Wintertime Emissions and Chemistry of Volatile Organic Compounds (VOCs)



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Outline:

- 1. VOCs and wintertime AQ: nitrate and SOA formation
- 2. Wintertime sources of VOCs: knowns and unknowns
- 3. Chemistry of VOCs: carbonyl and SOA formation
- 4. Necessary measurements for a wintertime AQ study

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Importance of VOCs for Wintertime Air Quality



Womack ... and Brown [GRL 2019]

- Nitrate formation is limited by VOCs
- Is this true for other episodes in SLC and other regions?
- If so, need to know the sources and OH reactivity of VOCs

Importance of VOCs for Wintertime Air Quality



Schroder ... and Jimenez [JGR 2018]

- SOA formation in urban air is also observed in the winter
- What are the precursors of SOA?
- What are their emission sources?

Wintertime Sources of VOCs: Motor Vehicles



Koss [PhD Thesis 2017]

- Road-side measurements: exhaust vs. fuel vapor emissions
- Are VOC emissions from motor vehicles different in winter?

Wintertime Sources of VOCs: Volatile Chemical Products



McDonald, de Gouw et al. [Science 2018]

- Volatile chemical products (VCPs) were found to be a large source of VOCs, OH reactivity and SOA potential in LA
- Is this true for other cities and in the winter?
- Need measurements of more VCP species and marker compounds, e.g. siloxanes for care products

Wintertime Sources of VOCs: Wood Burning



Coggon ... and de Gouw [GRL 2016]

- Winter emissions from wood burning in Boulder
 - ✓ Dominant VOC source at low ambient temperatures
 - ✓ Low nitrogen content of wood is reflected in emissions
- Likely smaller source in Salt Lake City, but how small exactly?

Wintertime Sources of VOCs: Cooking



Schauer [ES&T 1999]

Is cooking an important source of VOCs in urban areas?

Wintertime Sources of VOCs: Agriculture



Yuan ... and de Gouw [ACP 2017]

- OH reactivity: <u>alcohols</u>, carbonyls, sulfur species, phenols; Odors: sulfur species; NO₃ reactivity: phenols
- How important is this VOC source for wintertime AQ?

Chemistry of VOCs: Carbonyl Formation



Edwards, Brown et al. [Nature 2014]

- Winter ozone studies: secondary carbonyls are OH precursors
- Does this play a role in urban areas at higher NOx?
- Are such processes described well in lumped mechanisms?

Chemistry of VOCs: SOA Formation



Zhao ... and Robinson [ES&T 2014]

- IVOCs are more important than aromatics for SOA formation
- What are the sources of IVOCs in winter? VCPs?

Necessary Measurements for a Wintertime AQ Study

Particle nitrate formation

1. Detailed VOC measurements on ground

- ➢ GC-MS
- > PTR-TOF with GC interface
- Subset of VOCs from aircraft
 PTR-TOF
- 3. OH reactivity on the ground
 - Flow tube with LIF detection of OH

Additional for SOA formation

- IVOCs and SVOCs on the ground
 SV-TAG
- 2. Potential aerosol mass on the ground
 - OFR measurements of SOA formation

Holy grail: Closure and source attribution of:

- OH reactivity
- SOA formation potential

New Tools for VOC Measurements: Vocus PTR-TOF

Vocus PTR-TOF:

- 1. Ionization of VOCs by reaction with H_3O^+
- 2. Mass spec detection of products ions

Krechmer ... and de Gouw [Anal Chem 2018]

- Higher sensitivity due to use of RF fields in reactor
- Higher mass resolution due to longer time-of-flight region





<u>GC-Vocus:</u> VOC identification through use of a GC interface