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## 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 elements (PTE) (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 cannot 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 were 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.

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### 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  $\mu\text{m}$ . 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

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been focused on the characterization of their very fine size fractions (below 10  $\mu\text{m}$ ) due to their easy penetration to the innermost regions of the lung (Samet et al., 2000). However, particles with a diameter up to 100  $\mu\text{m}$  can be inhaled or ingested and those below 32  $\mu\text{m}$  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  $\text{m}^2$ ) 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  $\text{m}^3$  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

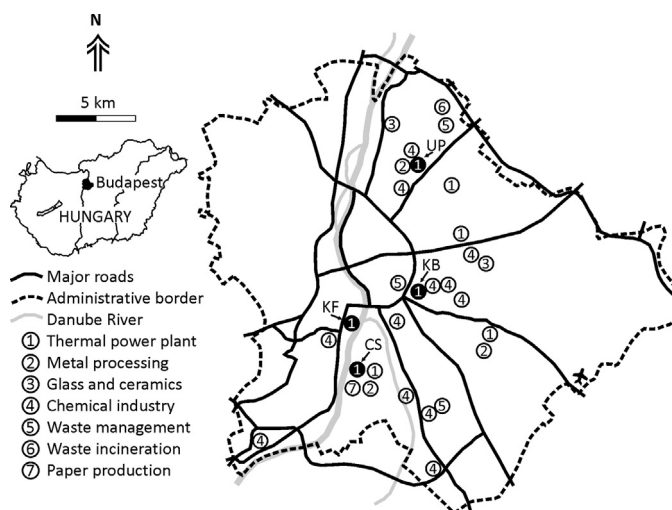


Fig. 1. Sampling sites and potential ambient air pollution sources nearby.

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 (Fig. 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  $\mu\text{m}$  with maximum frequency around 11  $\mu\text{m}$ . A secondary maximum for the UP samples at 35  $\mu\text{m}$  and a slight shoulder at 3  $\mu\text{m}$  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  $\mu\text{m}$ ) in an agate mortar before the chemical extractions.

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