted low risk in the case of As, high risk in the case of Tl and very high risk in the case of Cd. In 2018, the situation regarding As content in the soils studied did not change. Low risk resulting from the presence of this metalloid was determined in all sites. However, in the case of Tl the situation deteriorated in one site (no. 3). In other sites the situation did not change as compared to the year 1998. In the case of Cd the situation improved in two sites (no 1 and 3). Environmental risk decreased from very high to high, which was reflected in an improved general assessment for Cd.

Table 6
Risk Assessment Code (RAC) calculated for As, Cd and Tl content in 1998 and 2018 year in soils collected nest to the zinc-works.

Sampling sites	1998			2018		
	As	Cd	Tl	As	Cd	Tl
RAC[1]						
1	L	VH	M	L	H	M
2	L	VH	VH	L	VH	VH
3	L	VH	M	L	H	VH
4	L	VH	M	L	VH	M
For all samples	L	VH	H	L	H	H
RAC[2]						
1	L	VH	M	N	M	L
2	L	VH	H	N	M	M
3	L	VH	H	N	M	M
4	L	VH	M	N	M	L
For all samples	L	VH	H	N	M	M

RAC[1] − based on (%) extracted by the EDTA solution.
RAC[2] − based on (%) extracted by the I step of BCR.
N − no risk (RAC<1).
L − low risk ($1 \leq$ RAC<10).
M − medium risk ($10 \leq$ RAC<30).
H − high risk ($30 \leq$ RAC<50).
VH − very high risk ($50 \leq$ RAC).

In the second case, when using the number of cations on ion exchange positions and bound to carbonates (including those present in the substrate in the form of ore-bearing dolomites) to calculate RAC, the environmental risk evaluation results are completely different, especially for samples collected in the second sampling cycle (2018).

For samples collected in 1998, the As and Cd content in the soils studied did not change, compared to the results obtained using EDTA extraction. The sites presented low and very high risk, respectively. However in the case of Tl, the result was medium risk in the case of two sites (no. 1 and 4), while in site no. 2 the result improved slightly, changing from very high risk to high risk. In site no. 3, the result changed from medium to high risk. The general assessment performed for all samples collected in 1998 in all sites studied did not differ from the assessment formulated on the basis of EDTA extraction results.

In the case of the 2018 samples, the general assessment was completely different and improved in the case of all sites and elements. In the case of As, the result was no risk in all sites, in the case of Cd, the result was medium risk in all sites. When it comes to Tl, the result was low risk in two sites (no. 1 and 4), while in two other sites (no. 2 and 3) the result was medium risk. The general assessment based on the results obtained for individual samples taken in 2018 at all sites was: no risk in the case of As, and medium risk in the case of Cd and Tl.

Due to the environmental conditions related to the presence of plants, the quantity of metals extracted using EDTA solution should also be taken into consideration when calculating RAC. EDTA acid is a commonly used complexing agent for a number of metal cations. Owing to their stability and high effectiveness in extracting the majority of metals, EDTA solutions (of various concentrations) are commonly used in remediation of soil and sediments polluted with metals. On the other hand, extraction with acetic acid (Step I of BCR) allows for determining the quantity of metals readily soluble in an acidic environment. This includes (1) labile metals in the soil solution and those bound to the solid fraction of soil by physical and chemical adsorption and ion-exchange sorption, as well as (2) carbonates of heavy metals and forms adsorbed or coprecipitated with calcium carbonate, sulphides and phosphates. This fraction usually comprises about 10−20% of the total content of elements in the soil, whereas in the case of heavy metals the effectiveness of

their extraction from sediments and soils using EDTA solutions may reach up to 60−80% (Polettini et al., 2007; Nair et al., 2008).

5. Discussion

High levels of As, Cd and Tl found in soils heavily affected by the mining and metallurgical industry in post-soviet countries are not uncommon. In mining cities in Armenia, the team led by Akopyan et al. (2018) found similarly high quantities of As (9−276 mg kg^{-1}) and Pb (15−30 083 mg kg^{-1}), which denote high environmental risk. The calculated I$_{geo}$ values representing the As pollution level of Armenian soils put them in class 4 i.e. moderately to strongly polluted areas. High concentrations of metals were also found in the vicinity of Zn−Pb works located in Shaoguan City in China (Liu et al., 2018a, 2018b). The content of Tl in sediments sampled from the nearby river ranged from 4.17 to 13.09 mg kg^{-1}, while the content of Cd was considerably higher, ranging from 71.63 to 385 mg kg^{-1}. The results of multi-step BCR extraction conducted by Liu et al. (2018a, 2018b) were almost identical to the results obtained in this study when it comes to Tl in the residual fraction (about 40%) and in labile forms (10% of total content). Also the environmental risk evaluation results were similar. The I$_{geo}$ indices for Cd, Zn, Pb and Cu were >5, denoting extreme contamination (class 6). Another location with extremely high concentrations of metals and metalloids is the area around La Crus Smelter in Southern Spain. The contents of As, Cd and Tl in the soils in the vicinity of that plant reached 1318, 215 and 39.5 mg kg^{-1} respectively (Cortada et al., 2018), which denoted a very high environmental hazard level. The authors of that study demonstrated that the major cause of extreme contamination was the pollution zone which is usually connected with the operations of metallurgical plants, and in particular with two different mechanisms of pollutant dispersion. The first mechanism is related to the emissions of gas and dust produced by metallurgical processes and their transport by the prevailing winds. The second one is associated with the leachate produced in smelter residues.

Long-term mining and processing of metal ores in mining and industrial areas caused considerable changes in the dominating forms of elements and their availability to soil fauna and flora as discussed by e.g. Liu et al. (2018a, 2018b), Ghayoraneh and Qishlaqi (2017) and Liu et al. (2016). The increased share of As, Cd and Tl cations bound to silicates or crystalline Fe-oxides, and in the case of Tl bound to organic matter and sulphides, is a very positive environmental change.

Numerous authors studying the presence of particularly toxic elements (i.e. As, Cd and Tl) in soils of areas neighbouring metallurgical plants indicated that the highest content of the elements was found in top layers of soil profiles (e.g. Ghayoraneh and Qishlaqi, 2017; and Shen et al., 2017) that it decreased by 50−75% (for Cd, Zn and Pb) as the depth increased.

Pollution may pose a serious risk due to potential immobilisation and biological absorption of elements. Inhabitants of areas near zinc-works are at risk of much greater influence of toxic elements accompanying Zn−Pb ores such as As, Tl and Cd. Another important problem is related to spreading awareness of the existing hazards and the necessity to take action to improve the current situation as mentioned by Akopyan et al. (2018) and Ghayoraneh and Qishlaqi (2017).

6. Conclusions

This paper addresses the very important and difficult subject of evaluating the condition of the environment and environmental risk in areas affected by metal processing for numerous centuries. An important problem is that apart from the main metals processed i.e. Zn and Pb, other accompanying metals are released into the environment, enter the soil structure and vegetation and may become a hazard to living organisms. Based on the laboratory experiments and field studies conducted over a period of twenty years, the following conclusions were formulated.

1. Increased quantities of Zn, Pb and Cd (4.7, 4.1 and 0.4% mass respectively) were found in soils apart from the typical micro- and macro-elements. Also found were As, Ba, Bi, Cr, Ni and Tl (less than 1% mass).

2. Mineral composition of all soil samples analysed (for the entire study area) is based on silicates and aluminosilicates with considerable share of carbonates (dolomite and calcite) and silty minerals (illite and kaolinite).

3. Pseudo-total contents of As, Cd and Tl in top layer soil samples collected in 2018 vary between 113 and 689, 47−3056 and 5−143 (mg·kg^{-1}) respectively, and are considerably higher than the values determined 20 years earlier in the same sites: 13−195, 9−188, 17−47 (mg·kg^{-1}) respectively.

4. In the case of all soil samples collected in 2018, upper limits stipulated in legal regulations regarding As and Cd content were exceeded in the case of category II and IV soils. Also, natural contents of As, Cd and Tl determined for Polish soils were exceeded, which means that the soil environment is considerably polluted with these elements.

5. The main source of pollution changed over the years. In 1998, it was the zinc-works. However, in 2018, the main sources of emissions were the erosion and deflation processes in old, unprotected mining and industrial waste dumps located near the zinc-works.

6. The most polluted soil layers are the top layers of soil profiles. The contents of As, Cd and Tl determined in them were 10 times greater than for the layers located deeper in the profiles. Even though concentrations of elements decrease greatly as the depth increases, natural levels were exceeded. This means that the elements mentioned had been penetrating the soil profile for many years. This may pose a considerable hazard to ground water as the fraction extracted using an aqueous solution may comprise 0.05% (As), 0.19% (Cd) or 2.30% (Tl) of the total content.

7. Within the last 20 years, a positive environmental change occurred related to an increase in the share of sparingly soluble fractions, fractions bound with organic fraction and built into crystal lattice of minerals (residual fraction). The quantity of these fractions increased by 9% for As, 13% for Tl and 73% for Cd. Thus, the number of readily exchangeable fractions (i.e. ion exchange and bound with carbonates) decreased.

8. In the majority of sites, the absolute quantity of phytoavailable As, Cd and Tl has increased over the last two decades.

9. Despite good buffer properties of soils in the study area, a decrease in pH may cause the release of considerable quantities of As, Cd and Tl.

10. Depending on geochemical background and readily available/mobile fraction values used in environmental risk calculations, it was found that in the last 20 years:
    - contamination with As, Cd and Tl remained very high and ecological risk remained very high when comparing the determined contents to natural contents and to contents stipulated for category II soils;
    - the condition of soil environment deteriorated if using limits stipulated for category IV soils as reference values;
    - environmental conditions related to forms of elements and quantities of readily mobile forms of As, Cd and Tl improved slightly when quantities extracted with EDTA

solution were used for RAC calculations and in step I of BCR extraction. This means that the existing ecosystems are slowly recovering and the direction of change is positive.

Q - quartz, I - illite, A - albite.

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References

Akopyan, K., Petrosyan, V., Grigoryan, R., Melkomian, D.M., 2018. Assessment of residential soil contamination with arsenic and lead in mining and *smelting* towns of northern Armenia. J. Geochem. Explor. 184 (Part A), 97–109. https://doi.org/10.1016/j.gexplo.2017.10.010.

Antonkiewicz, J., Kołodziej, B., Bielińska, E., Witkowicz, R., Tabor, S., 2018. Using Jerusalem artichoke to extract heavy metals from municipal sewage sludge amended soil. Pol. J. Environ. Stud. 27 (2), 513–527. https://doi.org/10.15244/pjoes/75200.

Bączek-Kwinta, R., Antonkiewicz, J., Łopata-Stasiak, A., Kępka, W., 2018. Smoke compounds aggravate stress inflicted on *Brassica* seedlings by unfavourable soil conditions. Photosynthetica 57 (1), 1–8. https://doi.org/10.32615/ps.2019.026.

Cortada, U., Hidalgo, C., Martínez, J., Rey, J., 2018. Impact in soils caused by metal(loid)s in lead metallurgy. The case of La Cruz Smelter (Southern Spain). J. Geochem. Explor. 190, 302–313. https://doi.org/10.1016/j.gexplo.2018.04.001.

Data on Poland, 2019. Data on Poland. http://www.oecd.org/poland/.

Davidson, C.A., Duncan, A.L., Littlejohn, D., Ure, A.M., Garden, L.M., 1998. A critical evaluation of the tree-stage BCR extraction procedure to assess the potential mobility and toxicity of heavy metals in industrially-contaminated land. Anal. Chim. Acta 363, 45–55.

De Miguel, E., Iribarren, I., Chacon, E., Ordonez, A., Charlesworth, S., 2007. Risk-based evaluation of the exposure of children to trace elements in playgrounds in Madrid (Spain). Chemosphere 66, 505–513. https://doi.org/10.1016/j.chemosphere.2006.05.065.

De Miguel, E., Izquierdo, M., Gómez, A., Mingot, J., Barrio-Parra, F., 2016. Risk assessment from exposure to arsenic, antimony, and selenium in urban gardens (Madrid, Spain). Environ. Toxicol. Chem. 36 (2), 544–550. https://doi.org/10.1002/etc.3569.

European Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs, Official Journal of the European Union L 364/5.

Ghayoraneh, M., Qishlaqi, A., 2017. Concentration, distribution and speciation of toxic metals in soils along a transect around a *Zn/Pb smelter* in the northwest of Iran. J. Geochem. Explor. 180, 1–14. https://doi.org/10.1016/j.gexplo.2017.05.007.

Håkanson, L., 1980. An ecological risk index for aquatic pollution control. A sedimentological approach. Water Res. 14 (8), 975–1001.

Hansen, H.K., Pedersen, A.J., Ottonsen, L.M., Villumsen, A., 2001. Speciation and mobility of cadmium in straw and wood combustion fly ash. Chemosphere 45, 123–128.

IARC, 1987. Arsenic and Arsenic Compounds, vol. 7. IARC Monographs, Suppl., Lyon.

IARC, 1990. In: IARC Monographs on the Evaluation of Carcinogenic Risk to Human, vol. 49. Lyon.

Kabata-Pendias, A., Szteke, B., 2012. Trace Elements in Geo- and Biosphere. IUNG-PIB, Pulawy [In Polish].

Kabata-Pendias, A., Mukherjee, A.B., 2007. Trace Elements Form Soil to Human. Springer.

Kabata-Pendias, A., Pendias, H., 2000. Trace Elements in Soils and Plants. CRC Press, Boca Raton.

Karczewska, A., Gałka, B., Kocan, K., 2009. A carryover effect of the chelating agents EDTA and EDDS applied to soils on the uptake of copper and iron by maize in the second year of a pot experiment. Journal of Elementology 14 (4), 693–703.

Kicińska, A., 2017. Health risk assessment related to an effect of sample size fractions: methodological remarks. Stoch. Environ. Res. Risk Assess. 32, 1867–1887. https://doi.org/10.1007/s00477-017-1496-7.

Kicińska, A., 2019. Chemical and mineral composition of fly ashes from home furnaces, and health and environmental risk related to their presence in the environment. Chemosphere 215, 574–585. https://doi.org/10.1016/j.chemosphere.2018.10.061.

Kicińska, A., Bożęcki, P., 2017. Metals and mineral phases of dusts collected in different urban parks of Krakow and their impact on the health of city residents. Environ. Geochem. Health 40, 473–488. https://doi.org/10.1007/s10653-017-9934-5.

Kicińska, A., Jelonek-Waliszewska, A., 2017. As and Pb and their potential source in the hair of residents of Cracow. Journal of Elementology 22 (2), 517–528. https://doi.org/10.5601/jelem.2016.21.3.1223.

Kicińska, A., Mamak, M., 2017. Health risks associated with municipal waste combustion on the example of Laskowa commune (southern Poland). Hum. Ecol. Risk Assess. Int. J. 23 (8), 2087–2096. https://doi.org/10.1080/10807039.2071.1364131.

Kicińska-Świderska, A., 1999. Heavy Metals in Soils and Plants in Selected Areas of the Steel Industry's Impact. PhD thesis,AGH, Kraków [in Polish].

Kosa, B., Kicińska, A., 2016. Coal from the waste disposal site of the Siersza mine (Trzebinia, Poland) and its properties as a possible alternative fuel. E3S Web of Conferences Volume: 10. https://doi.org/10.1051/e3sconf/20161000039. Article Number: UNSP 00039.

Liu, J., Wang, J., Chen, Y., Xie, X., Qi, J., Lippold, H., Luo, D., Wang, C., Su, L., He, L., Wu, Q., 2016. Thallium transformation and partitioning during Pb–Zn smelting and environmental implications. Environ. Pollut. 212, 77–89. https://doi.org/10.1016/j.envpol.2016.01.046.

Liu, J., Wang, J., Xiao, T., Bao, Z., Lippold, H., Luo, X., Yin, M., Ren, J., Chen, Y., Linghu, W., 2018a. Geochemical dispersal of thallium and accompanying metals in sediment profiles from a smelter-impacted area in South China. Appl. Geochem. 88, 239–246. https://doi.org/10.1016/j.apgeochem.2017.05.013.

Liu, T., Li, F., Jin, Z., Yang, Y., 2018b. Acidic leaching of potentially toxic metals cadmium, cobalt, chromium, copper, nickel, lead, and zinc from two *Zn* smelting slag materials incubated in an acidic soil. Environ. Pollut. 238, 359–368. https://doi.org/10.1016/j.envpol.2018.03.022.

Lo, I.M.C., Yang, X.Y., 1999. EDTA extraction of heavy metals from different soil fractions and synthetic soils. Water. Air & Soil Pollution 109, 219. https://doi.org/10.1023/A:1005000520321.

Manouchehri, N., Besancon, S., Bermond, A., 2006. Major and trace metal extraction from soil by EDTA: equilibrium and kinetic studies. Anal. Chim. Acta 559 (1), 105–112. https://doi.org/10.1016/j.aca.2005.11.050.

Müller, G., 1981. The heavy metal pollution of the sediments of Neckars and its tributary. A Stock taking Chemische Zeit 150, 157–164.

Nair, A., Juwarkar, A.A., Devotta, S., 2008. Study of speciation of metals in an industrial sludge and evaluation of metal chelators for their removal. J. Hazard Mater. 152, 545–553.

Pan, Y., Wu, Z.M., Zhou, J.Z., Zhao, J., Ruan, X.X., Liu, J.Y., Qian, G.R., 2013. Chemical characteristics and risk assessment of typical municipal solid waste incineration (MSWI) fly ash in China [J]. J. Hazard Mater. 261, 269–276.

Piekut, A., Gut, K., Ćwieląg-Drabek, M., Domagalska, J., Marchwińska-Wyrwał, E., 2019. The relationship between children's non-nutrient exposure to cadmium, lead and zinc and the location of recreational areas - based on the Upper Silesia region case (Poland). Chemosphere 223, 544–550. https://doi.org/10.1016/j.chemosphere.2019.02.085.

Pietrzykowski, M., Antonkiewicz, J., Gruba, P., Pająk, M., 2018. Content of Zn, Cd and Pb in purple moor-grass in soils heavily contaminated with heavy metals around a zinc and lead ore tailing landfill. Open Chemistry 16, 1143–1152. https://doi.org/10.1515/chem-2018-0129.

Polettini, A., Pomi, R., Rolle, E., 2007. The effect of operating variables on chelant-assisted remediation of contaminated dredged sediment. Chemosphere 66, 866–877.

Quevauviller, P., 2003. Book Review. Methodologies for soil and sediment fractionation studies. Sci. Total Environ. 303, 263–264.

Regulation of the Minister of Environment of November 18, 2014 on Conditions to Be Met when Introducing Sewage into Waters or into the Ground, and on Substances Particularly Harmful to the Aquatic Environment, 2014. Dz. U item 1800.

Regulation of the Minister of the Environment 2016 on the Method of Conducting the Assessment of Surface Pollution, 2016. Dz. U item 1395.

Shen, F., Liao, R., Ali, A., Mahar, A., Guo, D., Li, R., Sun, X., Awasthi, M.K., Wang, Q., Zhang, Z., 2017. Spatial distribution and risk assessment of heavy metals in soil near a Pb/Zn smelter in Feng County, China. Ecotoxicol. Environ. Saf. 139, 254–262. https://doi.org/10.1016/j.ecoenv.2017.01.044.