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Marine and Terrestrial Sources of Methylated Arsenic Species in Atmospheric Deposition

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Arsenic cycling in the environment impacts ecosystem and human health, with atmospheric transport representing a key pathway that cycles an estimated 31 Gg annually. While pioneering work by Britta Planer-Friedrich revealed the importance of volatile methylated arsenic species (arsines) in volcanic and geothermal systems, the atmospheric transport and fate of their oxidized forms have remained largely unexplored.

We studied atmospheric arsenic and its source contributions at the high-altitude station Pic du Midi Observatory (2877 m a.s.l., France). Through sub-event-based sampling during 2019 (precipitation n=26; cloud water n=58) and a 2015-2020 weekly aerosol time series (n=134) at this site, we revealed significant levels of oxidized methylated arsenic species, demonstrating the potential for long-range atmospheric transport of arsenic. Source signatures were studied by integrating arsenic speciation analyses by LC-ICP-MS/MS with Lagrangian moisture source analyses and multiple chemical tracers. The oxidized forms dimethylarsinic acid ($DMAs^{V}$) and trimethylarsine oxide ($TMAs^{V}O$), derived from their volatile arsine precursors, exhibited contrasting source patterns: $DMAs^{V}$ showed clear marine signatures with strong correlations to marine tracers and Atlantic moisture sources, while $TMAs^{V}O$ displayed mixed terrestrial and marine biogenic sources with important coastal contributions [1].

Interestingly, methylated species showed enhanced water solubility in aerosols compared to inorganic arsenic, leading to their enrichment in wet deposition where they constituted on average 28±10% of total arsenic in precipitation and 46±20% in cloud water. These findings underscore their quantitative importance in wet deposition processes. This is further illustrated by our findings that atmospheric deposition fluxes of methylated arsenic species (0.005-3.38 $\mu g \times L^{-1} \times d^{-1}$) exceeded previously reported soil methylation rates, highlighting atmospheric deposition as a significant and overlooked source of potentially bioavailable methylated arsenic to terrestrial systems [1].

Overall, our study demonstrates that biogenic methylation processes, both marine and terrestrial, make substantial contributions to atmospheric arsenic cycling and should be included in global atmospheric arsenic budgets. This work, which highlights the importance of methylated species in atmospheric transport and deposition, builds on pivotal analytical developments from Britta Planer-Friedrich to trace arsenic methylation across environmental compartments.

[1] Breuninger, E.S., Tolu, J., Winkel, L.H.E. et al. (2024), *Nature Communication* 15, 9623.