Triple oxygen isotopes indicate that urbanization causes differences in the sources of nitrate between dry and wet atmospheric deposition

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The production of nitrogen oxides by human activities and to lesser extent natural processes significantly influences the chemical composition and reactivity of the troposphere, nitrogen deposition, and ultimately human and environmental health. However, significant uncertainties remain concerning (1) the relative important of the photochemical pathways that transform NO_x to HNO_3 and (2) the relative contributions of local vs. long-distance NO_x emissions to dry vs. wet deposition in various environmental settings. To address these uncertainties we determined the $\Delta^{17}O$ values of wet and dry deposited HNO_3 in 2009 at two sites along the western coast of northern Japan, downwind of the East Asian continent where NO_x emissions have increased approximately four-fold during the past forty years. At a remote site, nitrate $\Delta^{17}O$ values in wet and dry deposition showed similar seasonal variation, ranging between ~23 and 30‰. These results suggesting that both forms of deposition experienced similar photochemical reactions during their formation, with O_3 as the dominant oxidant in winter and a combination of O_3 and OH in summer. In contrast, at an urban site, nitrate $\Delta^{17}O$ values in wet deposition were larger (range of 24-31‰) than those in dry deposition (range of 19-25‰), particularly during the winter. These results suggest an important role of an alternative photochemical pathway for the formation of dry deposition in urban environments: oxidation of NO by peroxy radicals that originate from reactive hydrocarbons. Wet deposition at the urban site likely originates from long-distance transport, whereas most dry deposition likely originates from local NO_x emissions. These results illustrate the value of stable isotope tracers for assessing the sources, transport distances, and sinks of dry and wet atmospheric deposition.

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