

Real-Time Detection of Arsenic Cations from Ambient Air in Boreal Forest and Lake Environments

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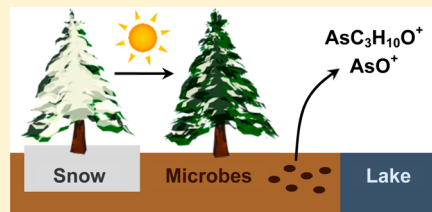
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Supporting Information

ABSTRACT: We present the first observation of airborne organic and inorganic arsenic cations, detected in real time within the boreal forest in Hyytiälä, Finland, and over nearby Lake Kuivajärvi. The technique of atmospheric-pressure interface time-of-flight mass spectrometry provides online, *in situ* monitoring as well as chemical information about the arsenic species, identified as protonated trimethylarsine oxide ($\text{AsC}_3\text{H}_{10}\text{O}^+$) and $\text{AsO}(\text{H}_2\text{O})_n^+$ clusters ($n = 0-4$). Quantum chemical calculations confirm that the proposed cations are stable under atmospheric conditions. Our most remarkable discovery is that minimal arsenic appeared during spring 2011 until after the ground began to thaw, triggering a sharp increase in airborne arsenic levels as snowmelt flooded the soil with water and stimulated microbial activity. These findings reveal that volatile arsenic species, detected here as atmospheric ions, link the biogeochemical cycling of arsenic through air, soil, water, and living organisms.



INTRODUCTION

Arsenic (As) is a highly toxic, carcinogenic trace element present throughout the environment. Natural sources of arsenic include weathering and erosion of rocks and soil. Humans introduce additional arsenic through fertilizers and pesticides, ore mining and smelting, and fossil fuel combustion. Background concentrations of arsenic typically range from 5 to 10 mg kg^{-1} in soil and from 0.2 to 2 $\mu\text{g L}^{-1}$ in lakes, but these levels rise by several orders of magnitude in groundwater in Bangladesh, India, China, Hungary, and elsewhere.¹ In response to this widespread contamination, the World Health Organization has named arsenic as one of the top 10 chemicals for major public health concern.²

Traditionally, the discussion of the biogeochemical cycle of arsenic has been limited to terrestrial and aquatic reservoirs, but emerging studies now recognize contributions from gas-phase species, which account for arsenic concentrations of 10^{-5} to $10^{-3} \mu\text{g m}^{-3}$ in unpolluted air.³⁻⁶ Volatile arsenic typically enters the atmosphere through microbial detoxification processes, generating arsine (AsH_3) and its methylated derivatives (methylarsine, dimethylarsine, and trimethylarsine) according to the Challenger mechanism for reduction and oxidative methylation.^{7,8} The resulting arsines are far more poisonous than their inorganic precursors, but because they are expelled as gases, biovolatilization is considered a detoxification

pathway for microorganisms. Once released to the atmosphere, arsines have a lifetime of ~ 8 h during the day and can persist for weeks under dark conditions before they are oxidized to form arsenite, arsenate, or methylarsonates.^{3,4} Of particular note, trimethylarsine is converted to trimethylarsine oxide (TMAO), a common form of arsenic in air, soil, and water across the globe.

The lack of field-deployable, real-time measurement techniques for identifying volatile arsenic compounds and their oxidation products, such as TMAO, has left a gap in our understanding of the arsenic biogeochemical cycle.^{3,5,9,10} Furthermore, simply measuring total arsenic levels does not sufficiently characterize health risks because the toxicity of arsenic is highly dependent on its chemical form. Here we address this gap and apply atmospheric-pressure interface time-of-flight mass spectrometry (API-TOF) to monitor arsenic ion concentrations within a Finnish boreal forest and over a boreal lake.

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METHODS

Measurement Sites. The measurements were conducted at SMEAR II (Station for Measuring Forest Ecosystem–Atmosphere Relations) in Hyytiälä, Finland, located in a managed 50-year-old Scots pine forest (*Pinus sylvestris*) at 61°51'N, 24°17'E.¹¹ The terrain in the forest is mostly flat but has height variations of up to 40 m. A thin layer of soil at most 2 m deep sits above igneous and metamorphic bedrock, and the thickness of organic (humus) layer is approximately 5–10 cm.

Kuivajärvi is a small, oblong-shaped lake (area of 61.3 ha, length of 2.6 km, maximal depth of 13 m, elevation of 141 m) located ~600 m southwest of SMEAR II and surrounded by a mainly forested catchment. Its waters are meso-eutrophic and humic with an anoxic hypolimnion layer in summer.¹² Both measurement sites are north of the glacial moraines that contribute to an arsenic “hot spot” covering >700 km², where As concentrations exceed 10 mg kg⁻¹.¹³ See the [Supporting Information](#) for additional details.

API-TOF Mass Spectrometer. API-TOF instruments (Tofwerk AG) measuring in positive ion mode were deployed to Hyytiälä from May 5 to 8, 2009 in the forest, from March 24 to April 29, 2011 in a clearing, and from August 24 to September 13, 2012 on a raft ~5 m off the shore of Lake Kuivajärvi. No ionization source is coupled to the mass spectrometer; the ions detected exist naturally in the atmosphere, chiefly formed as a result of high-energy galactic cosmic rays colliding with atomic nuclei in air.¹⁴ The API-TOF samples ambient ions through a 300 μ m inlet at a flow rate of 0.8 L min⁻¹. Three differential pumping stages reduce the background pressure in the mass spectrometer to 10⁻⁶ mbar. Two quadrupole ion guides and an ion lens stack direct ambient ions to the time-of-flight detector, which distinguishes the ions according to their mass-to-charge ratios (m/Q). The typical mass accuracy is 0.2% with a mass resolving power of 3000 Th/Th, where Th = Thompson is a unit of m/Q . Further instrumental characteristics are given elsewhere.^{15,16}

Data Analysis. The data were averaged in hourly increments. Raw ion counts were converted to concentration estimates by assuming a fixed transmission between 0.5 and 1.0%. We corroborated the scaling with cluster ion concentrations measured by a balanced scanning mobility analyzer (BSMA). We consider the resulting arsenic ion concentrations to be approximate and intend them for relative comparisons rather than absolute quantification. A detailed discussion of the concentration uncertainties and the criteria for peak assignment are provided in the [Supporting Information](#).

Computations. Initial guesses for molecular geometries were constructed by hand with the graphical user interface of the ADF quantum chemistry program.¹⁷ These initial geometries were then used as input for quantum chemical calculations providing standard enthalpies, Gibbs free energies, and structural data, which were performed using the multi-step method CBS-Q3 implemented in Gaussian 09.^{18–21} Proton affinities were calculated from standard enthalpies of reaction for $B + H^+ \rightarrow BH^+$. The enthalpy of the proton was taken to be exactly 2.5RT, where R is the gas constant.

RESULTS AND DISCUSSION

Identification of Arsenic Ions. We report the first ever detection of airborne inorganic and organic arsenic ions in the environment, building on previous studies of ambient cations.^{16,22} The principle ion detected was AsC₃H₁₀O⁺

(TMAsO⁺). Our simulations suggest that this ion should be stable under standard atmospheric conditions, allowing us to monitor a derivative of TMAsO for the first time in the gas phase with an online, field-deployable technique. We also detected several other organic ions, along with a series of AsO(H₂O)_n⁺ clusters that may form as fragments during oxidation, ionization, or sampling of other precursors, such as AsH₃, within the mass spectrometer.^{23–26} [Table 1](#) lists all 11

Table 1. Identification of Arsenic Ions

integer m/Q	chemical formula	exact mass
91	AsO ⁺	90.9160
107	AsCH ₄ O ⁺	106.9473
109	AsO(H ₂ O) ⁺	108.9265
119	AsC ₂ H ₄ O ⁺	118.9473
125	AsCH ₆ O ₂ ⁺	124.9578
127	AsO(H ₂ O) ₂ ⁺	126.9371
137	AsC ₃ H ₁₀ O ⁺	136.9942
143	AsCH ₈ O ₃ ⁺	142.9684
145	AsO(H ₂ O) ₃ ⁺	144.9477
163	AsO(H ₂ O) ₄ ⁺	162.9582
273	As ₂ C ₆ H ₁₉ O ₂ ⁺	272.9811

arsenic-containing cations identified in the Finnish boreal zone through high-resolution mass spectrometry. We confirmed the API-TOF peak assignments to these ions with electrospray measurements of cacodylic acid, (CH₃)₂AsO₂H, as outlined in the [Supporting Information](#). We focus our analysis here on TMAsO⁺, which provided the strongest signal.

Arsenic cations were present in all locations (forest, clearing, and lake), but the data from spring 2011 suggest that the arsenic ions originate from microbial activity in the soil. As shown in [Figure 1a](#), the concentration of TMAsO⁺ depended strongly on the volumetric water content of the soil surface, with the highest TMAsO⁺ levels appearing for volumetric water fractions of ~0.3–0.4, in good agreement with the range of optimum soil moisture of 0.25–0.35 for microbial arsenic methylation.⁶ Furthermore, elevated TMAsO⁺ concentrations were observed during periods of thawing when 0 °C < T_{soil} < 1 °C ([Figure 1b](#)) and 0 °C < T_{air} < 5 °C ([Figure 1c](#)). As discussed later, springtime freeze/thaw events triggered arsenic release from soil by exposing moist litter and heightening microbial activity.

During autumn, TMAsO⁺ concentrations from the 2012 lake campaign increased steadily with T_{soil} ([Figure 1e](#)). We maintain that the arsenic over Lake Kuivajärvi originates from microbial activity in soil because the same set of arsenic ions was detected over the lake as in the forest and clearing. Moreover, the instrument raft was only ~5 m from shore, so airborne arsenic could have easily traveled to the spectrometer from land. Field measurements elsewhere have also shown that terrestrial sources transfer arsenic to bodies of water within an ecosystem.⁸

Springtime Freeze/Thaw Events Trigger Arsenic Release. Our most remarkable finding, shown in [Figure 2a](#), is that minimal TMAsO⁺ was present during the 2011 campaign until April 3, when the snow cover began to melt. The soil moisture also increased sharply at this time, as previously discussed. These results match field studies from wetlands in Greenland (69°12'N), where Jessen et al. predict the release of soluble arsenic once the permafrost thaws.²⁷ In addition, measurements over an 18 year period in Pallas,

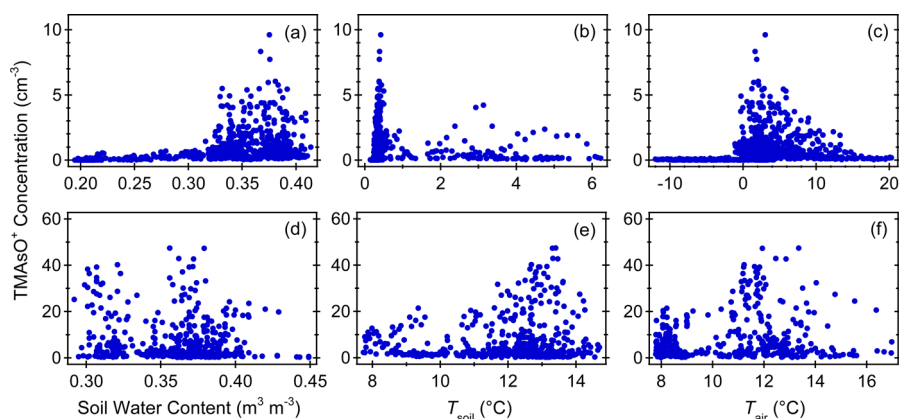


Figure 1. Arsenic ion concentrations as a function of soil conditions and temperature. Median hourly TMAso⁺ concentration measured by atmospheric-pressure interface time-of-flight mass spectrometry (Api-TOF), plotted vs (a) volumetric soil water content in the organic layer, (b) soil surface temperature, and (c) ambient temperature in Hyytiälä, Finland, from March 24 to April 29, 2011. (d–f) Analogous plots for measurements over Lake Kuivajärvi from August 24 to September 13, 2012. Ion concentrations are approximate and are intended for relative comparisons rather than absolute quantification. The brief 2009 campaign in Hyytiälä provided insufficient data to draw meaningful comparisons (see the [Supporting Information](#)).

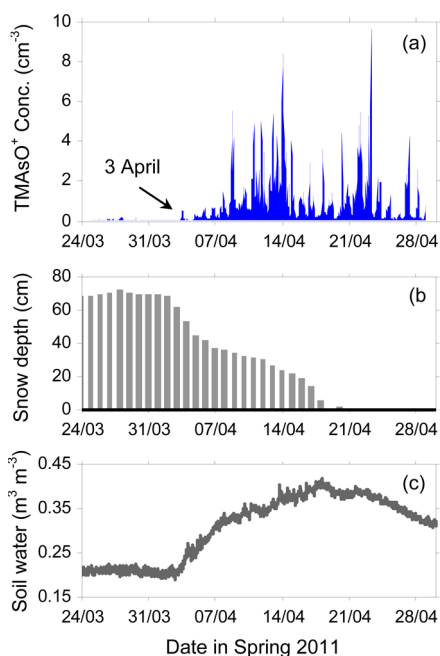


Figure 2. Springtime freeze/thaw events. (a) TMAso⁺ concentrations measured by Api-TOF, (b) snow depth, and (c) volumetric water content of the organic soil layer, all from March 24 to April 29, 2011 in Hyytiälä, Finland.

Finland consistently show a small arsenic spike each June, which corresponds to the time of snowmelt at this location (67°60'N).²⁸ Farther south in Hyytiälä (61°51'N), snowmelt increases the area of land temporarily inundated with water in April, including the riparian zone surrounding Lake Kuivajärvi. Soil moisture and rising temperatures affect volatile arsenic concentrations at all times of year, but freezing and thawing of soil particularly enhance atmospheric arsenic concentrations in early spring.

These springtime freeze/thaw cycles release arsenic through redox solubilization and increased microbial activity. Arsenic is often immobilized in soils as complexes with iron oxides, hydroxides, and oxyhydroxides, or in complexes with Mn(III), Mn(IV), Al(III), Ca, humic substances, clay, and natural

organic matter.²⁹ When dissolved O₂ concentrations in soil are low, e.g., from springtime flooding of soil with snowmelt, the reductive dissolution of iron and other metals can free arsenic. Often, this dissolution is bacterially mediated, and the available As(V) is reduced during anaerobic respiration.³⁰ Bacteria, fungi, and certain eukaryotes can also eliminate toxic arsenic from their environment through methylation, which generates volatile compounds like trimethylarsine that escape into the gas phase.^{1,30–32} In general, methylation and biovolatilization of arsenic occur more readily as the soil redox potential decreases.

The thawing of snow and ground frost in early spring not only increases soil water content, establishing anoxic conditions, but also allows litter to accumulate on the soil, further stimulating microbial activity. Field measurements in forests and wetlands typically detect more arsenic in the growing season than in the dormant season. For example, Huang et al. linked organic arsenic in soil to litterfall of leaves, twigs, and detritus to the forest floor,³³ and the addition of organic matter to soil has been widely shown to enhance microbial volatilization of arsenic.^{6,30} Furthermore, rising air and soil temperatures in spring can also facilitate microbial metabolism by helping overcome the ~12 kcal mol⁻¹ barrier toward arsenic methylation,³⁴ and warm temperatures promote diffusive transport of arsenic in the gas phase.

Emissions of volatile arsenic should be enhanced at the soil–water interface of Lake Kuivajärvi, where the ground is saturated with water and decomposable organic matter is readily available. In summer, and probably in late spring and early autumn as well, microbial activity generates arsenic at the interface between anoxic sediments and eutrophic waters.¹ The depletion of O₂ from biological activity favors the As(III) oxidation state at the lake bottom in summertime, but arsenic speciation in lakewater is often more nuanced and certainly depth-dependent. At the surface of Lake Biwa in Japan, for example, As(V) concentrations in the form of dimethylarsenic acid are well-correlated with temperature, whereas As(III) levels are correlated with chlorophyll *a* from photosynthesis, together maximizing the total surface arsenic concentration in late summer.³⁵ For comparison, we detected arsenic ions in both oxidation states above Lake Kuivajärvi. Atmospheric deposition further affects arsenic levels in lakes: Grahn et al. show that boreal lakes gain between 3 and 90 mg of arsenic/kg

of sediments (dry weight) per annum.³⁶ Future campaigns involving coordinated APi-TOF measurements in wetlands, peatlands, lakes, and other environments should specifically address the links between lacustrine, terrestrial, and airborne arsenic, including whether upwelling of arsenic-rich, anoxic water from the lake bottom contributes to arsenic concentrations in the gas phase.

Formation of Arsenic Ions. The airborne concentrations of neutral arsenic compounds in Hyytiälä are likely many orders of magnitude greater than the ion concentrations measured by APi-TOF. Because no ionization source is coupled to the mass spectrometer, the APi-TOF technique detects only those species that have already been ionized in ambient air, comprising just a tiny fraction of their neutral precursors. In positive ion mode, APi-TOF is most sensitive to abundant ions and to compounds that easily add a proton. More specifically, the proton affinity quantifies the propensity for a gas-phase molecule to add a proton through the reaction $B + H^+ \rightarrow BH^+$, and stronger bases with greater proton affinities will out-compete weaker bases for the available proton sources. As a result, cations formed from bases like ammonia, amines, and pyridines tend to dominate the positive ion population in the atmosphere.^{16,22} Our calculations suggest that TMA₂O is a good base, with a proton affinity of 234 kcal mol⁻¹ relative to an affinity of 204 kcal mol⁻¹ for NH₃,³⁷ allowing us to detect TMA₂O⁺ even when its neutral parent concentration is much lower than those of other more common atmospheric bases.

Atmospheric Implications and Future Needs. Ultimately, a combination of modeling and field work is necessary to explore the role of airborne arsenic in the biogeochemical cycle. Here we utilized real-time, *in situ* measurements with APi-TOF mass spectrometry to detect arsenic cations for the first time in the field. This approach fills the gap within the existing suite of arsenic measurement techniques because APi-TOF not only provides chemically specific identification based on mass-to-charge ratio, but also offers rapid time resolution on the order of ~0.1 Hz. The arsenic ions we detected in the boreal environment were strongly correlated with soil moisture and ambient temperature in early spring 2011, highlighting the contributions of microbial activity in the soil related to springtime freeze/thaw events. Future field campaigns should employ complementary measurement techniques to search for positive and negative arsenic ions, along with neutral arsenic compounds. To assess the biogeochemical relevance of gas-phase arsenic, and its contributions to arsenic in drinking water, more quantitative work is needed to explore arsenic concentrations and lifetimes in the atmosphere, and long-term studies are needed to monitor atmospheric arsenic across the globe, especially as climate change alters seasonal temperatures and the frequency of freeze/thaw events.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.5b00308.

Additional characteristics of measurements sites, procedure for peak assignments and calibration with cacodylic acid (Table S1 and Figure S1), concentration uncertainties and diurnal As cycles (Figure S2), discussion of AsO⁺ cluster ions (Figures S3 and S4), and analysis of the 2009 forest campaign (Figure S5) (PDF)

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Notes

The authors declare no competing financial interest.

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