Atmospheric Environment 55 (2012) 213–219

Contents lists available at SciVerse ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Bioaccessibility of palladium and platinum in urban aerosol particulates

Christoph Puls [a,b,*], Andreas Limbeck [a], Stephan Hann [b]

[a] Institute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9/164, Vienna A-1060, Austria
[b] Department of Chemistry, University of Natural Resources and Life Sciences, Muthgasse 18, Vienna A-1190, Austria

ARTICLE INFO

Article history:
Received 15 November 2011
Received in revised form
23 February 2012
Accepted 9 March 2012

Keywords:
Airborne particulate matter
Platinum group elements
Bioaccessibility

ABSTRACT

To evaluate potential health hazards caused by environmental Platinum Group Elements (PGEs), bioaccessibility of the metals in question needs to be assessed. To gain appropriate data, airborne particulate matter samples of different size fractions (total suspended particles as well as PM_{10} and $PM_{2.5}$) were taken in downtown Vienna, an urban site primarily polluted by traffic. Total PGE concentrations in these samples were in the low picogram per cubic meter range, as determined by ID-ICP-MS after microwave digestion. For elimination of elements interfering with the accurate quantification, the digested samples were subjected to a cleaning procedure involving cation exchange. For determination of the bioaccessible fraction, it was assumed that inhaled particles are removed from the respiratory system by mucociliary clearance and subsequently ingested. Accordingly, the solubility of PGE in synthetic gastric juice was investigated by batch extraction of particulate matter samples followed by microwave assisted UV-digestion, cation exchange cleanup and ID-ICP-MS. The acquired data was used to calculate the bioaccessible fraction of Pd and Pt in airborne particulate matter. Average GIT-extractable fractions for Pd and Pt in TSP were 41% and 27%, in PM_{10} 34% and 26%, respectively, thus exceeding previously determined values for bioaccessibility of PGE from ground catalyst materials by up to an order of magnitude.

1. Introduction

In recent years the focus of research on airborne particulate matter (PM) has shifted from the quantification of the total amount of different size classes and the determination of the size and shape to the investigation of the composition of those particles. This knowledge is essential for toxicological evaluation extending beyond the scope of epidemiologic studies considering particle size only (Pakkanen et al., 2001; Utsunomiya et al., 2004).

Since the introduction of three-way-catalysts (TWCs) for combustion engines, automobiles have become a main source for the emission of the platinum group elements (PGE) Pt, Pd and Rh, especially near motorways and in urban areas. Emission of these elements occurs mostly through abrasion and deterioration of the catalyst surface at a rate of several ng km^{-1} (Limbeck et al., 2007), elevating the concentration of PGE in urban regions substantially over the past two decades (Zereini et al., 2007).

The impact of particulate matter on human health depends to a great extent on the fate of the inhaled material in the respiratory tract. Particles of less than 2.5 μm in aerodynamic diameter can reach the pulmonary alveoli, where deposited material can attain residence times of month or even years. A particle size of 2.5–10 μm results in deposition in the tracheal and bronchial tract, where mucociliary clearance mechanisms are responsible for adoral transport. Subsequently particles removed from the respiratory tract are mainly swallowed, thereby reaching the gastrointestinal tract (GIT) (BAuA, 2001).

In the presented work it is assumed that 100 % of the inhaled PM_{10} particles are deposited in the thoracic or extrathoracic region, transported to the gastrointestinal tract und subsequently ingested. This assumption is based on several simplifications, as the rate of particle deposition is dependent on several factors. The mode of breathing is influencing the rate of deposition, since the nose filters most particles larger than 2.5 μm. When inhaled by mouth, total deposition in the thoracic and extrathoracic areas is still depending on particle diameter, with a maximum of 80% for particles of 10 μm decreasing to a minimum for particle diameters ranging from 0.1 to 1.0 μm. Deposition rates for smaller particles are increasing again, but this is due to alveolar deposition (ICRP, 1994). The fate of large deposited particles ($d = 6.2$ μm) has been studied by Falk et al. (1997) who determined that 50% had cleared within 24 h, of the remaining particles, 20% had a $t_{1/2}$ of 2 days, whereas the remaining part was retained much longer ($t_{1/2} = 50$ days). The fate of smaller particles deposited in alveolar region is most likely different, since the primary alveolar clearance mechanism is macrophage

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* Corresponding author. Institute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9/164, Vienna A-1060, Austria. Tel.: +43 1 58801 15106; fax: +43 1 58801 15199.
E-mail address: cpuls@mail.tuwien.ac.at (C. Puls).

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doi:10.1016/j.atmosenv.2012.03.023

phagocytosis, a small fraction may also be cleared via the lymphatic system (US-EPA, 2009). Therefore, determination of $PM_{2.5}$ bioaccessibility would require a different study design, e.g. extraction with lung fluid or a model for phagocytosic pathways.

In order to assess the toxicological potential of the thus ingested PGE correctly, it is necessary to determine the bioaccessible fraction. Hamel et al. (1998) defined bioaccessibility as the maximal amount of trace metal soluble in synthetic gastric fluid and therefore potentially available for uptake across the intestinal lumen, whereas bioavailability is defined as the actual amount of trace metal taken across the cell membranes. Synthetic gastric juice is used for assessment of bioaccessibility, since it is the most acidic of the digestive juices. In addition to the trace metal compound solubility increased by the contained pepsin, synthetic gastric juice is most likely to yield the maximal fraction of soluble trace metals of the digestive juices.

Different approaches to determine the fate of trace metals in a physiological environment were employed in the past. To quantify the bioaccessible fraction of trace metals in ingested soil, elaborate extraction schemes were developed, simulating saliva as well as gastric fluid under gastric and intestinal pH-conditions (Hamel et al., 1999). While modeling the pathway of potential pathogens through a large part of the human digestive tract, sequential extraction schemes tend to be laborious and time-consuming and therefore unsuitable for the processing of large sample sets. Furthermore, the number of chemicals required for such an elaborate scheme bears a high potential of contamination, hampering analysis especially if low-abundant elements are investigated. Trace metals in airborne particulate matter were investigated using a reduced protocol focusing on bioaccessibility using batch extraction with synthetic gastric juice without consideration of oral or intestinal conditions (Falta et al., 2008).

Bioaccessibility of PGE under gastrointestinal conditions has been determined employing both road dust and ground catalyst material (Colombo et al., 2008a,b; Turner and Price, 2008). Results showed quite substantial differences between the emitting catalyst material and the investigated road dust reference materials, posing the question for the toxicological impact of PGE in airborne particulate matter.

The aim of the present work was to assess bioaccessibility of palladium and platinum originating from TWCs. For the first time aerosol samples of different size fractions taken at an urban site were investigated according to an analytical protocol designed on the assumption that inhaled particles are ingested after inhalation, deposition and mucociliary clearance in the bronchiotracheal tract, thus giving an insight into the bioaccessibility of PGE from urban aerosols under simulated physiological conditions.

Total concentrations of PGE were determined by isotope dilution (ID) high resolution-inductively coupled plasma-mass spectrometry (HR-ICP-MS) after a multi-step sample digestion procedure and cation exchange for reduction of interfering elements. Batch extraction was carried out to assess the fraction soluble in synthetic gastric juice. The extracts were centrifuged to remove solid residues, digested employing a novel microwave assisted UV-digestion procedure and equally analyzed with ICP-SFMS in high resolution mode and quantified via isotope dilution analysis.

2. Experimental section

2.1. Reagents and standards

Chemical preparations were carried out in a class 100 000 cleanroom on metal free workbenches. ICP-MS measurements were performed in a class 10 000 clean room. Purified water was obtained by using a reagent I grade water (>18 MΩ cm -resistance according to ISO 3696 water specifications) purification system (HQ, USF, Vienna, Austria) and was further purified in a quartz sub-boiling system (Milestone-MLS GmbH, Leutkirch, Germany). Analytical reagent grade hydrochloric acid (VWR, Darmstadt, Germany) was additionally cleaned by sub-boiling distillation. Analytical grade nitric acid (VWR, Darmstadt, Germany) was sub-boil distilled twice. Ultrapure HF (48%), H_2O_2 (30%) and NaCl were purchased in suprapure quality at VWR (Darmstadt, Germany), Pepsin from porcine mucosa (456 units mg^{-1} solid) from Sigma Aldrich (Steinheim, Germany).

PGE standard solutions were prepared by diluting 1000 mg L^{-1} single element standard solutions (Pd: Fluka Atomic Spectroscopy Standard No. 76035; Pt: Merck Certipur Pt Standard No. 1.70219). Isotopically enriched ^{108}Pd and ^{196}Pt standards (abundance 98.25% and 97.25%, respectively; Science Technical Centre “Stable Isotopes” of State Scientific Centre of the Russian Federation—Institute of Physics and Power Engineering, Obninsk, Kaluga Region, Russia) were prepared and quantified using reverse ID-MS as described elsewhere (Kanitsar et al., 2003).

Cation exchange for reduction of interfering cations was performed with a polymer based benzenesulphonic acid modified solid phase extraction sorbent in cartridges containing 155 mg each (Chromafix S HR-XC) purchased from Macherey-Nagel (Düren, Germany).

All digestions were carried out with a Multiwave 3000 microwave digestion unit (Anton Paar, Graz, Austria). Employed rotor systems were XF100-8 and XQ100-8 with microwave energized UV-lamps for *aqua regia* and microwave assisted UV-digestions, respectively.

All polyethylene flasks, vials and pipette tips were subjected to a cleaning process with diluted nitric acid prior to disposable use. PFA vessels were cleaned with boiling *aqua regia*; appropriate cleaning runs were used to remove residual contaminations from quartz and PTFE digestion vessels.

2.2. Sample collection

Particulate matter was sampled in downtown Vienna (48°12′04.61″ N, 16°21′49.08″ O) during the period from 2009-11-09 to 2011-12-03 near a main road with 5 lanes and occasional stop-and-go traffic conditions. To minimize the exposure to road dust, the sampling equipment was positioned directly above the sidewalk in a height 5.7 m above street level, which may reduce the contribution of larger particles to the taken samples (especially for TSP) when compared to the breathing height of a human adult. Concerning airborne particulate matter the effect should not be as pronounced. Daily samples with a 24 h sampling period (filter change at 9 a.m.) were collected on cellulose ester filters (GN-4, 47 mm in diameter, Pall Life Sciences, Michigan, USA) using three different sampling lines. Size segregation was implemented by employing PM_{10} and $PM_{2.5}$ sampling heads (Digitel, Switzerland) with an intake volume of 2.3 $m^3 h^{-1}$. Total suspended particles (TSP) were sampled with open face filter assembly with an average intake volume of 1.4 m^3h^{-1}.

For the investigation of airborne particulate matter, it is common practice to divide collected aerosol samples into various parts. The purpose is to share one sample for different analytical measurements such as determination of elemental, organic and total carbon, analysis of various ions and sugars, crustal elements etc., which are required for a complete characterization of the sample. For the successful application of this approach a homogenous distribution of the airborne particles throughout the surface of the sampling substrate is essential, a pre-condition which could be fulfilled with the use of adequate sampling equipment (Puxbaum et al., 2004; Hueglin et al., 2005; Pio et al., 2007).