Ambient measurements of amines and related nitrogen-containing compounds in a rural environment using protonated ethanol chemical ionization high-resolution mass spectrometry

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Methods
Measurement Technique(s): Chemical-Ionization High-Resolution Time-of-Flight Mass Spectrometry

<table>
<thead>
<tr>
<th>Instrument specifications</th>
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<tbody>
<tr>
<td>Tofwerk/Aerodyne high-resolution mass spectrometer</td>
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<tr>
<td>Measurement frequency 1 Hz</td>
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<td>Mass-to-charge range 0-1200</td>
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Ionization technique: Protonated Ethanol

n EtOH + H₂ (g) → n EtO⁺ (g) + H₂O (g), n=1-3

Analyte detection: clustering or proton transfer

<table>
<thead>
<tr>
<th>Analytes</th>
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<tbody>
<tr>
<td>Reduced nitrogen compounds</td>
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<tr>
<td>Silyl-derivatives</td>
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<tr>
<td>Some organics</td>
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</tbody>
</table>

Data Analysis: Tofware

- Precise mass-to-charge calibration
- Constrained peak fitting (provisional peak width and shape)
- High resolution data analysis separates isotopic compounds, e.g., ammonia and methane (accurate at 108.0653 and C3H8 at 106.1226)

Take-home messages

- Ethanol-CIMS detects ammonia, amines and many more reduced nitrogen compounds
- Time-of-flight mass spectrometry allows simultaneous detection
- High-resolution mass spectrometry allows specification and separation of individual compounds
- Laboratory and field calibrations give absolute concentrations
- Inlet design reduces residence times, but still needs improvement
- Field measurements show temporal variation of most detected compounds before new particle formation events
- Strong changes in compounds not always correlated with new particle formation
- Frequent zeroing gives backgrounds and time-responses for individual compounds
- Statistical analysis (PMF) promises to specify sources and compound classes

Field Measurements

- Southern Great Plains ARM site, Oklahoma
- Rural environment
- Some influence from oil and gas extraction

Compound types present in mass spectra

- Dilution system for ammonia, methyl amine (MA), dimethyl amine (DMA), diethyl amine (DEA)
- Frequent standard additions of around 500-1000 ppt
- Regular zeroing

New particle formation events (NPF)

- Changes in most compounds slightly before events
- Strongest increase when no particle were formed
- Gas-phase compounds did not partition into particle phase

Preliminary results!

- Separate time-series and spectra show potential for source apportionment and compound assignment

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Time series shows different temporal behavior for isotopic compounds