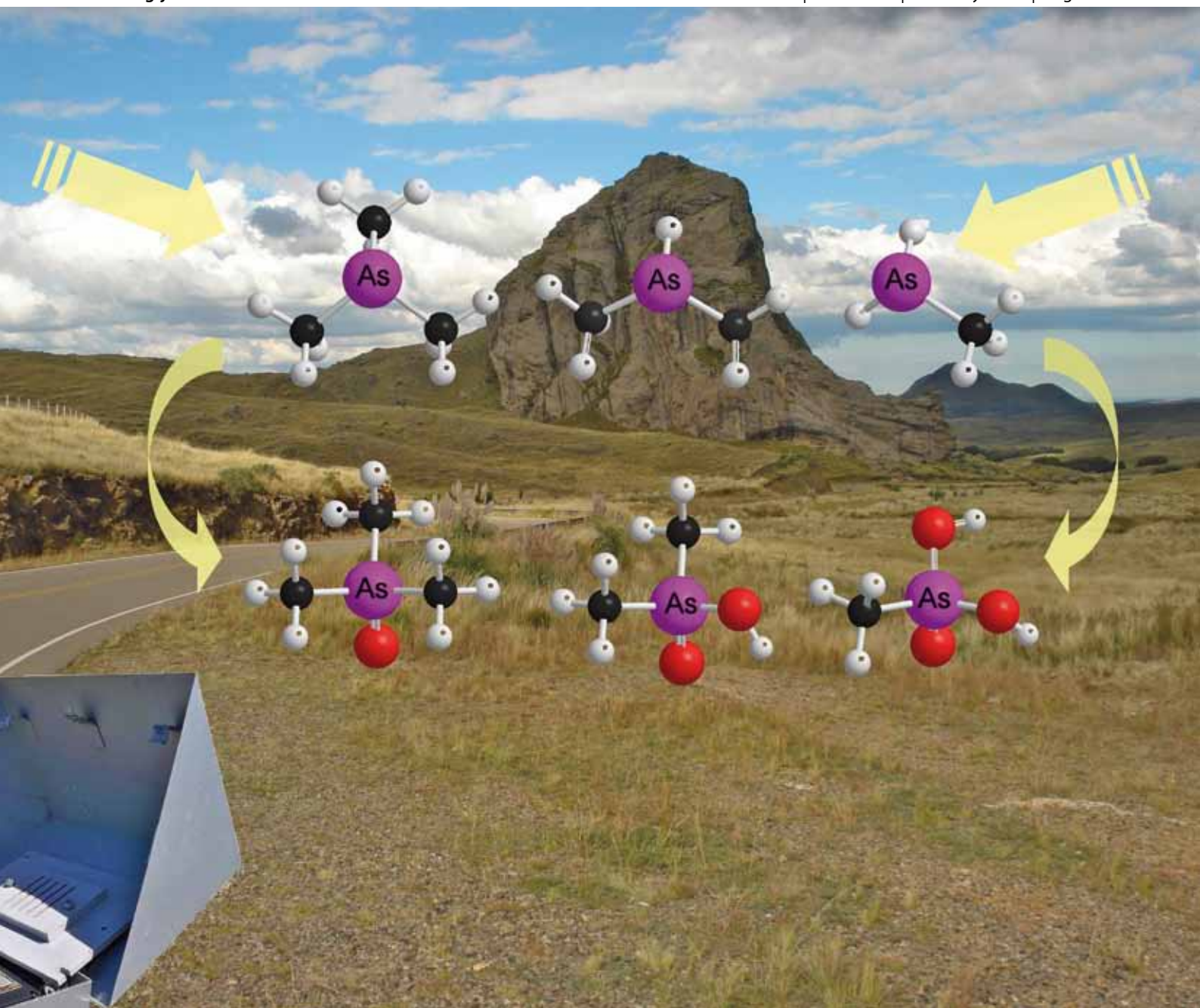


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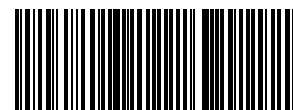
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# Atmospheric stability of arsines and the determination of their oxidative products in atmospheric aerosols (PM<sub>10</sub>): evidence of the widespread phenomena of biovolatilization of arsenic†

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Biovolatilisation of arsenic as their arsines in the form of AsH<sub>3</sub>, and mono-, di and trimethylarsine has often been determined under laboratory conditions. Although environmental point sources such as landfill sites or hot springs have been characterised, only limited knowledge is available on how widespread the formation of volatile methylated arsenic compounds are in the environment. Here we studied the atmospheric stability of the different arsines and quantified their oxidation products in atmospheric particulate matter (PM<sub>10</sub>) in two locations in Argentina. The atmospheric half-life of the arsines range from 19 weeks for AsH<sub>3</sub> to 2 d for trimethylarsine (TMAs) at 20 °C in the dark, while during simulated daytime conditions the stability is reduced for all arsines and in particular for the methylated arsines by three orders of magnitude which suggests that TMAs can only be dispersed at night. At both locations the arsenic concentration was in all samples below 1 ng As m<sup>-3</sup>, which is considered as rural background for arsenic. The oxidation products, *i.e.* methylarsonate (MA), dimethylarsinate (DMA) and trimethylarsine oxide (TMAO) were identified by using HPLC-ICP-MS/ES-MS in more than 90% of the 49 PM<sub>10</sub> samples taken from 8 sampling points at the two geographically different locations. TMAO was the predominate organoarsenicals in both locations (66 and 69%, respectively) while DMA was determined to be between 13 and 19% of all organoarsenicals at the two locations. The concentration of the organoarsenicals ranged from 4 to 60 pg As as TMAO m<sup>-3</sup>, while the maximum concentration for DMA and MA were 16 and 6 pg As m<sup>-3</sup>, respectively. No difference in terms of the concentration or distribution of the organoarsenicals in the PM<sub>10</sub> samples was identified as significant. Since the two locations were different in climate and industrial impact and sampled in different seasons, these data suggest that methylated arsenicals do occur as background chemicals in the environment. Due to the low atmospheric stability of the methylated arsines, it is suggested that biovolatilization of arsenic as methylated arsines is a widespread phenomenon. More studies however are necessary to identify the major sources and determine the flux of the volatilization process in order to determine whether or not the process has environmental significance.

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## Introduction

Arsenic is a category I carcinogen and it is ubiquitous in the environment. Hence, its biogeochemical cycling is of importance and is extensively studied. Those studies focus on mobilisation in the hydrosphere and volatilization through hot temperature processes such as volcanoes or incinerators. The latter determines the arsenic in particulate matter in the atmosphere. However, the low temperature volatilization pathway has not

### Environmental impact

The volatilization pathway within the biogeochemical cycle of elements influences not only their flux from the condensed spheres to the atmosphere; it enhances also the distribution of the elements in the environment. Arsenic is heterogeneously distributed due to the release of large quantities from mining/industrial processes or the release of arsenic containing groundwater for irrigation. In order to understand how arsenic distributes from these hot spots, it is pertinent to gain a full understanding of its biogeochemical cycle and the formation of volatile arsenic compounds in the environment.

been studied extensively mainly due to the lack of suitable analytical methods to quantify arsenic's biovolatilization. A range of fungi and bacteria isolated from the environment are capable to form trivalent arsines through methylation and hydridization of arsenic to give four compounds arsine ( $\text{AsH}_3$ ), methylarsine ( $\text{MeAsH}_2$ ), dimethylarsine ( $\text{Me}_2\text{AsH}$ ) and trimethylarsine (TMAs).<sup>1-3</sup> Only limited knowledge is available of the generation of those arsines in the environment.<sup>5-11</sup> However, due to the difficulty that the generated arsines are in small concentrations and due to their reactive nature<sup>4</sup> only sophisticated analytical methods such as cryotrapping with subsequent gas chromatographic separation and ICP-MS detection are capable to determine those species as described earlier.<sup>6,8,9</sup> Hence, only restricted studies of point sources have been performed so far, notably in soils,<sup>5</sup> natural gas,<sup>6,7</sup> landfill sites<sup>8,9</sup> and hot springs.<sup>10,11</sup> The used analytical method cryotrapping GC-ICP-MS is not a field-deployable method, hence no data are available to determine whether or not the volatilization of arsenic by the formation of methylated arsines is a widespread phenomenon or restricted to specific point sources.

It has been reported that arsine is oxidised to arsenite or arsenate, while the methylated arsines oxidise under atmospheric conditions rapidly to their pentavalent methylated arsenic oxides such as methylarsinate (MA), dimethylarsinate (DMA) and trimethylarsine oxide (TMAO).<sup>4</sup> Since, methylation to non-volatile compounds can take place in the soil or sediments,<sup>12</sup> the determination of the pentavalent arsine oxides needs to be done in atmospheric particles which are unlikely sources of soil and plant re-suspension. The  $\text{PM}_{10}$  fraction routinely measured for air quality purposes can be used to determine the oxidation products of the methylated arsines by arsenic speciation analysis. So far only one earlier study suggested that methylated arsenicals may appear in particulate matter,<sup>13</sup> most attempts have been made to differentiate between arsenite and arsenate in  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$ .<sup>14,15</sup>

Here, we report for the first time the atmospheric lifetime of the main four arsines and measure the oxidised methylated arsenic compounds in  $\text{PM}_{10}$  samples taken at two different sites in Argentina. The atmospheric lifetime was measured in static air samples with and without UV-light at two different temperatures to simulate day and night cycles using cryotrapping GC-ICP-MS, while the  $\text{PM}_{10}$  particles were leached selectively and the oxidised arsenic products (MA, DMA and TMAO) were quantified in the extract by using HPLC coupled to both inductively-coupled plasma mass spectrometry (ICP-MS) and electrospray mass spectrometry (ES-MS).

## Experimental

### Chemicals and standards

Arsenic stock solutions used were prepared from sodium arsenite (100%) and disodium methyl arsonate (MA) (99.0%), both from Chem Service Inc., West Chester, USA and dimethylarsinate (DMA) 98% from Sigma-Aldrich Inc., Dorset, U.K. The trimethylarsine oxide (TMAO) standard was produced by treating trimethylarsine (TMAs) with concentrated nitric acid. The ammonium carbonate for the anionic HPLC buffer was obtained from VWR International Ltd., Poole, England as well as the 28%

ammonia solution. Formic acid 90% from Fisher Scientific UK Limited, Leicestershire, UK and Pyridine from Fisons plc. Scientific Equipment Division, Loughborough, England were used to prepare the buffer for the cationic HPLC.

All tubes and the microwave bombs were treated in a solution of 10% v/v nitric acid for 24 h and then washed with deionised water before use. Hydrogen peroxide about 30% (VWR International S.A.S, Briare, France) was used for sample preparation. Ultra pure water produced by UHQ (ELGA) was used for sample preparation as well as for the dilution of the stock solutions to prepare the standards of DMA, MA and As(v), which were obtained from Sigma-Aldrich Chemie GmbH, Steinheim, Germany (DMA), Chem. Service, West Chester (MA) and Hopkins & Williams, LTD, London (As(v)) as sodium salts.

The microwave used for sample extraction was a CEM, XP-1500. The freeze drying was run with a Heto Power Dry LL3000 from Thermo Electron Corporation in 50 mL Greiner tubes. The first centrifugation was performed in an ALC 4218 Centrifuge the second one in a MSE Micro CE 39 (Sanyo). All standards were prepared in 15 mL Greiner or Fisherbrand® tubes.

### Experimental set up to determine the atmospheric stability of arsines

The experiments were conducted in pillow-shaped 10 L Tedlar bags suitable for the simulation of atmospheric reactions.<sup>16</sup> The bags were transparent for UV and visible light up to 290 nm, and the experiments were carried out indoors at 20 and 50 °C with the absence of artificial light. The exposure of the Tedlar bags to the UV-light was realised by using a 300 W halogen lamp at a fixed distance of 45 cm to the bags, resulting in a light intensity of around 5000 Lux. Tedlar bags were filled with air containing arsines in relevant atmospheric concentrations. For the generation of arsines a static hydride generation method was used as described elsewhere.<sup>17</sup> Briefly, for the generation of  $\text{AsH}_3$ ,  $\text{MeAsH}_2$  and  $\text{Me}_2\text{AsH}$ , Tedlar bags were filled using a batch hydride generation system. This was conducted by mixing 4 mL of 10  $\mu\text{g As L}^{-1}$  as As(v), MA and DMA, with 1 mL HCl (0.1 M), to keep the pH at  $\sim 2$  in a 50 mL reaction vessel where the head-space was continuously flushed with filtered air (200 mL  $\text{min}^{-1}$ ). Through a septum 1 mL of  $\text{NaBH}_4$  (2%) and NaOH (4%) solution was added drop wise into air flushed reaction vessel and 3 L of gas was then collected from the flushed reaction vessel during hydride generation, *i.e.* 15 min at 200 mL  $\text{min}^{-1}$  gas flow rate. Since the hydride generation method was checked to be quantitative, gas samples with a defined concentration of volatile arsines in filtered but moisturized air were generated.

### Speciation of volatile arsines in air

Gas samples were taken from the Tedlar bags with a 100 mL gas tight syringe. The gas samples were then immediately trapped at  $-196$  °C (liquid nitrogen) without using a NaOH-cartridge in a U-shaped cryotrap (a fused silica capillary  $l = 40$  cm) as described elsewhere.<sup>17</sup> The cryotrap was connected to a capillary GC column, which was equipped with a cryofocusing unit before

GC-ICP-MS.<sup>6</sup> The chromatographic column used was a CP-Sil 5CB Ultimetal capillary (25 m × 0.53 mm i.d.,  $d = 1 \mu\text{m}$ ) from Chrompack (Chrompack UK Ltd., London, England). The transfer line Ultimetal tubing, 0.53 mm i.d., methyl-deactivated) was heated to 150 °C and connected to the ICP-MS (Spectromass 2000). After removing the liquid nitrogen the GC was heated from 50 °C with a ramping of 10 °C min<sup>-1</sup>. The analytes were then eluted out of the capillary and subsequently into the plasma in the sequence of their boiling points.

### Sampling of PM<sub>10</sub> particles

Airborne particulate matter samples, PM<sub>10</sub>, were taken for one week in summer in Luján de Cuyo (LC) (18–25 February 2001) as well as one week in winter in San Nicolás (SN) (27 July–7 August 2001). The city of San Nicolas is located 200 km northwest of Buenos Aires city (33° 19' S, 60° 12' W). It is located on a flat terrain with the Paraná River on the northeast representing a temperate climate. The urban area is about 30 km<sup>2</sup> with relatively low traffic, except for the city centre. Pasture and farm fields stretch around the urban area. There is an important industrial activity in the area composed by a 650 MW coal-burning power plant, an integrated steel mill, cement factories and insecticide and herbicide manufacturing plants. In contrast to SN the second sampling site the city of Luján de Cuyo (33° 30' S, 62° 58' W) is representing an arid climate and has a different industrial impact. LC is situated on a flat terrain at an altitude of 900 m at a distance of 30 km south of the centre of Mendoza. The area reaches to the piedmont of the Andes 5 km west from the sampling sites. Since this area is located on an oil and gas field, the main industry is an oil refinery, a petrochemical plant, a gas power plant in addition to other industrial plants including a silicone inorganic chemical factory, a coke plant and a gypsum plant. Since it has emerged that oil and gas may contain large quantities of volatile arsines mainly in the form of TMAAs,<sup>6,7</sup> this place was chosen to identify the potential of liberated TMAAs from natural gas in contrast to SN where oil and gas operations are absent.

The samples were collected at four different stations in each location on ash-free glass-fibre filters with a high volume sampler equipped with a standardized PM<sub>10</sub> collection head. Sampling time was 24 h which collected an average of 1440 m<sup>3</sup> ambient air. More details can be found elsewhere.<sup>18</sup> Each filter was stored in a clean polyethylene bag.

### Extraction method for organoarsenicals in airborne particles

The filters were cut in quarters and placed in a Teflon bomb. A mixture of 6 mL H<sub>2</sub>O<sub>2</sub> (30%) and 6 mL H<sub>2</sub>O was added. Using a microwave, the compounds were then heated up to 75 °C within 5 min and temperature was held for 20 min. After cooling down the residual filter was washed with purified water and the solution was decanted into a 50 mL tube. The solvent was then removed by freeze-drying. 1 mL of H<sub>2</sub>O was added next in two steps; the mixtures centrifuged after each step at a speed of 4 × 1000 rpm for 5 min and then the water was filled in an Eppendorf safe-lock tube. The Eppendorf tubes were centrifuged again for another 15 min at a speed of 13 × 1000 rpm and stored in the freezer before analysis.

### Speciation method for organoarsenicals in extract

An HPLC-ICP-MS system was used for the speciation analysis of the organoarsenicals. An anion exchange column (Dionex AS 14) was used with a 100 mM ammonium carbonate at pH 10 with a flow rate of 1 mL min<sup>-1</sup>. The sample volume was 100 μL. As internal standard 10 μg rhodium L<sup>-1</sup> was added. Agilent 7500c (Agilent Technologies, Tokyo, Japan) was used in the collision cell mode with H<sub>2</sub>. In addition to  $m/z$  103 for rhodium and  $m/z$  75 for arsenic,  $m/z$  77 and 82 was measured to ensure that no chloride interference on  $m/z$  75 was recorded. For the calibration a stock solution of 1 mg L<sup>-1</sup> DMA was diluted to 5, 10, 20, 30 μg As L<sup>-1</sup>. All quantification was performed with this set-up while for the identification of TMAO in the extract a cation exchange (Varian Ion Sphere C) was necessary; because of the TMAO's retention time was too close to the void and would not be different than other arsenicals cationic under these conditions. As mobile phase 50 mM pyridine adjusted to pH 2.7 with formic acid with a flow rate of 1 mL min<sup>-1</sup> was used. The outflow was split 80 : 20 using a flow splitter (Upchurch), with 80% going into an electrospray mass spectrometer (Agilent 1100) and 20% to the ICP-MS. The fragmentor voltage was set to 100 V and the mass spectrometer on single ion monitoring ( $m/z$  137 for the protonated molecular mass of TMAO). This method was also used to determine the amount of extractable inorganic arsenic as arsenate.

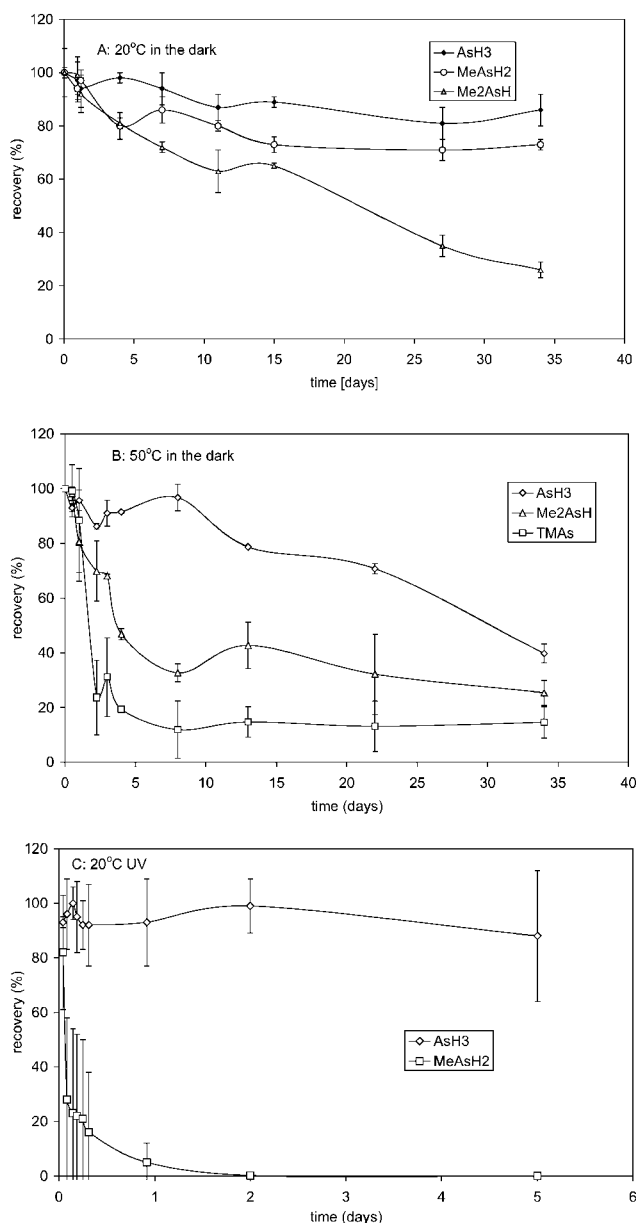
### Quality control of the organoarsenic in PM<sub>10</sub> analysis

For quality controls of the sample preparation method two different approaches were followed. In order to identify the homogeneous distribution of the organoarsenicals on the filter, one filter was quartered and every quarter was measured for the mass of loaded particles and concentration of each organoarsenicals in the dust. To document the extraction efficiency a standard reference material was used. Although no SRM exists for organoarsenicals in PM<sub>10</sub> particles, the SRM NIST 1648 urban particulate matter which contains 115 ± 10 mg kg<sup>-1</sup> total arsenic was used. In order to identify the extraction efficiency of the organoarsenicals 100 ng As as TMAO and DMA were spiked on an unloaded filter and treated in the same way as the samples.

## Results

### Arsine stability in air

All arsines were tested in moisturized filtered air at two different temperatures in the dark and under UV illumination. At 20 °C in the dark it can easily be seen that with increasing methyl groups on the arsenic the stability decreases (Fig. 1). Hence, AsH<sub>3</sub> is the most stable compound, while MeAsH<sub>2</sub> and Me<sub>2</sub>AsH were less stable. The degradation can be modelled as a first order kinetic reaction with satisfactory correlation coefficient of better than 0.8. (Table 1). Using this kinetics an estimated atmospheric half-life was calculated and expressed in hours. While the half-life of more than 130 d for AsH<sub>3</sub> is estimated, the methylated species exhibit smaller lifetimes of 67 d for MeAsH<sub>2</sub> and 17 d for Me<sub>2</sub>AsH. The half life of the arsines decrease linearly with the number of As–C bonds ( $R^2 = 0.99$ ). This is probably due to the lower stability of the As–C bond (262 kJ mol<sup>-1</sup>)<sup>19</sup> in comparison



**Fig. 1** Atmospheric stability of volatile arsines in moisturized air. (A) shows the stability of  $\text{AsH}_3$ ,  $\text{MeAsH}_2$  and  $\text{Me}_2\text{AsH}$  at  $20^\circ\text{C}$  in the dark, (B) shows the stability of  $\text{AsH}_3$ ,  $\text{Me}_2\text{AsH}$  and TMA at  $50^\circ\text{C}$  in the dark, while (C) displays the stability of all four arsines under UV illumination; only  $\text{AsH}_3$  and  $\text{MeAsH}_2$  were detectable after 1 h. The error bars represent the reproducibility of nine measurements of three different gas mixtures ( $n = 3$ ).

to the As–H bond ( $352\text{ kJ mol}^{-1}$ ).<sup>20</sup> When this linear relationship was used to estimate the atmospheric half-life of TMA under these conditions approximately 2 d was calculated. This could be confirmed by the stability data of TMA measured at  $50^\circ\text{C}$  in the dark, at which the atmospheric half-life is reduced to approximately 1.5 d, while the other methylated arsines show also a small but significant temperature dependent destabilizing effect; an estimation of the activation energy is between 0.2 and 0.7  $\text{kJ mol}^{-1}$  using the Arrhenius plot. In summary TMA is the least stable compound of the arsines, but it can be transported in its

**Table 1** kinetic constants of the atmospheric stability of arsines at the concentration level of about  $10\ \mu\text{g As m}^{-3}$ .<sup>a</sup>

	20 °C (dark)		50 °C (dark)		20 °C (UV)	
	<i>R</i>	<i>t</i> <sub>1/2</sub> /h	<i>R</i>	<i>t</i> <sub>1/2</sub> /h	<i>R</i>	<i>t</i> <sub>1/2</sub> /h
$\text{AsH}_3$	0.86	3178	0.93	753	0.45	>100
$\text{MeAsH}_2$	0.84	1620	n.m.	n.m.	0.93	2
$\text{Me}_2\text{AsH}$	0.99	428	0.85	122	n.d.	<1
TMA	n.m.	n.m.	0.61	37	n.d.	<1

<sup>a</sup> n.d.: not detectable, n.m. not measured.

volatile form over large distances during night-time conditions. The stability of all arsines decreased however rapidly when the gas was illuminated with UV light simulating daytime conditions. TMA and  $\text{Me}_2\text{AsH}$ , the least stable compounds in the dark were not detectable after 1 h, while about 30% of  $\text{MeAsH}_2$  and more than 80% of  $\text{AsH}_3$  were recovered. Hence, the transport of TMA and  $\text{Me}_2\text{AsH}$  during daytime as volatile compounds is very much diminished and is probably in the order of minutes. The most likely reaction is an oxidation of the arsenic from the trivalent to pentavalent arsenic. Pentavalent arsenic forms water-soluble and not volatile oxo-acids. It has been shown in the past,<sup>17,21</sup> that the atmospheric oxidation of TMA forms TMAO, while  $\text{Me}_2\text{AsH}$  and  $\text{MeAsH}_2$  forms DMA and MA respectively. It can be assumed that photo-oxidative reactions presumably with OH radicals, which are generated at daytime conditions, are responsible for those reactions. Hence, if arsines are formed in the environment their oxidation products should be found their way into rain water and adsorbed onto atmospheric particles.

### Organoarsenicals in $\text{PM}_{10}$

The SRM 1648 was extracted with the hydrogen peroxide method. It contained no arsenoarsenicals, hence the extraction efficiency for those species could not be established. The extraction efficiency for the inorganic arsenic was only  $42 \pm 17\%$  ( $n = 3$ ). The total amount of arsenic in the extract was not significantly different from the arsenate concentration measured by HPLC-ICPMS (see below). It should be noted that the analytical method was designed only to extract organoarsenicals, hence the low extraction efficiency for mineralised inorganic arsenic was expected. The extractability of the spiked TMAO and DMA gave slightly higher efficiencies of 69%. The used samples in combination with the analytical method give a detection limit for methylated arsenic of approximately  $0.3\ \mu\text{g m}^{-3}$ . This was achieved using three times the standard deviation of the blank level. The homogeneity study of the filters showed that between the four quarters the concentration of TMAO varied  $\pm 35\%$ .

Overall 49 samples were collected at eight sampling points, four in each location. At all sampling points a minimum of six samples were taken except for D at (Lujan de Cuyo) where only three samples were available for this study. The amount of dust collected was recorded. No significant difference between the different sampling points at each location was exhibited for the amount of  $\text{PM}_{10}$  in the air, although for San Nicolas only three

of the four sites were influenced by the emission of the thermal power station as reported earlier.<sup>22</sup> But a location difference was significant ( $p < 0.05$ ) with  $0.169 \pm 0.024 \text{ mg m}^{-3}$  at Lujan de Cuyo and  $0.103 \pm 0.046 \text{ mg m}^{-3}$  at San Nicolas (Fig. S1†).

TMAO was detected in all  $\text{PM}_{10}$  samples, while the frequency of DMA and MA detection was 90 and 86%, respectively. A typical HPLC-ICP-MS chromatogram of an extract containing all four arsenic species is shown in Fig. 2a. The extracted inorganic arsenic is oxidised to arsenate, which was well separated from the other three organoarsenicals. DMA and MA had a characteristic retention time and could unequivocally be identified by spiking of the respected standards. TMAO however eluted close to the void volume and had therefore no characteristic retention time. Its identification was confirmed when the extract was analysed by cation exchange high performance liquid chromatography, which was coupled to the ICP-MS to give a peak for arsenic after around 12 min, the eluent was also fed in parallel into the ES-MS as described elsewhere,<sup>23</sup> which recorded the protonated molecular mass of TMAO ( $m/z$  137) at the same retention time as the arsenic signal. TMAO was successfully identified in the extract of the  $\text{PM}_{10}$  filter.

The concentrations of all TMAO, DMA and MA in every individual  $\text{PM}_{10}$  sample expressed as nanogram arsenic per cubic metre air were ranked for the two locations highlighting the different sampling points and displayed in Fig. 3. The mean concentrations and the variability of all methylated compounds are not significantly different for both locations. The different sampling points at each location show no characteristically low

or high concentration of any organoarsenicals. The mean proportions of those methylated species are not significantly different for both locations (Fig. 4). In all the samples TMAO was the predominate organoarsenic species with  $68.8 \pm 16.7\%$  for Lujan de Cuyo (LC) and  $65.8 \pm 18.4\%$  for San Nicolas (SN), while DMA and MA were found always in lower concentrations making up  $18.7 \pm 9.4\%$  and  $13.2 \pm 9.4\%$  in LC and  $21.8 \pm 10.8\%$  and  $12.4 \pm 11.9\%$  in SN for DMA and MA, respectively.

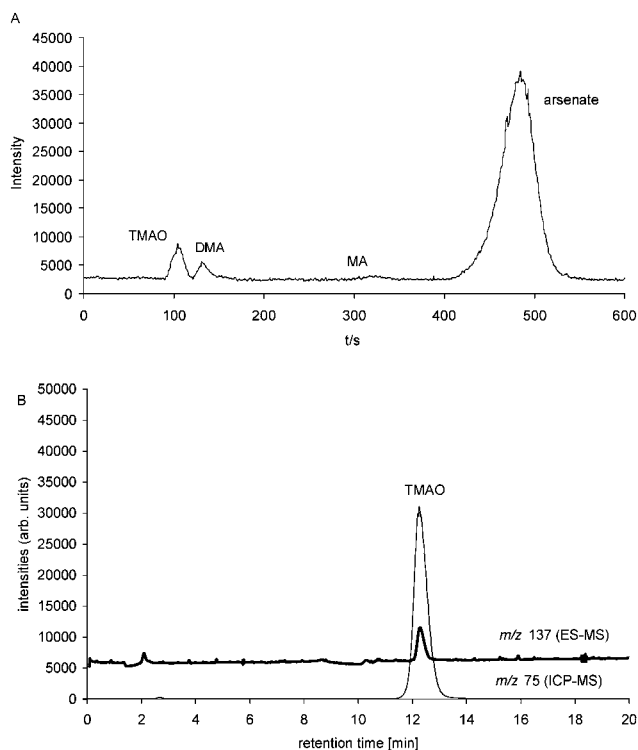
The arsenic content can however also be expressed as concentration of arsenic in the particles. The concentrations of the methylated arsenicals in the  $\text{PM}_{10}$  were significantly higher in SN ( $0.333 \pm 0.203 \text{ ng As mg}$ ) than in LC ( $0.187 \pm 0.090 \text{ ng As mg}$ ) ( $p < 0.05$ ). This difference is however cancelled out if the concentration of organoarsenicals is expressed in  $\text{ng As per m}^{-3}$  air:  $0.028 \pm 0.014 \text{ ng m}^{-3}$  in LC and  $0.024 \pm 0.13 \text{ ng m}^{-3}$  for SN due to the higher amounts of  $\text{PM}_{10}$  in the air of LC.

Significant was also the location difference in the proportion of methylated arsenic to the extractable total arsenic with  $15 \pm 6\%$  for the  $\text{PM}_{10}$  collected in the arid climatic area of LC, while the particles collected in the temperate SN at the Parana river  $24 \pm 9\%$  were found. The distribution of the individual methylated arsenicals exhibits no location difference (Fig. 5). The only trend, which could be conducted from the analysis is that if the extractable arsenic concentration was below  $0.1 \text{ ng As/mg}$ , the proportion of organoarsenicals were the dominant arsenic in the  $\text{PM}_{10}$  fraction (Fig. 6).

## Discussion

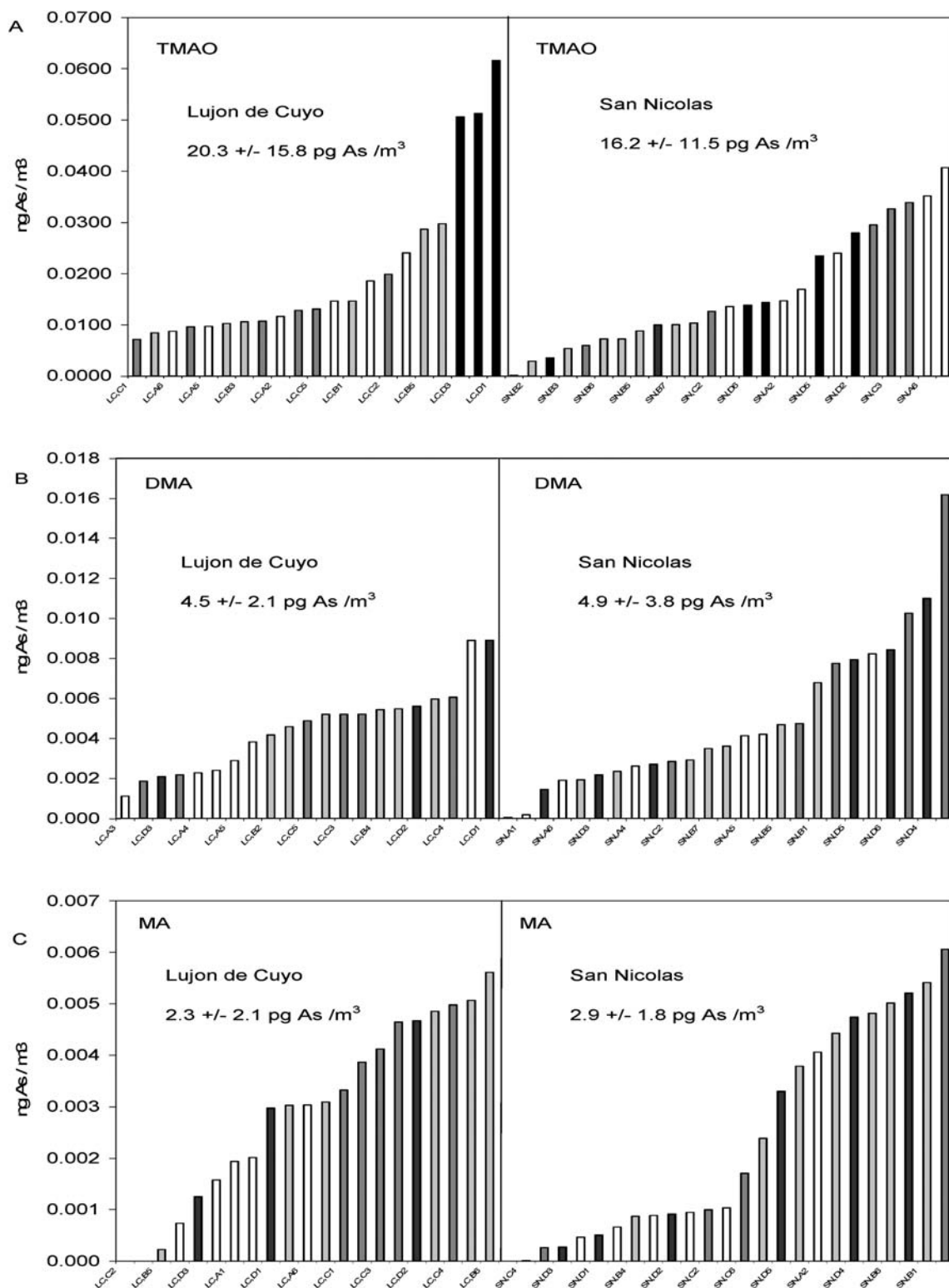
The concentration of  $\text{PM}_{10}$  is relatively high and by factor of 3–4 higher than reported in other areas.<sup>14,15</sup> Referring to the total extractable arsenic, the measured concentrations at both locations is below 1 nanogram per cubic metre. It is below the EU recommended guideline of  $6 \text{ ng As m}^{-3}$ .<sup>24</sup> Although the EC directive does not contain any species information but refers to total arsenic only the value do not constitute any health risk. It is however interesting to note that in all samples methylated arsenicals could have been measured, although the level of the methylated and extractable arsenic is at the lower end of what has been reported for total arsenic from the World Health Organisation for the rural and remote areas ( $0.02\text{--}4 \text{ ng As m}^{-3}$ ).<sup>25</sup>

The low variability and occurrence at two different sampling locations, which differed in climate, industrial impact and were sampled in two different seasons, is a strong indicator for a widespread phenomenon of the occurrence of methylated arsenicals in atmospheric particulate matter. This confirms earlier reports from Japan, in which airborne particles were sampled and methylated arsenic was measured.<sup>13</sup> The authors did not use any size discrimination when collected the particles, hence the interpretation that TMAO is the result of the bio-volatilization of arsenic was ambiguous. They reported approximately ten times higher values of TMAO than what we found, while their concentration of TMAO in the winter months are comparable to those in our study. Here in this study, the collection of the particulate fraction  $\text{PM}_{10}$  should have prevented the collection of re-suspended soil particulates and bio-particles such as pollen. The absence of the latter was confirmed by using scanning electron microscopy (data not shown). This is important since then the origin of the methylated compound can only



**Fig. 2** Chromatogram of a  $\text{PM}_{10}$  hydrogen peroxide extract measured by anion exchange ICP-MS is shown in (A) as  $m/z$  75 (arsenic), while in (B) the identification of TMAO by cation exchange coupled to both ICP-MS ( $m/z$  75) and by ES-MS ( $m/z$  137) is shown.

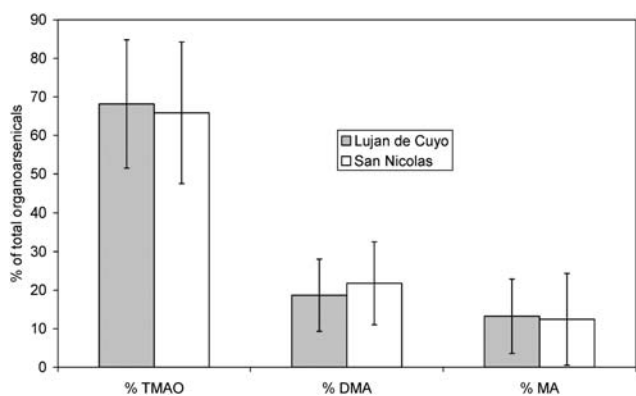




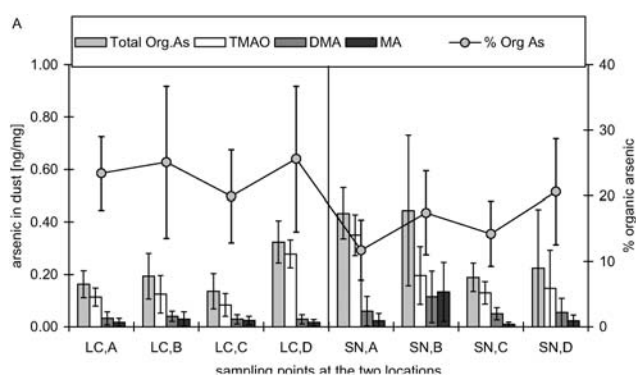
**Fig. 3** A–C: the ranking of the individual PM<sub>10</sub> samples for each location according to the concentration of the methylated species: TMAO (a), DMA (B) and MA(C). Concentration is given in ng As per m<sup>-3</sup> air. The different sample points are highlighted in four different shades of grey.

result from a volatilization processes and not from pollen or other plant material. Although it cannot be excluded at this stage that industrial products such as the herbicides disodium methylarsonate or cacodylic acid resulted in the occurrence of DMA

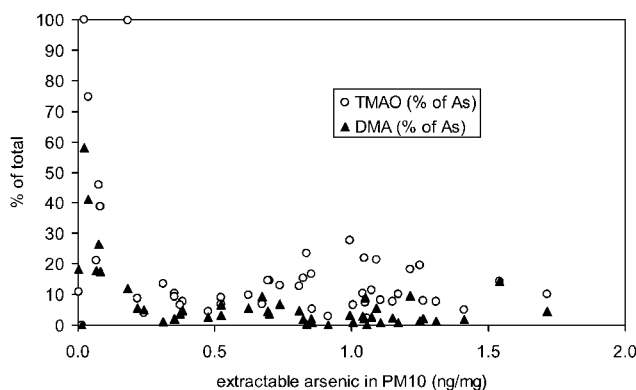
and MA in the particles, it is an unlikely source for all methylated species. The main organoarsenicals TMAO is trimethylated and to the authors' knowledge no trimethylated industrial product is produced as an industrial product except for indoor applications



**Fig. 4** Median distribution of methylated arsenicals in collected PM<sub>10</sub> at two different locations in Argentina. The error bars represent  $N = 22$  for LC and 27 for SN.



**Fig. 5** The mean amounts of organic arsenic and the individual methylated arsenicals TMAO, DMA and MA in the PM<sub>10</sub> particulate fraction at the four different sampling points for the two locations overlaid with the proportion of methylated arsenic on the total extractable arsenic in the dust. The error bars represent the standard error from 6–7 individual PM<sub>10</sub> samples taken on consecutive days during the sampling campaign. LC is Lujan de Cuyo and SN is San Nicolas.



**Fig. 6** Proportion of TMAO and DMA of the extractable arsenic in PM<sub>10</sub> particles for all individual samples. With low total arsenic, the proportion of the TMAO and DMA increase, emphasising the constant flux.

such as TMAs in the semiconductor industry.<sup>26</sup> Methylation of arsenic in the soil has been reported to be widespread, but also here mainly DMA and MA have been reported to occur in pore

water.<sup>27,28</sup> In most cases is the concentration however very low and TMAO has only occasionally been identified in plants<sup>29</sup> and in soil pore water.<sup>5</sup> On the other hand is the biovolatilization of arsenic by fungi and bacteria well documented,<sup>1</sup> of which TMAs had been described to be the most common volatile arsenic species. It has been reported that TMAs is a common constituent in natural gas,<sup>6</sup> has been released from hot springs,<sup>10,11</sup> landfill sites,<sup>8</sup> anaerobic sewage gas<sup>9</sup> and recently been demonstrated to be released from matured paddy soils.<sup>30</sup> The fact that at LC, the location dominated by the oil and gas industry, had no significantly higher concentrations of TMAO, would suggest that natural gas was probably not the major contributor for TMAO in PM<sub>10</sub>. The list of other possible sources emphasises that the release of volatile arsines into the atmosphere might be a widespread phenomenon and the fact that in almost all PM<sub>10</sub> samples collected at two different locations exhibit that methylated compounds are ubiquitous in the atmosphere. Once those volatile arsines have been released into the atmosphere, they can travel long distances over night indicated by the long atmospheric half-life of many hours in the absence of light. But during daytime a rapid oxidation to their pentavalent non volatile oxoacids takes place and been adsorbed onto small particles or washed out by rain.

So far no arsenic flux (from soil/water to atmosphere) data are available which would illustrate the importance of this pathway for the biogeochemical cycle of arsenic. This is mainly due to the lack of a field-deployable sampling method for the volatile arsines. Here we present an alternative: the analysis of PM<sub>10</sub> for the oxidation products of arsines. It may help to identify whether or not bio-volatilization of arsenic is a widespread phenomenon or defined to particular environments. The atmospheric stability of arsine measured for the first time in relevant environmental concentrations exhibits that arsines cannot be transported over a vast distance in the volatile form, but its distribution might be linked to that particulate matter in the atmosphere.

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