

Bioaccessibility of selected trace metals in urban PM_{2.5} and PM₁₀ samples: a model study

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Abstract Bioaccessibility of trace metals originating from urban particulate matter was assessed in a worst case scenario to evaluate the uptake and thus the hazardous potential of these metals via gastric juice. Sampling was performed over a period of about two months at the Getreidemarkt in downtown Vienna. Concentrations of the assayed trace metals (Ti, Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, Cd, Sn, Sb, Tl and Pb) were determined in PM_{2.5} and PM₁₀ samples by ICP-MS. The metal concentrations in sampled air were in the low picogram to high nanogram per cubic metre range. The concentrations in PM_{2.5} samples were generally lower than those in PM₁₀ samples. The average daily intake of these metals by inhalation for a healthy adult was estimated to be in the range of <1 ng (Tl) to >1,000 ng (Zn). To estimate the accessibility of the inhaled and subsequently ingested metals (i.e. after lung clearance had taken place) in the size range from 2.5- to 10- μ m aerodynamic equivalent diameter, a batch-extraction with synthetic gastric juice was performed. The data were used to calculate the bioaccessibility of the investigated trace metals. Extractable fractions ranged from 2.10% (Ti in PM_{2.5}) to 91.0% (Cd in PM_{2.5}), thus yielding bioaccessible fractions (PM_{2.5-10}) from 0.16 ng (Ag) to 178 ng (Cu).

Keywords Bioaccessibility · Inductively coupled plasma mass spectrometry · Trace metals · Urban particulate matter · Synthetic gastric juice

Abbreviations

ICP-MS	Inductively coupled plasma mass spectrometry
ICP-QMS	Inductively coupled plasma quadrupole mass spectrometry
DRC	Dynamic Reaction Cell™
PM	Particulate matter
PM ₁₀	PM with an aerodynamic diameter of $\leq 10 \mu\text{m}$
PM _{2.5}	PM with an aerodynamic diameter of $\leq 2.5 \mu\text{m}$
PM _{2.5-10}	PM with an aerodynamic diameter between 2.5 and 10 μm
GIT	Gastrointestinal tract
LOD	Limit of detection
LOQ	Limit of quantification

Introduction

Recent epidemiological studies have provided solid evidence for the association of airborne particulate matter (PM) concentrations with adverse respiratory health effects [1]. Particle size and shape are critical factors controlling the extent to which airborne particles penetrate the human respiratory tract [2, 3]. As a consequence, dedicated efforts have been made to evaluate the hazardous effects of this special kind of dust. However, the potential adverse health effects from the inhalation of PM depend on a number of factors: thus in addition to the simple determination of the particle size and shape, a qualitative description of the

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particles for a detailed toxicological evaluation of PM exposure is essential [2, 3].

Atmospheric PM consists of carbonaceous and metallic particles originating from primary emission, i.e. combustion, industrial processes and crustal material from erosion of soil and rock, and secondary pollutants, which are derived from precursor gases emitted at the source and subsequently formed in atmospheric processes, such as sulfates, nitrates and secondary organic aerosols [4]. One particular group of PM fractions that are known to exert toxic effects are transition metals such as Cd, Ni, Pb or Tl [2, 5]. These metals are associated with several adverse health effects including cancer [2, 5]. For this reason, a great deal of research has focussed on the metal composition of atmospheric suspended particulate matter. Most studies to date have determined total elemental concentrations in airborne particulate matter. However, toxic effects of trace metals in airborne PM are only expected if the metals are biologically available [5]. In this context, the fate of inhaled and deposited trace metals is the key question for toxicological assessment of human exposure to these metals. Inhaled airborne particles can be deposited in various places of the respiratory tract, depending on their chemical properties, shape and particle size, which can be altered by different moisture contents of the inhaled air [6–8]. Particles less than 10 μm in size can reach the lower respiratory tract, where they can cause adverse respiratory health effects. More than 80% of the particles smaller than 2.5 μm reach the pulmonary alveoli, where a small fraction is deposited and can stay for months to years [6, 9, 10]. Particles in the 2.5- to 10- μm particle size fraction are in most cases deposited in the tracheal and the bronchial region, from where they are transported within hours by the so-called mucociliary clearance adoral and are mainly swallowed [10]. This fraction reaches the gastrointestinal tract (GIT), where it comes into contact with gastric juice. Since several trace and heavy metals can be dissolved by gastric juice [11], thereby forming the bioaccessible metal fraction, the 2.5- to 10- μm particle size fraction of the investigated trace and heavy metals deserves closer attention.

According to Hamel et al. [11] the bioaccessibility of a metal is defined as the maximal amount of the metal that is soluble in a synthetic gastric fluid and therefore potentially available for uptake across the intestinal lumen, whereas bioavailability is the amount that is actually taken across the cell membranes. The determination of the bioaccessible/bioavailable metal fraction originating from particulate matter is an emerging topic in environmental analysis [5, 12, 13]. Birmili et al. determined the concentrations of Al, Ti, Mn, Fe, Co, Ni, Cu, Zn, Se, Ag, Cd, Sn, Ba, Pt, Hg and Pb in deionized water by using inductively coupled plasma mass spectrometry (ICP-MS) to simulate the solubility of these metals in human lung fluid [5]. Fernández Espinosa et al. used inductively coupled plasma atomic

emission spectrometry (ICP-AES) in combination with a speciation scheme to characterize four different degrees of metal solubility for 11 elements (Mg, Ca, Ti, V, Mn, Fe, Co, Ni, Cu, Cd and Pb), whereas for the “soluble and exchangeable metals”, which were postulated to present the most easily available metal fractions to the human body through breathing, water was used as leaching reagent [13]. Voutsas and Samara applied flame or electrothermal atomic absorption spectrometry (AAS) to the determination of the labile and the bioaccessible metal fractions of Cd, Cu, Mn, Ni, Pb and Zn, using 0.1 N HCl and a mild neutral (pH=7.40) synthetic serum solution, respectively [12].

However, none of these methods were designed to assess the solubility of trace metals in gastric juice, which is the most acidic of the digestive juices and is therefore likely to yield the greatest fractions of soluble metal compounds or complexes [11]. Thus, it possesses on the one hand a higher acidity than water or synthetic serum solution and on the other hand a lower acidity than 0.1 N HCl. However, since gastric juice also contains pepsin, which can increase metal solubility, dilute HCl alone is not a suitable model for the chemical conditions in the GIT [14]. The aim of the present work was the assessment of the bioaccessibility of the inhaled metal fraction which is ingested after clearance of the bronchiotracheal tract.

In the present work, total concentrations of several trace metals were determined in PM₁₀ and PM_{2.5} samples to provide information about the bioaccessibility of trace metals in urban particulate matter. Thus, the average daily intake of these metals by inhalation could be estimated for a healthy adult. Furthermore, model experiments were accomplished, which should give information about the accessibility of the inhaled and subsequently ingested metals (i.e. after lung clearance had taken place). By using a batch-extraction with synthetic gastric juice the bioaccessible metal fraction in PM samples—which is potentially available for uptake across the intestinal lumen—could be determined under simulated physiological conditions of the stomach [11]. This extraction procedure can be characterized as an easy to handle and effective model to estimate the solubility of trace metals in the gastric juice. Other methods for the extraction of these metals with synthetic digestive fluids include the additional simulation of the conditions in the intestinal tract [15, 16] and the use of synthetic saliva [17]. Although these methods deliver more realistic models for the uptake of those metals, they are quite time consuming, and thus not suitable for the analysis of a large set of samples, and/or use chemicals which form a complex matrix and result in high blank concentrations that could hamper analysis by ICP-MS. To evaluate the efficiency of the chosen extraction procedure, for each PM sample the extraction ratios of the investigated metals were calculated by comparison of the extractable part of the respective metal with its total available amount.

Experimental

Reagents and standards

All reagents used for sample pretreatment and ICP-QMS analysis were of high purity. Purified water, which was obtained by using a reagent I grade water ($>10 \text{ M}\Omega \text{ cm}^{-1}$ resistance according to ISO 3696 water specifications) purification system (HQ, USF, Vienna, Austria), was further purified in a quartz sub-boiling system (Milestone-MLS GmbH, Leutkirch, Germany). Analytical grade hydrochloric acid (HCl, 37%, Merck, Darmstadt, Germany) and nitric acid (HNO_3 , 65%, p.a., Merck, Darmstadt, Germany) were additionally cleaned by sub-boiling distillation (once for HCl; twice for HNO_3) in an ultra pure quartz apparatus (Milestone-MLS GmbH, Leutkirch, Germany). Aqueous hydrofluoric acid (HF_{aq} , 48%, Merck, Darmstadt, Germany) and hydrogen peroxide (H_2O_2 , 31%, Merck, Darmstadt, Germany) were of Ultrapur[®] quality; perchloric acid (HClO_4 , 70%, Merck, Darmstadt, Germany) and sodium hydroxide monohydrate ($\text{NaOH}\cdot\text{H}_2\text{O}$, 99.99%, Merck, Darmstadt, Germany) were of Suprapur[®] quality. Pepsin from porcine stomach mucosa (456 units mg^{-1} solid) was purchased from Sigma Aldrich Chemie GmbH, Steinheim, Germany. For all measured elements (Ti, Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, Cd, Sn, Sb, Tl and Pb) 1,000 mg L^{-1} ICP-MS single element standards were obtained from Merck. All pipette tips, polyethylene (PE) flasks, vials and materials which come in contact with the samples were cleaned prior to their disposable use according to a special cleaning process with diluted nitric acid.

Sampling

Sampling of $\text{PM}_{2.5}$ and PM_{10} samples was performed at the Getreidemarkt in downtown Vienna ($16^\circ 24' \text{ E}$, $48^\circ 12' \text{ N}$), near to a heavy traffic road with occasional stop and go traffic, at approximately 10 m in height over a period of about 6 weeks (16 February 2006 to 27 March 2006). For collection of size-segregated aerosol samples PM_{10} and $\text{PM}_{2.5}$ pre-separation heads (DIGITEL Elektronik GmbH, Ludesch, Austria) with an intake volume of $2.3 \text{ m}^3 \text{ h}^{-1}$ (equivalent to 40 L min^{-1}) were equipped with GN-4 Metricel[®] mixed cellulose ester filters (diameter 47 mm, pore size $0.8 \mu\text{m}$; PALL Life-sciences, Michigan, USA, product number 64679) as sampling substrates. Sampling intervals were 24 h. Filter changes were performed at 8.00 a.m.. Collected air volumes were measured using a gas meter. The aerosol samples were stored in petri dishes at room temperature.

Sample preparation

For determination of the total and the bioaccessible fraction the filters were cut into halves and weighed using a Sartorius

MC 210P (Data Weighing Systems Inc., Illinois, USA) balance in a humidity-controlled room. One filter half was digested by using aqua regia and a microwave-assisted digestion procedure. For this purpose the filter half was placed into a HF 100 digestion vessel (Anton Paar, Graz, Austria) and 2 mL HNO_3 , 3 mL HCl and 0.5 mL HF were added. Microwave digestion was performed using a Rotor 16 HF 100 (Anton Paar, Graz, Austria) and a Multiwave 3000 microwave system (Anton Paar, Graz, Austria), which was equipped with an IR sensor for monitoring the temperature of all vessels. Since the temperature and the pressure in the digestion vessels are crucial during microwave operation, one digestion vessel was equipped with a contact temperature–pressure sensor for accurate temperature/pressure reading of this “reference” vessel. The settings of the microwave digestion program are shown in Table 1.

After cooling down, the samples were transferred to PFA vessels and 100 μL HClO_4 was added. The samples were then evaporated at 120°C to about 200 μL . After addition of 2 mL aqua regia, the samples were again evaporated at 120°C to about 200 μL . Subsequently the samples were evaporated at 150°C to about 100 μL and finally diluted with 5 mL of 2.5% (v/v) HCl, transferred to 10-mL PE bottles and filled to about 5 g with 2.5% (v/v) HCl. The samples were stored at 4°C until the day of measurement. Prior to measurement with ICP-QMS, 0.5-mL aliquots of the samples were diluted 1:10 with 1% (v/v) HNO_3 , and 0.5 mL of a $110 \mu\text{g L}^{-1}$ In solution was added as internal standard.

The second half of each filter was subjected to a batch-extraction procedure with synthetic gastric juice, which was prepared according to a US Pharmacopeia methodology [11]: 0.497 g ultrapure $\text{NaOH}\cdot\text{H}_2\text{O}$ was dissolved in a solution of 2.6 mL sub-boiled HCl and 100 mL sub-boiled water in a 250-mL PE flask; 0.8 g of pepsin was added and the solution was filled up to 250 g with sub-boiled water. After placing the filter halves into 100-mL PE flasks, 10 mL synthetic gastric juice was added. The flasks were closed and the samples were shaken for 2 h at 37°C and 70 rpm in a Julabo SW20 (Julabo, Seelbach, Germany) water bath. Afterwards the liquid was decanted into PE vials, which were centrifuged with a SIGMA 2–5 centrifuge (SIGMA Laborzentrifugen, Osterode am Harz, Germany) for 10 min at 3,400 rpm. Centrifugation was preferred,

Table 1 Microwave digestion program

Step	Time	Power (W)
1	5 min. Ramp + 7 min. Hold	400
2	16 min. Ramp	800
3	12 min. Ramp	1,000
4	10 min. Hold	0

since filtration via precleaned cellulose acetate filters led to higher blank levels. A 1-mL aliquot of the supernatant of each sample was diluted 1:5 with 1% (v/v) HNO₃ and stored in a PE vial at 4 °C until measurement. Prior to measurement with ICP-QMS, 0.5 mL of a 110 µg L⁻¹ In solution was added as internal standard.

Analysis with ICP-QMS

For ICP-QMS analysis a multielement calibration standard, which contained the highest expected concentration of each element (varying from 0.1 µg L⁻¹ for Tl to 100 µg L⁻¹ for Ti, Cu and Zn), as well as its 1:1.3, 1:2, 1:4, 1:10 and 1:100 dilutions were prepared. Sample measurement was carried out using a PerkinElmer ELAN DRC-II ICP-Quadrupole-MS under the conditions listed in Table 2. Sample introduction was performed by using a PerkinElmer Autosampler AS-93 and a PFA-nebulizer (Elemental Scientific, Omaha, Nebraska, USA) with a flow rate of 0.4 mL min⁻¹, which was maintained by a peristaltic pump.

The isotopes selected for measurement are listed in Table 2. NH₃ was employed as the reaction gas for the measurement of Cr and Ni with the DRC.

Trueness of daily calibrations was checked against certified reference material (TM27.2 acidified surface water, Environment Canada, National Water Research Institute, Burlington, Canada). We selected BCR-723 road dust material (BCR, Geel, Belgium) for validation of the abovedescribed digestion procedure using the indicative values, which were acquired through the certification campaign of this material for platinum group elements [18].

Calculations

Daily intake

To determine the average daily amount of trace metals inhaled by a healthy adult, the metal concentrations in the sample air were multiplied by the average respiratory volume of an adult (Eq. 1). An average respiratory volume of 15.12 m³ day⁻¹ was obtained by using the estimation that a healthy adult

possesses an average respiratory rate of 15 breathes per minute (without physical strain) and a respiration volume of 0.5–0.8 L per breath (dependent on the body weight, whereat per kilogram body weight a respiration volume per breath of about 10 mL has to be reckoned with, thus leading by assumption of an average body weight of 70 kg to a respiration volume of 0.7 L per breath) [19].

$$M_T = c_{\text{aerosol}} \cdot V_{\text{Resp}} \quad \text{with} \quad (1)$$

$$c_{\text{aerosol}} = c_{\text{digestion}} \cdot \frac{V_{\text{digestion}}}{V_{\text{air filterhalf}}}$$

In Eq. 1 M_T (ng) represents the average daily intake by inhalation, c_{aerosol} (ng m⁻³) represents the concentration of the respective metal in the sample air, $c_{\text{digestion}}$ (ng mL⁻¹) represents the concentration of the respective metal in the sample solution after total digestion, $V_{\text{digestion}}$ (mL) represents the volume of the sample solution after total digestion, $V_{\text{air filterhalf}}$ (m³) represents the air volume that was sucked through the respective filter half and V_{Resp} (m³ day⁻¹) represents the average respiration volume (15.12 m³ day⁻¹) of a healthy adult, respectively.

The total daily amount of the PM_{2.5–10} fraction, which was deposited on the filter samples, was calculated for each metal as the difference between the metal content in the PM₁₀ and PM_{2.5} aerosol fraction (Eq. 2),

$$D_{2.5-10} \mu\text{m} = c_{\text{PM}_{10}} \cdot V_{\text{sample PM}_{10}} \cdot \frac{w_{\text{filter PM}_{10}}}{w_{\text{filter half PM}_{10}}} - c_{\text{PM}_{2.5}} \cdot V_{\text{sample PM}_{2.5}} \cdot \frac{w_{\text{filter PM}_{2.5}}}{w_{\text{filter half PM}_{2.5}}} \quad (2)$$

where $c_{\text{PM}_{10}}$ (ng mL⁻¹) and $c_{\text{PM}_{2.5}}$ (ng mL⁻¹) represent the measured metal concentrations in the corresponding PM₁₀ and PM_{2.5} samples; $V_{\text{sample PM}_{10}}$ (mL) and $V_{\text{sample PM}_{2.5}}$ (mL) represent the sample volume of those PM₁₀ and PM_{2.5} samples; $w_{\text{filter PM}_{10}}$ (mg) and $w_{\text{filter PM}_{2.5}}$ (mg) represent the weight of the respective PM₁₀ and the PM_{2.5} filter; and as $w_{\text{filter half PM}_{10}}$ (mg) and $w_{\text{filter half PM}_{2.5}}$ (mg) represent the weight of the corresponding PM₁₀ and PM_{2.5} filter halves, respectively.

Furthermore, the average daily intake of this particle fraction by inhalation for a healthy adult, which is accessible via ingestion, was calculated by subtraction of the average daily intake of the PM_{2.5} fraction from the average daily intake of the PM₁₀ fraction.

Results and discussions

Analytical figures of merit

For each element the limit of detection (LOD) and the limit of quantification (LOQ) were determined as three and ten

Table 2 ICP-MS parameters and measured isotopes

RF power	1,300 W
Plasma gas flow	15 L min ⁻¹
Auxiliary gas flow	1.3 L min ⁻¹
Nebulizer gas flow	0.94 L min ⁻¹
Isotopes measured without using the DRC	⁴⁷ Ti, ⁵⁵ Mn, ⁵⁹ Co, ⁶⁵ Cu, ⁶⁶ Zn, ⁹⁸ Mo, ¹⁰⁷ Ag, ¹¹¹ Cd, ¹¹⁸ Sn, ¹²¹ Sb, ²⁰⁵ Tl and ²⁰⁸ Pb
Isotopes measured by using the DRC (NH ₃ as reactive gas)	⁵² Cr and ⁶⁰ Ni

Table 3 LODs and LOQs of the investigated elements for the total digestion and the extracted samples collected via DIGITEL pre-separation heads

Measured isotope	Total digestion samples		Extraction samples	
	LOD (ng m ⁻³)	LOQ (ng m ⁻³)	LOD (ng m ⁻³)	LOQ (ng m ⁻³)
¹⁰⁷ Ag	0.054	0.18	0.028	0.094
¹¹¹ Cd	0.031	0.10	0.033	0.11
⁵⁹ Co	0.017	0.057	0.011	0.038
⁵² Cr	3.0	10	0.28	0.94
⁶⁵ Cu	1.5	5.1	0.68	2.3
⁵⁵ Mn	0.58	1.9	0.19	0.64
⁹⁸ Mo	0.20	0.66	0.027	0.090
⁶⁰ Ni	0.82	2.7	0.92	3.1
²⁰⁸ Pb	0.70	2.3	0.060	0.20
¹²¹ Sb	0.49	1.6	0.069	0.23
¹¹⁸ Sn	0.43	1.4	0.046	0.15
⁴⁷ Ti	19	65	2.0	6.7
²⁰⁵ Tl	0.0032	0.011	0.00065	0.0022
⁶⁶ Zn	16	54	3.1	10

times the standard deviation, respectively, which was derived from the measurement of ten clean aerosol filters. For determination of LOD and LOQ of total digestion and extraction, ten filter halves were totally digested and the ten other halves were extracted with synthetic gastric juice according to the extraction procedure described above. Table 3 lists the LODs and LOQs of the investigated elements for the total digestion and the extraction samples, which were recalculated by using an average for the air volumes sampled throughout the study.

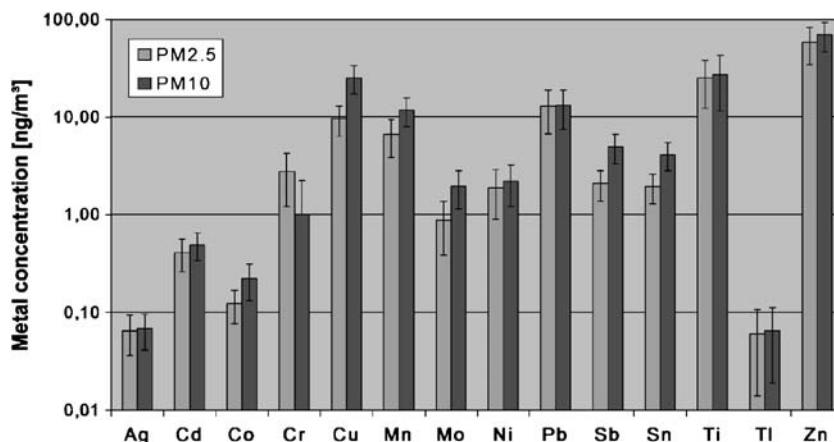
By comparing the LODs and LOQs of the digested and the extracted samples it is obvious that, although a complex organic matrix is used, the applied extraction procedure can be seen as an easy to handle and effective method, since it shows comparable or even better LODs and LOQs than the total digestion method, which is state of the art and free of organic compounds. Thus, this extraction method provides

a basis for the adequate determination of the bioaccessibility of the assayed metals.

Trace metal concentrations in urban aerosols

The 24-h samples ($n=27$ sampling days), which were collected in downtown Vienna over a period of 6 weeks, were subjected to the digestion procedure described above. In the investigated samples the total metal concentrations ranged from some picograms per cubic metre to several nanograms per cubic metre. Averaged results for PM₁₀ and PM_{2.5} samples are depicted in Fig. 1.

The PM_{2.5} fraction is relevant in terms of metals. Indeed the differences of the trace metal concentrations in PM_{2.5} and PM₁₀ samples were generally low, indicating that the PM_{2.5} fraction is dominant for most of the metals except Cu, Mo, Sb and Sn. The contribution of the trace metals present in PM_{2.5} to PM₁₀ concentrations differed from element to element indicating differences in the main emission sources. Comparison with literature data showed that our results were in agreement with other studies on urban aerosol [20–24]. Moreno et al. determined the average annual concentrations of various metals—including Cd, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Sn, Ti and Zn, which were also measured in this study—in PM₁₀ and PM_{2.5} samples from six sampling sites in Spanish towns [20]. Metal concentrations varied strongly among these sampling sites. For example Zn concentrations varied between 15 and 417 ng m⁻³ in PM₁₀ and from 14 to 239 ng m⁻³ in PM_{2.5} samples [20]. For comparison, in this survey Zn concentrations of 70 ± 23 ng m⁻³ for PM₁₀ and 59 ± 24 ng m⁻³ for PM_{2.5} samples were determined. Götschi et al. [21] calculated annual means for the PM_{2.5} concentrations of Cu, Mn, Pb, Ti, Zn and other elements originating from 21 central urban monitoring sites in 20 cities. For instance mean Zn concentrations ranged from 2.2 ng m⁻³ in Reykjavik (Iceland) to 185 ng m⁻³ in Grenoble (France) [21], thus demonstrating that the Zn concentrations for PM_{2.5} samples obtained in the present study are well within this

Fig. 1 Average trace metal concentrations (ng m⁻³) in urban aerosol samples. The values represent the outlier-corrected average of 27 sampling days

range. Manalis et al. [22] measured As, Cd, Cr, Cu, Mn, Ni, Pb and V in PM₁₀ samples from four sampling sites in the greater Athens area. Copper concentrations for example varied among these sampling sites between 13±7.5 and 141±64 ng m⁻³, whereas Cd concentrations ranged from 1.9±1.8 to 3.7±2.4 ng m⁻³ and Mn concentrations from 4.4±3.7 to 21±19 ng m⁻³ [22]. For comparison, in this study Cd, Cu and Mn showed concentrations in PM₁₀ of 0.49±0.15, 25±8.2 and 12±3.8 ng m⁻³, respectively. Voutsas and Samara found average concentrations of Cd, Cu, Mn, Ni, Pb and Zn of 1.2±0.72, 118±100, 33±23, 6.8±5.3, 77±25 and 127±119 ng m⁻³, respectively, in PM_{7.2} samples from urban sampling sites of the greater Thessaloniki area [12]. While Cd, Cu, Mn Ni and Zn concentrations in PM₁₀ samples determined in the present survey are comparable, the average Pb concentration found by Voutsas and Samara significantly exceeds the corresponding average PM₁₀ concentration measured in this study (13±5.7 ng m⁻³). On the other hand Birmili et al. measured average metal (Ag, Cd, Co, Cu, Mn, Ni, Pb, Sn, Ti and Zn) concentrations for PM_{7.2} samples in Birmingham background air (in the vicinity of the University of Birmingham), which were generally lower than the corresponding average PM₁₀ concentrations and—except for Ag and Cu—were even lower than the corresponding average PM_{2.5} concentrations measured in this study [5]. Metal concentrations measured in fine urban particles (PM_{0.61}) sampled in the city of Seville [13] showed on the one hand a significantly higher average lead concentration (43.7 ng m⁻³) than the average lead concentration measured for PM₁₀ samples in this study (13±5.7 ng m⁻³), and on the other hand a significantly lower average titanium concentration (3.2 ng m⁻³) than the average titanium concentration measured for PM_{2.5} samples in this survey (25±13 ng m⁻³). Furthermore Fernández Espínosa et al. [13] found in PM_{0.61} samples an average cobalt concentration of 0.29 ng m⁻³ and

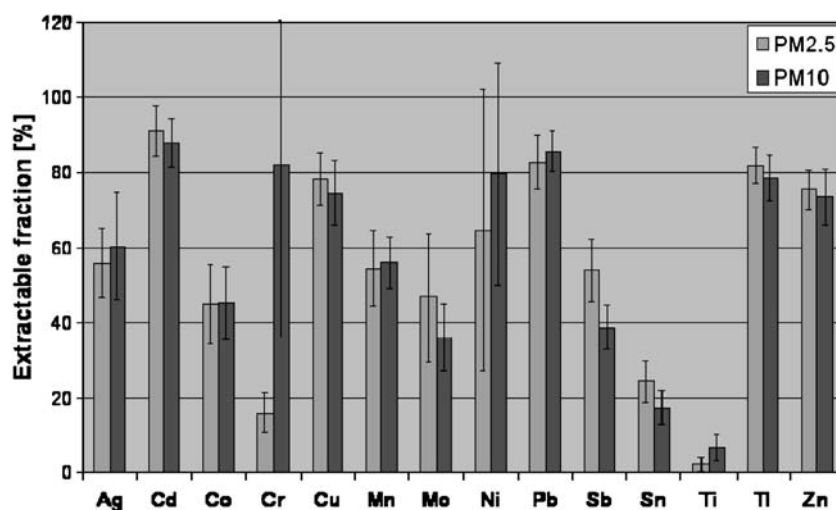
an average manganese concentration of 7.4 ng m⁻³, thus being in the range of the average cobalt concentration measured for PM₁₀ samples in this study (0.22±0.091 ng m⁻³) and the average manganese concentration measured for PM_{2.5} samples in this survey (6.6±2.8 ng m⁻³). The mean cadmium concentration in PM_{0.61} was reported to be 0.21 ng m⁻³ [13], thus being lower than the average cadmium concentration measured for PM_{2.5} samples in this study (0.41±0.15 ng m⁻³), while the average copper concentration of 9.6 ng m⁻³ [13] corresponds very well to the average copper concentration measured for PM_{2.5} samples in this survey (9.6±3.3 ng m⁻³).

Metal fractions extractable in synthetic gastric juice

The filter samples obtained from 27 sampling days were subjected to the described extraction procedure. The metal concentrations extractable with synthetic gastric juice were found to be generally lower than the respective total concentrations, indicating that the investigated metals were only partially soluble in this solvent. Based on the results derived for total and extractable metal concentrations in airborne PM, average extractable fractions for the individual trace metals were calculated (see Fig. 2).

No significant differences were observed between the averaged extraction ratios of PM₁₀ and PM_{2.5} samples. The considerable fluctuations of the individual daily samples can be attributed to the aerosol composition varying from day to day. Enhanced average extraction ratios were observed for the toxic metals cadmium, thallium and lead, which are also known to possess a significant carcinogenic potential. Distinctly reduced ratios were found for tin and titanium, which is in accordance with the low solubility of the airborne form of these metals in diluted hydrochloric acid, since in particulate matter Sn and Ti are mainly

Fig. 2 Average extractable fractions (%) for the extraction of urban aerosol samples with synthetic gastric juice. The values represent the outlier-corrected average of 27 sampling days



present as oxides: while 89% of Sn is emitted by fossil fuel combustion [25], titanium, which predominantly occurs as TiO_2 in the Earth's crust, mainly enters the environment by brake lining wear emissions (the high temperature during the braking process leads to the formation of titanium oxide) and resuspension of road dust [26]. Automobile brake linings are also responsible for the high enrichment factor of Sb in urban aerosol [27, 28]. Sb metal is mainly present as Sb_2S_3 , which may be the reason for the moderate extraction efficiency of $39 \pm 5.8\%$ in PM_{10} and $54 \pm 8.5\%$ in $\text{PM}_{2.5}$ samples, respectively.

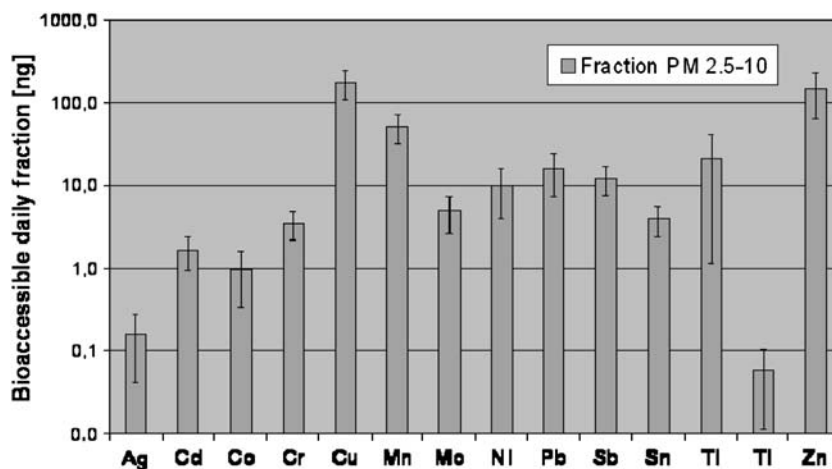
Comparison of the extraction ratios obtained in this study with literature data is not straightforward, since there are many parameters (investigated size fraction, composition of the extraction fluid, extraction time, etc.) which differ with respect to the conditions used in this survey. Voutsas and Samara, who used 0.1 N HCl as extractant to leach $\text{PM}_{7.2}$ samples, also showed that the sampling site can have a significant impact on the extraction efficiency, since different PM sources possess varying mineralogical composition and relative contribution [12]. Birmili et al. [5] and Fernández Espínosa et al. [13] used water as extractant; however, Birmili et al. extracted $\text{PM}_{7.2}$ samples, whereas Fernández Espínosa et al. leached $\text{PM}_{0.61}$ samples. Extraction ratios for Ag, Cd, Co, Cu, Mn, Ni, Pb, Sn and Zn (i.e. those elements for which literature data were available for comparison) were generally higher when using synthetic gastric juice as extractant instead of water [5, 13]. Cadmium, which showed the highest extraction yield in this study ($88 \pm 6.4\%$ for PM_{10} and $91 \pm 6.6\%$ for $\text{PM}_{2.5}$ samples), for example exhibited extraction ratios in water of 25% [13] and about 50% [5] for $\text{PM}_{0.61}$ and $\text{PM}_{7.2}$ samples, respectively, whereas it had an extraction ratio of about 90% [12] in 0.1 N HCl for $\text{PM}_{7.2}$ samples (for urban sample sites), which is in accordance to this survey. The use of 0.1 N HCl as extractant generally led to extraction ratios for Cu, Mn, Ni and Zn for $\text{PM}_{7.2}$ samples (from urban sample sites) [12] which were higher than those

reported in this study, since this extractant possesses a higher acidity than the synthetic gastric juice, which exhibits an acidity equal to 0.07 N HCl. However, Pb showed higher extraction ratios in synthetic gastric juice ($86 \pm 5.3\%$ for PM_{10} and $83 \pm 7.0\%$ for $\text{PM}_{2.5}$ samples) than in 0.1 N HCl (66% for $\text{PM}_{7.2}$ samples from urban sites) [12]. This could be due to the use of pepsin in the synthetic gastric juice, which tends to form complexes with certain metals and, owing to the enzymatic digestion of organic matter, can make metal-bearing particles available to acid attack [14]. Fernández Espínosa et al. [13] found an average extraction ratio for titanium of 7.7% in water for $\text{PM}_{0.61}$ samples, which is slightly above the extraction ratios for PM_{10} ($6.9 \pm 3.6\%$) and $\text{PM}_{2.5}$ ($2.1 \pm 2.0\%$) samples reported in the present study and definitely higher than those found by Birmili et al. [5] for $\text{PM}_{7.2}$ samples (<1% in water).

Inhaled bioaccessible fraction

Based on the derived aerosol concentrations and the estimation of the daily respiration volume, the daily intake of the investigated metals was calculated from Eq. 1. As mentioned above, the 2.5- to 10- μm particle size fraction is mainly deposited in the tracheal and bronchial region of the human respiratory tract and is subjected to the mechanism of mucociliary clearance, i.e. this fraction can be expected to be the main one available in the GIT. Accordingly, the extractable part (in synthetic gastric juice as extractant) of this size fraction, which is taken up in one day, was defined for the present study as the bioaccessible daily fraction (see Fig. 3). To estimate the bioaccessible daily fraction of a metal, its daily intake by inhalation of the 2.5- to 10- μm particle size fraction was multiplied by its average extraction ratio for this fraction. Assuming that the inhaled particles of this particle size fraction were quantitatively transported into the gastrointestinal tract by mucociliary clearance, bioaccessible fractions ranging from < 1 to > 100 ng day^{-1} were calculated.

Fig. 3 Average bioaccessible daily fraction (ng) calculated for urban aerosol samples. The values represent the outlier-corrected average of 27 sampling days



Voutsas and Samara calculated “daily respiratory uptakes” (DRU_is) in a comparable way to the “bioaccessible daily fraction” reported in the present study under the assumption of an inhalation rate of 20 m³ day⁻¹ for PM_{7.2} samples, thus obtaining mean daily respiratory uptakes for Cd (3.4 ng), Cu (1290 ng), Mn (375 ng), Ni (56 ng), Pb (3.8 ng) and Zn (574 ng) for urban sample sites in the greater Thessaloniki area [12]. The DRU_is of Cd, Cu, Mn, Ni and Zn are significantly higher than the corresponding mean bioaccessible daily fractions calculated in this survey. In addition to the low inhalation volume applied in our study, this can be explained since Voutsas and Samara [12] extracted PM_{7.2} samples by a mild neutral solution, simulating serum, while we used synthetic gastric juice for the extraction of the PM_{2.5–10} fraction. Pb showed a significantly lower mean respiratory uptake than the mean bioaccessible daily fraction calculated in our study (16±8.7 ng for the PM_{2.5–10} fraction), thus suggesting that simulated serum is a poor model for the bioaccessibility of Pb [12].

Conclusion

A fit-for-purpose extraction procedure for trace metals with synthetic gastric juice was developed and applied to estimate the bioaccessible fraction of these metals after inhalation. For the majority of the metals, extractable fractions over 50% could be obtained. Thus, the metal fraction, which is ingested after inhalation and subsequent mucociliary clearance and hence actually available for the uptake across the intestinal lumen, could be determined for downtown Vienna. Although the calculated trace metal uptakes are far below the safety levels for human intake, even at low concentrations, long-term effects cannot be excluded, since some of these metals (e.g. cadmium) tend to accumulate in the human body [29–31].

Metal uptake into the human body from food or drinking water generally occurs at much higher levels than the intake of aerosol-bound metals [29–31]. However, the comparison of metal intake via food or water and via inhalation and subsequent ingestion of aerosol is not straightforward. Metals ingested via food and drinking water reach the gastrointestinal region in a highly diluted or complexed form, whereas aerosol-bound metals are present as ultra-fine, highly reactive particles. The higher reactivity of these metals may compromise the apparently lower intake via aerosol inhalation and ingestion.

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