Maritime deposition of organic and inorganic arsenic

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ABSTRACT

The speciation of arsenic in wet and dry deposition are ambiguously described in current literature. Presented here is a two-year study quantifying arsenic species in atmospheric deposition collected daily from an E. Atlantic coastal, semi-rural site, with comparative urban locations. Inorganic arsenic (As_i) was the principal form of arsenic in wet deposition, with a mean concentration of 0.54 \( \mu \text{mol/m}^3 \). Trimethylarsine oxide (TMAO) was found to be the dominant form of organic arsenic, determined as above the LoD in 33% of wet deposition samples, with a mean concentration of 0.12 \( \mu \text{mol/m}^3 \). Comparison with co-deposited trace elements and prevailing weather trajectories indicated that both anthropogenic and marine sources contribute to atmospheric deposition. Analysis of dry deposition revealed it to be a less significant input to the land-surface for As_i, contributing 32% of that deposited by wet deposition. Dry deposition had a larger proportion of As_i than was found in wet deposition, with TMAO making up only 12% of the sum of species. In comparison, urban sites showed large spatial and temporal variations in organic arsenic deposition, indicating that local sources of methylated species may be likely, and that further understanding of biogenic arsine evolution and degradation are required to adequately assess the atmospheric arsenic burden and subsequent contribution to terrestrial ecosystems.
INTRODUCTION

Studies on arsenic speciation in deposition, wet or dry, are rare.\textsuperscript{1–3} Short-term maritime studies have recently shown that organic arsenic species, primarily trimethylarsine oxide (TMAO), are present in wet deposition at ~20% of sum of arsenic species.\textsuperscript{2,3} Weather trajectory modeling indicates that the TMAO is of marine origin\textsuperscript{2,3}, derived from the atmospheric photooxidation of trimethylarsine (TMA)\textsuperscript{4}, emitted from seawater\textsuperscript{3}. Inorganic arsenic (As\textsubscript{i}) is the dominant species in atmospheric deposition\textsuperscript{1–3}, but its origin is less clear\textsuperscript{2,3}. The sole continental arsenic speciation deposition campaign reported in the literature found that As\textsubscript{i} dominated, and that organic species, again dominated by TMAO, were low and infrequent.\textsuperscript{1} The authors attributed the presence of TMAO to phylosphere metabolism of As\textsubscript{i} in their forested site.\textsuperscript{1} Atmospheric particulate studies routinely pick up TMAO as the major organic arsenic species\textsuperscript{4–6}, but this has been hypothesized to be of terrestrial origin, with soil microbes thought to be the source.\textsuperscript{5} Volcanic emissions have also been considered a source for TMA/TMAO.\textsuperscript{7,8}

The lack of arsenic speciation data in atmospheric deposition studies has meant that the source modeling of atmospheric arsenic has been conducted on totals\textsuperscript{9,10}, potentially confounding industrial and natural emissions. This confusion is exacerbated further by the poor understanding of natural sources of atmospheric arsenic, which may enter the atmosphere in gaseous form, including from biovolatilization and volcanic activity, or in particulate form from volcanic activity in addition to ocean spray and soil dust entrained to the atmosphere by wind.\textsuperscript{10–12} Mass balance modeling of the global
atmospheric flux of arsenic determined a total input of 30.7 Gg yr\(^{-1}\). However, this was calculated with the assumption that volcanic emissions were the only significant natural source of atmospheric arsenic, ignoring other natural sources and leading to only 2.1 Gg yr\(^{-1}\) of the calculated total as being of natural origin.\(^\text{11}\) This calculation was conducted without the knowledge garnered from recent studies that ~20% of arsenic in atmospheric deposition is organic and of natural origin\(^2,3\), either from terrestrial or marine microbial metabolism of arsenic.\(^{13-15}\)

A review of global arsenic modeling noted\(^\text{10}\) that there is an inherent problem with arsenic flux calculations in that the actual data used was both limited in scale/scope, and that where speciation was considered, antiquated methodologies had been used. While short-term studies lead to a better mechanistic understanding of arsenic deposition, in particular that there is rapid washout of TMAO in wet deposition samples\(^3\), longer runs of data are needed to conduct both yearly mass-balances, and to look at seasonal variation. Also, arsenic speciation in the dry deposition of atmospheric particulates is unstudied, and this omission is important for understanding sourcing of arsenic species. Here we present a 2-year run of wet deposition, and a 1-year run of dry deposition, arsenic speciation in a maritime setting known to have a maritime TMAO input.\(^3\)
MATERIALS AND METHODS

Atmospheric deposition samples were collected from a semi-rural, non-industrially impacted site in Northern Ireland, 54.617 N, -5.817 W (Figure 1) over a two-year period from May 2015 to May 2017, with daily samples collected in duplicate throughout year 1, and in triplicate throughout year 2. To complement the main site, three urban sites in were also sampled for wet deposition, implementing the same sampling conditions outlined above for the main site, for 2-5 months situated in domestic gardens within central Belfast: site 1: 54.575 N, -5.957 W; site 2: 54.584 N, -5.948 W; site 3, 54.577 N, -5.933 W.

Samples were collected at a height of 1.5 m in a flat open-lawn location, 5 m distant from hedge or tree cover, as shown in the equipment set-up in Figure S1. Bulk deposition samples were collected in pre-weighed 56 mm diameter, 120 ml volume, polypropylene cups (supplied by VWR), as received from supplier, which were capped and added to a freezer immediately after each 24-h collection period. The cups were disposable and were single use only, to avoid microbial and chemical contamination. They were set in a wider container (a colander) to provide stability. In the 2nd year of sample collection, sample cups left for a 24-h period where no wet deposition was collected were frozen in the same way. Dry sample cups were then treated with the addition of Milli-Q water (>18.2 MΩ.cm), determined gravimetrically, with 1 ml of Milli-Q water added to each sample assigned for arsenic speciation analysis and 4 ml added to sample cups assigned for analysis of trace
elements. These were then left overnight before preparation and analysis as per wet depositional samples.

All samples were weighed prior to sample preparation and volume of wet deposition was determined gravimetrically. Analytical protocols for speciation and multi-elements are given in detail in references 2 and 3. During year 1, 162 samples were analyzed for arsenic species, and a subset of 90 samples were analyzed for trace elements (B, Na, Mg, K, V, Mn, Ni, Cu, Zn, As, Se, Rb, Sr, I) by ICP-MS (Thermo Scientific ICAP-Q) in full-scan mode. In year 2, one sample from each daily set of triplicate samples was analyzed for arsenic speciation, a 2nd sample was prepared with acid for trace element analysis and the 3rd sample was treated with tetramethylammonium hydroxide solution (TMAH) for iodine analysis.

Samples for arsenic speciation were 0.45 micron filtered directly into 1 ml polypropylene vials, with hydrogen peroxide added to a final concentration of 0.3 % prior to analysis by ion chromatography (a Thermo Scientific AS7 column fitted to a Thermo Scientific IC5000 system) coupled to an ICP-MS detector (Thermo Scientific ICAP-Q). A representative rainwater arsenic speciation chromatogram of rainwater is given in Figure 2. Note, slight differences in retention times, but this is normal variation and identify of species in rain water was confirmed by spiking authentic standards into rainwater samples, along with cross confirmatory cation exchange chromatography for TMAO². Dimethylarsinic acid (DMAA) was used as the calibrant, as it sits in the middle of the species eluted. The limit of detection
(LoD) derived from the DMAA calibration curve was calculated for each batch. The highest LoD across all batches was determined and then applied to give a uniform LoD across the whole data set. This was to avoid any confounding of batch difference in LoD in subsequent statistical analysis (Table S1). The average percent recovery of As from a synthetic surface water certified reference material (CRM) (SPS-SW2, obtained from LGC, Middlesex, UK), was 108% (n=142, standard error of mean=0.99%), Table S1. CRMs were prepared in triplicate with each set of samples received by the laboratory, with 2-3 sets of prepared samples then run with each analytical batch (n=25). No CRMs were available of organic arsenic speciation in waters.

Samples for analysis by full scan ICP-MS were 0.45 micron filtered before further preparation. Samples for trace element determination by ICP-MS were acidified to 0.1 M with nitric acid before analysis and for the analysis of iodine by ICP-MS samples were prepared with TMAH (0.5%, m/m). All analytical methods were carried out as per Savage et al.²

Potential arsenic contamination by bird feces or plant debris was controlled as a replicate sample was always collected by an adjacent cup, samples were then analyzed for both arsenic species via chromatography and for total arsenic by direct scanning mode. The samples were tested for outliers using the ROUT protocol (a new method based on robust nonlinear regression and the false discovery rate) in GraphPad Prism (v. 6 for Mac), using a Q of 1%.
For the logged data, which was used in subsequent linear regression comparison between the two data sets (Figure 3), no outliers were identified.

Basic statistical analysis (regression, identification of outliers) was conducted using GraphPad Prism. Factor analysis was conducted using SPSS (v.25) using a correlation matrix, with equimax rotation. Weather back-trajectories (72-h) were calculated using Hysplit as per Savage et al², and origins determined, as shown in Figure 1.
RESULTS

An illustrative rainwater chromatogram is shown in Figure 2. All potentially expected arsenic species [monomethylarsonic acid (MMAA), DMAA, TMAO, arsenobetaine (AsB), tetramethylarsonium (Tetra), arsenate (Asi)] separated, with the exception of AsB and TMAO. A Thermo Scientific CS12A cation exchange column was used to identify that the AS7 AsB/TMAO peak was TMAO, as expected from our previous studies. MMAA and Tetra were not found to be present above the LoD in any samples. At the semi-rural site, DMAA was only found above the LoD in wet deposition on 3 sampling dates over the 2-year period. TMAO was the second most frequently occurring arsenic species, present in 104 out of 312 wet deposition samples. Asi dominated arsenic species detected. The wet deposition concentrations of Asi and TMAO, as well as wet deposition volume, for the 2-year period are shown in Figure 4. Asi was the predominant form of arsenic in dry deposition, found above the LoD in 170 out of 184 samples. This compared with only 59 samples from the same subset containing TMAO above the LoD. The sum of arsenic species by speciation analysis had an 83% recovery when compared to total arsenic by ICP-MS, a regression of the data ($R^2 = 0.55$) is shown in Figure 3. It is likely that particulate minerogenic arsenic constitutes the difference between sum of species and total arsenic.

Bulk deposition of arsenic species was calculated by assuming concentration values below the global arsenic species LoD (Table S1) to be half that value. Minimum and maximum values were also calculated by ascribing sample concentration for those below the LoD to be zero, or the LoD value,
respectively. Table S2 shows the average concentration (µmol/m³), average daily deposition (nmol/m²/day) and annual flux (nmol/m²/year) for these three scenarios for wet deposition samples in year 1 (n=162) and year 2 (n=150), and for dry deposition samples collected in year 2 (n=184). For Asᵢ concentration per event, values ranged from 0.44 to 0.47 µmol/m³ in year 1 wet deposition, 0.63 to 0.64 µmol/m³ in year 2 wet deposition and 0.77 to 0.78 µmol/m³ in year 2 dry deposition, when zero and the LoD were used in this calculation for samples below LoD, respectively. For bulk deposition Asᵢ values for wet deposition were between 0.81 and 0.89 nmol/m²/day in year 1, between 1.28 and 1.38 nmol/m³/day in year 2, and a single figure of 0.35 nmol/m²/day for dry deposition in year 2, when zero and the LoD were used in this calculation for samples below LoD, respectively. The single figure in place of a range for average dry deposition of Asᵢ is due to there being very few samples (n=14) below the LoD, meaning that the scenarios of accounting for samples below the LoD with zero, half or full value of the LoD has negligible effect. There was larger variation between average TMAO concentrations under the different scenarios than was found for Asᵢ, reflecting the larger proportion of samples with TMAO below the LoD. For TMAO in wet deposition, average concentration ranged from 0.09 to 0.15 µmol/m³ in year 1 wet deposition and 0.09 to 0.14 µmol/m³ in year 2 wet deposition. In dry deposition the range was from 0.07 to 0.13 µmol/m³ under the different scenarios, with the almost 2-fold difference due to the small number of dry deposition samples with TMAO above the LoD.
The results presented in Table S2 show that rainwater accounts for a higher proportion of the atmospheric deposition of all arsenic species than dry deposition. When assuming samples below the LoD to be half the LoD value, wet deposition accounted for 61.9 nmol/m²/yr of TMAO in year 1 and 37.9 nmol/m²/yr in year 2, compared to 8.89 nmol/m²/yr of TMAO from dry deposition in year 2. Similarly, the annual contribution of Asᵢ was also considerably larger from wet deposition, with 265 nmol/m²/yr in year 1 and 200 nmol/m²/yr in year 2, compared to 63.9 nmol/m²/yr of Asᵢ deposited from dry deposition in the second year.

Year 2 was 30% drier than year 1, with 573 mm of wet deposition recorded, compared to 823 mm, which was reflected in the sum of arsenic species found in wet deposition, with 28% less arsenic found in year 2 than in year 1. The decline disproportionately affected TMAO, with 39% less recorded in drier conditions compared to a reduction of 25% for Asᵢ.

Asᵢ and TMAO concentrations in wet deposition were plotted against each other and against elemental analysis, and meteorological factors, in Figures 5 and 6, respectively, with only significant regressions shown. In Figure 5, statistical analysis was carried out on the concentration (log µmol/m³) of Asᵢ in wet deposition samples, for all samples with concentration of Asᵢ determined to be higher than the global speciated arsenic LoD (n=245). Results below the global LoD were removed from this analysis. A significant relationship between Asᵢ in wet deposition and a number of different elements and parameters was determined, with a positive trend with
for boron, vanadium, manganese, zinc, selenium, strontium, iodine, as well as with longitude (all P<0.001). \(\text{As}_i\) also correlated positively with TMAO (P=0.001) and iodine (P=0.01). There were negative relationships with length of 72-hour weather trajectory and with average daily rainfall mm (both P<0.001). For TMAO (Figure 6), there were positive correlations with nickel and \(\text{As}_i\) (P<0.001), copper (P=0.001), vanadium (P=0.002), boron (P=0.003), sodium (P=0.004) and selenium (P=0.007). There was also a negative relationship with rainfall deposition (P<0.001). All other parameters were not significant for TMAO. Seasons, based on equinox’s, also had no contribution to \(\text{As}_i\) or TMAO concentration in wet deposition, using 2-way ANOVA on ranked data. When the same statistical analysis was carried out for \(\text{As}_i\) in dry deposition samples, longitude (P<0.001) as well as with boron (P=0.004) and iodine (P=0.005) were significant for season.

The relationship between arsenic species concentration and rainfall was further analyzed by fitting exponential decay functions to the non-logged data (Figure 7), showing strong wash-out of TMAO, with R² values given in Table S3. This sharp decline in TMAO concentration with rain water volume was also observed in 3 urban sites monitored for shorter periods. Median data of the complete data series for the inner-city sites are reported in Table S4, and exponential decay curves shown in Figure S2, with fitting statistics reported in Table S3.

To further analyze the interrelationships between arsenic species and element concentrations, weather trajectory data and rainfall, Principle
Components Analysis (PCA) was conducted, as shown in Figure 8. There was no clear separation of data based on As₃ concentration, but the factor analysis showed the association between elements and environmental factors. PCA1 separated on rainfall (mm), as expected from the regression plots in Figures 5-6 and washout curves demonstrated in Figure 7. The factor analysis for PCA2 v. PCA3 was more revealing with respect to associations between elements. As₃ separated with selenium and vanadium and zinc, as well as longitude. TMAO was between this cluster and a cluster for copper, nickel, rubidium and potassium. Boron, strontium, sodium and magnesium were diagonal to the cluster bounded by As₃ and TMAO.
As$_i$ was found to be the dominant form in rainwater collected daily from an Atlantic seaboard site, comprising approximately 80% of the mean concentration for the sum of arsenic species analyzed. TMAO was the only routinely observed organic arsenic compound, accounting for 20% of deposited arsenic, with DMAA found to be a minor constituent rarely detected in Irish atmospheric deposition. The proportion of inorganic to organic arsenic reported here corresponds to previous data from Indian Ocean summer monsoon wet deposition data, which reported median concentrations of 1.33 $\mu$mol/m$^3$ As$_i$ and 0.30 $\mu$mol/m$^3$ TMAO. Here, TMAO showed no strong relationship to weather trajectories or season, only to wet deposition volume, suggesting ubiquitous and non-seasonal local source, which we attribute to the ocean and sea that surround Ireland. It would be expected that a primarily terrestrial source of TMAO would show a stronger seasonal pattern as soils have a greater temperature variation, and thus reduced microbial activity during the winter would be expected, as illustrated by the seasonal dependence on soil microbe produced NO$_2$. Sea temperatures are more buffered against extremes of temperature, as illustrated by time trends in CO$_2$ production, especially in the Gulf Stream dominated location of the study. The rapid washout or UV-mediated degradation of methylated species would reduce long-distance transport, further strengthening the dominant marine origin hypothesis, and may explain why TMAO is elevated in this current study, and at other Irish locations, but is only intermittently observed in continental Germany. While evidence from Irish and South Asian sites have pointed to marine environments as ubiquitous sources of biovolatilized
arsenic, the low frequency of TMAO detection in continental Germany may suggest that terrestrial sources of biovolatilized arsenic are less abundant or biome-specific.

Di- and tri-methyl arsines are biogenic products, emitted to the atmosphere from soils and waters through microbial biovolatilization, with atmospheric oxidation leading to the occurrence of DMAA and TMAO respectively, which have been identified in atmospheric particulates in several locations globally, but is still poorly understood. The biovolatilization of arsenic by bacteria and fungi to arsines has been identified in terrestrial environments, by freshwater cyanobacteria, and the marine microalgae Ostreococcus tauri. While it has been acknowledged that TMAO is ubiquitous in the atmosphere, identifying the sources, flux and transport is confused. A maritime Japanese study attributed DMAA and TMAO in atmospheric particulates to terrestrial origin, but in light of more recent evidence a marine source is more likely. This is not to say that terrestrial arsine production will not contribute to TMAO deposition, and indeed the continental German intermittent observation of TMAO in wet deposition could emanate from soils, although the TMAO here could also have been from long distance transport with a marine origin as discussed above. However, the study reported here, and our previous investigations, show that on seaboard locations that TMAO is carried on weather trajectories that either originate, or pass over, marine water bodies.
Here, $\text{As}_i$ was dominated by European mainland sources. The mean concentration of the sum of arsenic species in wet deposition reported was $0.71 \, \mu \text{mol/m}^3$, as compared to total arsenic of $1.99 \, \mu \text{mol/m}^3$ in a long-term study of a remote area in Wales$^{21}$. Non-ferrous smelting and fossil fuel production are the main sources globally of anthropogenic arsenic, with the replacement of coal burning for natural gas a major factor in the 4-fold decline in arsenic emissions in the UK since 1970.$^{19}$ The long-term Welsh study recorded a decline in rainwater arsenic concentrations, halving over the decade 1999 to 2009, in line with the reduction in industrial emissions.$^{21}$ Despite this marked decline in emissions and subsequent deposition reported for historic investigations, the data presented here, corresponding to the findings in that Welsh investigation, show that for even in the most remote areas of Europe there is still an anthropogenic baseline input of atmospheric arsenic. In this study, positive correlations in Irish wet deposition were observed between $\text{As}_i$ and industrial elements Ni, Cu and Zn, suggesting a common anthropogenic source; and while the UK has prevailing Atlantic weather systems, higher concentrations of $\text{As}_i$ were found to correlate with air mass trajectories originating from the east. This demonstrates an impact from urban and industrial regions of mainland UK and continental Europe. Factor analysis showed that $\text{As}_i$ was most closely associated with ferrous industries associated vanadium and zinc, as well as a loser association with copper and nickel. Also, this factor analysis showed that $\text{As}_i$ was diagonal in its influence in the PCA to marine derived boron, magnesium, sodium and strontium. Additionally, length of weather trajectory showed strong negative correlations with $\text{As}_i$ as well as with longitude, which
may indicate a dominant influence from nearby anthropogenic sources in mainland UK. The Irish concentrations for total arsenic reported here were considerably lower (8-fold) than those found in a year-long study in a forested catchment in Germany. This German study concluded that arsenic in rainwater was predominantly from industry and atmospheric entrainment of polluted soils.

However, as well as linking of Asi to industrial/terrestrial elements, positive correlations were found between Asi and marine elements Se, I and B, suggesting a link between Asi and the prevailing Atlantic weather systems which dominate the Irish landmass, supporting the hypothesis of a contribution from marine sources of arsenic to terrestrial ecosystem wet deposition. Wet deposition has also been found to play a significant role in the cycling of marine arsenic, with Asi being identified as the most abundant form in seawater, and with little variation found in surface concentrations throughout the oceans. Concentrations of Asi in seawater are higher than those found in rainwater, which, when coupled with prevailing marine weather trajectories, make the physical entrainment of ocean water a likely source of Asi. If Asi is derived from marine aerosols, as well as from anthropogenic emissions, this may also explain the high temporal variation, but lack of seasonal trend, as both sources may provide relatively constant emissions, but subject to significant shifts in air-mass trajectories and associated meteorology. The source of arsenic in atmospheric deposition was modelled for rural Welsh wet deposition using source proxies and similar to the relationships with Asi data reported here, exposure to urban
emissions was the most important factor explaining Asi, with exposure to chlorophyll $a$ also found to be significant\cite{16}, corresponding with the potential marine source identified in this study.

ASSOCIATED CONTENT

The supporting information contains 4 tables and 2 figures. The tables pertaining to quality control, quantification of atmospheric deposition of arsenic species over the 2-year period, median concentration of arsenic species in wet deposition and statistical analysis of the data presented. The Figures pertain to images of the main sampling site and sampling equipment, and to arsenic species relationship to rainfall (mm).
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Notes

The authors declare no competing financial interest.
REFERENCES


(7) Hirner, A. V; Feldmann, J.; Krupp, E.; Grümping, R.; Goguel, R.; Cullen, W. R. Metal(loid)organic compounds in geothermal gases and


(15) Yin, X. X.; Wang, L. H.; Zhang, Z. C.; Fan, G. L.; Liu, J. J.; Sun, K. Z.; Sun, G. X. Biomethylation and volatilization of arsenic by model protozoan Tetrahymena pyriformis under different phosphate regimes.


Figure 1. Origin of 72 h weather trajectories as modelled by Hysplit, indicated by orange circles. The Belfast sampling location indicated by blue star.
Figure 2. An arsenic speciation mixed standard (A) and a representative rainfall (B) chromatogram.
Figure 3. Regression of rainwater samples analyzed by IC-ICP-MS (sum of arsenic species) versus ICP-MS (total arsenic), $R^2 = 0.55$. 
Figure 4. Concentration of As (A) and TMAO (B), and rainfall (C), plotted against time, for the main study site, with samples <LoD denoted as half LoD (0.04 μmol/m³).
Figure 5. Regressions of log Asi concentration in wet deposition with weather trajectory data and other species/elements. Only data with significant regressions (P>0.05) are presented. Only data above LoD were plotted and regressed.
Figure 6. Regressions of log TMAO concentration in wet deposition with weather trajectory data and other species/elements. Only data with significant regressions (P>0.05) are presented. Only data above LoD were plotted and regressed.
Figure 7. Relationship between rainfall and concentration of Asi (A), DMAA (B) and TMAO (C), modelled using a single exponential decay function.
Figure 8. PCA of 2-year study - arsenic species and trace element concentrations, rainwater and weather trajectory data. PCA1 v. PCA2 (A), factor analysis for PCA1 v. PCA2 (B), PCA2 v. PCA3 (C) and PCA2 v. PCA3 factor analysis (D) are shown. PCA1 explained 35.9% of variance; PCA2, 12.0%; and PCA3 8.5%; cumulative variance explained being 56.5%.
Atmospheric deposition of inorganic + organic arsenic

- As$_i$
  - Physical entrainment of inorganic arsenic from ocean

- TMA
  - Bio-volatilization of organic arsenic from ocean

- As$_i$ + TMAO

- As$_i$
  - Anthropogenic emissions of inorganic arsenic