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Analysis of toxic metals and assessment of their bioaccessibility from urban particulate matter by inductively coupled plasma mass spectrometry (ICP-MS)

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Abstract

During the recent decades the exposure of humans to particulate matter (PM) has continuously increased. As a consequence, dedicated efforts have been made to evaluate the hazardous potential of this special kind of dust. Since PM with an aerodynamic diameter $\leq 10 \mu\text{m}$ (PM_{10}) can pass the larynx and thus reach the lower part of the respiratory tract, limit values for the PM_{10} concentration in ambient air have been defined in the Air Quality Protection Act (Immissionsschutzgesetz-Luft (IG-L), Federal Law Gazette I 115/1997). PM with an aerodynamic diameter $\leq 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) can even reach the pulmonary alveoli and deserves therefore special attention.

In addition to the simple determination of the particle size, a qualitative description of the particles for a detailed toxicological evaluation of the particulate matter exposure is essential. Since certain trace and heavy metals are associated with several adverse health effects – including cancer - the main goal of this diploma thesis was the assessment of the hazardous potential of the metallic fraction emitted over the particulate matter. For this purpose, the concentrations of several trace and heavy metals (Ti, Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, Cd, Sn, Sb, Hg, Tl and Pb) were determined in PM_{10} and $\text{PM}_{2.5}$ samples. Sampling was performed over a period of about two months (February and March 2006) at the Getreidemarkt in downtown Vienna. The concentrations of the assayed metals in sampled air were in the range of $0.0599 \pm 0.0485 \text{ ng/m}^3$ (Hg) to $70.0 \pm 23.2 \text{ ng/m}^3$ (Zn) for PM_{10} as well as in the range of $0.0451 \pm 0.0299 \text{ ng/m}^3$ (Hg) to $58.7 \pm 24.3 \text{ ng/m}^3$ (Zn) for $\text{PM}_{2.5}$. The average daily intake of these metals by inhalation could be estimated for a healthy adult to be in the range of $0.906 \pm 0.733 \text{ ng}$ (Hg) to $1058 \pm 350 \text{ ng}$ (Zn) for PM_{10} and in the range of $0.682 \pm 0.452 \text{ ng}$ (Hg) to $887 \pm 367 \text{ ng}$ (Zn) for $\text{PM}_{2.5}$. Furthermore, model experiments were accomplished, which give information about the mobility of the inhaled and subsequently – after lung clearance had taken place – ingested metals. By using a so called “batch”-extraction - which is an extraction under equilibrium condition – the bioaccessible metal fraction of PM-samples was determined simulating the physiological conditions of the human stomach. 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. For the majority of the metals extraction ratios of over 50 % were obtained.

The presented diploma thesis contains three chapters. After a general introduction, the possible sources of trace and heavy metals in urban aerosol are examined in the first chapter. Due to the high potential health risks originating from the three heavy metals lead, cadmium and mercury, these metals are discussed in detail. Since traffic is one of the largest polluters in Austria and many trace and heavy metals are attributed to this emission source, a special section in this chapter deals with trace and heavy metals emitted by traffic.

Furthermore, the potential health risks originating from the human exposure to toxic metals via inhalation of PM are discussed. In the final section of the first chapter the principles of elemental analysis by ICP-DRCMS, which is an inductively coupled plasma mass spectrometer (ICP-MS) equipped with a so called Dynamic Reaction Cell™ (DRC), are presented.

The second chapter deals with the analysis of toxic metals in size classified aerosol, which is derived from PM₁₀ and PM_{2.5} filter samples. After an introduction, the experimental section of the chapter lists the used reagents and samples and describes the sample treatment procedures (total digestion and extraction) for the filter-samples as well as the analysis with ICP-quadrupole-MS (ICP-QMS). In the next section, the results obtained by the analysis of the total digestion and extraction samples are presented and discussed. In the final section of the second chapter conclusions from the obtained results are drawn.

Since biological monitoring (“biomonitoring”) – which is the measurement of concentrations of harmful substances and/or their metabolites in biological materials like urine, blood or faeces – plays a decisive role for the assessment of the individual human exposure to the noxious metals and the associated health risks, the third chapter contains an article about the “Ultra-trace analysis of palladium in human urine samples via flow-injection coupled with the ELAN 6100 DRC II ICP-MS” that was submitted to “Atomic Spectroscopy” journal. Hence, the abstract that was written for this article is quoted below:

The use of palladium as catalyst material in vehicles, which are equipped with Otto engines, has dramatically increased in recent years, since Pd is cheaper and less sensitive to catalyst-poisons than platinum. Furthermore, Pd-catalysts can easier meet the strict threshold limits for exhaust emissions, which were introduced within the European Union in 2000 and 2005 by the EU-directives Euro Stage 3 and 4. As consequence of these developments the automotive catalytic converter became the main emission source of Pd into the environment. For a better assessment of the hence resulting health-risks, intensive efforts have been made in recent years for the development of analytical methods, which can routinely be applied in the field of biomonitoring. Beneath the use of ETAAS, the application of ICP-MS has proven advantageous, since this analytical method possesses a high sensitivity and provides the opportunity of isotope dilution mass spectrometry (IDMS). The very low Pd-concentrations, as they are present e.g. in urine-samples, as well as comparatively high concentrations of interfering matrix-elements, make the application of special sample pre-treatment- and enrichment-techniques an absolute prerequisite for performing accurate Pd-analysis.

The presented method for ultra-trace analysis of Pd in human urine therefore includes the destruction of the organic matrix by UV-digestion, separation of interfering cations by cation-exchange-chromatography, on-line-enrichment via an automated flow-injection-analysis-system (FIAS) and accurate quantification of Pd via IDMS.

Zusammenfassung

Da die Feinstaubbelastung des Menschen in den letzten Jahren kontinuierlich zugenommen hat, wurden Versuche unternommen, um das Risikopotential dieser speziellen Form von Staub zu bewerten. Da Feinstaub mit einem aerodynamischen Durchmesser $\leq 10 \mu\text{m}$ (PM_{10}) über den Kehlkopf hinaus in die unteren Atemwegsorgane gelangen kann, wurden im Immissionsschutzgesetz-Luft (IG-L, BGBl. I 115/1997) Grenzwerte für die PM_{10} Konzentration in der Umgebungsluft definiert. Feinstaub mit einem aerodynamischen Durchmesser $\leq 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) kann sogar bis in die Lungenbläschen (Alveolen) gelangen und verdient daher spezielle Aufmerksamkeit.

Zusätzlich zu der einfachen Bestimmung der Partikelgröße ist für eine detaillierte toxikologische Bewertung eine qualitative Beschreibung des Feinstaubes unentbehrlich. Da zahlreiche Spuren- und Schwermetalle mit schädlichen Auswirkungen auf die Gesundheit – inklusive Krebs - in Verbindung gebracht werden, war das Hauptziel dieser Diplomarbeit die Abschätzung des Risikopotentials der über den Feinstaub emittierten Metall-Fraktion. Zu diesem Zweck wurden die Konzentrationen von einigen Spuren- und Schwermetallen (Ti, Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, Cd, Sn, Sb, Hg, Tl and Pb) in PM_{10} und $\text{PM}_{2.5}$ Proben bestimmt. Die Proben wurden über einen Zeitraum von ca. zwei Monaten (Februar und März 2006) am Getreidemarkt in der Wiener Innenstadt gesammelt. Die Konzentrationen der untersuchten Metalle in der Probenluft waren in einem Bereich von $0.0599 \pm 0.0485 \text{ ng/m}^3$ (Hg) bis $70.0 \pm 23.2 \text{ ng/m}^3$ (Zn) für PM_{10} sowie in einem Bereich von $0.0451 \pm 0.0299 \text{ ng/m}^3$ (Hg) bis $58.7 \pm 24.3 \text{ ng/m}^3$ (Zn) für $\text{PM}_{2.5}$. Damit konnte abgeschätzt werden, dass die durchschnittliche tägliche Aufnahme dieser Metalle durch Inhalation für einen gesunden Erwachsenen in einem Bereich von $0.906 \pm 0.733 \text{ ng}$ (Hg) bis $1058 \pm 350 \text{ ng}$ (Zn) für PM_{10} und in einem Bereich von $0.682 \pm 0.452 \text{ ng}$ (Hg) bis $887 \pm 367 \text{ ng}$ (Zn) für $\text{PM}_{2.5}$ liegt. Weiters wurden Modell-Versuche durchgeführt, die Aufschluss über die Mobilisierbarkeit der inhalierten und anschließend – nach erfolgter Lungenclearance - ingestierten Metalle geben. Mit Hilfe eines „batch“-Extraktionsverfahrens, das eine Extraktion unter Gleichgewichtsbedingungen darstellt, konnte die mobilisierbare und damit bio-verfügbare Metallfraktion in Staubproben unter Simulierung der physiologischen Verhältnisse des Magens erfasst werden. Für jede Feinstaub-Probe wurden die Extraktionsraten der untersuchten Metalle durch Vergleich des extrahierbaren Anteils des jeweiligen Metalls mit seiner jeweils verfügbaren Gesamtmenge berechnet. Für die Mehrzahl der Metalle wurden auf diese Weise Extraktionsverhältnisse von über 50 % erhalten.

Die hier präsentierte Diplomarbeit ist in drei Kapitel gegliedert. Im ersten Kapitel werden nach einer allgemeinen Einleitung mögliche Quellen von Spuren- und Schwermetallen im Stadtaerosol untersucht. Aufgrund der potentiell hohen Gesundheitsrisiken, die von den drei

Schwermetallen Blei, Cadmium und Quecksilber ausgehen, werden diese Metalle näher diskutiert. Da der Verkehr einer der größten Emittenten in Österreich ist und viele Spuren- und Schwermetallen diesem Emissions-Quelle zugeordnet werden können, befasst sich ein spezieller Abschnitt dieses Kapitels mit vom Verkehr emittierten Spuren- und Schwermetallen. Weiters werden die möglichen Gesundheitsrisiken, die von der Belastung des Menschen mit toxischen Metallen durch die Inhalation von Feinstaub ausgehen, diskutiert. Im letzten Abschnitt des ersten Kapitels werden die Prinzipien der Elementaranalyse mit ICP-DRCMS - einem induktiv gekoppelten Plasma-Massenspektrometer (ICP-MS) das mit einer so genannten Dynamic Reaction Cell™ (DRC) ausgestattet ist - präsentiert.

Das zweite Kapitel behandelt die Analyse von toxischen Metallen in größenklassiertem Aerosol, welches von den PM₁₀ und PM_{2.5} Filterproben erhalten wurde. Nach einer Einleitung werden im Abschnitt „Experimentelles“ die verwendeten Reagenzien und Proben aufgeführt und die Probenaufbereitungs-Techniken (Total-Aufschluss und Extraktion) für die Filterproben sowie die Analyse mit ICP-Quadrupol-MS (ICP-QMS) beschrieben. Im nächsten Abschnitt werden die Ergebnisse, die durch die Analyse der Total-Aufschluss-Proben und der Extraktions-Proben erhalten wurden, präsentiert und diskutiert. Im letzten Abschnitt des zweiten Kapitels werden anhand der vorgelegten Ergebnisse Schlussfolgerungen gezogen.

Da die biologische Überwachung („Biomonitoring“) – dies ist das Messen der Konzentrationen von Schadstoffen und/oder ihrer Metaboliten in biologischen Materialien wie Urin, Blut oder Kot – eine entscheidende Rolle für die Abschätzung der individuellen menschlichen Belastung gegenüber schädlichen Metallen und der damit verbundenen Gesundheitsrisiken spielt, enthält das dritte Kapitel einen Artikel über die „Ultrapurenanalyse von Palladium in menschlichen Urinproben mittels Fließinjektion gekoppelt mit dem ELAN 6100 DRC II ICP-MS“, der bei der Zeitschrift „Atomic Spectroscopy“ eingereicht wurde. Daher wird die für diesen Artikel verfasste Zusammenfassung im Folgenden wiedergegeben:

Die Verwendung von Palladium als Katalysatormaterial in Kraftfahrzeugen, die mit Otto-Motoren ausgestattet sind, hat innerhalb der letzten Jahre dramatisch zugenommen, da Pd billiger und unempfindlicher gegen Katalysatorgifte ist als Platin. Zudem können mit Pd-Katalysatoren die mit den EU-Direktiven Euro Stage 3 und 4 im Jahr 2000 bzw. 2005 innerhalb der EU eingeführten Grenzwerte besser eingehalten werden. Als Folge dieser Entwicklungen wurde der Autokatalysator zur Hauptemissionsquelle von Pd in die Umwelt. Um die sich daraus ergebenden Gesundheitsrisiken besser abschätzen zu können wurde in den letzten Jahren intensiv an der Entwicklung analytischer Methoden für den

routinemäßigen Einsatz im Biomonitoring-Bereich gearbeitet. Neben der ETAAS hat sich ICP-MS als vorteilhaft erwiesen, da diese Methode eine hohe Empfindlichkeit aufweist sowie die Möglichkeit der massenspektrometrischen Isotopenverdünnungsanalyse (IDMS) bietet. Die äußerst geringen Pd-Konzentrationen – wie sie z.B. in Urinproben vorliegen – sowie die vergleichsweise hohen Konzentrationen störender Matrix-Elemente, machen allerdings auch bei der Verwendung von ICP-MS als Detektionsmethode den Einsatz spezieller Probenvorbereitungs- und Anreicherungstechniken erforderlich.

Die hier präsentierte Methode zur Ultrapurenanalyse von Pd in Urin umfasst daher die Zerstörung der organischen Matrix mit Hilfe eines UV-Aufschlusses, die Abtrennung störender Kationen mittels Kationen-Austausch-Chromatographie, die on-line-Anreicherung über ein automatisiertes Fließinjektions-Analyse-System (FIAS) sowie die genaue Quantifizierung von Pd mittels Isotopenverdünnungsanalyse (ID-ICP-MS).

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1 Introduction

The exposure of humans to particulate matter has continuously increased in recent years. The toxicological evaluation of the dust exposure is done in the first step by determination of the particle size (classing). "Dust" can be distinguished between "airborne particulates", which describes particles with a diameter of up to 30 μm - showing decelerated sedimentation as well as a relative high dwell time (of several days) in the atmosphere - and "particulate matter", which denotes particles with a diameter $< 10 \mu\text{m}^1$. The highest potential threat to the population's health emanates from particulate matter. Especially particles with a diameter between 1 to 6 μm , which can reach the pulmonary alveoli, are problematic².

Atmospheric particulate matter (PM) consists on the one hand of carbonaceous and metallic particles from combustion and industrial processes as well as crustal material from erosion of soil and rock – the so called primary emissions - and on the other hand of secondary pollutants, which are derived from precursor gases emitted at the source and subsequently formed in atmospheric processes, such as sulphates, nitrates and secondary organic aerosols³. Therefore, in addition to the simple determination of the particle size, a qualitative description of the particles for a detailed toxicological evaluation of the particulate matter exposure is essential. Since certain trace and heavy metals are associated with several adverse health effects – including cancer - the main goal of this diploma thesis was the assessment of the hazardous potential of the metallic fraction emitted over the particulate matter. For this purpose, the concentrations of several trace and heavy metals (Ti, Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, Cd, Sn, Sb, Hg, Tl and Pb) in urban aerosol samples were determined. 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 mobility of the inhaled and subsequently – after lung clearance had taken place – ingested metals. By using a so called "batch"-extraction - which is an extraction under equilibrium condition – the bioaccessible metal fraction in PM-samples under simulation of the physiological circumstances of the stomach could be determined. 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.

1.1 Possible sources of trace and heavy metals in urban aerosol

Many trace metals are ubiquitous in various raw materials (fossil fuels, metal ores, etc.) as well as in industrial products⁴, thus leading to emissions of these metals from power suppliers, small consumers, industry, traffic, agriculture and other sources (e.g. waste treatment)⁵. According to Pacyna et al.⁴ the use of raw materials in the high-temperature production of industrial goods as well as the combustion of fuels and the incineration of municipal and industrial wastes can lead to the partial or even entire evaporation of the therein embodied trace metals, thus entering the ambient air with exhaust gases. The volatilization and entrainment of several trace metals may also be a result of their releases to other environmental compartments (e.g. spills to water bodies, landfills, sewage lagoons, and holding ponds)⁴. Trace metals, which were emitted to the atmosphere, are subjected to transport within air masses and migration through the ecosystem. This can lead to deleterious effects for humans and the environment, either directly over the air path or by accumulation of trace and heavy metals in the soil and the ecosystems, hence resulting in a possible uptake over the food chain⁵.

According to Pacyna et al.⁴ the first quantitative worldwide estimate of the annual industrial input of 16 trace metals into the air and other environmental compartments at the beginning of the 1980s (published 1988 by Nriagu and Pacyna in *Nature*) revealed that pyrometallurgical processes in the primary non-ferrous metal industry were the major sources of atmospheric As, Cd, Cu, In, Sb and Zn as well as an important source of Pb and Se. Furthermore the combustion of coal was identified to be the major source of anthropogenic Hg, Mo and Se as well as a significant source of As, Cr, Mn, Sb and Tl. It was also shown that the most important source of V and Ni is the combustion of oil. Furthermore it was stated that the major source of Pb is the combustion of leaded gasoline and that the iron and steel industry is the primarily source for atmospheric Cr and Mn.

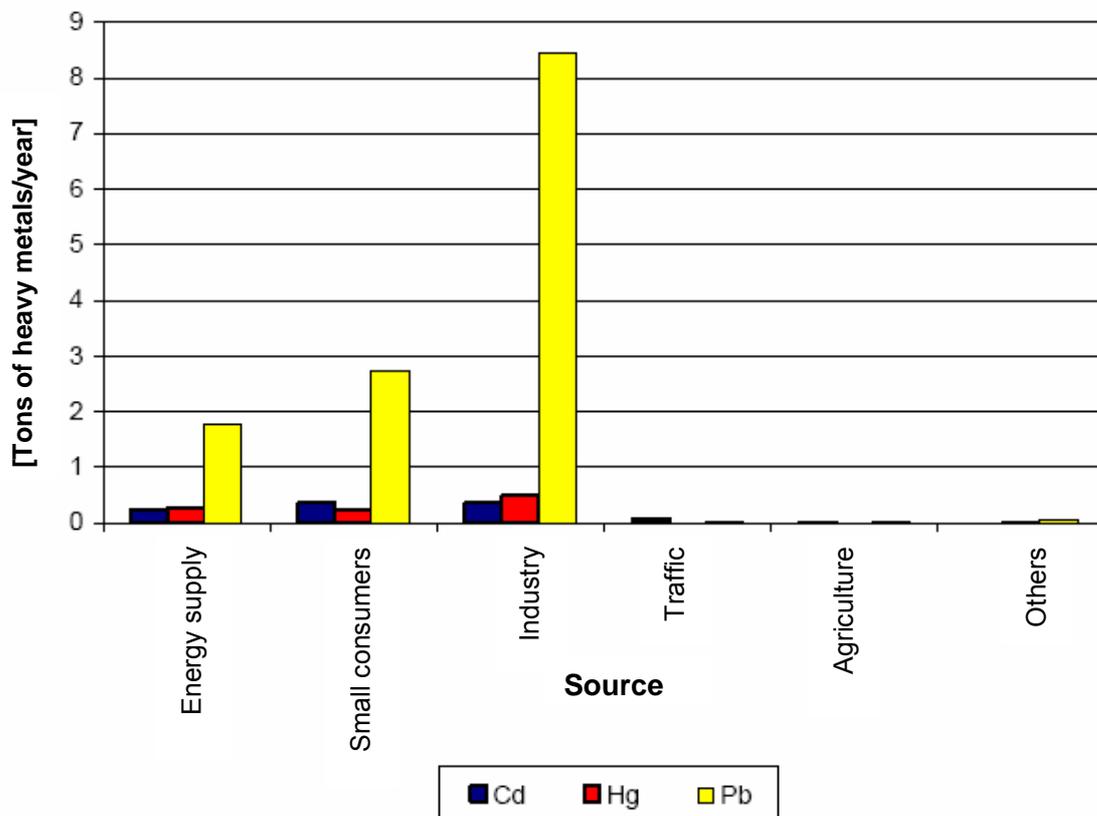
Beneath the anthropogenic emissions of trace metals there also exist natural sources for these metals like releases from deflated soil and sediment, volcanic emissions, forest fire debris as well as biogenic and oceanic emissions⁴. Since natural emission estimates are extrapolated from very sparse data sets, they vary widely, thus leading to significant uncertainties, when comparing anthropogenic and natural emissions of trace metals – particularly on a global scale⁴. Nevertheless Pacyna et al.⁴ presented a comparison of global anthropogenic emission estimates with the global natural emission estimates published by Nriagu (1989) in *Nature*, thus suggesting that on a global scale the anthropogenic emissions of Pb and V are by one order of magnitude higher than the natural emissions of these metals. It was further stated that for Cd and Ni the anthropogenic emissions are a factor of 2 to 3 higher than the natural emissions. The anthropogenic emissions of Cu, Hg, Mo, Sb and Zn were declared to be comparable to the

natural emissions of these metals. On the other hand it was stated that the global natural emissions of As, Cr and Se are by a factor of 2 to 3 larger than the global anthropogenic emissions of these elements. The natural sources of Mn were declared to be far more significant than its anthropogenic sources. It should be underlined that the comparisons of anthropogenic versus natural sources for trace metals made above are only valid on a global scale. When discussing the situation on a local scale (e.g. around a volcano or a waste incinerator) and even on regional scale (e.g. in the Mediterranean Sea basin or in Central Europe) the results of this comparisons can be completely different⁴.

According to the Austrian Umweltbundesamt GmbH the emission sources in Austria can be divided into six sectors⁵: The power supply being the first sector encloses the electrical- and the district heating-power plants (including the energetic waste-utilization), refineries, energy input at the oil- and gas-production as well as volatile emissions of fuels (pipelines, petrol stations). The small consumers form the second sector, which includes the heating systems of private households, private and public services, (small) trade and agricultural companies as well as mobile instruments of private households (e.g. lawnmowers), agricultural- and forest instruments (e.g. tractors, power saws, etc.) and mobile instruments for other services (e.g. tracked vehicles for ski pistes, etc.). The industry being the third sector encloses the process- and pyrogenic emissions as well as off-road vehicles of the industry. Traffic including road traffic, railway traffic, shipping and national air traffic forms the fourth sector. Agriculture being the fifth sector encloses emissions caused by the ingestion of the cattle, emissions from liquid manure and dung as well as fertilizing with organic and mineral N-fertilizers. The sixth sector is defined as "Others" including waste treatment – like emissions from rubbish tips, waste incineration without energetic utilization, sewage and composting – as well as solvent applications for paint and lacquer, cleaning, degreasing and the production or processing of chemical products.

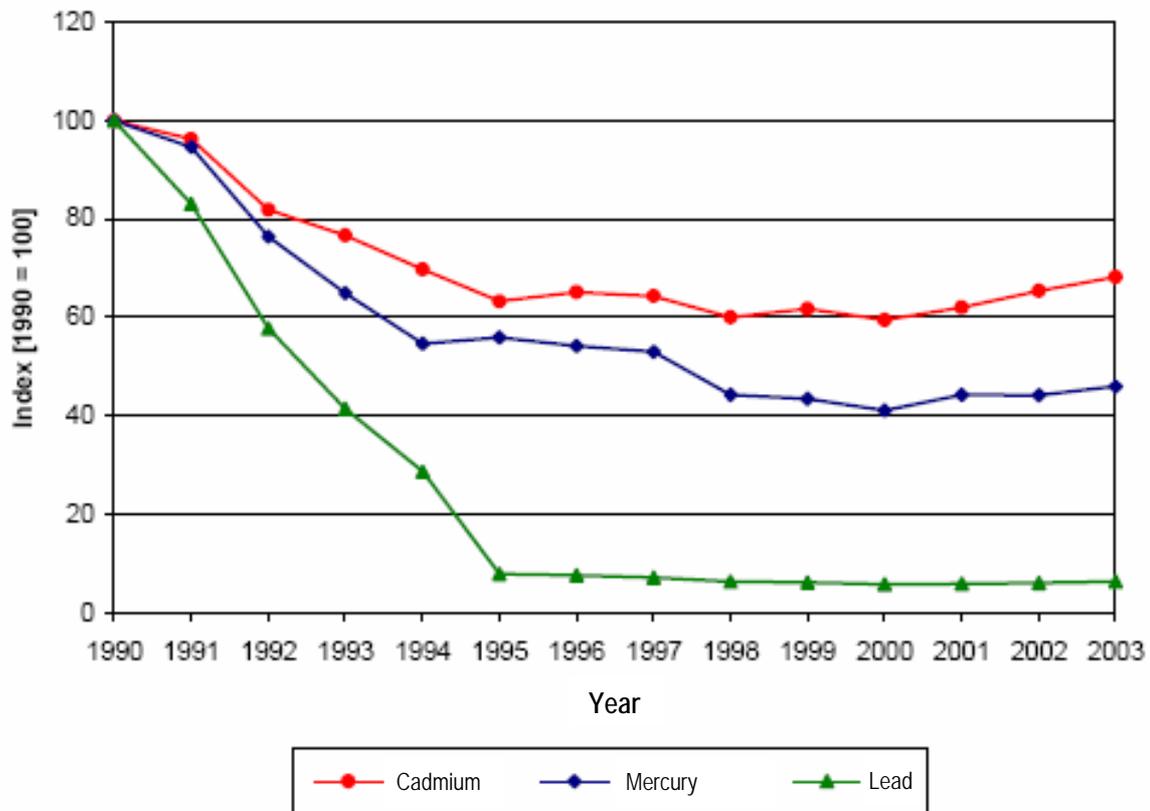
Looking at the origins of heavy metal emissions in Austria the industry, small consumers and power suppliers have been identified as main sources, whereby in 2003 the industry was the main emission source by far⁵. Thereby especially the emissions of Pb^{5,6,7,8}, Cd⁵⁻⁸ and Hg^{5,8} were taken into account by the Austrian Umweltbundesamt GmbH, since for these elements international reporting commitments are in force. In Figure 1 the emissions of Cd, Hg and Pb in Austria are depicted depending on their sources for the year 2003:

Figure 1: Emissions of Cd, Hg and Pb in Austria depending on their sources for the year 2003.
 Source: M. Anderl et al., Emissionstrends 1990-2003 – Ein Überblick über die österreichischen Verursacher von Luftschadstoffen mit Datenstand 2005, Umweltbundesamt GmbH, Wien, 2005, published on the web (<http://www.umweltbundesamt.at/umweltschutz/luft/emiberichte/>)



With about 87% (13 tons) the Pb-emissions in 2003 form the largest part of heavy metal emissions in Austria, whereby 65% of the lead emissions can be attributed to the industry⁵. The Cd- and Hg-emissions, which are caused by the three main emission sources (industry, small consumers and power suppliers) on nearly equal rates, amount about one ton each⁵. In Figure 2 the trend of the anthropogenic Cd-, Hg- and Pb-emissions in Austria from 1990 to 2003 is depicted:

Figure 2: Trend of the anthropogenic Cd-, Hg- and Pb-emissions in Austria from 1990 to 2003 [%].
 Source: M. Anderl et al., Emissionstrends 1990-2003 – Ein Überblick über die österreichischen Verursacher von Luftschadstoffen mit Datenstand 2005, Umweltbundesamt GmbH, Wien, 2005, published on the web (<http://www.umweltbundesamt.at/umweltschutz/luft/emiberichte/>)



As can be seen in Figure 2 lead emissions could be continuously reduced by about 94% from 206 tons per year in 1990 to about 13 tons per year in 2003, by implementing a number of steps for the reduction of Pb-emissions - especially for those from traffic (the ban on the use of leaded gasoline) and industry (by improving emission abatement techniques)^{5,8}. During the same period the emissions of Cd and Hg were reduced by 32% (Cd) and 54% (Hg), respectively⁵.

Due to the high potential health risks originating from the three heavy metals Pb, Cd and Hg, these metals will be discussed in the following sections in detail. Since traffic is one of the largest polluters in Austria⁵ and many trace and heavy metals are attributed to this emission sector⁹, a special section will deal with trace and heavy metals emitted by traffic.

1.1.1 Lead (Pb)⁵⁻⁸

Till the prohibition of the addition of lead to petrol in 1986, lead tetraethyl ($\text{Pb}(\text{C}_2\text{H}_5)_4$) was used as antiknock additive in gasoline, thus turning road traffic into the major emission source of Pb in Austria. The high hazardous potential of Pb (high Pb-concentrations in the environment can lead to serious problems in the central nervous system, peripheral nervous system and the vascular system of humans¹⁰) as well as the introduction of

automotive catalytic converters, for which Pb is a catalyst-poison, led to the development and implementation of unleaded gasoline. Therefore, today Pb is mainly used in accumulators, for noise protection in the building industry as well as for the protection against X-rays and radioactivity in medical engineering, for the lining of pipelines and instruments in the chemical industry and furthermore as alloy material. Lead oxide – being classified as a potential carcinogenic compound¹⁰ - is used in optical glasses and for the production of pigments, which are used for paint and lacquer.

The main emission sources of Pb in Austria today are therefore the iron- and steel industry, the domestic fuel as well as commercial and industrial combustors. Further important sources are the secondary copper- and lead production (e.g. in Brixlegg), the glass production as well as the combustion of refinery residues, firewood, coke and coal. Overall in Austria 65% of the Pb-emissions in 2003 were derived from industry, 21% from small consumers and 13% from power suppliers. As can be seen in Figure 1, the Pb-emissions in Austria from the other three emission sectors – Traffic, Agriculture and Others - played in 2003 only a negligible role.

Measurement series recorded by the Austrian Umweltbundesamt GmbH for Pb in PM₁₀ are available in Austria since 1999 for the test points in Brixlegg, Arnoldstein and Salzburg Rudolfsplatz. In a larger extend Pb measurements were started in 2002. The test points Brixlegg and Arnoldstein are both mainly influenced by local industry, thus showing for the years 1999-2004 the highest Pb concentrations in PM₁₀ in Austria. For all other measurement points, which are either situated in large cities or close to industrial sites in Austria, significantly lower Pb concentrations in PM₁₀ were measured for the same period. In this period the calculated yearly average values were below the threshold limit of 0.5 µg/m³ for all evaluated test points.

1.1.2 Cadmium (Cd)⁵⁻⁸

In low concentrations Cd is ubiquitous in the environment. In Austria Cd is mainly emitted by the combustion of heavy fuel oil, coal, coke and household waste. Cd-emissions are also caused by the burning of firewood in small firing plants as well as by the combustion of industrial waste and refinery residues. Further Cd-sources are the iron- and steel-production, especially the scrap recycling with Cd-containing adhesions of paint and lacquer, as well as the production of cement, zinc and lead. Cd is also used in the semiconductor industry, as alloy element as well as for the production of paint pigments and stabilizers, which are used in the glass-, ceramics- and plastics industry. The continuous increasing volume of traffic – especially in the heavy load domain – led in the traffic sector to an increase in the Cd-emissions, mainly originating from the abrasion of tires and brakes.

Thus, in the year 2003, 34% of the Cd-emissions in Austria originated from the industry and the small consumers, respectively, 23% were derived from the energy supply, 8% from traffic and 1% from agriculture. Additionally to the Cd sources mentioned above, tobacco smoking is a considerable source for the exposure of Cd to humans. Furthermore Cd can be enriched over the food chain, since it shows a long half-life period in the human and animal organism. Cd and its compounds are classified as “definite carcinogenic substances”.

1.1.3 Mercury (Hg)^{5,8}

The main emission sources of Hg in Austria are the industry, small consumers and the power supply. Hg is mainly emitted by the combustion of heavy fuel oil, coke, coal, refinery residues and fire wood as well as industrial production. Being the only metal, which is liquid at room temperature, there are numerous fields of application. Hg is used in thermometers, batteries, fluorescent lamps and plant protection products. Thus, in 2003 49% of the Hg-emissions in Austria stemmed from the industry, 27% from the power supply sector and 23% originated from small consumers. The Hg-emissions of the other sectors (Traffic, Agriculture, Others) were negligible. Hg can be brought into the environment by waste water, waste incineration and incorrect handling. Enduring exposure to Hg vapour can lead to irreversible i.e. chronic harms to human health.

1.1.4 Trace and heavy metals emitted by traffic

Traffic and its consequences is an emerging topic in today's political, economical, ecological and social discussions. On the one hand fast, efficient and flexible transport systems play in an increasing degree an important role in the world's economy as well as in our every day's life; on the other hand traffic – and thereby especially road traffic – shows negative environmental impacts like energy consumption, pollutant emissions, noise emissions, land consumption, sealing of the surface and negative effects on the natural scenery^{5,9}. These environmental impacts lead to environmental problems - like climate changes, acidification, air pollution, noise and the destruction of ecosystems - thus having direct and indirect consequences for human beings, animals and plants^{5,9}. Among the substances, whose emission can mainly be assigned to road traffic, many – like the heavy metals Pb, Cu, Sb, Cd or Zn - are qualified as toxic⁹. In Austria the number of licensed motor vehicles has increased by nearly 50% in the last 15 years⁹. Furthermore goods traffic (heavy duty vehicles), which showed particularly high grow rates, was even nearly doubled over the last 20 years⁹. These developments made an effective emission control an absolute necessity.

There are many processes, like the burning process, emissions from tire abrasions, abrasion from brake processes, the release of metals from the car body, the loss of engine and lubricating oils as well as releases from the automotive catalytic converter, which contribute to the road traffic emissions⁹. According to Zechmeister et al.⁹ the elements Cr, Mo, Sb, Zn, As, Fe, V, Cu, Ni and Co can be identified as road traffic emissions, which are mainly deposited within a distance of 250 m from major roads. Additionally, as a result of the introduction of automotive catalytic converters in 1987 in Austria, increasing amounts of Pt, Pd and Rh are released into the environment. As the demand of these noble metals for production of auto catalysts in Europe rose in only one decade (1994 - 2004) from 18820 kg to 52255 kg for Pt as well as from 8090 kg to 34370 kg for Pd, this emission source will be discussed in the following paragraph in detail^{11,12}.

Automotive catalytic converters¹³ were developed for the reduction of the emissions of gaseous pollutants, like nitrogen oxides (NO_x), carbon monoxide (CO) and hydrocarbons (HCs). These pollutants are removed from the exhaust gases of a properly tuned combustion engine either by reduction or by oxidation. The noble metals mentioned above combined with heat facilitate these heterogeneous reactions in the catalytic converter. On the one hand NO_x and CO are eliminated together by a redox reaction on an Rh catalyst, by which NO_x can oxidize CO to carbon dioxide (CO₂) and is reduced to nitrogen gas (N₂); on the other hand remaining CO and HCs are oxidized by air to CO₂ and water on a Pt or Pd catalyst¹³. In modern “three-way converters” (TWCs) these reactions proceed parallel to each other, thus converting over 90% of CO, HCs and NO_x into less harmful compounds. A constant air-to-fuel-mixture at the stoichiometric ratio ($\lambda=1$), which is regulated by the lambda probe, is an absolute prerequisite for the proper functionality of a TWC.

TWCs consist of a monolithic honeycomb support, which is made of a special stainless steel or cordierite (2MgO·2Al₂O₃·5SiO₂), embedded in a stainless steel box, and coated with an activated, high-surface alumina layer, the so called “washcoat”¹³. The washcoat is composed of approximately 90% γ -Al₂O₃ and a mixture of base metal additives, mainly oxides of Ce, Zr, La, Ni, Fe, Ti, Y, W and some alkaline earth metals, which are used to improve the performance of the catalyst by acting as promoters of the desired catalytic reactions and to serve as stabilizers against deterioration and aging¹³. To fix the precious metals Pt, Pd and Rh on its surface, the washcoat is impregnated with hexachloroplatinic (IV) acid (H₂PtCl₆·6H₂O), palladium chloride (PdCl₂) and rhodium chloride (RhCl₃) precursor salts, respectively¹³. For achieving catalytically “active”, highly dispersed, metallic particles of the platinum group elements (PGE), with diameters in the 1-10 nm range, the precursors are reduced in an H₂ stream at 500°C¹³.

High temperatures of the exhaust gases, changing oxidative / reductive conditions and mechanical abrasion lead – by stressing the surface of the washcoat and thus also the

catalytic active layer physically and chemically – to the emission of PGE containing particles into the environment^{13,14}. The amount and rate of PGE emissions are influenced by the speed of the automobile, the type of the engine, the age of the catalyst as well as the used fuel additives. Unfavourable operating conditions like misfiring or excessive heating can intensify these emissions and even lead to the destruction of the catalyst¹³. PGEs released from TWCs are mainly emitted in particulate form (Pt>95%, Pd>85% and Rh>90%) into the environment at a rate of up to 200 ng PGE per km per car, whereupon the PGEs are often still bound to ablated washcoat particles¹³.

1.2 Exposure to toxic metals via inhalation of PM

Inhaled airborne particles can be deposited in various places of the respiratory tract, depending on the chemical properties and the particle size, which can be altered by different moisture contents of the inhaled air¹⁵: Large particles (> 3 µm after nasal inspiration) are deposited in the nasal and pharyngeal region¹⁵. Smaller particles can reach the bronchia and the pulmonary alveoli¹⁵. Particulate matter with a particle size of about 0.5 µm is mainly exhaled¹⁵.

According to the Bundesanstalt für Arbeitsschutz und Arbeitsmedizin (2001)¹⁶ particles, which reach the pulmonary alveoli – as far as they are insoluble - can stay there for months to years (half-life up to 400 days). For the elimination (clearance) of alveolar deposited particles macrophages play a decisive role. They can take up these particles and remove them via the bronchial-, the lymph- or the blood- system. An elevated particle-uptake over a long period can lead to a disturbed balance between uptake and elimination causing the so called “Overload-phenomenon”, which means that from a certain particle-loading of the macrophages the clearance of the alveolar deposited dust is reduced or completely stopped in case of overloading (if ≥60% of the macrophage-volume are filled out with particles).

In most cases particles deposited in the bronchia are transported relative fast (within hours) adoral and are either coughed out or swallowed¹⁶. The latter fraction reaches the gastrointestinal-tract (GIT), where it comes in contact with gastric juice, which main components are hydrochloric acid and pepsin. Thus, gastric juice is the most acidic of the digestive juices and is therefore likely to yield the greatest fractions of soluble metal compounds or complexes¹⁷. According to S.C. Hamel et al.¹⁷ for the present work 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, while bioavailability is the amount that actually is taken across the cell membranes.

After their resorption in the lunge or the GIT the noxious metals are transported over the blood stream into various tissues and organs like liver and kidney, where accumulation,

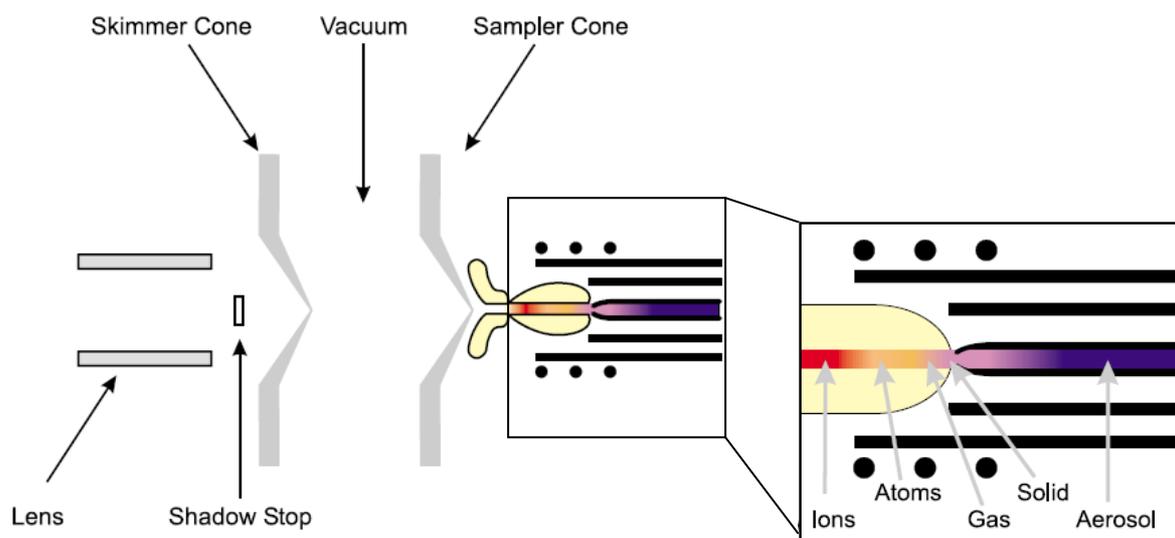
metabolic transformation or elimination can occur¹⁵. The main excretion paths of these metals are therefore the elimination over the urine and/or over the faeces, whereupon for water-soluble substances the renal excretion is most important¹⁵. Thus, urine can be considered to be one of the most useful materials for biological monitoring (“biomonitoring”), also due to its ease of sampling¹⁸. Biomonitoring, which is the measurement of concentrations of harmful substances and/or their metabolites in biological materials, plays a decisive role for the assessment of the individual human exposure to the noxious metals and the associated health risks^{15,18}. Thus, the human biomonitoring of PGEs in urine samples, which will be further discussed in chapter 3 of this diploma thesis, was already used as a marker of the load of these metals in the urban environment¹⁸. However, up to date human biomonitoring was performed mostly in the case of platinum, since there is a lack of analytical methods for accurate quantification of ultra-trace concentrations of rhodium and palladium in human urine. Hence the development of such methods was one major aim of this work.

1.3 Elemental analysis by ICP-DRCMS

For performing trace metal analysis highly sensitive, fast and reliable analytical instruments like inductively coupled plasma mass spectrometers (ICP-MS) are an absolute prerequisite. An ICP-MS basically consists of a sample introduction system, an ICP torch, an interface, a vacuum system, an ion lens system, a mass filter, a detector as well as a data handling and control system¹⁹. The sample introduction system, which transports the sample to the ICP-MS, is generally consisting of a peristaltic pump, a nebulizer and a spray chamber. The introduction system generates a fine sample aerosol that is introduced via the sample injector tube of the ICP torch. At the end of the ICP torch a high-temperature argon-plasma is formed, which serves as the ion source of the ICP-MS. In the various temperature zones of the argon plasma the sample aerosol is dried, vaporized, atomized and finally ionized^{19,20}. As depicted in Figure 3, the thus generated positively charged ions enter the ICP-MS interface, which is one of the most critical parts of the ICP-MS and of decisive importance for its functionality.

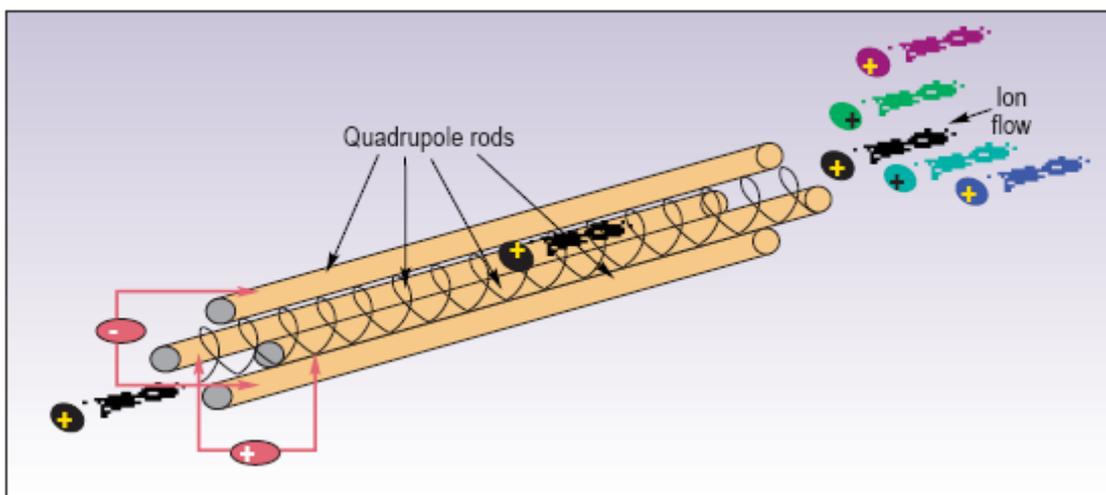
Figure 3: Interface region of the ICP-MS. *Enlarged Detail:* State of the sample in the various temperature zones of the plasma.

Source: Perkin Elmer Sciex, Technical Note „The 30-Minute Guide to ICP-MS”, 2001, published on the web



The importance of the interface belongs to the fact that a high temperature- and pressure-difference exists between the plasma, which is at 6000 °C and under atmospheric pressure, and the ion lens system, which works nearly at room temperature under high vacuum conditions. The ions, which were generated in the plasma, initially pass the orifice of the sampler-cone, which has an inner diameter of 0.8-1.2 mm, thus entering the rough-vacuum area of the ICP-MS. Afterwards the ions pass the skimmer cone orifice, which has an inner diameter of 0.4-0.8 mm, thus reaching the ion lens system of the ICP-MS. At the beginning of the lens system the so called shadow-stop is located that stops photons of the plasma, which could otherwise overload the detector, as well as non-ionized material. Afterwards the ions are focussed by an ion-lens system and the resulting ion-beam is transmitted into the mass filter. The separation of the ions according to their mass-to-charge ratio (m/z) is performed in a mass analyzer – normally a quadrupole mass spectrometer. In Figure 4 the scheme of a quadrupole mass separation device is depicted:

Figure 4: Scheme of the functionality of a quadrupole mass filter.
Source: R. Thomas, Spectroscopy **16**(10), 2001, 44-48



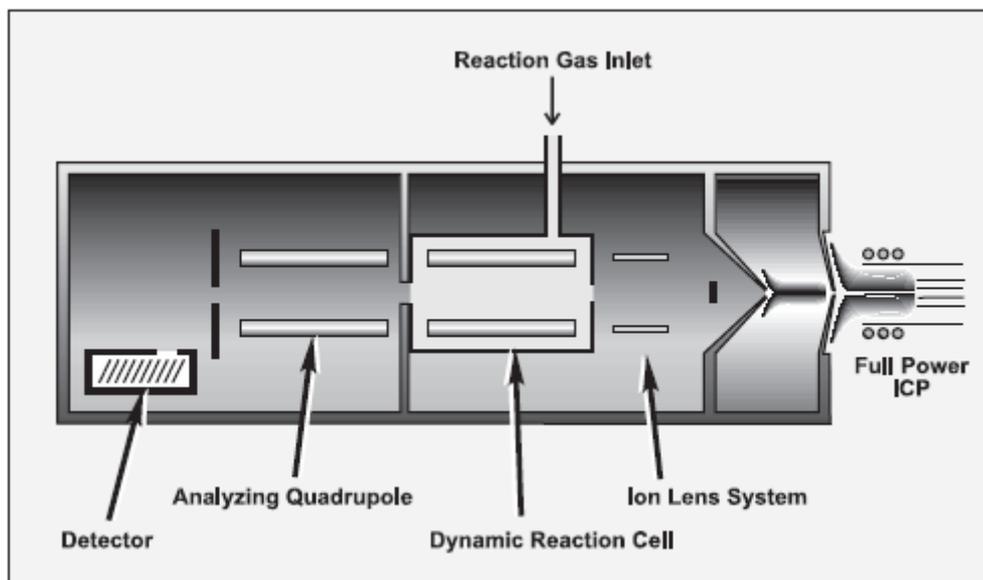
The opposite electrodes of the quadrupole mass filter are on the same potential, while a direct and an alternating voltage is applied between the vicinal electrodes. The ratio between the direct and the alternating voltage (at constant frequency of the alternating voltage) determines which ions can pass the mass separation device. Thus only the ions of interest can reach the detector. The other ions, which possess a different mass-to-charge ratio pass through the spaces between the rods and are ejected from the quadrupole or collide with the electrodes²¹. The ions exiting the mass spectrometer finally reach the detector - normally a secondary electron multiplier – where they generate a measurable electronic signal. This signal is finally read out into a data handling unit, which is used for the evaluation of the thus generated data sets as well as to control the entire ICP-MS system.

The rapid multielement capabilities, the ability to detect the individual isotopes of each element as well as the superb detection limits are the most attractive feature of ICP-MS. Nevertheless, for some elements the achievable detection limits by ICP-MS are poor, since these elements suffer from major spectral interferences generated by ions derived from the plasma gas, matrix components or the used chemicals (solvent, etc.)²². Examples for these interferences include $^{40}\text{Ar}^{16}\text{O}$ mitigating the determination of ^{56}Fe as well as $^{40}\text{Ar}^{35}\text{Cl}$, $^{40}\text{Ar}^{12}\text{C}$ and $^{23}\text{Na}^{37}\text{Cl}$ hampering the determination of ^{75}As , ^{52}Cr and ^{60}Ni , respectively. For the elimination of these interferences the so called collision/reaction cells were implemented into ICP-MS instruments in the late 1990s²². Such cells consist of a multipole (a quadrupole, hexapole or octapole) into which a collision/reaction gas is introduced. According to S.D. Tanner et al.²³ it can be shown that the preferred multipole configuration is a quadrupole, as it is used in PerkinElmer's Dynamic Reaction Cell™ (DRC™). The main advantage of using a quadrupole inside the collision/reaction cell is that - contrary to higher order multipoles - highly reactive gases, such as ammonia, oxygen or methane, can be

used, which tend to be more efficient at interference reduction, since quadrupoles show well-defined stability boundaries and are able to efficiently suppress interferences that would otherwise be produced by the reactive gases through a complex sequence of reactions^{22,23}. As depicted in Figure 5 the DRC is positioned between the ion lens system and the analyzer quadrupole.

Figure 5: Scheme of an ICP-DRCMS.

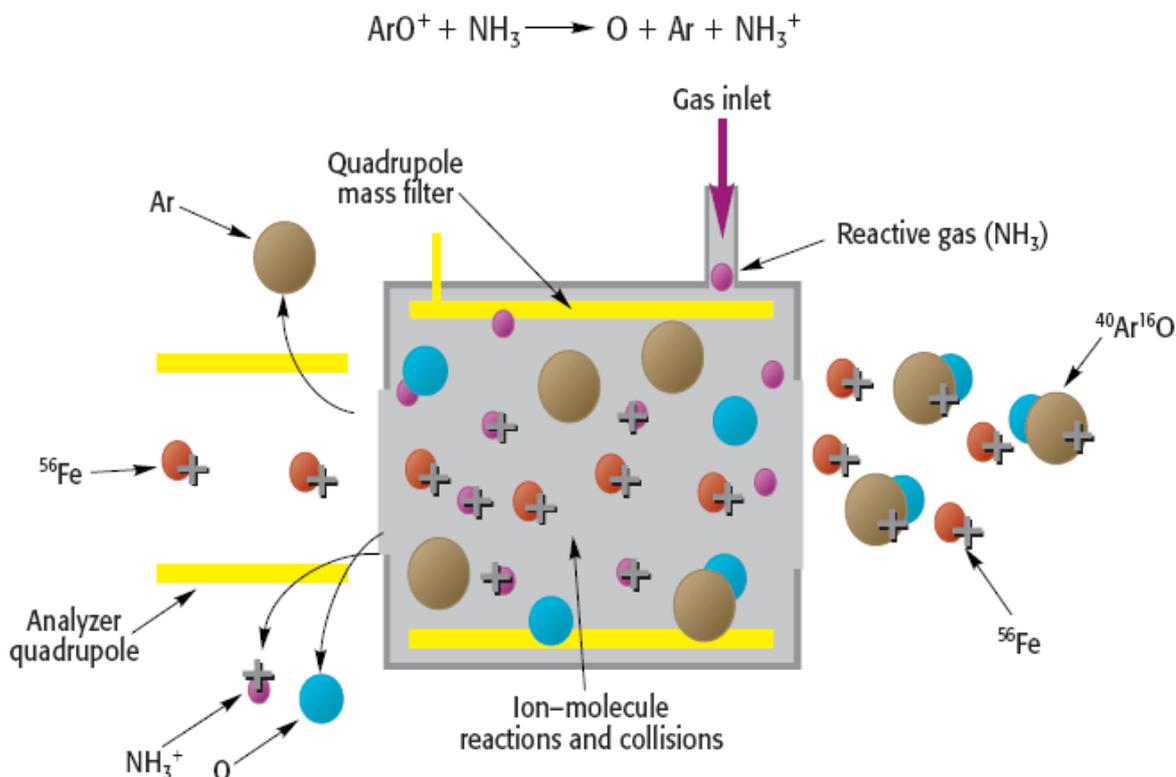
Source: S.D. Tanner and V.I. Baranov, Atomic Spectroscopy Vol. 20(2), 1999, 45-52



Ions emerging from the ion lens system enter the DRC where interfering ions react with a very low volume of reaction gas, which pressurizes the reaction cell, to non-interfering reaction products²⁴. As depicted in Figure 6 these reaction products, which must not be transmitted through the analyzing quadrupole, are ejected from either the quadrupole inside the DRC or from the analyzer quadrupole^{22,24}.

Figure 6: Example for the functionality of the DRC. The ArO interference on the determination of ^{56}Fe is removed by the NH_3 reaction gas, which reacts with the ArO^+ ions according to the given formula. The non interfering reaction products Ar, O and NH_3^+ are ejected from either the quadrupole inside the DRC or from the analyzer quadrupole. Thus, the NH_3^+ is prevented from reacting further to produce new interfering ions.

Source: R. Thomas, Spectroscopy 17(2), 2002, 42-48



Therefore only analyte ions can pass both quadrupoles and finally reach the detector, thus making an ICP-DRCMS to an instrument with an outstanding interference reduction power as it is necessary for the ultra-trace determination of many isotopes²⁴.

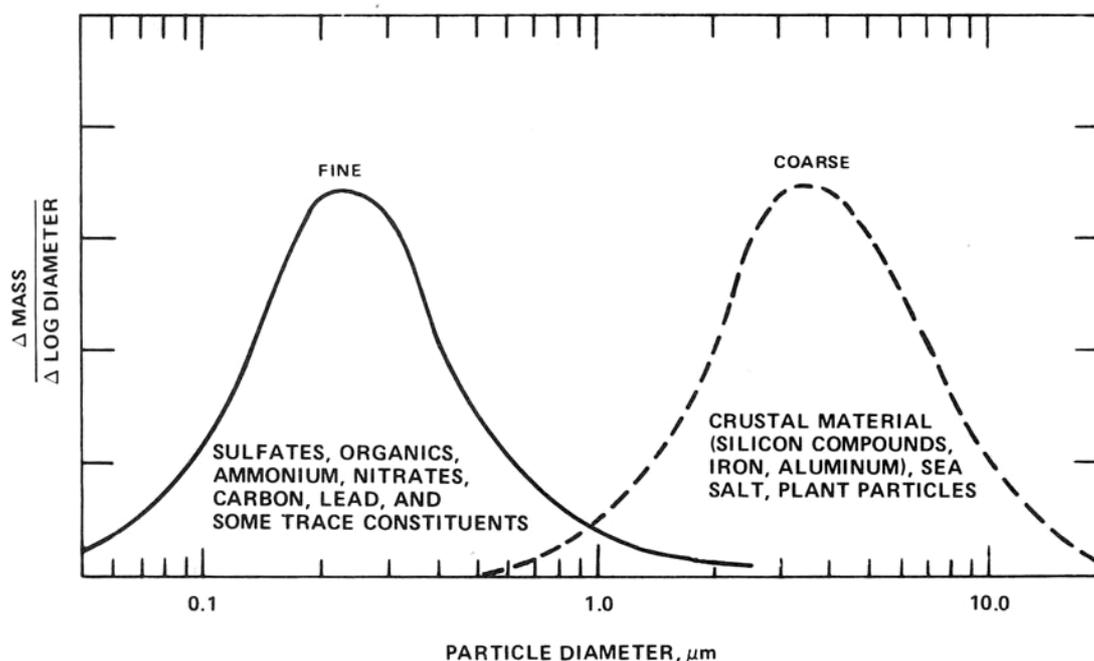
2 Analysis of toxic metals in size classified aerosol

An assembly of liquid (forming fog / mist) or solid (forming airborne particulates) particles suspended in a gaseous medium – normally air - long enough to enable observation and measurement is termed aerosol¹. In the atmosphere different types and concentrations of aerosols exist. On the one hand these can be aerosols of natural origin, like smoke from forest fires, windblown dust, airborne sea salt and emissions from volcanoes, on the other hand the aerosols can emanate from anthropogenic sources like automotive exhausts, smoke from power plants or agricultural burning and test aerosols generated in laboratories¹. For airborne particles the size and the chemical composition are important parameters, influencing the particles behaviour in the environment as well as its toxicological potential. Worldwide, there exist three main types of aerosols, which are the

“continental” aerosol (that over land masses), the “marine” aerosol (that over the ocean) and the “urban” aerosol (that in the cities)¹. It is obvious that the urban aerosol is that with the largest anthropogenic impact. In Figure 7 the typical chemical composition of the fine and coarse fractions of a typical urban aerosol are depicted.

Figure 7: Particle size fractions and chemical composition (the chemical species are listed in approximate order of their relative mass contribution) of a typical urban aerosol.

Source: K. Willeke and P. A. Baron (editors), *Aerosol measurement – principles, techniques, and applications*, Van Nostrand Reinhold, New York 1993



Actual, urban aerosol is an aerosol-mixture originating from various sources. It is difficult to identify these sources, since aerosol measurements are usually immission measurements, which give only information about the concentration and/or the size of certain aerosol compounds. Nevertheless, two main groups of aerosol sources can be identified: local and regional sources on the one hand, as well as long-range transport on the other hand. Looking at the origins of the PM₁₀-exposure in Austria, the contribution of local and regional sources predominantly consists of primary emission particles from road traffic, domestic fuel, industry and off-road as well as ammonium nitrate, whose precursor substances are NO_x and NH₃, which are mainly emitted by road traffic and agriculture⁶. In eastern Austria long-range transported PM₁₀ shows up to 60% of secondary aerosols – mainly ammonium sulphate, which points at a considerable contribution of large SO₂-emitters in Eastern Europe to the PM₁₀-exposure in Austria⁶.

Aerosol particles can be biological, organic or inorganic, like trace and heavy metals, which are associated with several adverse health effects – including cancer – as well as with deleterious impacts on the environment^{1,4}. For the assessment of the hazardous potential

of the metallic fraction, which is emitted over particulate matter, it is necessary to measure the total concentration of these harmful metals as well as their bioaccessible fraction.

2.1 Experimental

2.1.1 Reagents and Samples

Sampling of PM_{2.5} and PM₁₀ samples was performed at a sample site at Getreidemarkt in downtown Vienna (16° 24' E, 48° 12' 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 (16th February 2006 to 27th March 2006, see Table 1).

Table 1: Sample name, date and weekday of sampling. Sample GM_TU-F6 was sampled for 72 hours, all other samples for 24 hours, corresponding to a sampling volume of 51.3-72.4 m³ per day. After sample changing, which was performed at about 8:00, the aerosol samples were stored in petri dishes at room temperature.

Sample	Date	weekday	Sample	Date	weekday
GM_TU-F5	16.02.2006	Thursday	GM_TU-F20	08.03.2006	Wednesday
GM_TU-F6	17.02.2006	Friday	GM_TU-F21	09.03.2006	Thursday
GM_TU-F7	20.02.2006	Monday	GM_TU-F22	10.03.2006	Friday
GM_TU-F8	21.02.2006	Tuesday	GM_TU-F23	13.03.2006	Monday
GM_TU-F9	22.02.2006	Wednesday	GM_TU-F24	14.03.2006	Tuesday
GM_TU-F10	23.02.2006	Thursday	GM_TU-F25	15.03.2006	Wednesday
GM_TU-F11	24.02.2006	Friday	GM_TU-F26	16.03.2006	Thursday
GM_TU-F12	26.02.2006	Sunday	GM_TU-F27	17.03.2006	Friday
GM_TU-F13	27.02.2006	Monday	GM_TU-F28	20.03.2006	Monday
GM_TU-F14	28.02.2006	Tuesday	GM_TU-F29	21.03.2006	Tuesday
GM_TU-F15	01.03.2006	Wednesday	GM_TU-F30	22.03.2006	Wednesday
GM_TU-F16	02.03.2006	Thursday	GM_TU-F31	23.03.2006	Thursday
GM_TU-F17	03.03.2006	Friday	GM_TU-F32	24.03.2006	Friday
GM_TU-F18	06.03.2006	Monday	GM_TU-F33	27.03.2006	Monday
GM_TU-F19	07.03.2006	Tuesday			

For sample collection of the PM₁₀-samples a DIGITEL PM₁₀ pre-separator (DIGITEL Elektronik GmbH, Ludesch, Austria, see Figure 8) with an intake volume of 2.3 m³/h (being equivalent to 40 L/min) was equipped with a GN-4 Metricel® mixed cellulose ester filter (diameter: 47 mm, pore size: 0.8 µm; PALL Life-sciences, Michigan, USA, product number 64679). For PM_{2.5} sample collection a sampling head with an identical construction – except a different geometry of the pre-separator's nozzles (different diameter) and thus a different separation performance – was used.

Figure 8: DIGITEL PM₁₀ pre-separator for 2.3 m³/h according to EN12341.
Source: DIGITEL Elektronik GmbH, Ludesch, Austria



The air volume, which was actually sucked in by the DIGITEL pre-separator, was determined for each filter sample by using a gas meter. Since the gas meter of the PM_{2.5} pre-separator unit did not function properly – maybe caused by clogging of the gas meter by a spoiled filter – the determination of the sucked in air volume of the PM_{2.5} samples was accomplished by multiplying the sucked in air volume of the corresponding PM₁₀ samples with a constant factor ($f = 42/40 = 1.05$). This factor is resulting from the fact, that the effective pump output of the PM_{2.5} pre-separator unit was 42 L/min and the effective pump output of the PM₁₀ pre-separator unit was 40 L/min.

All reagents used for sample pre-treatment and ICP-QMS analysis were of the highest available 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, order number 1.00317.2500) and nitric acid (HNO₃, 65%, p.a., Merck, Darmstadt, Germany, order number 1.00456.2500) were additionally cleaned by sub-boiling distillation (once for HCl; twice for HNO₃) in an ultra pure quartz apparatus (Milestone-MLS GmbH, Leutkirch, Germany). Aqueous hydrofluoric acid (HF_{aq}, 48%, Merck, Darmstadt, Germany, order number 1.01513.1001) and hydrogen peroxide (H₂O₂, 31%, Merck, Darmstadt, Germany, order number 1.06097.1001) were of Ultrapur[®] quality;

perchloric acid (HClO₄, 70%, Merck, Darmstadt, Germany, order number 1.00517.0250) and sodium hydroxide monohydrate (NaOH·H₂O, 99,99%, Merck, Darmstadt, Germany, order number 1.06466.0500) were of Suprapur[®] quality. Pepsin from porcine stomach mucosa (456 units/mg solid, order number P-7000) 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, Hg, Tl and Pb) 1000 mg/L ICP-MS single element standards were obtained from Merck. All casks (pipette tips, polyethylene (PE)-flasks and vials, etc.) were cleaned prior to their disposable use according to a special cleaning process.

2.1.2 Sample digestion

All filters were weighed before and after use with a Sartorius MC 210P (Data Weighing Systems Inc., Illinois, USA) balance.

The filters were cut into halves by using ceramic scissors and tweezers, and subsequently the halves were weighed again. One filter-half was totally digested by using aqua regia and an acid microwave-assisted digestion procedure. For this purpose the filter-half was placed into a lockable HF 100 digestion vessel (Anton Paar, Graz, Austria) and 2 mL HNO₃, 3 mL HCl and 0.5 mL HF were added. After sealing, four of these digestion vessels were set into a Rotor 16 HF 100 (Anton Paar, Graz, Austria), which was finally fixed in a Multiwave 3000 microwave system (Anton Paar, Graz, Austria). The settings of the microwave digestion program are shown in Table 2.

Table 2: Settings of the microwave digestion program. The ventilator of the microwave was operated during the whole program at power level 1. Thus, during step 4 the samples were slowly cooled down. After step 4 the samples were quickly cooled down by operating the ventilating fan at full power.

STEP	TIME	POWER
1	5 min. Ramp + 7 min. Hold	400 W
2	16 min. Ramp	800 W
3	12 min. Ramp	1000 W
4	10 min. Hold	0 W

Since the temperature and the pressure in the digestion vessels are crucial parameters during microwave operation, one digestion vessel was equipped with a contacting-temperature-pressure-sensor for accurate temperature/pressure reading of this “reference” vessel. Additionally the microwave system was equipped with an IR-sensor for monitoring the temperature of all vessels. When the temperature or the pressure exceeded the given threshold limits (240 °C, 40 bar and a pressure increase rate of 0.5 bar/s for the contacting-temperature-pressure-sensor; 210 °C for the IR sensor, since this sensor measures the temperature from outside the vessels) the microwave power input was automatically reduced.

After cooling down, the samples were transferred to PFA-vessels, 100 μL HClO_4 were added and subsequently the samples were evaporated at 120 $^\circ\text{C}$ to about 200 μL . After addition of 2 mL aqua regia, the samples were again evaporated at 120 $^\circ\text{C}$ to about 200 μL . Subsequently the samples were evaporated at 150 $^\circ\text{C}$ 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 $^\circ\text{C}$ until the day of measurement. Prior to measurement with ICP-quadrupole-MS (ICP-QMS) 0.5 mL of the samples were diluted 1:10 with 1% (v/v) HNO_3 . To 5 mL of the diluted samples, 0.5 mL of a 110 ppb In-solution were 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 an US-Pharmacopeia methodology as described by S.C. Hamel et al.¹⁷: In a 250 mL-PE-flask about 0.497 g $\text{NaOH}\cdot\text{H}_2\text{O}$ were dissolved in a solution of 2.605 mL HCl and about 100 mL of subboiled water; 0.8 g of Pepsin were added and the solution was filled up to 250 g with subboiled water. After placing the filter-halves into 100 mL-PE-flasks, 10 mL synthetic gastric juice were added. The flasks were closed and the samples were shaken for 2 h at 37 $^\circ\text{C}$ 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 3400 rpm. One mL of the supernatant of each sample was diluted 1:5 with 1% (v/v) HNO_3 and stored in a PE-vial at 4 $^\circ\text{C}$ until the day of measurement. Prior to measurement with ICP-QMS 0.5 mL of a 110 ppb In-solution were added as internal standard.

2.1.3 Analysis with ICP-QMS

For ICP-QMS analysis a multi-element calibration standard, which contained the highest expected concentration of each element, as well as its 1:1.3, 1:2, 1:4, 1:10 and 1:100 dilutions were prepared. The measurement of the samples was carried out using PerkinElmer's ELAN DRC-II plus ICP-Quadrupole-MS under the plasma conditions listed in Table 3.

Table 3: Used plasma conditions.

RF power	1300 W
Plasma gas flow	15 L/min
Auxiliary gas flow	1.3 L/min
Nebulizer gas flow	0.94 L/min

For sample introduction PerkinElmer's Autosampler AS-93 and a PFA-nebulizer (Elemental Scientific, Omaha, Nebraska, USA) with a flow rate of 0.4 mL/min were used. The isotopes ^{47}Ti , ^{52}Cr , ^{55}Mn , ^{59}Co , ^{60}Ni , ^{65}Cu , ^{66}Zn , ^{98}Mo , ^{107}Ag , ^{111}Cd , ^{118}Sn , ^{121}Sb , ^{202}Hg , ^{205}Tl and ^{208}Pb were selected for measurement and subsequent quantification of all samples. For the measurement of Cr and Ni the DRC with NH_3 as reactive gas was used. For each element the limit of detection (LOD) and the limit of quantification (LOQ) were determined as threefold (3σ -criterion for the LOD) and tenfold (10σ -criterion for the LOQ) of the standard deviation, which was derived from the measurement of 10 clean filter-halves (blank samples).

The settings in the method section of the ELAN ICP-MS-software (ELAN 3.0 HotFix 3) used for the measurements are depicted in Figure 9.

The evaluation of the data sets was also performed by using the ELAN ICP-MS-software. Thereby the mean intensity (the averaged intensity of the three replicates, which were performed by each measurement as depicted in Figure 9) was used to determine the mean concentration [$\mu\text{g/L}$] of the measured elements for each sample according to the linear calibration function, which was obtained for each element by measurement of the calibration standards and subsequent linear regression.

Figure 9: Settings in the method section of the ELAN software.

Sweeps / Reading		20	Est. Reading Time :		0:00:19,160		Get Cell Parameters						
Readings / Replicate		1	Est. Replicate Time :		0:00:19,160								
Replicates		3	Est. Sample Time :		0:01:57,480								
Tuning File		default.tun	Select...		<input type="checkbox"/> Enable QC Checking								
Optimization File		mein.dac	Select...										
	Int Std	Analyte (*)	Mass (amu)	Scan Mode (*)	MCA Channels	Dwell Time per AMU (ms)	Integration Time (ms)	Corrections	Cell Gas A	Cell Gas B	RP a	RP q	Mode
1		Ti	46.9518	Peak Hopping	1	50	1000		0	0	0	0.25	Standard
2		Mn	54.9381	Peak Hopping	1	50	1000		0	0	0	0.25	Standard
3		Co	58.9332	Peak Hopping	1	50	1000		0	0	0	0.25	Standard
4		Cu	64.9278	Peak Hopping	1	50	1000		0	0	0	0.25	Standard
5		Zn	65.926	Peak Hopping	1	50	1000		0	0	0	0.25	Standard
6		Mo	97.9055	Peak Hopping	1	50	1000		0	0	0	0.25	Standard
7	▶	In	114.904	Peak Hopping	1	50	1000	Sn	0	0	0	0.25	Standard
8		Ag	106.905	Peak Hopping	1	50	1000		0	0	0	0.25	Standard
9		Cd	110.904	Peak Hopping	1	50	1000		0	0	0	0.25	Standard
10		Sn	117.902	Peak Hopping	1	50	1000		0	0	0	0.25	Standard
11		Sb	120.904	Peak Hopping	1	50	1000		0	0	0	0.25	Standard
12		Hg	201.971	Peak Hopping	1	50	1000		0	0	0	0.25	Standard
13		Tl	204.975	Peak Hopping	1	50	1000		0	0	0	0.25	Standard
14	⌋	Pb	207.977	Peak Hopping	1	50	1000		0	0	0	0.25	Standard
15	⌋	Cr_1	51.9405	Peak Hopping	1	50	1000		0.7	0	0	0.45	DRC
16	⌋	Ni_1	59.9332	Peak Hopping	1	50	1000		0.7	0	0	0.45	DRC
17	⌋	In_1	114.904	Peak Hopping	1	50	1000	Sn	0.7	0	0	0.45	DRC

2.2 Results and discussion

2.2.1 Total digestion samples

2.2.1.1 Concentrations in air

The amount of trace and heavy metals per cubic metre air volume that was determined for the totally digested samples is listed in Table 4 (PM₁₀) and Table 5 (PM_{2.5}) for each investigated element. Elements (Cr, Ni), which were measured by using the DRC are indicated by “_1” after the element symbol (thus: Cr_1, Ni_1). The values in these tables were obtained by multiplying the measured mean concentration [µg/L] of the totally digested samples with the corresponding sample volume [g] and dividing by the air volume [m³], which was sucked through the respective filter-half. The resulting average aerosol concentrations of the metals in the sampled air [ng/m³] are additionally depicted in Figure 10 to Figure 17, thus showing the variation of the aerosol concentration of the respective metal with time, which is caused by changes in meteorological conditions and/or contributions of local emission sources.

Table 4: Concentrations [ng/m³] of the assayed metals in the respective sample-air, which were obtained by the analysis of the totally digested PM₁₀-filter-samples. *Italic* typed values are between the limit of detection (LOD) and the limit of quantification (LOQ) of the respective element. The values in the magenta colored cells lie outside of the selected calibration range for the total digestion samples. The values in the red colored cells are outliers according to the Grubbs-outlier-test. Outliers and values outside the calibration range were not used for the calculation of the average, the standard deviation (STD) or the relative standard deviation (RSD).

Analyte:	⁴⁷ Ti	⁵⁵ Mn	⁵⁹ Co	⁶⁵ Cu	⁶⁶ Zn	⁹⁸ Mo	¹⁰⁷ Ag	¹¹¹ Cd	¹¹⁸ Sn	¹²¹ Sb	²⁰² Hg	²⁰⁵ Tl	²⁰⁸ Pb	⁵² Cr_1	⁶⁰ Ni_1
Sample	Conc. Mean [ng/m ³]														
F5_10	<LOD	10,9	0,260	34,2	84,1	3,82	<i>0,0777</i>	0,629	4,98	6,37	<i>0,0104</i>	0,0568	20,8	<LOD	5,07
F6_10	<i>13,0</i>	11,8	0,162	31,7	51,5	2,77	<i>0,0489</i>	0,281	4,58	6,35	<i>0,0343</i>	0,0258	9,51	<LOD	3,63
F7_10	<i>19,5</i>	18,8	0,336	44,7	103	3,74	<i>0,0926</i>	0,700	6,93	8,77	<i>0,0845</i>	0,0403	13,3	<LOD	3,57
F8_10	28,6	13,0	0,208	23,1	80,2	1,72	<i>0,139</i>	0,528	3,88	4,85	<i>0,0219</i>	0,101	15,4	<LOD	2,54
F9_10	<LOD	10,5	0,185	18,6	<i>50,7</i>	1,38	<LOD	0,319	3,24	3,61	<LOD	0,0567	8,58	<LOD	12,0
F10_10	<LOD	11,0	0,148	17,8	73,4	1,32	<i>0,0555</i>	0,596	3,69	3,89	<LOD	0,155	17,2	<LOD	<i>1,31</i>
F11_10	<LOD	13,8	0,772	20,5	121	1,42	<i>0,0912</i>	0,856	3,66	4,14	<i>0,0621</i>	0,234	26,6	<LOD	<i>1,87</i>
F12_10	<LOD	5,45	0,103	14,5	58,8	1,04	<LOD	0,676	2,44	3,30	<LOD	0,154	16,1	<LOD	<i>0,989</i>
F13_10	<LOD	12,3	0,478	29,9	79,0	2,45	<i>0,121</i>	0,575	4,36	5,59	<i>0,0802</i>	0,0376	10,2	<LOD	3,70
F14_10	<LOD	10,9	0,183	27,4	56,5	2,16	<i>0,0484</i>	0,468	4,21	5,39	<i>0,0240</i>	0,0377	10,8	<LOD	2,31
F15_10	21,8	7,12	0,249	18,1	34,2	1,35	<i>0,0658</i>	0,416	3,10	3,52	<i>0,00877</i>	0,0163	5,40	<LOD	<i>1,03</i>
F17_10	<i>13,8</i>	13,2	0,196	32,0	64,5	2,68	<i>0,0386</i>	0,509	5,00	6,24	<i>0,0489</i>	0,0313	9,18	<LOD	3,07
F18_10	<LOD	6,80	0,105	19,8	45,6	1,78	<i>0,0690</i>	0,401	3,36	3,77	<i>0,0671</i>	0,0298	8,58	<LOD	2,39
F19_10	26,1	10,8	0,159	25,3	49,3	1,91	<LOD	0,281	3,98	4,75	<i>0,0197</i>	0,0203	5,17	<LOD	<i>1,35</i>
F20_10	16,7	7,26	0,251	12,9	33,0	1,13	<LOD	0,302	2,07	2,33	<i>0,0303</i>	0,0142	5,26	<LOD	2,23
F21_10	25,6	8,22	0,258	26,6	1172	1,68	<LOD	0,428	2,73	3,15	<i>0,148</i>	0,0249	7,23	<LOD	<i>2,03</i>
F22_10	<i>19,1</i>	8,06	0,166	16,5	36,6	1,19	<LOD	0,229	2,56	3,06	<i>0,170</i>	0,0146	4,46	<LOD	<i>1,76</i>
F23_10	<i>17,6</i>	10,4	0,197	19,2	58,4	1,39	<i>0,0408</i>	0,395	3,08	3,84	<LOD	0,0628	12,1	<LOD	<i>2,06</i>
F24_10	<LOD	8,35	0,129	21,1	74,8	1,57	<i>0,0438</i>	0,666	3,41	4,47	<LOD	0,142	18,8	<LOD	<i>1,42</i>
F25_10	<i>17,5</i>	15,9	0,212	30,9	104	27,0	<i>0,0450</i>	0,921	4,92	6,20	<LOD	0,267	21,4	1,76	2,31
F26_10	<i>17,1</i>	19,0	0,263	30,7	166	18,1	<i>0,0906</i>	1,59	5,57	7,06	<LOD	0,550	38,5	<LOD	<i>1,90</i>
F27_10	25,3	9,30	0,131	23,5	69,0	43,0	<LOD	0,648	5,09	26,3	<LOD	0,118	16,3	0,379	<i>0,555</i>
F28_10	53,4	27,6	0,452	46,4	95,5	27,0	<i>0,0768</i>	0,745	7,60	8,74	<LOD	0,0642	15,7	3,22	8,08
F29_10	64,8	17,5	0,247	29,6	84,0	29,2	<i>0,0834</i>	0,700	5,72	5,51	<LOD	0,0505	14,4	<LOD	<i>2,11</i>
F30_10	61,5	16,3	0,249	24,7	94,0	27,6	<i>0,0640</i>	0,827	4,20	4,94	<LOD	0,102	18,3	0,175	<i>1,78</i>
F31_10	25,6	15,2	0,260	25,4	85,5	34,2	<i>0,0436</i>	0,786	4,14	5,05	<LOD	0,132	16,6	0,446	<i>2,01</i>
F32_10n	24,7	13,9	0,216	18,9	64,1	2,85	<i>0,0430</i>	0,500	2,94	3,78	<i>0,0884</i>	0,0902	15,4	0,0201	<i>1,98</i>
Average	27,3	11,8	0,223	25,3	70,0	1,97	0,0689	0,494	4,13	4,95	0,0599	0,0657	13,2	1,00	2,20
STD	15,8	3,76	0,0907	8,21	23,2	0,829	0,0278	0,153	1,32	1,65	0,0485	0,0466	5,70	1,25	0,993
RSD [%]	57,7	32,0	40,6	32,4	33,1	42,1	40,4	31,1	32,0	33,3	80,9	70,9	43,3	125	45,2

Table 5: Concentrations [ng/m³] of the assayed metals in the respective sample-air, which were obtained by the analysis of the totally digested PM_{2.5}-filter-samples. *Italic* typed values are between the limit of detection (LOD) and the limit of quantification (LOQ) of the respective element. The values in the magenta colored cells lie outside of the selected calibration range for the total digestion samples. The values in the red colored cells are outliers according to the Grubbs-outlier-test. Outliers and values outside the calibration range were not used for the calculation of the average, the standard deviation (STD) or the relative standard deviation (RSD).

Analyte:	⁴⁷ Ti	⁵⁵ Mn	⁵⁹ Co	⁶⁵ Cu	⁶⁶ Zn	⁹⁸ Mo	¹⁰⁷ Ag	¹¹¹ Cd	¹¹⁸ Sn	¹²¹ Sb	²⁰² Hg	²⁰⁵ Tl	²⁰⁸ Pb	⁵² Cr_1	⁶⁰ Ni_1
Sample	Conc. Mean [ng/m ³]														
F5_2.5	<LOD	4,86	0,136	11,0	68,9	2,03	<i>0,0469</i>	0,509	1,90	2,31	<i>0,00520</i>	0,0487	18,8	<LOD	3,68
F6_2.5	<LOD	4,76	0,0869	11,6	38,1	1,21	<i>0,0330</i>	0,229	1,76	2,56	<i>0,0346</i>	0,0225	7,78	<LOD	2,47
F7_2.5	<LOD	8,95	0,136	16,9	78,2	1,35	<i>0,0665</i>	0,577	2,80	3,40	<i>0,0239</i>	0,0391	11,2	<LOD	2,46
F8_2.5	<LOD	5,86	0,102	8,09	61,6	0,774	<i>0,138</i>	0,449	2,00	2,09	<LOD	0,0980	14,3	<LOD	<i>1,29</i>
F9_2.5	<LOD	4,24	0,0793	5,91	36,3	<i>0,413</i>	<LOD	0,220	1,38	<i>1,25</i>	<i>0,0476</i>	0,0534	7,49	<LOD	4,02
F10_2.5	<LOD	6,67	0,0937	8,20	65,6	0,608	<i>0,0688</i>	0,502	2,20	2,04	<LOD	0,156	16,8	<LOD	<i>1,22</i>
F11_2.5	<LOD	10,1	0,571	9,66	107	0,685	<i>0,0874</i>	0,867	2,29	2,23	<i>0,0477</i>	0,249	27,2	<LOD	<i>1,42</i>
F12_2.5	<LOD	3,00	0,0900	5,32	56,2	0,616	<LOD	0,517	1,15	<i>1,51</i>	<i>0,122</i>	0,152	15,5	<LOD	<i>0,987</i>
F13_2.5	<LOD	4,47	0,228	9,79	72,5	0,788	<i>0,133</i>	0,497	1,43	1,79	<i>0,0616</i>	0,0383	9,44	<LOD	2,93
F14_2.5	<i>16,1</i>	4,11	0,103	9,38	44,5	0,745	<LOD	0,309	1,53	2,05	<LOD	0,0335	9,97	<LOD	<i>1,71</i>
F15_2.5	<i>17,4</i>	3,84	0,0808	8,29	31,5	0,570	<i>0,0535</i>	0,340	1,53	<i>1,48</i>	<i>0,0228</i>	0,0160	4,97	<LOD	<i>0,982</i>
F16_2.5	<LOD	6,17	0,110	15,1	36,2	1,28	<LOD	0,237	2,51	2,88	<i>0,0607</i>	0,0155	5,58	<LOD	<i>1,53</i>
F18_2.5	<i>14,7</i>	3,62	0,106	7,97	36,5	4,13	<i>0,0596</i>	0,316	1,30	<i>1,34</i>	<i>0,0309</i>	0,0289	7,19	<LOD	16,1
F19_2.5	<i>14,0</i>	5,21	0,0968	10,5	38,6	0,770	<LOD	0,187	1,74	1,98	<i>0,0167</i>	0,0196	4,39	<LOD	<i>0,962</i>
F20_2.5	<i>16,6</i>	4,72	0,225	5,73	27,9	0,616	<LOD	0,231	1,20	<i>0,972</i>	0,187	0,0144	4,87	<LOD	<i>1,48</i>
F21_2.5	<i>36,3</i>	2,30	0,0381	3,87	37,9	<i>0,309</i>	<LOD	0,304	<i>0,844</i>	<i>0,636</i>	<i>0,0693</i>	0,0212	7,05	<LOD	<i>1,40</i>
F22_2.5	100	26,8	0,133	6,36	26,3	0,632	<i>0,0473</i>	0,124	0,936	1,22	<i>0,0432</i>	0,0134	72,6	30,0	7,59
F24_2.5	<LOD	5,56	0,0784	5,47	61,0	<i>0,478</i>	<i>0,0460</i>	0,539	1,18	1,60	<LOD	0,131	23,5	1,06	<i>1,11</i>
F25_2.5	<LOD	8,72	0,132	11,9	86,8	13,1	<i>0,0558</i>	0,756	2,68	2,91	<LOD	0,268	19,8	1,12	<i>1,52</i>
F26_2.5	29,7	11,8	0,133	9,89	132	7,84	<i>0,0734</i>	1,26	2,76	3,02	<LOD	0,506	48,7	4,09	<i>2,19</i>
F27_2.5	20,8	5,22	0,0805	8,60	57,6	22,0	<LOD	0,502	2,85	22,0	<LOD	0,111	15,6	<LOD	<LOD
F28_2.5	52,0	11,1	0,195	16,4	66,2	12,0	<i>0,0711</i>	0,521	2,83	3,31	<LOD	0,0573	15,8	4,53	4,44
F29_2.5	47,7	7,75	0,165	9,90	63,5	12,9	<i>0,0567</i>	0,550	2,99	2,04	<LOD	0,0505	12,9	2,00	<i>1,11</i>
F30_2.5	12,6	9,28	0,118	8,89	72,4	17,0	<i>0,0473</i>	0,659	1,86	1,98	<LOD	0,0953	19,9	3,06	<i>1,25</i>
F31_2.5	18,8	9,46	0,160	9,48	70,0	24,9	<i>0,0450</i>	0,571	2,11	2,38	<LOD	0,130	15,1	1,46	<i>1,30</i>
F32_2.5	34,0	10,8	0,173	11,1	55,1	1,88	<LOD	0,492	1,94	2,55	<LOD	0,0835	15,5	2,27	<i>1,50</i>
F33_2.5	20,9	9,47	0,128	13,9	56,1	18,8	<i>0,0453</i>	0,548	2,72	2,90	<LOD	0,0266	10,3	5,12	2,31
Average	25,1	6,61	0,123	9,60	58,7	0,875	0,0652	0,414	1,94	2,09	0,0451	0,0607	12,8	2,74	1,89
STD	12,8	2,77	0,0459	3,29	24,3	0,484	0,0286	0,152	0,656	0,723	0,0299	0,0467	6,14	1,53	0,992
RSD [%]	51,0	41,9	37,2	34,2	41,4	55,3	43,9	36,8	33,8	34,5	66,2	76,9	47,8	55,7	52,6

Figure 10: Concentrations [ng/m³] of the metals Ti, Cu, Zn and Pb in the respective sample-air, which were obtained by the analysis of the totally digested PM₁₀ samples. The relative standard deviation of the values given in the figure is 11.8 %.

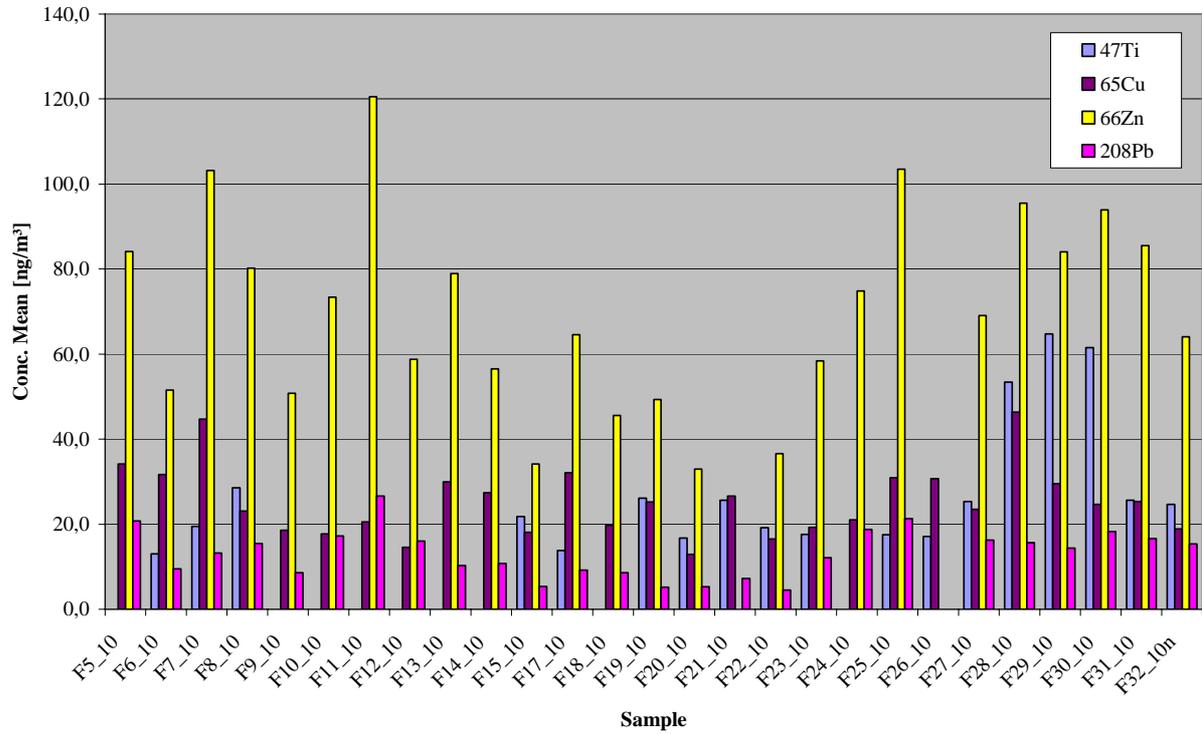


Figure 11: Concentrations [ng/m³] of the metals Ti, Cu, Zn and Pb in the respective sample-air, which were obtained by the analysis of the totally digested PM_{2.5} samples. The relative standard deviation of the values given in the figure is 11.8 %.

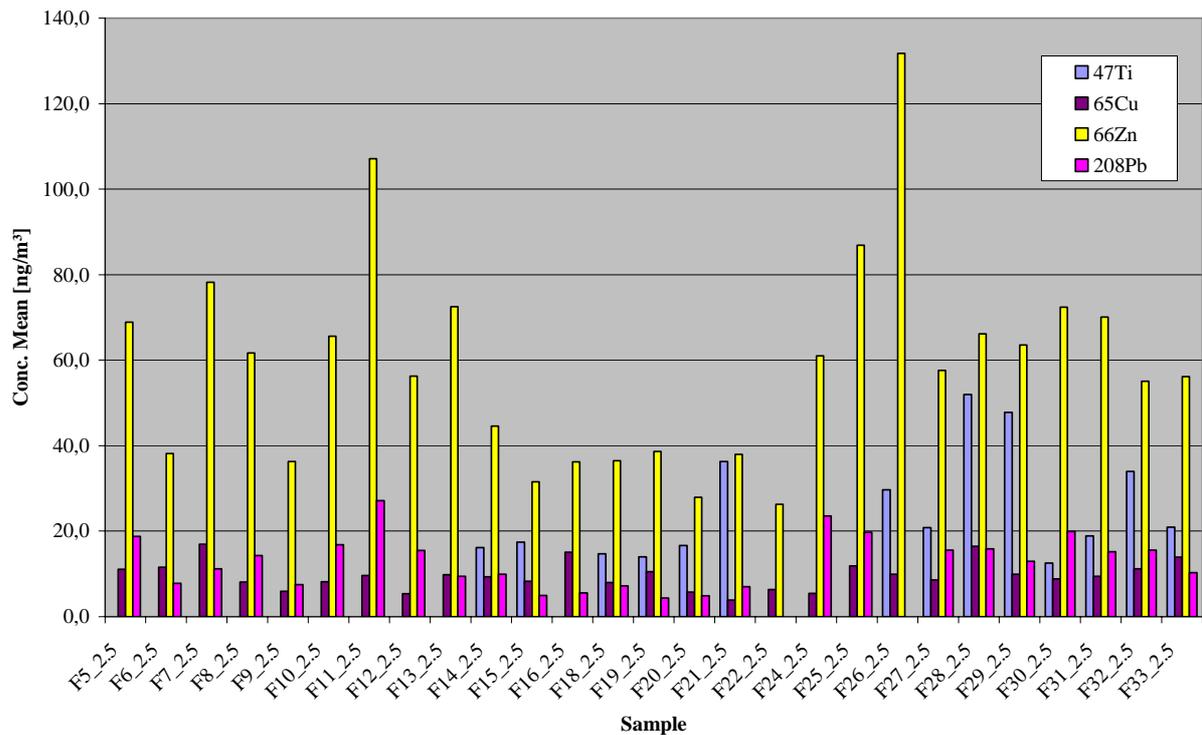


Figure 12: Concentrations [ng/m³] of the metals Mn, Ni, Sn and Sb in the respective sample-air, which were obtained by the analysis of the totally digested PM₁₀ samples. The relative standard deviation of the values given in the figure is 11.8 %.

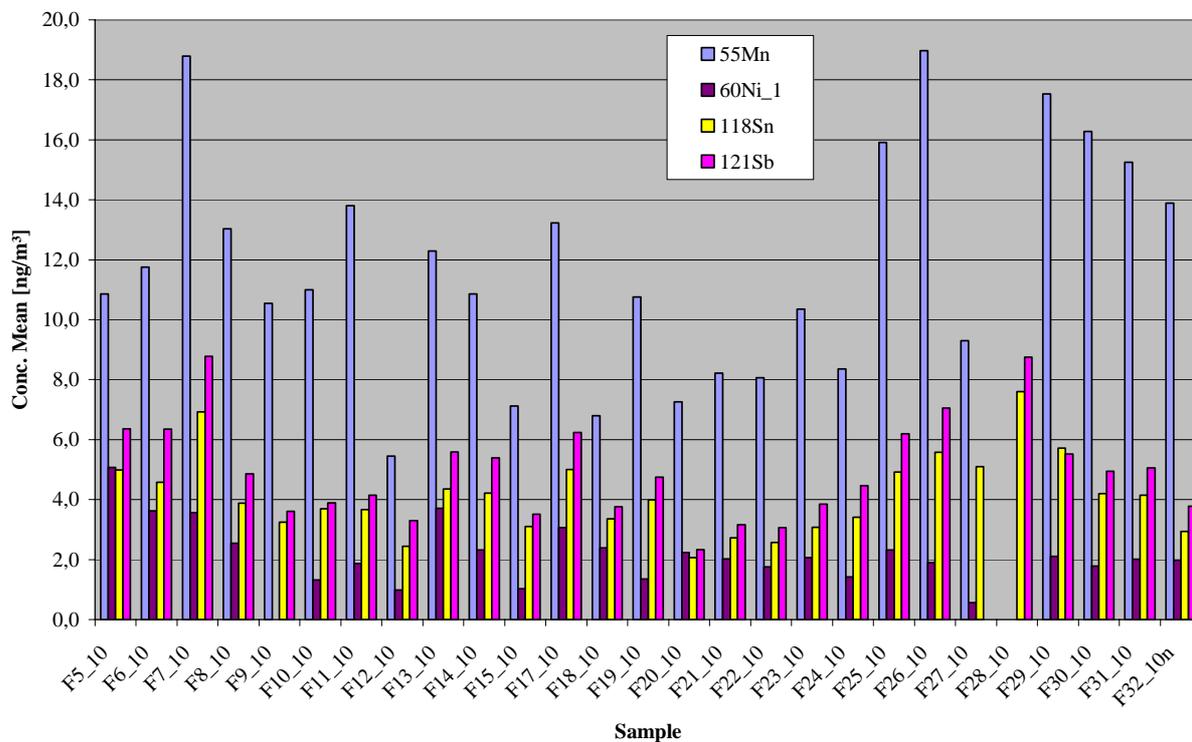


Figure 13: Concentrations [ng/m³] of the metals Mn, Ni, Sn and Sb in the respective sample-air, which were obtained by the analysis of the totally digested PM_{2.5} samples. The relative standard deviation of the values given in the figure is 11.8 %.

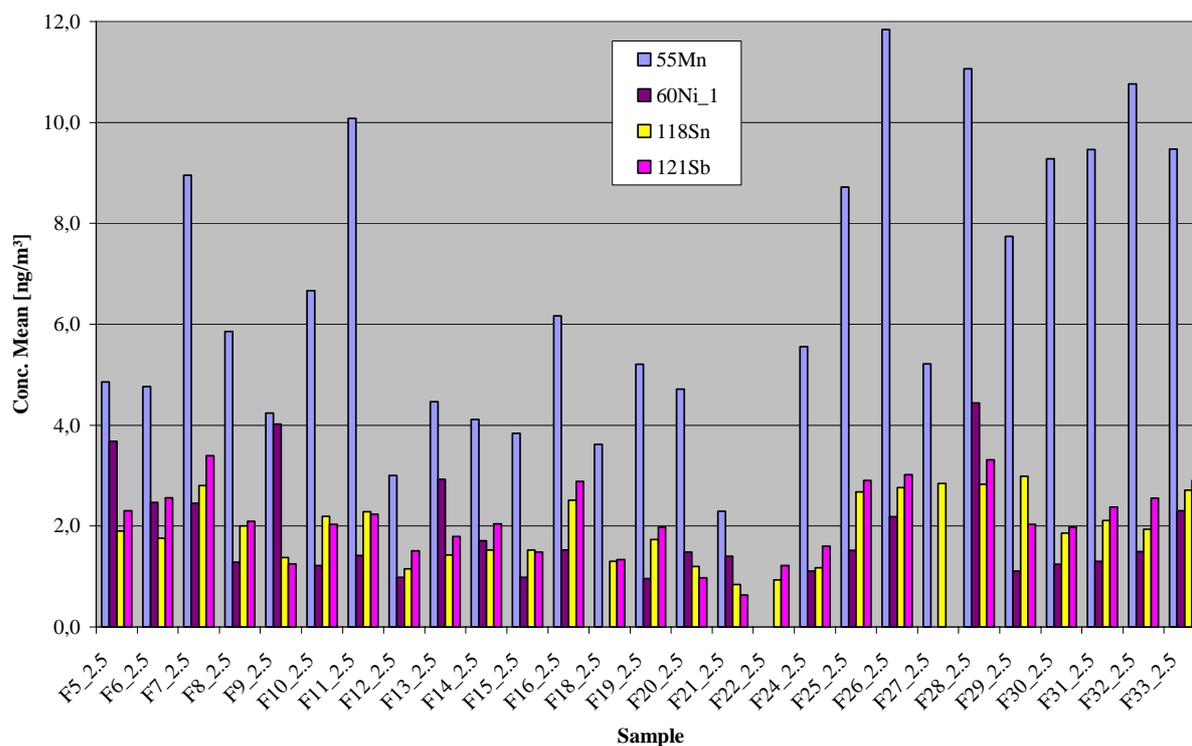


Figure 14: Concentrations [ng/m³] of the metals Cr, Co, Mo and Cd in the respective sample-air, which were obtained by the analysis of the totally digested PM₁₀ samples. The relative standard deviation of the values given in the figure is 11.8 %.

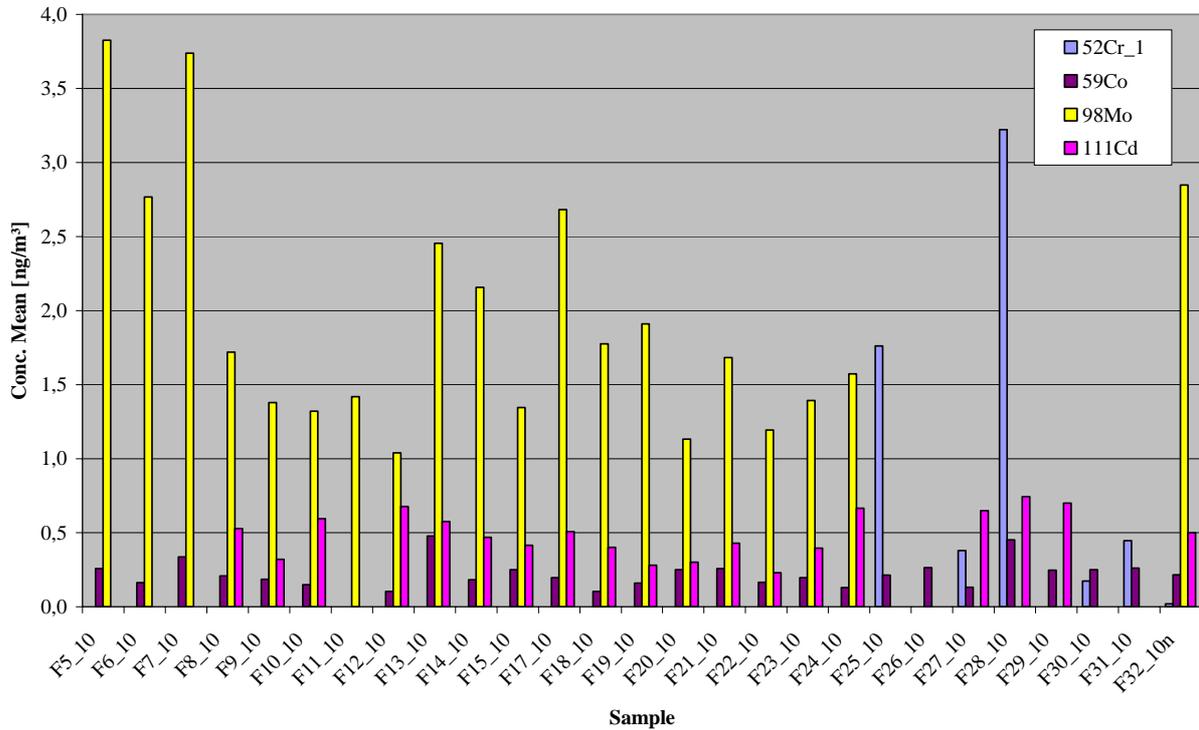


Figure 15: Concentrations [ng/m³] of the metals Cr, Co, Mo and Cd in the respective sample-air, which were obtained by the analysis of the totally digested PM_{2.5} samples. The relative standard deviation of the values given in the figure is 11.8 %.

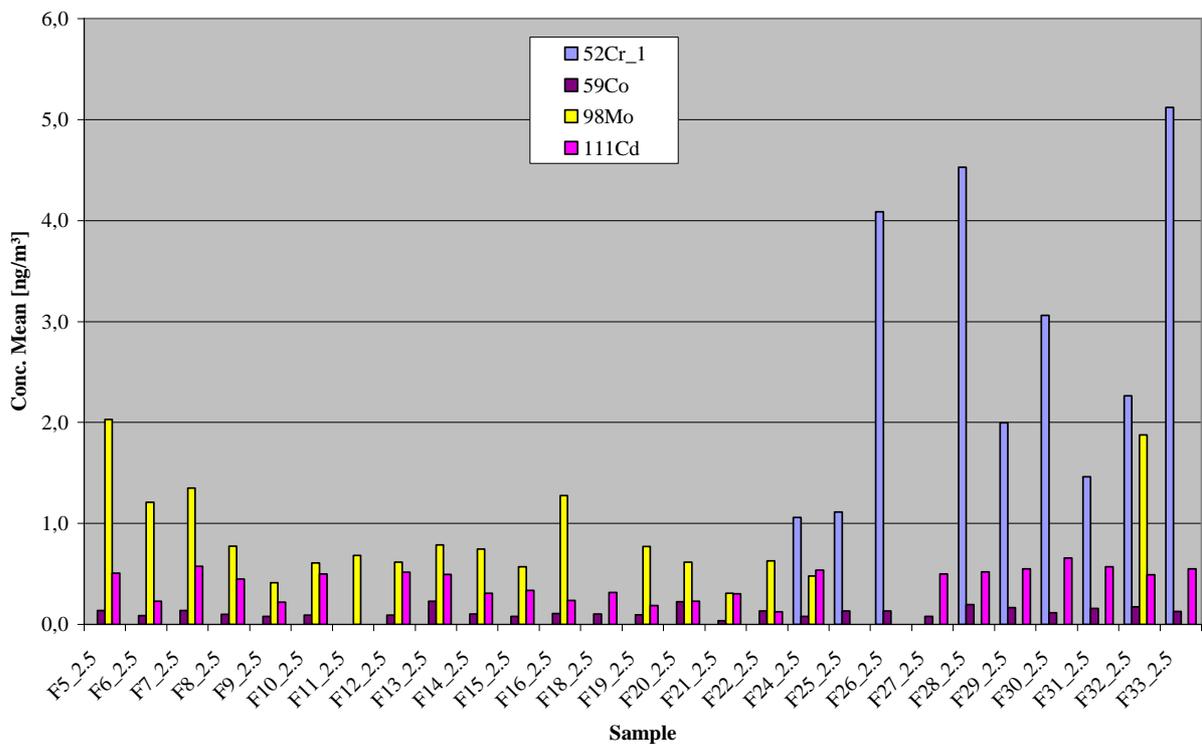


Figure 16: Concentrations [ng/m³] of the metals Ag, Hg and Tl in the respective sample-air, which were obtained by the analysis of the totally digested PM₁₀ samples. The relative standard deviation of the values given in the figure is 11.8 %.

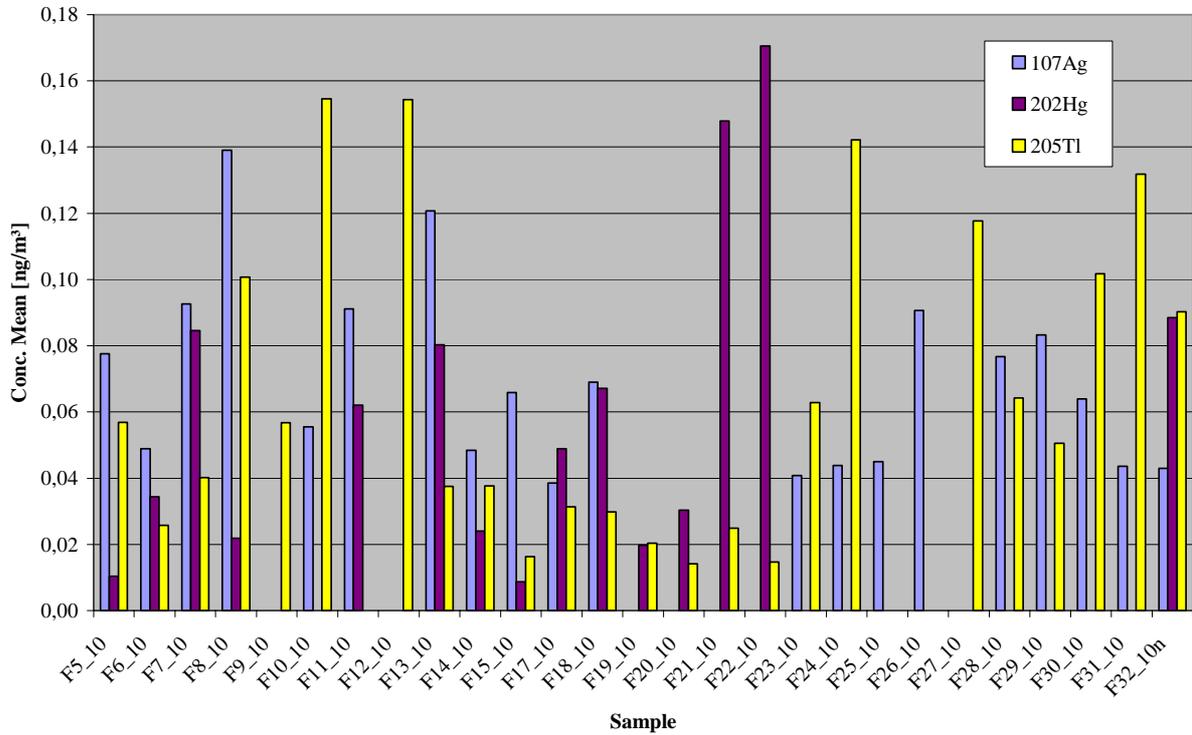
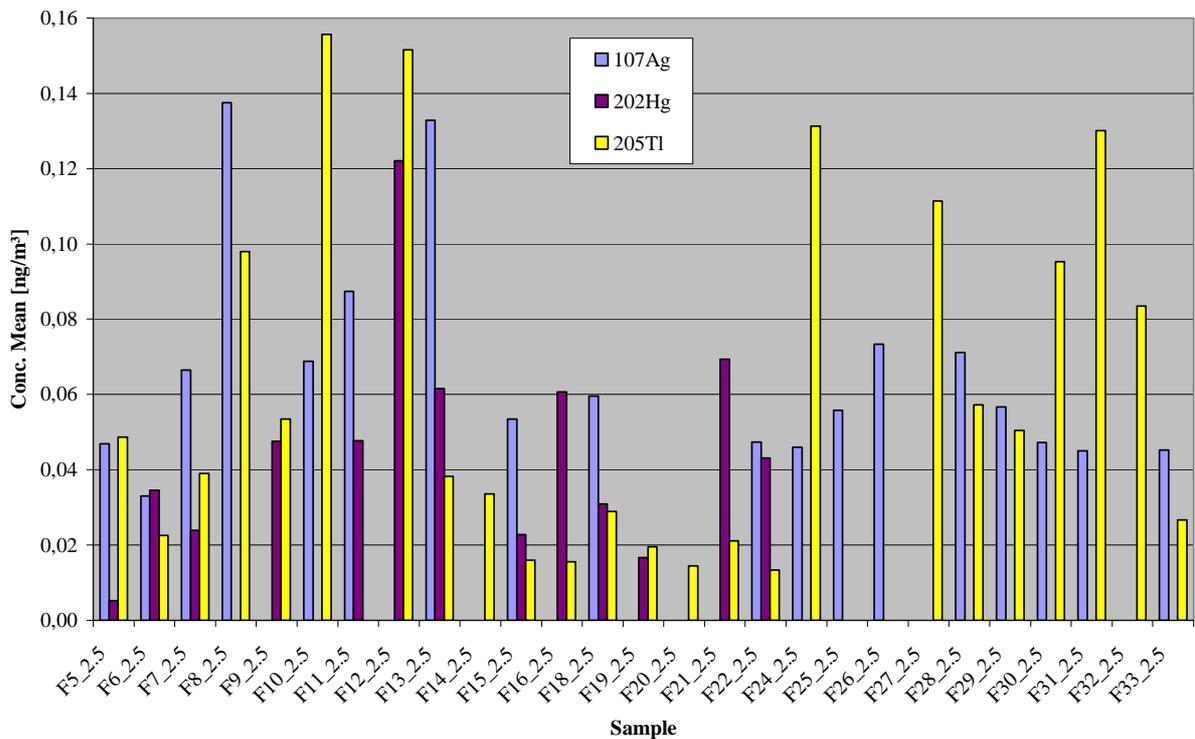


Figure 17: Concentrations [ng/m³] of the metals Ag, Hg and Tl in the respective sample-air, which were obtained by the analysis of the totally digested PM_{2.5} samples. The relative standard deviation of the values given in the figure is 11.8 %.



As can be seen in Figure 10 and Figure 11 **zinc** is the element with the highest concentration of the investigated elements in PM₁₀ and PM_{2.5} samples. The metal is used as zinc coating for surface protection of ironware and as sheet zinc for roofs, gutters and dry batteries²⁵. Zinc dust is applied in the chemical industry and metallurgy as reduction agent²⁵. Zinc is also needed for alloys, especially for brass, which is a Cu-Zn-alloy. Zinc is mainly emitted into the environment by waste incinerators, whereupon the thus emitted particles rather belong to the fine particle fraction, as well as by abrasion processes from vehicle tires (tire stock contains about 1.5% Zn; abrasion is estimated to be 1.2 mg/km), which rather contributes to the coarse particle fraction²⁶. Further emission sources are mining, zinc and metal production facilities, corrosion of galvanized structures, coal and fuel combustion as well as the use of zinc-containing fertilizers and agrochemicals²⁶. Zinc dust in ambient air consists to 52-70 % of particles with diameters < 5 µm²⁶. Zinc-concentrations of 10 to 2400 ng/m³ were found in European urban areas²⁶. Thus, the average Zinc-concentrations presented in this work for PM₁₀ (average: 70 ± 23.2 ng/m³) and PM_{2.5} (average: 58.7 ± 24.3 ng/m³) samples are within this range, also showing that the main part of this metal can be found in the fine particle fraction.

As can be seen in Table 4 and Table 5 **titanium** is the metal with the second highest average concentration of the investigated elements in PM₁₀ and PM_{2.5} samples. Titanium and its alloys are used in applications where strength, lightness and resistance to corrosion are desirable, like surgical implants and prostheses, tubings as well as applications in the space industry²⁶. Nevertheless, the most important form of titanium is its dioxide (TiO₂), which is a brilliant white pigment used in paints, lacquers and enamels, ceramics, paper coatings, leather finishing, detergents, food additives, toothpastes and so on²⁶. According to E. Merian et al.²⁶ atmospheric concentrations of titanium in urban regions are usually < 0.5 µg/m³, which is in agreement with the results presented in this work.

As can be concluded from Table 4 and Table 5 **copper** mainly occurs in the coarse particle fraction of the particulate matter. Copper is a heavy metal, which combines outstanding properties like ductility, durability, malleability as well as electrical and thermal conductivity²⁶. Thus, copper has a wide field of applications, like the use in electrical wire and cable, electronic applications, water piping, roofing material, kitchenware, pigments as well as for chemicals and pharmaceutical equipment²⁶. Copper is further used in alloys, like brass (zinc), bronze (tin) and money metal (nickel) as well as in many metallic amalgams (e.g. mercury amalgams used in dentistry)²⁶. Copper compounds – like copper sulphate – can be used in algicides and molluskicides, fungicides, feed additives and pigments²⁶.

Contrary to copper, **lead** mainly occurs in the fine particulate fraction of the particulate matter – as can be seen in Table 4 and Table 5 - with a mass medium diameter of 0.55 µm²⁶. Softness, a low melting point, a high resistance to corrosion and a high density

are important properties of lead, making it easy to handle and fashion²⁶. Thus, the heavy metal is used for paint pigments, glass, plastics, ceramics, in ammunition, cable-covering materials, casting materials, solders, pipes, traps, bends, for weatherproofing buildings, for the equipment used in the manufacture of acids and so on^{26,27}. However, lead-acid storage batteries are the most important use of lead today²⁶. In the past lead tetraethyl ($\text{Pb}(\text{C}_2\text{H}_5)_4$) was used as antiknock additive in gasoline, thus turning road traffic into the major emission source of lead into the environment. The high hazardous potential of lead (high Pb-concentrations in the environment can lead to serious problems in the central nervous system, peripheral nervous system and the vascular system of humans¹⁰) as well as the introduction of automotive catalytic converters, for which lead is a catalyst-poison, led to the development and implementation of unleaded gasoline. For 2005 the share in unleaded gasoline was estimated to be about 85 % of the worldwide sold gasoline²⁶. In Austria the ban on leaded gasoline led to a reduction in lead-emissions of 94 % for the period of 1990 – 2003⁵. According to the Austrian Umweltbundesamt GmbH (W. Spangl et al.)⁶ the yearly mean values of the lead concentrations in PM_{10} samples measured in urban areas in Austria were for the year 2004 in the range of 6 – 20 ng/m^3 . Thus, the average lead concentration presented in this work for PM_{10} samples (average: $13.2 \pm 5.70 \text{ ng}/\text{m}^3$) is within this range.

By comparing Figure 12 and Figure 13 as well as Table 4 and Table 5 it can be concluded that **manganese** has nearly equal parts occurring in the fine and the coarse particle fraction of the particulate matter. The main part of manganese (over 90 %) is used in the iron, steel and aluminium industries as an alloying, deoxidising and desulfurizing agent for improving the properties of many metallurgical products, like cast iron, steel and nonferrous metals²⁶. However, manganese is also used in non-metallurgical applications, such as glass, dry-cell batteries, welding rods, brick and ceramic colouring, electrolytic and chemical manganese dioxide and other manganese chemicals²⁶. According to E. Merian et al.²⁶ the average annual manganese content in urban areas without significant manganese pollution in the USA was found to be between 30 and 70 ng/m^3 . Thus, the average manganese concentrations presented in this work for PM_{10} (average: $11.8 \pm 3.76 \text{ ng}/\text{m}^3$) and $\text{PM}_{2.5}$ (average: $6.61 \pm 2.77 \text{ ng}/\text{m}^3$) samples are significantly below this range.

As can be seen in Table 4 and Table 5 **antimony** mainly occurs in the coarse particle fraction of the particulate matter. Antimony is mainly used in alloys for motor bearings, brake linings, batteries and solders²⁶. Antimony compounds are used in the vulcanization of rubber (e.g. for tires), the manufacture of flame retardants as well as in fireworks, ammunition, ceramics and glass²⁶. Coal-fired power plants, smelters, volcanoes and vehicle emissions release antimony oxides into the environment²⁶. According to E. Merian et al.²⁶ in the air over Chicago antimony concentrations in the range of 1.4 to 55 ng/m^3 have

been measured. Thus, the average antimony concentrations presented in this work for PM₁₀ (average: 4.95 ± 1.65 ng/m³) and PM_{2.5} (average: 2.09 ± 0.723 ng/m³) samples are comparable to these results.

By comparing Table 4 and Table 5 it can be concluded that **tin** has nearly equal parts occurring in the fine and the coarse particle fraction of the particulate matter. Tin is mainly used for tinning of metals, welding alloys and the production of various chemical products²⁶. Inorganic tin compounds as well as organotin compounds possess a wide field of applications, for example in the textile industry, the electronics industry, the pharmaceutical industry, the plastics industry, in various plating processes, tin-plate electrolysis as well as for agrochemicals²⁶.

As can be concluded from Table 4 and Table 5 **nickel** mainly occurs in the fine particle fraction of the particulate matter. Nickel is used for the manufacturing of Ni-Cd batteries, in electroplating, in pigments for paints and ceramics, in rods for arc welding, in surgical and dental prostheses, in magnetic tapes and computer components as well as in Ni-catalysts^{26,27}. Furthermore nickel alloys are used for corrosion resistant equipment (e.g. Cr-Ni-steel), food processing and cooking utensils, chemical and petroleum equipment, coinage, magnets and aircraft parts^{26,27}. Nickel is emitted into the environment by natural sources, like volcanoes and windblown dust produced by weathering of rocks and soils, as well as anthropogenic sources, such as the combustion of fossil fuels, mining and refining operations, metal consumption in industrial processes and waste incineration²⁶. The "4. Luftqualitäts-Tochterrichtlinie 2004/107/EG", which is in force since 2005, defines a target value of 20 ng/m³ (yearly mean value) for nickel in PM₁₀ samples⁶. According to the Austrian Umweltbundesamt GmbH (W. Spangl et al.)⁶ the yearly mean values of the nickel concentrations in PM₁₀ samples measured in urban areas in Austria were for the year 2004 in the range of 1.69 – 3.37 ng/m³. Thus, the average nickel concentration presented in this work for PM₁₀ samples (average: 2.20 ± 0.993 ng/m³) is within this range.

By comparing Figure 14 and Figure 15 as well as Table 4 and Table 5 it can be concluded that **molybdenum** has nearly equal parts occurring in the fine and the coarse particle fraction of the particulate matter. Molybdenum is mainly used for the production of alloys, e.g. the addition of molybdenum to steel alloys increases their strength as well as thermal and corrosion resistance, as necessary in gas and steam turbines used for power generation, in aircrafts and missiles²⁶. Molybdenum compounds are used as catalysts for desulphurization of petroleum, petrochemicals and coal-delivered liquids, as lubricants (especially MoS₂), flame retardants, smoke repressants and molybdenum pigments²⁶. Molybdenum concentrations in ambient air are usually rather low²⁶. However, in the vicinity of fossil fuel combustion sites, elevated molybdenum concentrations can be measured²⁶. According to E. Merian et al.²⁶ molybdenum concentrations in urban areas were found to

be in the range of 10 - 30 ng/m³. Thus, the average molybdenum concentrations presented in this work for PM₁₀ (average: 1.97 ± 0.829 ng/m³) and PM_{2.5} (average: 0.875 ± 0.484 ng/m³) samples are significantly below this range.

As can be seen in Figure 14 and Figure 15 only few data are available for **chromium**. Chromium is mainly used in metallurgical, chemical and refractory industries, e.g. for the production of stainless steel, the electroplating of chromium on other metals to impart corrosion resistance, decoration purposes as well as for forming bricks and shapes^{26,27}. Chromium compounds have a wide field of applications, including tanning, wood preservatives, metal finishing and pigments^{26,27}.

As can be concluded from Table 4 and Table 5 **cadmium** mainly occurs in the fine particle fraction of the particulate matter. Cadmium is used in pigments, plating (Cd-coated steel), batteries and as a stabilizer in polyvinyl chloride (e.g. for outdoor window frames)^{26,27}. Cadmium emission is limited to the production of the heavy metal as well as to cadmium plating and technical applications as welding, since in batteries, pigments and polyvinyl chloride, cadmium is tightly bound to the matrix^{26,27}. In Austria cadmium is mainly emitted by the combustion of heavy fuel oil, coal, coke and household waste⁵. The “4. Luftqualitäts-Tochterrichtlinie 2004/107/EG”, which is in force since 2005, defines a target value of 5 ng/m³ (yearly mean value) for cadmium in PM₁₀ samples⁶. According to the Austrian Umweltbundesamt GmbH (W. Spangl et al.)⁶ the yearly mean values of the cadmium concentrations in PM₁₀ samples measured in urban areas in Austria were for the year 2004 in the range of 0.18 – 0.37 ng/m³, thus being significantly below the above mentioned target value. These values however, do not include data from Vienna. For PM₁₀ samples in Vienna average cadmium concentration in the range of 0.40 – 0.56 ng/m³ were found in 2002⁶. Thus, the average cadmium concentration presented in this work for PM₁₀ samples (average: 0.494 ± 0.153 ng/m³) is within this range, but above the concentration range found in 2004 for other urban areas in Austria.

By comparing Table 4 and Table 5 it can be concluded that **cobalt** has nearly equal parts occurring in the fine and the coarse particle fraction of the particulate matter. Cobalt is mainly used for steel making and in alloys, such as the so-called superalloys, which are used for machines operating at high temperatures like jet engines and gas turbines²⁶. Cobalt compounds are used for glasses, ceramic glazes, pigments and as chemical catalyst²⁶.

By comparing Figure 16 and Figure 17 as well as Table 4 and Table 5 it can be concluded that **silver, thallium and mercury** mainly occur in the fine particle fraction of the particulate matter. **Silver** is used in electrical circuit boards, batteries, clinical applications, jewellery, adornment and decoration, dental amalgams and other alloys²⁶. Silver

compounds are used for photographic industry, as explosives and to “produce” rain (especially from hail bearing clouds)²⁶.

Thallium alloys and its compounds are used for semiconductor materials, low-temperature thermometers, low-melting point glasses with a high refractive index, and until recent years as rodenticide^{26,27}. However, the main anthropogenic emissions into the environment are caused by some industrial processes and the combustion of some types of coal²⁶.

Mercury and its compounds are used in the chloro-alkali production, in batteries, dental amalgams, batteries, electric and electronic switches, pharmaceuticals and so on^{26,27}. In Austria mercury is mainly emitted into the environment by the combustion of heavy fuel oil, coke, coal, refinery residues and fire wood as well as by industrial production⁵. Major natural emissions sources for mercury are volcanoes²⁷. According to E. Merian et al.²⁶ atmospheric concentrations of mercury in urban areas are in the range of 10 to 170 ng/m³, thus being significantly higher than the average mercury concentrations presented in this work for PM₁₀ (average: 0.0599 ± 0.0485 ng/m³) and PM_{2.5} (average: 0.0451 ± 0.0299 ng/m³) samples.

2.2.1.2 Daily intake

To determine the amount of trace and heavy metals, which is inhaled day after day by a healthy adult, the concentrations of these metals in the sample air were multiplied with the average air volume an adult is breathing each day. A healthy adult was estimated to possess an average respiratory rate of 15 breathes per minute (without physical strain) and a respiration volume of 0.5 – 0.8 Litre per breath (dependent on the body weight, whereat per kg body weight a respiration volume per breath of about 10 mL has to be reckoned with)^{28,29}. Thus, by assumption of an average body weight of 70 kg, a respiration volume of 0.7 L was obtained. The multiplication of this value with the above mentioned average respiratory rate results in an average respiration volume of 10.5 Litre per minute or 15.12 m³ per day. The latter value was used to determine the average daily intake [ng] of trace and heavy metals for an adult as listed in Table 7 and Table 8 for PM₁₀ and PM_{2.5} samples, respectively. For example, the average daily intake calculated for PM₁₀ samples, was 1058 ± 350 ng for zinc and 383 ± 124 ng for copper, whilst for PM_{2.5} samples it was 887 ± 367 ng for zinc and 145 ± 49.7 ng for copper. However, since the average respiratory rate and the respiration volume vary considerably for each human individual, the values given in Table 7 and Table 8 are expected to be afflicted with a high standard uncertainty. For estimation of this error the total combined uncertainty of the results obtained by Equation 1, was calculated according to EURACHEM/CITAC³⁰. Table 6 gives the values and standard uncertainties as well as the individual contribution of the different quantities to the total combined uncertainty.

Equation 1: Calculation of the average daily intake by inhalation M_T [ng], where $c_{Aerosol}$ [ng/m³] represents the concentration of the respective metal in the sample-air, $c_{digestion}$ [ng/mL] represents the concentration of the respective metal in the sample solution after total digestion, $V_{digestion}$ [mL] represents the volume of the sample solution after total digestion, $V_{air\ filterhalf}$ [m³] represents the air-volume that was sucked through the respective filter-half and F_{Resp} [min⁻¹] as well as V_{Resp} [m³] represent the average respiratory rate and the respiration volume of a healthy adult, respectively. To give the average number of breathes per day the respiratory rate is multiplied with a factor of $60 \cdot 24 = 1440$, which is the length of a day in minutes.

$$M_T = c_{Aerosol} \cdot V_{Resp} \cdot F_{Resp} \cdot 60 \cdot 24 \quad \text{with} \quad c_{Aerosol} = c_{digestion} \cdot \frac{V_{digestion}}{V_{air\ filterhalf}}$$

Table 6: Calculation of the total combined uncertainty of the average daily intake by inhalation, which is given with a coverage factor of 2 (being equivalent to the twofold standard deviation or 95 % significance when assuming a Gaussian distribution). For this purpose the standard uncertainties of each parameter used in Equation 1, and thus its contribution to the total combined uncertainty, were estimated by using the values of a specific sample (sample F5_10; for $c_{digestion}$ and $c_{Aerosol}$ the values of Mn in this sample were used).

Quantity	Value	Standard Uncertainty	Uncertainty Contribution	Contribution to total combined uncertainty
V_T	15.12 m ³	3.72 m ³		
F_{Resp}	15	3	33 ng	54,90%
V_{Resp}	$700 \cdot 10^{-6}$ m ³	$100 \cdot 10^{-6}$ m ³	23 ng	28,00%
$c_{Aerosol}$	10.85 ng/m ³	1.21 ng/m ³		
$c_{digestion}$	73.8 ng/mL	7.38 ng/mL	16 ng	13,70%
$V_{digestion}$	5.1222 mL	$2.96 \cdot 10^{-3}$ mL	0.095 ng	0,00%
$V_{airfilterhalf}$	34.84 m ³	1.74 m ³	-8.2 ng	3,40%

Total combined uncertainty of average daily intake by inhalation: 54 % (coverage factor 2)

Table 7: Average daily intake [ng] by inhalation of the PM₁₀ fraction of the assayed trace and heavy metals for an adult. *Italic* typed values are based on concentration-values between the LOD and the LOQ of the respective element. The values in the magenta colored cells are based on concentration-values that lie outside of the selected calibration range for the total digestion samples. The values in the red colored cells are based on concentration-values that are outliers according to the Grubbs-outlier-test. Outliers and values outside the calibration range were not used for the calculation of the average, the standard deviation (STD) or the relative standard deviation (RSD).

Analyte:	⁴⁷ Ti	⁵⁵ Mn	⁵⁹ Co	⁶⁵ Cu	⁶⁶ Zn	⁹⁸ Mo	¹⁰⁷ Ag	¹¹¹ Cd	¹¹⁸ Sn	¹²¹ Sb	²⁰² Hg	²⁰⁵ Tl	²⁰⁸ Pb	⁵² Cr_1	⁶⁰ Ni_1
Sample	Daily intake [ng]	Daily intake [ng]													
F5_10		164	3,93	517	1272	57,8	<i>1,17</i>	9,51	75,3	96,3	<i>0,157</i>	0,859	314		76,6
F6_10	<i>197</i>	178	2,45	479	779	41,9	<i>0,740</i>	4,25	69,3	96,0	<i>0,519</i>	0,390	144		54,9
F7_10	295	284	5,08	676	1561	56,5	<i>1,40</i>	10,6	105	133	<i>1,28</i>	0,609	200		53,9
F8_10	<i>433</i>	197	3,15	349	1212	26,0	<i>2,10</i>	7,99	58,7	73,4	<i>0,331</i>	1,52	233		38,4
F9_10		159	2,80	282	767	20,9		4,82	49,0	54,6		0,858	130		181
F10_10		166	2,23	268	1110	20,0	<i>0,840</i>	9,01	55,7	58,9		2,34	261		19,9
F11_10		209	11,7	310	1822	21,4	<i>1,38</i>	12,9	55,3	62,6	<i>0,939</i>	3,54	402		28,3
F12_10		82,4	1,56	220	889	15,7		10,2	37,0	49,8		2,33	243		15,0
F13_10		186	7,22	452	1194	37,1	<i>1,82</i>	8,70	65,9	84,5	<i>1,21</i>	0,568	155		56,0
F14_10		164	2,77	414	855	32,6	<i>0,732</i>	7,08	63,7	81,5	<i>0,363</i>	0,570	163		35,0
F15_10	<i>330</i>	108	3,77	273	517	20,4	<i>0,995</i>	6,28	46,9	53,2	<i>0,133</i>	0,247	81,6		15,6
F17_10	<i>209</i>	200	2,97	484	976	40,6	<i>0,583</i>	7,70	75,6	94,3	<i>0,740</i>	0,473	139		46,4
F18_10		103	1,59	299	689	26,8	<i>1,04</i>	6,07	50,7	57,0	<i>1,01</i>	0,451	130		36,1
F19_10	<i>394</i>	163	2,41	382	745	28,9		4,24	60,2	71,8	<i>0,297</i>	0,307	78,2		20,4
F20_10	253	110	3,79	195	498	17,1		4,56	31,3	35,3	<i>0,458</i>	0,214	79,5		33,7
F21_10	387	124	3,90	402	17717	25,5		6,48	41,2	47,7	2,24	0,377	109		30,7
F22_10	289	122	2,51	249	553	18,0		3,46	38,8	46,3	2,58	0,221	67,4		26,6
F23_10	266	157	2,98	291	883	21,1	<i>0,617</i>	5,97	46,6	58,1		0,950	183		31,2
F24_10		126	1,94	318	1131	23,8	<i>0,663</i>	10,1	51,5	67,6		2,15	284		21,5
F25_10	265	241	3,21	467	1565	408	<i>0,681</i>	13,9	74,3	93,7		4,04	323	26,6	35,0
F26_10	259	287	3,98	465	2517	273	<i>1,37</i>	24,1	84,3	107		8,31	582		28,7
F27_10	383	141	1,98	355	1044	651		9,80	77,0	398		1,78	246	5,72	8,39
F28_10	807	417	6,83	701	1444	408	<i>1,16</i>	11,3	115	132		0,970	237	48,7	122
F29_10	979	265	3,73	447	1270	442	<i>1,26</i>	10,6	86,5	83,4		0,764	218		31,9
F30_10	930	246	3,76	373	1421	417	<i>0,967</i>	12,5	63,5	74,6		1,54	276	2,65	27,0
F31_10	387	231	3,93	383	1293	518	<i>0,659</i>	11,9	62,7	76,4		1,99	251	6,75	30,4
F32_10n	373	210	3,27	285	969	43,1	<i>0,650</i>	7,55	44,5	57,2	<i>1,34</i>	1,36	233	0,303	29,9
Average	413	178	3,37	383	1058	29,8	1,04	7,47	62,4	74,8	0,906	0,994	199	15,1	33,3
STD	238	56,9	1,37	124	350	12,5	0,421	2,32	20,0	24,9	0,733	0,704	86,2	18,9	15,0
RSD [%]	57,7	32,0	40,6	32,4	33,1	42,1	40,4	31,1	32,0	33,3	80,9	70,9	43,3	125	45,2

Table 8: Average daily intake [ng] by inhalation of the PM_{2.5} fraction of the assayed trace and heavy metals for an adult. *Italic* typed values are based on concentration-values between the LOD and the LOQ of the respective element. The values in the magenta colored cells are based on concentration-values that lie outside of the selected calibration range for the total digestion samples. The values in the red colored cells are based on concentration-values that are outliers according to the Grubbs-outlier-test. Outliers and values outside the calibration range were not used for the calculation of the average, the standard deviation (STD) or the relative standard deviation (RSD).

Analyte:	⁴⁷ Ti	⁵⁵ Mn	⁵⁹ Co	⁶⁵ Cu	⁶⁶ Zn	⁹⁸ Mo	¹⁰⁷ Ag	¹¹¹ Cd	¹¹⁸ Sn	¹²¹ Sb	²⁰² Hg	²⁰⁵ Tl	²⁰⁸ Pb	⁵² Cr_1	⁶⁰ Ni_1
Sample	Daily intake [ng]	Daily intake [ng]													
F5_2.5		73,4	2,06	167	1042	30,7	<i>0,709</i>	7,70	28,8	34,9	<i>0,0786</i>	0,736	284		55,7
F6_2.5		72,0	1,31	175	577	18,3	<i>0,499</i>	3,46	26,6	38,8	<i>0,524</i>	0,341	118		37,4
F7_2.5		135	2,05	256	1182	20,5	<i>1,00</i>	8,73	42,3	51,4	<i>0,361</i>	0,591	170		37,1
F8_2.5		88,5	1,54	122	932	11,7	<i>2,08</i>	6,78	30,3	31,6		1,48	217		<i>19,5</i>
F9_2.5		64,1	1,20	89,3	<i>549</i>	<i>6,24</i>		3,33	20,8	<i>18,9</i>	<i>0,719</i>	0,808	113		60,8
F10_2.5		101	1,42	124	992	9,19	<i>1,04</i>	7,59	33,2	30,8		2,35	254		<i>18,5</i>
F11_2.5		152	8,63	146	1620	10,4	<i>1,32</i>	13,1	34,6	33,8	<i>0,721</i>	3,76	411		<i>21,5</i>
F12_2.5		45,4	1,36	80,5	850	9,31		7,81	17,4	22,8	<i>1,85</i>	2,29	234		<i>14,9</i>
F13_2.5		67,6	3,44	148	1096	11,9	<i>2,01</i>	7,52	21,6	27,1	<i>0,931</i>	0,579	143		44,3
F14_2.5	244	62,2	1,56	142	673	11,3		4,68	23,1	30,9		0,507	151		25,9
F15_2.5	263	58,0	1,22	125	476	8,62	<i>0,809</i>	5,14	23,1	22,4	<i>0,344</i>	0,243	75,1		<i>14,9</i>
F16_2.5		93,3	1,66	228	548	19,3		3,59	38,0	43,6	<i>0,917</i>	0,235	84,3		23,1
F18_2.5	222	54,8	1,60	121	552	62,4	<i>0,901</i>	4,78	19,7	20,2	<i>0,467</i>	0,437	109		244
F19_2.5	211	78,7	1,46	159	584	11,6		2,82	26,3	29,9	<i>0,253</i>	0,296	66,4		<i>14,5</i>
F20_2.5	251	71,3	3,39	86,6	423	9,31		3,49	18,2	14,7	2,82	0,218	73,7		22,4
F21_2.5	549	34,7	0,576	58,5	574	4,67		4,60	12,8	9,61	<i>1,05</i>	0,320	107		21,2
F22_2.5	1520	406	2,01	96,2	398	9,55	<i>0,716</i>	1,87	14,2	18,4	<i>0,653</i>	0,202	1098	453	115
F24_2.5		84,1	1,19	82,7	922	7,23	<i>0,695</i>	8,15	17,8	24,2		1,99	356	16,0	16,8
F25_2.5		132	1,99	180	1313	198	<i>0,844</i>	11,4	40,5	44,0		4,05	299	16,9	23,0
F26_2.5	449	179	2,01	150	1991	119	<i>1,11</i>	19,0	41,7	45,7		7,65	736	61,8	33,1
F27_2.5	315	78,9	1,22	130	871	333		7,59	43,1	333		1,68	235		
F28_2.5	786	167	2,95	248	1000	181	<i>1,08</i>	7,87	42,7	50,0		0,866	240	68,5	67,2
F29_2.5	722	117	2,50	150	960	195	<i>0,857</i>	8,31	45,2	30,8		0,764	196	30,2	16,8
F30_2.5	190	140	1,79	134	1094	257	<i>0,715</i>	9,97	28,1	29,9		1,44	302	46,3	18,8
F31_2.5	285	143	2,41	143	1059	377	<i>0,680</i>	8,63	31,9	36,0		1,97	229	22,1	19,7
F32_2.5	514	163	2,62	169	833	28,4		7,44	29,3	38,6		1,26	235	34,3	22,6
F33_2.5	316	143	1,94	210	849	284	<i>0,685</i>	8,29	41,1	43,9		0,403	156	77,4	34,9
Average	380	100	1,87	145	887	13,2	0,986	6,26	29,3	31,7	0,682	0,917	194	41,5	28,5
STD	194	41,9	0,694	49,7	367	7,31	0,433	2,31	9,92	10,9	0,452	0,705	92,9	23,1	15,0
RSD [%]	51,0	41,9	37,2	34,2	41,4	55,3	43,9	36,8	33,8	34,5	66,2	76,9	47,8	55,7	52,6

The extent to which airborne particles can penetrate the human respiratory tract is mainly determined by the particle size and shape. 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 can reach the pulmonary alveoli, where they can be deposited for month and years^{16,2}. Particles, which belong to the 2.5 - 10 μm particle size fraction, are mainly deposited in the tracheal and the bronchial region, from where they are transported relative fast (within hours) by the so-called mucociliary clearance adoral and are either coughed out or swallowed¹⁶. The latter fraction reaches the gastro-intestinal-tract (GIT), where it comes in contact with gastric juice, which main components are hydrochloric acid and pepsin. Since the gastric juice is the most acidic of the digestive juices, it is likely to yield the greatest fractions of soluble metal compounds or complexes¹⁷. Thus, the 2.5 - 10 μm particle size fraction of the investigated trace and heavy metals deserves closer attention. Therefore the total daily-amount of this fraction, which was collected by the filter samples, was calculated according to Equation 2 for each metal (see Table 9).

Equation 2: Calculation of the daily amount $D_{2.5-10\mu\text{m}}$ [ng] of the 2.5 - 10 μm particle size fraction, which was collected by the filter samples, where $c_{\text{PM}_{10}}$ [ng/mL] and $c_{\text{PM}_{2.5}}$ [ng/mL] represent the measured metal concentrations in the corresponding PM_{10} and $\text{PM}_{2.5}$ samples; $V_{\text{sample PM}_{10}}$ [mL] and $V_{\text{sample PM}_{2.5}}$ [mL] represent the sample volume of those PM_{10} and $\text{PM}_{2.5}$ samples; $w_{\text{filter PM}_{10}}$ [mg] and $w_{\text{filter PM}_{2.5}}$ [mg] represent the weight of the respective PM_{10} and the $\text{PM}_{2.5}$ filter as well as $w_{\text{filter half PM}_{10}}$ [mg] and $w_{\text{filter half PM}_{2.5}}$ [mg] represent the weight of the corresponding PM_{10} and $\text{PM}_{2.5}$ filter halves, respectively.

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

Furthermore, the average daily intake by inhalation of this particle fraction was calculated – for a healthy adult – by subtraction of the average daily intake of the $\text{PM}_{2.5}$ fraction from the average daily intake of the PM_{10} fraction (for detailed results see Table 10), thus ranging from 0.0568 ± 0.0457 ng for thallium to 243 ± 91.5 ng for copper.

Table 9: Total daily-amount [ng] of the 2.5 - 10 µm particle size fraction, which was collected by the filter samples. *Italic* typed values are based on concentration-values (either PM₁₀ or PM_{2.5}) between the LOD and the LOQ of the respective element. The values in the magenta colored cells are based on concentration-values (either PM₁₀ or PM_{2.5}) that lie outside of the selected calibration range for the total digestion samples. The values in the red colored cells are outliers according to the Grubbs-outlier-test. Outliers and values outside the calibration range were not used for the calculation of the average, the standard deviation (STD) or the relative standard deviation (RSD).

Analyte:	⁴⁷ Ti	⁵⁵ Mn	⁵⁹ Co	⁶⁵ Cu	⁶⁶ Zn	⁹⁸ Mo	¹⁰⁷ Ag	¹¹¹ Cd	¹¹⁸ Sn	¹²¹ Sb	²⁰² Hg	²⁰⁵ Tl	²⁰⁸ Pb	⁵² Cr_1	⁶⁰ Ni_1
Sample	Daily amount [ng]	Daily amount [ng]													
F5		396	8,03	1554	811	117	<i>1,96</i>	6,48	206	272	<i>0,341</i>	0,393	72,2		82,5
F6	<i>698</i>	362	3,80	1045	616	80,4	<i>0,765</i>	2,20	146	196		0,115	72,0		55,4
F7	<i>1198</i>	578	11,9	1658	1299	143	<i>1,40</i>	5,75	245	320	<i>3,66</i>		90,3		60,8
F8	<i>1722</i>	414	6,08	876	931	54,5		3,45	107	160	<i>1,32</i>		23,1		71,7
F9		366	6,12	745	757	56,8		5,26	108	138		0,0359	43,1		464
F10		234	2,89	536	266	40,0		4,03	80,9	103					1,77
F11		190	10,2	613	476	41,2			74,2	106	<i>0,711</i>				22,3
F12		132	0,486	517		22,8		7,69	71,5	98,7					
F13		435	13,7	1125	165	93,3		3,05	164	213	<i>0,892</i>		19,2		36,1
F14		375	4,31	1008	563	78,9	<i>2,78</i>	8,24	150	186	<i>1,38</i>	0,144	17,6		29,4
F15	<i>208</i>	181	9,65	550	<i>64,2</i>	43,9	<i>0,567</i>	3,45	87,7	<i>115</i>			10,7		
F18		177		674	428		<i>0,379</i>	4,10	118	<i>140</i>	<i>2,05</i>		60,7		
F19	<i>670</i>	311	3,37	835	<i>512</i>	64,7		4,97	127	157	<i>0,125</i>		32,9		20,1
F20		139	0,884	414	<i>217</i>	29,0		3,53	48,3	78,6			8,33		40,3
F21		299	11,2	<i>1159</i>	<i>58165</i>	69,9		5,58	94,6	<i>128</i>	3,86	0,138			28,5
F22			1,57	588	536	31,8		5,94	94,8	<i>107</i>	<i>7,50</i>	0,0347			
F24		143	2,64	874	614	<i>61,2</i>		5,70	124	159		0,245			14,9
F25	<i>1012</i>	391	4,26	1065	714	<i>766</i>		<i>7,37</i>	121	182			34,2	34,1	<i>41,2</i>
F26		358	6,78	1116	1545	<i>540</i>	<i>0,742</i>	<i>14,8</i>	147	213		<i>1,03</i>			
F27	<i>202</i>	222	2,69	840	496	<i>1158</i>		7,01	122	<i>185</i>		0,0382		22,0	32,2
F28		<i>943</i>	14,6	1718	1535	<i>848</i>	<i>0,124</i>	11,7	273	311		0,236			<i>201</i>
F29	<i>847</i>	543	4,23	1107	1001	<i>907</i>	<i>1,38</i>	7,12	149	195			47,8		54,4
F30	<i>2793</i>	378	7,19	886	1039	<i>564</i>	<i>0,828</i>	<i>7,79</i>	130	165		0,0958			27,5
F31	<i>334</i>	306	5,31	886	691	<i>463</i>		<i>10,7</i>	111	147			42,3		37,0
F32		148	1,97	410	356	50,1	<i>2,46</i>		51,8	62,9	<i>5,06</i>	0,146			23,2
Average	968	308	5,99	912	680	63,4	1,22	5,68	126	165	2,44	0,147	41,0	28,1	37,7
STD	796	128	4,05	358	400	31,7	0,865	2,28	53,7	66,8	2,32	0,109	25,2	8,58	20,5
RSD [%]	82,1	41,6	67,5	39,3	58,9	50,1	71,1	40,2	42,6	40,6	94,7	73,9	61,4	30,6	54,4

Table 10: Average daily intake [ng] by inhalation of the 2.5 - 10 µm particle size fraction of the assayed trace and heavy metals for an adult. *Italic* typed values are based on concentration-values (either PM₁₀ or PM_{2.5}) between the LOD and the LOQ of the respective element. The values in the magenta colored cells are based on concentration-values (either PM₁₀ or PM_{2.5}) that lie outside of the selected calibration range for the total digestion samples. The values in the red colored cells are outliers according to the Grubbs-outlier-test. Outliers and values outside the calibration range were not used for the calculation of the average, the standard deviation (STD) or the relative standard deviation (RSD).

Analyte:	⁴⁷ Ti	⁵⁵ Mn	⁵⁹ Co	⁶⁵ Cu	⁶⁶ Zn	⁹⁸ Mo	¹⁰⁷ Ag	¹¹¹ Cd	¹¹⁸ Sn	¹²¹ Sb	²⁰² Hg	²⁰⁵ Tl	²⁰⁸ Pb	⁵² Cr_1	⁶⁰ Ni_1
Sample	Daily intake [ng]	Daily intake [ng]													
F5		90,6	1,86	349	230	27,1	<i>0,465</i>	1,81	46,5	61,4	<i>0,0787</i>	0,123	30,1		20,9
F6	<i>197</i>	106	1,14	304	203	23,6	<i>0,241</i>	0,795	42,6	57,2		0,0495	26,2		17,5
F7	295	149	3,03	421	379	36,1	<i>0,396</i>	1,85	62,4	81,2	<i>0,917</i>	0,0181	30,7		16,8
F8	<i>433</i>	108	1,61	226	280	14,3	<i>0,0225</i>	1,21	28,4	41,8	<i>0,331</i>	0,0413	16,6		<i>19,0</i>
F9		95,3	1,60	192	<i>218</i>	<i>14,6</i>		1,49	28,1	35,6		0,0495	16,5		120
F10		65,5	0,816	144	118	10,8		1,42	22,5	28,0			6,68		<i>1,38</i>
F11		56,4	3,04	164	203	11,1	<i>0,0563</i>		20,7	28,8	<i>0,218</i>				6,78
F12		37,0	0,195	139	38,8	6,42		2,40	19,6	27,0		0,0424	8,79		<i>0,0238</i>
F13		118	3,78	304	98,2	25,2		1,18	44,3	57,4	<i>0,282</i>		12,2		11,7
F14		102	1,21	273	<i>182</i>	21,3	<i>0,732</i>	2,40	40,6	50,5	<i>0,363</i>	0,0632	12,2		<i>9,05</i>
F15	<i>66,9</i>	49,6	2,55	148	<i>40,4</i>	11,7	<i>0,186</i>	1,15	23,8	30,7		0,00437	6,52		<i>0,718</i>
F18		48,0		178	<i>137</i>		<i>0,142</i>	1,29	31,0	36,7	<i>0,547</i>	0,0137	20,9		
F19	<i>183</i>	83,9	0,941	223	<i>161</i>	17,2		1,42	34,0	41,8	<i>0,0449</i>	0,0114	11,8		5,89
F20	<i>2,10</i>	38,5	0,393	109	<i>75,9</i>	7,79		1,07	13,1	20,6			5,78		<i>11,3</i>
F21		89,6	3,32	<i>344</i>	<i>17144</i>	20,8		1,87	28,5	<i>38,1</i>	<i>1,19</i>	0,0567	2,70		9,45
F22			0,497	153	<i>155</i>	8,49		1,59	24,6	27,9	<i>1,92</i>	0,0188			
F24		42,2	0,758	236	209	<i>16,6</i>		1,92	33,7	43,4		0,164			4,78
F25	<i>265</i>	109	1,21	288	252	<i>210</i>		<i>2,50</i>	33,8	49,7			23,9	9,77	<i>11,9</i>
F26		108	1,97	315	526	<i>155</i>	<i>0,260</i>	<i>5,04</i>	42,5	61,0		<i>0,665</i>			
F27	<i>68,3</i>	61,7	0,761	225	<i>173</i>	<i>318</i>		2,21	33,9	<i>64,9</i>		0,0942	10,8	5,72	8,39
F28	<i>21,1</i>	<i>250</i>	3,88	453	444	<i>227</i>	<i>0,0857</i>	3,39	72,2	82,2		0,104			<i>55,0</i>
F29	258	148	1,23	297	310	<i>247</i>	<i>0,403</i>	2,28	41,3	52,5		0,0000548	22,3		<i>15,1</i>
F30	<i>740</i>	106	1,97	238	326	<i>160</i>	<i>0,252</i>	<i>2,53</i>	35,4	44,8		0,0971			<i>8,13</i>
F31	<i>102</i>	87,5	1,52	240	235	<i>141</i>		<i>3,25</i>	30,8	40,4		0,0260	22,6		<i>10,7</i>
F32		47,2	0,652	117	<i>136</i>	14,7	<i>0,650</i>	0,109	15,1	18,6	<i>1,34</i>	0,102			7,25
Average	219	84,6	1,66	243	214	16,9	0,299	1,67	34,0	44,1	0,657	0,0568	16,0	7,75	9,84
STD	208	33,2	1,08	91,5	120	7,90	0,221	0,735	13,5	16,8	0,605	0,0457	8,65	2,86	5,92
RSD [%]	94,7	39,2	64,9	37,6	56,0	46,7	73,7	44,0	39,8	38,2	92,1	80,4	54,2	36,9	60,2

2.2.2 Extraction samples

To determine the bioaccessible metal fraction, which is defined for the present work as the maximal amount of a metal that is soluble in a synthetic gastric fluid and therefore potentially available for the uptake across the intestinal lumen¹⁷, the second filter half of each filter was subjected to a batch-extraction procedure as described in the experimental section. Being the most acidic of the digestive juices, gastric juice is likely to yield the greatest fractions of soluble metal compounds or complexes¹⁷. Thus, the used extraction procedure can be characterised as an easy to handle, but nevertheless effective model to estimate the solubility of trace and heavy 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^{31,32} and the use of synthetic saliva³³. 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 probably hamper analysis by ICP-MS.

2.2.2.1 Concentrations

The amount of trace and heavy metals per cubic metre air volume, which was derived by analysis of the extraction samples, is listed in Table 11 (PM₁₀) and Table 12 (PM_{2.5}) for each investigated element. The values in these tables were obtained by multiplying the measured mean concentration [$\mu\text{g/L}$] of the extracted samples with the corresponding sample volume [g] and dividing by the air volume [m^3], which was sucked through the respective filter-half. The thus obtained results for the average concentrations of the assayed metals in the sample-air ranged for PM₁₀ samples from $0.0422 \pm 0.0188 \text{ ng/m}^3$ for silver to $50.5 \pm 17.2 \text{ ng/m}^3$ for zinc as well as for PM_{2.5} samples from $0.0365 \pm 0.0152 \text{ ng/m}^3$ for mercury to $41.7 \pm 15.0 \text{ ng/m}^3$ for zinc. The daily-amount of the 2.5 - 10 μm particle size fraction, which was extracted from the filter samples, was calculated according to Equation 2 for each metal as described above (see Table 13), thus ranging from $0.160 \pm 0.197 \text{ ng}$ for thallium to $621 \pm 228 \text{ ng}$ for copper.

Table 11: Concentrations [ng/m³] of the assayed metals in the respective sample-air, which were obtained by the extraction of the PM₁₀-filter-samples with synthetic gastric fluid. *Italic* typed values are between the limit of detection (LOD) and the limit of quantification (LOQ) of the respective element. The values in the magenta colored cells lie outside of the selected calibration range. The values in the red colored cells are outliers according to the Grubbs-outlier-test. Outliers and values outside the calibration range were not used for the calculation of the average, the standard deviation (STD) or the relative standard deviation (RSD).

Analyte:	⁴⁷ Ti	⁵⁵ Mn	⁵⁹ Co	⁶⁵ Cu	⁶⁶ Zn	⁹⁸ Mo	¹⁰⁷ Ag	¹¹¹ Cd	¹¹⁸ Sn	¹²¹ Sb	²⁰² Hg	²⁰⁵ Tl	²⁰⁸ Pb	⁵² Cr_1	⁶⁰ Ni_1
Sample	Conc. Mean [ng/m ³]														
F5G_10	0,850	6,96	0,121	27,7	67,2	2,19	0,0336	0,530	1,05	2,93	0,0387	0,0471	19,2	0,838	3,08
F6G_10	1,17	7,39	0,0888	26,2	40,7	0,875	0,0256	0,253	0,601	2,04	0,0360	0,0201	8,25	0,630	2,48
F7G_10	2,85	11,8	0,179	38,2	87,6	1,19	0,0503	0,612	1,05	2,94	0,0931	0,0339	12,2	0,960	3,54
F8G_10	1,89	6,97	0,0970	16,3	59,7	0,586	0,0929	0,482	0,739	1,89	0,0519	0,0829	13,7	0,606	1,96
F9G_10	1,80	6,75	0,0830	14,7	37,0	0,463	<LOD	0,290	0,597	1,36	0,0215	0,0485	7,52	0,823	3,73
F10G_10	2,50	7,15	0,0885	15,9	59,5	0,552	0,0484	0,549	0,927	1,94	0,0508	0,134	15,9	0,644	4,34
F11G_10	1,78	6,17	0,231	13,7	76,2	0,523	0,0487	0,718	0,680	1,61	0,111	0,178	21,6	0,810	1,55
F12G_10	1,20	2,53	0,0445	9,70	43,5	0,355	<LOD	0,504	0,419	1,38	0,0377	0,120	13,2	0,355	1,28
F13G_10	1,78	7,48	0,171	23,3	60,7	0,731	0,0791	0,522	0,609	1,91	0,0413	0,0323	8,95	0,686	2,43
F14G_10	1,50	5,07	0,0765	17,9	38,2	0,581	<LOD	0,353	0,514	1,75	0,0471	0,0289	8,74	0,475	3,44
F15G_10	1,64	5,07	0,0777	16,6	27,5	0,478	0,0385	0,394	0,416	1,31	0,0477	0,0135	4,91	0,442	1,26
F16G_10	2,23	5,81	0,0747	21,9	31,3	0,740	0,0269	0,304	0,660	1,97	0,0377	0,0132	5,17	0,643	1,80
F17G_10	1,90	7,07	0,0929	22,8	45,0	0,892	0,0376	0,426	0,713	2,02	0,0605	0,0204	7,49	0,835	2,47
F18G_10	1,31	3,79	0,0441	16,1	35,8	0,601	0,0450	0,356	0,491	1,44	0,0577	0,0230	6,71	0,426	0,852
F19G_10	1,53	6,35	0,0630	19,7	33,5	0,497	0,0310	0,238	0,461	1,42	0,0502	0,0135	4,37	0,648	1,19
F20G_10	1,45	4,04	0,236	9,51	22,1	0,391	<LOD	0,298	0,374	1,06	0,0300	0,0112	4,57	0,554	1,79
F21G_10	0,955	4,56	0,185	19,0	906	0,749	0,0240	0,398	0,382	1,13	0,0242	0,0271	6,38	0,893	2,26
F22G_10	1,20	4,39	0,0555	13,8	33,9	0,330	<LOD	0,200	0,237	0,955	0,0227	0,0108	4,43	0,299	3,74
F23G_10	1,32	5,67	0,0813	15,1	41,0	0,464	<LOD	0,331	0,527	1,54	0,0317	0,0460	10,1	0,569	1,10
F24G_10	0,779	4,09	0,0703	14,4	50,4	0,564	<LOD	0,577	0,610	1,88	0,0397	0,106	14,6	0,420	1,20
F25G_10	1,71	10,1	0,113	24,2	74,8	22,7	0,0221	0,895	1,05	2,85	0,0495	0,230	18,8	0,861	2,04
F26G_10	1,65	9,98	0,116	19,6	120	14,2	0,0597	1,45	1,20	3,26	0,0767	0,464	32,8	0,921	1,50
F27G_10	0,768	5,30	0,0700	19,1	46,5	38,3	<LOD	0,532	1,16	17,6	0,0284	0,0910	13,2	0,450	0,662
F28G_10	1,78	14,7	0,184	31,1	65,4	20,3	0,0351	0,651	1,10	2,66	0,0440	0,0485	12,4	1,17	3,51
F29G_10	1,84	9,65	0,111	20,7	69,7	24,0	0,0468	0,609	1,64	2,22	0,0490	0,0401	12,3	0,811	1,70
F30G_10	1,36	9,08	0,248	17,1	70,9	25,2	0,0332	0,809	0,921	2,13	0,0629	0,0912	16,4	0,589	0,935
F31G_10	1,18	6,52	0,0900	14,1	52,6	27,9	0,0237	0,646	0,682	1,84	0,0634	0,104	13,4	0,556	1,06
F32G_10	1,47	7,36	0,0854	12,5	41,0	1,68	<LOD	0,483	0,614	1,77	0,0331	0,0685	12,1	0,526	1,14
Average	1,55	6,85	0,114	19,0	50,5	0,609	0,0422	0,450	0,730	1,90	0,0455	0,0510	11,0	0,658	2,07
STD	0,487	2,63	0,0588	6,39	17,2	0,213	0,0188	0,145	0,319	0,604	0,0165	0,0377	4,87	0,208	1,05
RSD [%]	31,4	38,4	51,8	33,7	34,1	35,0	44,6	32,3	43,7	31,8	36,4	73,9	44,3	31,5	50,6

Table 12: Concentrations [ng/m³] of the assayed metals in the respective sample-air, which were obtained by the extraction of the PM_{2.5}-filter-samples with synthetic gastric fluid. *Italic* typed values are between the limit of detection (LOD) and the limit of quantification (LOQ) of the respective element. The values in the magenta colored cells lie outside of the selected calibration range. The values in the red colored cells are outliers according to the Grubbs-outlier-test. Outliers and values outside the calibration range were not used for the calculation of the average, the standard deviation (STD) or the relative standard deviation (RSD).

Analyte:	⁴⁷ Ti	⁵⁵ Mn	⁵⁹ Co	⁶⁵ Cu	⁶⁶ Zn	⁹⁸ Mo	¹⁰⁷ Ag	¹¹¹ Cd	¹¹⁸ Sn	¹²¹ Sb	²⁰² Hg	²⁰⁵ Tl	²⁰⁸ Pb	⁵² Cr_1	⁶⁰ Ni_1
Sample	Conc. Mean [ng/m ³]														
F5G_2.5	<LOD	2,81	0,0532	9,79	59,1	1,56	0,0244	0,497	0,522	1,40	0,0331	0,0432	16,8	0,402	1,26
F6G_2.5	0,0192	2,62	0,0470	9,30	30,5	0,517	0,0184	0,207	0,316	1,21	0,0201	0,0189	6,89	0,280	1,87
F7G_2.5	<LOD	3,96	0,0589	11,4	57,8	0,577	0,0325	0,511	0,595	1,48	0,0434	0,0298	9,30	0,434	0,838
F8G_2.5	<LOD	2,86	0,0460	5,66	45,7	0,310	0,0806	0,357	0,476	1,10	0,0287	0,0793	11,5	0,311	0,628
F9G_2.5	<LOD	3,01	0,0393	4,99	29,5	0,203	<LOD	0,186	0,450	0,748	0,0138	0,0474	6,92	0,279	0,802
F10G_2.5	<LOD	3,94	0,0544	6,45	51,9	0,290	0,0363	0,454	0,712	1,26	0,0420	0,130	14,7	0,428	0,678
F11G_2.5	<LOD	3,65	0,160	6,76	70,7	0,337	0,0508	0,642	0,556	1,16	0,103	0,187	21,7	0,434	0,242
F12G_2.5	<LOD	1,77	0,0363	3,88	41,3	0,190	<LOD	0,435	0,280	0,888	0,0423	0,124	12,9	0,215	0,207
F13G_2.5	<LOD	3,52	0,0917	9,10	59,4	0,342	0,0793	0,448	0,344	1,00	0,0309	0,0332	8,48	0,314	1,36
F14G_2.5	<LOD	2,20	0,0424	6,79	33,1	0,316	<LOD	0,281	0,301	1,02	0,0452	0,0293	8,52	0,227	0,472
F15G_2.5	0,199	2,69	0,0458	7,14	24,5	0,245	0,0419	0,324	0,346	0,681	0,0409	0,0130	4,53	0,224	0,521
F16G_2.5	0,184	3,88	0,0578	12,5	29,2	0,475	0,0448	0,217	0,437	1,26	0,0315	0,0136	8,45	0,488	2,09
F18G_2.5	0,0986	2,13	0,0297	6,64	26,4	0,314	0,0705	0,264	0,292	0,656	0,0530	0,0244	6,26	0,340	0,550
F19G_2.5	0,729	3,30	0,147	8,11	25,2	0,332	<LOD	<LOD	0,314	0,812	0,0374	0,0147	3,66	0,544	0,833
F20G_2.5	0,323	2,49	0,104	4,67	20,3	0,202	0,0496	0,208	0,210	0,532	0,0253	0,0112	3,82	0,353	1,28
F21G_2.5	<LOD	0,963	0,0174	2,94	19,5	0,193	<LOD	0,269	0,208	0,385	0,0156	0,0155	5,79	0,216	0,884
F22G_2.5	<LOD	2,13	0,0255	5,12	19,3	0,188	<LOD	<LOD	0,111	0,433	0,0203	0,0100	3,51	0,161	0,400
F24G_2.5	0,0745	2,32	0,0424	4,48	49,2	0,320	<LOD	0,545	0,391	1,11	0,0286	0,115	15,1	0,223	0,901
F25G_2.5	0,107	4,61	0,0656	8,65	62,6	10,7	0,0198	0,697	0,590	1,53	0,0429	0,224	16,8	0,577	1,24
F26G_2.5	0,0349	5,75	0,0765	7,97	102	6,51	0,0440	1,14	0,633	2,03	0,0719	0,444	29,8	0,526	2,97
F27G_2.5	0,00186	2,33	0,0391	5,92	43,8	20,2	<LOD	0,428	0,784	16,3	0,0207	0,0910	12,8	0,262	0,558
F28G_2.5	0,625	6,63	0,104	13,0	52,0	9,89	0,0352	0,521	0,710	1,65	0,0317	0,0486	11,4	0,691	2,60
F29G_2.5	0,659	4,05	0,0517	7,29	46,8	10,6	0,0346	0,525	1,05	1,15	0,0370	0,0406	10,6	0,378	0,777
F30G_2.5	0,227	5,54	0,0696	7,11	58,7	15,9	0,0280	0,694	0,600	1,40	0,0553	0,0827	14,6	0,355	1,82
F31G_2.5	1,18	4,89	0,0735	8,04	48,8	21,1	<LOD	0,512	0,554	1,31	0,0735	0,101	12,5	0,363	1,11
F32G_2.5	0,641	4,28	0,0539	7,10	36,2	1,18	<LOD	0,406	0,452	1,32	0,0409	0,0652	11,1	0,329	1,24
F33G_2.5	0,748	4,75	0,0609	11,7	42,7	16,7	0,0236	0,532	0,781	1,60	0,0234	0,0206	9,39	0,483	1,41
Average	0,366	3,45	0,0627	7,50	41,7	0,315	0,0420	0,411	0,482	1,12	0,0365	0,0501	10,3	0,364	1,09
STD	0,350	1,34	0,0337	2,58	15,0	0,116	0,0193	0,145	0,213	0,400	0,0152	0,0387	4,62	0,129	0,688
RSD [%]	95,7	38,7	53,7	34,5	35,9	36,7	45,9	35,3	44,2	35,7	41,6	77,3	44,8	35,4	62,8

Table 13: Daily-amount [ng] of the 2.5 - 10 µm particle size fraction, which was extracted from the filter samples. *Italic* typed values are based on concentration-values (either PM₁₀ or PM_{2,5}) between the LOD and the LOQ of the respective element. The values in the magenta colored cells are based on concentration-values (either PM₁₀ or PM_{2,5}) that lie outside of the selected calibration range. The values in the red colored cells are outliers according to the Grubbs-outlier-test. Outliers and values outside the calibration range were not used for the calculation of the average, the standard deviation (STD) or the relative standard deviation (RSD).

Analyte:	⁴⁷ Ti	⁵⁵ Mn	⁵⁹ Co	⁶⁵ Cu	⁶⁶ Zn	⁹⁸ Mo	¹⁰⁷ Ag	¹¹¹ Cd	¹¹⁸ Sn	¹²¹ Sb	²⁰² Hg	²⁰⁵ Tl	²⁰⁸ Pb	⁵² Cr_1	⁶⁰ Ni_1
Sample	Daily amount [ng]	Daily amount [ng]													
F5G	58,6	276	4,52	1202	353	38,5	<i>0,548</i>	0,544	34,7	101	0,275	0,121	109	28,6	<i>121</i>
F6G	61,4	249	2,11	883	464	17,8	<i>0,335</i>	1,88	14,4	41,2	0,798	0,0128	54,3	18,0	27,6
F7G	175	470	7,18	1617	1652	36,1	<i>0,994</i>	4,60	26,3	85,7	2,93	0,161	151	31,0	<i>164</i>
F8G	114	239	2,93	626	706	15,6	0,498	6,45	14,4	44,5	1,31		99,3	16,8	78,6
F9G	108	215	2,51	570	357	15,0		<i>5,67</i>	7,47	34,7	0,421		15,5	31,8	<i>173</i>
F10G	147	176	1,84	532	294	14,5	<i>0,604</i>	4,28	10,5	36,4	0,396		25,4	11,4	<i>212</i>
F11G	105	138	3,71	390	113	9,98		2,57	5,65	23,4	0,111			20,9	<i>76,3</i>
F12G	69,2	39,0	0,368	325	11,3	9,00		2,77	7,26	26,0				7,44	<i>61,4</i>
F13G	102	217	4,29	787		21,3		2,96	14,2	49,3	0,512		2,62	20,4	<i>57,3</i>
F14G	86,2	158	1,83	618	202	14,3		3,28	11,4	38,4				13,6	<i>169</i>
F15G	84,2	132	1,74	537	102	12,9		3,13	3,12	34,9	0,282		9,04	12,2	<i>42,0</i>
F16G	119	101	0,819	511	38,8	14,1		<i>4,44</i>	11,8	37,9	0,269			7,65	
F18G	71,4	92,2	0,765	539	476	16,0		4,65	10,9	44,2	0,122		7,80	4,05	<i>16,2</i>
F19G	45,0	169		655	416	8,71	<i>1,82</i>	14,0	7,73	33,6	0,638		30,8	4,53	<i>18,4</i>
F20G	66,8	85,1	7,61	276	50,0	10,7		<i>4,79</i>	9,20	29,9	0,207		33,3	11,0	<i>26,6</i>
F21G	49,1	183	8,58	819	45505	28,1	<i>1,23</i>	5,93	8,37	37,5	0,398	0,554	15,7	34,3	<i>68,4</i>
F22G	71,8	129	1,72	506	815	7,93		12,0	7,22	30,0	0,0815	0,0149	44,2	7,75	<i>199</i>
F24G	40,0	94,3	1,47	551		13,1		0,262	11,4	40,9	0,551			10,6	<i>14,2</i>
F25G	92,3	301	2,56	872	524	667	<i>0,0773</i>	9,46	25,0	71,9	0,257		68,1	14,8	<i>42,5</i>
F26G	88,3	216	1,94	618	701	406	<i>0,742</i>	13,8	29,6	62,2	0,0680		79,6	20,2	
F27G	44,5	166	1,68	747	32,0	992		4,83	19,3	32,0	0,390			10,1	<i>4,41</i>
F28G	66,1	453	4,43	1026	639	585		6,19	21,0	54,3	0,628		22,3	25,9	<i>46,2</i>
F29G	66,4	312	3,31	752	1192	745	<i>0,607</i>	3,31	31,2	58,7	0,588		64,0	23,9	<i>51,0</i>
F30G	65,1	189	10,1	557	533	495	<i>0,218</i>	4,65	16,9	38,1	0,279	0,250	59,6	12,5	
F31G		80,0	0,737	327	81,5	331	<i>1,36</i>	6,23	5,81	27,2			14,0	10,1	
F32G	45,6	164	1,65	290	170	24,7		3,27	8,00	21,9		0,00332	26,4	10,4	
Average	81,7	194	3,22	621	376	17,3	0,753	3,91	14,3	44,1	0,364	0,160	46,6	16,2	79,5
STD	33,1	105	2,60	228	308	8,78	0,511	1,76	8,67	19,2	0,206	0,197	39,2	8,70	65,7
RSD [%]	40,6	54,1	80,8	36,7	81,9	50,8	67,8	45,0	60,5	43,5	56,6	123	84,3	53,9	82,6

2.2.2.2 Extraction ratios

Based on the results derived for extractable and total PM₁₀ and PM_{2.5} concentrations the extraction ratios [%] of the assayed metals were determined (see Table 14 for PM₁₀ samples and Table 15 for PM_{2.5} samples as well as Figure 18) in accordance to Equation 3.

Equation 3: Calculation of the extraction ratio R [%] for the PM₁₀ and PM_{2.5} filter samples, where $c_{\text{extraction}}$ [ng/mL] represents the measured metal concentration in the extracted samples, and $c_{\text{digestion}}$ [ng/mL] represents the measured metal concentration in the corresponding totally digested samples; $V_{\text{extraction}}$ [mL] and $V_{\text{digestion}}$ [mL] represent the sample volume of the extracted and the totally digested samples; $w_{\text{filter half dig.}}$ [mg] and $w_{\text{filter half extr.}}$ [mg] represent the weight of the corresponding filter halves for the total digestion and extraction samples, respectively.

$$R = 100 \cdot \frac{c_{\text{extraction}} \cdot V_{\text{extraction}}}{c_{\text{digestion}} \cdot V_{\text{digestion}}} \cdot \frac{w_{\text{filter half dig.}}}{w_{\text{filter half extr.}}}$$

Furthermore the extraction ratio [%] for the 2.5 - 10 μm particle size fraction (see Table 16) was calculated according to Equation 4.

Equation 4: Calculation of the extraction ratio $R_{2.5-10 \mu\text{m}}$ [%] for the 2.5 - 10 μm particle size fraction, where $D_{2.5-10 \mu\text{m}, \text{extraction samples}}$ [ng] represents the daily amount of this particle size fraction, that was found in the extraction samples according to Equation 2, and $D_{2.5-10 \mu\text{m}, \text{digestion samples}}$ [ng] represents the corresponding amount of this particle size fraction in the totally digested samples, which was also determined according to Equation 2.

$$R_{2.5-10 \mu\text{m}} = 100 \cdot \frac{D_{2.5-10 \mu\text{m}, \text{extraction samples}}}{D_{2.5-10 \mu\text{m}, \text{digestion samples}}}$$

As depicted in Figure 18, the majority of the investigated metals show average extraction ratios above 50 % for PM₁₀ and PM_{2.5} samples. For the toxic heavy metals cadmium, thallium and lead average extraction ratios of over 75 % were obtained. As can be seen in Table 16 the average extraction ratios for the 2.5 - 10 μm particle size fraction, which are used to determine the bioaccessible daily fraction, are also quite high.

Table 14: Extraction ratios [%] of the assayed metals as determined according to Equation 3 for the PM₁₀ samples. *Italic* typed values are based on concentration-values (either of the extraction or of the total digestion samples) between the LOD and the LOQ of the respective element. The values in the magenta colored cells are based on concentration-values that lie outside of the selected calibration range. The values in the red colored cells are outliers according to the Grubbs-outlier-test. Outliers and values outside the calibration range were not used for the calculation of the average, the standard deviation (STD) or the relative standard deviation (RSD).

Analyte:	⁴⁷ Ti	⁵⁵ Mn	⁵⁹ Co	⁶⁵ Cu	⁶⁶ Zn	⁹⁸ Mo	¹⁰⁷ Ag	¹¹¹ Cd	¹¹⁸ Sn	¹²¹ Sb	²⁰² Hg	²⁰⁵ Tl	²⁰⁸ Pb	⁵² Cr_1	⁶⁰ Ni_1
Sample	Extr.- Ratio [%]														
F5_10		64,1	46,8	81,2	79,9	57,3	<i>43,3</i>	84,2	21,1	46,0	372	82,9	92,4		60,8
F6_10	8,95	62,9	54,7	82,9	78,9	31,6	52,3	89,8	13,1	32,1	105	77,7	86,7		68,4
F7_10	14,6	62,8	53,2	85,5	84,8	31,9	54,3	87,4	15,2	33,6	110	84,1	92,2		99,3
F8_10	6,60	53,5	46,6	70,9	74,5	34,1	66,8	91,2	19,0	39,0	237	82,3	89,0		77,3
F9_10		64,0	44,8	79,2	72,9	33,6		90,9	18,4	37,8		85,5	87,6		31,2
F10_10		65,0	60,0	89,3	81,1	41,7	87,2	92,2	25,1	49,8		86,9	92,1		330
F11_10		44,6	29,9	66,8	63,2	36,9	53,4	83,8	18,6	39,0	178	76,0	81,1		82,7
F12_10		46,4	43,2	66,7	74,1	34,1		74,7	17,2	42,0		78,0	81,9		130
F13_10		60,9	35,8	77,9	76,9	29,8	65,5	90,7	14,0	34,2	51,5	85,9	87,3		65,5
F14_10		46,7	41,7	65,3	67,6	27,0		75,3	12,2	32,4	196	76,6	81,1		149
F15_10	7,53	71,3	31,2	92,0	80,4	35,5	58,6	94,8	13,4	37,2	544	82,4	91,0		123
F17_10	13,7	53,4	47,3	71,3	69,8	33,3	97,4	83,7	14,2	32,3	124	65,2	81,5		80,5
F18_10		55,8	42,0	81,4	78,5	33,8	65,2	88,7	14,6	38,1	86,0	77,0	78,2		35,6
F19_10	5,87	59,0	39,6	77,9	68,0	26,0		84,7	11,6	30,0	255	66,3	84,5		87,9
F20_10	8,68	55,6	94,1	73,6	67,1	34,6		98,9	18,1	45,3	99,0	79,1	86,9		80,2
F21_10	3,73	55,5	71,8	71,5	77,3	44,5		92,9	14,0	35,9	16,3	109	88,3		111
F22_10	6,25	54,5	33,5	83,8	92,6	27,6		87,4	9,24	31,2	13,3	73,7	99,4		212
F23_10	7,50	54,8	41,2	78,5	70,2	33,3		83,8	17,1	39,9		73,3	83,6		53,1
F24_10		49,0	54,7	68,2	67,3	35,9		86,7	17,9	42,1		74,8	77,8		83,9
F25_10	9,77	63,2	53,3	78,2	72,3	84,2	49,1	97,2	21,4	46,1		86,2	88,2	48,9	88,3
F26_10	9,61	52,6	43,9	63,9	72,2	78,8	65,9	91,0	21,6	46,2		84,3	85,2		78,9
F27_10	3,03	57,0	53,5	81,3	67,4	89,0		82,2	22,7	67,0		77,4	81,4	119	119
F28_10	3,33	53,1	40,7	67,0	68,5	75,2	45,8	87,4	14,5	30,4		75,6	78,9	36,2	43,5
F29_10	2,84	55,0	45,1	69,9	83,0	82,1	56,2	86,9	28,7	40,3		79,4	85,1		80,4
F30_10	2,22	55,8	99,8	69,4	75,5	91,5	51,8	97,8	21,9	43,2		89,6	89,6	337	52,4
F31_10	4,60	42,8	34,6	55,7	61,5	81,6	54,3	82,1	16,5	36,5		78,6	80,6	125	53,0
F32_10n	5,96	53,0	39,4	66,4	63,9	58,8		96,7	20,9	46,9	37,5	75,9	78,6	2624	57,5
Average	6,94	56,0	45,1	74,7	73,5	36,1	60,4	87,9	17,5	38,8	162	78,6	85,6	133	79,7
STD	3,55	6,80	9,60	8,61	7,42	8,71	14,5	6,38	4,46	5,77	145	6,01	5,30	121	29,7
RSD	51,1	12,1	21,3	11,5	10,1	24,2	23,9	7,26	25,5	14,9	89,7	7,65	6,20	90,6	37,3

Table 15: Extraction ratios [%] of the assayed metals as determined according to Equation 3 for the PM_{2.5} samples. *Italic* typed values are based on concentration-values (either of the extraction or of the total digestion samples) between the LOD and the LOQ of the respective element. The values in the magenta colored cells are based on concentration-values that lie outside of the selected calibration range. The values in the red colored cells are outliers according to the Grubbs-outlier-test. Outliers and values outside the calibration range were not used for the calculation of the average, the standard deviation (STD) or the relative standard deviation (RSD).

Analyte:	⁴⁷ Ti	⁵⁵ Mn	⁵⁹ Co	⁶⁵ Cu	⁶⁶ Zn	⁹⁸ Mo	¹⁰⁷ Ag	¹¹¹ Cd	¹¹⁸ Sn	¹²¹ Sb	²⁰² Hg	²⁰⁵ Tl	²⁰⁸ Pb	⁵² Cr_1	⁶⁰ Ni_1
Sample	Extr.- Ratio [%]														
F5_2.5		57,9	39,0	88,6	85,8	76,6	52,1	97,6	27,4	60,6	637	88,7	89,3		34,2
F6_2.5		55,1	54,1	80,3	79,9	42,8	55,8	90,5	17,9	47,1	58,1	83,8	88,6		75,8
F7_2.5		44,3	43,4	67,2	73,9	42,7	48,9	88,6	21,3	43,4	182	76,2	82,9		34,1
F8_2.5		48,8	45,1	70,0	74,2	40,1	58,6	79,5	23,7	52,6		81,0	80,3		48,8
F9_2.5		71,0	49,6	84,5	81,4	49,2		84,5	32,7	59,8	28,9	88,7	92,4		20,0
F10_2.5		59,2	58,1	78,6	79,2	47,7	52,8	90,3	32,4	61,6		83,5	87,5		55,5
F11_2.5		36,2	28,0	69,9	66,0	49,2	58,1	74,1	24,3	51,9	217	75,3	79,8		17,0
F12_2.5		58,8	40,4	72,8	73,4	30,8		84,1	24,4	58,8	34,7	81,7	83,5		20,9
F13_2.5		78,8	40,3	93,0	82,0	43,4	59,6	90,0	24,1	55,8	50,1	86,7	89,8		46,4
F14_2.5		53,5	41,2	72,4	74,3	42,4		90,9	19,7	50,1		87,5	85,4		27,5
F15_2.5	1,14	70,2	56,7	86,1	77,8	43,1	78,4	95,5	22,6	45,9	180	81,3	91,3		53,1
F16_2.5		62,9	52,5	83,1	80,6	37,2		91,6	17,4	43,8	52,0	87,6	152		137
F18_2.5	0,671	58,7	28,0	83,3	72,4	7,61	118	83,5	22,4	49,0	172	84,6	87,1		3,41
F19_2.5	5,21	63,4	152	77,1	65,2	43,1			18,1	41,0	224	75,1	83,4		86,6
F20_2.5	1,94	52,9	46,1	81,6	72,5	32,9		90,0	17,4	54,7	13,6	77,5	78,4		86,3
F21_2.5		42,0	45,8	75,9	51,5	62,4		88,3	24,7	60,5	22,6	73,5	82,1		63,0
F22_2.5		7,93	19,2	80,5	73,4	29,8			11,8	35,6	47,0	75,0	4,84	0,538	5,27
F24_2.5		41,7	54,1	81,9	80,7	66,8		101	33,3	69,4		87,2	64,3	21,1	81,3
F25_2.5		52,9	49,7	72,8	72,1	81,4	35,5	92,2	22,0	52,7		83,4	85,0	51,7	81,7
F26_2.5	0,118	48,5	57,6	80,6	77,6	83,1	59,9	90,7	22,9	67,1		87,9	61,3	12,9	136
F27_2.5	0,00892	44,7	48,5	68,9	76,0	91,9		85,2	27,5	73,8		81,7	82,3		
F28_2.5	1,20	59,9	53,3	79,2	78,6	82,4	49,6	100	25,1	49,9		84,8	72,1	15,3	58,5
F29_2.5	1,38	52,3	31,2	73,6	73,6	82,0	61,0	95,6	35,1	56,2		80,3	82,1	19,0	69,8
F30_2.5	1,81	59,7	58,8	80,0	81,2	93,5	59,2	105	32,2	71,1		86,8	73,3	11,6	146
F31_2.5	6,26	51,7	46,0	84,9	69,7	84,8		89,6	26,2	54,9		77,8	82,8	24,9	85,2
F32_2.5	1,89	39,8	31,1	63,7	65,7	63,1		82,4	23,3	51,8		78,1	71,4	14,5	83,1
F33_2.5	3,58	50,1	47,6	83,7	76,1	89,1	52,1	97,1	28,8	55,1		77,4	90,9	9,44	61,0
Average	2,10	54,4	44,8	78,3	75,5	46,7	55,8	91,0	24,4	53,9	98,5	81,9	82,7	16,1	64,6
STD	1,95	10,1	10,5	7,00	5,27	17,2	9,33	6,60	5,60	8,52	81,3	4,78	6,97	5,19	37,2
RSD	92,9	18,6	23,3	8,94	6,98	36,9	16,7	7,25	22,9	15,8	82,5	5,84	8,42	32,3	57,6

Figure 18: Average extraction ratios [%] of the assayed metals for the PM_{2,5} and PM₁₀ samples. The error bars indicate the average plus/minus one σ (standard deviation).

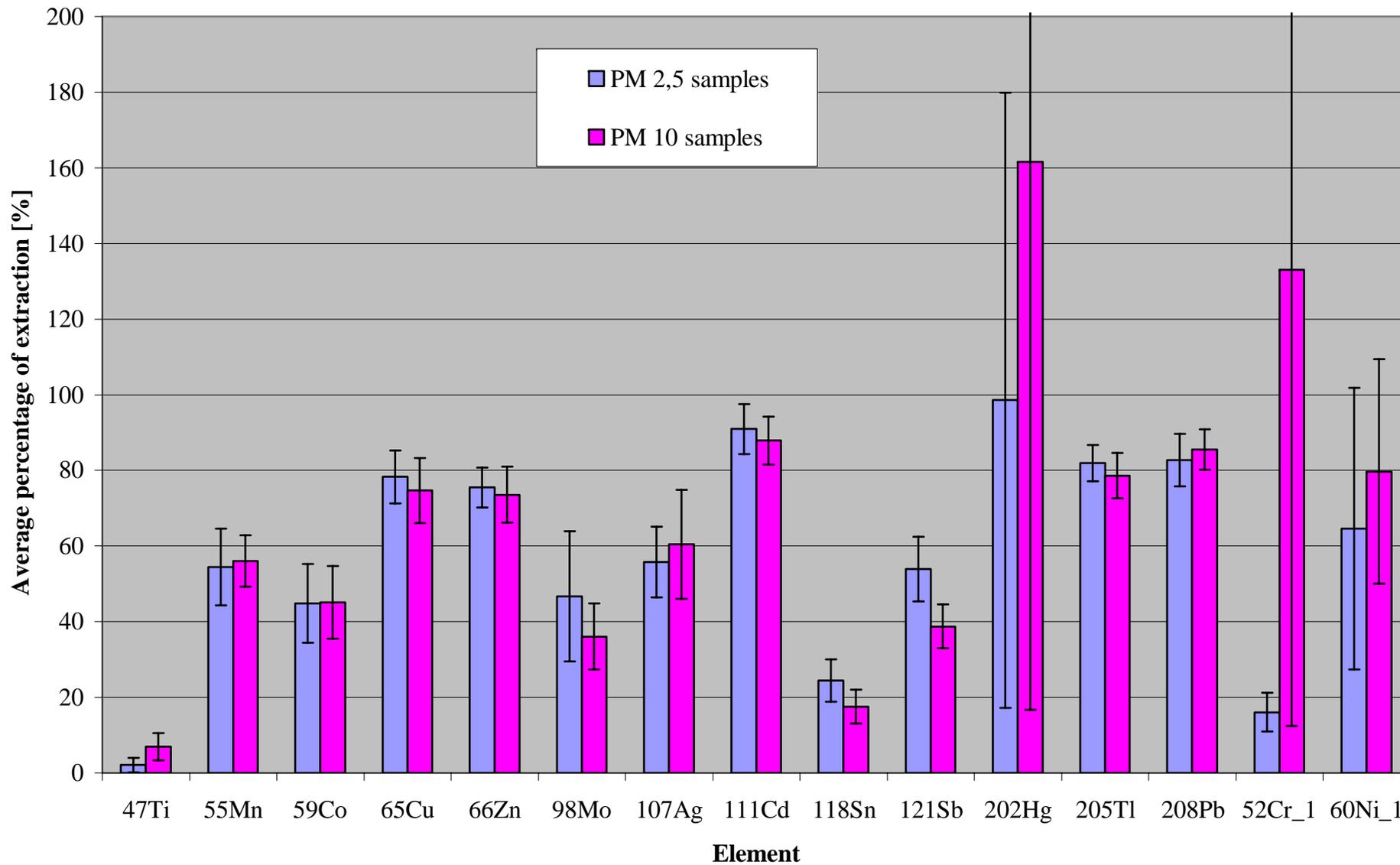


Table 16: Extraction ratios [%] of the assayed metals as determined according to Equation 4 for the 2.5 - 10 µm particle size fraction. *Italic* typed values are based on concentration-values (either PM₁₀ or PM_{2,5} of the extraction or the total digestion samples) between the LOD and the LOQ of the respective element. The values in the magenta colored cells are based on concentration-values (either PM₁₀ or PM_{2,5}) that lie outside of the selected calibration range. The values in the red colored cells are outliers according to the Grubbs-outlier-test. Outliers and values outside the calibration range were not used for the calculation of the average, the standard deviation (STD) or the relative standard deviation (RSD).

Analyte:	⁴⁷ Ti	⁵⁵ Mn	⁵⁹ Co	⁶⁵ Cu	⁶⁶ Zn	⁹⁸ Mo	¹⁰⁷ Ag	¹¹¹ Cd	¹¹⁸ Sn	¹²¹ Sb	²⁰² Hg	²⁰⁵ Tl	²⁰⁸ Pb	⁵² Cr_1	⁶⁰ Ni_1
Sample	Extr.- Ratio [%]	Extr.- Ratio [%]													
F5		69,6	56,3	77,4	43,6	33,0	28,0	8,39	16,9	37,1	80,8	30,9	150		147
F6	8,79	68,6	55,5	84,5	75,4	22,2	43,7	85,3	9,87	21,0		11,1	75,5		49,8
F7	14,6	81,4	60,4	97,5	127	25,3	70,8	79,9	10,7	26,8	80,0		167		270
F8	6,60	57,8	48,2	71,4	75,9	28,7		187	13,5	27,8	99,1		430		110
F9		58,9	41,0	76,5	47,2	26,4		108	6,95	25,2			36,0		37,3
F10		75,3	63,7	99,4	110	36,1		106	13,0	35,4					12008
F11		72,5	36,5	63,7	23,7	24,2			7,62	22,1	15,6				343
F12		29,4	75,7	62,8		39,6		36,1	10,2	26,3					
F13		49,8	31,3	70,0		22,8		97,1	8,67	23,2	57,4		13,7		159
F14		42,2	42,6	61,4	36,0	18,2		39,9	7,58	20,7					574
F15	40,4	72,6	18,0	97,6	159	29,5		90,7	3,55	30,4			84,1		
F18		52,1		80,1	111			114	9,27	31,6	5,94		12,8		
F19	6,72	54,5		78,5	81,2	13,5		281	6,09	21,5	509		93,6		91,7
F20		61,4	860	66,6	23,0	36,8		136	19,0	38,0			399		66,0
F21		61,2	76,6	70,7	78,2	40,2		106	8,85	29,3	10,3	400			240
F22			110	86,1	152	25,0		202	7,62	28,1	1,09	42,9			
F24		65,8	55,8	63,0		21,3		4,59	9,20	25,7					95,7
F25	9,12	77,2	60,1	81,9	73,4	87,1		128	20,6	39,6			199	43,2	103
F26		60,3	28,6	55,4	45,4	75,1	100	92,9	20,2	29,2					
F27	22,0	74,6	62,5	89,0	6,45	85,7		68,9	15,8	17,3				46,1	13,7
F28		48,1	30,4	59,8	41,6	69,0		52,9	7,70	17,5					22,9
F29	7,85	57,4	78,2	67,9	119	82,2	44,1	46,5	20,9	30,1			134		93,7
F30	2,33	50,0	141	62,9	51,3	87,8	26,3	59,7	13,0	23,0		261			
F31		26,2	13,9	36,9	11,8	71,5		58,0	5,24	18,5			33,1		
F32		111	83,5	70,8	47,9	49,3			15,5	34,9		2,28			
Average	9,76	61,6	57,7	73,3	69,6	28,9	52,2	105	11,5	27,6	43,8	125	141	44,7	123
STD	6,02	17,5	29,5	14,5	44,9	9,15	28,4	70,7	5,07	6,21	39,8	166	135	2,06	95,0
RSD	61,7	28,5	51,1	19,8	64,4	31,6	54,4	67,5	44,1	22,5	90,9	133	96,1	4,62	77,4

2.2.2.3 Bioaccessible daily fraction

To estimate the bioaccessible daily fraction of a metal, its daily intake by inhalation of the 2.5 - 10 µm particle size fraction (see Table 10) was multiplied with its average extraction ratio for this fraction (before multiplication the given "Average"-values in Table 16 were divided by 100). If the average extraction ratio was over 100 %, the bioaccessible daily fraction of the respective metal was set equal to its daily intake by inhalation of the 2.5 - 10 µm particle size fraction. The thus obtained results are listed in Table 18 and depicted in Figure 19 to Figure 22.

To assess the toxicological relevance of these results, the bioaccessible daily fraction was compared with the daily intake of trace and heavy metals by drinking water from the first and second Viennese "Hochquellenleitung", which are the two main water supply lines for the city of Vienna (more than 95 % of the Viennese water originate from founts in Styria and Lower Austria, wherefrom it is transported via the two "Hochquellenleitungen" towards Vienna)^{34,35}. In Table 17 the metal concentrations [µg/L], which were found in the first and second Viennese "Hochquellenleitung" according to the yearly inspection reports^{36,37}, are listed:

Table 17: Metal concentrations [µg/L] in the water from the first and second Viennese „Hochquellenleitung“, as determined for the inspection report 2005.

Source: Institut für Umweltmedizin der Stadt Wien – IV/5, Überwachungsbericht – Jährliche Untersuchung des gechlorten Trinkwassers (I. HQ) in Wien gemäß Trinkwasserverordnung BGBl. II Nr. 304/2001 (Prüfbericht 05-3865), Stadt Wien – MA15 Gesundheitswesen und soziales Dezernat – Gesundheitsvorsorge, Wien 2006; and: Institut für Umweltmedizin der Stadt Wien – IV/5, Überwachungsbericht – Jährliche Untersuchung des gechlorten Trinkwassers (II. HQ) in Wien gemäß Trinkwasserverordnung BGBl. II Nr. 304/2001 (Prüfbericht 05-3866), Stadt Wien – MA15 Gesundheitswesen und soziales Dezernat – Gesundheitsvorsorge, Wien 2006

All values in µg/L	Sb	Pb	Cd	Cr	Cu	Mn	Ni	Hg
1. „Hochquellenleitung“	<1.00	1.3	<0.50	<5.0	2.8	<10	3.4	<0.10
2. „Hochquellenleitung“	<1.00	<1.00	<0.50	<5.0	1.1	<10	<2.0	<0.10

Dependent on various parameters like body weight, age, metabolic conditions, physical strain and environmental factors (temperature, humidity, etc.) the average daily water demand of a healthy adult is about 2.5 Litre, whereat about 1.5 Litre have to be taken up as fluid (the rest is taken up by food)³⁸. Thus, a healthy adult living in Vienna, who quenches his thirst by drinking water from one of the "Hochquellenleitungen", has an average daily intake of up to 2 µg lead, 4.2 µg copper and 5.1 µg nickel over the drinking water.

Table 18: Bioaccessible daily-fraction [ng] of the assayed metals, which was determined for the 2.5 - 10 µm particle size fraction. *Italic* typed values are based on concentration-values (either PM₁₀ or PM_{2.5} of the extraction or the total digestion samples) between the LOD and the LOQ of the respective element. The values in the magenta colored cells are based on concentration-values (either PM₁₀ or PM_{2.5}) that lie outside of the selected calibration range. The values in the red colored cells are outliers according to the Grubbs-outlier-test. Outliers and values outside the calibration range were not used for the calculation of the average, the standard deviation (STD) or the relative standard deviation (RSD).

Analyte:	⁴⁷ Ti	⁵⁵ Mn	⁵⁹ Co	⁶⁵ Cu	⁶⁶ Zn	⁹⁸ Mo	¹⁰⁷ Ag	¹¹¹ Cd	¹¹⁸ Sn	¹²¹ Sb	²⁰² Hg	²⁰⁵ Tl	²⁰⁸ Pb	⁵² Cr_1	⁶⁰ Ni_1
Sample	Bioaccessible Daily-Fraction [ng]														
F5		55,8	1,08	256	160	7,85	<i>0,242</i>	1,81	5,35	17,0	<i>0,0345</i>	0,123	30,1		20,9
F6	<i>19,2</i>	65,1	0,657	222	141	6,83	<i>0,126</i>	0,795	4,90	15,8		0,0495	26,2		17,5
F7	28,8	91,6	1,75	308	264	10,4	<i>0,206</i>	1,85	7,17	22,4	<i>0,402</i>	0,0181	30,7		16,8
F8	<i>42,2</i>	66,8	0,926	166	195	4,13	<i>0,0117</i>	1,21	3,26	11,5	<i>0,145</i>	0,0413	16,6		<i>19,0</i>
F9		58,7	0,924	141	<i>152</i>	4,23		1,49	3,23	9,85		0,0495	16,5		120
F10		40,3	0,470	106	82,4	3,12		1,42	2,59	7,75			6,68		<i>1,38</i>
F11		34,7	1,75	120	141	3,21	<i>0,0293</i>		2,38	7,96	<i>0,0955</i>				<i>6,78</i>
F12		22,8	0,113	102	<i>27,0</i>	1,86		2,40	2,25	7,46		0,0424	8,79		<i>0,0238</i>
F13		72,8	2,18	223	68,4	7,29		1,18	5,09	15,9	<i>0,123</i>		12,2		11,7
F14		62,8	0,700	200	<i>127</i>	6,18	<i>0,382</i>	2,40	4,67	14,0	<i>0,159</i>	0,0632	12,2		<i>9,05</i>
F15	<i>6,53</i>	30,5	1,47	108	<i>28,1</i>	3,40	<i>0,0973</i>	1,15	2,73	8,49		0,00437	6,52		<i>0,718</i>
F18		29,5		131	<i>95,4</i>		<i>0,0740</i>	1,29	3,56	<i>10,1</i>	<i>0,240</i>	0,0137	20,9		
F19	<i>17,8</i>	51,7	0,543	163	<i>112</i>	4,99		1,42	3,91	11,6	<i>0,0196</i>	0,0114	11,8		5,89
F20	<i>0,205</i>	23,7	0,227	79,7	<i>52,9</i>	2,25		1,07	1,50	5,68			5,78		<i>11,3</i>
F21		55,1	1,92	252	<i>11939</i>	6,02		1,87	3,27	10,5	<i>0,520</i>	0,0567	2,70		9,45
F22			0,287	112	<i>108</i>	2,46		1,59	2,83	7,70	<i>0,843</i>	0,0188			
F24		26,0	0,437	173	145	4,80		1,92	3,88	12,0		0,164			<i>4,78</i>
F25	25,8	67,0	0,701	211	176	60,9		2,50	3,89	13,7			23,9	4,37	<i>11,9</i>
F26		66,4	1,14	231	366	44,8	<i>0,136</i>	5,04	4,89	16,9		0,665			
F27	<i>6,66</i>	38,0	0,439	165	<i>120</i>	92,0		2,21	3,90	17,9		0,0942	10,8	2,56	8,39
F28	<i>2,06</i>	154	2,24	332	309	65,6	<i>0,0447</i>	3,39	8,30	22,7		0,104			55,0
F29	<i>25,1</i>	91,1	0,711	218	216	71,5	<i>0,210</i>	2,28	4,75	14,5		0,0000548	22,3		<i>15,1</i>
F30	72,2	65,1	1,14	175	227	46,4	<i>0,132</i>	2,53	4,07	12,4		0,0971			8,13
F31	<i>9,97</i>	53,9	0,876	176	163	40,7		3,25	3,54	11,2		0,0260	22,6		<i>10,7</i>
F32		29,1	0,376	85,6	<i>94,5</i>	4,24	<i>0,339</i>	0,109	1,74	5,13	<i>0,585</i>	0,102			7,25
Average	21,4	52,1	0,960	178	149	4,90	0,156	1,67	3,91	12,2	0,288	0,0568	16,0	3,46	9,84
STD	20,3	20,4	0,623	67,1	83,3	2,29	0,115	0,735	1,55	4,65	0,265	0,0457	8,65	1,28	5,92
RSD [%]	94,7	39,2	64,9	37,6	56,0	46,7	73,7	44,0	39,8	38,2	92,1	80,4	54,2	36,9	60,2

Figure 19: Bioaccessible daily fraction [ng] determined for the 2.5 – 10 µm particle size fraction of the metals Ti, Mn, Cu and Zn.

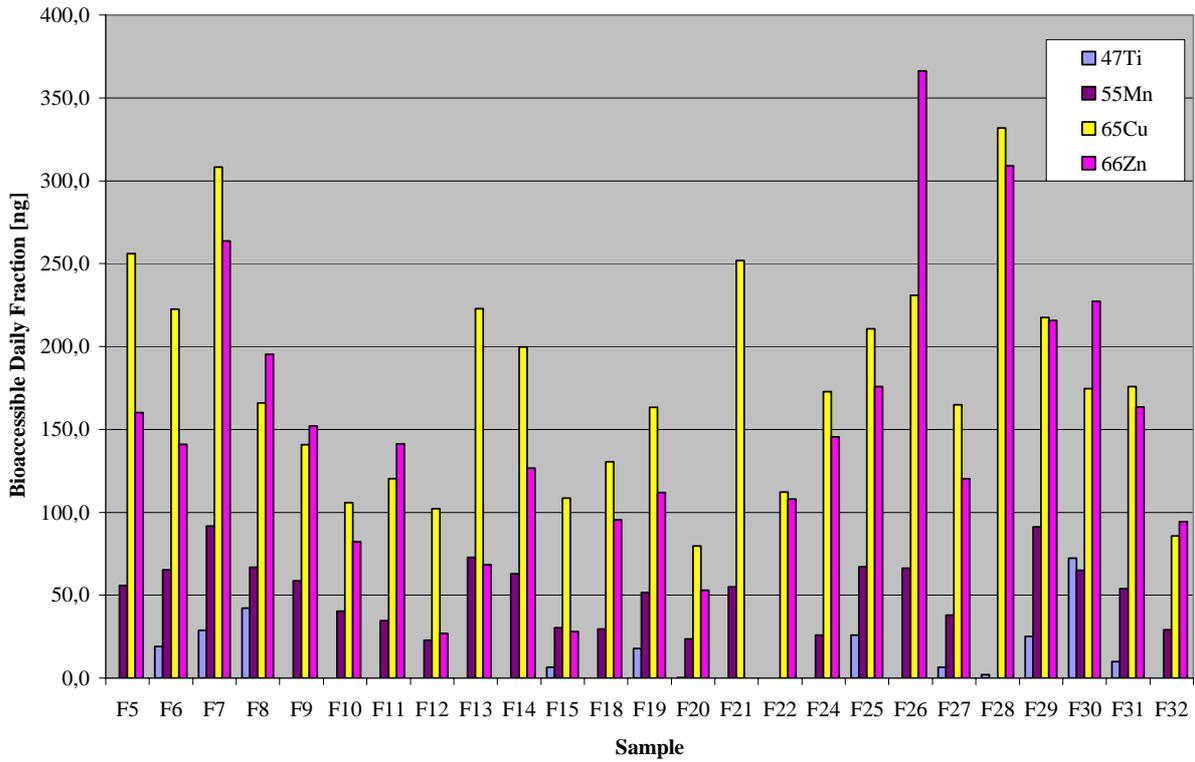


Figure 20: Bioaccessible daily fraction [ng] determined for the 2.5 – 10 µm particle size fraction of the metals Ni, Mo, Sb and Pb.

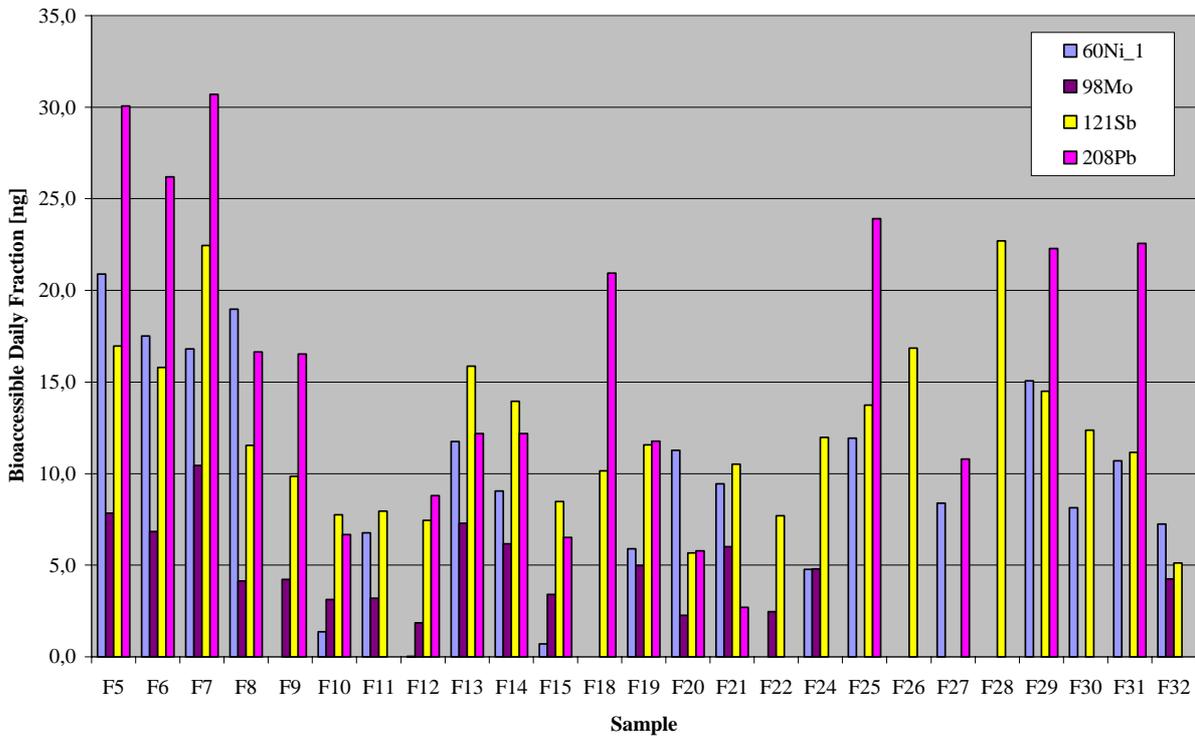


Figure 21: Bioaccessible daily fraction [ng] determined for the 2.5 – 10 µm particle size fraction of the metals Cr, Co, Cd and Sn.

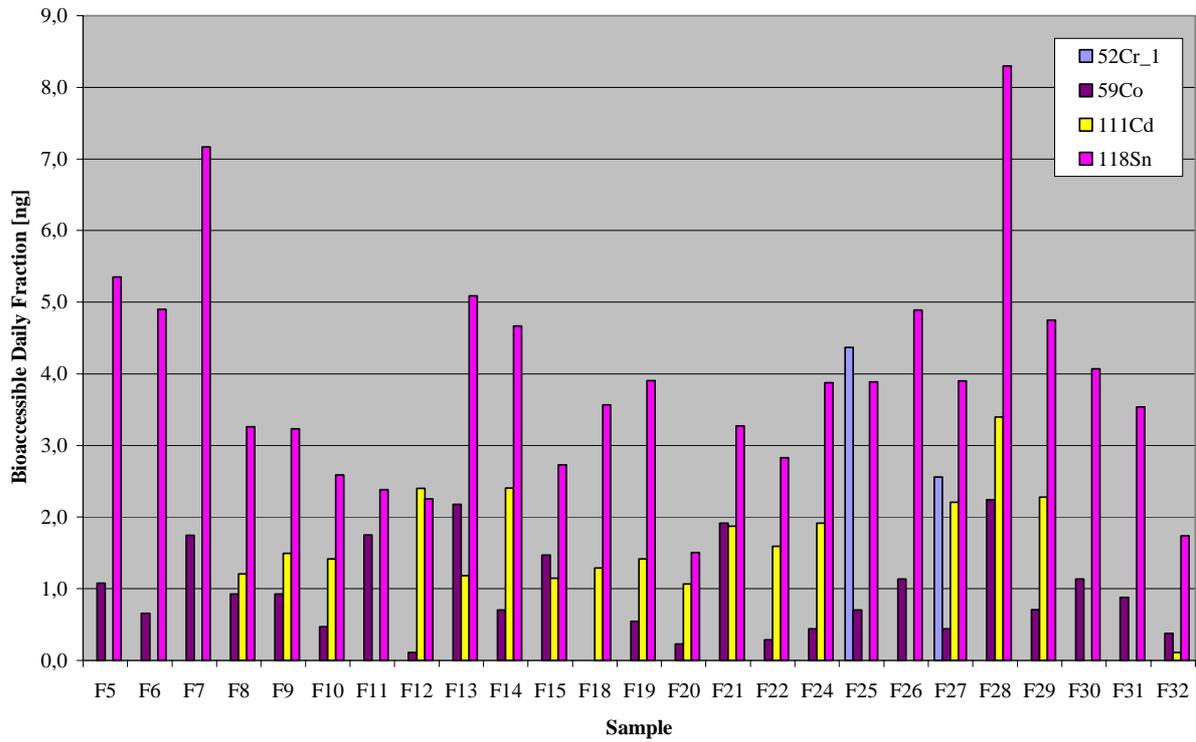
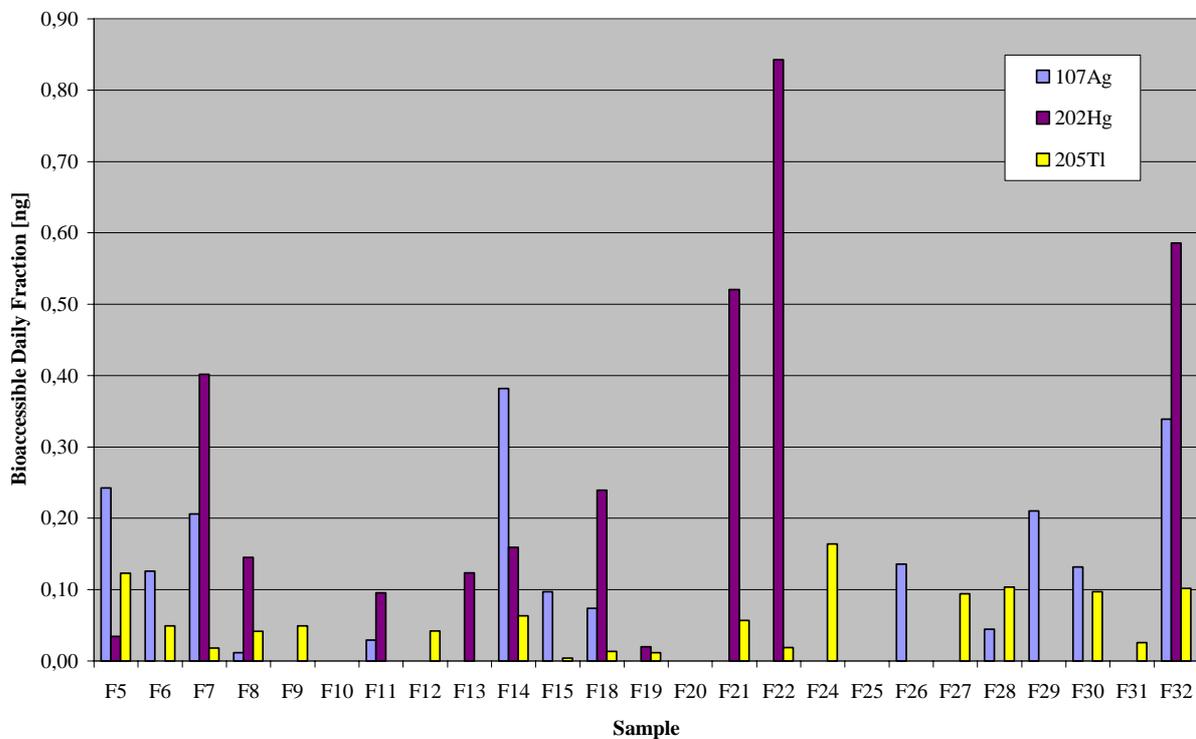


Figure 22: Bioaccessible daily fraction [ng] determined for the 2.5 – 10 µm particle size fraction of the metals Ag, Hg and Tl.



By comparing the obtained values for the daily intake of lead, copper and nickel over the drinking water with the bioaccessible daily fraction of the respective elements, it is obvious

that the intake over the drinking water is significantly higher. However, these results were found for adults. For a baby, whose estimated daily water intake will not exceed 0.25 litres, the situation might be different.

Copper, being the metal that shows the highest bioaccessible daily fraction (see Table 18 and Figure 19), is both an essential and potentially toxic (cytotoxic) element^{15,26}. Since the recommended daily intake (RDI) of copper by food is 0.5 – 0.7 mg for children in the first years of life, and 2.0 – 3.0 mg for adults²⁶, the obtained values for the bioaccessible daily fraction (average: 178 ± 67.1 ng), which result from the inhalation and subsequent digestion of copper-containing aerosols, are only a small part of the RDI.

As can be seen in Table 18 and Figure 19 **zinc** is the element showing the second highest bioaccessible daily fraction. Like copper, zinc is also an essential trace element that can impair the human life functions either by deficiency or surplus²⁶. According to E. Merian et al.²⁶ an additional zinc intake of 10 – 15 mg per day does not constitute a health hazard. Thus, the obtained values for the bioaccessible daily fraction (average: 149 ± 83.3 ng) can be seen as harmless to human health.

Being a constituent and an activator of several enzymes and proteins, **manganese** is an essential nutrient but also a toxicant for humans, for whom the range between deficiency and toxicity of the metal is narrow²⁶. According to E. Merian et al.²⁶ the U.S. Environmental Protection Agency (EPA) estimated for a 70-kg individual a no-observed-adverse-effect level (NOAEL) of 10 mg Mn per day for the ingestion from food. The obtained values for the bioaccessible daily fraction (average: 52.1 ± 20.4 ng, see Table 18) are even significantly below the required mean manganese intake for an adult of about 2 mg per day²⁶. Nevertheless, potential health risks of airborne concentrations of manganese are quite high, since the inhalation of Mn-rich dust can increase susceptibility of the respiratory tract to infection and can also induce multiple damage to the central nervous system due to an accumulation of manganese in the brain²⁶. According to E. Merian et al.²⁶ the EPA estimated the workplace-base lowest-observed-adverse-effect level (LOAEL) to be $150 \mu\text{g Mn m}^{-3}$. From this value an exposure-adjusted LOAEL of $50 \mu\text{g Mn m}^{-3}$ for non-occupational lifetime exposure was derived, which resulted – by implicating an uncertainty factor of 1000 - in an inhalation reference concentration (RfC) of 50 ng Mn (respirable) per m^3 ²⁶. The average Mn-concentration in the sample-air, which was derived from total digestion analysis of the PM_{10} samples, was found to be 11.8 ± 3.76 ng/ m^3 (see Table 4). Thus, it is only a factor of 4 to 5 below the RfC-value.

For **titanium** an average value of 21.4 ± 20.3 ng for the bioaccessible daily fraction was determined (see Table 18). Since the total daily intake of titanium (over an average of 7 days) ranges from 30 to 525 μg for women and from 25 to 700 μg for men, the

bioaccessible daily fraction of this metal is only a small part of its total daily intake²⁶. However, titanium dioxide pigment is classified as a nuisance because of its small particulate size (about 20 µm)²⁶. Thus, the UK Health and Safety Executive and the American Conference of Governmental Hygienists (ACGIH) have specified “long-term exposure limits” of 10 mg/m³ total dust and 5 mg/m³ respirable dust²⁶. The average Ti-concentration in the sample-air, which was derived from the total digestion of the PM₁₀ samples, was found to be 27.3 ± 15.8 ng/m³ (see Table 4). Thus, it is significantly below the above-mentioned long-term exposure limits, even when assuming that the total part of the measured titanium was originally in the form of the dioxide.

For **lead** an average value of 16.0 ± 8.65 ng for the bioaccessible daily fraction was determined (see Table 18). Since the average daily uptake of a European is about 200 µg lead^{15,29}, the contribution of the bioaccessible daily fraction to this average daily uptake is only small. The high hazardous potential of lead (high Pb-concentrations in the environment can lead to serious problems in the central nervous system, peripheral nervous system, blood and blood forming organs, kidneys and the vascular system of humans^{10,15,26}) led in Austria to the definition of a threshold limit according to the “Immissionsschutzgesetz-Luft” for lead in PM₁₀ of 0.5 µg/m³ air (as yearly average value)⁶. The average Pb-concentration in the sample-air, which was derived from the total digestion of the PM₁₀ samples, was found to be 13.2 ± 5.70 ng/m³ (see Table 4). Thus, it is significantly below the above-mentioned threshold limit.

For **antimony** an average value of 12.2 ± 4.65 ng for the bioaccessible daily fraction was determined (see Table 18). Since the antimony content, which was measured in 10 adult human diets during the period 1970 to 1991, ranged from 0.2 to 20 µg per day, the contribution of the bioaccessible daily fraction to the average daily uptake is rather small²⁶. According to E. Merian et al.²⁶ inhalation exposure to antimonials can produce pneumoconiosis, fibrosis, bone marrow damage and carcinoma. For limiting worker’s exposure to antimony particulates, industrial standards in the range of 0.2 to 2 mg Sb per cubic metre air were defined²⁶. The average Sb-concentration in the sample-air, which was derived from the total digestion of the PM₁₀ samples, was found to be 4.95 ± 1.65 ng/m³ (see Table 4). Thus, it is significantly below the above-mentioned industrial standards, which were defined for occupational exposure.

For **nickel** an average value of 9.84 ± 5.92 ng for the bioaccessible daily fraction was determined (see Table 18). According to E. Merian et al.²⁶ the nickel requirement of humans has been estimated to be 25 to 35 µg per day. However, human diets generally contain much greater amounts of nickel (130 µg to 900 µg per day)²⁶. Thus, the contribution of the bioaccessible daily fraction to the average daily nickel uptake is only small. Nevertheless, workers who are chronically exposed to nickel aerosols can develop

chronic respiratory diseases²⁶. Since nickel compounds are carcinogenic to humans and metallic nickel is possibly carcinogenic to humans, in Austria technical guiding concentrations of 50 µg Ni m⁻³ for nickel and its compounds are in force²⁶. The average Ni-concentration in the sample-air, which was derived from the total digestion of the PM₁₀ samples, was found to be 2.20 ± 0.993 ng/m³ (see Table 4). Thus, it is significantly below the above-mentioned technical guiding concentrations, which were defined for occupational exposure.

Molybdenum has been recognized as an essential element for humans and animals²⁶. For humans an intake of 25 µg per day is required and the Recommended Dietary Allowance (RDA) for molybdenum in adults is 45 µg per day²⁶. Thus, the obtained values for the bioaccessible daily fraction (average: 4.90 ± 2.29 ng, see Table 18) are significantly below the required mean molybdenum intake level. However, elevated molybdenum intake via foodstuffs can lead to higher blood levels of uric acid and thus to symptoms of gout²⁶. Since occupational exposure levels for soluble molybdenum compounds are as high as 5 mg/m³, the average Mo-concentration of 1.97 ± 0.829 ng/m³ (see Table 4) in the sample-air, which was derived from the total digestion of the PM₁₀ samples, is significantly below this limit.

For **tin** an average value of 3.91 ± 1.55 ng for the bioaccessible daily fraction was determined (see Table 18). Since the daily intake of tin in the human diet is about 10 mg (5 % of which is most likely absorbed)²⁶, the contribution of the bioaccessible daily fraction to the average daily intake is rather small.

Chromium is both an essential and potentially toxic element to humans^{15,26}. According to E. Merian et al.²⁶ the adequate intake (AI) for chromium is about 25 µg per day for women and 35 µg for adult men. Thus, the obtained values for the bioaccessible daily fraction (average: 3.46 ± 1.28 ng) are only a small part of the AI. Inhalation of dusts from chromates, dichromates and chromium containing ores at concentration levels of about 0.1 mg Cr /m³ can lead to various adverse health effects in the respiratory tract and after long time exposure even to lung cancer²⁷. The average Cr-concentration in the sample-air, which was derived from the total digestion of the PM₁₀ samples, was found to be 1.00 ± 1.25 ng/m³ (see Table 4). Thus, it is unlikely that the determined chromium concentrations can induce the above described adverse health effects.

Cadmium is a nonessential, toxic heavy metal that is mainly taken up into the human body by cigarette smoke and foodstuff^{15,26,27}. Especially for non-smokers the daily intake of cadmium clearly depends on personal diets, since the cadmium exposure via food may be up to several hundred µg per day²⁶. The average total daily intake of cadmium in most European countries is most likely in the range of 10 to 30 µg per day²⁶. Thus, the obtained values for the bioaccessible daily fraction (average: 1.67 ± 0.735 ng) are only a small part of the average daily intake. However, chronic Cd exposure can lead to pulmonary lesions,

severe kidney diseases and adverse effects on bone mineral density^{15,26,27}. According to E. Merian et al.²⁶ there is also sufficient evidence in humans for the carcinogenicity of cadmium and its compounds.

For **cobalt** an average value of 0.960 ± 0.623 ng for the bioaccessible daily fraction was determined (see Table 18). According to E. Merian et al.²⁶ human dietary cobalt intakes are in the order of 10 – 30 µg per day. Thus, the obtained values for the bioaccessible daily fraction are only a small part of the average daily intake. However, workers exposed to cobalt containing dusts developed chronic lung damages like progressive pulmonary fibrosis²⁶. Elemental cobalt as respirable dusts or aerosols and cobalt compounds of low solubility are unmistakably carcinogenic in animals under experimental conditions, which are comparable to human occupational exposure²⁶. Thus, for Germany a Technical Reference Concentration of 0.5 mg/m³ was defined, while in Belgium 0.01 mg/m³ is the limit for cobalt and cobalt oxide in air²⁶. The average Co-concentration in the sample-air, which was derived from the total digestion of the PM₁₀ samples, was found to be 0.223 ± 0.0907 ng/m³ (see Table 4). Thus, it is unlikely that this cobalt concentration can induce the above described adverse health effects.

For **mercury** an average value of 0.288 ± 0.265 ng for the bioaccessible daily fraction was determined (see Table 18). According to E. Merian et al.²⁶ the average daily mercury vapour intakes from dental amalgam are in the order of 3.8 – 21 µg. Additionally a total of 4.3 µg (ionized) inorganic mercury (on average) as well as 2.4 µg methyl-mercury are taken up by the general population per day - mainly by consuming foodstuff²⁶. Thus, the obtained values for the bioaccessible daily fraction are only a small part of the average daily intake. Exposure to elemental mercury vapour mainly affects the nervous system. Therefore, a European expert group proposed for mercury vapour a limit of 50 ng/m³ in ambient air²⁶. The average Hg-concentration in the sample-air, which was derived from the total digestion of the PM₁₀ samples, was found to be 0.0599 ± 0.0485 ng/m³ (see Table 4) and thus significantly below the above-mentioned limit.

For **silver** an average value of 0.156 ± 0.115 ng for the bioaccessible daily fraction was determined (see Table 18). According to E. Merian et al.²⁶ an average silver intake of about 16.6 µg per day was calculated. Thus, the obtained values for the bioaccessible daily fraction are only a small part of the average daily intake. Since silver and its compounds show only minimal toxic effects on humans, the maximum allowable concentration at the workplace (MAK-value) has been set at 0.1 mg/m³ for metallic silver and 0.01 mg/m³ for silver salts as Ag²⁶. The average Ag-concentration in the sample-air, which was derived from the total digestion of the PM₁₀ samples, was found to be 0.0689 ± 0.0278 ng/m³ (see Table 4) and thus significantly below the above-mentioned MAK-value.

Thallium, being the metal that shows the lowest bioaccessible daily fraction of the investigated elements (see Table 18) is a nonessential and toxic trace element^{15,26,27}. In non-polluted areas the normal human daily intake of thallium (mainly via food) is estimated to be about 2 – 5 µg, whereas for people living within the emission region of a coal-fired power plant 10.5 – 12.6 µg can be calculated²⁶. Thus, the obtained values for the bioaccessible daily fraction (average: 0.0568 ± 0.0457 ng, see Table 18) are only a small part of the average daily intake. Chronically exposed humans can show polyneuropathy, psychiatric changes and eye defects^{15,26}. Thus, in many countries the threshold limit value for occupational exposure to thallium was defined to be 0.1 mg/m^3 ^{26,27}. The average TI-concentration in the sample-air, which was derived from the total digestion of the PM₁₀ samples, was found to be $0.0657 \pm 0.0466 \text{ ng/m}^3$ (see Table 4) and thus significantly below the above-mentioned threshold limit value.

2.3 Conclusion

Within this work, an easy to perform extraction procedure for trace and heavy metals with synthetic gastric juice was developed and applied to estimate the bioaccessible fraction of these metals. 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 the majority of the metals extraction ratios of over 50 % could be obtained. Furthermore, the PM₁₀ and PM_{2.5} concentrations of the assayed metals as well as the average daily intake of these particle size fractions by inhalation were determined.

As discussed in the previous section the concentrations of the trace and heavy metals in the city aerosol of Vienna are at present rather low. However, this was not always the case: Before the ban on leaded gasoline, lead concentrations in Austria – especially in cities with high traffic volume like Vienna – were significantly higher than nowadays. Today, acute toxic effects originating from trace and heavy metals in the Viennese city aerosol need not to be taken into account. Nevertheless, even at low concentrations, long-term effects cannot be excluded, since some of these metals – like cadmium – tend to accumulate in the human body^{15,26,27}.

Generally 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 gastro-intestinal region in a highly diluted or complexed form, whereas aerosol bound metals are present as ultrafine highly reactive particles. The higher reactivity of these metals may compromise the apparently lower intake via aerosol inhalation and ingestion.

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3 Ultra-trace analysis of palladium in human urine samples via flow-injection coupled with the ELAN 6100 DRC II ICP-MS

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Ultra-trace analysis of palladium in human urine samples via flow-injection coupled with the ELAN 6100 DRC II ICP-MS

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ABSTRACT

The use of palladium as catalyst material in vehicles, which are equipped with Otto engines, has dramatically increased in recent years, since Pd is cheaper and less sensitive to catalyst-poisons than platinum. Furthermore, Pd-catalysts can easier meet the strict threshold limits for exhaust emissions, which were introduced within the European Union in 2000 and 2005 by the EU-directives Euro Stage 3 and 4. As consequence of these developments the automotive catalytic converter became the main emission source of Pd into the environment. For a better assessment of the hence resulting health-risks, intensive efforts have been made in recent years for the development of analytical methods, which can routinely be applied in the field of Biomonitoring. Beneath the use of ETAAS, the application of ICP-MS has proven advantageous, since this analytical method possesses a high sensitivity and provides the opportunity of isotope dilution mass spectrometry (IDMS). The very low Pd-concentrations, as they are present e.g. in urine-samples, as well as comparatively high concentrations of interfering matrix-elements, make - even by using ICP-MS as the method of detection - the application of special sample pre-treatment- and enrichment-techniques to an absolute prerequisite for performing accurate Pd-analysis.

The here presented method for ultra-trace analysis of Pd in human urine therefore includes the destruction of the organic matrix by UV-digestion, the separation of interfering cations by cation-exchange-chromatography, the on-line-enrichment via an automated flow-injection-analysis-system (FIAS) as well as the accurate quantification of Pd via isotope dilution mass spectrometry (IDMS).

INTRODUCTION

Palladium (Pd) is a soft silver-white platin-group element (PGE) with a natural occurrence in the continental crust of 0.4 µg/kg on average¹. The largest use of palladium today is in automotive catalytic converters of gasoline-operated engines. The lower firing temperatures of diesel engines prohibit the application of palladium as the catalytic active material in the diesel catalyst. Nevertheless, in the period from 1994 to 2004 – thus within just one decade – there was a huge increase in the Pd demand in Europe for autocatalysts (see Table 1).

Table 1: Palladium Demand in Europe^{2,3}

Application	1994 (kg)	2004 (kg)
Autocatalyst (gross)	8090	34370
Autocatalyst (recovery)	0	-3420
Chemical industry	1870	2180
Dental	7930	2490
Electronics	7930	3580
Jewellery	933	1090
Other	778	778
Total	27530	41060

The main reasons for this remarkable development are that palladium is cheaper and less sensitive to catalyst poisons than platinum⁴. Additionally, palladium-based catalysts are able to meet stricter emission limits – like they are in force since the introduction of EURO Stage III in January 2000⁴. On the other hand these developments made the automotive catalytic converter to the main emission-source of palladium into the environment.

Modern automotive catalytic converters are usually designed as “three-way converters” (TWCs), which convert over 90% of carbon monoxide (CO), hydrocarbons (HCs) and nitrogen oxides (NO_x) into carbon dioxide (CO₂), water and nitrogen. Combination of heat with the noble metal catalysts facilitates these heterogeneous reduction- and oxidation-reactions. In TWCs the oxidation of CO and HCs to CO₂ and H₂O as well as the reduction of NO_x to nitrogen are parallel operations. As a prerequisite for these reactions a constant air-to-fuel-mixture has to be maintained at the stoichiometric ratio ($\lambda=1$), which is regulated by the lambda probe.

Most TWCs consist basically of a monolithic honeycomb support, which is made of cordierite (2MgO·2Al₂O₃·5SiO₂) or a special stainless steel and coated with an activated, high-surface alumina layer, the so-called “washcoat”⁴. The washcoat is composed of approximately 90% γ -Al₂O₃ and a mixture of base metal additives, mainly oxides of Ce, Zr, La, Ni, Fe, Ti, Y, W

and some alkaline earth metals. On the one hand these additives serve as stabilizers against deterioration and aging; on the other hand they improve the performance of the catalyst by acting as promoters of the desired catalytic reactions⁴. The fixing of the precious metals Pt, Pd and Rh on the surface of the washcoat is usually performed by impregnation with hexachloroplatinic (IV) acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), palladium chloride (PdCl_2) and rhodium chloride (RhCl_3) precursor salts, respectively⁴. To achieve catalytically “active”, highly dispersed, metallic PGE particles with diameters in the 1-10 nm range, the precursors are reduced in an H_2 stream at 500°C ⁴.

The surface of the washcoat – and thus also the catalytic active layer - is chemically and physically stressed by high temperatures of the exhaust gases, changing oxidative / reductive conditions and mechanical abrasion, thus leading to the emission of PGE containing particles into the environment^{4,5}. The amount and rate of PGE emission are influenced by the age of the catalyst, the speed of the automobile as well as the type of the engine and the used fuel additives. For palladium emission-rates up to 200 ng km^{-1} were measured in dynamometer-experiments using fresh TWCs⁴. Aged TWCs showed significantly lower emission-rates of palladium.

The release of palladium from TWCs occurs in particulate form, whereas the major fraction of the nano-particles is still bound to μm -size washcoat-particles⁴. 82% of palladium present in the inhalable aerosol size range $< 30 \mu\text{m}$ is bound to particles with a diameter of $10\text{-}30 \mu\text{m}$, about 4% and 13 % of palladium are present in the size range of $2.5\text{-}10 \mu\text{m}$ (tracheal-bronchial-fraction) and $1\text{-}2.5 \mu\text{m}$ (alveolar fraction), respectively⁶. Therefore palladium is mainly taken up into the human body by inhalation but also by ingestion (after lung-clearance), dermal contact and – due to the fact that palladium is the most mobile PGE - to an increasing degree over the food-chain^{4,5,7,8}. Palladium can cause allergic reactions similar to those of nickel, whereupon about 90% of those persons, which suffer from a nickel-allergy, are also sensitive against palladium^{4,7,8}. Up to day the possible carcinogenic potential of palladium has not been sufficiently investigated⁹.

Palladium is mainly eliminated over the urine¹⁰, making urine samples suitable for the bio-monitoring of palladium concentrations in humans.

The discussed increase of palladium emissions led to the necessity to design powerful analytical methods for ultra-trace analysis of palladium: Schuster et al.¹¹ developed in 1996 an on-line enrichment-procedure for graphite furnace atomic absorption spectrometry (GFAAS) receiving a limit of detection (LOD) of $25 \text{ ng}\cdot\text{L}^{-1}$. Messerschmidt et al.¹² developed a method for the separation and enrichment of palladium (and gold) in biological and environmental samples, which is based on the reductive co-precipitation with mercury. After evaporation of mercury palladium measurement was performed by total reflection X-ray fluorescence (TXRF) resulting in a LOD of $2.5 \text{ ng}\cdot\text{L}^{-1}$. Philippeit et al.¹³ reached for urine

samples a LOD of $10 \text{ ng}\cdot\text{L}^{-1}$ by using a UV-digestion, followed by an off-line solid-phase-extraction (SPE) method and analysis with a HPLC, which was equipped with a UV-detector. ICP-MS is regarded as a powerful technique for PGE analysis. However, ultratrace analysis of palladium in environmental or biological samples with ICP-MS is hampered by several interfering ions. Table 2 shows the major interferences on the palladium isotopes ^{105}Pd , ^{106}Pd and ^{108}Pd , which we selected for our measurements.

Table 2: Major interferences on ^{105}Pd , ^{106}Pd and ^{108}Pd as well as required mass resolution, necessary to separate the respective interference¹⁴.

Isotope	Abundance (%)	Main interferences	Abundance (%)	Required mass resolution ($m/\Delta m$)		
$^{105}\text{Pd}^+$	22.33	$^{65}\text{Cu}^{40}\text{Ar}^+$	30.71	7042		
		$^{89}\text{Y}^{16}\text{O}^+$	99.76	24373		
		$^{88}\text{Sr}^{17}\text{O}^+$	0.03	328855		
		$^{87}\text{Sr}^{18}\text{O}^+$	0.01	35263		
		$^{87}\text{Rb}^{18}\text{O}^+$	0.06	32102		
		$^{88}\text{Sr}^{16}\text{O}^1\text{H}^+$	82.36	31984		
		$^{68}\text{Zn}^{37}\text{Cl}^+$	4.5	7319		
		$^{70}\text{Zn}^{35}\text{Cl}^+$	0.45	9615		
		$^{106}\text{Pd}^+$	27.33	$^{66}\text{Zn}^{40}\text{Ar}^+$	27.79	7033
				$^{90}\text{Zr}^{16}\text{O}^+$	51.34	27492
$^{106}\text{Cd}^+$	1.25			35468		
$^{108}\text{Pd}^+$	26.46			$^{68}\text{Zn}^{40}\text{Ar}^+$	18.72	6474
		$^{92}\text{Zr}^{16}\text{O}^+$	17.07	27386		
		$^{92}\text{Mo}^{16}\text{O}^+$	15.01	49724		
		$^{108}\text{Cd}^+$	0.89	369535		

Beside the isobaric interferences of ^{106}Cd and ^{108}Cd on ^{106}Pd and ^{108}Pd matrix-elements as Cu, Y, Sr, Zn, Zr and Mo can generate interferences in the plasma (oxides, hydroxides and hydrides are preferably generated in the cooler zones of the plasma – directly in front of the interface). The last column of Table 2 lists the mass resolutions necessary for separation of the respective interference signal from the analyte signal. Regarding the fact that the maximum resolution of a modern sector-field-MS is in the range of 12000, it is obvious that most of the interfering ions can not be separated by this technique. Therefore an appropriate sample pre-treatment, which separates the analyte from potential interferences, is an absolute prerequisite for the accurate determination of palladium in environmental and biological samples.

Hann et al.¹⁴ have employed ion chromatography for separation of interfering elements and accurate quantification of palladium by isotope dilution mass spectrometry. Together with an alternative off-line enrichment procedure using anion-exchange the method was applied for measurement of certified reference materials (e.g. road dust) with inductively coupled plasma

sector-field mass spectrometry (ICP-SFMS), reaching detection limits of $125 \text{ pg}\cdot\text{g}^{-1}$ and $14 \text{ pg}\cdot\text{g}^{-1}$ liquid sample, respectively.

Limbeck et al.¹⁵ advanced the on-line enrichment-system of Schuster et al. for the analysis of roaddust- and aerosol-samples and increased the robustness of the method, thus leading to a LOD of $23 \text{ ng}\cdot\text{L}^{-1}$. Rudolph et al.¹⁶ adapted this on-line enrichment-system for ICP-SFMS, using the benefits of the higher sensitivity – compared to GFAAS – and isotope dilution mass spectrometry (IDMS, showing a measurement-uncertainty of about 2%). For analysis of roaddust a LOD of $240 \text{ pg}\cdot\text{g}^{-1}$ solid sample could be reached. This LOD corresponds to an approximate LOD of 5 ng L^{-1} in the digested sample solution. However, the used flow injection analysis system (FIAS) was not automated (the valves had to be operated by hand) and therefore not suitable for routine-analysis like the human-biomonitoring in urine samples. The aim of the present work was therefore the automation of the FIAS to allow routine-analysis and to conduct the measurements with ICP-quadrupole-MS (ICP-QMS).

EXPERIMENTAL

Reagents and Samples

All chemical preparations prior to measurement were conducted on metal-free class 100 workbenches inside a class 100.000 clean room laboratory. Furthermore, all used reagents were of the highest available purity. Purified water - obtained 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 (37%, Merck, Darmstadt, Germany, order number 1.00317.2500) was additionally cleaned by sub-boiling distillation in an ultra pure quartz apparatus (Milestone-MLS GmbH, Leutkirch, Germany). Methanol (Merck, Darmstadt, Germany, order number 1.06007.2500) was of gradient grade. ICP-MS single element standards (Pd) were purchased from SPEX. Human urine samples were obtained from a volunteer, non-occupationally i.e. “normally” exposed adult female.

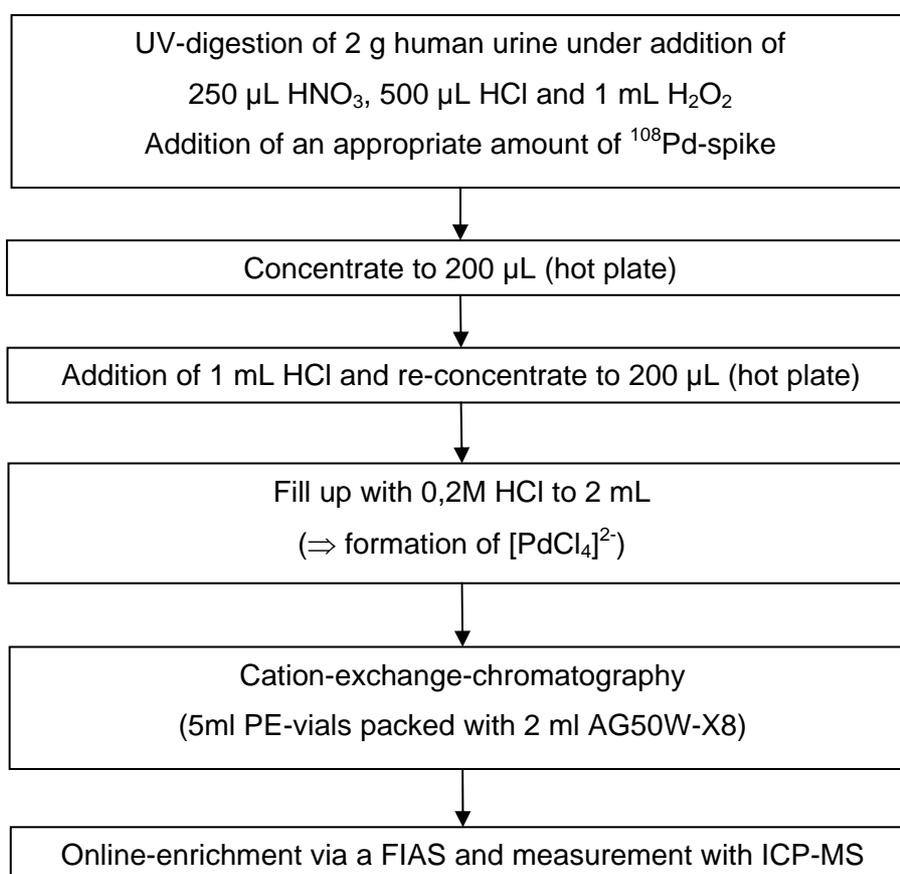
AG50W-X8 (200-400 mesh, hydrogen form, Bio-Rad Laboratories, 2000 Alfred Nobel Drive, Hercules, CA, order number 142-1451/500g) was used for the cation exchange procedure¹⁶. The complexing agent N,N-diethyl-N'-benzoylthiourea (DEBT) was prepared from benzoyl-isothiocyanate and aminoethanol as described by Douglas and Dains in 1934¹⁷. The ligand solution was prepared by dissolving 10 mg of solid DEBT in 10 ml Methanol and subsequent dilution with high purity water to a final volume of 100 ml.

For isotope dilution mass spectrometry (IDMS) isotopically enriched ^{108}Pd (abundance 98.25 %, Science-Technical Centre “Stable Isotopes” of State Scientific Centre of the Russian Federation – Institute of Physics and Power Engineering, Obninsk, Kaluga Region, Russia) was selected. The preparation and quantification of the ^{108}Pd spike via IDMS was described elsewhere in detail⁶.

Sample pre-treatment

The urine samples were subjected to the following sample pre-treatment procedure:

Figure 1: Scheme of the sample pre-treatment procedure.



The UV-digestion of the spiked urine-samples – necessary for the complete removal of the organic matrix - was performed in quartz-vessels using a Methrom 705-UV-Digester (Methrom AG, Herisau, Switzerland). After conversion of the solute palladium into an anionic $[\text{PdCl}_4]^{2-}$ - complex, the samples were subjected to cation-exchange-chromatography as described elsewhere in detail¹⁶. In digested urine most of the metals mitigating palladium-determination exist as cations and are therefore retained by the functional groups of the strong cation exchange resin (SCX). The solution passing the SCX-column contained $[\text{PdCl}_4]^{2-}$ and other anionic and neutral compounds, which were not retained by the SCX-

material. In order to remove interfering matrix constituents, which passed the SCX-column, on-line enrichment via a FIAS was employed.

Flow injection analysis system (FIAS)

The FI system used for the on-line enrichment procedure was realised with a PerkinElmer FIMS 400, equipped with a 9-port-valve and two peristaltic pumps, an additional four-port valve, a magnetic valve, a micro-column and a PerkinElmer Autosampler AS-93. The schematic design of the FI system is depicted in Figure 2. The FIMS 400 and the ELAN DRC II ICP-MS were directly controlled by the ELAN ICP-MS-software (ELAN 3.0 HotFix 3). The FIMS settings in the ELAN software are listed in Table 3. The two peristaltic pumps of the FIMS 400 were equipped with polyvinyl chloride tubes (Spetec GmbH, Erding, Germany, order number 38-0243 (red/red)); all other tubes of the FI system were made of inert Teflon. Therefore both sample-losses caused by the adsorption of the non-polar metal complexes to the pump tubes and contaminations of the sample were prohibited.

Table 3: FIMS settings in the ELAN software. The “X” in the “Read” column marks the step, at which the ICP-MS measurement was started. The Duration of each step is given in seconds. Step 3 was carried out five-times. Pump 1 and Pump 2 correspond to the pumps P1 and P2 in Figure 2 (see below); the pump speeds (rpm) are given as negative values, because both peristaltic pumps were operated in counter clockwise direction. In the “Valve” column the position of the 9-port-valve is shown (“1” corresponds to position 1a or 1b in Figure 2, “2” to position 2 in Figure 2). In the “Autosampler Location” column the Autosampler position is determined, whereupon in Step 3 the Autosampler was moved to the respective sample position, which was defined in the “Sample” section of the ELAN software. Switch 2 controlled the four-port-valve (in the marked (X) step the valve was switched to the position depicted in “Position 1a” in Figure 2). Switch 3 controlled the magnetic valve (in the marked (X) step the valve was opened for the argon gas stream).

Step Number	Read	Duration (s)	Pump 1 (rpm)	Pump 2 (rpm)	Valve	Autosampler Location	Switch 2	Switch 3
1		60	0	-30	1	1		
2		60	0	-30	1	0	X	
3		60	0	-30	1			
4		80	0	-30	1	1		
5		80	0	-30	1	1		
6		20	-60	0	1	1		
7	X	60	0	0	2	1		X

In the first step of the FI-procedure (Step 1 in Table 3; position 1b in Figure 2) the micro-column was conditioned by sucking washing-liquid (0.2 N HCl with ca. 15% (v/v) MeOH) over the column. The micro-column consisted of a 1/8-inch polyvinyl chloride tube (Spetec GmbH, Erding, Germany, order number 38-0252 (yellow/blue)) filled with C18 Polygosil (IST, 221-0020-H, UK, average particle diameter: 59 µm) and sealed with two porous discs.

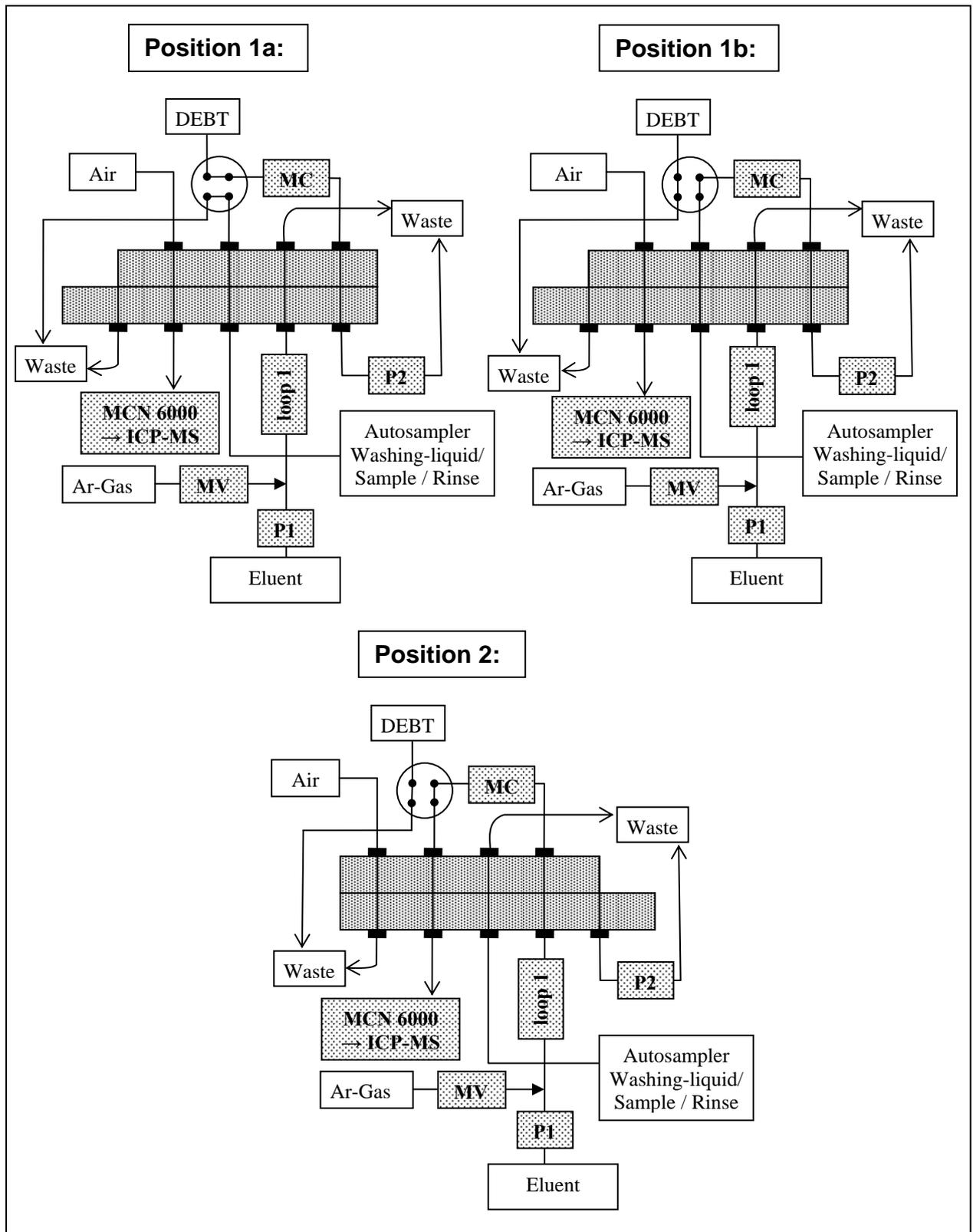
In the second step (Step 2 in Table 3; position 1a in Figure 2) the complexing agent DEBT was applied onto the micro-column, where it was retained by the C18-material. Meanwhile –

to avoid a possible contamination of the sample – the Autosampler-tip was washed with 5% (v/v) HNO₃.

In the next step (Step 3 in Table 3; position 1b in Figure 2) the application of the sample took place, leading to the formation of the Pd-DEBT₂-complex on the column. This step was followed by a wash-step (Step 4 + 5 in Table 3; position 1b in Figure 2), which was used on the one hand to accomplish complete sample-uptake and on the other hand to remove surplus sample-solution from the column and the tubes. In the next step (Step 6 in Table 3; position 1b in Figure 2) the eluent-loop – in Figure 2 marked as “loop 1” – was filled with the eluents (MeOH + 3% (v/v) HCl).

After switching the 9-port-valve (Step 7 in Table 3; position 2 in Figure 2), the ICP-MS-measurement was started. An argon gas stream pressed the eluent with a flow-rate of about 200 µl/min over the column towards the MCN 6000AT⁺ nebulization and desolvation unit (Cetac Technologies Inc., USA), thus starting the elution of the Pd-complex. The MCN6000AT⁺ was equipped with a PFA-Nebulizer, a heated (75°C) PFA-spray-chamber and a membrane desolvation unit, where the main part of the solvent was removed at 160°C.

Figure 2: Schematic design of the used FI-system (MC: Micro-Column; P1, P2: peristaltic pumps; MV: magnetic valve; MCN 6000: Micro Concentric Nebulizer (desolvation-unit)).



Analysis with ICP-QMS

The measurement of the samples was carried out using PerkinElmer's ELAN DRC-II plus ICP-Quadrupole-MS under the instrumental parameters listed in Table 4.

Table 4: Used instrumental parameters for ICP-MS analysis.

RF power	1350 W
Nebulizer gas flow	1.3 – 1.5 L/min
Scan Mode	Peak Hopping
Sweeps / Reading	3
Readings / Replicate	1000
Replicates	1
Dwell Time per AMU	50 ms

^{105}Pd , ^{106}Pd and ^{108}Pd were selected for measurement and subsequent quantification of palladium in the investigated samples.

IDMS was performed according to Equation 1, where R_B represents the ratio of the peak-areas of the transient signals of $^{105}\text{Pd}/^{108}\text{Pd}$ and $^{106}\text{Pd}/^{108}\text{Pd}$ in the spiked sample, respectively. R_X and R_Y are the corresponding ratios in the unspiked sample and the spike, respectively. K represents the mass bias factor as well as f_{iX} and f_{iY} the isotopic abundance of the reference isotope (^{108}Pd) in the unspiked sample and the spike, respectively.

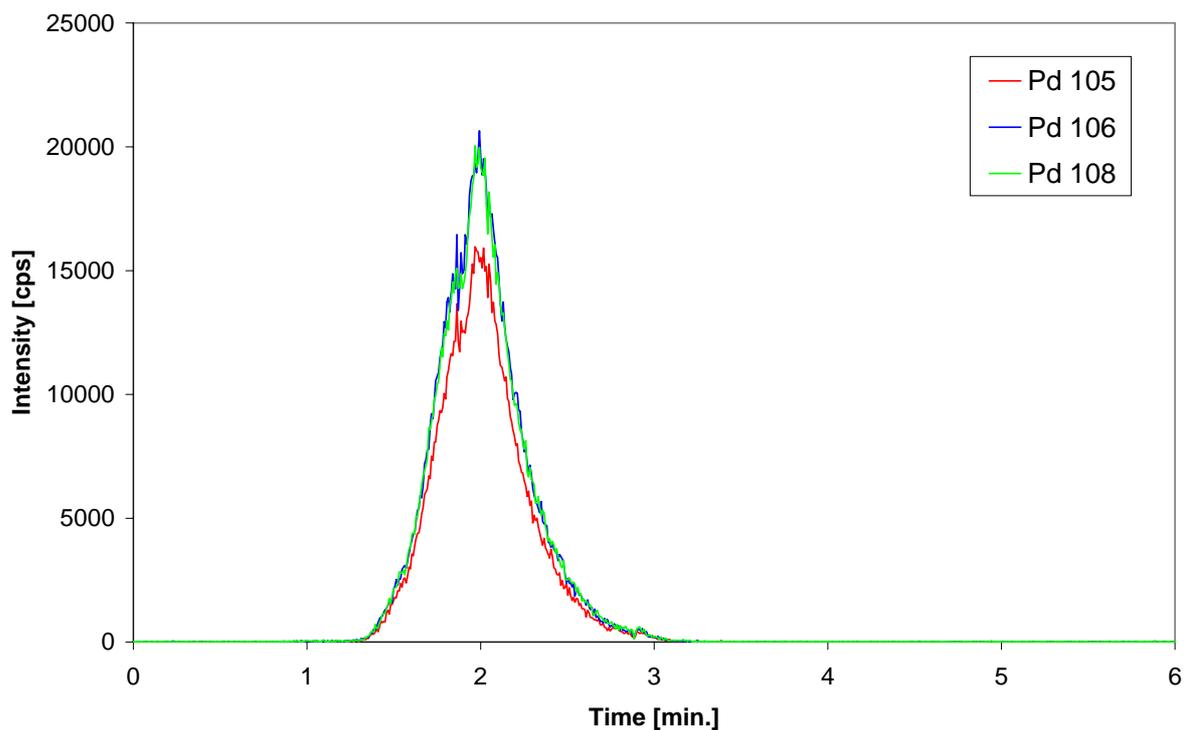
Equation 1: IDMS-calculation for the determination of the concentration of the unspiked sample c_X (mol/g), where c_Y (mol/g) represents the concentration of the spike as well as m_X and m_Y the mass of the unspiked sample and the spike, respectively. This formula can only be used if R_X is equal to the natural isotopic ratio and R_Y is known from a certificate.

$$c_X = \frac{c_Y \cdot m_Y}{m_X} \cdot \frac{R_Y - K \cdot R_B}{K \cdot R_B - R_X} \cdot \frac{f_{iY}}{f_{iX}}$$

RESULTS AND DISCUSSION

Figure 3 depicts the signals obtained by the described FIMS procedure after injection of a standard solution containing $100 \text{ ng}\cdot\text{L}^{-1}$ palladium.

Figure 3: Transient signal of a 100 ng·L⁻¹-Palladium-Standard. The applied sample quantity was about 2.0 g.



For the IDMS-calculations the natural isotopic ratio R_X was determined by four independent measurements of a 100 ng·L⁻¹-Palladium-Standard. Dead time correction of all measured signals was performed using the built-in dead-time correction algorithm of the ELAN 3.0 software. The mass bias factor K was calculated according to Equation 2 (see Table 5). Thereby the ratio $^{105}\text{Pd}/^{108}\text{Pd}$ as well as the ratio $^{106}\text{Pd}/^{108}\text{Pd}$ was determined, which could both be measured with a relative standard deviation of < 1%.

Equation 2: Calculation of the mass bias factor K , where $R_{X, \text{True}}$ represents the natural isotopic ratio, which can be seen as a true value, and $R_{X, \text{Observed}}$ the observed (measured) isotopic ratio in the unspiked sample.

$$K = \frac{R_{X, \text{True}}}{R_{X, \text{Observed}}}$$

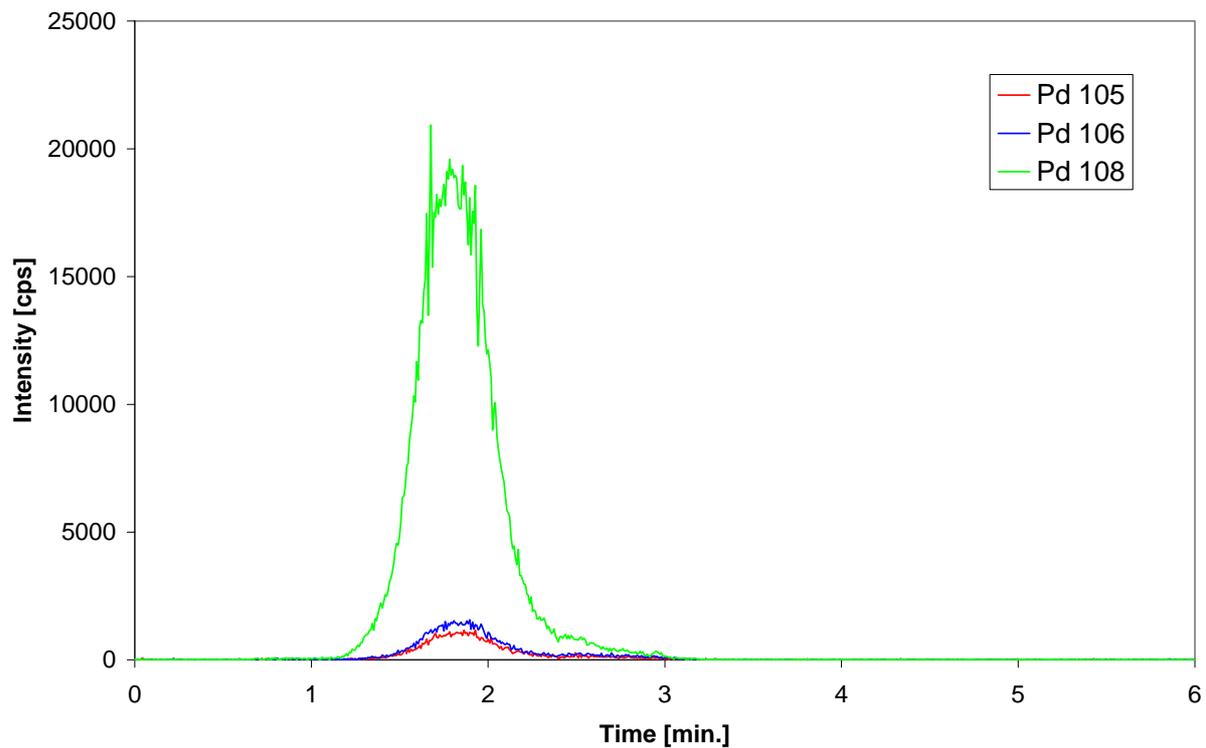
Table 5: Determination of the isotopic ratio R_X and the mass bias factor K by four independent measurements of a 100 ng·L⁻¹-Palladium-Standard.

Measurement	Isotopic ratio R_X		Mass bias factor K	
	¹⁰⁵ Pd / ¹⁰⁸ Pd	¹⁰⁶ Pd / ¹⁰⁸ Pd	¹⁰⁵ Pd / ¹⁰⁸ Pd	¹⁰⁶ Pd / ¹⁰⁸ Pd
Theoretical isotopic ratio	0.8439	1.0329		
100 ng/L-Std. 1	0.8312	1.0210	1.0154	1.0116
100 ng/L-Std. 2	0.8300	1.0180	1.0168	1.0146
100 ng/L-Std. 3	0.8274	1.0208	1.0199	1.0118
100 ng/L-Std. 4	0.8181	1.0154	1.0315	1.0172
Average	0.8267	1.0188	1.0209	1.0138
Std.-Dev.	0.0059	0.0027	0.0073	0.0027
RSD (%)	0.71	0.26	0.72	0.26

The deviation of the measured isotopic ratio R_X from the theoretical value of the natural isotopic ratio, which is expressed by the mass bias factor K, is for ¹⁰⁵Pd/¹⁰⁸Pd about 2.1%, for ¹⁰⁶Pd/¹⁰⁸Pd about 1.4%. This results in a mass bias per mass unit of 0.7%.

To evaluate the procedure spiked urine samples from a volunteer, non-occupationally i.e. “normally” exposed adult female were analysed. Figure 4 shows the transient signal of a 2 g urine-sample, which was digested according to the method described above. Prior to digestion the sample was spiked with 100 pg ¹⁰⁸Pd (10 mg of a 10 µg·L⁻¹-¹⁰⁸Pd-Spike).

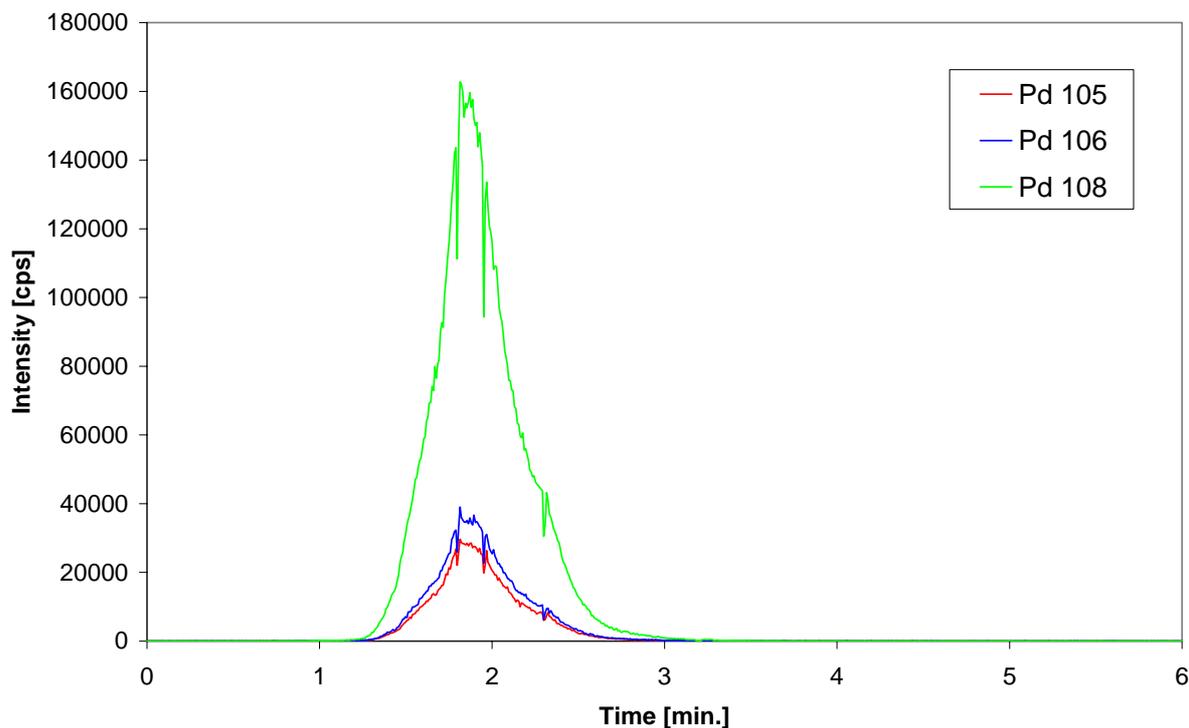
Figure 4: Transient signal of a urine-sample spiked with 10 mg of a $10 \mu\text{g}\cdot\text{L}^{-1}$ ^{108}Pd -Spike. The applied sample quantity was about 2.0 g.



None of the spiked urine samples showed palladium concentrations above the LOD of the method.

The trueness and recovery of the developed method was determined by addition of 1 ng of palladium to the 2 ml of urine samples prior to digestion. Figure 5 shows the transient signal of the respective sample.

Figure 5: Transient signal of a urine-sample spiked with 100 mg of a $10 \mu\text{gL}^{-1}$ - ^{108}Pd -Spike and 500 pg/ml of ^{nat}Pd . The sample intake was about 2.0 g.



From the received data the recovery of the added standard in the urine samples (see Table 6) as well as the expanded measurement uncertainty, the LOD and the limit of quantification (LOQ) were calculated.

Table 6: Recovery of the added standard in the analysed urine samples.

Sample	Theoretical Conc. (Standard) ($\text{ng}\cdot\text{L}^{-1}$)	Conc. ($\text{ng}\cdot\text{L}^{-1}$) $^{105}\text{Pd}/^{108}\text{Pd}$	Conc. ($\text{ng}\cdot\text{L}^{-1}$) $^{106}\text{Pd}/^{108}\text{Pd}$
Urine-blank 1	0	< LOD	< LOD
Urine-blank 2	0	< LOD	< LOD
Urine-blank 3	0	< LOD	< LOD
Urine-sample A	505	481 ± 46	481 ± 46
Urine-sample B	494	465 ± 45	466 ± 45

An expanded measurement uncertainty ($k=2$) of 9.6% was determined by the GUM Workbench software (Version 1.2.4 06.07.1999, Metrodata GmbH, Grenzach-Wyhlen, Germany) according to EURACHEM/CITAC. According to the 3σ -criterion the LOD was $15 \text{ ng}\cdot\text{L}^{-1}$ Pd. Accordingly a LOQ of $50 \text{ ng}\cdot\text{L}^{-1}$ Pd was obtained (10σ -criterion).

As can be seen in Table 6 the palladium concentrations obtained using the isotopic ratios $^{105}\text{Pd}/^{108}\text{Pd}$ and $^{106}\text{Pd}/^{108}\text{Pd}$ correspond excellent. Moreover the values agree within the limits

of their uncertainty of measurement with the theoretical concentrations calculated from the added quantity of the palladium standard.

CONCLUSION

It could be shown that flow injection-inductively coupled plasma mass spectrometry (FI-ICP-MS) in combination with cation exchange is suitable for interference-free ultra-trace analysis of palladium in urine samples. The automation of the FIA-system, developed for the online pre-concentration of the samples, enables routine analysis as essential for human bio-monitoring. The LOD of $15 \text{ ng}\cdot\text{L}^{-1}$ enables accurate measurement of samples from occupationally exposed persons. Future research will focus on the improvement of sensitivity aiming at LODs in the $1 \text{ ng}\cdot\text{L}^{-1}$ range in order to apply the method for measurement of palladium background values of non-occupational exposed persons.

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