Contributions of organic nitrogen to the gas phase and speciation of amines in ambient samples

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Organic Nitrogen:

Exists in gas, aerosol, and precipitation

Mix of compounds – both oxidized and reduced

In both precipitation and aerosol organic nitrogen contributes 10-30% on average

Many questions remain…

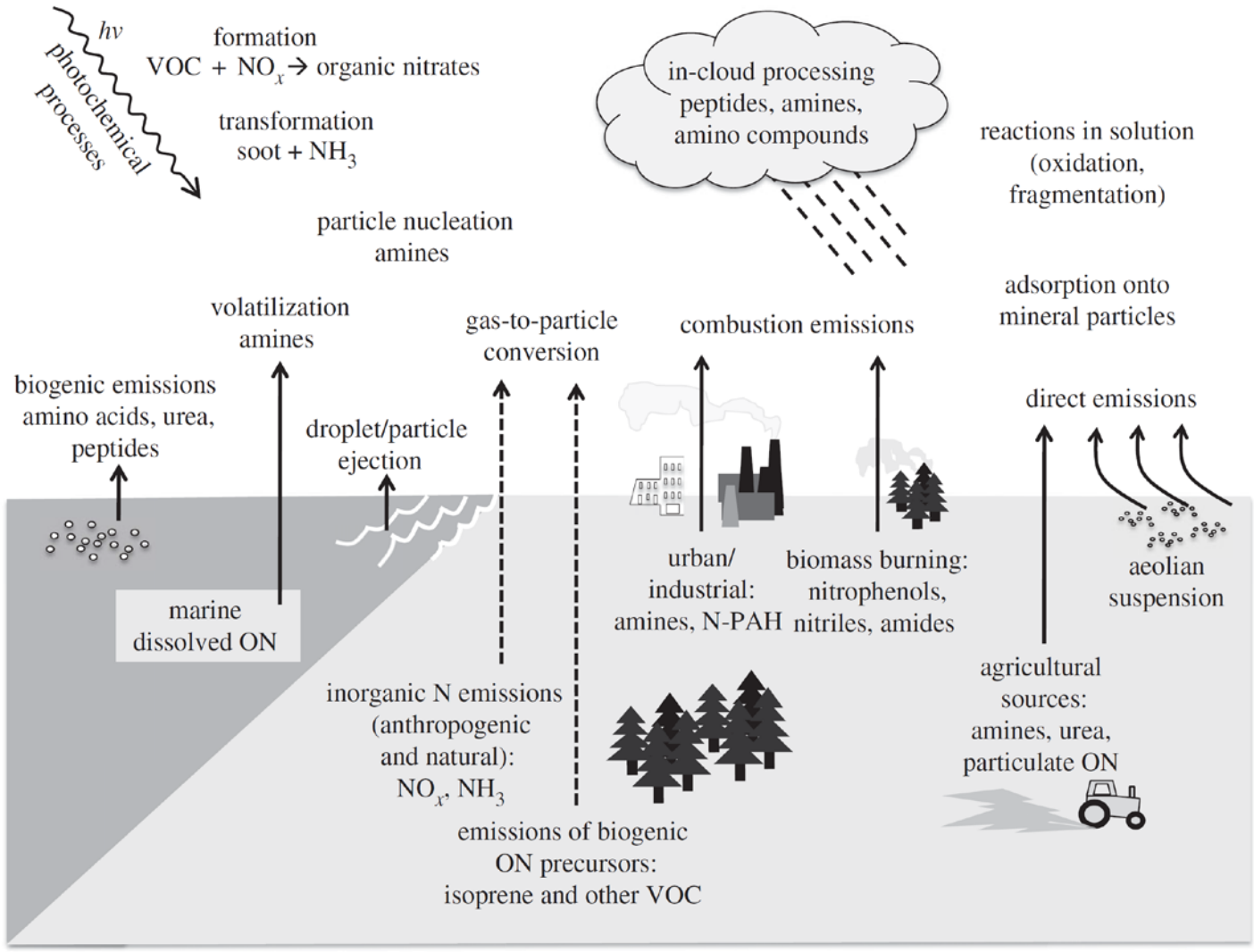

Figure 2. A cartoon illustrating the diversity of atmospheric ON precursors including primary sources and formation by secondary processes (VOC, volatile organic carbon; N-PAH, nitrogen containing polycyclic aromatic hydrocarbons).

Figure from Jickells et al 2013 – The cycling of organic nitrogen in the atmosphere

How can we learn more about organic nitrogen in the atmosphere?

DENUDER TESTING FOR GAS PHASE ORG. N

Measuring organic nitrogen by TN-inorganic N

Interferences and cross-contamination

Efficiency of denuders for methyl-, dimethyl-, and trimethyl-amine

Stability of denuder extracts for TN analysis

AMINE ANALYSIS OF $PM_{2.5}$ FILTER SAMPLES

New Separation method by Ion Chromatography – with conductivity detection

Analysis of May-Sept of nylon filter samples from Rocky Mountain National Park

Which are most abundant? What fraction of NH_4^+ do amines account for?

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Water-soluble organic nitrogen in the gas phase measured by the denuder–filter pack method

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ABSTRACT

The WSON in the gas phase and aerosols were simultaneously measured by the denuder–filter pack method. Approximately 33 ± 18% of the WSON in the atmosphere existed in the gas phase. A large portion (approximately 76 ± 33%) of the gaseous WSON collected in the present sampling method was occupied by basic species. The gaseous basic and acid WSON showed about one-sixth of the nitrogen concentrations of the gaseous NH_3 and HNO_3, respectively. These results indicate that the gaseous WSON is also an important fixed nitrogen species in the atmosphere.

What is the collection efficiency for different organic nitrogen compounds?

How abundant are basic and acidic organic nitrogen compounds in the atmosphere?

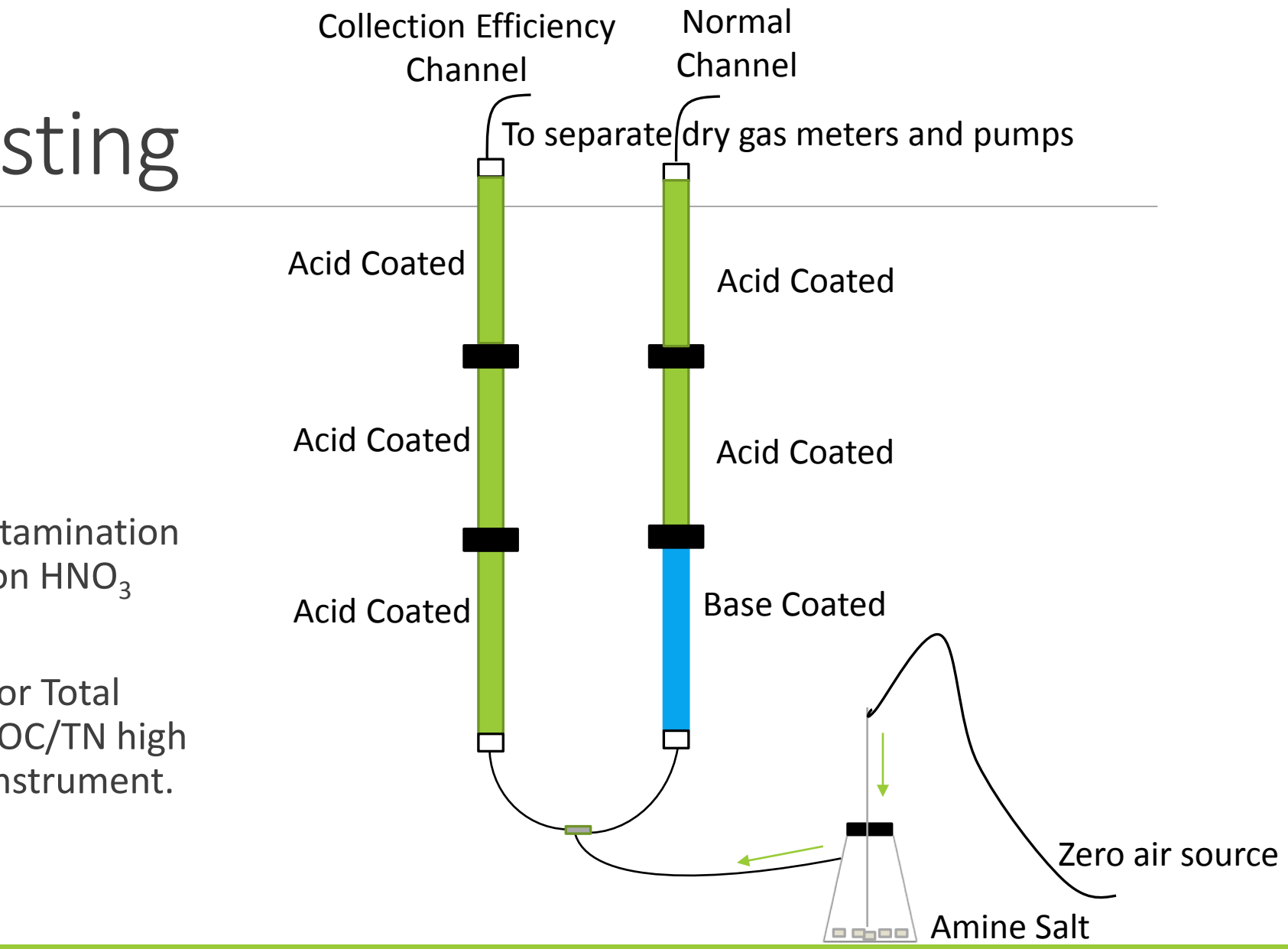
- Matsumoto and Yamato (2016 & 2017) tested ambient samples with a focus on water soluble organic nitrogen (WSON) in $PM_{2.5}$
- Estimated positive and negative artifacts in aerosol sampling of WSON. (32.5% loss)
- Demonstrated the ability to collect WSON in the gas phase by a denuder method.

Denuder Testing

Collection efficiency
- Ammonia
- Methylamine
- Dimethylamine
- Trimethylamine

Is there any cross-over contamination (increase in TN measured on HNO_3 denuder)?

Measurement of extracts for Total Nitrogen using Shimadzu TOC/TN high temperature combustion instrument.



Denuder Testing for determining ON by TN

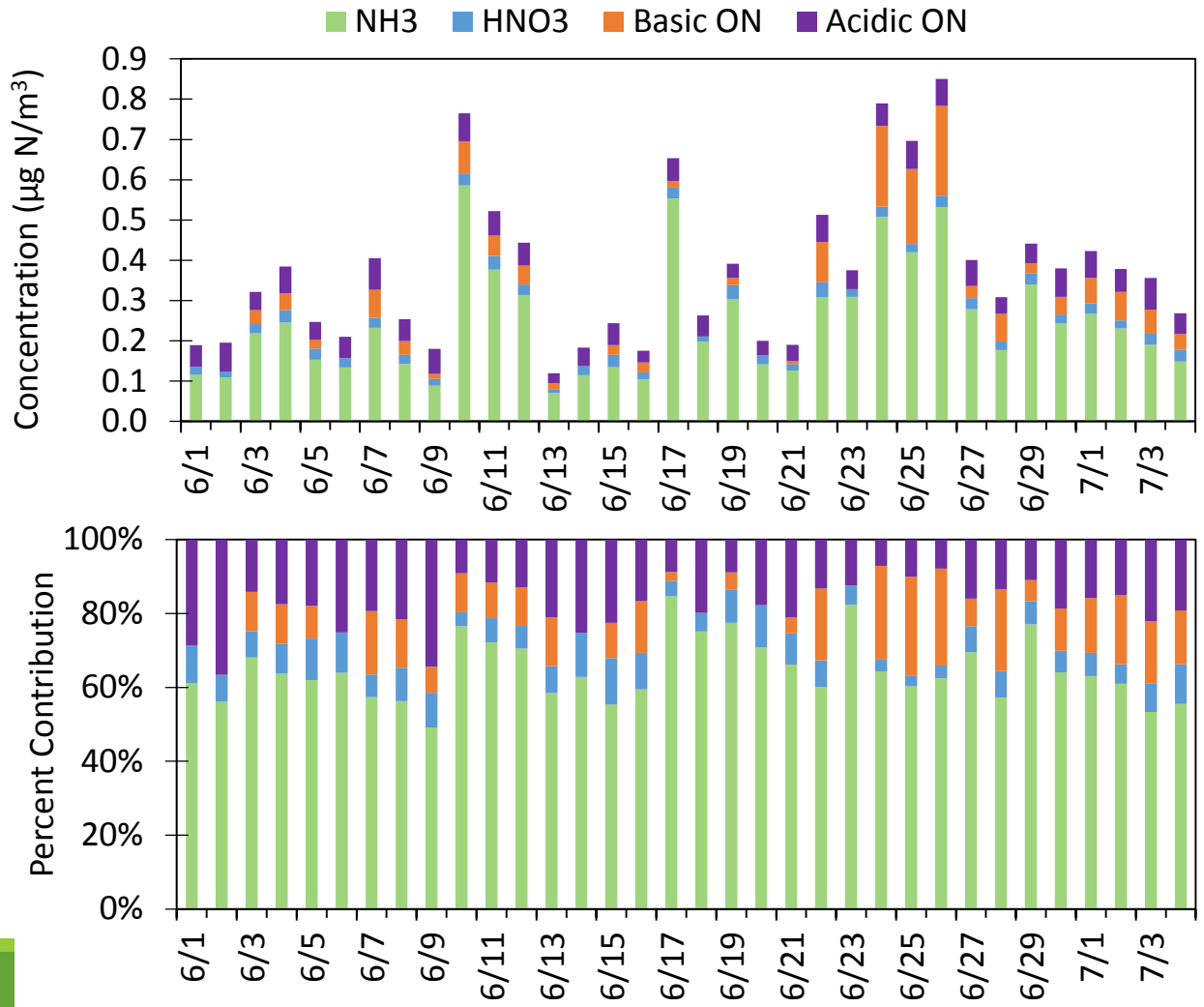
Efficiency of Amine Collection

	N experiments	Efficiency	Carry over in base-coated denuder
Ammonia	3	99±1 %	
Methylamine	7	91±7 %	Not significant above blank
Dimethylamine	7	92±9 %	Not significant above blank
Trimethylamine	6	97±2 %	Not significant above blank

Stability Testing (36 days)– variability of approx. 10% but no consistent increasing or decreasing trends

These may be issues related to the injection technique which we are working to address

Denuder Data from Rocky Mountain National Park



- Approximately 1 month of denuder samples analyzed.
- Ammonia is dominant N species. Depending on the day the relative contribution of the other species change but generally NH_3 is followed by the acidic and basic organic nitrogen categories.
- Unable to compare to filter ON because we were using nylon filters which have high ON background.

How can we learn more about ON?

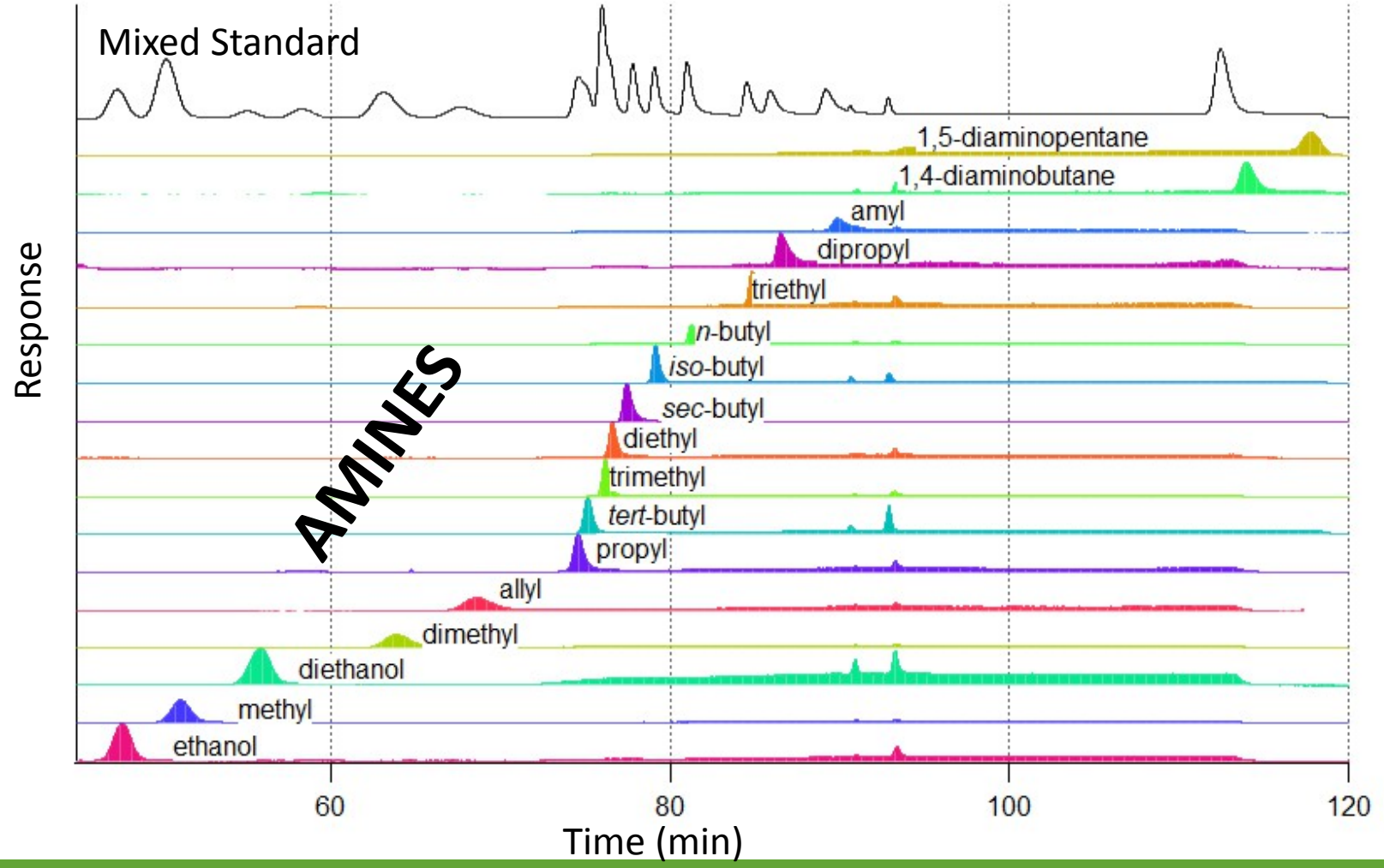
Development an ion chromatography separation to look at different amines.

We observe 17 different amines type compounds. Including:

Methylamine – animal operations, industry, automobiles, sewage, landfill, biomass burning
Ethanolamine – industry, natural gas processing
Dimethylamine – animal operations, industry, automobiles, biomass burning
Butylamine and diethylamine – animal operations, industry, landfill, sewage
Iso-butylamine – dairy, tobacco smoke
Sec-butyl – tobacco smoke, CO_2 capture
Tert-butylamine – tire repair
Diethanolamine – industry, CO_2 capture

From Ge et al. 2011 and source therein

New Amine Separation by IC



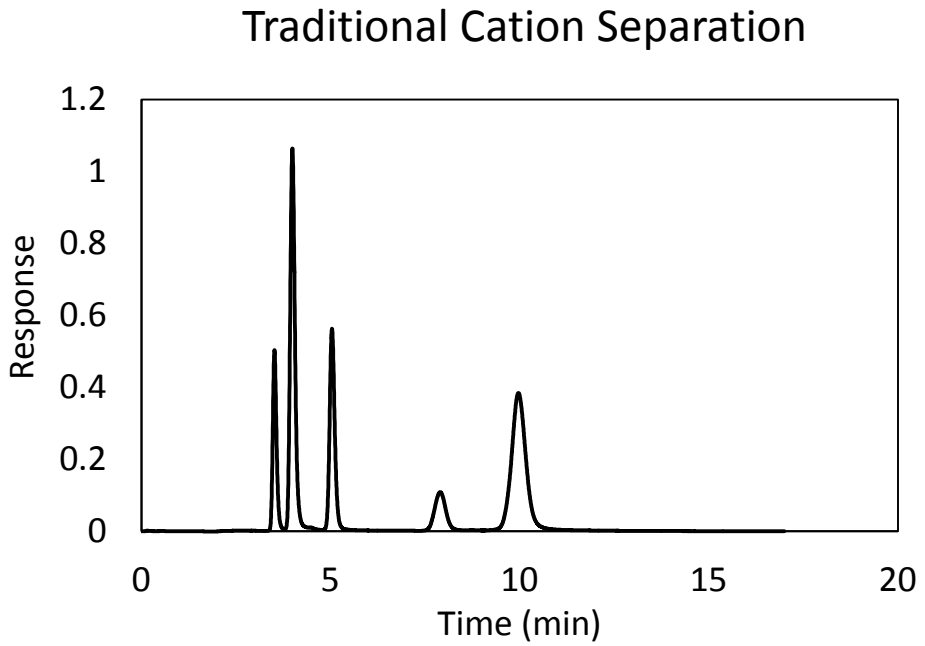
ThermoScientific CS19 4mm Column with MSA gradient at 40°C

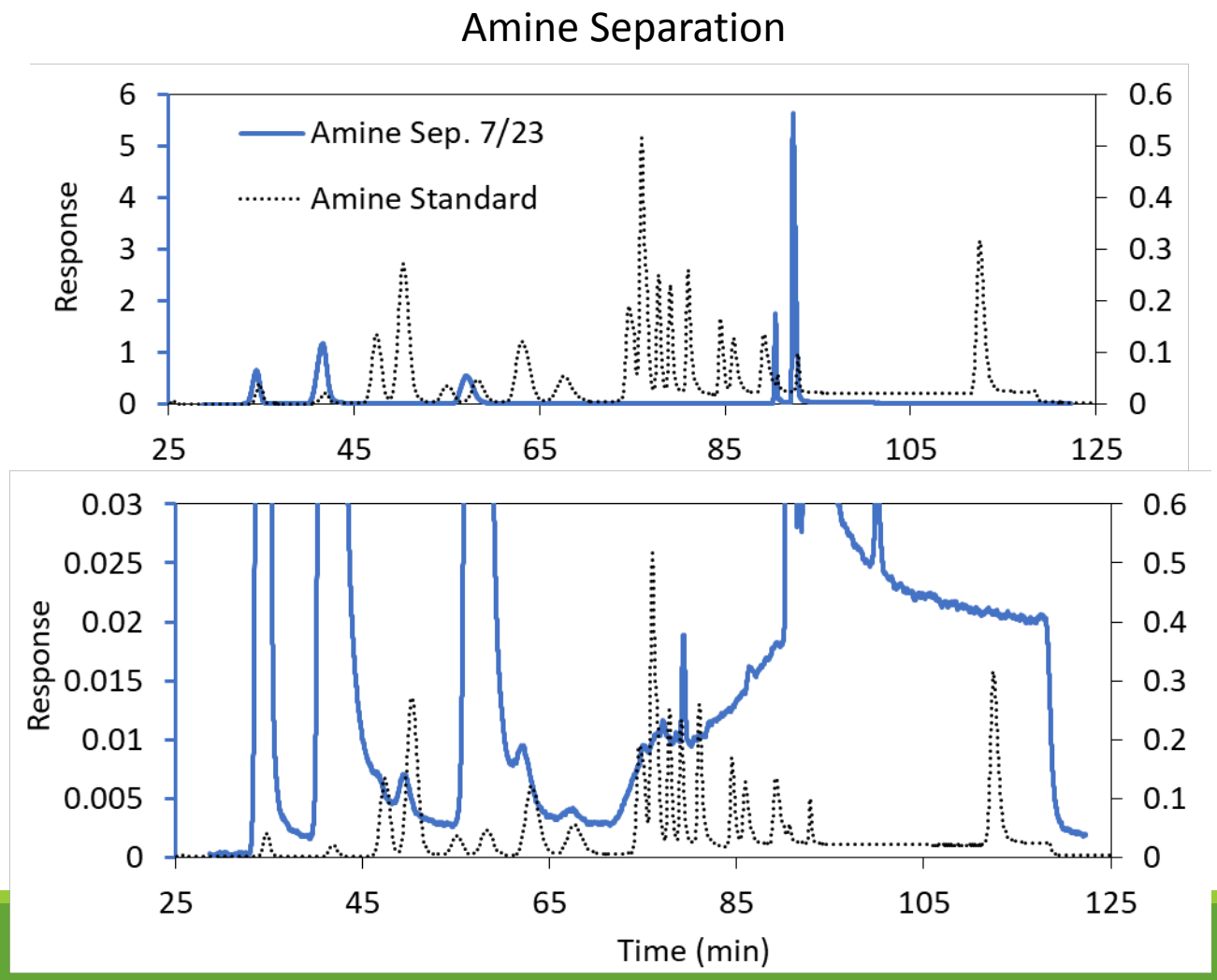
- Methylamines
- Ethylamines
- Ethanolamines
- Propylamines
- 4 isomers of butylamine

- Detection Limit:
  2-4 µg/L, ~1 ng/m^3

Comparison of cation and amine separation

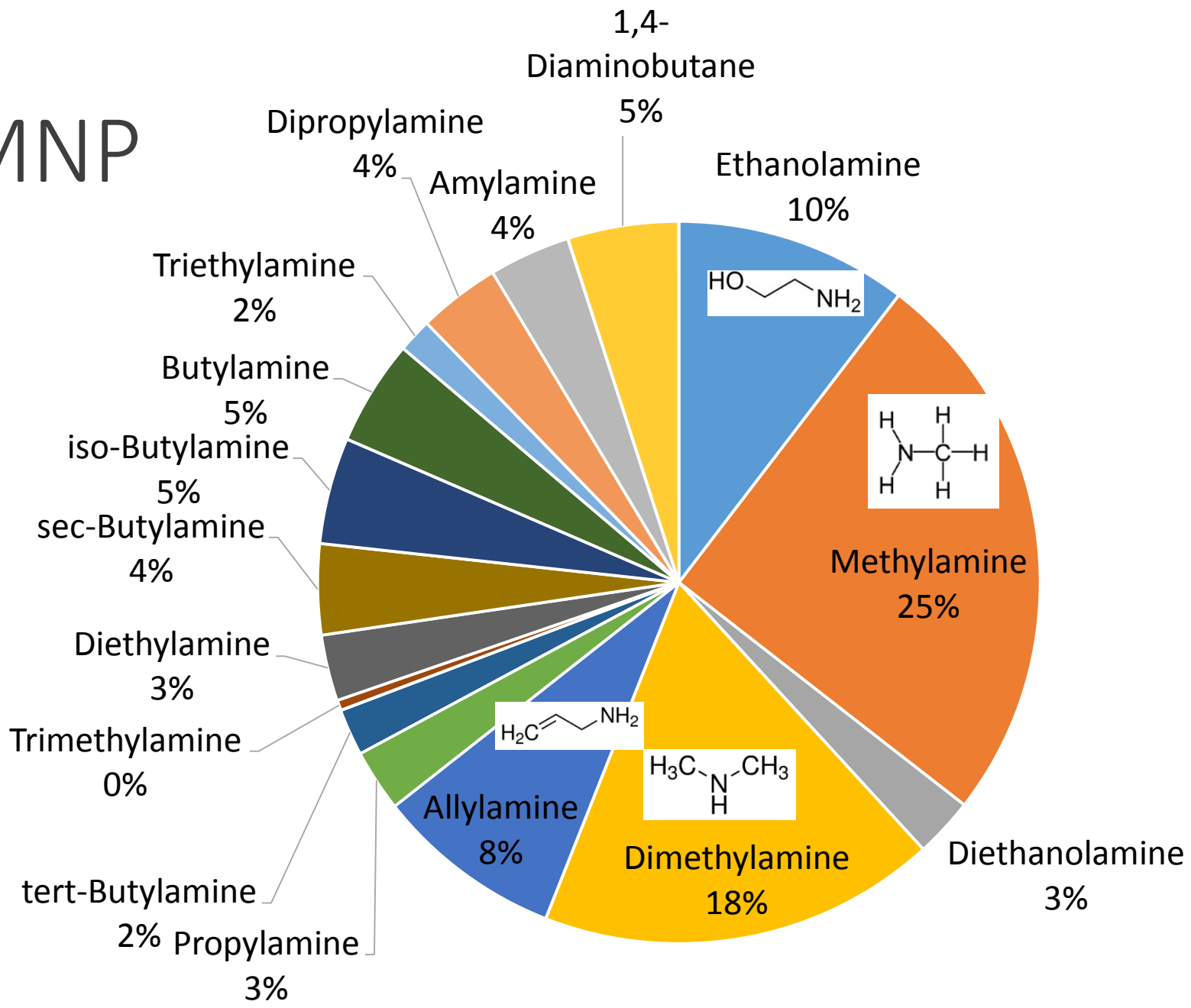
Nylon filter sample from RMNP 7/23/2017



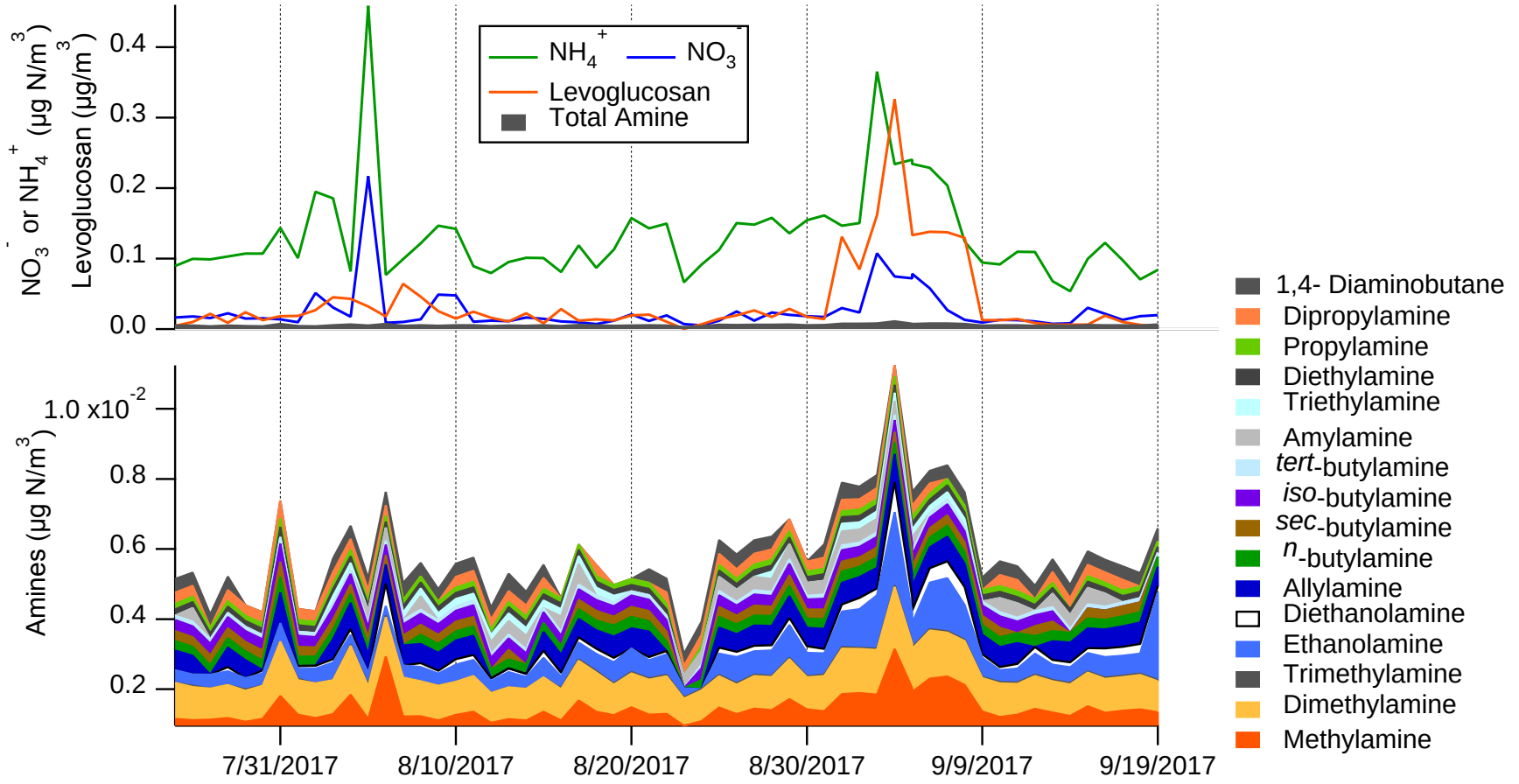


$PM_{2.5}$ Amines at RMNP

- 7/25-9/17 Nylon filter samples
- On average 5% of NH_4^+ (1-33%)



Enhancement of amines during smoke impacts at RMNP



Conclusions

There is potential to use denuder sampling to determine bulk organic nitrogen in the gas phase. But we still need to address:

- Collection efficiency for other organic nitrogen species beyond the methylamines
- Long-term stability of collected samples (>1 months) – can we go back and analyze samples in cold storage?
- Improve injection technique for small volume (total sample volume $\geq$ 2 mL)

The amine separation is long (2 hours) but we are getting a lot of information about amines in the remote atmosphere that we haven't had before.

- We plan to analyze more samples from other locations to get a better idea of which amines are important in other environments.
- Compare the total amine concentration to ON using a different type of filter (quartz).

Take Home Messages