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Arsenic speciation in aerosols of a respiratory therapeutic cave: A first approach to study arsenicals in ultrafine particles

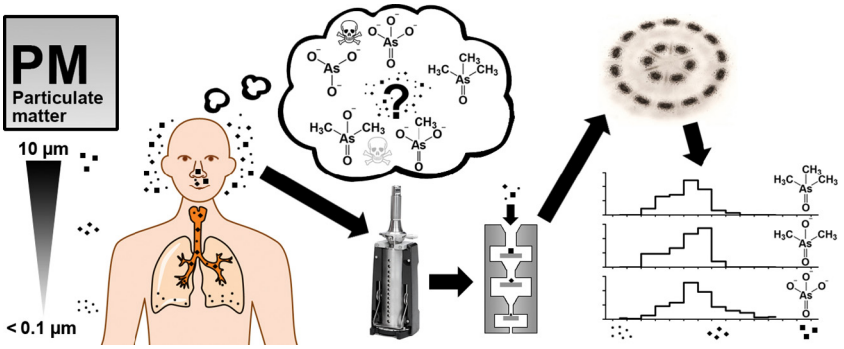
Stefan Tanda [a], Roman Ličbinský [b], Jitka Hegrová [b], Jiří Faimon [b,c,d], Walter Goessler [a,*]

[a] University of Graz, Institute of Chemistry, Analytical Chemistry for Health and Environment, Universitaetsplatz 1, 8010 Graz, Austria
[b] Transport Research Centre, Division of Sustainable Transport and Transport Buildings Diagnostics, Líšeňská 33a, 619 00 Brno, Czech Republic
[c] Masaryk University, Faculty of Sciences, Department of Geological Sciences, Kotlářská 2, 611 37 Brno, Czech Republic
[d] Palacký University, Faculty of Science, Department of Geology, 17. Listopadu 1192/12, 771 46 Olomouc, Czech Republic

HIGHLIGHTS

- Knowledge of arsenic and its compounds in ambient air is of relevance to human health.
- This study investigated arsenicals in size-resolved (ultra)fine particles.
- Particles in the nanometer scale exhibited an enormous diversity of arsenic species.
- The developed method is not only limited to urban environments or point sources.

GRAPHICAL ABSTRACT



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ABSTRACT

Arsenic is ubiquitous in the environment and of special concern due to its varying toxicity depending on the chemical form present. Less is known about arsenic in air, especially about organoarsenicals, their sources and fate. There is also a lack of knowledge regarding arsenic in airborne nanoparticles that are critical for understanding with respect to human health effects due to their size. Here we show results from an arsenic speciation analysis in size-resolved airborne particles with aerodynamic diameters down to 15 nm. Analysis of aerosols from a respiratory therapeutic cave showed temporarily higher concentrations of trimethylarsine oxide than inorganic arsenic and substantial amounts of organoarsenicals, especially in smaller particles. Our method provides guidance for future studies investigating arsenicals in ultrafine particles and their health implications. Furthermore, the method developed can be used to widely monitor particle-bound organoarsenicals to fully understand the importance of As biovolatilization in the environment.

1. Introduction

For many decades, the study of arsenic and the compounds containing in environmental samples has been of great interest, particularly as a result of the metalloid's species-specific toxicity. Presence of arsenic in ground and drinking water, fauna and flora, soils, and food has always been the focal point of interest and concern, in stark contrast to arsenic present in the Earth's atmosphere (Mandal, 2002). Although a target value for total arsenic in ambient air of 6 ng m^{-3} in PM_{10} averaged over a calendar year was established in the European Union (European Parliament and the Council of the European Union, 2004),

* Corresponding author.
E-mail address: walter.goessler@uni-graz.at (W. Goessler).

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existing reviews dealing with arsenic determination in air (considering both particulate and vapor phases) illustrate the lack of knowledge we are still facing today (Lewis et al., 2012; Mestrot et al., 2013; Sánchez-Rodas et al., 2015). In particular little is known about arsenic biovolatilization, the processes leading to volatile arsenicals and their fate (Mestrot et al., 2013). Furthermore, there is a need to determine arsenicals in airborne particles of smaller diameters, since arsenic tends to concentrate in this size fraction (Slejkovec et al., 2000). To our knowledge, there is no study available dealing with arsenicals in ultrafine particles (UFPs, <100 nm in diameter), although exposure to them is associated to a wide range of adverse health effects (Oberdörster, 2001). Reasons for these knowledge gaps and the analytical challenges arising from them might be the following: volatile arsenicals can be reactive depending on the conditions (Jakob et al., 2010; Parris and Brinckman, 1976) and are only present in small concentrations in air. Determination of particle-bound arsenic is complicated by issues of small sample amounts. This is particularly true for the apportioning of particles with different diameters using cascade impactors. Furthermore, arsenic concentrations in particulate matter (PM) can vary widely with locality, season (Mukai et al., 1986) and nearby sources. Metal production and burning of fossil fuels are the most important anthropogenic As inputs (Chilvers and Peterson, 1987). Natural sources include hot (such as volcanoes and forest fires) and low temperature processes (e.g., microbial metabolism, wind erosion and sea spray) (Chilvers and Peterson, 1987). Volatile arsenicals known to be found in air are arsine (AsH_3) and its methylated forms – monomethylarsine ($(CH_3)AsH_2$, dimethylarsine $(CH_3)_2AsH$ and trimethylarsine $(CH_3)_3As$. Arsine is oxidized to arsenite As^{III} and arsenate As^{V}, while mono-, di- and trimethylarsine are oxidized to their pentavalent methylated arsenic oxides, namely monomethylarsonate (MA), dimethylarsinate (DMA) and trimethylarsine oxide (TMAO) (Parris and Brinckman, 1976), reported to be present in PM (Jakob et al., 2010; Lewis et al., 2012; Tziaras et al., 2015).

Existing studies dealing with arsenic speciation analysis in PM are often restricted to urban areas (Rabano et al., 1989; Sánchez-Rodas et al., 2007; Slejkovec et al., 2000) or point sources (Sánchez dela Campa et al., 2008; Sánchez-Rodas et al., 2007; Solomon et al., 2014), larger PM fractions (Farinha et al., 2004; Huang et al., 2014; Jakob et al., 2010; Mukai and Ambe, 1987; Rabano et al., 1989; Sánchez dela Campa et al., 2008; Sánchez-Rodas et al., 2007; Slejkovec et al., 2000; Solomon et al., 2014; Tziaras et al., 2015), or just the inorganic forms of arsenic, arsenite and arsenate (Farinha et al., 2004; Sánchez de la Campa et al., 2018; Rabano et al., 1989; Sánchez dela Campa et al., 2008; Sánchez-Rodas et al., 2007; Solomon et al., 2014; Tirez et al., 2015). Organoarsenicals and TMAO in particular are often overlooked in recent studies, even though they were first detected in PM in the mid 1970s (Johnson and Braman, 1975). The reason for this is obvious: the concentration of organoarsenicals (typically found in the pg m^{-3} range) is very low compared to inorganic arsenic species (typically found at the ng m^{-3} level), when studying larger PM fractions (PM_{10} and $PM_{2.5}$) in outdoor environments (Lewis et al., 2012). For example, concentrations for different organoarsenicals determined at two locations in Argentina ranged from 4 to 60 pg As m^{-3} as TMAO, while the maximum concentrations for DMA and MA were 16 and 6 pg As m^{-3}, respectively, but on the other hand these organoarsenicals were identified in >90% of the 49 PM_{10} samples analyzed (Jakob et al., 2010). Therefore, it would be necessary to study these organic compounds, since low-level diffuse biovolatilization in soils, sediments and water seems to be a wide-spread phenomenon (Mestrot et al., 2011; Mestrot et al., 2013; Savage et al., 2018) that is potentially highly underestimated. Since approximately 90% of atmospheric arsenic is present in the particulate phase (Matschullat, 2000) and rapid oxidation of volatile arsines (Jakob et al., 2010) can take place, the determination of their pentavalent arsine oxides needs to be done in airborne particles. A better understanding of these processes could also have implications in terms of environmental exposure and impacts to humans and other organisms.

In a nutshell, there is a need for an analytical method that allows the study of all relevant arsenic species in different PM fractions, including UFPs, whose use is not restricted to point sources.

2. Material and methods

2.1. Chemicals and standards

Nitric acid (HNO_3, 65%, Carl Roth GmbH + Co. KG, Karlsruhe, Germany), used for sample digestion and standard preparation, was purified via sub boiling prior to use. Ultrapure water (18.2 MΩ cm, produced by a Milli-Q™ water purification system, Merck Millipore, Darmstadt, Germany) was used for sample preparation, preparation of mobile phases, as well as for the dilution of all solutions, it will be referred to as 'water' for the remainder of this document. Hydrogen peroxide (≥30%, for trace analysis, Carl Roth GmbH + Co. KG, Karlsruhe, Germany) was used for sample preparation. Arsenic, germanium and indium stock solutions (single element standards, 1000 mg L^{-1}, Merck Millipore, Darmstadt, Germany) were used to prepare the standard and internal standard for analysis of total arsenic content. The anionic HPLC buffer was prepared from phosphoric acid (TraceSELECT® Ultra, for trace analysis, ≥85%, Sigma-Aldrich Chemie GmbH, Steinheim, Germany) and an ammonia solution (≥25% p.a., Carl Roth GmbH + Co. KG, Karlsruhe, Germany). Pyridine (CHROMASOLV® Plus, for HPLC, ≥99.9% p.a., Sigma-Aldrich Chemie GmbH, Steinheim, Germany) and formic acid (≥98%, Sigma-Aldrich Chemie GmbH, Steinheim, Germany) were used to prepare the buffer for cationic HPLC. Arsenic stock solutions (1000 mg L^{-1}), used to prepare the standards for arsenic speciation analysis were prepared from sodium arsenate dibasic heptahydrate (As^{V}) (Merck KGaA, Darmstadt, Germany) and sodium dimethylarsinate (DMA) (Fluka, Buchs, Switzerland). Additionally, trimethylarsine oxide (TMAO) stock solution was synthesized in-house according to Merijanian and Zingaro (1966) as well as the methylarsonic acid (MA) stock solution according to the Meyer reaction (Scheer et al., 2012). All dilutions and preparations were made in 15 or 50 mL Cellstar® tubes (polypropylene, Greiner Bio-One International GmbH, Kremsmuenster, Austria).

2.2. Sampling methodology

Two different types of devices were used for the sampling of particulate matter, including an electrical low pressure impactor (ELPI+, Dekati Ltd., Kangasala, Finland) and sequential samplers (SEQ 47/50, Sven Leckel Ingenieurbuero GmbH, Germany).

ELPI+ is a real-time particle spectrometer consisting of 15 stages, including 14 impactor stages plus a filter stage. The device separates and measures particles in the range from 6 nm to 10 μm (50% cut off diameters (D_{50}, μm) were 9.83, 5.34, 3.64, 2.46, 1.62, 0.942, 0.599, 0.379, 0.254, 0.154, 0.095, 0.053, 0.029, 0.015 and 0.006). Fourteen impactor stages operating in the range from 15 nm to 10 μm collect particulate matter on suitable substrates for chemical analysis. During presented measurements, ELPI+ was operated as recommended by manufacturer. Flow rate of sampling air was set to 10 L min^{-1} and particles were captured on polycarbonate collection foils (25 mm in diameter, Whatman® Nuclepore™, GE Healthcare, USA) suitable for chemical analysis. Prior to sampling, collection substrates were greased (Dekati® DS-515 Collection Substrate Spray, Dekati Ltd., Kangasala, Finland) in order to prevent bouncing of the particles during collection. ELPI+ was equipped with the Dekati® Dryer DD 603 (Dekati Ltd., Kangasala, Finland) to remove humidity from the sample based on a co-polymer Nafion® tube.

Sequential samplers SEQ 47/50 were equipped with a PM_x inlet and jets for the sampling of PM_{10}. Particles were captured on nitrocellulose membrane filters (1.2 μm pore size, 47 mm in diameter, Merck Millipore Ltd., Cork, Ireland). For the determination of PM_{10} concentrations, filters were weighed before and after sampling in accordance with EN 12341 Ambient air – Standard gravimetric measurement method for the