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# Arsenic Speciation in Lichens and in Coarse and Fine Airborne Particulate Matter by HPLC–UV–HG–AFS

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**Abstract.** A three-step sequential extraction procedure with Milli-Q, $CaCl_2$ and $H_3PO_4$ was applied for extraction of arsenic species in lichen transplants and airborne particulate matter (fine and coarse fractions). The samples used in this work were collected in 1994–1995 near coal-fired power plants. Both transplant lichens and airborne particulate matter were submitted to the same environment simultaneously. Arsenic species identification and quantification was performed by HPLC–UV–HG–AFS. Inorganic forms of arsenic (arsenite and arsenate) were present in significant amounts in most of the samples. Only in lichens also organic forms of arsenic (monomethyl arsonic acid and dimethyl arsinic acid) were identified which may indicate biotransformation of inorganic arsenic.

**Key words:** arsenic speciation, fine and coarse airborne particulate matter, lichens

## 1. Introduction

Arsenic is widely distributed in the environment and it occurs in various organic and inorganic species with $-3$, $+3$ and $+5$ oxidation states. It originates from natural and anthropogenic sources (Iffland, 1994). Arsenic is ubiquitous and cannot be destroyed in the environment, it can only change its chemical form, reacting with oxygen or other molecules present in air, water, soil or become attached to particles. Arsenic toxicity depends on its chemical form. Inorganic arsenic compounds are more toxic than organic arsenic compounds (Amran *et al.*, 1995). In several environmental studies compounds like arsenite (As(III)), arsenate ((As(V)), monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA), arsenobetaine (AsB), arsenocholine ion (AsC), tetramethylarsonium ion (TETRA) and trimethylarsine oxide (TMAO), as well as arsenolipids and arsenosugars were determined (Koch *et al.*, 2000; Kuehnelt *et al.*, 1997, 2000).

Atmospheric arsenic is assumed to be entirely in particulate form and contained totally within the troposphere. Mass size functions of arsenic in marine and continental aerosol indicate that atmospheric particulate arsenic has a mass median diameter of about 1 $\mu$m and that 90% of the arsenic is in particles $\leq$3.5 $\mu$m diameter (Walsh *et al*., 1979).

Lichens are associations of fungi (mycobionts) and green algae or cyanobacteria (photobionts). These organisms depend mainly on the atmospheric input of mineral nutrients. These features of lichens, combined with the extraordinary capability of some species to grow at a large geographical range and to accumulate mineral elements far above their need, rank them among the best bioindicators of air pollution (Garty, 2001).

Although determination of the total element concentration in biomonitors and in fine (aerodynamic diameter $<$2.5 $\mu$m) and coarse (2.5 $\mu$m $<$ aerodynamic diameter $<$ 10 $\mu$m) fractions is common practice, speciation is still very scarcely applied, even in small-scale environmental studies. Hardly any arsenic speciation data can be found for lichens and for fine and coarse fractions of aerosols. However, when comparing speciation data of biomonitors with airborne particulate matter, information may be gathered on the possible bioconversion of the elements in the biomonitors.

## 2. Experimental

### 2.1. SAMPLE HANDLING

*Parmelia sulcata* transplants and coarse and fine airborne particulate matter used in this study are from an experiment held in Portugal in the period of 1994–95. The experiment was described in detail previously (Reis *et al*., 1999). In short, Tapada do Outeiro and Sines were chosen for this study. Tapada do Outeiro is a rural site located in the north of Portugal with an old power station (100 MW) burning 80% national coal and 20% of fuel oil during the sampling period. Sines is a small town located south of Lisbon in an industrial area including the largest and more modern coal-powered station of the country (1256 MW) during the sampling time.

### 2.2. DETERMINATION OF TOTAL ARSENIC CONCENTRATIONS

For arsenic determination, samples were analysed by instrumental neutron activation analysis (INAA) and concentrations were calculated by the $k_0$-method (De Corte, 1987). These results were reported elsewhere (Freitas *et al.*, 2003). Beside lichens and airborne particulate matter, the power plants related products such as coal, fuel oil, fly ashes and ashes were also analysed in both locations. On average total arsenic concentrations for coal, fly ashes, ashes and fuel oil from Tapada do Outeiro and Sines were respectively: (1) in coal, 38 mg $kg^{-1}$ and 1.3 mg $kg^{-1}$; (2) in fly ashes, 78 mg $kg^{-1}$ and 14 mg $kg^{-1}$; (3) in ashes 2.4 mg $kg^{-1}$ and 1.7 mg $kg^{-1}$. For fuel oil only in Tapada do Outeiro arsenic was found with an average concentration of 0.05 mg $kg^{-1}$.

## 2.3. IDENTIFICATION OF ARSENIC SPECIES

### 2.3.1. *Reagents*

$As_2O_3$, $As_2O_5$ and DMAA were purchased from Merck (Darmstadt, Germany), AsB from Community Bureau of Reference (BCR) and MMAA, TMAO, AsC and TETRA-iodide were gifts from the late Prof. K.J. Irgolic (Karl-Franzens University Graz, Austria). The chemicals used were at least of analytical reagent grade. Stock solutions of the arsenic compounds containing 1000 mg $l^{-1}$ arsenic were prepared in water and kept at 4 °C. Working solutions with arsenic concentrations of 5–50 ng $ml^{-1}$ were prepared fresh, daily. Milli-Q Plus water (Millipore-waters, Milford, MA, USA) was used for the solution preparations.

### 2.3.2. *Sequential Extraction Procedure*

The sequential extraction procedure is explained in detail below. In contrast to conventional sequential extraction procedures the extractant was not replaced in each step but additions were made to the extractant to gradually increase the extractability of arsenic; in each step small aliquots were withdrawn for analysis. For this procedure, two reference *in situ* lichens (a, b duplicates), two exposed lichens transplants from Tapada do Outeiro (a, b duplicates) and two from Sines (a, b duplicates) were prepared. Lichen transplant samples used were exposed during the whole aerosol sampling period. Composite filters were made up of 47 and 43 filters quarters (both fine and coarse) over a ca. one-year period from Tapada do Outeiro and Sines, respectively.

*Step 1: Milli-Q extraction.* Ten ml of Milli-Q water were added to different amounts (range: 0.2–0.5 g) of the powdered *Parmelia sulcata* transplants in a 50 ml polypropylene centrifuge tube (Nalgene Nunc International, Rochester, New York, USA). Two parallel extracts were prepared for lichens transplants. For Nuclepore filters, 15 ml Milli-Q water were added to the 47 coarse and fine filters from Tapada do Outeiro and the 43 coarse and fine filters from Sines. The suspensions were sonicated for 30 min at room temperature. From the water extract, 2 ml were taken and filtered using a 0.45 $\mu$m membrane filter (Millex-HV, Millipore) and kept in the refrigerator (4 °C) until analysis.

*Step 2: $CaCl_2$ extraction.* To each lichen and filter extract from step 1, 0.2 ml and 0.3 ml of 1 mol $L^{-1}$ $CaCl_2$ were added respectively. In order to keep the initial volume constant and to obtain a final solution of 20 mM of $CaCl_2$, 1.8 ml and 1.7 ml of Milli-Q water were added. The suspensions were sonicated for 30 min at room temperature. From $CaCl_2$ extracts for lichens and filters, 2 ml and 3 ml were taken respectively, and filtered and kept in the refrigerator (4 °C) until analysis.

*Step 3: $H_3PO_4$ extraction.* 1.6 ml and 2.4 ml of 1.9 mol $L^{-1}$ $H_3PO_4$ were added respectively to the remaining lichens and filters Milli-Q + $CaCl_2$ extracts. In order to keep the initial volume constant and to obtain a final solution of 0.3 mol $L^{-1}$ of $H_3PO_4$, 0.4 and 0.6 ml of Milli-Q water were added, respectively. The suspensions were sonicated for 30 min at room temperature. $H_3PO_4$ extracts were filtered and kept in the refrigerator (4 °C) until analysis.

### 2.4. ARSENIC DETERMINATION IN EXTRACTS

The speciation system used is a combination of the following techniques High-Performance Liquid Chromatography (HPLC), UV-Reactor, Hydride Generation (HG), and Atomic Fluorescence Spectrometry (AFS) (Van Elteren and Šlejkovec, 1997). Experimental details are given in Table I. Since the arsenic concentrations in aerosols were extremely low, separation on an analytical column would result in a too high limit of detection; for that reason separation was carried out on a precolumn as described elsewhere (Šlejkovec *et al*., 2000). For each of the two extracts, duplicate separation and quantification runs were made on anion and cation exchange columns. In this study only anion exchange chromatography results will be discussed, since only anionic arsenic species were found. Analytical results were based on measurement of peak heights. Arsenic species were quantified by external calibration in the concentration range from 5 to 50 ng $mL^{-1}$. The analytical results were corrected for the field blanks. Each lichen solution was analysed twice while each filter solution was analysed four times. Analytical data obtained were averaged resulting in a relative uncertainty $<10\%$, and were expressed in atmospheric concentration units (ng $m^{-3}$) for filters and in mass concentrations (mg $Kg^{-1}$) for lichens.

## 3. Results and Discussion

To distinguish between water-extractable arsenic, phosphate-extractable and non-extractable arsenic (refractory) the extraction procedure described below was performed with lichens and airborne particulate matter (fine and coarse fractions). Arsenic extracted in step 1 is associated with the surface of aerosols or environmentally mobile As, while As extracted in step 3 is the As which is more strongly bound but still available and non-extractable arsenic is associated with the matrix or refractory. $CaCl_2$ was used to increase the ionic strength but extracts were not further analysed since no additional arsenic extractability was found. The extracts from steps 1 and 3 were analysed with anion as well as cation exchange HPLC–UV–HG–AFS.

### 3.1. AIRBORNE PARTICULATE MATTER

#### 3.1.1. *Total Arsenic Concentration*

Total arsenic concentrations are approximately 4 and 13 times higher in fine than in coarse fractions for Tapada do Outeiro and Sines, respectively (see Table II).

*Table I.* Experimental conditions for arsenic speciation with the HPLC–UV–HG–AFS system

| | |
|---|---|
| HPLC | |
| Anion exchange: | |
| Column (for lichens) | Hamilton PRP-X100, 250 × 4.1 mm |
| Column (for aerosols) | Alltech Adsorbosphere SAX precolumn |
| Mobile phase (for both columns) | $KH_2PO_4$ solution, 15 mmol $L^{-1}$, pH 6.1 ($NH_4OH$) |
| Cation exchange: | |
| Column | Alltech Adsorbosphere SCX 5U, 250 × 4.6 mm |
| Mobile phase | pyridine, 2.5 mmol $L^{-1}$, pH 2.65 (HCl) |
| Flow rate | 1 ml $min^{-1}$ |
| Injection volume | 100 $\mu$l |
| On-line UV-reactor (optional) | |
| Ultraviolet lamp | 8 W (Camag), 254 nm |
| Digestion coil | FEP Teflon tubing (3.1 m, 0.5 mm i.d.) |
| $K_2S_2O_8$ | 2% (m/v) in 2% (m/v) NaOH, (anion exchange) or 4% (m/v) in 4% (m/v) NaOH, (cation exchange) |
| Flow rate | 1.35 ml $min^{-1}$ |
| Hydride generation | |
| HCl | 4.4 mol $l^{-1}$, 3.0 $ml^{-1}$ |
| $NaBH_4$ | 1.5% (m/v) in 0.1% (m/v) NaOH, 3 ml $min^{-1}$ |
| Argon (gas–liquid separator) | 340 ml $min^{-1}$ |
| Nitrogen (drying) | 1 L $min^{-1}$ |
| AFS | |
| Detector | Excalibur (PS Analytical, Kent, UK) |
| Lamp | Arsenic, 189.04, 193.76 and 197.26 nm (Photron Pty. Ltd., Superlamp 803S) |
| Primary current | 27.5 mA |
| | 35 mA |

This suggests what was mentioned above that more than 90% of arsenic is in particles with aerodynamic diameter below 3.5 $\mu$m. Total arsenic concentrations are higher in Tapada do Outeiro than Sines which was expected taking into account the arsenic concentrations for the power plants related products.

### 3.1.2. *Amount of Arsenic Extracted with Milli-Q*

The amount of arsenic extracted in the fine fraction (see Table II) is also higher in Tapada do Outeiro (14%) than in Sines (6.2%), but in Sines only As(V) was found. In the coarse fraction, 8.5% was extracted in Tapada do Outeiro and in Sines any species were found. The amounts of As extracted are smaller when

*Table II.* Total amount of As, and the extracted amount and the arsenic species extractability with Milli-Q and CaCl2 + $H_3PO_4$ from coarse and fine fractions collected at Tapada do Outeiro and Sines

| Sampling site | Size fraction | Total As conc.[a] | | Extractability of As (% of total As) | | | As species in Milli-Q | | | | As species in $CaCl_2 + H_3PO_4$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | ng $m^{-3}$ | mg $kg^{-1}$ | Milli-Q | $CaCl_2 + H_3PO_4$ | Refractory | As(III) ($10^{-2}$ ng $m^{-3}$) | Extracted (%) | As(V) ($10^{-2}$ ng $m^{-3}$) | Extracted (%) | As(III) ($10^{-2}$ ng $m^{-3}$) | Extracted (%) | As(V) ($10^{-2}$ ng $m^{-3}$) | Extracted (%) |
| Tapada Outeiro | Fine | 2.71 | 135 | 14.1 | 31.6 | 54.3 | 9±2 | 3.1 | 30 ± 1 | 11.0 | n.d. | – | 84 ± 7 | 31.6 |
| | Coarse | 0.69 | 51 | 8.5 | 71.3 | 20.2 | 1.3 ± 0.2 | 1.9 | 5 ± 1 | 6.6 | 1.9 ± 0.8 | 2.8 | 50 ± 10 | 68.5 |
| Sines | Fine | 1.90 | 116 | 6.2 | 15.8 | 78.0 | n.d. | – | 12 ± 2 | 6.2 | 3.7 ± 0.3 | 2.0 | 30 ± 10 | 13.8 |
| | Coarse | 0.15 | 10 | – | 52.5 | 47.5 | n.d. | – | n.d. | – | 2.5 ± 0.2 | 16.7 | 0.05[b] | 35.8 |

[a]5% analytical error based on one replicate.
*Note*: n.d. below detection limit.
[b]Based on a single measurement.

compared with results obtained previously (Šlejkovec *et al.,* 2000). These authors found values in the order of magnitude of 50% (fine fraction) and 12% (coarse fraction). This fact may be explained by different extraction conditions, such as shorter sonication time (30 min instead of 3 h) and use of only water instead of methanol + water. Also our samples were not frozen and freeze dried. Furthermore, the large number of filter quarters may have hindered the contact of particles with the extractant.

The amount of arsenic extracted in Milli-Q water is slightly dependent with the aerosol size fraction. This is different from the results observed by the authors mentioned above.

### 3.1.3. *Amount of Arsenic Extracted with $CaCl_2 + H_3PO_4$*

The amount of arsenic extracted with $CaCl_2 + H_3PO_4$ (see Table II) is higher in the coarse fraction for both sampling sites. The arsenic extractability for Tapada do Outeiro filters is 31.6% and 71.4% for fine and coarse fractions, respectively. For Sines lower arsenic extractability values were observed (15.8% and 52.4% for fine and coarse fractions, respectively). The remaining As was non-extractable leaving about 54% in the fine fraction for Tapada do Outeiro and 78% for Sines. For the coarse fraction 20% was non-extractable for filters from Tapada do Outeiro and 48% for filters from Sines. The refractory As for the fine fraction is higher when compared with the coarse fraction. This differs from earlier results (Šlejkovec *et al.,* 2000) where 78% of the coarse As and about 40% of the fine As were not extracted (collected in Hungary). Different compositions of the atmospheric particles in both countries might explain the different results. Besides the poor vegetal coverage of soil, Portugal has a strong influence of dust coming from the north of Africa, namely from the Sahara desert (Reis *et al*., 2002). When a major influence of soil is observed the water solubility is lower since the elements are strongly bound. Since soil particles are mostly associated with the coarse fraction, extraction is only possible with under more aggressive conditions, e.g. acids, as it is observed in Table II.

### 3.1.4. *Arsenic Species in the Milli-Q Extracts*

Concerning arsenic species found with Milli-Q (see Table II), in Tapada do Outeiro As(III) and As(V) were found in both size fractions. At this site, the amount of As(III) extracted is similar for both fractions (3.2% and 1.9% in fine and coarse fractions, respectively). The amount of As(V) extracted is 11% and 6.6% in fine and coarse fractions respectively. In Sines As(III) was not identified and As(V) was identified in the fine fraction with an extractability of 6.2%. At both sites the extraction of As(V) in the fine fraction is similar and probably also in the coarse fraction taking into account that total arsenic in the coarse fraction for Sines is much smaller than in Tapada do Outeiro.

### 3.1.5. *Arsenic Species in the $CaCl_2 + H_3PO_4$ Extracts*

Concerning arsenic species found with $CaCl_2 + H_3PO_4$ (see Table II) both As(III) and As(V) were extracted from Sines filters. As(III) for Tapada do Outeiro filters was observed only in the coarse fraction. Comparing with the species extracted with Milli-Q, higher concentrations were found for As(V), leading to the conclusion that a substantial part of the extracted arsenic measured is in this form. However, part of the As(V) may have resulted from oxidation of As(III) during the sampling, storage, extraction, etc.

## 3.2. LICHENS

### 3.2.1. *Total Arsenic Concentration*

Total arsenic concentrations and the amounts of arsenic extracted in lichen transplants are shown in Table III. The arsenic reference values for the unexposed lichen were 0.82 and 0.97 mg $Kg^{-1}$ (duplicate samples). The total arsenic concentration increased about 100% for both sampling sites during the exposure.

### 3.2.2. *Amount of Extracted Arsenic and Arsenic Species in the Milli-Q Extracts*

Table III shows that the accumulated arsenic is mostly refractory for lichens from both Sines and Tapada do Outeiro; only a small fraction (ca. $<10\%$) is accessible under Milli-Q conditions. These results are in agreement with the results of earlier studies with different or equal species of lichens; the amount of water-extractable As is reported between 1.1–42% (Koch *et al*., 2000), 7–28% (Kuehnelt *et al*., 2000) and 1.7–32% (M.M. Farinha, personal communication).

At both sampling sites four arsenic species were found, viz. As(III), DMAA, MMAA and As(V) for almost all the samples (see Table III). Since in both fractions of airborne particulate matter organic arsenic was not detected the presence of these species in lichens may indicate the biotransformation of inorganic arsenic. This transformation was observed in several terrestrial organisms, such as fungi, bacteria, mushrooms, freshwater algae, animals, and humans (Byrne *et al*., 1995; Kuehnelt *et al*., 1997). The presence of the methylated species appears to be a self-defence mechanism. This appears more evident for Tapada do Outeiro lichens where a higher arsenic extractability from aerosols was found (Table II).

### 3.2.3. *Amount of Extracted Arsenic and Arsenic Species in the $CaCl_2 + H_3PO_4$ Extracts*

No improvement was achieved in terms of extracted amount in these conditions. Only from Tapada do Outeiro the four species were extracted. From the remaining lichen samples the following species were detected: *Reference a,* DMAA; *Sines b,* As(III) and As(V). In the majority of the samples the use of more aggressive

*Table III.* Total As concentrations, sequential arsenic extractability and arsenic species concentrations in lichens (mg $kg^{-1}$ dry mass) in Milli-Q and in $CaCl_2 + H_3PO_4$ extracts for lichens exposed at Tapada do Outeiro and Sines (a and b denote duplicate for lichen transplant and in in situ samples)

| | Total As conc.[a] (mg $kg^{-1}$) | Extractability of As (% of total As) | | | As species in Milli-Q ($10^{-2}$ mg $kg^{-1}$) | | | | As species in $CaCl_2 + H_3PO_4$ ($10^{-2}$ mg $kg^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Milli-Q | $CaCl_2$+$H_3PO_4$ | Refractory | As(III) | DMAA | MMAA | As(V) | As(III) | DMAA | MMAA | As(V) |
| Reference a | 0.82 | ≈3 | 1.5 | 96 | 0.9 ± 0.1 | n.d. | n.d. | n.d. | n.d. | 1.4 ± 0.2 | n.d. | n.d. |
| Reference b | 0.97 | 2.6–6.2 | – | 94–97 | 1.6 ± 0.2 | 1.6 ± 0.4 | 0.8 ± 0.2 | 1.8 ± 0.1 | n.d. | n.d. | n.d. | n.d. |
| Tapada Outeiro a | 2.8 | ≈7 | 4.6–6.2 | ≈88 | 3.7 ± 0.3 | 13 ± 1 | n.d. | 2.5 ± 0.5 | 3.3 ± 0.2 | 1.9 ± 0.9 | 1.9 ± 0.3 | 7.7 ± 0.9 |
| Tapada Outeiro b | 1.6 | 7.5–9.3 | 1.0–1.8 | ≈90 | 2.3 ± 0.4 | 7.3 ± 1 | 1.1 ± 0.3 | 2.5 ± 0.6 | 0.9 ± 0.5 | n.d. | 0.5 ± 0.4 | 3 ± 2 |
| Sines a | 2.1 | ≈2 | – | ≈98 | 1.1 ± 0.6 | 0.011[b] | 0.011[b] | 2.4 ± 0.9 | n.d. | n.d. | n.d. | n.d. |
| Sines b | 2.3 | ≈2 | 0.7 | ≈97 | 1.5 ± 0.1 | 1.2 ± 0.1 | n.d. | 1.5 ± 0.6 | 0.6 ± 0.4 | n.d. | n.d. | 1.5 ± 0.8 |

[a]5% analytical error based on one replicate.

[b]Based on a single measurement.

extracts (acid) leads to small extracted amounts of each species. This may indicate that the As is strongly bound to the matrix.

## 4. Conclusions

The As species concentrations in aerosols from Tapada do Outeiro were higher than from Sines, for both fine and coarse fractions, which agrees with the total arsenic concentrations. For both size fractions, only inorganic As was found (As(III) and As(V)) for the applied sequential extraction procedure.

For lichens, in spite of a total As concentration after exposure being similar for both sampling sites, the extractability of As species was more extensive for Tapada do Outeiro. Four arsenic species were found, two inorganic species (As(III) and As(V)) and two organic species (DMAA and MMAA) for both sampling sites and for Milli-Q extractions.

Concluding we may say that in lichens the presence of organic arsenic may indicate the biotransformation of inorganic As, since in the fine and coarse aerosol fractions these species were not identified.

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