Combination of single and sequential chemical extractions to study the mobility and host phases of potentially toxic elements in airborne particulate matter

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Abstract

Risk assessment of metals associated to airborne particulate matter (PM) has usually been based on the analysis of their total concentrations, which is a poor indicator of metal mobility. Chemical fractionation processes may provide an additional level of information, however, chemical complexity and small sample sizes do not allow to combine several extraction methods. Additionally, analysing the metal concentrations during the extractions exceptionally provides restricted information about metals' speciation. To overcome these limitations we collected total suspended particulate matter (TSP) samples from the air filters placed in the air supply channel of methane-heated turbines of thermal power stations which allows collecting large amounts of TSP materials. Additionally, we combined single and sequential chemical extractions in which not only the concentrations of potentially toxic metals (Cd, Cr, Cu, Ni, Pb, Zn) but also that of the major chemical components (Al, Ca, Fe, K, Mg, Mn, Na, P, S, Ti) were analysed. Our aims were to study these metals' mobility and speciation through the study of their association to major chemical components.

Accumulation of the studied PTEs in the TSP material suggests moderate contamination for Ni, Cd and Cr whereas a heavy one for Cu, Zn and Pb. Three groups of these PTEs could be distinguished based on their mobility. The highly mobile Zn and Cd (large ratios of water and weak acid soluble fractions) can be considered as especially harmful elements to environment. The moderately mobile Pb and Cu (large ratios of reducible and oxidizable fractions, respectively) may potentially have a negative effect on the environment, whereas the immobile Cr and Ni can not be expected to pose a serious risk. Based on the statistical evaluation of extraction data, the potential phases for Zn and Cu are presented by metal-sulphates, -nitrates, -chlorides, -carbonates and -hydroxides, as well as sorbed forms. Lead primarily hosted by metal-carbonates and sorbed forms, as well as by -hydroxides, whereas Cu by organic matter. Finally, Cr and Ni are mostly incorporated into very resistant phases, most probably by magnetite or other resistant metal-oxides.

Combination of single and sequential extractions, as well as that of the analysis of not only the target elements but also the major chemical components was found to be a very effective tool to study the host phases of PTEs in the TSP material. The necessity for relatively large sample amounts for such analyses could be fulfilled using special sampling methodology; however, obvious disadvantages of this kind of sampling must be taken into account when resulted data are evaluated.

1. Introduction

Airborne particulate matter (PM) is a stable suspension of solid and/or liquid particles in the atmosphere having an aerodynamic diameter from 0.001 to 100 μm. It has been widely associated to health disorder primarily due to its fine particles and also to potentially toxic components (Kim et al. 2015). Recent attention has been focused on the characterization of their very fine size fractions (below 10 μm) due to their easy penetration to the innermost regions of the lung (Samet et al. 2000). However, particles with a diameter up to 100 μm can be inhaled or ingested and those below 32 μm may reach the bronchial tubes too (UNEP and WHO 1992).

Airborne PM generally shows significant enrichment in several potentially toxic elements (PTE) in the urban environment. As such particles are of a relatively long residence time in the atmosphere, they may cause contamination both locally and far away from their sources. After sedimentation, these particles can also contaminate soils, groundwater, and even the food chain (Seiler et al. 1988). Studies on sources, compositions, and distribution of airborne particulate matter components are necessary for their risk assessment of atmospheric quality, ecology and human health. This is especially true for the urban environment, where population and traffic density are relatively high, and a harmful effect of airborne PM is expected to be significantly increased (Vardoulakis et al. 2003).

Environmental risk assessment of metals associated with PM has usually been based on the analysis of their total concentrations. However, it is a poor indicator of metal bioavailability, mobility and toxicity, because these properties depend on the chemical association of the trace elements with the different components of the solid matrix (Dabek-Zlotorzynska et al. 2003). Unfortunately, there is no known universal analytical technique capable of identifying as well as quantifying all metal species present in airborne PM. Furthermore, owing to the chemical complexity, extremely small particle sizes, and typically small total sample size of ambient PM samples collected on filters, such samples can pose significant problems for analysis (Huggins et al. 2000). In this context, a chemical fractionation process may provide an additional level of information because it allows classifying trace elements according to their solubility in specific reagents, which can be associated to bonding to some specific matrix component (Richter et al. 2007). Sequential chemical extractions are still rarely used to characterize metal speciation or mobility in PM materials. Most of these studies are restricted to only one or a few metal, and analysis of these metals together with the major chemical components to study their association is almost absent (Samontha et al. 2007). Studies using such approach were published only recently, however each location exhibited high variance in local emission sources (e.g. Richter et al. 2007, Schleicher et al. 2011). Moreover, no combination of different extraction methods was used on such materials primarily due to the very small sample amounts.

To overcome this latter limitation we collected total suspended particulate (TSP) matter samples from the air filters placed in the air supply channels of methane-heated turbines of thermal power stations. Such filters clearing the outdoor air can be characterized by large surface area (0.36 m^2) and they are in use as long as their transmission is high enough (from several months up to a year). They may filter more than one million m^3 of air monthly enabling to collect several tens of grams material from one sampling site. When compared

to standardized air sampling methods, additional contribution of soil to the TSP material can be neglected in this case as the filters are placed at 5-15 m height. However, that of soot and carbonaceous particles may be overrepresented due to the by-products of methane combustion (Sipos et al. 2012). Additionally, sampling localizations are restricted which do not allow to collect samples at optional sites where effect of given sources could be excluded or included. That is why we do not expect to have a useful sampling method for air quality monitoring but we think that metal speciation in airborne PM can be further specified when such samples are studied as well. The aim of this study was to characterize the concentration, mobility, operationally defined speciation and associations to major chemical elements (Al, Ca, Fe, K, Mg, Mn, Na, P, S, Ti) of potentially toxic elements (Cd, Cr, Cu, Ni, Pb and Zn) in the TSP material from Budapest, Hungary using the combination of single and sequential chemical extractions to get a deeper insight into the characteristics of host phases of potentially toxic metals.

2. Materials and Methods

2.1 Sampling and sample preparation

Total suspended particulate matter samples (TSP) were collected from the air filters placed in the air supply channels of methane-heated turbines in four thermal power stations from Budapest, Hungary. Each power station is placed in or close to industrialized areas. Besides traffic, metal processing and paper production in Csepel (CS), chemical industry in Kelenföld (KF), chemical and pharmaceutical industries as well as waste management in Kőbánya (KB), metal processing, glass industry, chemical industries and waste incineration in Újpest (UP) are the major potential emission sources (Figure 1). Altogether 4 samples were collected from the Kelenföld, 3 samples from the Kőbánya, 2 samples from the Újpest and 1 sample from the Csepel thermal power station. The filters were in use for 3-6, 6-13, 6-11 and 15 months, respectively. Samples were removed from the filters mechanically as powder samples received by such separation method did not show any differences in their total metal concentrations to those separated using ultrasonic bath or to those digested together with the filter. Large plant and animal debris were removed by passing the powder through a 0.5 mm sieve. The TSP samples are composed of particles smaller than 60 μm with maximum frequency around 11 μm. A secondary maximum for the UP samples at 35 μm and a slight shoulder at 3 μm for each sample were also found. Between 45 and 80% of their particles belong to the PM10 fraction. Based on their chemical and mineralogical composition, the collected TSP samples are dominantly composed of minerals from the natural geological background (40-60 wt%), like quartz, carbonates, clay minerals and feldspar. Anthropogenic phases, such as magnetite, gypsum, halite, (alkaline earth metal sulphates, hematite) and their weathering products (ferrihydrite) are also present in significant amounts (altogether 15-20 wt%). Carbonaceous materials, like soot and organic matter compose 15-25 wt% of the samples. More detailed characterization of the samples can be found in paper by Sipos et al. (2013). Samples were grounded to fine powder (<10 μm) in an agate mortar before the chemical extractions.

2.2. Chemical extractions

Summary of the extraction procedures used in this study are shown in Table 1. Single chemical extractions were carried out as follows. Water-soluble amounts of the studied elements were determined from 2.5 g samples and 25 mL of distilled water at 21°C with continuous agitation for 2 h. Aqua regia digestion was carried out on 0.5 g sample with 12 mL concentrated aqua regia in the heating block of a hot water bath at 95°C for 1 h. Before evaporation the cooled sample was made up to 10 mL with dilute hydrochloric acid. The solutions from both extractions were filtered and analysed with a Perkin-Elmer Elan 9000 ICP-MS instrument. The BCR sequential chemical extraction was carried out according to the following steps: 1) the weak acid soluble fraction was obtained by 0.11 M acetic acid at solid:solution ratio of 1:40 with continuous shaking for 16 h at 22°C; 2) the reducible fraction was obtained using 0.5 M hydroxylamine hydrochloride at solid:solution ratio of 1:40 at pH 2 (set by nitric acid) with continuous shaking for 16 h at 22°C; the oxidizable fraction was extracted in two steps. In the first one, 8.8 M hydrogen peroxide was used at solid solution ratio of 1:10 for 1 h at 22°C and for another 1 h at 85°C. The extract was evaporated to get moist residue which was cooled and then extracted by 1 M ammonium acetate at solid solution ratio of 1:50 at pH 2 (set by nitric acid) with continuous shaking for 16 h at 22°C. The extracts were separated from the solid residues by centrifugation at 3000 g for 20 minutes in each case. The residues were washed after each step by adding 20 mL distilled water, shaking for 15 minutes and centrifuging. Concentrations of the elements were analysed in the extracts using an Agilent 710 simultaneous ICP-OES. The residue from step 3 was digested with 4 mL concentrated nitric acid, 3 mL perchloric acid and 15 mL hydrofluoric acid to dryness for 16 h at increasing temperature from 90 to 160°C. The remaining material was then taken up in 5 mL of 5 M hydrochloric acid at 70°C for 1 h and diluted to 25 mL with distilled water. The solutions were filtered and analysed with a Perkin-Elmer Elan 9000 ICP-MS instrument. Concentrations of 6 potentially toxic metals (Cd, Cr, Cu, Ni, Pb and Zn) as well as that of 10 major elements (Al, Ca, Fe, K, Mg, Mn, Na, P, S, Ti) were analysed in the solutions. Total metal concentrations were calculated as the sum of the concentrations in the BCR extraction steps and in the residual digestion.

Each extraction was carried out in triplicates. Average relative standard deviations for each analysed elements in the parallel measurements are 5.7%, 4.1%, 2.5%, 1.8%, 2.5% and 2.5% for the water extraction, aqua regia digestion, BCR step 1, step 2, step 3 extractions and the multi-acid digestion, respectively (Table 2). The following standard reference materials (SRM) were also analysed for their composition: STD DS3 for water dissolution, STD DS9 for the aqua regia digestion and OREAS45E for the multi acid digestion. The measured concentrations for SRM materials were found to be within the expected concentration ranges. For the sequential extraction, BCR-701 SRM was analysed. Metal recoveries were generally within 90-110% of expected values (Table 2) except for Pb where slightly lower values suggesting partial re-adsorption of Pb onto TSP components (Bacon and Davidson 2008).

2.3. Calculation of the geoaccumulation index

Geoaccumulation index (I_{geo}) was successfully applied both to contaminated sediments, soils and soil dusts (Ji et al. 2008). It enables the assessment of the degree of contamination by comparing the contaminated and background metal concentrations. It can be calculated using the formula:

$$\text{Igeo} = \ln \frac{Cn}{1.5 * Bn}$$

where Cn is the measured concentration of the element in the TSP material and Bn is the geochemical background value of the same element. The constant 1.5 allows us to analyse the natural fluctuations in the content of a given substance in the studied material. It consists of several classes as follows: 0) practically uncontaminated ($I_{geo} < 0$), 1) uncontaminated to moderately contaminated ($0 < I_{geo} < 1$), 2) moderately contaminated ($1 < I_{geo} < 2$), 3) moderately to heavily contaminated ($2 < I_{geo} < 3$), 4) heavily contaminated ($3 < I_{geo} < 4$), 5) heavily to extremely contaminated ($4 < I_{geo} < 5$) and 6) extremely contaminated ($5 < I_{geo}$). As the natural sources of the TSP material are the surface soils and sediments, local geochemical background values were selected on the basis of the geochemical map of Hungary (Ódor et al. 1997). Geochemical background values are 0.65 mg/kg for Cd, 25 mg/kg for Cu, 25 mg/kg for Cr, 22 mg/kg for Ni, 21 mg/kg for Pb and 95 mg/kg for Zn.

2.4. Statistical analysis

To find the associations between the concentrations of PTEs and that of the major chemical elements in the different extraction steps, hierarchical cluster analysis was carried out on our dataset using squared Euclidean distance. Cluster analysis classifies a set of observations into two or more mutually exclusive unknown groups based on a combination of internal variables. Therefore, it can be applied to distinguish among phase associations and sources of metals in environmental media effectively (Lu et al. 2010).

3. Results

3.1 Metal content and accumulation

Average PTE concentrations in the studied TSP samples are as follows: 7.37 ± 2.72 mg/kg for Cd, 327 ± 64 mg/kg for Cr, 629 ± 127 mg/kg for Cu, 299 ± 184 mg/kg for Ni, 1795 ± 1685 mg/kg for Pb and 4470 ± 3544 mg/kg for Zn (Figure 2). These concentration values showed significant differences among the sampling sites whereas no differences were found among samples from a single sampling site from this point of view (Table 3). KF samples can be characterized by the highest Pb (3538 ± 1304 mg/kg) and Cd (8.88 ± 2.72 mg/kg) contents, KB samples with the highest Cu (737 ± 114 mg/kg) and Ni (505 ± 180 mg/kg) concentrations and that of Cd (8.00 ± 1.48 mg/kg) is also high there. UP samples contain the highest Zn amounts (10 712 ± 1983 mg/kg) whereas the CS sample can be characterized by one of the lowest concentrations for almost each studied PTEs.

Average geoaccumulation indexes (I_{geo}) of the PTEs increases in the following order in the studied TSP samples: 2.0 ± 0.7 for Ni, 2.2 ± 0.3 for Cd, 2.3 ± 0.2 for Cr, 3.1 ± 0.2 for Cu, 3.6 ± 0.7 for Zn and 3.9 ± 0.9 for Pb (Figure 2). Differences among the sampling sites show the same pattern as the total concentration values (Table 3). The highest Pb (4.9 ± 0.4) and Cd (2.4 ± 0.3) I_{geo} values were found in the KF samples, that of Cu (3.2 ± 0.2) and Ni (2.7 ± 0.4) was found in the KB samples whereas Zn (4.7 ± 0.1) showed the highest accumulation in the UP samples. The CS sample can be characterized by the one of the lowest accumulations for almost each PTEs again.

3.2. Single extractions

The two single extractions used in this study aimed at the estimation of the ratios of the most mobile (water soluble forms) and that of the most resistant (forms not soluble in aqua regia) PTE host phases. The results are shown on Figure 3. The ratios of the water soluble forms were the highest for Zn and Cd, on average 15.8% and 11.4%, respectively. However, it showed high variance among the sampling sites as UP samples with highest Zn content showed very high water soluble Zn and Cd ratios (55.5% and 32.1%, respectively), whereas samples (KF and KB) with highest Cd behaved oppositely (4-6% and 3-5%, respectively). All other studied PTEs could not be characterized by such a high variance in their water soluble ratios. Copper and Ni showed moderated water soluble ratios, on average 7.8 ± 2.8% and 3.2 ± 2.6%, respectively. On the other hand, Pb and Cr showed very low values, the water soluble ratio for Pb was 0.34 ± 0.28%, whereas Cr could not be detected in these extracts (<0.01%).

The results of the aqua regia digestion showed a slightly different feature for the studied metals (Figure 3). Still the highest ratios were extracted for Zn and Cd (88.2 ± 14.6% and 87.9 ± 13.0%, respectively), meaning the lowest ratio of the presence of resistant phases in the TSP material for these elements. Contrarily, the lowest extraction ratios were found for Ni (45.2 ± 6.0%) and Cr (35.7 ± 7.7%). In this case, Cu and Pb represented the medium ratios with values of 73.5 ± 5.0% and 71.4 ± 11.4%, respectively. In contrast to the water soluble metal ratios, there was not found any high variance among the aqua regia soluble metal fractions for each PTE.

3.3. Sequential extraction

Sequential extraction aimed not only at the further specification of the mobility sequence of the studied PTEs between the mobile and resistant range but also at that of mobilization conditions characteristic of the natural environment (Figure 3). No significant variation among the samples was found with respect to the metals' fractionation. The ratio of the weak acid soluble fraction was the highest for Zn (47.7 ± 17.2%) and Cd (44.5 ± 5.2%), medium for Cu (10.5 ± 3.5%) and Ni (5.3 ± 1.4%) and low Pb (2.7 ± 0.9%) and Cr (1.2 ± 0.3%). The difference between the ratio of water and weak acid soluble fraction was found to be significant only for Zn and Cd with values of 32.0 ± 8.6 and 33.3 ± 11.1%, respectively. This difference is below 2.5% for the other studied PTEs. The ratio of the reducible fraction was relatively high for Pb (51.4 ± 11.2%), Cd (38.2 ± 5.9%) and Zn (30.0 ± 7.8%) whereas moderate for Cu (15.9 ± 8.1%), Ni (8.3 ± 2.9%) and Cr (8.2 ± 4.6%). High ratio of total metal content was extracted in the oxidizable step of the sequential extraction only for Cu (31.9 ± 6.3%), whereas it was moderate for all other PTEs with slightly decreasing ratios in the sequence of Cr, Pb, Cd, Ni and Zn from 8.2 ± 4.6% to 4.5 ± 2.6%. Very high residual fractions were found for Cr (83.2 ± 5.3%) and Ni (81.2 ± 4.1%), a moderate one for Cu (41.8 ± 8.0%) and Pb (38.9 ± 11.5%), whereas a relatively low one for Zn (17.8 ± 8.6%) and Cd (11.6 ± 2.6%). The ratio of the BCR residual fraction and the aqua regia insoluble fraction show large similarity for the mobile metals (difference is below 10%) and the difference between the two fractions increases with increasing immobility of the PTEs for the benefit of the BRC residual fraction (between 20 and 30% for Cr and Ni).

3.4. Cluster analysis

To assess the potential host phases for the studied PTEs, also chemical elements forming the major compounds of the TSP material were analysed both in single and sequential extractions. The fractionation behaviour of all studied chemical elements was compared using cluster analysis for the data from each extraction step (Figure 4). Two major groups of the studied chemical elements could be distinguished after the water extraction. Elements showing relatively high water solubility are present in the first one. The major anion-forming element is the sulphur here with the highest water-solubility and besides the prevailing alkaline elements (Na, Mg, K and Ca) also significant amounts of Mn and Zn was found in this fraction, and also Cd in the UP samples. The potential host phases of the second group of elements show low solubility in water formed by components like Al, P, Ti and Fe and most of the studied PTEs (Cr, Cu, Ni, Pb) could be related to them as well. After the aqua regia digestion, two major groups could be also distinguished. In the first one consisting of Ca, Cd, Cu, Mn, Pb, S and Zn, at least the half of the total element content was dissolved. On the contrary, elements present mostly in aqua regia-resistant phases form the second group with Cr, Fe, K, Mg, Na, Ni, P, and also along with a subgroup of Al and Ti of which the aqua regia soluble ratio is very low.

The distribution of the elements in the weak acid soluble fraction of the sequential extraction shows large similarity to that of in the water soluble fraction. The only exception is the Cd which is transferred to the element group characterized by high solubility in this case. For the reducible fraction, three major groups of elements were distinguished as follows. In the first one, Pb, Cd and Zn are present of which more than the third of their total amounts could be mobilized at this step. Much less but still significant ratio of total Ca, Cu, Fe, Mn, Mg and P was dissolved here, whereas only slight amount of Al, Cr, K, Na, Ni, S and Ti composing the second and third group at this step, respectively. The oxidizable fraction is the more important for Cu and P showing significantly different and relatively high extractability here as compared to the other studied elements. Much less but still significant portion of Cd, Cr, Ni, Pb, S and Zn could be also mobilized at this extraction step. The third group of elements in the oxidizable fraction is for those which do not show high extractability here, like Al, Ca, Fe, K, Mg, Mn, Na and Ti. The ratio of the residual fraction is the highest for Al, Cr, Fe, K, Ni and Ti among the studied elements. More than 70% of their total contents could be mobilized only by this extraction step. The second group of elements consisting of Cu, Mg, Mn, Na, P and Pb could be characterized still by high ratios in the residual fraction: nearly half of their total amounts could be extracted there. Elements with low ratio of the residual phases are Ca, Cd, S and Zn suggesting that they could be characterized by high mobility generally in the studied materials.

4. Discussion

4.1. Accumulation of the potentially toxic elements

Metal amounts at similar concentration ranges to those we have observed were reported both for street dusts (Sysalova and Szakova 2006) and even for fine PM (Feng et al. 2009) although the general observation is that such elements tend to concentrate in the fine particulate matter (e.g. Fernandez-Espinoza and Ternero-Rodriguez 2004) despite that reverse trend were also found in certain cases (Mateus et al. 2013). This is, however, largely dependent on the prevailing local metal source as some of them may also emit large-sized

particles, for example Cu of vehicle part origin (Ewen et al. 2009) or Zn of smelter origin (Zajzon et al. 2013). According to the enrichment factors of the studied PTEs, Pb, Zn and Cu showed heavy contamination, whereas Cr, Cd and Ni only moderate contamination in the TSP material suggesting the dominating presence of anthropogenic source(s) for these elements (Richter et al. 2007). The earliest studies on the metal concentrations in the TSP material from Budapest also found similar enrichment characteristics for the studied metals (Hlavay et al. 1996) and this is the case for TSP and fine PM from other sampling sites (Hu et al. 2013) suggesting a general feature for them in airborne PM. Differences in metal concentrations and enrichments among the sampling sites suggest differences in the local metal sources there and/or in their distances as well, as local sources are generally prevailing for TSP material (Mateus et al. 2013). Salma et al. (2001) found that Cd, Cu, Pb and Zn exhibit very high enrichment both in coarse and fine particulate matter in Budapest, Hungary, whereas Cr and Ni do moderate one when compared to their crustal abundances. They also found that strong accumulation of these metals in the fine PM points to high-temperature sources. However, they showed also high variability among various sampling sites which could be related to the variation of local sources. Kukkonen et al. (2003) estimated the relative contribution of source categories to ambient trace elements concentrations in the PM from Budapest. They found that substantial amount of Cd, Pb and Zn are originated from waste incineration (65-70%) whereas contribution of traffic ranges from 11 to 17%. Other sources (like coal or oil burning) account for 5-7% additional contribution. Potential metal emission from local sources shows high variability also in our case (Figure 1). For example, the highest Zn content in the TSP material in the UP samples may be related to the vicinity of the waste incinerator. Such objects are known as significant emission sources for potentially toxic metals, primarily for Zn, but also for Pb, Cu, Cr and Cd (Liu et al. 2005). On the other hand, high amount of Pb in the KF samples may be the result that this power station is placed next to a busy road directly (while the other studied stations do not) which environment is a huge reservoir of former (but also of recent) Pb emission of traffic origin (Johansson et al. 2009). Contrarily, the lowest metal content of the CS samples may be related to the fact that this station is placed next to the Danube River which provides the major wind channel in Budapest. When samples from one single site are compared, however, we found large similarities among them. This suggests that the long-term (from 3 to 13 months) sampling result in samples unaffected by the seasonal variation of the contribution of emission sources as it is observed in airborne PM otherwise (e.g. Schleicher et al. 2011). These data show that TSP samples collected from the filters placed in the air supply channels of thermal power stations can be also used to study metals' speciation due to their similar metal enrichment characteristics to that of samples collected by air samplers on the one hand, as well as to the high variability in local sources on the other.

4.2. Mobility of the potentially toxic elements

High variance in the chemical fractionation of PTEs can be found among sampling sites and particle size fraction of PM in other studies (Richter et al. 2007). However, it can be expected as different sources may emit metals in different chemical forms which affects its potential dissolution at given conditions (Kocak et al. 2007). In our case, when the results of both single and the sequential extractions are taken into account, no significant differences in the behaviour of the studied metals can be observed among the samples, except for Zn and Cd in their most mobile fractions. Despite these facts, it is a general observation that large

proportion of total Zn and Cd contents are mostly found in the most mobile fractions (water and weak acid soluble) of PM materials both in total and fine PM fractions (Fernandez et al. 2000; Handt et al. 2008). In our case, this can be related to the major contribution of the waste incinerator to the Zn and Cd content of the PM in Budapest (Kukkonen et al., 2003). Several studies showed that Zn and Cd in waste incinerator fly ashes show high mobility and significant ratios of their total content can be leached by weak acids or even by water (e.g. Liu et al. 2005). This phenomenon is the most expressed for the UP samples in our case which were collected close to the waste incinerator. Additionally, metal processing activities, like smelting may also emit water-soluble forms (sulphate, chloride or nitrate) of metals as found by Fernandez-Espinoza et al. (2004). Besides these forms, large portion of Zn and Cd were also found in the reducible fraction, which was found to mobilize not only metal oxides dissolving at redox conditions but also metal-carbonates susceptible to stronger pH-drop (Fernandez et al. 2000). Such forms of metals can be also related to metal processing activities or certain combustions processes (Fernandez-Espinoza et al. 2004). Consequently, the high mobility can be due to the prevailing presence of Zn and Cd both as water soluble, (weak) acid soluble and reducible forms on the one hand, and to their very subordinate role in resistant phases on the other in our case. The reducible fraction, however, is the most significant for Pb in the studied samples. This behaviour of lead was also found both in TSP (Fernandez et al. 2000), PM10 (Fernandez-Espinoza and Ternero-Rodriguez 2004) and PM2.5 (Feng et al. 2009) materials. Such forms of Pb are generally related to smelting, combustion or traffic related sources (Zajusz-Zubek et al., 2015). This fraction is less but still important for Cu which was rather found in the oxidizable fractions in large proportions showing the high affinity of this metal to organic materials even in such environment, as it was found also by others in PM materials (e.g. Richter et al. 2007). Fernandez-Espinoza et al. (2004) found that organic-bound Cu can be related to traffic emissions and oil combustion, as well. Additionally, both Pb and Cu were found to be present in the residual fraction at similar rate to those found in reducible and oxidizable fractions, respectively. That is why these two PTEs can be characterized by moderate mobility among the studied metals. Zajzon et al. (2013) found that both steel plants and traffic may emit magnetite, a highly resistant iron-oxide with significant Pb and Cu content which may contribute to the residual fraction of these metals in the TSP material in our case. However, the residual fractions are prevailing for Cr and Ni showing the lowest mobility for them. For these elements the largest portion of the residual fraction is insoluble even in aqua regia. Both Cr and Ni were often found in the residual fraction in dusts (Schleicher et al. 2011) and TSP materials (Handt et al. 2008) suggesting their presence in very resistant phases. Although they may originate from several anthropogenic sources in this form, like coal and oil combustion or waste incineration (Zajusz-Zubek et al., 2015), their highly resistant natural forms can not be excluded either as suggested by their lowest geoaccumulation indexes in the TSP material. Consequently, our results show that three groups of the studied PTEs can be distinguished based on their mobility in the TSP material of Budapest: the highly mobile Zn and Cd, the moderately mobile Cu and Pb as well as the highly immobile Ni and Cr. Highly similar behaviour for these metals were observed by Schleicher et al. (2011) in the TSP material of Beijing, China, although differences in local sources are present (for example coal combustion is a major temporal source in Beijing whereas it can be excluded in Budapest). Despite this, similar conclusions can be reached regarding the environmental risk for the studied metals. Zinc and Cd can be considered as especially harmful metals to the environment and exposed people also in our case due to their high solubility in water and weak acid. Additionally, Pb and Cu

can also be considered as mobile with a negative impact on the environment and the human health as they showed high extractabilities in the reducible and oxidizable fractions, respectively.

4.3. Potential host phases for the potentially toxic elements

Water soluble forms are characteristic primarily for Zn (an in the UP samples for Cd). It is present in this fraction together with alkaline and alkaline earth elements and sulphur forming mostly sulphates together and probably also nitrates and chlorides are present in the TSP material. Literature data show that these major elements made an important contribution to the water-soluble aerosol mass (Dos Santos et al. 2009). Sulphates, nitrates and chlorides of Zn and Cd are all highly soluble in water. Such phases may arise for example from the fly ash of fossil fuel combustion or waste incineration (Pinzani et al. 2002). The weak acid soluble fraction is expected to mobilize elements present in some carbonates and in the sorption-pool of the TSP material, as well as the water soluble forms too. The same elements were found to be characteristic of this fraction as in the water soluble one suggesting that high mobility could be related to large variety of potential phases. The high affinity of Zn towards clay mineral surfaces is a well-known phenomenon which was observed in urban dusts together with its carbonates (Sipos et al. 2014). The strongly similar behaviour of Zn and Cd could be due to the common Cd impurities in Zn materials which seem to survive anthropogenic processes as well (Monaci et al. 2000). The reducible fraction was found to mobilize not only metal oxides dissolving at redox conditions but also metal-carbonates susceptible to stronger pH-drop (Fernandez et al. 2000). This fraction is mostly characteristic for Pb, Zn ad Cd and partly for Ca, Cu, Fe, Mn, Mg and P. Mobilization of Fe (and Mn) suggest the presence of their hydroxides in the TSP material, whereas that of carbonates can be related to the appearance of Ca and Mg (but also of Fe and Mn). Continuous flow extraction studies of Pb by Samontha et al. (2007) showed that significant amount of Pb dissolved just before Fe in this step suggesting the close association of this metal with Fe-hydroxides in airborne PM. Additionally, dissolution of metal carbonates may start in this or continue from the previous extraction step and that of metal oxides and hydroxides may also take place in this step as suggested by the dissolution experiments of Funasaka et al. (2013). Such Pb compounds, like sulphate, carbonate and (hydr)oxide are often found in emission sources including waste incineration and smelters in urban environment (Sobonska et al. 1999). Among the studied PTEs, Cu can be characterized the highest association to organic matter in TSP based on its large ratio in the oxidizable fraction together with P. As compared to other transitional metals, the very high extractability of Cu by organic solvents also suggest its close association with organic matter in airborne PM (Molinelli et al. 2006). Largest number of elements could be associated to the residual fraction composed of highly resistant phases. Aluminium, K, Mg and Na are the major components of silicates originating from the geological environment. They are expected to contain PTEs only in trace amounts. On the contrary, magnetite ($FeFe_2O_4$) is a widespread phase of anthropogenic origin in the airborne PM (Zajzon et al. 2013). Besides the high resistance (it is insoluble in aqua regia), the ability to incorporate relatively large amounts of trace metals into its structure are its common characteristic. Among the studied metals, Cr and Ni show the highest compatibility into magnetite at various genetic conditions (Dare et al. 2014). The high ratio of both Cr and Ni in the residual and aqua-regia non-soluble fraction suggest that they are primarily associated to magnetite in the studied TSP material. Table 4.

summarizes the operationally defined speciation and potential host phases of the studied PTEs in the TSP material. Our results show that evaluation of major element extractability together with that of the trace metals is an effective tool in the estimation of potential host phases of the potentially toxic metals.

5. Conclusions

The heavy (Pb, Zn, Cu) and moderate (Cd, Cr, Ni) enrichment of the studied metals in the TSP material suggest significant contribution to their concentrations from anthropogenic sources. The high variance of metal concentrations among sampling sites could be related to differences in the local metal sources and/or in their distances. On the contrary, fractionation of metals could be characterized by large similarities among the sampling sites except that of the most mobile fractions of the most mobile elements. Three major groups of the studied metals could be distinguished based on their mobility. Zinc and Cd showed the highest mobility with large proportion in water and (weak) acid soluble fractions. Lead and Cu could be characterized by moderate mobility due to their presence in acid soluble and reducible as well as in oxidizable fractions, respectively. The lowest mobility was found for Cr and Ni which were found in the residual fraction dominantly. Metals with highest mobility can be considered as elements posing the highest risk to the environment and human health.

Host phases for the most mobile Zn and Cu are presented by metal-sulphates, -nitrates, -chlorides, -carbonates and -hydroxides, as well as sorbed forms. Moderately mobile Pb primarily hosted by metal-carbonates and sorbed forms, as well as by -hydroxides, whereas Cu by organic matter. The least mobile Cr and Ni are mostly incorporated into very resistant phases, most probably by magnetite or other metal-oxides.

Combination of single and sequential extractions, as well as that of the analysis of not only the target elements but also the major chemical components was found to be a very effective tool to study the host phases of PTEs in the TSP material. The necessity for relatively large sample amounts for such analyses could be fulfilled using special sampling methodology practically resulting in similar type of samples to those collected by standardized air sampling methods. Investigation of former samples may provide significant additional information about the speciation of potentially toxic elements in the airborne particulate matter. However, obvious disadvantages of this kind of sampling must be kept in mind as they do not allow using them for air quality monitoring.

Acknowledgements

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Figure captions

Figure 1. Sampling sites and potential ambient air pollution sources nearby.
Figure 2. Concentrations (mg/kg) and geoaccumulation indices of the studied PTEs in the TSP material.
Figure 3. Results of single and sequential chemical extractions.
Figure 4. Association of the studied PTEs to the major chemical components of the TSP material in the different extraction steps.

Table 1

Table 1. Single and sequential extraction procedures used in this study.

Extraction type	Fraction	Extractant
Single	Water soluble	H_2O
	Aqua regia-soluble	cc. HNO_3, cc. HCl (1:3)
Sequential (BCR)	Weak acid-soluble	0.11M CH_3COOH
	Reducible	0.5M $NH_2OH \cdot HCl$
	Oxidizable	8.8M H_2O_2; 1M NH_4OAc
	Residual*	cc. HNO_3, cc. $HClO_4$, cc. HF, 5M HCl (4:3:15:5)

* It is not part of the BCR method but was carried out sequentially.

Table 2

Table 2. Relative standard deviations (RSD) of the parallel analyses and recoveries (REC) of the measured and expected concentrations of the standard reference materials for the studied elements. Note that there are generally no reference values for the major elements in the sequential extractions. nd = not detectable, WS = water soluble, AR = aqua regia-soluble, BCR S1, S2, S3 = step 1, 2 and 3 of the sequential extraction, RES = residual fraction

RSD (%)	Cd	Cr	Cu	Ni	Pb	Zn	Al	Ca	Fe	K	Mg	Mn	Na	P	S	Ti
WS	5.7	nd	3.8	3.6	10.6	4.1	10.9	4.3	3.1	3.3	5.8	4.8	4.3	6.9	6.0	8.4
AR	4.0	6.8	3.9	2.1	7.3	3.5	0.5	4.2	5.6	2.0	3.9	2.4	1.8	5.2	8.0	4.8
BCR S1	1.1	0.8	0.6	1.0	3.2	0.4	1.7	2.9	5.3	2.0	1.8	2.3	1.0	5.6	3.4	6.9
BCR S2	1.0	0.7	1.0	1.0	0.9	0.6	1.5	2.3	1.7	3.5	3.2	4.4	1.1	0.9	1.8	3.5
BCR S3	4.9	1.7	0.5	1.3	1.5	1.2	1.6	2.6	3.5	2.7	2.5	3.4	1.1	3.2	2.6	5.2
RES	8.0	1.5	2.9	2.0	4.0	2.2	1.2	1.6	1.4	1.4	1.1	1.4	1.9	3.8	3.7	1.4

REC (%)	Cd	Cr	Cu	Ni	Pb	Zn	Al	Ca	Fe	K	Mg	Mn	Na	P	S	Ti
WS	100	105	104	95	104	134	95	105	96	102	99	101	107	105	132	97
AR	100	96	97	99	102	97	98	97	101	96	99	99	93	104	99	102
BCR S1	93	98	93	90	93	99										
BCR S2	100	95	88	96	105	108										
BCR S3	100	96	97	110	77	102										
RES	117	100	104	107	111	114	100	92	101	105	103	103	107	106	109	103

Table 3

Table 3. Average, minimum and maximum concentrations and geoaccumulation index values of potentially toxic elements in the studied total suspended particulate matter samples.

Sampling sites		Concentrations (mg/kg)						Geoaccumulation indexes					
		Cd	Cr	Cu	Ni	Pb	Zn	Cd	Cr	Cu	Ni	Pb	Zn
All	Average	7.37	327	629	299	1795	4470	2.2	2.7	3.3	2.3	4.1	3.9
n = 10	*Minimum*	*4.33*	*233*	*406*	*87.2*	*387*	*1447*	*1.8*	*2.4*	*2.9*	*1.3*	*3.0*	*3.0*
	Maximum	*12.5*	*398*	*832*	*647*	*4668*	*12114*	*2.8*	*2.9*	*3.6*	*3.3*	*5.5*	*5.2*
Csepel (CS)	Average	4.92	376	625	146	387	2843	1.9	2.9	3.3	1.8	3.0	3.7
n = 1	Minimum												
	Maximum												
Kőbánya (KB)	Average	8.00	372	737	505	713	1548	2.4	2.8	3.5	3.0	3.6	3.1
n = 3	*Minimum*	*6.82*	*348*	*610*	*302*	*586*	*1447*	*2.2*	*2.8*	*3.3*	*2.5*	*3.4*	*3.0*
	Maximum	*9.65*	*392*	*832*	*647*	*790*	*1631*	*2.6*	*2.9*	*3.6*	*3.3*	*3.7*	*3.2*
Kelenföld (KF)	Average	8.88	326	640	287	3538	3947	2.4	2.7	3.3	2.5	5.1	4.0
n = 4	*Minimum*	*6.73*	*276*	*575*	*276*	*2377*	*2973*	*2.2*	*2.5*	*3.2*	*2.4*	*4.8*	*3.8*
	Maximum	*12.5*	*398*	*710*	*306*	*4668*	*4608*	*2.8*	*2.9*	*3.5*	*2.5*	*5.5*	*4.2*
Újpest (UP)	Average	4.64	236	446	91.2	637	10712	1.8	2.4	3.0	1.3	3.4	5.0
n = 2	*Minimum*	*4.33*	*233*	*406*	*87.2*	*437*	*9310*	*1.8*	*2.4*	*2.9*	*1.3*	*3.1*	*4.9*
	Maximum	*4.94*	*238*	*486*	*95.2*	*837*	*12114*	*1.9*	*2.4*	*3.1*	*1.4*	*3.8*	*5.2*

Table 4

Table 4. Summary of the operationally defined speciation and potentially host phases of the studied potentially toxic elements in the studied total suspended particulate materials.

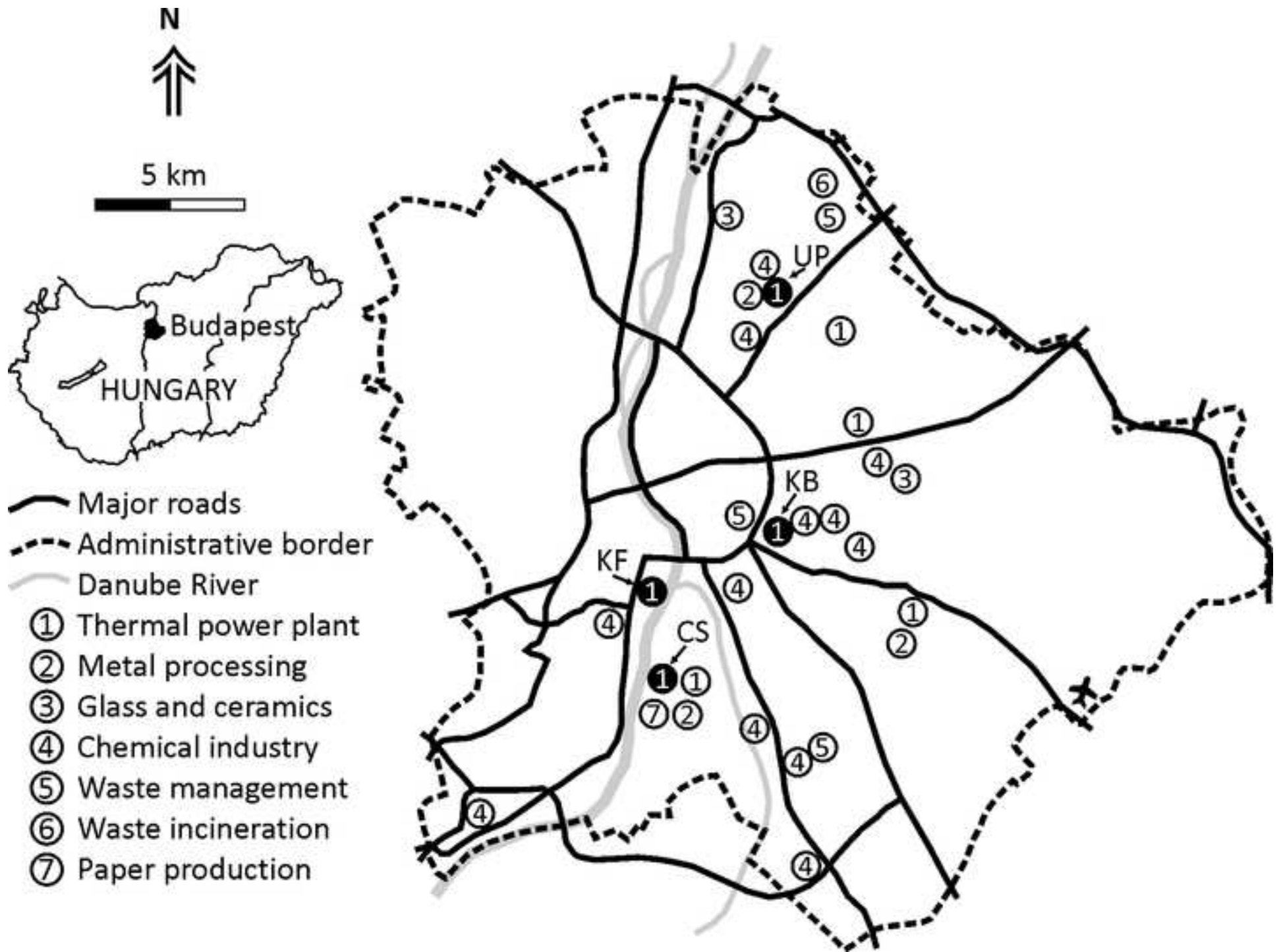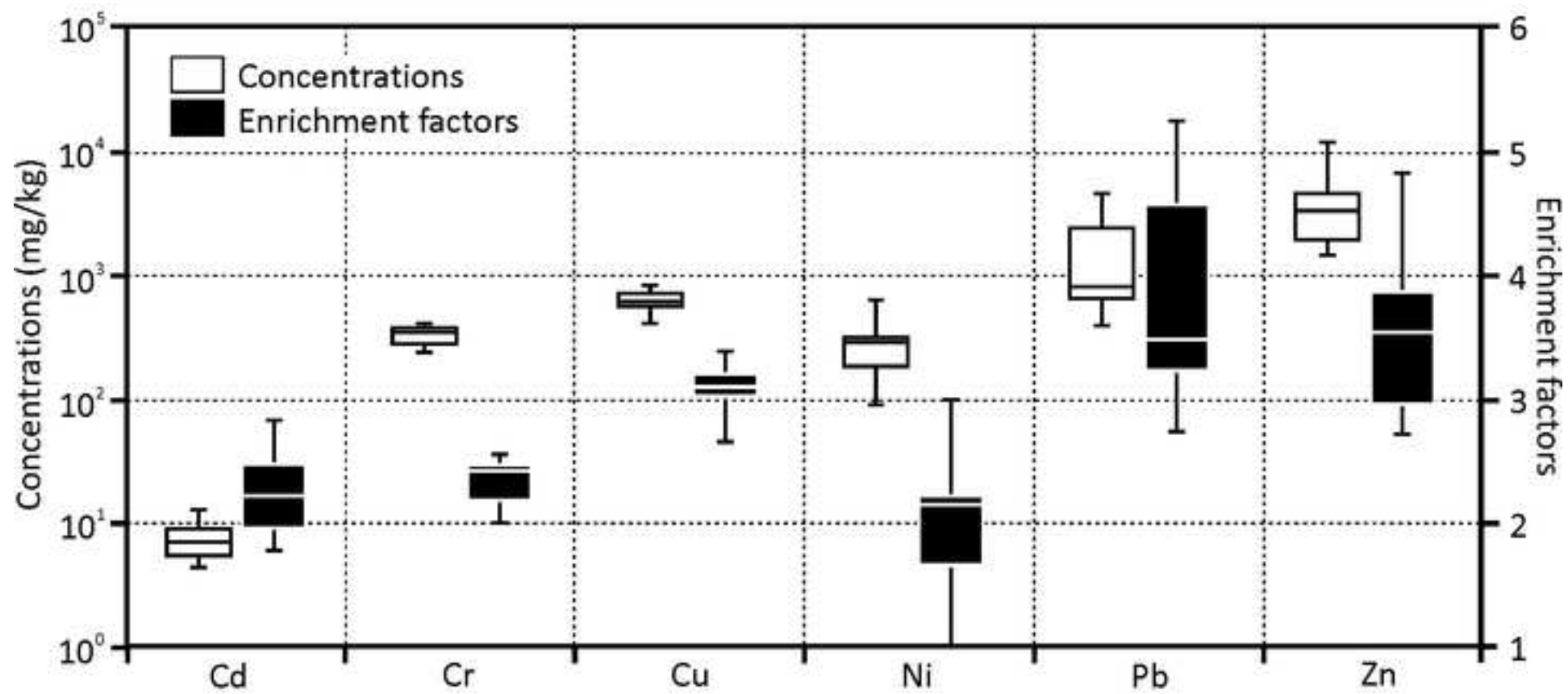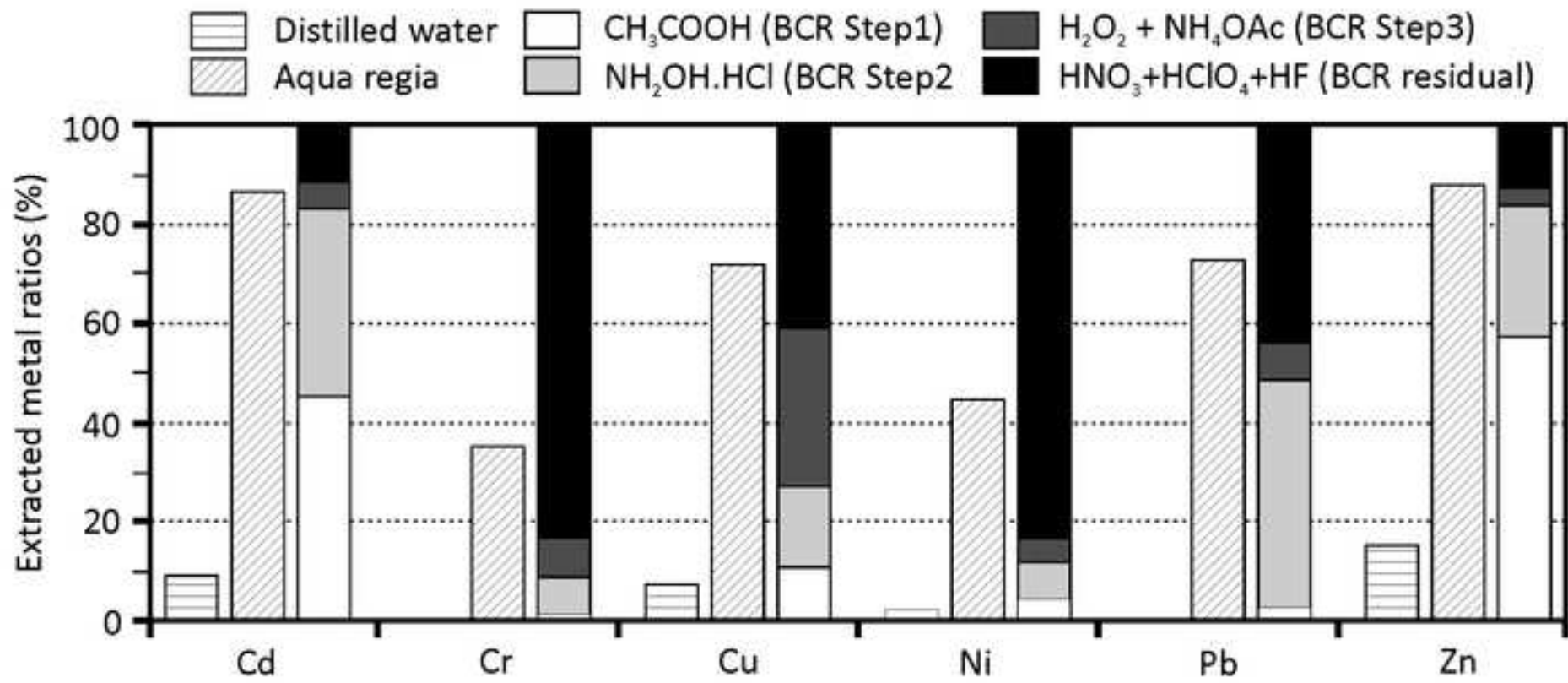| Operationally defined speciation	Potential host phases	Characteristic metal
Water soluble	metal-sulphates (chlorides, nitrates)	Zn > Cd (> Cu)
Weak acid soluble	metal-sulphates, carbonates, sorbed surfaces	Zn ≥ Cd >> Cu
Reducible and acid soluble	metal-(hydr)oxides, carbonates, metals co-precipitated with Fe (and Mn) hydroxides	Pb > Cd > Zn > Cu > (Ni ≥ Cr)
Oxidizable	organic matter, soot	Cu >> (Cr ≥ Pb)
Residual (highly resistant)	metal-oxides, magnetite (silicates)	Cr ≥ Ni >> Cu ≥ Pb >> Zn ≥ Cd

Figure 1

Figure 2

Figure 3

Figure 4