Quantifying Urban Emissions Influencing Wintertime Ammonium Nitrate Formation

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AQUARIUS Workshop (September 25, 2019)
During Cold Pool Episodes Ammonium Nitrate Dominates PM$_1$

All Flight Data:

- Pollution Episode #5
- Episode #6
- Clear Conditions and start of Episode #7

Average Mass Fractions:

- NO$_3$
- NH$_4$
- SO$_4$
- Cl
- Org

Source: 2017 Utah Winter Fine Particulate Study – Final Report
Overview

What gas-phase emission sources could contribute to ammonium nitrate formation?

(1) Potential gaps in mobile source NO$_x$ emissions
   • Lack of wintertime roadside emission factor studies
   • Can satellite data help fill measurement gap?

(2) Emergence of volatile chemical products as sources of VOCs
Are mobile source NO\textsubscript{x} emissions overestimated or not?

**Summer** field campaigns suggested mobile source NO\textsubscript{x} **overestimated**

**Winter** field campaigns suggested mobile source NO\textsubscript{x} **not overestimated**
Debate over Summertime Mobile Source NO$_x$ Emission Factors

Gasoline EF was ~2x higher, now within ~20%

Diesel EF within ~30%

Adapted from McDonald et al. (Environ. Sci. Technol., 2018)
Is there seasonal variability in mobile source NO\textsubscript{x} EF?

 adapt from McDonald et al. (Environ. Sci. Technol., 2018)

 Nearly all studies of heavy-duty NO\textsubscript{x} in CA (i.e., mild winters)

 One recent winter and summer tunnel study in Baltimore (HEI Report, 2019)

 Factor of $\sim$2 difference

 Adapted from McDonald et al. (Environ. Sci. Technol., 2018)
Utilizing Satellite Data to Evaluate NO\textsubscript{x} Emission Inventories

TROPOMI (12 km x 12 km) – July, 2018

Measures NO\textsubscript{2}, HCHO, CO, and CH\textsubscript{4} at ~3 km x 7 km resolution (currently operational)

Recalculated AMF using model NO\textsubscript{2} profile (apples-to-apples)

Meng Li (NOAA)
Good Consistency between Model and TROPOMI NO₂

WRF-Chem (12 km x 12 km) – July, 2018

(1) Updated mobile sources with FIVE (McDonald et al., Environ. Sci. Technol., 2018)

(2) Updated power plants with CEMS

(3) Updated other point + area sources to NEI14
Ground-Based Truthing of Satellite Retrieval w/ Pandorases in NYC

WRF-Chem (12 km x 12 km)
Bias = +10%, r = 0.65

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Preliminary Modeling of Wintertime NO$_2$ Columns

Hypothesis: If mobile source NO$_x$ is underestimated in winter, then the model NO$_2$ will be biased low versus TROPOMI.
Model Systematically Under-Predicts NO$_2$ Columns in Winter

WRF-Chem (12 km x 12 km) – March 2019

Bias = -32%
R$^2$ = 0.67

Bias = -59%
R$^2$ = 0.66

Can higher mobile source NO$_x$ emissions in winter close gap?

~33% of US NO$_x$ Emissions
Approaches to Measuring Heavy-Duty Diesel Truck Emissions

Mobile laboratory
(Dallmann et al., Environ. Sci. Technol. 2011)

Tunnel study
(Dallmann et al., Environ. Sci. Technol. 2012)

IR Remote Sensing
(Haugen and Bishop, Environ. Sci. Technol. 2017)

Ideally measure CO, CO₂, VOC, NOₓ, NH₃, N₂O, and PM₂.₅ (including speciation)
VOCs Can Also Influence Ammonium Nitrate Formation

Womack et al. (Geophys. Res. Letters, 2019)
Source Apportionment of New York City VOCs (Winter 2018)

Manhattan (Winter 2018)

- Consumer VCPs: 52%
- Off-Road Gas: 28%
- On-Road Gas: 8%
- Evap Gas: 8%
- Diesel: 8%
- Other O&G: 8%

VOC Emissions = 46 ± 12 g/person/d

Coggon et al. (in preparation)

Beginning to identify markers with PTR-ToF-MS

Limited measurements of VCP markers via aircraft

Inlet

Matthew Coggon
Georgios Gkatzelis
Jessica Gilman
Suggestions for a Future Winter Field Campaign

(1) Satellites will measure during campaign (and beyond)
   • Ground-based remote sensing measurements helpful for truthing
   • Can help with constraining urban/regional emissions (e.g., NO$_x$)

(2) Roadside measurements could be helpful for estimating mobile source NO$_x$ and other co-emitted species
   • Potential for GHG co-related benefits

(3) Aircraft measurements of non-traditional urban VOC sources have been limited
   • Helpful for evaluating emissions + chemistry of 3-D photochemical models