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Poster Session Day 2

Feedbacks of Emission Regulation on Atmospheric Nitrate Formation Chemistry in the Northeastern US: Insight from Oxygen Isotopes

Heejeong Kim[1], Wendell W. Walters[2], & Meredith Hastings[1,3]*

[1] Department of Earth, Environment, and Planetary Sciences, Brown University, Providence, RI 02912, USA

[2] Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, USA.

[3] Institute at Brown for Environment and Society, Brown University, Providence, RI 02912, USA.

*Presenting Author Email: heejeong_kim@brown.edu

Nitrogen oxides (NO_x = NO + NO_2) play a crucial role in atmospheric chemistry by influencing the oxidizing efficiency in the atmosphere. Atmospheric particulate nitrate (pNO_3^-), a product of NO_x oxidation, has important implications for air quality, acid deposition, and climate change. Due to effective regulations by the Clean Air Act, NO_x emissions in the northeastern US have dramatically decreased over the last several decades. However, the relationships between NO_x reduction and changes in nitrate formation and acid deposition have significant uncertainties due to non-linear chemical feedbacks.

Stable oxygen isotopes ($\delta^{18}O$ and $\Delta^{17}O = \delta^{17}O - 0.52 * \delta^{18}O$) of nitrate have proven to provide powerful observational constraints on NO_x oxidation, enabling us to probe the connections between changes in emissions and atmospheric chemistry. Here, oxygen isotopes in nitrate from a unique long-term aerosol record (2005–2018) in the northeastern US were analyzed to understand the changes in NO_x oxidation chemistry in response to emission reductions. A significant shift in oxygen isotopes in nitrate was observed on decadal timescales, particularly for $\delta^{18}O$ of nitrate ($p < 0.01$) with an average rate of –0.5 ‰/years; annual $\delta^{18}O$ values changed from 68.0 (±9.0) ‰ to 65.3 (±7.6) ‰ from 2005 to 2015. In addition, distinct seasonality of higher values in the cold season (Oct-Mar) and lower values in the warm season (Apr-Sep) was driven by a seasonal shift from ozone (O_3) dominated chemistry (cold season) to HO_x/RO_x (warm season) chemistry associated with NO_x photochemical cycling and nitrate formation. Two different atmospheric chemistry models were deployed to evaluate NO_x oxidation chemistry, and our results reveal that emission regulation responses have increased NO_x oxidation efficiency in heavily urbanized locations, particularly during nighttime and colder months due to an increase in O_3 concentration over the years. Increased oxidation efficiency has shortened urban NO_x lifetime, leading to enhanced nitrate formation, especially in wintertime in the northeastern US. This direct observational constraint by oxygen isotopes explains the continued elevated wintertime nitrate that plagues air quality in the eastern US.