# Ambient Measurements of Amines by PTR-QiTOF-MS



# Instrument Performance Assessment and Results from Field Measurements in the Vicinity of TCM, Mongstad

Tomas Mikoviny<sup>a</sup>, Claus J. Nielsen<sup>a</sup>, Wen Tan<sup>a</sup>, Armin Wisthaler<sup>a</sup>, Liang Zhu<sup>a</sup>, Anne Kolstad Morken<sup>b</sup>, Terje Niøten Nilsen<sup>b</sup>



<sup>a</sup> Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, 0315 Oslo, Norway <sup>b</sup> CO<sub>2</sub> Technology Centre Mongstad (TCM DA), 5954 Mongstad, Norway



c.j.nielsen@kjemi.uio.no

#### **Overview**

**Routine monitoring** stack gas measurements\*

\*PTR-ToF-MS (version: PTR-TOF 8000)

## Challenging task

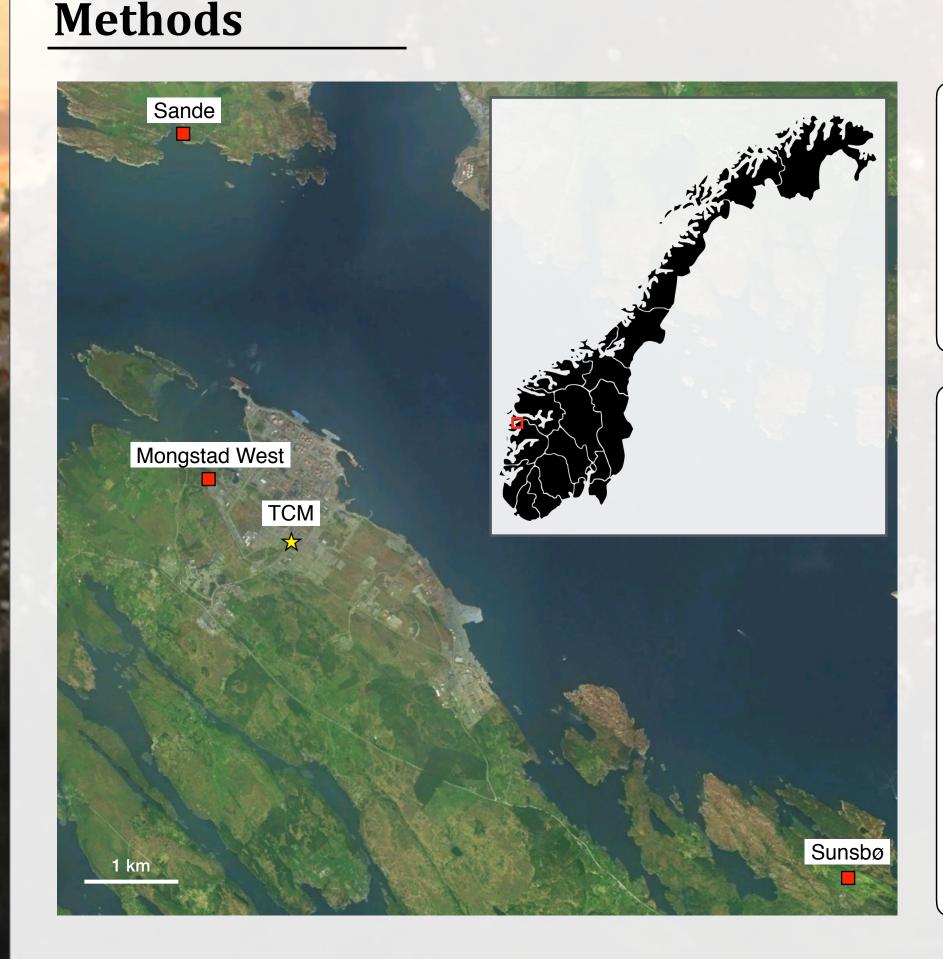
atmospheric measurements are problematic due to low ambient concentrations and sampling artefacts

### PTR-QiToF-MS\*

instrument is capable of detecting trace gases at single-digit pptv\*\* levels on-line and in real time

\*Proton-Transfer-Reaction Quadrupole ion guide Time-of-Flight Mass Spectrometer

\*\*1 pptv = 1 pmol/mol =  $10^{-12}$  v/v



# **Locations:**

Sunsbø (60°46'10.1"N, 5°09'08.6"E) Sande (60°50'56.6"N, 5°00'21.0"E) Mongstad West (60°48'45.7"N, 5°00'43.4"E)

### Target compounds:

Methylamine (MA) CH<sub>5</sub>N

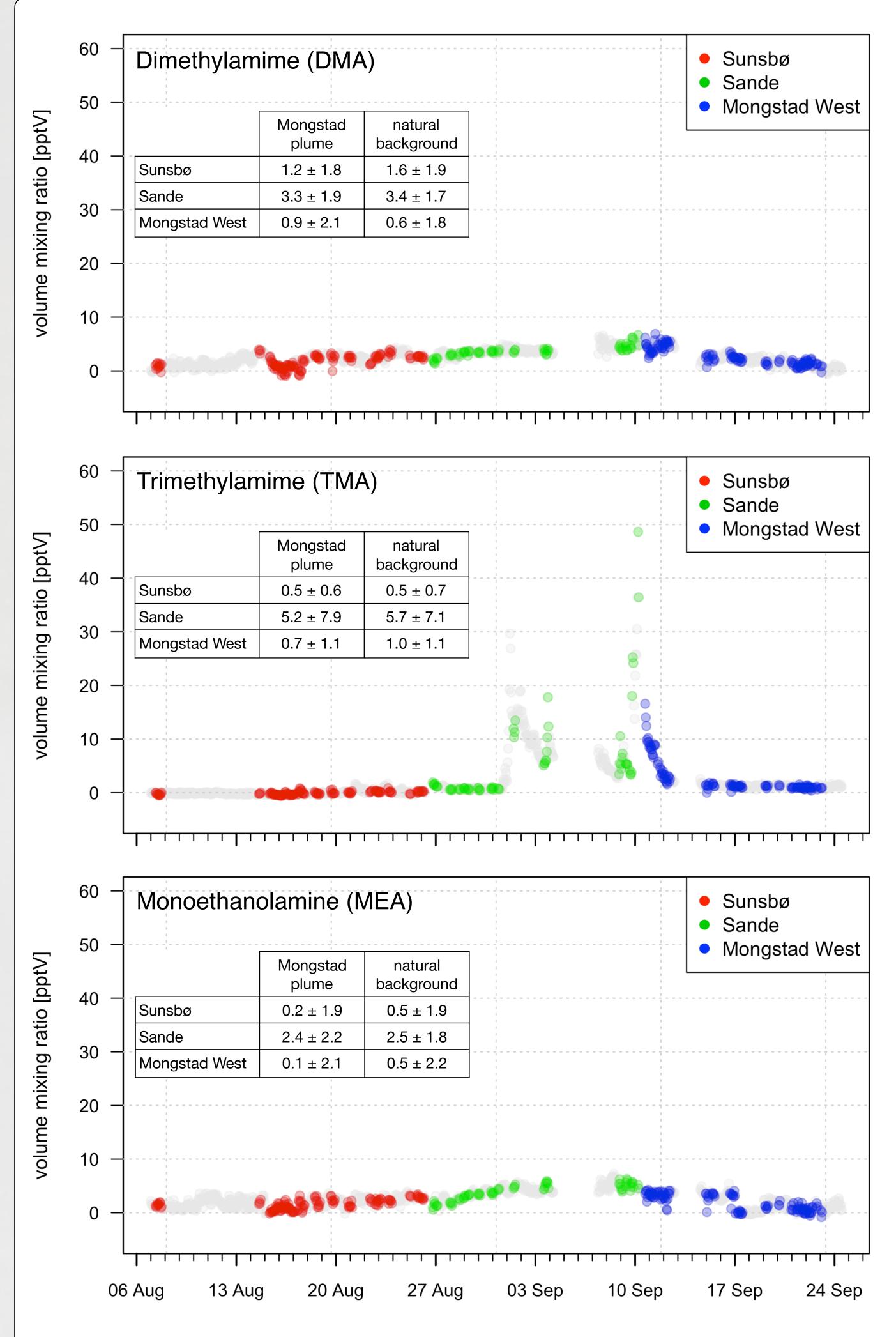
Dimethylamine (DMA) C<sub>2</sub>H<sub>7</sub>N Trimethylamine (TMA) C<sub>3</sub>H<sub>9</sub>N Monoethanolamine (MEA) C<sub>2</sub>H<sub>7</sub>NO

2-amino-2-methylpropanol (AMP) C<sub>4</sub>H<sub>11</sub>NO Diethylamine (DEA) C<sub>4</sub>H<sub>11</sub>N Piperazine (PZ) C<sub>4</sub>H<sub>10</sub>N<sub>2</sub>

#### Setup:

- routine mode of operation
- H<sub>3</sub>O<sup>+</sup> chemical ionisation
- drift tube pressure 3.8 mbar, drift tube temperature 60 °C
- optimised inlet system
- ambient air sampled at a flow rate of 12 litres per minute
- passivated stainless steel tube material (SilcoNert® 2000)
- OD: 6.35 mm, length: 115 cm, temperature: 60 °C
- zero air generation
- amine-free zero air from ambient air
- catalytically cleaned (Pt/Pd at 325 °C)
- instrumental background
- periodically checked every 12 hours for 30 minutes

### Results



Hourly average time series of DMA, TMA and MEA amine as measured at Sunsbø, Sande and Mongstad West in August and September of 2015. The color-coded data points identify the time periods when the Mongstad outflow was advected to the sampling sites.

# **MEA**

**DMA** 

**TMA** 

- instrument is not capable to detect MEA due to the abundant O<sub>2</sub>+ signal that distorts the mass spectrum in the region where MEA is detected.
- measured values were within single-digit pptv levels which is close to the instrumental detection limit
- 2-minute average data show episodic short-term enhancements in the 10 to 22 pptv range at all three measurement sites
- enhancements were found both in natural background air and in the outflow from the Mongstad complex.
- levels were typically close to zero
- episode (Sept 1-12) hourly average volume mixing ratios up to 49 pptv
- enhanced levels of TMA were observed at the Sande and the Mongtad West site, both in natural background air and in the outflow from the industrial site.
- within the single-digit pptv
- 1-2 pptv enhancement was observed (Aug 31-Sept 10) both in natural background air and in the Mongstad outflow
- surprising since MEA is believed not to have natural sources
- further research is needed to confirm these findings and exclude potential signal interferences for MEA

# **AMP**

DEA

PZ

**MEA** 

- were not detected at levels above 10 pptv
- it was not possible to measure these species at single-digit pptv levels due to mass spectral interferences
- A PTR-QiTOF instrument was successfully deployed in the field for the first time to measure amines in ambient air
- The time series data indicate that amine levels were not enhanced in the Mongstad outflow when compared to natural background conditions (see tables in respective amine time series plots)
- TCM was operating on MEA during the ambient measurements when singledigit pptv levels of MEA were observed in ambient air - no indications were found that these small enhancements were caused by emissions from TCM.
- further analytical work is required