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Speciation of inorganic arsenic in particulate matter by combining HPLC/ICP-MS and XANES analyses

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Abstract

Inorganic arsenic species in ambient particulate matter (PM_{10} and $PM_{2.5}$) have been determined in an urban area, in the vicinity of a metallurgical industrial plant. The developed high performance liquid chromatography inductively coupled plasma mass spectrometry (HPLC/ICP-MS) method allows monitoring of particulate As(III) and As(V)-species, with a limit of quantification of 0.34 ng m^{-3} As(III) and 0.23 ng m^{-3} As(V) respectively. A good agreement was obtained between the sum of the concentrations of As(III) and As(V) determined by HPLC/ICP-MS and the total As concentrations determined by XRF, indicating a complete extraction of the As species. During the measuring campaigns for PM_{10} and $PM_{2.5}$, a significant conversion (oxidation) up to 54% of exogenous spiked As(III) was observed. The total amount of the spiked As(III) was well-recovered (PM_{10} and $PM_{2.5}$ on average 108% and 101%, respectively). The extraction of the filter in combination with the sampled air matrix is likely to induce the As(III) conversion.

The average measured As concentration in PM_{10} during a 40 days monitoring campaign (30 ng m^{-3}) at the hot spot location is above the European target value of 6 ng m^{-3}. The measured As concentration in $PM_{2.5}$ was half the value of the measured concentration in PM_{10} and no relative enrichment of total As was observed in one of both particulate matter fractions. However, in PM_{10}, As (V) was the main component, while in $PM_{2.5}$, As(III) was the dominant species. During the monitoring campaign, the fraction of particulate As(III) varied between 19-61 % in PM_{10} and a trend towards a higher fraction of As(III) with increasing concentration of total As was observed. XANES and XRD analyses were used for the identification of arsenic species in local PM sources and confirmed the presence of $Ca_3Sr_2(AsO_4)_{2.5}(PO_4)_{0.5}(OH)$, As_2O_3 and As_2O_5 species.

Introduction

Notwithstanding the arsenic concentrations in particulate matter are generally quite low, typical arsenic levels for the European region are between 0.2 and 1.5 ng m^{-3} in rural areas and 0.5 and 3.0 ng m^{-3} in urban areas, in some hotspot regions increased concentration levels occur due to local industrial activities.[1] Arsenic in atmospheric particulate matter exists in two oxidation states, As(III) and As(V), in inorganic and/or organometalloid forms. Five different species of As have been detected in ambient atmospheric particulate matter so far.[2,3] The two inorganic species arsenite (As(III)) and arsenate (As(V)) and the organoarsenic species methylarsonate (MA), dimethylarsinate (DMA) and trimethylarsine oxide (TMAO), all tree methylated forms of As(V). TMAO has been identified as the predominate organoarsenical species in PM, with maximum concentrations up to 0.09 ng m^{-3}.[2,3]

Because of the relatively high toxicity and carcinogenicity of arsenic through inhalation, special attention is required to assess the health risks of arsenic in air.[4] The two inorganic species, arsenite and arsenate, are reported to be more toxic than the organoarsenic species. There is also a toxicological difference between the two inorganic As species, where trivalent arsenic is considered to be the more toxic species. However, taken into account the difference within the variation of the toxicological data, the difference in toxicity, a factor of 2-3, is considered small.[4] As a result of adverse effects of exposure to air pollutants in ambient air, the European Union, amongst others, has developed an extensive body of legislation which establishes health based standards and objectives for a number of pollutants in air. For arsenic, an European target value of 6 ng m^{-3} came into effect at the end of 2012 as an annual mean concentration.[5]

With regard to arsenic determinations in ambient air, the European Committee for Standardisation (CEN) has published sampling and analysis procedures. The European reference method specifies a microwave digestion followed by analysis with either ICP-MS or ET AAS.[8,9] For the determination of the individual species of arsenic, several combinations of techniques (separation + element-selective detection) have been attempted, but high-performance liquid chromatography (HPLC) in conjunction with ICP-MS or hydride generation atomic fluorescence spectrometry (HG-AFS) has emerged as one of the best combination for monitoring purposes.[1-3,6,7,10-23]

Most arsenic analytical techniques require samples to be extracted or digested prior to instrumental analysis. This approach was used consistently in the majority of the literature reviewed when particulate matter was collected on filter media.[6,12-22,24] In this case, the focus on the extraction procedure is the complete recovery of the arsenic species avoiding possible species inter-conversion (As(III) $\leftrightarrow$ As(V)). Based on literature, air samples were prepared in a variety of ways but, in nearly every case, wet digestion or extraction of the air sampling media was performed using an acid. For example, Oliveira et al. evaluated several extraction methods, comparing water, NH$_2$OH, HCl, and H$_3$PO$_4$ digestion followed by either microwave or ultrasonic radiation;[14] the NH$_2$OH, HCl, and H$_3$PO$_4$ extraction procedures were all determined to be acceptable extraction methods. Sánchez de la Campa et al., performed sample digestion using HNO$_3$ and HF, as well as a NH$_2$OH-HCl digestion method incorporating microwave digestion.[12] Tsopelas et al., evaluated HCl versus H$_3$PO$_4$ extraction of both polycarbonate and glass fiber filters;[13] they determined that HCl led to a higher recovery from both filter types, and the HCl-polycarbonate filter was the optimal preparation method. Thus, although some differences in sample preparation approaches were identified in the articles reviewed, most seemed to be effective for determining speciated arsenic in air samples. A few studies compared multiple extraction methods in an attempt to identify the most efficient technique and to allow selection of the most robust methods.[14,20] Based on the studies reviewed, extraction of quartz fiber filters in NH$_2$OH-HCl or HCl appeared to be the optimal preparation method.

Certified reference materials (CRM) are available for total arsenic and were evaluated in several studies to verify the recovery of the extraction procedure.[26] For example, Tsopelas *et al.* reported recoveries for total As of 98–103% on a reference soil sample;[13] Sanchez de la Campa *et al.* reported nearly 100% recovery of total As on Coal Fly Ash (SRM 1633b);[12] Yang *et al.* reported recoveries for total As of 92% on a reference soil sample.[1] However, in general, limited information is available on the identification and concentration of specific arsenic species in CRMs.[15]

Rabano *et al.*, evaluated the species inter-conversion (As (III) $\leftrightarrow$ As(V)) in several ways during their study.[6,19] First, they evaluated recovery of speciated arsenic standards on unexposed PFTE filters; recoveries were on the order of 95% and 100% for As(III) and As(V), respectively. This was followed by determination of recoveries of known concentrations of speciated arsenic standards added to exposed filters (similar to matrix spikes); recoveries of the standards were 79 ± 22% and 97 ± 23% for As(III) and As(V), respectively. The authors concluded that the complex nature of the PM slightly affected measurement of the arsenic species; matrix interferences may also have been an issue but, in general, recoveries were very good. Several of the studies reviewed evaluated accuracy in terms of extraction efficiency, comparing the summed concentrations of speciated arsenic (i.e., As(III) + As(V)) to the total arsenic results and calculating % recoveries. As an example, to evaluate the efficiency of their extraction procedures, Sánchez de la Campa *et al.*, compared the results of $PM_{2.5}$ to total arsenic in dry-ashed samples; comparing the sum of the As(III) and As(V), a mean extraction efficiency of 97% was found, indicating excellent recovery.[12]

As stated above, different extracting solutions have been used to perform the extraction of arsenic species. In these studies, the yield of extraction, the possible inter-conversion of As species, and their recoveries were sometimes evaluated by spiking with exogenous As(III) and As(V). The use of speciated isotope dilution mass spectrometry (SIDMS) to study possible arsenic species inter-conversions occurring during the extraction is not applicable.[27-29] In literature, use of X-ray absorption near edge structure (XANES) spectroscopy as a benchmark for validation of extraction methods is often reported.[29,30] XANES is a non-destructive element-specific technique for characterising electronic configurations of both amorphous and crystalline materials.[31,32] In synchrotron-based characterisation of arsenic species in urban particulate matter and particulate matter derived from coal combustion, As(V) was reported to be the most dominant form.[33,34]

Ambient air monitoring focusses on particulate matter, however and especially in the case of high temperature metallurgical processing, besides arsenic in particles, gaseous arsenic emissions may be of concern. Impregnated filters have been found to be able to capture simultaneously both particulate arsenic and arsenic oxide vapour and have been used for total arsenic collection, amongst others, in the vicinity of a copper smelter.[25] The volatile arsenic trioxide can be collected by reaction with the chemical agent on the impregnated filter, e.g. sodium carbonate (As_2O_3 + $Na_2CO_3 \rightarrow 2\ NaAsO_2 + CO_2$) and thereafter, a determination of the total arsenic content is performed.[24,25] For example, the presence of arsenite, arsenate, arsenic sulfide and As_2O_3 vapour have been reported in copper smelter emissions.[24]

The work in this paper describes the determination of inorganic arsenic species in ambient particulate matter (PM) near a metallurgical industrial plant situated in Antwerp (Belgium), where according to recent modelling data (2011) the European target value of 6 ng m^{-3} is exceeded in an area of ca. 0.6 km² with 3000 inhabitants.[35] For this purpose a monitoring campaign was organized, where PM_{10}, $PM_{2.5}$ and arsenic vapour were collected on filters and the total element concentration of arsenic and its speciation were determined. The determination of total As concentration was performed using Energy Dispersive X-ray fluorescence spectrometry (EDXRF). The determination of

particulate As(III) and As(V) was performed using a microwave extraction in combination with HPLC/ICP-MS on one hand and XANES spectroscopy on the other.

Experimental section

Sampling

Sampling for total arsenic concentration in PM

Ambient particulate matter (PM_{10} and $PM_{2.5}$) was collected at 24 hour intervals in an urban area in the vicinity of a metallurgical site in the Flemish region of Belgium with a filter sampler (Leckel SEQ47/50 sequential sampler, Germany). Sampling was performed at a flow rate of 2.3 m^3 h^{-1} on PTFE filters (Teflo 47mm, Pall Life Sciences).

Sampling for particulate As(III) and As(V)

Ambient particulate matter (PM_{10} and $PM_{2.5}$) was collected at 24 hour intervals with a Partisol 40201 Speciation Sampler (Thermo Fisher Scientific Inc, Waltham, USA). Sampling was performed at a flow rate of 0.6 m^3 h^{-1} on ashless cellulose filters (grade 40, Whatman International Ltd., Maidstone, UK).

Sampling for total As (particulate arsenic compounds and arsenic trioxide vapour)

Sampling was performed according to NIOSH standard 7901 (1984), in which a methodology is described to collect particulate arsenic compounds as well as arsenic trioxide vapour. Air is sucked through a filter impregnated with a 20:1 Na_2CO_3: glycerol solution. Sampling was performed with a Partisol 2300 Speciation Sampler (Thermo Fisher Scientific Inc.).

Instrumentation

Particulate As(III) and As(V) by HPLC/ICP-MS

For the determination of particulate As(III) and As(V), filters were extracted during 20 min with 100 mM ascorbic acid and 1 M H_3PO_4 at 80°C using microwave heating (Anton Paar, Multiwave 3000). After 10-fold dilution, extraction solutions were analysed using a quadrupole-based ICP-MS instrument (Nexion 300S, Perkin Elmer), equipped with an ESI Microflow PFA-ST concentric nebulizer (Elemental Scientific Inc or ESI, NE, USA) coupled to a 50 mL baffled cyclonic spray chamber (Perkin Elmer). The ICP-MS operation parameters are summarized in Table 1. The speciation was carried out using a Flexar LC system (PerkinElmer, Waltham, MA, USA) consisting of Flexar Quaternary LC pump FXQ pump, a Flexar Solvent Manager and a Flexar LC autosampler. The speciation was carried out using a ESI CF-As-01 column (ESI).[36] The eluent was pushed through the column at a flow rate of 400 µL min^{-1} using a 50 µL sample loop with the following program: 2.5 min eluent 1 (1.06 ml 25% NH_3 + 1.36 ml 8.5% H_3PO_4 in 500 ml); 6 min eluent 2 (1.05 ml 25% NH_3 + 3.41 ml 8.5% H_3PO_4 in 50 ml); 8 min eluent 1. Cesium was added at a concentration level of 1 µg L^{-1} in both eluents and monitored along the chromatogram as an internal standard.

Total As (particulate arsenic compounds and arsenic trioxide vapour) by ICP-SFMS

For the determination of total As in PM, the NIOSH standard 7901 prepared filters were extracted during 20 min with 100 mM ascorbic acid and 1 M H_3PO_4 min at 80°C using microwave heating. After 5-fold dilution, extraction solutions were analysed using inductively coupled plasma sector field mass spectrometry (ICP-SFMS, Element II, Thermo).

Total As in PM by EDXRF

The elemental concentration of As on the filters was measured using a high performance energy dispersive XRF spectrometer with polarised X-ray excitation geometry (HE XEPOS, Spectro Analytical Systems, Kleve, Germany). This instrument is equipped with a 50 W tungsten end-window tube (max. 60 kV, 2 mA) and a Silicon Drift Detector. For signal optimisation the used targets were Mo, Al_2O_3, Co and Pd(L) target. The calibration of the XRF spectrometer was performed using in-house made standard filters. An in-house developed aerosol generation system based on the ultrasonic nebulisation of a multi-element solution was used for the collection of aerosols on a filter.[37]

XANES

The XANES measurements were performed at the ANKA SUL-X Beamtime (Proposal ENV-247). XANES spectra are recorded by tuning the energy of incident X-ray photons across an absorption edge of a specific element present in the sample (here, As at the K-edge). The XANES contains information about the chemical state of the absorbing element. One common method (fingerprinting) is to compare spectra of unknown samples. The X-ray source of SUL-X is a 27-pole wiggler operating at K = 8.5 (wiggler gap, 16 mm). A silicon (111) crystal pair with a fixed beam exit was used as monochromator. The X-ray beam was aligned with an intermediate focus, and finally focused by Kirkpatrick–Baez mirrors to about 100 mm (horizontal) x 20 mm (vertical) for measurements at the tidemark and to about 200 mm (horizontal) x 150 mm (vertical) for data acquisition. The fluorescence radiation was collected using a seven element Si(Li) solid-state detector (Gresham, now e2v) and a digital signal-processing system (DXP) from XIA. The absorption spectra were recorded summing all fluorescence emission counts within the As-Ka region of interest. The resulting XANES spectra were analyzed using ATHENA, which is included in the IFEFFIT package for XAS analysis (Newville, 2001; Ravel & Newville, 2005; Newville, 2009). Each scan was normalized to an edge jump of unity and its energy scale was calibrated with respect to the Au-L3 edge. This energy calibration was based on the transmission of an elemental gold foil that was recorded simultaneously for each sample. The first maximum of the derivative of the Au XANES was calibrated to 11919 eV (Au L3 edge) for each scan. The LSLC fitting range was restricted to -20 to +50 eV around the absorption edge (defined as the first maximum of the derivative).

XRD

The X-ray diffractograms were analysed with an X-Pert Pro from PANalytical (Eindhoven, Netherlands). The measurements were done on a standard sample holder. The measurement conditions were : Cu-K-alfa : 40kV; 40mA; step 0.04°2theta; time: 4s; continuous scan. A monochromator and soller slits were used combined with a spinner and a proportional detector

Standard solutions and reagents

For the preparation of all solutions, ultra-pure water with a resistivity of 18 MΩ cm^{-1} obtained from a Milli-Q water purification system (Millipore, MA, USA) was used.

Stock standard solutions for the calibration of the HPLC/ICP-MS were prepared from a 1 g L^{-1} As (III) and As(V) standard solutions purchased from Chem-Lab (Zedelgem, Belgium). A stock standard solution of 10 mg L^{-1} As form Spex CertiPrep Inc. (NJ, USA) was used for the calibration of the ICP-SFMS. For the HPLC, eluent 1 was prepared by dissolving 1.06 ml 25% NH_3 (Merck, Darmstadt Germany) and 1.36 ml 8.5% H_3PO_4 (Merck) in 500 ml Milli-Q water. Eluent 2 was prepared by dissolving 1.05 ml 25% NH_3 and 3.41 ml 8.5% H_3PO_4 in 50 ml Milli-Q water.

For the extraction solution L(+)-ascorbic acid (BDH Prolabo, Leuven, Belgium) and H_3PO_4 (Merck) was used. For the sampling according to NIOSH standard 7901, filters were impregnated in a 50 ml 85 % glycerol (Merck) and 95 g Na_2CO_3 (Merck) in 1 L Milli-Q water solution.

For XANES reference compounds, the following reagent-grade As compounds were purchased: $NaAsO_2$, As_2O_5, As_2O_3, As_2S_3, FeAsS, $Ca_3(AsO_4)_2$ (Alfa Aesar GmbH, Karlsruhe, Germany). Supplementary, a residue produced at the lead refinery, $Ca_3(AsO_4)_2$ (135 g As kg^{-1}) and a fly ash sample (filtered by a bag filter) containing As_2O_3 (273 g As kg^{-1}) were collected at the monitoring site.

Spiking of filters
Ashless cellulose filters (grade 40, 47 mm, 8 µm, Whatman International Ltd., Maidstone, UK) were selected for sample collection. The addition of As(III)/As(V) was performed by spiking with an automatic pipette 50-100 µl of a prepared As(III)/As(V) solution (Chem-Lab) on the filter.

Results and Discussion

Performance characteristics of the HPLC/ICP-MS speciation monitoring method

At first, the extraction according to Oliveira *et al.*, also used by Sanchez-Rodas *et al.* for PM_{10} and by Sánchez de la Campa *et al.* for $PM_{2.5}$ was evaluated.[12,14,15] The procedure consists of a microwave extraction (150 W) of the filter during 4 min with 100mM NH_2OH-HCl. According to Oliveira *et al.* recoveries between 82 – 109 % of the total arsenic content are to be expected.[14] However, the recovery of total As using this extraction procedure on 10 air filters collected at the sampling site ranged between 5-100 %. Therefore a more rigorous microwave extraction method as described by Sun et al. using 100 mM ascorbic acid (used as an antioxidant) and 1 M H_3PO_4 during 20 min at 80°C was used.[38,39]

The accuracy of this procedure was verified by extracting NIST 2583 trace elements in indoor dust (certified value is 7.0 ± 1.6 mg kg^{-1} As, but using digestion procedures an indicative mean of 5.2 mg kg^{-1} As is reported). An average As(III) concentration of 0.12 ± 0.08 mg kg^{-1} (n = 6) and average As(V) concentration of 5.85 ± 0.27 mg kg^{-1} (n = 6) was measured. The accuracy was further verified by comparing the total As content determined by EDXRF and the As(III)+ As(V) content determined by HPLC/ICP-MS on 6 PM_{10} air filters collected at the sampling site (see Table 2).The comparison of total As measured with EDXRF and total As calculated as the sum of measured As(III) and As(V) with HPLC/ICP-MS shows a good correlation (range 97-108%).

In order to control possible species inter-conversion, separate solutions containing 5 µg L^{-1} As(III) and As(V) respectively were extracted with the above mentioned procedure and measured by HPLC/ICP-MS. An average As(III) concentration of 5.06 ± 012 µg L^{-1} (n = 6 , RSD 2.4 %, bias = + 1.3 %) and average As(V) concentration of 5.09 ± 0.07 µg L^{-1} (n = 6 , RSD 1.4 %, bias = + 1.8 %) were derived. These results confirm that the extraction procedure itself does not induce arsenic species inter-conversion.

Based on 7 separate measurements of a 10-fold dilution extraction solution (10 mM ascorbic acid + 100 mM H_3PO_4) containing 0.1 µg L^{-1} As(III), respectively As(V), a limit of quantification (6 * st. dev.) of 0.020 en 0.013 µg L^{-1} was derived for the HPLC/ICP-MS method. Taking into account the 10-fold dilution of the extraction solution and a sampled air volume of 14 m^3 per filter, this corresponds to an LoQ of 0.34 ng m^{-3} As(III) and 0.23 ng m^{-3} As(V) for the monitoring method. The possible co-elution of As(III) with trimethylarsine oxide (TMAO) using an anion exchange column, leading to a possible overestimation of the As(III) concentration, has been recently reported.[2,3] However, the maximum observed concentrations of TMAO in PM (0.09 ng m^{-3}) is below the LoQ of the monitoring method and negligible in the present case study.

Based on 26 duplicate measurements of extraction solutions of sampled filters, a relative precision (95 % confidence interval) of 9.6 % for As(III) and of 12.2 % for As(V) was derived for the HPLC/ICPMS method. This is in line with reported precision in literature, *e.g.*, Rabano et al. reported precision error of 8% for unexposed filters versus 23% for exposed filters, based on the addition of speciated arsenic standards to these matrices.[6,19] Šlejkovec *et al.* reported a study with an RSD of <10%.[17]

The precision (st. dev.) of the ICP-SFMS method, used for the determination of total As (particulate arsenic compounds and arsenic trioxide vapour) according to NIOSH standard 7901, was verified by extracting NIST 2583 in every measurement run. An average total As concentration of 5.43 ± 0.19 mg kg^{-1} As (n = 4) was found.

Stability of the arsenic species

Stability studies offer another potential method of evaluating accuracy. Based on our review, little information is available on the stability of arsenic species in air, but the oxidation of As(III) to As(V) in the atmosphere by oxidants such as ozone has been reported.[13] Sánchez-Rodas et al., evaluated short- (within 1 day of sampling) and long- (sample analysed monthly for 1 year) term chemical stability in a sample exhibiting elevated arsenic concentrations;[15] no increase, decrease, or conversion of arsenic species (As(III) and As(V)) was noted. Oliveira et al., also evaluated sample stability for both total and speciated arsenic (As(III) and As(V)) after both extraction and speciation analyses.[14] According to their findings, no changes in the distribution of arsenic species occurred during a 33-month period. Neither of these studies reported how the samples were stored during the stability analysis. Therefore, at least among these studies, the form of arsenic species in the sample appeared stable over time for a given method.

Stability of arsenic species during conservation

To study the stability of the arsenic species during conservation, filters were spiked in 4-fold with respectively As(III) and As(V) (at a level of 2000 ng/filter) and stored at different conditions during 28 days at < -18°C, at < 5°C and at room temperature (21°C). The results are summarised in Figure 1. The results confirm the stability of As(III) and As(V) species over a period of 28 days, when preserved under < 5°C conditions and, in case of As(III), the need for keeping filters cool during storage.

Stability of arsenic species during sampling

To further study the stability of As(III) and As(V) species during sampling, 12 filters were spiked with As(III) (2000 ng/filter) and another set of 12 filters was spiked with As(V) (2000 ng/filter). Those filters were used in a preliminary sampling campaign (period 2-14/11/2013) in the vicinity of the industrial site. At the same time, sampling was also performed on non-spiked filters in order to correct for the As species present in the sampled PM (local background concentration). The filters were sampled on a daily basis and were left on-site (in the sample holder) during the 12 days sampling campaign. The results are summarised in Table 3. The recovery of the spikes was calculated as given in the following example: on 2/10/2013 the concentration of As(III) and As(V), respectively, on the non-spiked filter amounted 0.44 and 4.6 ng m^{-3}. On the spiked filter (where a theoretical value of 36.3 ng m^{-3} As(III) was added), a concentration of As(III) and As(V) of 20.2 and 19.7 ng m^{-3}, respectively, was measured. The As(III) recovery was calculated as (20.2-0.44)/36.3 ~ 54%, the recovery for total As concentration of the spike, total As recovery = (20.2+19.7-0.44-4.6)/36.3 ~ 96%. In Figure 2 the recoveries for the spiked As(III), As(V) and total As are summarised.

More than 70 % of the total content of the arsenic spike concentration is recovered in all cases. It must be mentioned that for the calculation of the recovery, the uncertainty includes the measurement as well as the sampling (two separate filters were used). A different stability is observed for the As species. No conversion from As(V) spike to As(III) spike is observed, while significant conversion from the As(III) to As(V) spike is observed during sampling. The As(III) spike is recovered as As(III) in the range of 45 – 65 %, while the remainder is oxidised to As (V). To further address the As(III) conversion, exogenous As(III) spiked filters were also processed during the final monitoring campaign.

Results of the monitoring campaign (40 days)

Monitoring setup

A daily monitoring campaign was organised between 7 November and 16 December 2013 in an urban area, in the vicinity of an industrial plant situated in Antwerp (Belgium), where according to modelling data of 2011, an exceedance of the European target value for arsenic of 6 ng m^{-3} was to be expected.[35] During the campaign, the meteorological conditions were normal for the time of the year; an average temperature of 6°C, a precipitation of 55 mm and a wind mainly coming from the SW. During the campaign, the following parameters were determined: total As in PM_{10} and $PM_{2.5}$ (PTFE filter/EDXRF), As(III) in PM_{10} and $PM_{2.5}$ (Whatman filter, HPLC/ICP-MS), As(V) in PM_{10} and $PM_{2.5}$ (Whatman filter, HPLC/ICP-MS), total As (particulate arsenic compounds and arsenic trioxide vapour) in PM_{10} and $PM_{2.5}$ (filter prepared according to NIOSH 7901/ICP-SFMS). During the monitoring campaign, PM_{10} was also sampled and analysed on a daily basis by two other laboratories. These laboratories used Wavelength Dispersive (WD)XRF and EDXRF for the determination of the total As content and cellulose nitrate and quartz filters for sampling respectively.

As concentration in PM_{10}

In Figure 3 an overview is given of the total As concentration in PM_{10} measured on a daily basis during the monitoring campaign. A good correlation is observed between the total As concentration determined by the three laboratories using different sampling units, different types of filter and different types of XRF instruments and the total As concentration in PM_{10} measured by HPLC/ICP-MS. Total As in PM_{10} was determined by HPLC/ICP-MS as the sum of the measured As(III) and As(V) concentration (for clarity, only results > 6 ng m^{-3} are shown in Figure 3). For the EDXRF/WDXRF measurements, 55 m^3 of air was sampled (Leckel), while in case of HPLC/ICP-MS 14 m^3 of air was sampled (Speciation) within 24 h. For the results > 6 ng m^{-3} (Figure 3), a 84 % median recovery (N = 23) was found between particulate As collected on ashless cellulose filter and measured by HPLC/ICP-MS on one hand and the average XRF result on the other.

Particulate arsenic compounds and arsenic trioxide vapour

During 11 days, a supplementary sampling set-up was performed in order to verify the presence of volatile As species (As_2O_3 vapour). During this campaign, two filters were placed in series, the first consisted of an ashless cellulose filter (sampling of particulate As(III) and (As(V)), the second filter was a Na_2CO_3/glycerol solution impregnated ashless cellulose filter (sampling of arsenic trioxide vapour, NIOSH 7901). This set-up was used for PM_{10} as well as for $PM_{2.5}$ sampling (see Table 4 and Table 5). For the results > 6 ng m^{-3} reported in Table 4 and Table 5, a 84 % median recovery (N = 9) for PM_{10} and a 86 % median recovery (N = 6) for $PM_{2.5}$ was found between particulate As collected on ashless cellulose filter and measured by HPLC/ICP-MS on one hand and the XRF (collected on PTFE filter) result on the other.

These 15 % lower results of particulate As collected on ashless cellulose filter and measured by HPLC/ICP-MS as compared to the XRF results collected on PTFE filter are in contrast to the results of the validation study on 6 PM_{10} air filters collected at the sampling site (see Table 2), for which a good correlation was found (range 97-108%). However, the results of the validation study were based on the analysis of the same filter. Therefore a filter efficiency test was performed to evaluate the particle retention of the ashless cellulose filter. With the use of 2 optical particle counters (Grimm 1.108 dustmonitor (Grimm Technologies, Inc.) for the fine particles and a 8025 P-Trak (TSI, Inc.) for the ultrafine particles) a filter efficiency of approx. 85 % for both fine and ultrafine particles was determined on a set of blank ashless cellulose filters in the lab. These results indicate that the amount of As found on the second filter might in fact be particulate As and not As_2O_3 vapour. The results reported as As_2O_3 vapour in Table 4 and Table 5 can therefore be considered as an artefact

of the sampling and the sum As(III)+ As(V)+ As_2O_3 vapour can be interpreted as consisting of particulate As only.

Inter-conversion of As species

In the stability study (see above), As(III) conversion up to 55% was observed on spiked filters during sampling. In order to further study this As(III) oxidation, spiked As(III) filters were processed during this sampling campaign (in concentrations of 2000 and 1000 ng As/filter). In order to calculate the recovery of the As(III) spike, sampling was also simultaneously performed on non-spiked filters (PM background concentration). Four control spiked filters were stored at < -18°C and extracted and analysed at the same time as the spiked filters that were sampled. No significant oxidation of As(III) was observed in the (non-sampled) control filters stored at -18°C and the recovered total concentrations were in good agreement with the theoretical values (see Table 6). The recoveries of the spiked As(III), calculated as the recovery of the total spiked As concentration and as the recovery of the As(III) species, are summarised in Table 7 for PM_{10} and Table 8 for $PM_{2.5}$.

The total content of the spiked arsenic is well retrieved during the PM_{10} sampling (106-110%). However, a significant portion of the As (III) spike is converted to As (V) (conversion varies between 0 up to 54%) and these values are in line with the conversions observed in the preliminary sampling campaign performed in the stability study (see Figure 2).

The total content of the arsenic spike is well retrieved during the $PM_{2.5}$ sampling (average 101%). Similar to the observations for PM_{10} sampling, a significant fraction of the As(III) is converted to As(V) (conversion varies between 8 and 53%)(see also Figure 4). It is remarkable that on two days, where (very limited) sampling was performed due to a defect in the sampling device (12/11 and 19/11) almost no conversions of the exogenous spiked As(III) are observed (7 and 1%). This strongly indicates the effects of ambient sampling conditions and ambient particles on the As(III) recoveries and that the extraction of the filter in combination with the sampled air matrix is likely to induce the As conversions. While this inter-conversion information is relevant for interpretation of the data, correction for the As(III) conversion itself is ambiguous because of the possible difference in oxidation between the added exogenous As(III) spike species and the As(III) species actually present in the sample.[29]

As in PM_{10} versus $PM_{2.5}$

The average results of the measurements performed during the monitoring campaign are summarised in Table 9. The average concentration of As in the $PM_{2.5}$ fraction (25 ng m⁻³) is half the value of the PM_{10} fraction (50 ng m⁻³) during the sampling period 7-18/11. The reported total As (HPLC/ICP-MS + ICP-SFMS) represents the sum of the particulate As(III)+As(V) measured with HPLC/ICP-MS and the arsenic collected on the second impregnated filter placed in serie, which also represents particulate arsenic species caused by insufficient separation efficiency of the first filter (see discussion above, Table 4 and Table 5), and measured with ICP-SFMS. Based on the simultaneous sampling of the PM_{10} en $PM_{2.5}$ fractions, an average concentration of *ca*. 4.1 ng As per μg PM_{10} and 4.2 ng As per μg $PM_{2.5}$ was found (see Table 10). These results suggest that no relative enrichment is observed for total As in one of the particulate matter fractions as no significant difference is found between the amount of As per mass of PM for PM_{10} and $PM_{2.5}$. An enrichment of arsenic in the fine fraction ($PM_{2.5}$) of airborne particulate matter was observed by Tsopelas *et al.* and Sanchez de la Campa *et al.*[12,13]

A similar calculation was performed to determine whether the contribution of As(III) is increased in the $PM_{2.5}$ fraction compared to the PM_{10} fraction. The As(III) concentration (in ng m⁻³) was divided

by the PM concentration (in µg m^{-3}) respectively for PM_{10} and $PM_{2.5}$ (see Table 10). The amount of As(III) is slightly enriched in the $PM_{2.5}$ fraction. In PM_{10}, As (V) is the main component, while in $PM_{2.5}$, As(III) is the dominant species.

Fraction As(III) versus As(V) in PM_{10}

The measurement results of the monitoring campaign show that there is a trend towards a higher fraction of As(III) with increasing concentrations of total As (see Table 11). This conclusion is visualised in Figure 5, in which the As (III) percentage is given as a function of the wind direction and as a function of the total As-concentration. The industrial site was situated SW of the monitoring location. For the layout of this figure, daily monitored As concentrations of PM_{10} (total As and the percentage of As(III)) were merged to hourly wind direction measurements. Each combination of total As concentration (one daily averaged value) and hourly wind direction (24 measurements per day) are plotted as a pollution rose, where total As concentrations are given with respect to a concentric circle scaling (in ng m^{-3} As, 30 ng/m³ wide intervals) and wind directions with respect to the N, E, S and W axes (10° wide intervals). The colouring of these 'bins' is in accordance with the percentage of As(III) of the total As concentration as represented by different colours (see legend). At low concentrations of total As the As(III) contribution is limited, with increasing concentration, the As(III) contribution increases as well.

XANES analysis

X-ray based techniques are generally regarded as reference methods for solid state speciation since they enable the identification and quantification of oxidation states while being non-destructive.[31] A number of studies have been published on arsenic speciation with XANES.[33,34,41] A great advantage of XANES is that it can distinguish between different compounds of the same element, including different oxidation states (e.g., As(III), As(V)) as well as different compounds with the same oxidation state (e.g., As_2O_3, As_2S_3). For this study, the following reagent-grade As compounds were purchased: As_2O_5, As_2O_3, As_2S_3, $Ca_3(AsO_4)_2$. Besides those compounds, also an arsenic containing residue produced at the lead refinery and a fly ash sample (filtered by a bag filter), both originating from the metallurgical site, were analysed as well as they were likely to be representative for the sources of As pollution at the monitoring site.

Reference compounds

In a preliminary study, the residue produced at the lead refinery and the fly ash sample, both likely to represent sources of As at the monitoring site, were analysed by XRF, XRD and EXAFS to further elucidate the kind of arsenic species present.

In the fly ash sample, the following components were identified by XRD: As_2O_3 (Arsenite), $Pb_5(AsO_4)_3Cl$ (Mimetite) and a structure isomorphous with tetragonal $(Sn_{0.8}Sb_{0.2})O_2$. The content of major elements, measured by EDXRF, amounted 270 g kg^{-1} As, 190 g kg^{-1} Sb, 190 g kg^{-1} Pb and 30 g kg^{-1} Sn. A qualitative evaluation of the EXAFS confirms the similarity between the reagent-grade As_2O_3 and the fly ash containing As_2O_3, only small structural differences might exist in the 1st and 2nd coordination shell: the As-O bond length seems a bit larger and the amplitude corresponding to the O atom at 3.45Å (O in the As_4O_6 cage) seems enhanced with respect to the amplitude corresponding to the O atom at 3.05Å (not in the As_4O_6 cage). This could be a hint that the As_4O_6 cages do exist but their arrangement is less regular. The XANES and EXAFS collected for fly ash clearly suggest that fly ash is almost identical to cubic As_2O_3 (Arsenolite), with a slightly changed crystalline structure and/or degree of crystallinity. In the remainder of this paper, this source will be denoted by As_2O_3 (fly ash).

The XRD analysis identified 3 components in the residue produced at the lead refinery. The main phase was $(Ca_{8.40}Sr_{1.60})(AsO_4)_{2.58}(PO_4)_{3.42}(F_{0.69}(OH)_{1.31})$ corresponding to Fermorite $(Ca_3Sr_2(AsO_4)_{2.5}(PO_4)_{0.5}(OH))$. The other phases were identified as $Ca(OH)_2$ (Portlandite) and $Ca(CO_3)$ (Calcite). The content of major elements, measured by EDXRF, amounted 260 g kg^{-1} Ca, 140 g kg^{-1} As and 0.2 g kg^{-1} Sr. In the remainder of this paper, this source will be denoted by $Ca_3Sr_2(AsO_4)_{2.5}(PO_4)_{0.5}(OH)$ (residue).

The reagent-grade As compounds As_2O_5, As_2O_3, As_2S_3 and $Ca_3(AsO_4)_2$ were also analysed by XRD. All compounds were positively identified, except $Ca_3(AsO_4)_2$ which was identified as Haidingerite, a calcium arsenate mineral with formula $Ca(AsO_3OH) \cdot H_2O$.

Filters

At first, to check possible beam damage, a filter spiked with an As(III) standard solution was measured. Immediately after the start of a series of quickscans a strong change in the scan curves was observed. A loopscan (1 sec measurements at same energy and point) at the whiteline of As(III) showed a rapid decline of As fluorescence radiation. When performing the analysis under vacuum condition, no change of the As(III) XANES spectrum was observed. To reduce the impact of the beam only very short measurements were done on a single point on the sample. To improve statistics (signal-to-noise-ratio) several XANES measurements were spread over different points and merged together.

A description of the filters, sampled in the vicinity of the industrial site, and analysed by XANES are summarised in Table 12. Based on the modelling, the best fitting of the spectra was obtained using As_2O_5, $Ca_3Sr_2(AsO_4)_{2.5}(PO_4)_{0.5}(OH)$ (residue) and As_2O_3 (fly ash) as reference compounds. An example of the fitting with these reference compounds is given for filter E in Figure 6. The relative contributions of the different As species as calculated based on the XANES measurements are summarised in Figure 7. The R-factor of each fit (the quality of fit parameter commonly used in XANES analysis) is also shown in Figure 7.[45] In the 5 filters analysed by XANES, the fraction $Ca_3Sr_2(AsO_4)_{2.5}(PO_4)_{0.5}(OH)$ residue (As(V)) varies between 23-44 %, the fraction As_2O_3 (As(III)) varies between 26-44 % and the fraction of As_2O_5 (As(V)) varies between 18-51 %. These results are in line with the fractions observed during the monitoring campaign (40 days), where the fraction of particulate As(III) varied between 19-61 % in PM_{10} and 19-69% in $PM_{2.5}$ (14 days).

Fraction As(III) versus As(V)

At this point, two hypothesis may be formulated. First, in the gas cleaning systems with injection of lime that are used to capture volatile arsenic in mettalurgical processing, the lime precipitates As(V) as hydroxyl and hydrated calcium arsenates.[24] However, it has been reported that these compounds may not have long-term stability, showing that calcium arsenate compounds decompose slowly in contact with atmospheric CO_2 to form calcium carbonate and soluble arsenic acid.[24] In this case it may be hypothesised that the fraction of As_2O_5 (As(V)) results from the decomposition of the fraction $Ca_3Sr_2(AsO_4)_{2.5}(PO_4)_{0.5}(OH)$ residue (As(V)). Second hypothesis, based on the exogenous As(III) spiked filters, oxidation up to ~50 % in case of PM_{10} and $PM_{2.5}$ samples has been observed during the monitoring campaign and stability study. The hypothesis that the fraction As_2O_5, as calculated by XANES, originates from oxidation of As_2O_3 is therefore likely as well and, consequently, two scenarios can be calculated for the fraction of As (III) and As (V). In the first scenario the fraction of As_2O_5 is included in the fraction of As(V), in the second scenario it is

assumed that As_2O_5 originates from oxidation of As_2O_3 and is therefore included in the As(III) fraction. The fact that proportionally more As_2O_5 is found in the samples collected in June-July (Filter A-D) in comparison to the filter that was collected in October (Filter E), may be assigned to oxidation of As_2O_3 during prolonged storage or to decomposition of the $Ca_3Sr_2(AsO_4)_{2.5}(PO_4)_{0.5}(OH)$ residue, considering that XANES measurements were performed in November.

In the first scenario (As_2O_5 originates from decomposition of the $Ca_3Sr_2(AsO_4)_{2.5}(PO_4)_{0.5}(OH)$ residue), the fraction of particulate As(III) would vary between 18-51%. In the second scenario (As_2O_5 originates from oxidation of As_2O_3), the fraction of particulate As(III) would vary between 62-77%.

Implications on toxicity

Because of the relatively high toxicity and carcinogenicity of arsenic via inhalation, special attention is required to assess the health risks of arsenic in air. Most literature data on inhalation toxicity are related to studies in workplace atmosphere.[4,40] In occupational exposure (smelters, chemical companies) the major form of arsenic is arsenic trioxide in the form of dust. There is convincing evidence that occupational exposure to arsenic via inhalation leads to an increased risk of lung cancer. Several studies also suggest that living near smelters or chemical plants where arsenic is processed an increased risk of lung cancer is expected. Several agencies have derived a unit risk for lung cancer by inhalation. In the derivation of the unit risks, differences in relative toxicity of arsenic species or particle size were not taken into account.[4,40] As stated earlier, different agencies point to a factor 2-3 difference between As (III) and As (V), with a higher toxicity for As (III), but consider the difference within the uncertainty on the toxicity data. There is currently insufficient scientific information to derive a separate unit risk for smaller ($PM_{2.5}$) and for larger particles (PM_{10}). In accordance with this unit risks and for a population of 1000 persons exposed for lifetime to 1 µg m^{-3} As, there will be a risk of 0.15 to 4.29 additional cancer cases.[40] For an additional lifetime cancer risk of 1 in 1 million lifetime-exposed persons, a number that is fixed in Europe for exposure calculations of the population, the corresponding air concentration with negligible cancer risk amounts to 0.23-6.7 ng m^{-3}As and is below the average concentration measured during this monitoring campaign.[4]

Conclusion

The developed HPLC/ICP-MS method allows monitoring of particulate As(III) and As(V)-species, with a LoQ of 0.34 ng m^{-3} As(III) and 0.23 ng m^{-3} As(V) respectively. The precision (95% confidence interval) of the method is 10% and a good agreement is obtained between the sum of the concentrations of As(III) and As(V) determined by HPLC/ICP-MS and the total As concentrations determined by XRF (indication of a complete extraction of the As species). There were no conversions As(III) <-> As(V) determined during the extraction and measurement of control solutions of both arsenic species. However, during sampling, significant conversion (oxidation) of exogenous spiked As(III) to As(V) was observed (conversion up to 54% in case of PM_{10} and up to 53% in case of $PM_{2.5}$). The total content of the spiked As (III) was well-recovered (PM_{10} and $PM_{2.5}$ on average 108% and 101%, respectively). This strongly indicates the effects of ambient sampling conditions and ambient particles on the As(III) recoveries and that the extraction of the filter in combination with the sampled air matrix is likely to induce the As conversions.

The average measured As concentration in PM_{10} (30 ng m^{-3}) at the hot spot location is above the European target value of 6 ng m^{-3}. The measured As concentration in $PM_{2.5}$ was half the value of the measured concentration in PM_{10}, but no relative enrichment of total As was observed in one of

both particulate matter fractions. However, in PM_{10}, As (V) was the main component, while in $PM_{2.5}$, As(III) was the dominant species. During the monitoring campaign (7/11-16/12/2013) the fraction of particulate As(III) varied between 23 – 63 % and a trend towards a higher fraction of As(III) with increasing concentration of total As was observed. The ashless cellulose filter used for the sampling of the particulate arsenic species showed an insufficient separation efficiency (~85 %) and biased the subsequent sampling of arsenic vapour (As_2O_3). Based on the comparison of total As measurements by ICP-MS (including sampling for arsenic vapour) and XRF (only particulate As), the presence of arsenic vapour (As_2O_3) at the sampling location is unlikely.

XANES and XRD analyses were used for the identification of arsenic species in local PM sources and confirmed the presence of $Ca_3Sr_2(AsO_4)_{2.5}(PO_4)_{0.5}(OH)$, As_2O_3 and As_2O_5 species. It was hypothesised that the fraction As_2O_5, as calculated by XANES, originated from oxidised As_2O_3 or the decomposition of calcium arsenate. The multi-disciplinary approach, including HPLC/ICP-MS, XRF, XRD and XANES has shown to be a powerful tool to study and monitor arsenic speciation in ambient particulate matter.

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Table 1: ICP-MS operating parameters

Parameter	Value
RF power	1500
Plasma gas flow rate	18 L/min
Auxiliary gas flow rate	1.2 L/min
Nebulizer gas flow rate	0.9-1.0 L/min daily tuning
Deflector voltage	- 8.13 V
Discriminator Threshold	15
Rpq	0.25 (Standard)
Dwell time	250 ms
Detector mode	Pulse
Measured m/z	^{75}As; ^{133}Cs

Table 2: comparison of total As measured with EDXRF and total As calculated as the sum of measured As(III) and As(V) with HPLC/ICP-MS.

	EDXRF ng As/filter	HPLC/ICP-MS ng As/filter	Recovery %	As(III) ng As/filter	As(V) ng As/filter
Filter 1	2006	2167	108%	804	1363
Filter 2	2907	2973	102%	284	2689
Filter 3	5696	5509	97%	2010	3499
Filter 4	4777	4656	97%	421	4235
Filter 5	1677	1680	100%	278	1402
Filter 6	6319	6101	97%	843	5258

Table 3: measured As(III) and As(V) concentrations during stability control sampling campaign.

Sampling day	Theoretical concentration added spikes		Measured concentration non-spiked filters		Measured concentration spiked filters	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}
2/10/2013	36.29		0.44	4.56	20.2	19.7
3/10/2013		36.32	0.40	3.39	0.5	39.4
4/10/2013	36.32		*	*	23.6	28.3
5/10/2013		36.30	3.64	5.42	3.1	39.9
6/10/2013	36.30		*	*	22.4	15.8
7/10/2013		65.00	54.93	42.81	52.3	89.8
8/10/2013	58.81		5.08	15.44	40.1	35.8
9/10/2013		36.31	*	*	56.6	56.0
10/10/2013	36.29		31.88	15.28	48.1	28.6
11/10/2013		36.31	0.28	1.34	0.1	37.6
12/10/2013	36.30		*	*	28.2	26.1
13/10/2013		36.30	16.70	29.65	14.3	58.4
14/10/2013	85.95		1.05	2.61	58.1	35.3

* measurements failed due to technical reasons

Table 4: measurement of individual particulate As(III), As(V) by HPLC/ICP-MS, As_2O_3 vapour by ICP-SFMS and total As by EDXRF in PM_{10} samples.

PM_{10}	As(III)	As(V)	As_2O_3 vapour[*]	sum As(III)+ As(V)+ As_2O_3vapour	XRF
	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}
7/11/2013	93.8	64.8	5.3	163.9	167.5
8/11/2013	13.8	17.9	1.9	33.6	34.5
9/11/2013	40.5	46.4	2.7	89.6	106.6
10/11/2013	9.1	35.3	1.5	46.0	49.5
11/11/2013	6.0	20.0	2.4	28.3	36.4
12/11/2013	5.9	17.9	2.4	26.2	30.1
14/11/2013	4.2	23.1	3.1	30.3	32.9
15/11/2013	1.9	4.4	2.4	8.7	5.8
16/11/2013	3.5	10.7	4.7	19.0	10.2
17/11/2013	1.3	3.6	3.4	8.3	5.1
18/11/2013	9.6	38.1	2.6	50.3	56.6

[*] artefact of the sampling

Table 5: measurement of individual particulate As(III), As(V) by HPLC/ICP-MS, As_2O_3 vapour by ICP-SFMS and total As by EDXRF in $PM_{2.5}$ samples.

$PM_{2.5}$	As(III)	As(V)	As_2O_3 vapour[*]	sum As(III)+ As(V)+ As_2O_3 vapour	XRF
	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}
7/11/2013	52.2	23.3	11.2	86.7	87
8/11/2013	8.6	11.1	< 0.9	19.6	22
9/11/2013	32.9	14.6	3.8	51.4	59
10/11/2013	3.8	10.0	1.3	15.1	13
11/11/2013	5.3	14.6	2.6	22.5	25
12/11/2013					13
14/11/2013	11.0		2.0	13.0	<4
15/11/2013	2.1	6.4	3.2	11.7	<4
16/11/2013	1.8	7.7	2.1	11.6	<4
17/11/2013	1.7	3.8	3.4	9.0	<4
18/11/2013	6.7	15.2	3.1	25.0	26

[*] artefact of the sampling

Table 6: measurement results of the As(III) spiked control filters stored at -18°C.

	ng As(III)/Filter	ng As(V)/Filter
Filter spike 2 µg As(III)	2020	20
Filter spike 2 µg As(III)	2070	20
Filter spike 1 µg As(III)	1010	20
Filter spike 1 µg As(III)	1040	10

Table 7: recovery of As(III)-spiked filters during monitoring campaign (PM_{10}).

PM_{10}		As(III)	As(V)	As spike*	Recovery total As	Recovery As(III)
		ng m^{-3}	ng m^{-3}	ng m^{-3}	%	%
05/12	Non spiked filter	10.6	22.1			
05/12	1 µg As(III) spiked filter	50.5	23.6	70	106%	73%
07/12	Non spiked filter	13.8	14.0			
07/12	2 µg As(III) spiked filter	102.1	47.8	139	108%	74%
09/12	Non spiked filter	24.1	25.6			
09/12	1 µg As(III) spiked filter	48.3	28.0	70	110%	69%
11/12	Non spiked filter	1.5	6.1			
11/12	2 µg As(III) spiked filter	139.0	11.0	139	108%	100%
13/12	Non spiked filter	7.4	21.5			
13/12	1 µg As(III) spiked filter	59.2	17.1	70	110%	85%
15/12	Non spiked filter	17.2	30.4			
15/12	2 µg As(III) spiked filter	64.1	84.1	139	107%	46%

*Approx. 14.4 m³ was sampled on the spiked filters

Table 8: recovery of As(III)-spiked filters during monitoring campaign ($PM_{2.5}$).

$PM_{2.5}$		As (III)	As (V)	As spike	recovery total As	recovery As(III)
		ng m^{-3}	ng m^{-3}	ng m^{-3}	%	%
7/11	Non spiked filter	52	23			
7/11	2 µg As(III) spiked filter	127	88	139	100%	54%
8/11	Non spiked filter	9	11			
8/11	2 µg As(III) spiked filter	91	68	140	100%	59%
9/11	Non spiked filter	33	15			
9/11	2 µg As(III) spiked filter	98	101	151	109%	47%
10/11	Non spiked filter	4	10			
10/11	2 µg As(III) spiked filter	72	79	137	99%	49%
11/11	Non spiked filter	5	15			
11/11	2 µg As(III) spiked filter	94	62	136	98%	64%
14/11	Non spiked filter	< 0.4	2			
14/11	2 µg As(III) spiked filter	83	71	138	109%	60%
15/11	Non spiked filter	2	6			
15/11	2 µg As(III) spiked filter	106	41	137	99%	75%
16/11	Non spiked filter	2	8			
16/11	2 µg As(III) spiked filter	125	21	147	99%	89%
17/11	Non spiked filter	2	4			
17/11	2 µg As(III) spiked filter	130	23	139	105%	92%
18/11	Non spiked filter	7	15			
18/11	2 µg As(III) spiked filter	129	32	143	100%	88%
		ng/filter	ng/filter	ng/filter		
12/11	Non spiked filter	12	27			
12/11	2 µg As(III) spiked filter	1880	107	2000	97%	93%
19/11	Non spiked filter	20	67			
19/11	2 µg As(III) spiked filter	2000	145	2000	103%	99%

Table 9: average concentrations of total As, As(III) and As(V) in PM_{10} and $PM_{2.5}$ during the monitoring campaign.

Species (ng m^{-3})	7-18/11/2013		7/11 – 16/12/2013
	PM_{10}	$PM_{2.5}$	PM_{10}
Total As (XRF)	50	25	33
Total As (HPLC/ICP-MS+ ICP-SFMS)	47	28	31
sum As(III)+As(V) (HPLC/ICP-MS)	44	25	29
As(III)	19	13	12
As(V)	26	12	18

Table 10: amount of As per mass PM, for total As, As(III) and As(V) in PM_{10} and $PM_{2.5}$ fractions.

	As total XRF/PM (ng As / µg PM)	As total ICP-MS/PM (ng As / µg PM)	As(III)/PM (ng As / µg PM)	As(V)/PM (ng As / µg PM)
$PM_{2.5}$	4.4	4.0	2.0	1.5
PM_{10}	4.2	3.9	1.7	2.0

Table 11: median values of the fraction of As(III) and As(V) in function of the total As-concentration in PM_{10}.

	Median fraction As(III)	Median fraction As(V)
All data	27%	72%
> 6 ng m^{-3} total As conc.	29%	69%
> 30 ng m^{-3} total As conc	40%	60%
> 60 ng m^{-3} total As conc	59%	41%

Table 12: description of the filters analysed by XANES.

	Date sampling	fraction	filter	ng As /filter	ng m^{-3} As
Filter A	24/06/2013	PM_{10}	PTFE	820	14.9
Filter B	1/07/2013	$PM_{2.5}$	PTFE	880	15.9
Filter C	2/07/2013	$PM_{2.5}$	PTFE	890	16.1
Filter D	3/07/2013	PM_{10}	PTFE	900	16.3
Filter E	4/10/2013	PM_{10}	ashless cellulose	1180	25.4

Figure 1: stability study of As(III) and As(V) spiked on filters (2 μg/filter) and preserved during 0 days and 28 days under different conditions. The error bars represent the standard deviation on the measurement of 4 filters.
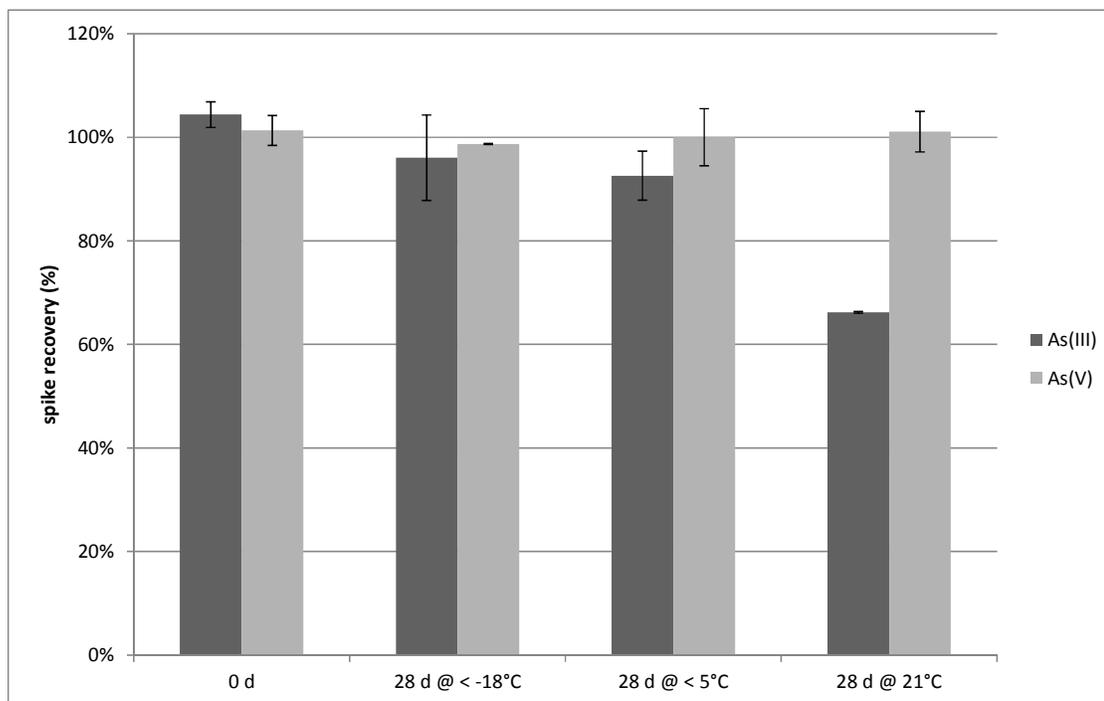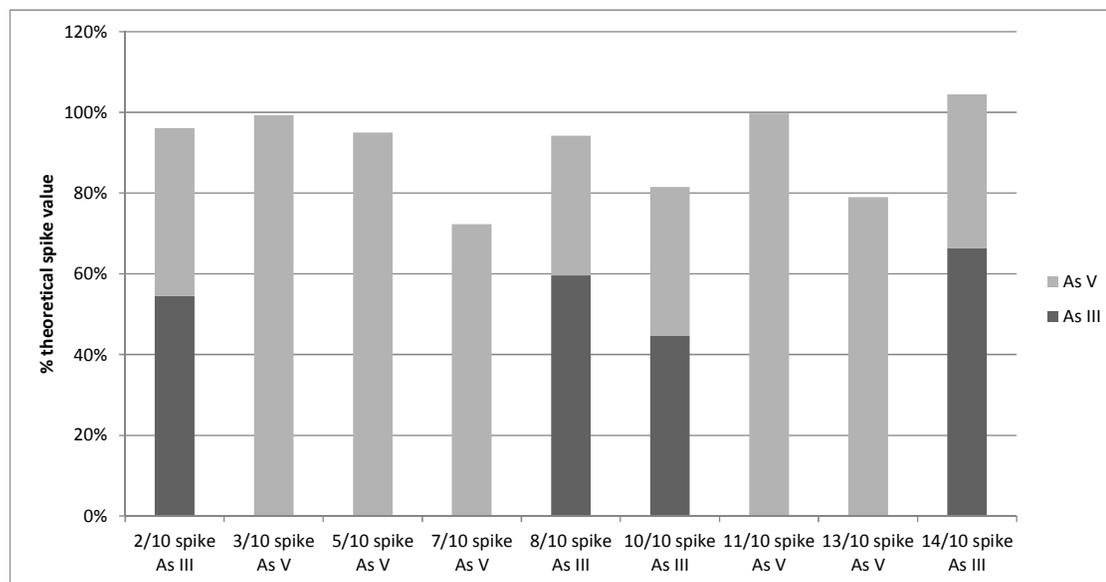
Figure 2: stability study of As(III) and As(V) spiked on filters (2 µg/filter) during sampling campaign.

Figure 3: summary of and correlation between the different analytical methodologies for the determination of total As concentration in PM_{10} during the monitoring campaign (for clarity, only results > 6 ng m^{-3} are represented).
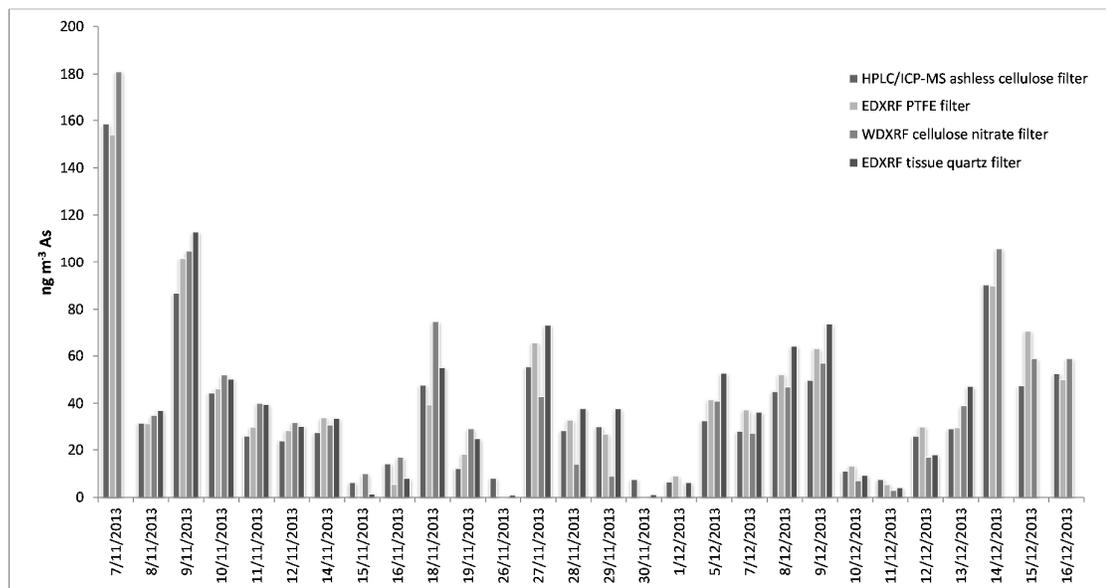
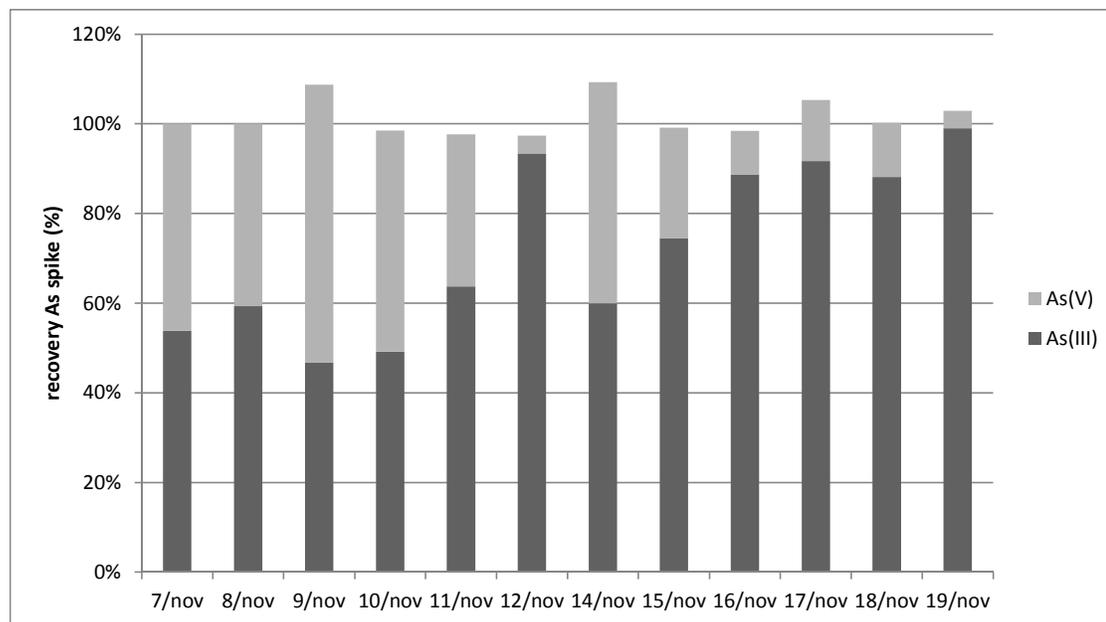Figure 4: stability study of As(III) spiked on filters (2 µg/filter) during PM$_{2.5}$ sampling campaign.

Figure 5: Percentage As(III) of the total As-concentration in PM_{10} and in function of wind direction at sampling location, situated NE of the industrial plant. Total As concentrations are given with respect to a concentric circle scaling (in ng m^{-3} As, 30 ng/m³ wide intervals) and wind directions with respect to the N, E, S and W axes (10° wide intervals). The colouring of these 'bins' is in accordance with the percentage of As(III) of the total As concentration as represented by different colours (see legend).
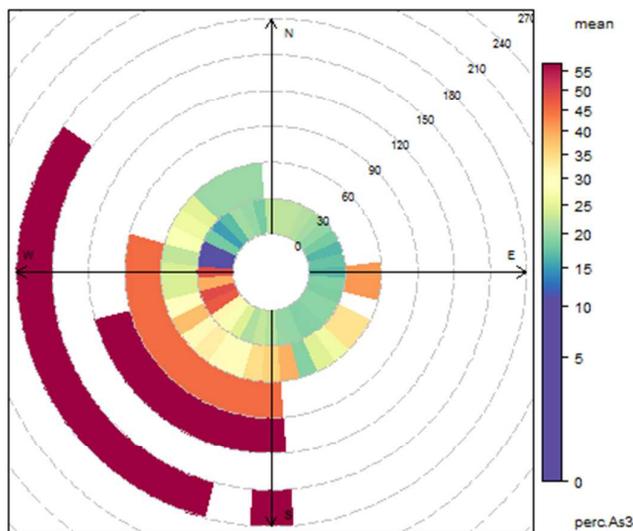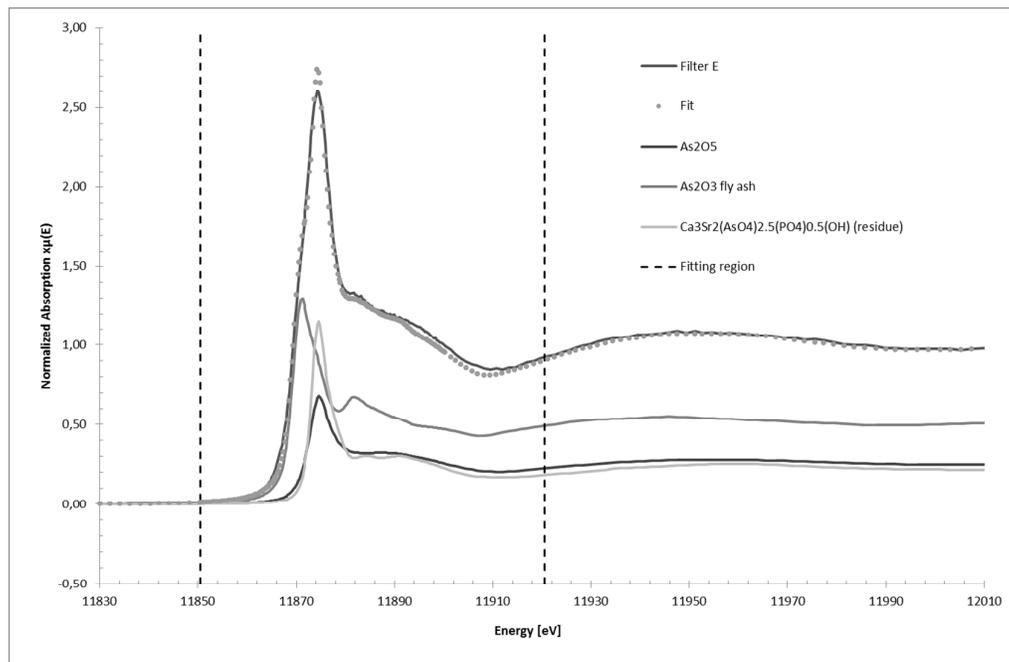
Figure 6: XANES fitting of filter E (PM$_{10}$, 1200 ng As/filter).

Figure 7: relative contributions of different As species in PM as calculated based on the XANES measurements (error bars represent the fit errors, which are calculated by the FEFFIT program (Newville, 1995) as described in the program documentation (Newville, 1998)).