Identification of chemical trends in ambient ion composition using Positive Matrix Factorization and Resolution-Enhanced Kendrick Mass Defect analysis

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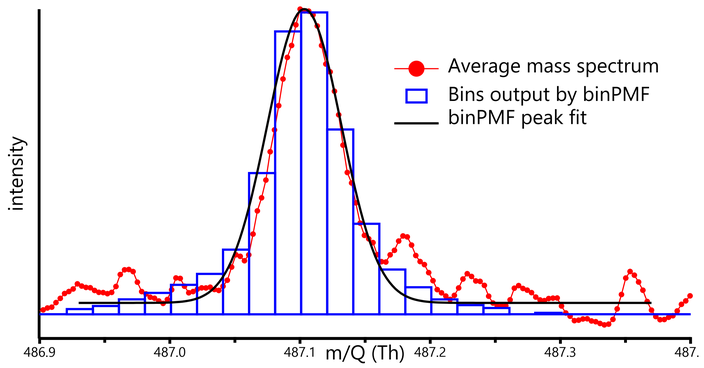
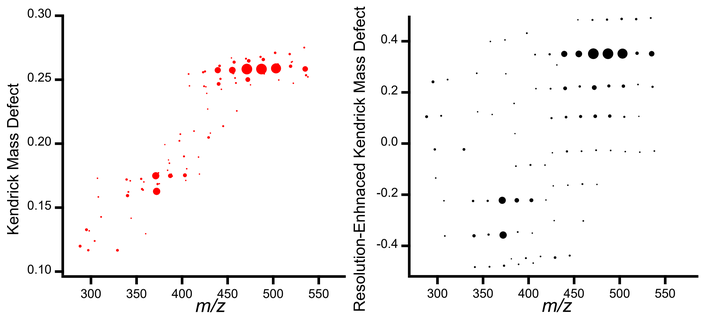
Introduction

- Ambient ions (AIs) affect new particle formation (NPF) rates through ion-mediated nucleation, control electrical properties of the atmosphere, and provide insight into neutral trace gases that participate in NPF[1].
- AIs have low concentrations (~10^3 cm^{-3}), short lifetimes (~10^2-10^3 s)[1].
- Fast, chemically resolved measurements of Ais are analytically challenging.
- Here, we demonstrate the use of binned positive matrix factorization (binPMF) and resolution-enhanced Kendrick mass defect (REKMD) analysis to chemically characterize AIs.

Methods

- Atmospheric pressure interface time-of-flight mass spectrometer[2,3] (APi-ToF) deployed in Southern Great Plains during 2016 HI-SCALE campaign.
- Positive and negative ambient ions observed alternatively for 24 hr at a time over one month.
- Binned positive matrix factorization[3] (binPMF) provides insight into temporally related chemical species.
- Peak fitting of binPMF results recovers chemical information.
- Resolution-enhanced Kendrick mass defect analysis[4] elucidates chemical trends in binPMF fitted peaks.





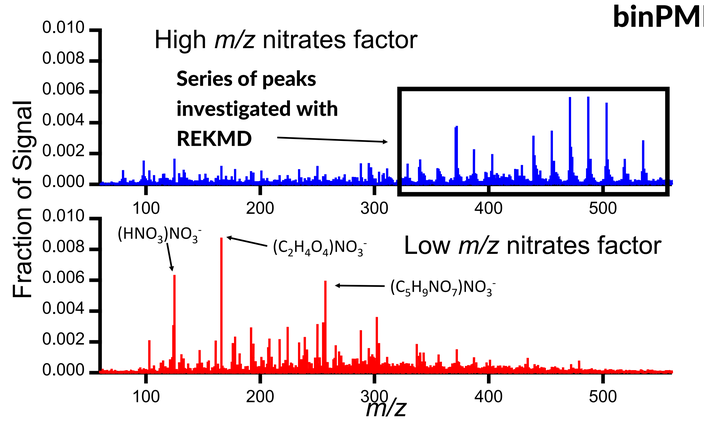
$$KM = m/z \cdot \frac{round(m_{base})}{m_{base}}$$

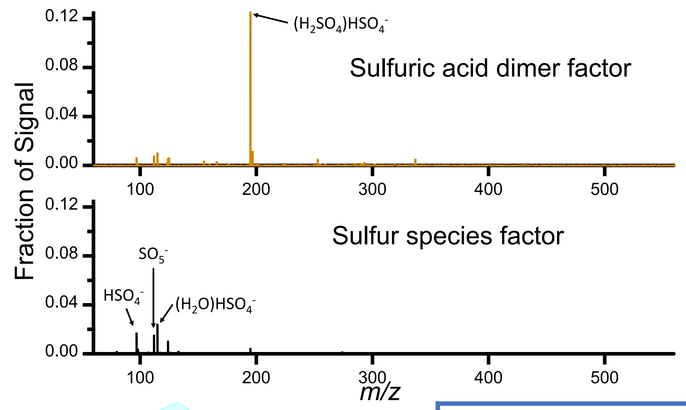
$$KMD = round(KM) - KM$$

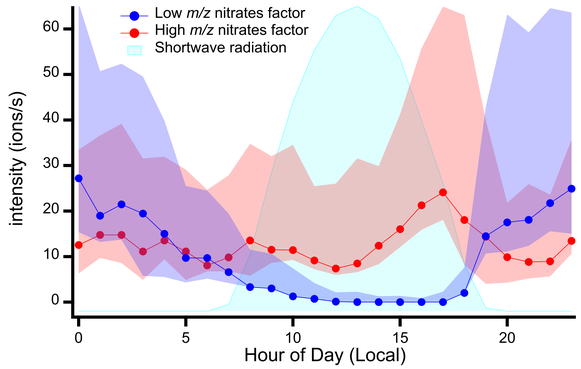
$$REKM = m/z \cdot \frac{round(m_{base}/x)}{m_{base}/x}$$

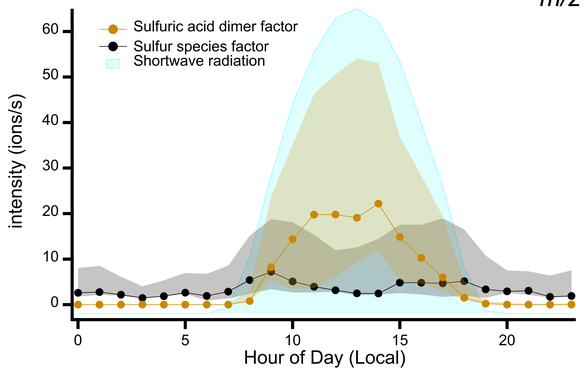
$$REKMD = round(REKM) - REKM$$

Negative Mode Results





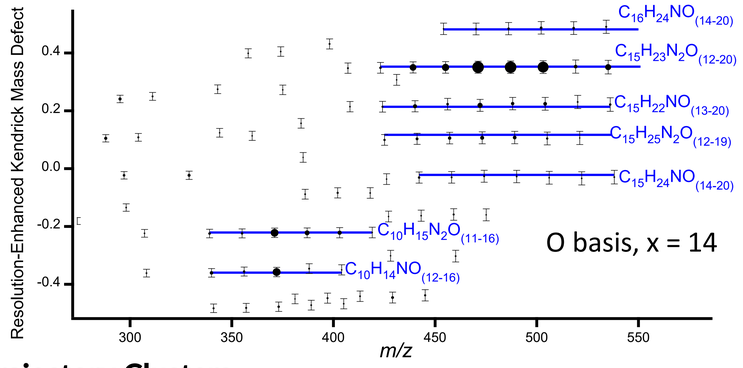




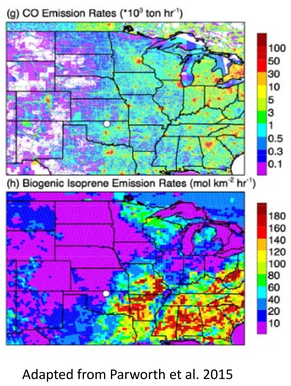
Scan code for positive mode results

Resolution-enhanced Kendrick mass defect analysis of high m/z nitrates factor

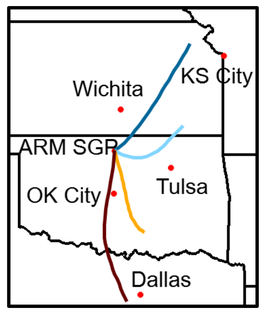
- REKMD with oxygen basis shows series of C10 and C15 highly-oxygenated molecules
- C10 compounds correspond to monoterpenes (MTs), known to participate in new particle formation and growth[6,7,8].
- C15 compounds may correspond to sesquiterpenes (SQTs), first identification in APi-ToF measurements.
- binPMF + REKMD reveals compounds relevant to new particle formation and growth.

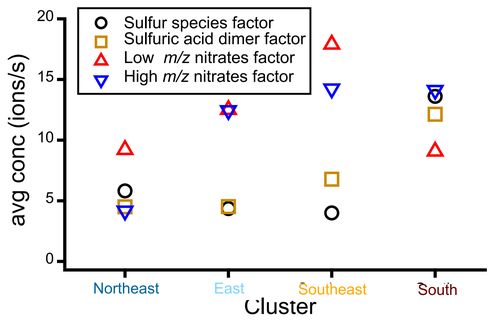


HYSPLIT Trajectory Clusters



Adapted from Parworth et al. 2015





- HYSPLIT back trajectories used to explore origin of air masses that contribute to each factor.
- Sulfur factors enhanced in cluster that passes over urban areas.
- High m/z nitrates factor highest in clusters that pass over regions with high biogenic emissions, consistent with MTs and SQTs.

References
(1) Shuman et al. *Chem. Rev.* **2015.** (2) Junninen et al. *Atmos. Meas. Tech.* **2010.** (3) Ehn et al. *Atmos. Chem. Phys.* **2010.** (4) Zhang et al. *Atmos. Meas. Tech.* **2019.** (5) Foquet and Sato. *Anal. Chem.* **2017.** (6) Bianchi et al. *Atmos. Chem. Phys.* **2017.** (7) Bianchi et al. *Science.* **2016.** (8) Heinritzi et al. *Atmos. Chem. Phys.* **2020.** (9) Parworth et al. *Atmos. Environ.* **2015.**

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