



Seasonal variations in stable isotope ratios of atmospheric nitrate in a tropical boundary layer environment (Cape Verde Observatory).

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Atmospheric nitrate (NO_3^-) is the end-product of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) oxidation, thus its production is sensitive to the oxidative state of the atmosphere. Unfortunately, revealing this complex chemical activity using only nitrate concentration appears to be an extremely difficult task if not impossible. More sophisticated approaches are thus needed to extract from this ubiquitous atmospheric species information on the chemical functioning of our atmosphere and its interaction with the climate.

Isotopic investigations have proven to be instrumental in deciphering sources and processes affecting nitrate. Combining the analysis of the two oxygen stable isotope ratios ($^{17}\text{O}/^{16}\text{O}$, $^{18}\text{O}/^{16}\text{O}$) with the nitrogen stable isotope ratio ($^{15}\text{N}/^{14}\text{N}$) on the same sample is a powerful tool to reveal unexpected processes happening in the air. $^{15}\text{N}/^{14}\text{N}$ ratio (expressed in terms of $\delta^{15}\text{N}$) is used to trace NO_x sources and mass transfers between reservoirs because $\delta^{15}\text{N}$ values are for the most part conserved during the chemical conversion of NO_x to nitrate. In contrast, the triple oxygen isotopic composition of nitrate provides original information about the nature and the relative importance of NO_x oxidation pathways, ultimately leading to atmospheric nitrate. This interpretation results directly from the fact that ozone possesses a unique and unconventional isotope composition ($\Delta^{17}\text{O} \simeq \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$) which is transferred to others atmospheric species during chemical attacks.

Despite recent successes in using the isotope composition of nitrate for deciphering atmospheric chemical processes in polar and mid latitude regions, the strong oxidative conditions prevailing in the sub tropical and tropical regions has been ignored hitherto. Forgetting to document these regions is particularly detrimental for modellers who want to use these new isotopic markers to place new constraints on their chemical and physical codes.

In order to partially fill this gap, we present a full seasonal cycle of the nitrate isotope systematic at the Cap Verde (lat. $16^\circ 85'\text{N}$, lon. $24^\circ 87'\text{W}$) characteristic of a tropical oceanic boundary layer. Both $\Delta^{17}\text{O}$ and $\delta^{15}\text{N}$ display a marked seasonal cycle in opposing phase. $\Delta^{17}\text{O}$ values are maximum in winter ($\simeq 30$ permil) and minimal in summer ($\simeq 26$ permil) while $\delta^{15}\text{N}$ display the opposite trend with maximum in summer (-2.9 permil) and minimum in winter (-8.8 permil). No correlation is found with the nitrate atmospheric loading for any of the isotope ratio. $\Delta^{17}\text{O}$ seasonal variations correlate with the monthly averaged daytime depletion of ozone whose seasonal variation have been attributed mainly to halogen oxides. This observation suggests that part of the maximum nitrate oxygen anomaly ($\Delta^{17}\text{O}$) could result from halogen chemistry in the marine boundary layer via probably the strong NO_x oxidant BrO . For $\delta^{15}\text{N}$, a broad correlation is found with the atmospheric concentration of NO and solar radiation intensity, confirming that $\delta^{15}\text{N}$ of nitrate retranscribes principally a source and/or a photochemical equilibrium effect between NO and NO_2 .