Concentration, distribution and speciation of toxic metals in soils along a transect around a Zn/Pb smelter in the northwest of Iran

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ABSTRACT

Non-ferrous metals smelting has been recognized as one of the most important point sources of toxic metals in soil. In this preliminary study, the concentration, distribution and speciation of toxic metals (Pb, Zn, Cd, Cr, Ni and Cu) in soils were investigated along a pre-selected transect around a Zn/Pb smelter in NW Iran. Two groups of the metals were identified in terms of range and variation: Pb, Zn and Cd (Group 1) whose mean concentrations (302, 311 and 9.83 mg/kg, respectively) are significantly higher than the concentrations in the control soil and exhibited high coefficients of variation (CV > 2). The concentrations of these three metals decreased exponentially or as power-law model with increasing distance downwind from the smelter, implying that their variations are mainly controlled by inputs from the smelter. Declining trend of concentration along the transect for Cd is different from that of the two other metals, i.e. Cd is levelled off at a longer distance (≈ 8000 m) whereas Pb and Zn concentrations are dropped at a shorter distance (≈ 3400 m) from the smelter. The total concentrations of these metals also decreased significantly with depth by decreasing rates of > 50%. By contrast, three other metals Cr, Ni and Cu (Group 2) are characterized by low variability (CV < 1) with mean values of 46.1 mg/kg (for Cr), 28.2 mg/kg (for Ni) and 24.8 mg/kg (for Cu). The total contents of these metals did not vary with distance from the smelter and tend to increase with depth, suggesting that they are derived mainly from geogenic source. Marked differences were found between the two groups of metals in terms of their geochemical fractionation in the soils: smelter-related metals (Pb, Zn and Cd) were distributed in all soil fractions, with the most relevant abundances in the reducible one (> 45% of their total contents). The amounts of these metals in the non-residual fractions decreased with increasing distance from the smelter. On the contrary, Cr, Ni and Cu had a large percentage of the residual fraction (> 80% of the total contents) and relatively small proportion of the non-residual fractions ($\leq 10\%$ of the total fraction). The mobility factors of all toxic metals studied are found to be low to moderate due to alkaline nature of the soils. The average single factor pollution index (SFPI) from the sampling sites decreased in the order of Cd > Pb > Zn > Ni > Cr > Cu. In view of the comprehensive pollution index (CPI), soils from the study area showed heavy to warning level of pollution along the transect. The results from this study clearly indicated that Zn smelting activity is responsible for soil contamination in the study area and not only led to significant increases in total contents of some metals but also altered their speciation in soils along the transect. This can pose a significant risk to health of local inhabitants particularly for those living closer to the smelter which should be assessed in future investigations.

1. Introduction

Soil as a geochemical sink receives chemical elements (including toxic metals) released from both natural and unnatural sources. However, due to rapid industrialization and urbanization over the last few years, the natural input of these metals to soils has been exceeded by the anthropogenic input even on global and regional scales. This has led to extensive soil contamination which continues to receive increasing attention from researchers and communities because of its adverse effect on human health and the environment.

A wide variety of anthropogenic sources contribute metals to the soil (Wuana et al., 2010). One of the most important sources is non-ferrous metal smelters. It is estimated that non-ferrous smelter emissions account for 40 to 73% of emissions of metals such as Zn, Cd and Pb into the environment including soil (Pacyna and Pacyna, 2001). Many cases of particularly severe soil contamination have been reported from areas surrounding non-ferrous metal smelters in many countries (Burt et al., 2003; Martley et al., 2004; Ettler et al., 2005;

Cappuyns et al., 2006; Cloquet et al., 2006; Ettler et al., 2007; Ettler et al., 2010; Kríbek et al., 2010; Juillot et al., 2011; Zhang et al., 2011; Douay et al., 2013; Ettler, 2016). Among non-ferrous metal industries, Zn/Pb smelters account for the highest rate of pollution (Manceau et al., 2000). During smelting of the Zn/Pb ores, lead and zinc and other associated metals (metalloids) such as Cd, Cu, As and Hg are typically released into the surrounding environment (Li and Thornton, 2001; Pacyna and Pacyna, 2001). These metals are primarily discharged with the smelting gases in the form of airborne particles or may be lost to solid wastes during refining or processing of the Zn/Pb ores. The metals, whether emitted from smelters in flue gases or incorporated into solid wastes, would eventually reach the soil leading to significant contamination at local-to-regional scale. The metal-contaminated soils may pose significant risks to other environmental compartments (groundwater, crops) because metals present in soils at elevated levels can be transferred or mobilized under certain conditions.

To assess more accurately the soil contamination by metals, it is necessary to have an insight into the fractionation and speciation of toxic metals in soils. It is now well established that the risk and the degree of soil contamination are determined by chemical forms of metals rather than by their total concentrations. This necessitates identification and quantification of geochemical forms of metals in the soils. The nature of metal speciation in the soil environment is commonly studied by sequential extraction techniques, which are still one of the most effective methods to predicate metal forms in soils. These methods have been widely applied to evaluate metal speciation in soils near metal smelters (Li and Thornton, 2001; Kabala and Singh, 2001; Burt et al., 2003; Ettler et al., 2005; Knight and Henderson, 2006; Cecchi et al., 2008).

Zanjan province (in northwest Iran) is richly endowed with Pb/Zn mineral resources and mines (e.g. Anguran Zn-Pb mine). These mines provide zinc-lead bearing raw materials for domestic Zn/Pb smelting plants. One of these plants is the Zanjan zinc smelting factory owned by the National Iranian Lead and Zinc Company (NILZ). This plant, as the first electrolytic zinc plant in Iran, started its operation in 1993 and is now one of the largest Pb and Zn producers in terms of production volume (20,000 Znt/d). In the zinc plant, the feed materials consist of zinc carbonate concentrate ($ZnCO_3$) and calcined zinc oxide (ZnO), which are passed through four successive steps (i.e. leaching - neutralization, refining, electrolysis and smelting). The products are zinc slab and lead ingot. The activity of the zinc plant, however, is also associated with production of large amounts of chemical solid wastes and air-born (gaseous) particles. Cd-Ni filter-cakes, as the most important solid residue, are produced continuously at the third purification step in the electrolytic process (Safarzadeh et al., 2009). These undesirable materials have been dumped on the east end of the smelter yard where they are left uncovered for a prolonged time. As a consequence, the solid waste materials are readily subjected to erosion by wind or water which can locally cause soil contamination in the vicinity of the Zn/Pb smelter. On the other hand, the NILZ also includes a Pb smelting/refining (pyro-metallurgical) plant in which Pb concentrates are melted at high temperature (1000–1200 °C). This plant generates a great deal of particulate emissions, including metals which are volatilized and those which are condensed and enriched in fine particles that escape from the particulate retention devices. These fine-particles are dispersed over a large area by local prevailing wind current toward Zanjan city about 11 km west of the zinc plant. Although steps have been taken to reduce emissions, fallout from this plant remains significant. This preliminary study was undertaken to investigate the influence of zinc/lead smelting on the contamination and distribution (horizontal and vertical) of selected metals in soils neighboring the Zanjan Zn/Pb smelting plant. To do so, in the first step, total metal concentrations (Pb, Zn, Cd, Cu, Cr and Ni) in soils collected along a pre-selected transect around the Zn/Pb smelter were measured. We also determined the chemical partitioning of toxic metals using the modified four-stage sequential extraction procedure (Community

Bureau of Reference; BCR) to gain a more precise understanding of the potential and actual impact of elevated levels of metals in the affected soils.

2. Materials and methods

2.1. Site description

Geographically, the NILZ smelter is situated about 11 km east of Zanjan in a vast plain. The area has a semiarid and cold climate with annual temperatures ranging from − 30 °C in winter to 40 °C in summer and an average annual rainfall over 309 mm. The soils in the study area, developed predominately on Quaternary alluvial sediments, are mainly composed of loam. According to soil taxonomy (Soil Survey Staff, 2006), these soils are mainly classified as Entisols. The topography of the region is characterized by a vast, nearly level plain surrounded by mountainous and hilly areas. Over the study area, the most frequent winds persistently blow from the east (at 2–20 knots (with a prevailing southeast-to-northwest pattern throughout the year (Bijnavand, 2012). Zanjan city lies in the line of the prevailing winds toward the west.

Geologically, the mountainous areas surrounding the central plain are mainly made up of volcano-clastic rocks (andesite, tufftic shale and agglomerate) and sedimentary rocks (limestone, sandstone and marl) of middle to late Eocene age.

2.2. Soil sampling and chemical analysis

Assuming the smelter at center and given the prevailing wind direction, SE-NW transect was considered as main contamination gradient around the NILZ smelter. Topsoil samples were collected along this transect up to a distance of 10 km from the point source. The location of the sampling sites is shown on the map in Fig. 1. The sites D1 to D11 and U1 to U9 are, respectively, downwind (NW direction) and upwind (SE direction) from the smelter. In addition, soil samples were taken from the closest proximity to open waste dump (site W1, Fig.1). Two control soil samples were also collected from sites that were far away from the present smelter and any other contamination sources (e.g. roads, cultivated lands). At each sampling location a stainless steel auger was used to collect five sub-samples from the topsoil layer at a depth of 0–20 cm. In order to evaluate the vertical distribution of toxic metals in soils, three soil profiles (in the downwind direction) were also sampled at 20 cm intervals to a depth of 140 cm. Profile 1 (P-1) was situated near the soil waste dumps and the two other profiles (P-2 and P-3) were located at different distances from the smelter. The samples were placed in labelled polyethylene bags for transport to the laboratory. In laboratory, the samples were air-dried at ambient temperature for 72 h, disaggregated and sieved to an adequate size for further analysis (< 2 mm or < 63 mm). Soil samples were then analyzed for their total metal contents. Briefly, 200 mg air-dried soils were digested in a 3- acid mixture (2 mL HF_{conc} + 2 mL HNO_{3conc} + 4 mL HCl_{conc}) and the concentrations of Cr, Ni, Cu, Zn, Cd and Pb in extracts were determined by inductively coupled plasma optical emission spectrometry (ICP/OES). The triplicate analyses were used to calculate overall precision which is in the range of 2–5% for Pb, Cu, Ni and Cr and 5% for Cd and Zn. The analytical accuracy was also assessed by the use of international certified reference soil material (CRM 141R, calcareous loam soil). A good agreement (t-test, $p < 0.05$) was found between the certified values and the obtained values (Table 1). The detection limits (three times the standard deviation of triplicate measurement of the blank) were as follows: Pb 0.1 μg/L; Cu 0.1 μg/L; Zn 0.5 μg/L; Cd 0.05 μg/L; Cr 1 μg/L; and Ni 0.2 μg/L. These detection limits are considered adequate for the needs of the study, in terms of being sufficiently low to survey the wide range of concentrations encountered.
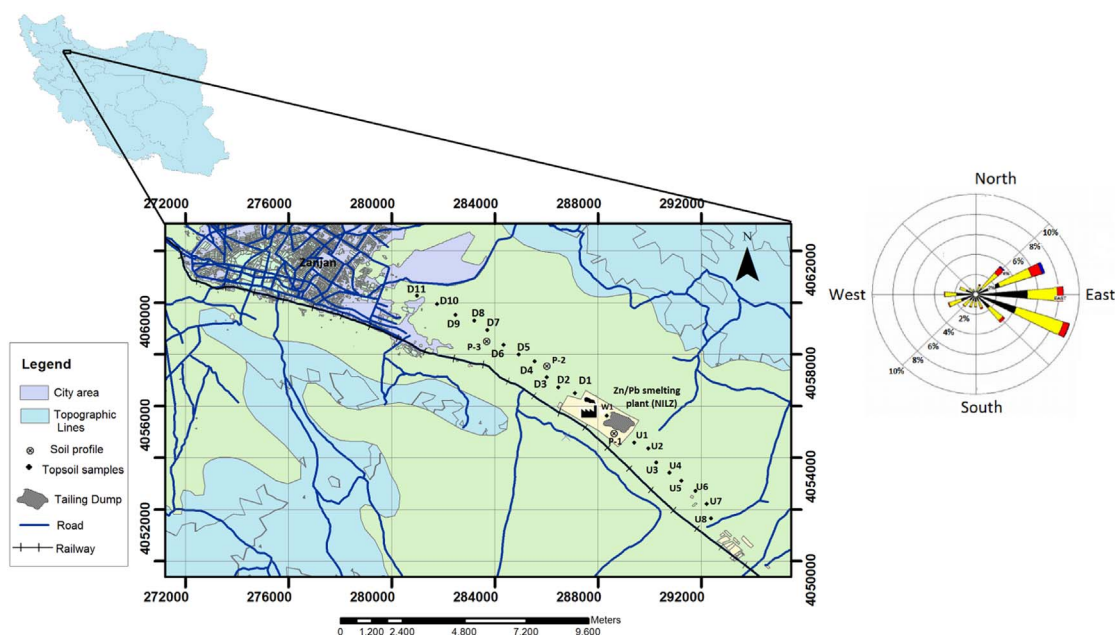
Fig. 1. A map showing the study area and soil sampling points around Zn/Pb smelting plant.

Table 1
Analytical validation against a certified reference material (CRM 141R, calcareous loam soil).

Metal	Content (mg/kg)		Accuracy (%)
	Certified[a]	Measured[b]	
Pb	51.3 ± 2.0	49.1 ± 3.0	95.7
Zn	270 ± 8	269 ± 6	99.6
Cu	46.9 ± 1.8	45.1 ± 1.1	96.1
Cr	138 ± 5	137 ± 3	99.2
Ni	94 ± 5	92 ± 6	97.7
Cd	14.1 ± 0.4	13 ± 0.2	92.8

[a] Mean ± uncertainty.
[b] Mean ± standard deviation (n = 3).

2.3. Determination of soil physico-chemical properties

The > 2 mm soil fraction was used for the pH, soil organic matter content (SOM) and granulometric measurements. Soil organic matter was measured by the Walkley-Black procedure (consisting of oxidation of soil organic matter in 0.5 mol/L potassium dichromate and concentrated sulphuric acid with back titration of excess dichromate by standard ferrous sulphate) (Walkley and Black, 1934). Soil pH was determined by mixing soil and ultra-pure water in a 1:2.5 (g:mL) ratio and shaking for 15 min before measuring pH using a pre-calibrated pH (model Jenway 3310). Particle size distribution was determined by the hydrometer method for silt and clay, and by dry sieving for sand fractions, following pre-treatments to remove organic matter, and chemical dispersion with sodium hexametaphosphorate (Reeuwijk, 1995).

2.4. Determination of chemical forms of metals in soils

In order to fractionate the chemical forms of selected metals in soil samples, the modified BCR method scheme was performed. The BCR procedure (proposed by the European Community Bureau of References) is more reproducible and more operationally effective than other sequential extraction methods. In this protocol, three fractions of metals are sequentially extracted with dilute acetic acid, a reducing agent and an oxidizing agent (Rauret et al., 1999). The fourth step (residual fraction) is only recommended and can be calculated by subtracting the non-residual fraction (defined as the sum of all the fractions except the residual one) from the total metal concentrations (Bacon and Davidson, 2008). As a modification (additional step), the residual from the third step was digested using the same three acids as for determination of total metal content (Rauret et al., 1999; Cappuyns et al., 2007; Passos et al., 2010). The extracts were then analyzed for Cu, Ni, Zn, Cd, Pb and Cr by ICP/OES. The extraction procedure, chemical reagents and the experimental conditions are reported in detail in the flow chart (Fig. 2). Reagents used throughout this experiment were of purris. p.a analytical grade. To evaluate the accuracy of the method for the determination of metal levels in soil fractions, known amounts of the target elements were added to extracts of soil fractions. These additions were within the range of the calibration curve standards.The analyses were repeated in triplicate using 1 g soil samples. The recovery values calculated by comparison of the concentrations of the metals with and without a spike ranged from 94 to 104%, with a repeatability of < 4.0%. As an internal check on the procedure, recovery percentages were also calculated by comparing the ratio of the modified BCR extracts for the four fractions with that of the total metal analysis multiplied by 100. The overall recovery rates were around 90 ± 8% for all of the metals in the soil samples, indicating good agreement between the total concentration and the sum of BCR results. It is noteworthy that the geochemical phases at each extraction step are largely operationally defined by the method and reagents used, and they can be considered as relative rather than absolute chemical speciation. Another remark is that the leachate composition (extracted from each fraction) may be influenced by kinetic parameters not by equilibrium with leaching solution. This is due to the fact that reagents used in sequential extraction schemes are non-selective for target phases. For example, the majority of iron oxyhydroxide-bound metals may be released in Step 1, rather than in Step 2 (the reduction step) as expected (Bacon and Davidson, 2008). In the present study, however, good recoveries of the six metals were obtained during sequential extraction, ensuring that the results obtained are satisfactorily reproducible and reliable.

2.5. Assessment of soil pollution

With the aim of assessing the degree of metal pollution in the soils of the study area, single factor-pollution index (SFPI) and comprehensive pollution index (CPI, Nemerow index) (Zhang et al., 2009; Ma et al., 2015) were calculated by the following equations:
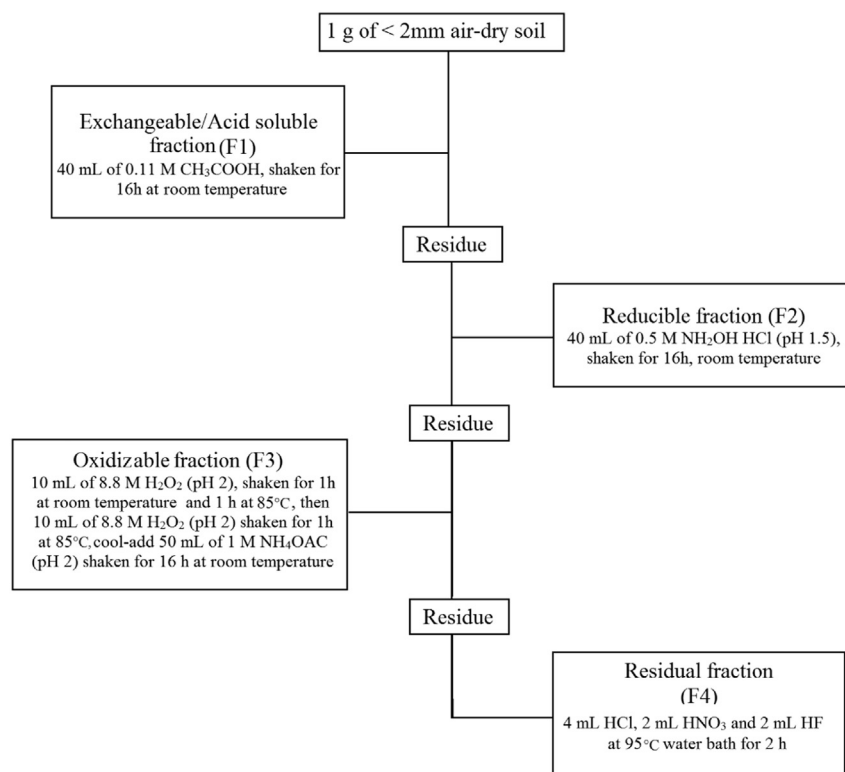
Fig. 2. Flow chart portraying the modified BCR procedure applied in this study.

$$SFPI_{ji} = \frac{C_{ji}}{C_{0i}}$$

$$CPI_j = \sqrt{\frac{[Average(C_{ji}/C_{0i})^2 + Max(C_{ji}/C_{0i})^2]}{2}}$$

where C_{ji} is the concentration of the ith metal at the jth sampling site, and C_{oi} is the criteria value or guideline for the ith metal (i.e., the background values in the control soils). Soil metal pollution is divided into four grades according to SFPI: SFPI ≤ 1, no pollution; 1 < SFPI ≤ 2, slight pollution; 2 < SFPI ≤ 3, moderate pollution; SFPI > 3, heavy pollution. According to the Nemerow multifactor index, the grades on soil pollution degree are also classified as five levels: CPI ≤ 0.7, safety; 0.7 < CPI ≤ 1, warning; 1 < CPI ≤ 2, slight pollution; 2 < CPI ≤ 3, moderate pollution; CPI > 3, serious pollution (Brady et al., 2014).

2.6. Sampling and analysis of solid wastes and dust

Ten grab samples of smelting wastes were taken from discarded heaps on east side of the smelter yard. These samples included Cd-Ni filter-cakes (produced from acidic leaching of Zn concentrates in the zinc plant) and smelting wastes (resulted from smelting/refining of lead concentrates in the lead plant). Seven bulk samples were also obtained from depots of the concentrated Pb ores which are fed into the furnace in the lead plant. In addition, seven composite (flue-gas) dust samples were collected from baghouse filter unit in the smelter. These materials were dried, weighted and dissolved in perchloric/nitric acids and metal levels were determined in the solutions by ICP/OES.

2.7. Statistical analysis

Descriptive statistics including mean, maximum, minimum, and coefficient of variation (CV) were calculated for soil variables. We adopt the CV as an indicator of the variability of soil properties. Pearson correlation coefficients were also used to identify the relationship between the metal concentrations and with soil physicochemical properties. Two sided *t*-tests were used to calculate statistical significance (p values). To determine if the distance to the smelter was influencing soil, linear regression was also performed on the data from study sites. Prior to statistical analyses, all soil variables were z-scale standardized to minimize the effects of different units and variance of variables and to render the data dimensionless. These analyses were performed using SPSS (Version 21.0).

3. Results and discussion

3.1. Total content of metals in solid wastes and flue gas dust

Results of bulk chemical analysis on the leaching residues (filter-cake) indicated that these materials have elevated concentrations of metals such as Pb, Zn and Cd with averages of 12,900, 450,000 and 139,000 mg/kg, respectively (Table 2). These materials are also characterized by low pH due to application of sulfuric acid during leaching step in the process of zinc production. Solid smelting wastes (produced in the lead plant) have extremely high levels of Pb, Zn and Cd (Table 2). Also, in the concentrated ores, the average concentrations of metals of interest are observed to be 368,600 mg/kg (for Pb), 194,000 mg/kg (for Zn) and 77,500 mg/kg (for Cd). It is interesting to note that the concentrations of Pb and Zn in the solid smelting wastes are relatively higher than those of the flue-gas dust samples. It seems that the high boiling point metals such as Pb and Zn prefer to retain in the smelting wastes whereas most Cd in the lead concentrates might evaporate and enter the gas-phase during the high temperature smelting process due to its low boiling points (767 °C) (Bi et al., 2006). These different behaviors of metals during lead smelting processes also result in higher Zn/Cd and Pb/Cd ratios in the smelting wastes than those in the flue gas dust (Table 2). Among the three other metals, Ni exhibited an extremely high level in the leaching residues (filter-cakes). Nickel substantially exists as impurity in the fed zinc concentrates which are removed efficiently through the leaching/purification process in the zinc plant.

Table 2
Metal contents in leaching residues, solid smelting wastes, concentrated ores and flue-gas dust samples (in g/kg) along with the calculated Zn/Cd and Pb/Cd ratios.

	Pb	Zn	Cd	Cu	Cr	Ni	Zn/Cd	Pb/Cd
Leaching residues (Filter-cake)								
Max	15.1	520	152	20.1	0.141	40.3	3.41	0.091
Min	11.1	400	130	15.1	0.082	35.1	3.21	0.083
Mean	12.9	450	139	17.2	0.101	37.2	3.18	0.083
Solid smelting wastes								
Max	175	21	5.71	0.370	0.142	0.054	6.72	56.4
Min	125	15	3.12	0.312	0.082	0.055	2.61	21.9
Mean	150	17.8	4.24	0.344	0.108	0.051	4.66	39.6
Concentrated Pb ores								
Max	395	250	98.2	1.51	0.102	1.11	4.92	7.11
Min	351	155	50.7	1.07	0.041	1.07	1.54	3.82
Mean	370	194	77.5	1.25	0.072	1.08	2.93	5.16
Flue-gas dust								
Max	4.71	2.51	8.73	0.191	0.071	0.172	0.312	0.512
Min	3.14	2.32	8.12	0.172	0.061	0.131	0.261	0.361
Mean	3.91	2.40	8.41	0.181	0.065	0.153	0.281	0.432

3.2. Physico-chemical properties of topsoil

Table 3 shows the main physico-chemical parameters of sampled topsoils. The results of particle size analysis indicated that the studied soils had a loam to clay loam texture (USDA classification), with clay contents ranging from 16 to 34%. Soil OM also varied from 0.12 and 2.43%. Neither of these soil variables (texture and SOM content) differed significantly between the sampling sites, suggesting soils around the smelter were derived from a single or uniform parent material (geologic substrate). As an exception, sample W1 which was collected close to solid waste pile showed an acidic pH (≈ 5.32). Due to application of acid sulfuric during the third stage of mineral processing in the smelter plant, the waste solids produced are acidic in nature (pH ≈ 3). These waste materials are dumped improperly inside and around the smelter plant. The long-term leaching of these materials

Table 3
Physico-chemical properties of soil samples.

Sampling site	Particle size distribution			OM (%)	pH$_w$
	% Silt	% Clay	% Sand		
D-1	40	22	38	1.82	7.60
D-2	35	19	46	1.69	7.10
D-3	43	20	37	1.63	7.08
D-4	32	20	48	1.50	7.00
D-5	40	26	34	2.43	7.00
D-6	37	24	39	1.40	6.98
D-7	42	22	36	0.89	7.20
D-8	40	16	44	0.80	7.40
D-9	41	19	40	1.70	7.10
D-10	35	18	47	1.68	7.01
D-11	30	20	50	1.77	7.18
U-1	33	21	46	1.46	7.20
U-2	42	25	33	1.58	7.86
U-3	47	27	26	0.65	7.61
U-4	34	26	40	0.63	7.70
U-5	35	23	42	1.53	7.03
U-6	41	18	41	1.21	7.12
U-7	39	26	35	1.25	7.01
U-8	46	25	29	0.34	6.79
U-9	40	34	26	0.12	7.22
W-1	30	20	50	0.69	5.32
Max	47	34	50	2.43	7.86
Min	30	16	26	0.12	5.32
Mean	38.25	22.64	39.26	1.27	7.07
CV	0.12	0.18	0.18	0.44	0.06

might lead to acidification and contamination of the surrounding soils (site W1). The remaining soil samples have neutral to slightly alkaline pH (6.98–7.18).

3.3. Depth -wise variation of soil properties

For two soil profiles sampled (P-3, and P-2), the organic matter content is the highest in surface horizons (0–20 cm) and declines at lower sampling depths (Fig. 3c and f). Soil pH does not show any obvious trend with depth (Fig. 3a and d) whereas the clay content displays a gradual rise across these soil profiles (Fig. 3b and e).

At soil profile P-1 near the solid waste pile, soil pH is extremely low in the uppermost 20 cm of the profile and then it increases gradually with depth (Fig. 3g). This indicates again the influence of the nearby solid waste pile on the pH of surface layers, although this appears to be on a localized scale. Variation of the clay content and organic matter in the profile 1 is almost the same as in the other two profiles (Fig. 3h and i).

3.4. Total concentration of metals in topsoil

The statistical summaries of total metal concentrations in topsoil samples are listed in Table 4. Soil samples collected from the control sites contained 0.76–1.31 mg/kg of Cd, 35–40 mg/kg of Cr, 19–21 mg/kg of Cu, 32–35 mg/kg of Pb, 45–52 mg/kg of Zn and 20–25 mg/kg of Ni. These results were comparable to their corresponding concentrations in worldwide uncontaminated soils (Fergusson, 1990), and therefore can represent regional baseline concentrations. Metals in soils near the Zn/Pb smelter can be grouped in terms of their ranges and variations:

3.4.1. Group (1)

This group includes Zn, Pb, and Cd. The concentration range of these metals is very wide (Table 4) and their coefficients of variation (C.V., calculated as [standard deviation]/[mean]) are greater than one. In almost 23% of the analyzed soil samples, total contents of these metals are well above background soil concentrations. This indicates that levels of these metals have high variability among sampling sites and are strongly influenced by an exogenous (non-pedogenic) source in the study area. In the soil samples collected from the downwind area of the smelter (D1 to D11), the concentrations of Pb and Zn reached values above 1000 mg/kg within a distance of 4300 m from the smelter. For Cd, total concentrations are still above the background level up to a distance of 8000 m from the smelter. These findings clearly suggest that the investigated metals (Pb, Zn and Cd) are being released into the atmosphere as air-borne particles, dispersed by the prevailing wind current along the transect and eventually deposited on the surface soil in the downwind direction at different distance from the smelter. In a similar study, Chrastný et al. (2012) found that the agriculture soils localized near the Olkusz smelter (southern Poland) are rich in Pb, Cd and Zn, compared to the site further from the smelter and a significant decrease (according to the Duncan test) in total metal concentration with the distance from the contamination source was found for Zn and Cd in both upper organic soil horizons A and mineral soil horizons C.

In the upwind soil samples (U1 to U9), concentrations of these metals are roughly comparable to their corresponding values in the control soils (C1 and C2). As can be seen in Table 4, extremely high concentrations of Pb, Zn and Cd are found in soil sampling site W1, located in closest proximity to the solid wastes dumps. It is evident again that the leaching of the solid wastes is responsible for the significantly higher levels of these metals in soil at this site.

3.4.2. Group (2)

This group comprising Ni, Cr and Cu is characterized by narrow range and a coefficient of variation of less than one (Table 4). In most
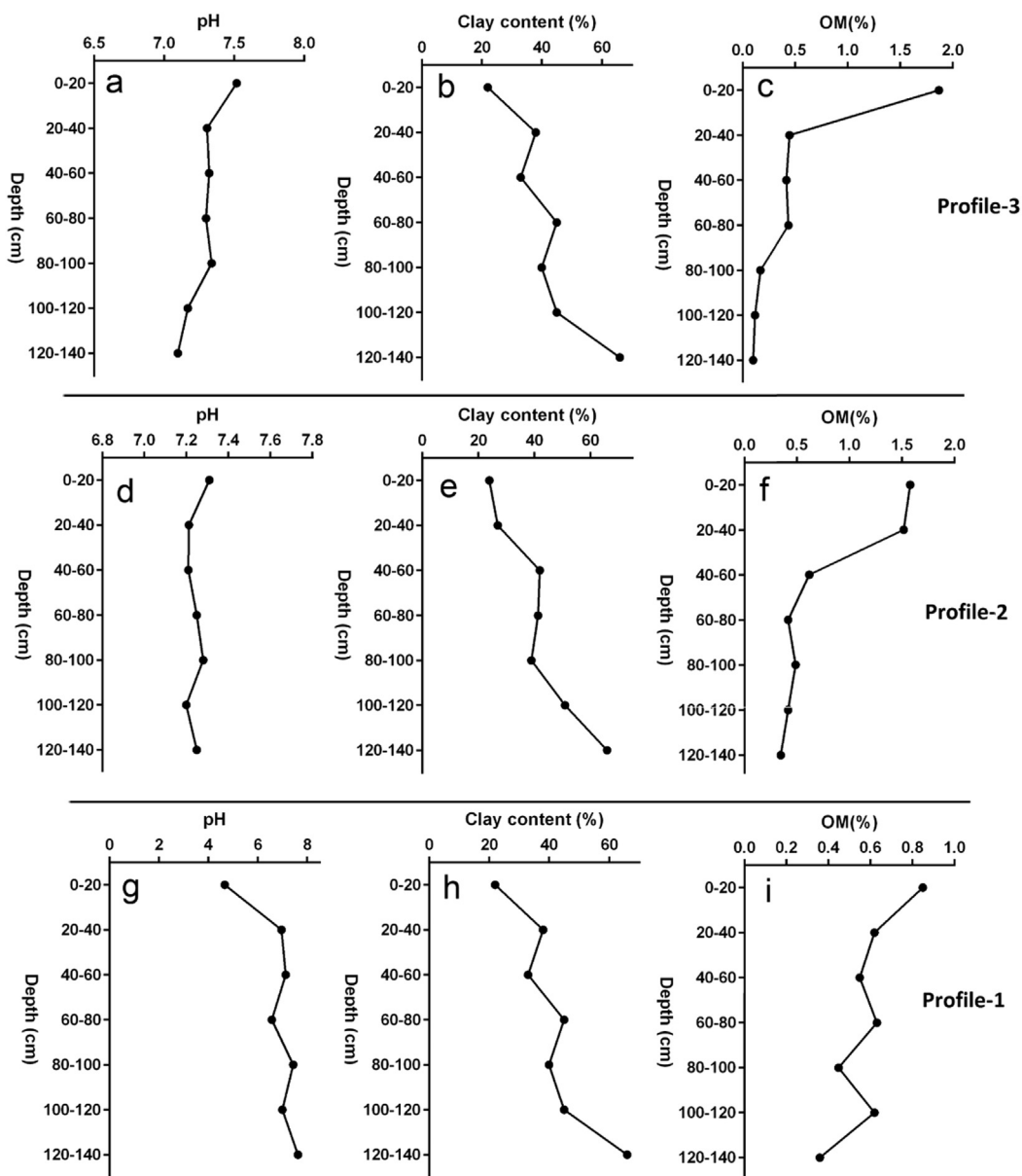
Fig. 3. Depth-wise variation of soil physico-chemical properties in the three soil profiles.

the samples, levels of these metals in soils are comparable to the background soil values, implying that the extrinsic inputs of these metals into the soils were limited. For this group, there is also no significant difference between their concentrations in the downwind and upwind directions (*t*-test, p < 0.01). The exception to this is yet again, site W1 that is marked by high level of Ni, owing to the presence of Ni-Cd bearing filter cakes in nearby solid waste dump.

3.5. Correlation analysis

Pearson's correlation analysis was used to examine the mutual relationships among metals investigated and with soil properties. From Table 5, it can be seen that there exist close correlations among Zn, Pb and Cd at significance level of 0.01. This degree of covariance is strongly suggestive of common (anthropogenic) source for these metals. The three other metals (Ni, Cr and Cu) are well correlated with each other (r > 0.612, p < 0.05) but show no significant mutual correlation with the other metals (i.e. Pb, Zn, and Cd). The results once again confirm that the concentrations of Pb, Zn, and Cd in soil around the smelter are mostly controlled by aerial emissions from the smelter

whereas Ni, Cr and Cu contents are not affected by the smelting activity in the study area. Chromium, Ni and Cu also have similar ionic radii (Dean, 1992), so they may exhibit similar geochemical behavior during pedogenic processes.

Among soil properties, soil pH showed a positive correlation with Cd, Pb, Zn and Cu with correlation coefficients all more than 0.50, implying that the neutral–alkaline soil environment substantially enhances the accumulation of these metals in soil.

Clay content only correlated positively with Cr and Ni (p < 0.05), and correlated poorly with other metals. It has been shown that Cr and Ni often participate with clay minerals during pedogenic processes, thus existing as structural components of clay minerals rather than as the exchangeable ions on the surface of clays.

Soil organic matter content does not indicate significant correlation with metals, probably due to its narrow range in soil samples.

3.6. Horizontal variation of metal concentrations in topsoil

In order to evaluate the impact of airborne emissions from the Zn/Pb smelter on soil metal contamination, concentration of the

Table 4
Descriptive statistics of total metals concentrations (mg/kg) in soil samples studied.

Sampling site	Distance from smelter (m)	Pb	Zn	Cd	Cu	Cr	Ni
D-1	1001	1600	2137	32.7	23.7	47.2	39.1
D-2	2201	1420	1557	24.4	22.1	42.5	30.9
D-3	3475	84.3	183	28.2	20.2	45.6	22.2
D-4	4280	74.9	122	22.4	26.9	46.6	36.7
D-5	5802	38.5	74.4	19.3	37.4	54.2	29.9
D-6	6100	35.2	56.8	27.7	26.4	46.3	33.6
D-7	6890	33.4	48.6	24.1	23.6	37.9	30.9
D-8	7528	21.3	59.4	2.91	30.4	49.3	39.5
D-9	8050	32.1	52.3	0.921	26.3	51.1	38.1
D-10	8689	28.5	51.2	0.713	19.7	34.5	34.6
D-11	9767	26.8	44.7	0.911	25.8	44.2	31.1
U-1	1500	149	170	2.11	22.8	53.4	22.9
U-2	2370	109	153	2.50	22.5	32.4	26.7
U-3	3500	75.6	105	1.21	26.5	43.9	25.4
U-4	4907	61.6	175	0.921	14.6	36.4	24.1
U-5	5709	40.9	42.6	1.01	24.8	47.5	30.2
U-6	6540	63.4	67.9	1.22	19.2	41.5	20.5
U-7	7700	43.1	74.8	1.61	24.1	46.1	22.4
U-8	8505	42.6	51.1	1.20	25.3	53.9	19.3
U-9	9630	50.3	47.2	1.41	24.9	40.9	23.9
Max		1600	2137	32.7	28.3	54.5	36.9
Min		21.3	79.4	0.713	22.8	36.4	19.3
Mean		302	311	9.82	24.8	46.1	28.2
CV		2.40	2.27	2.38	0.541	0.112	0.181
W-1[a]		22,630	44,178	1014	78.3	125	1005
C-1[b]		35	54	1.31	19	40	25
C-2[b]		32	45	0.762	21	35	20
World soils (average)[c]		25	62	1.12	14	42	18

[a] Soil sampling site (W1) close to solid waste dump.
[b] Control soils.
[c] Data from Fergusson (1990) after Kabata-Pendias (2010).

investigated metals at varying distances from the smelter are taken into consideration.

As shown in Fig. 4, concentrations of the three studied metals (Pb, Zn and Cd) in surface soils (D1 to D11) decrease gradually with increasing distance from the smelter in the downwind direction. The highest concentrations of Pb (1600 mg/kg) and Zn (2137 mg/kg) were observed within 3400 m from the Zn/Pb smelter (Fig. 4a and b, respectively). After this distance, concentrations of these two metals abruptly dropped and reached their reference levels at a distance of 6100 m from the smelter. The sharp decrement in the concentration of Pb and Zn in soils surrounding the smelter indicates that they are directly emitted from the stack (as dust particles) and deposited in close proximity to the smelter. The decreasing trend with distance indicates that the Cd level is still significant at distances up to 8000 m from the smelter (Fig. 4c). Therefore, difference exists in the distribution pattern

of this metal along the transect as compared with the two other metals (Pb and Zn). An important reason for this difference is that cadmium is more readily volatized during smelting and deposited over a longer distance to the smelter. Some studies showed that Cd was a volatile element and was less likely to deposit around the point source as it tended to remain in the atmosphere, where it was subject to long-range transport (Rasmussen, 1998).

Mathematically, the concentrations decrease for Pb and Zn is well-fitted with the power-law model according to the following equation:

$$y = \alpha x^{-\beta}$$

$$y = 1563.9x^{-1.92} \quad r^2 \geq 0.80 \text{(for Pb)}$$

$$y = 2074.9x^{-1.76} \quad r^2 \geq 0.80 \text{(for Zn)}$$

For Cd, the decreasing pattern with distance from the smelter follows an exponential equation:

$$y = \alpha e^{-\beta x}$$

$$y = 102.36e^{-0.42x} \quad r^2 \geq 0.7 \text{(for Cd)}$$

where α and β are coefficients and x is the distance from the smelter. The α coefficient stands for the theoretical maximum value of the anthropogenic component. A higher α value indicates greater anthropogenic activities. The α value for Pb and Zn is quite high, which confirms a greater accumulation of these metals as a result of smelting activity. The β coefficient indicates the rate of decreasing concentration. The $y = \alpha x^{-\beta}$ or $y = \alpha e^{-\beta x}$ is the trend which represents the anthropogenic component of a given element (Dao et al., 2014). Element concentrations with higher β values decrease more rapidly than those with smaller value with increasing distance (Wu et al., 2011; Dao et al., 2014). Pb have the lowest β value and its content in soil along the transect declines more rapidly as compared to the other two metals.

The statistical evaluation obtained from the regression analysis revealed that mean metal concentrations were negatively correlated with the distance from the smelter, giving r values of -0.924 (Pb), -0.943 (Zn) and -0.868 (Cd), respectively. It is worth noting that soil samples within 3400 m of the smelter have the features of high ratios of Zn/Cd (> 40) and Pb/Cd (> 6). This confirms that Pb and Zn are most likely carried in the form of dust particles rather than as volatile (flue gas) phase and, as a consequence deposited over short distances downwind from the smelter.

Unlike the former group of metals, concentrations of the three metals Cu, Ni and Cr do not exhibit any clear dependency with distance from the smelter (as shown in Fig. 4d,e and f, respectively), giving very low r^2 values in the regression fitting. This further supports the assumption that variations of these elements in the study area were not influenced by smelting activity. Contrary to our results, Sutkowska et al. (2013) found that levels of Cr, Ni and Cu in surface soils around Jaworzno smelter (southern Poland) are significantly greater than the
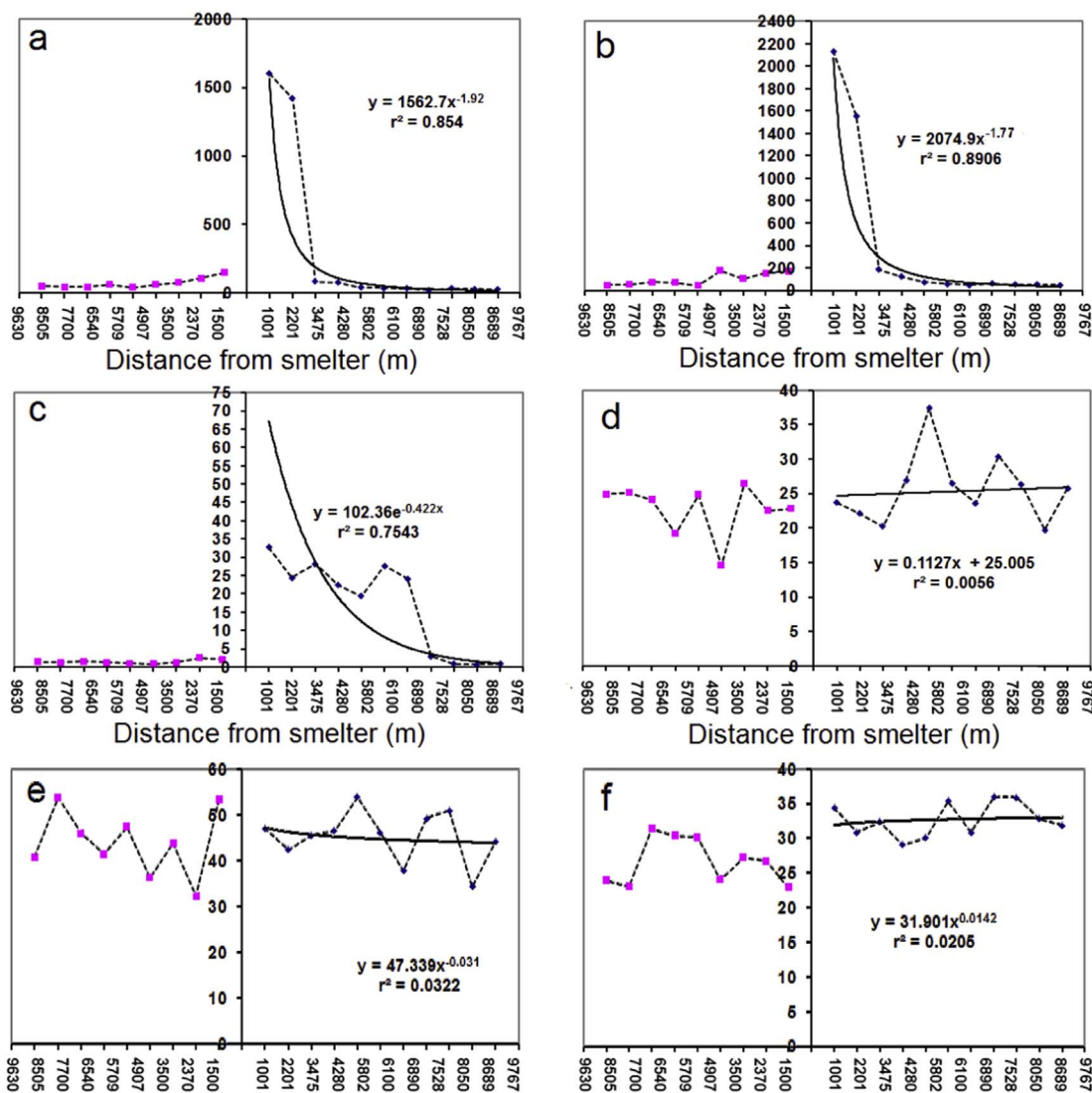
Table 5
Correlation matrix between metal concentrations and soil properties.

	Cd	Cr	Cu	Pb	Zn	Ni	pH	OM	CC
Cd	1								
Cr	−0.088	1							
Cu	0.081	0.795[a]	1						
Pb	0.942[a]	−0.041	0.190	1					
Zn	0.922[a]	−0.016	0.334	0.981[a]	1				
Ni	−0.077	0.807[a]	0.567[a]	−0.127	0.003	1			
pH	0.556[b]	0.219	0.699[a]	0.537[a]	0.606[b]	−0.297	1		
OM	−0.281	0.407	−0.325	−0.283	−0.318	−0.255	0.463	1	
CC	0.040	0.625[b]	−0.200	−0.060	−0.154	0.7514[b]	0.352	0.166	1

OM: organic matter.
CC: clay content.
[a] Correlation is significant at the 0.01 level (2-tailed).
[b] Correlation is significant at the 0.05 level (2-tailed).

Fig. 4. Variation of total metal concentration (mg/kg) in the topsoils along the pre-selected transect: (a) Pb; (b) Zn; (c) Cd; (d) Cu; (e) Ni; (f) Cr.

local background ranges and decrease gradually with increasing distance from the zinc smelter suggesting the anthropogenic input of these metals to topsoils.

It should be noted, however, that the effects of smelter emissions on the surrounding soils depend on other factors such as the mass of emitted contaminants, their specific size distribution, stack height, meteorological conditions (such as wind speed and direction) and topography which must be considered in evaluating the nature and extent of smelter-related impacts.

3.7. Vertical distribution of metals in soil profiles

In order to distinguish natural concentrations of the investigated metals from anthropogenic contamination in the study area, a concept of soil sampling at three soil profiles was used.

Figs. 5, 6 and 7 give the typical evolution of the total metal contents as a function of the depth in the three soil profiles. The percentage decrease in concentrations of these metals from the top layer of soil (0–20 cm) to the deepest layer (120–140 cm) was also calculated. In the profiles P-2 and P-3 (as shown in Fig. 5a–f and Fig. 6a–f, respectively), the three metals (Pb, Zn and Cd) showed content decreased with increasing soil depth. The mean of decreasing rates from 0 to 20 cm to 120–140 cm were 74% (for Pb), 58% (for Zn) and 54% (for Cd). This indicates that Cd, Pb and Zn mainly accumulated in the top 20 cm of the

soil. Interestingly, the decreasing rates of these metals in the profile 2 were much higher than those of profile 3, due to closer proximity of profile 2 to the smelting plant. In addition to distance from the source, the accumulation or mobility of toxic metals along the soil profile also depends on the soil physiochemical properties. For instance, in the profiles 2 and 3 neutral or slightly alkaline nature of the studied soils and accumulation of soil organic matter in the upper layers have apparently limited the mobility and migration of the metals into deeper layers. Sterckeman et al. (2000) and Chrastný et al. (2012) discussed the major physicochemical factors influencing the vertical distribution of Pb, Cd and Zn in smelter-affected soils.

However, as is noted by Chrastný et al. (2012), the vertical metal migration in the soil profile cannot be fully understood with only a meager knowledge of soil properties and without data about the appropriate mineralogical transformation processes. According to the results obtained by these authors, the mobilization of Pb, Zn and Cd in in smelter- affected soils depends to a great extent on the mineralogical transformation of the primary materials (in air and soil system) and is directly controlled by the pH of the target soil (Chrastný et al., 2012, 2015). The mineralogical characteristics of the solid wastes (fly ash, filter-cake…) and the affected soils have not been covered in the present study and remains as a subject for future research.

As observed in Figs. 5 and 6, the other three metals (Cu, Cr and Ni) display a different vertical distribution along the soil profiles. For the
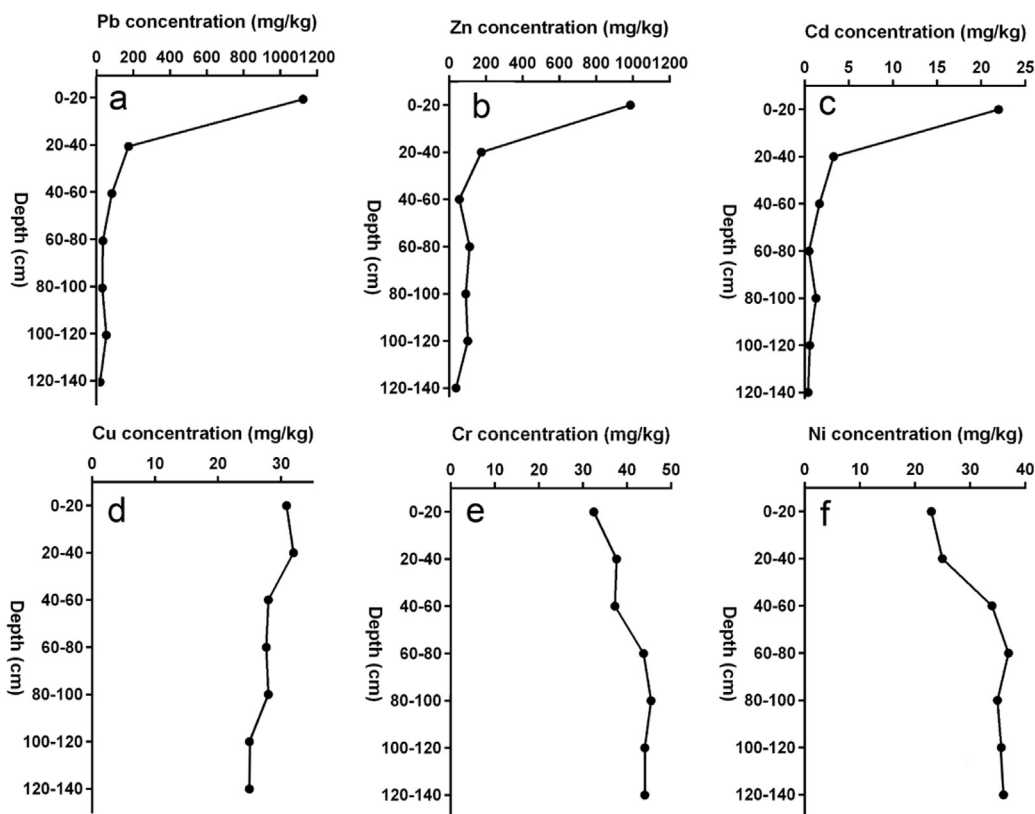
Fig. 5. Depth-wise variation of metals in the soil profile 2: (a) Pb; (b) Zn; (c) Cd; (d) Cu; (e) Cr; (f) Ni.

total concentrations of Ni and Cr, the striking pattern is that the concentrations of these metals in the soil profiles 2 (Fig. 5e and f) and 3 (Fig. 6e and f) increased slightly with depth and became constant at a depth of approximately 110 cm This could be related to the clay content which increases gradually with depth. Copper appears to have a more uniform surface and subsurface distribution. The decreasing rates for Ni, Cu and Cr are 0.6%, 1.5% and 2%, respectively, confirming their increasing contents with depth. This trend of increasing content with
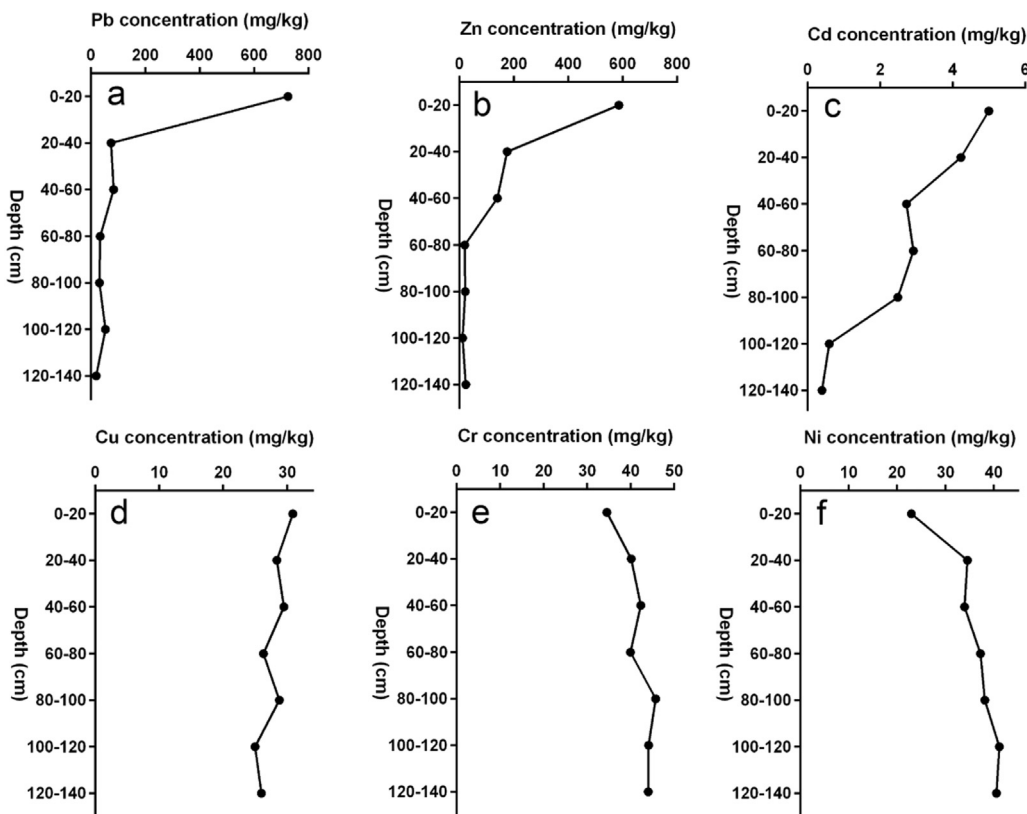
Fig. 6. Depth-wise variation of metals in the soil profile 3: (a) Pb; (b) Zn; (c) Cd; (d) Cu; (e) Cr; (f) Ni.
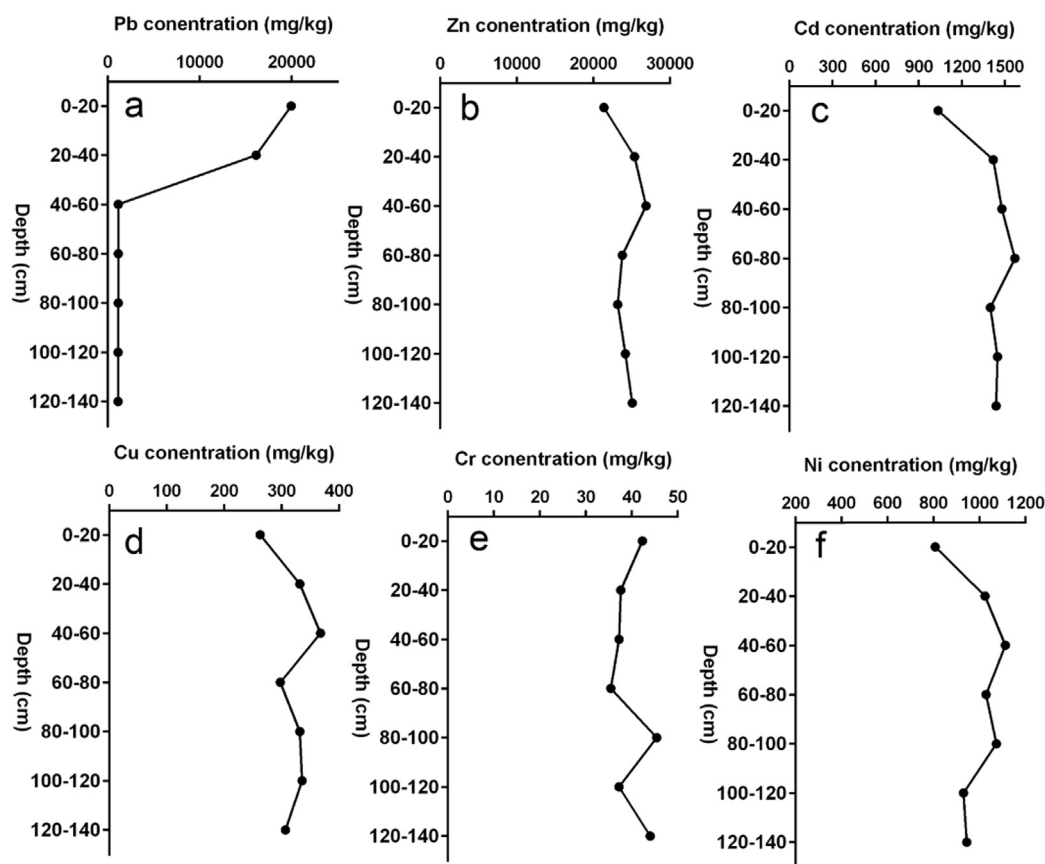
Fig. 7. Depth-wise variation of metals in the soil profile 1: (a) Pb; (b) Zn; (c) Cd; (d) Cu; (e) Cr; (f) Ni.

depth also suggests that these three metals have either more limited or no deposition from the smelter and their concentrations in the soil are most likely controlled by pedogenic processes.

In the soil profile 1 located close to solid waste dump, the depth-wise variation of the metals is totally different from that of the other two profiles (Fig. 7a–f). For this profile, total concentrations of all metals (except for Cr and Pb) increased significantly with depth. This is more discernable for Cd than other metals. The lower pH in the topsoil of profile-1 might accelerate the leaching of the metals down to the lower profile, as metal solubility tends to increase at lower pH (Brallier et al., 1996; Wang and Qin, 2005). This finding is in agreement with the results obtained by Chrastný et al. (2012) who observed a significant metal migration downwards to the deeper horizons in a soil profile due to acid leaching of the smelting wastes dumped close to the Olkusz smelter (southern Poland). Based on Cd isotope fractionation in the soil profiles adjacent to the same smelter, Chrastný et al. (2015) implied that soil processes (i.e. interaction of the dissolved Cd species with solid soil compounds) need to be taken into account in identifiyng the source and Cd distsribution pattern in the affected soils near the smelters.

3.8. Assessment of soil metal pollution

Fig. 8a shows the SFPI variations of metals at the sampling sites along the transect downwind. The SFPI of Cu, Ni and Cr are less than 1.0, which indicates that all the sampling sites were not polluted by these metals. On the contrary, the pollution degrees of Pb, Zn, and Cd in the soils were relatively heavy, and as the distance increased from the smelter, their pollution levels decreased gradually from heavy to medium. Among all the pollutants, Cd pollution was the most serious and shows heavy to moderate pollution level in 7500–8000 m from the smelter. For Pb and Zn, the SFPI values are more than 3.0 within 3400 m from the smelter and decreased with increasing distance from
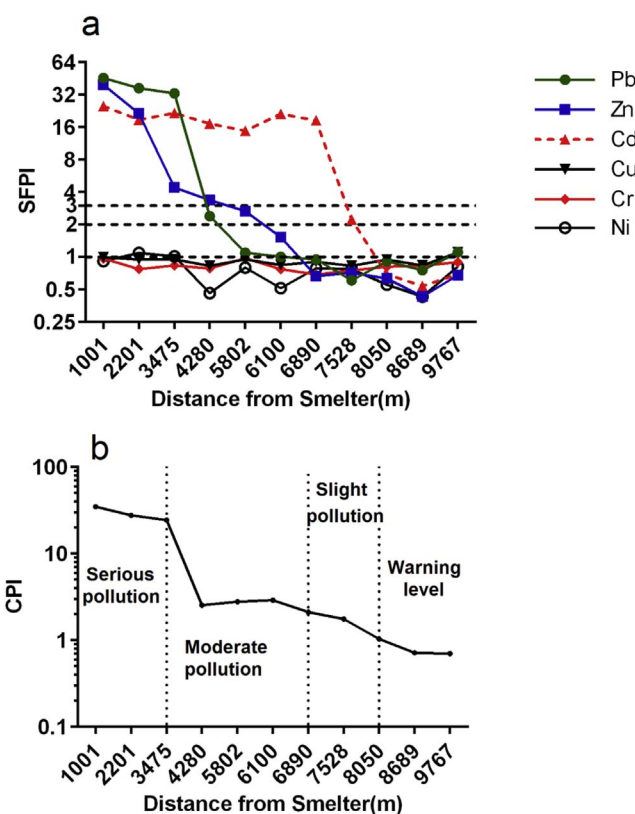

Fig. 8. (a) Plot of single factor pollution index (SFPI) for each metal and (b) comprehensive pollution index (CPI) for all soil sampling sites along the transect downwind.
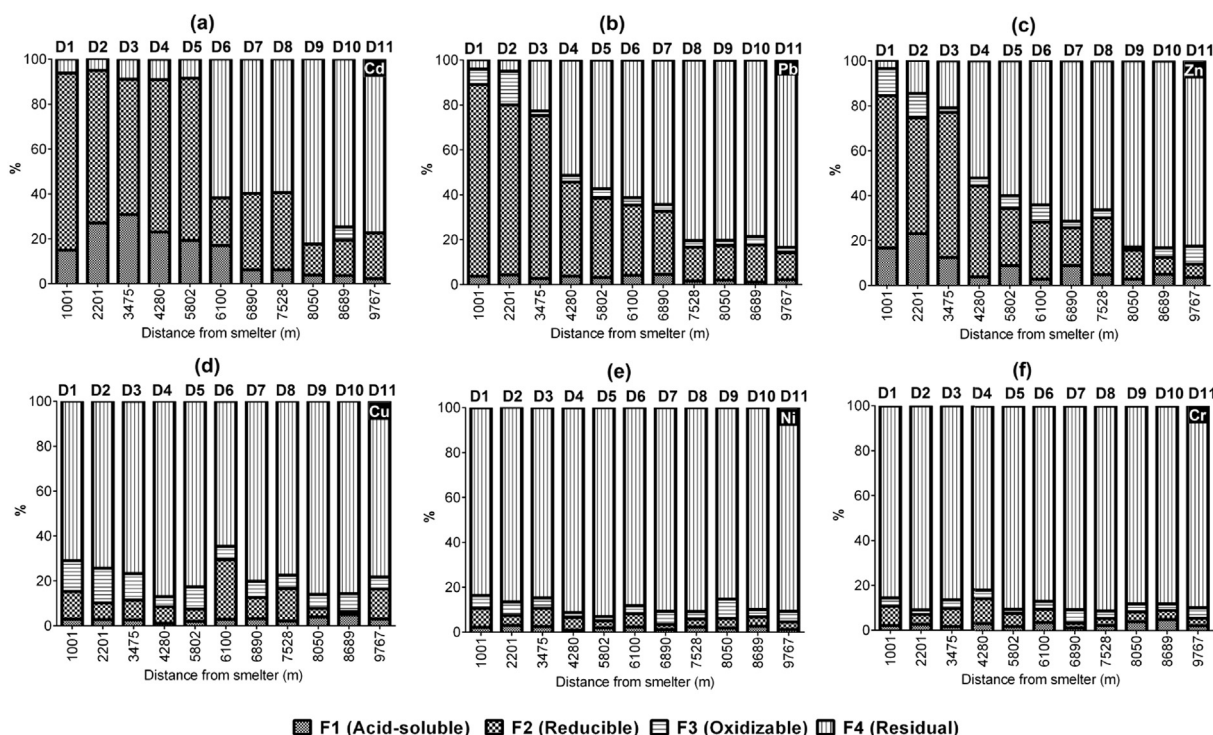
Fig. 9. Fractionation of metals in the topsoils along the transect downwind: (a) Cd; (b) Pb; (c) Zn; (d) Cu; (e) Ni; (f) Cr.

the point source. These trends roughly matched the concentration tendencies for these metals along the transect.

Based on the comprehensive pollution indices (CIPs), four pollution zones can be identified along the transect (Fig. 8b). The first is the serious pollution zone that is located within 3400 m from the smelter, where the CPI values are more than 10.0. The second is the moderate pollution zone located 3400–6800 m from the source where the CPI values are 2.5–3. The third is slight pollution zone with CPI values ranged from 1.7 to 2.1 located within 6800–8000 m and the fourth zone with CPI < 1 that is located more than 8000 m from the smelter and is at warning level in terms of metal pollution.

4. Chemical fractionation (forms) of metals in soils along the transect

In this work, an optimized four-stage BCR scheme was applied to assess the geochemical forms of Pb, Zn, Cd, Cu, Ni and Cr in the topsoil samples collected on downwind side of the Zn smelter. Among the four fractions of metals, the first three fractions (the sum of the exchangeable/acid soluble, reducible and organic-bound fractions) are typically considered the mobile and potentially bioavailable ones for living organisms (Ma and Rao, 1997; Chen et al., 2000). These three fractions include metals from anthropogenic sources. The metals present in the residual fraction are not available and can be regarded as a measure of the contribution by natural sources.

Fig. 9a–f depict the chemical fractionation of the studied metals in topsoils samples. Each chemical fraction was presented as the percentage of the sum of all the fractions and is discussed below on an element by element basis. Also, the results obtained for absolute concentrations (in mg/kg) of the six metals in each fraction are presented as supplementary data in Table S1.

4.1. Cd

Cadmium in topsoils was mainly associated with the reducible fraction with concentrations ranging from 1.14 mg/kg to 25.7 mg/kg which account for 13% to 78% of its total content (Fig. 9a). The

adsorption is highly pH dependent and increases dramatically from pH 6 to 8 (Johnson, 1990). Next to the reducible fraction, Cd is mainly bound to the residual fraction, which ranges from 6.2 to 82%. The remaining Cd is associated with the exchangeable phase (mean, 14%). This suggests that a portion of Cd was probably contained in acid-soluble carbonate phase such as calcite in which Cd may replace Ca. Cadmium generally has a special affinity with carbonate and may coprecipitate with carbonate minerals at high pH (Forstner and Wittmann, 1981). Except for site D10, Cd content in the oxidizable fraction was found below detection limit (0.05 μg/L) in all studied topsoils. The minor role for the organic fraction in the speciation of Cd noted in the present study is consistent with the low adsorption constant of Cd to organic matter (Baron et al., 1994; Chlopecka et al., 1996). A striking pattern is that in topsoil samples collected within 7500 (≈ 8000) m from the smelter, Cd is more often incorporated into the non-residual fractions (Fe-Mn oxides and exchangeable phases). These two fractions accounted for 70% of the total Cd in the soil sampling sites. The relatively high percentage of the non-residual fractions of Cd in these soils is an indication of its anthropogenic source. However, the calculated mobility factors (corresponding to the ratio of labile fractions (F1 + F2 + F3) to the sum of all fractions) indicated that Cd availability is generally moderate (19–58%), probably due to alkaline condition of the soil. Increasing the pH of soil rich in Fe-Mn oxides and clay minerals, the total percentage of Cd bound to oxide fraction increases, while at lower pH values the exchangeable Cd fraction increases. In this context, Chrastný et al. (2012) pointed out that the pH of the soil does not directly remobilize primary contamination material. In other words, the smelting process produces apparently chemically and mineralogically less stable metal forms. The consequent transformation process of such material is probably controlled by a persistence in the atmosphere (the distance from the smelter) and/or by the pH of the target soil system.

4.2. Pb

The major geochemical phase for Pb in the topsoils studied is the Fe-Mn oxide fraction (mean: 55%, 234 mg/kg), followed by the residual

phase (mean: 37%, 31 mg/kg) while lower percentage of the total Pb is bound to exchangeable-labile (mean: 3.1%, 11 mg/kg) and oxidizable phases (mean: 4.4%, 30 mg/kg) (Fig. 9b). The presence of Pb in the reducible fraction suggests that Fe-Mn oxides are involved in trapping this element for pH values above 7 (Nafeh Kassir et al., 2012). Many studies have also demonstrated the strong affinity of Pb for both Fe and Mn compounds (Burt et al., 2003; Kaasalainen and Yli-Halla, 2003; Davidson et al., 2006; Cuong and Obbard, 2006; Covelo et al., 2007). These compounds (commonly referred to as sesquioxides) sorb Pb via formation of inner sphere sorption complexes (Scheinost et al., 2001). In soils with low organic matter such as the studied soils, this process seems to be the major mechanism controlling the fate and transport of Pb. The sum of the non-residual fractions indicates that approximately 45% of the Pb might be potentially available at all sites. This is confirmed by low-moderate mobility factors for Pb with values ranging from 19 to 52%.

It was observed that the distribution of Pb among the geochemical fractions is dependent on the total Pb content in the soil. In soil samples with high lead contents near the smelter (sites D1, D2, D3), Pb is mainly concentrated in the non-residual fractions. The association of Pb with the non-residuals fraction in the soil samples containing high total Pb contents reflects dominance of anthropogenic sources through emissions from the nearby smelting plant. Conversely, average concentrations of Pb in the reducible fraction systematically decreased from 85.3 mg/kg at site D1 to 12.9 mg/kg at site D11 and in soil samples further away from the contamination source the residual fraction becomes clearly predominant indicating less impact by smelting activity. It is often argued that the incoming pollutants from external polluting sources initially exist in unstable chemical forms and continued pollutant accumulation leads to the formation of precipitates, especially as reducible forms (Lee, 2006). Comparable findings to this study have been reported by Chrastný et al. (2012). They observed that reducible and oxidizable fractions of Pb are dominant in the soils from the more contaminated area around the Olkusz smelter (southern Poland). At the site further from the smelter, Pb associated with the reducible fraction slightly exceeds the oxidizable one in soil surface horizons. They also deduced that Pb distribution in the upper soil horizon cannot be explained on the basis of soil properties and mineralogical transformations of the fly ash after its deposition into the soils, which may be responsible for the differences of fractionation in the affected soils.

4.3. Zn

The partitioning pattern of Zn was, in part, similar to that of Pb with an average of 54% (1168 mg/kg) in the reducible fraction, 7% (120 mg/kg) in the organic matter-bound fraction, 31% (667 mg/kg) in the residual fraction, and 8.4% (180 mg/kg) in the exchangeable/acid soluble fraction (Fig. 9c). In agreement with these results, several other workers have also reported the dominance of the Fe-Mn oxides bound in Zn (Narwal et al., 1999; Mahanta and Bhattacharyya, 2011). This may be due to the stability constants of Zn oxides being high enough to be concentrated in this fraction (Ramos et al., 1994). Kabala and Singh (2001) concluded that Zn sorption on Fe-Mn oxides is probably the most important mechanism that controls the behavior of this element in the soils. As can be seen in Fig. 9c, more Zn was retrieved from the exchangeable/acid soluble fraction as compared to Pb. This is likely related to carbonates such as Zn-rich calcite and/or smithsonite ($ZnCO_3$) which have relatively high stability under the alkaline pH conditions in soils. Also, as earlier stated, the principal ore being processed in the NILZ plant is $ZnCO_3$. Thus, the amount of Zn present in the non-residual fractions is appreciable from the standpoint of potential Zn mobility and bioavailability as highlighted by MF values from 17 to 81% with a mean of 40%. Several authors have reported the relatively high mobility of Zn in the soil environment, which makes it more mobile than lead (Wilson and Pyatt, 2007). Chrastný et al. (2012) also reports Zn carbonates are the main Zn phases of dust particles from

tailing ponds and around the mining and smelting area near the Olkusz smelter (southern Poland).

Similar to the results obtained for Pb, percentage of the Zn non-residual fractions showed a reducing trend with increasing distance from the source of contamination. This finding is consistent with the results obtained by Chrastný et al. (2012) who observed that the sum of non-residual Zn fractions to total concentration is higher in the soil profiles nearer to the smelter.

4.4. Cu

In the studied soils, large amounts of Cu were retrieved from the residual fraction with concentrations ranging from 15.5 mg/kg to 23.5 mg/kg. These concentrations represent high percentages of the total metal concentration (between 77 and 87%). As it can been seen in Fig. 9d, all the samples showed lower Cu concentrations in the reducible phase, with percentage ranging from 4% (D9) to 26% (D6) and a mean of 15%. A fairly low percentage of Cu was also extracted from the exchangeable fraction (mean 1.7%, 2.12 mg/kg). Cu is specifically adsorbed or fixed in soils, making it one of the trace metals which moves the least (Alloway, 1990). The high percentage of Cu in the residual phase is likely due to the fact that Cu is easily chemisorbed on or incorporated in clay minerals. Copper is also characterized by high complex constant with organic matter as it forms strong associations with oxygen and sulfur atoms at the organic matter surface (Evans, 1989). However, in this study, insignificant proportions of Cu were found in the oxidizable fraction. This can be explained by low level of organic matter content in the soils studied (on average 1.3%). In a similar study, Li (1993) found 65% of Cu in residual fraction and 25% in organic fraction of soils from historical Pb smelting site in the UK. As obvious in Fig. 9d, no trend exists in Cu fractionation with increasing distance from the smelter. High proportion of Cu in the residual fraction suggests that this metal is of geogenic source and consequently has very limited mobility in the studied soils (MF: 12–23%).

4.5. Ni

As shown in Fig. 9e, Ni in the soil samples is strongly associated with the residual fraction (83%–93% of the total content, 18.8–35.5 mg/kg). This metal had only a slight amount in the organic fraction (1.8%–8.6%, 0.54–3.21 mg/kg) and oxide phases (2.1%–8.5%, 2.67–3.33 mg/kg) with a negligible portion in the exchangeable phase (1.1%–3.1%, 1.59–1.33 mg/kg). The first three fractions were only about 13% of the total Ni. Therefore, the residual fraction of Ni was higher than the non-residual fractions and consequently Ni in soil samples was reasonably considered to be parent material-originated. Nickel that is of natural origin has been reported to be associated primarily in soil with residual fraction (Ma and Rao, 1997). It is also normal to find Ni particularly in the silicate phase when its compounds properties are considered. These results are in line with the observations from different studies (e.g. Abollino et al., 2006; Sarkar et al., 2014; Marković et al., 2016; Hseu et al., 2016; Hu and Cheng, 2016) indicating that a majority of Ni in soils is occluded in the residual fraction. The mobility factor for this metal was found in the range of 7% (for site D4) to 1.2% (for site D9), reflecting that Ni is also quite immobile under prevailing soil condition. Also, there were no marked differences in Ni fractionation among sampling sites along the transect (Fig. 9e).

4.6. Cr

The partitioning pattern of Cr was quite similar to those of Ni and Cu, with the highest proportion in the residual fraction (88% of its total content, on average) (Fig. 9f). This may be ascribed to the preferential incorporation of Cr into the lattice of silicate minerals and therefore are unlikely to be released through dissociation. Chromium had lower

concentrations in the reducible fraction (mean, 2.52 mg/kg), the oxidizable fraction (mean, 1.61 mg/kg) and the acid-soluble fraction (1.22 mg/kg) representing (corresponding to) < 10% of the total content. The phase distribution of Cr in this study is in agreement with the literature (e.g. Nannoni and Protano, 2016; Matong et al., 2016; Hu and Cheng, 2016) which found that Cr was mostly retained in the residual fraction. This partitioning shows that most of the Cr is relatively immobile in the studied soils, as confirmed by narrow range of mobility factors found for this metal (1.3 to 18%). The tendency of clay minerals to absorb Cr irreversibly by lattice penetration may explain the significant amounts of Cr found in the residual fraction. As for Cu and Ni, Cr fractionation does not show any trend with distance from the smelter, suggesting again that concentration and fractionation of these metals in the soils studied are not controlled by the smelting activity. This finding, however, contrasts with the other studies in similar type of metal smelting areas where distribution and fractionation of these three metals (Cr, Cu and Ni) are mainly impacted by Zn-smelting activity nearby (e.g. Bi et al., 2006; Sutkowska et al., 2013).

5. Summary and conclusions

In this preliminary study, the concentration, distribution and speciation of toxic metals (Pb, Zn, Cd, Cr, Ni and Cu) were investigated in soils along a pre-selected transect around NILZ smelter in NW Iran. Two groups of metals were identified based on their variations and means. The first group of metals (Group 1, smelter-related) is characterized by high coefficients of variation and their mean concentrations are significantly higher than the concentrations in the control samples. Horizontal distribution patterns along the transect showed that the concentrations of these three metals decreased exponentially or as power-law model with increasing distance in downwind direction. There is a marked difference in the concentration decline for these three metals along the transect, i.e. Cd concentration is dropped within an 8000 m distance from the smelter in the downwind direction while Pb and Zn concentrations abruptly level off within the relatively short distance from the smelter ($\approx$ 3400 m). This difference is related to the different behavior of these metals during ore smelting as reflected by high Zn/Cd and Pb/Cd ratios in the affected soils nearer the smelter. Depth-wise variation of Pb, Zn and Cd in the soil profiles also revealed that total concentrations of these metals decreased significantly with depth. The results from the modified BCR sequential extraction also showed that anthropogenic amounts of Pb, Zn and Cd were distributed in all soil fractions, with the most relevant enrichments in the reducible one. Interestingly, the amounts of these metals in the non-residual fractions were higher at the locations nearest to the pollution source and decreased with increasing distance, indicating again that they are mostly originated from anthropogenic inputs by the Pb/Zn smelting in the study area. The assessment results by the values of PI and CPI showed that the pollution level for these metals varied generally from high in soils nearer the smelter to a warning level in soils located far away from the smelter.

Unlike the former group, Cu, Cr, and Ni (Group 2, geogenic-originated) exhibited generally low coefficients of variation and their mean concentrations were comparable to back-ground values of topsoil in the study area. The horizontal distributions of these metals in topsoils along the transect showed a pattern which is independent of distance from the smelter. These metals also had a large percentage of the residual fraction and relatively small proportion of the mobile fraction and their concentrations tend to gradually increase with depth, suggesting that they were most likely contributed from the lithogenic source. Based on the IPI and CPI values, there was no obvious pollution of these metals in soils of the study area.

Although only one soil transect was investigated in this study and consequently limitation as to the conclusions may occur, the finding of this study clearly showed that Zn/Pb smelting activity is the major source of metal contamination in soils of the study area. Lead, Zn and

Cd emissions from the smelter not only led to significant increases in their total concentrations but also altered their speciation in soils along the transect. Even though the concentrations of these metals gradually decreased the further away from the smelter, long-term emission of airborne particles from the smelting plant would pose a significant risk to health of local inhabitants particularly for those living in the nearby town (Zanjan). This should be evaluated through a detailed health risk assessment in future investigations.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.gexplo.2017.05.007.

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