Exploring Gas-Particle Partitioning of Trimethylamine using Single Particle Mass Spectrometry

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Overview

- Sources of trimethylamine
- Importance of particle mixing state
- The Aerosol Time-of-Flight Mass Spectrometer (ATOFMS)
- Case Study 1: Ontario
- Case Study 2: MEGAPOLI campaign Paris
- Summary
Trimethylamine

- Particulate matter (PM) affects our air quality, health and climate

- Particulate phase amines are rarely measured using routine off-line and on-line chemical analyses

- Trimethylamine (TMA) is estimated to be the most abundant alkyl amine in the troposphere$^1$

- Multiple sources contribute to TMA emissions globally, and include rendering and leather manufacturing

- Animal husbandry is estimated to be the most significant source by far ($\sim 0.1$ Tg N a$^{-1}$)$^1$

$^1$Ge et al. Atmos. Environ. 2011
Single particle composition and mixing state

Externally mixed particles

Internally mixed particles

- Organic carbon
- Elemental carbon
- Sulphate
Bulk sampling

- Bulk sampling enables determination of the overall composition but all single particle information is lost.

- Can be difficult to identify sources of particles using bulk results.

- Single particle measurements avoid this problem.
ATOFMS: principles of operation

- TSI Model 3800
ATOFMS: capabilities

- Detects elemental carbon, organic carbon, metals, inorganic ions for single particles

- Can also detect amines

- Provides size-resolved chemical composition in real time

- Allows determination of chemical mixing state (internal or external)

- Some mixing states are unique to specific sources- can be useful for apportionment
Case Study 1: Ontario

Cloud and Fog Processing Enhanced Gas-to-Particle Partitioning of Trimethylamine

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Supporting Information

ABSTRACT: An aerosol time-of-flight mass spectrometer (ATOFMS) was used to detect trimethylamine (TMA) in 0.52–1.9 μm particles at urban and rural sites in Southern Ontario during the summer and winter of 2007. During the summer, TMA-containing particles were observed exclusively during high relative humidity or fog events at both the urban and rural sites. In the wintertime, greater concentrations of TMA-containing particles were linked to cloud processing of aerosol in air masses originating from over agricultural and livestock areas. A laboratory study revealed that, at high relative humidity (~100%), gas phase TMA at concentrations ranging from 2 to 20,000 ppt partitions preferentially to acidic particles present in the ambient air. On the basis of the field and laboratory studies, it appears that gas phase TMA present in ambient air partitions onto pre-existing particles preferentially during periods of acidic cloud/fog processing, leading to the presence of TMA-containing particles in the 0.52–1.9 μm size range.
Case Study 1: Ontario

Intensive agriculture and animal husbandry activities to the South and West
Trimethylamine mixing state- Toronto

Average particle mass spectrum for TMA-containing particles in Toronto (winter)
Dependence upon meteorology

- In the summer, particle phase TMA was associated with fog events.

- In the winter, although elevated particle phase TMA was observed at RH < 90%, this was typically under cloudy conditions.
TMA source regions

- Potential Source Contribution Function (PSCF) combines temporal trends with air mass back trajectories to identify source regions.

- Agricultural areas to the south and west of Toronto are likely sources of TMA.

- In the winter the ground is typically frozen and thus crop production seems an unlikely source.

- **Animal husbandry** is more sensible.
Laboratory test: TMA partitioning

- Ambient particles were mixed with increasing mixing ratios of gas phase TMA at high relative humidity prior to ATOFMS analysis

- 4 distinct mixing states for ambient particles were identified and compared

- TMA uptake was significantly enhanced for the acidic sulphate-containing particles relative to the others
Case Study 1: Conclusions

- **High relative humidity** enhances TMA uptake to ambient particles (liquid water layer)

- Gas-particle partitioning is enhanced for **acidic** particles (probably due to protonation inhibiting exchange back to the gas phase)*

\[
\text{N(CH}_3\text{)}_3 (\text{g}) \leftrightarrow \text{N(CH}_3\text{)}_3 (\text{aq}) + \text{H}_2\text{O (l)} \leftrightarrow \text{N(CH}_3\text{)}_3\text{H}^+ (\text{aq}) + \text{OH}^- (\text{aq})
\]

- Trimethylaminium salt formation may also be occurring but could not be confirmed here

*Pankow Atmos. Environ. 2003*
Case Study 2: Paris - MEGAPOLI Project

- ATOFMS deployed at the LHVP urban background site

Healy et al., Atmos. Chem. Phys. 2012
TMA mixing state - Paris

Average particle mass spectrum for TMA-containing particles in Paris (winter)
TMA particle size distribution - Paris

- TMA-rich particles are much larger than local wood burning particles
- Indicates significant ageing
TMA particle temporal trend- Paris

- TMA-containing particle concentrations appear to be dependent upon air mass origin.
TMA source regions for Paris using PSCF

- TMA particles associated with source regions in Central and Eastern Europe
- These regions also contributed significantly to sulphate concentrations
Overall Conclusions

- ATOFMS enables determination of TMA mixing state

- No significant local sources of TMA identified in Paris or Toronto, instead TMA is associated with animal husbandry activities in rural areas outside these cities

- Gas-particle partitioning of TMA in Toronto is dependent upon RH and particle acidity

- Appearance of TMA-containing particles in Paris associated exclusively with air mass origin
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