Isotopic Composition of Aerosol Nitrate in the Pacific Atmosphere

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Atmospheric nitrate (NO_3^-) makes up a major portion of atmospheric deposition (AD) in the Pacific (i.e., precipitation and aerosols), and is the primary sink of nitrogen oxides (NO_x = NO + NO_2) from the atmosphere. AD could be an important N source for the North Pacific. For example, only ~1.5 of the 2 mol C $m^{-2}y^{-1}$ measured at Station ALOHA (22.75° N, 158.00°W) can be accounted for via N_2 fixation and mesoscale mixing. Additionally, cruise-based data in the North Pacific show an excess of N in the last few decades that has been suggested to be the result of increased AD from emissions in Asia. We quantified the concentrations and stable isotopes of NO_3^- ($\delta^{15}N$-, $\delta^{18}O$-, $\Delta^{17}O$-NO_3^-) in aerosols collected during two GEOTRACES cruises: 1) Alaska to Tahiti in 2018 (GP15; 55.0 to -20.0°N, 152.0°W), and 2) Peru to Tahiti in 2013 (GP16; 4.1°S, 81.9°W to 10.5°S, 152.0°W). The $\delta^{15}N$-NO_3^- ranges from -1.1 to -13.1‰, with the lowest values occuring in the Equatorial Pacific, and away from the coasts, reflecting a combination of NO_x sources, transport and chemistry. The majority (75%) of NO_x in the atmosphere is derived from anthropogenic sources (e.g., fossil fuel combustion), with the remaining ~25% from natural sources (e.g., lightning). The ocean is not a direct source of NO_x; however, photolysis of alkyl nitrates ($RONO_2$) emitted from the ocean can alter the NO_x budget. The $\delta^{18}O$- and $\Delta^{17}O$-NO_3^- both show a decreasing trend from Alaska to Tahiti, as well as moving away from the coast of Peru, reflecting a change in the major oxidant chemistry. The $\delta^{18}O$ and $\Delta^{17}O$ of atmospheric NO_3^- are high (65.2-85.4‰ and 21.4-30.7‰, respectively) reflecting the isotopic influence of ozone oxidation on NO_x. Both $\delta^{18}O$ and $\Delta^{17}O$ decrease with increasing distance from high [NO_x] regions (i.e. continental), likely reflecting a decrease in atmospheric ozone concentrations. These lower values may also be associated with the influence of $RONO_2$ on NO_3^- production in the region, because the $\delta^{15}N$-, $\delta^{18}O$- and $\Delta^{17}O$-$RONO_2$ are expected to be low. This information betters our collective understanding of the oxidative capacity and atmospheric chemistry over the Pacific. The very low $\delta^{15}N$-NO_3^- throughout the Pacific atmosphere represents an isotopically light source of N to the surface ocean, and the uniquely high oxygen isotopic compostion could serve as a tracer of unclyced NO_3^-.