

## Atmospheric reactive nitrogen concentration and flux budgets at a Northeastern U.S. forest site

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### Abstract

We report concentrations of atmospheric  $\text{NO}_x$ , nitric acid ( $\text{HNO}_3$ ), peroxyacetyl nitrate (PAN), and  $\text{NO}_y$ ; eddy covariance fluxes of  $\text{NO}_x$  and  $\text{NO}_y$ ; inferred fluxes of  $\text{HNO}_3$  at the mixed deciduous Harvard Forest field site, June–November 2000. A novel Tunable Diode Laser Absorption Spectrometer (TDLAS) produced sensitive, hourly  $\text{HNO}_3$  concentration data, which were used to evaluate systematic error in the Dry Deposition Inferential Method (DDIM), often employed to estimate weekly  $\text{HNO}_3$  flux at deposition monitoring network sites. Due to the weak diurnal variation in  $\text{HNO}_3$  concentration at Harvard Forest, no systematic bias was found in the application of this method to compute daily and weekly average fluxes. The sum of individually measured reactive nitrogen species concentrations and fluxes were approximately equal to total  $\text{NO}_y$  concentrations and fluxes for clean Northwesterly flows, but fell short of the total  $\text{NO}_y$  values for the more polluted Southwesterly transport regime. The concentration and deposition velocity of the unmeasured reactive nitrogen compounds were consistent with prior estimates and recent measurements of alkyl- and hydroxyalkyl nitrates, suggesting that these compounds play an important role in reactive nitrogen deposition processes where anthropogenic  $\text{NO}_x$  emissions and natural hydrocarbons are present.

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### 1. Introduction

The partitioning of total reactive nitrogen,  $\text{NO}_y = \text{NO} + \text{NO}_2 + \text{NO}_3 + 2\text{N}_2\text{O}_5 + \text{HNO}_3 + \text{peroxyacetyl nitrate (PAN)} + \text{other organic nitrates} + \text{aerosol nitrate}$ , among the individual species has direct effects on photochemical production of ozone in rural and urban areas, on deposition of acidic species to ecosystems, on ecosystem nutrient status, and on the export of

atmospheric nitrogen from the continent to the global troposphere. Reactive nitrogen enters the atmosphere primarily as NO emitted by combustion or soil microbes, with additional contributions from lightning, ammonia oxidation, emission from the oceans, and transport from the stratosphere. NO and  $\text{NO}_2$  (the  $\text{NO}_x$  radicals) interconvert rapidly in the troposphere, with reaction timescales on the order of minutes. Conversion of  $\text{NO}_x$  to nitric acid ( $\text{HNO}_3$ ) and subsequent wet and dry deposition occur on longer timescales, hours to days. Such deposition is widely held to be the primary tropospheric loss process for reactive nitrogen. Atmospheric  $\text{NO}_x$  is converted to  $\text{HNO}_3$  via both homogeneous and heterogeneous chemical pathways.

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Because recycling of  $\text{HNO}_3$  back to  $\text{NO}_x$  is inefficient in the troposphere compared to wet and dry deposition, oxidation of  $\text{NO}_x$  to  $\text{HNO}_3$  terminates the  $\text{NO}_x$  photochemistry that produces  $\text{O}_3$ .  $\text{NO}_x$  also forms temporary non-radical reservoir species such as PAN and other organic nitrates, allowing alternative deposition pathways or export to remote regions where radicals can be regenerated.

The nitrate provided to ecosystems by reactive nitrogen deposition acts as an essential nutrient that may stimulate forests and crops if the dose is not too high. However, at high deposition rates excess nitrate is harmful; loss of base cations, mobilization of toxic elements such as aluminum in soils, disruption of nutrient balances, and other impacts have been observed (Aber et al., 1998; Magill et al., 2000). Due to the complexity of nutrient cycling in ecosystems, long-term effects on ecosystem growth due to deposition of acidic species such as  $\text{HNO}_3$  may take many decades to become apparent, and have important links to global climate through impacts on carbon uptake (Tomlinson, 2003). Deposition of  $\text{HNO}_3$  is the second most important atmospheric source of acidity after sulfuric acid in the Northeastern U.S. (U.S. Environmental Protection Agency, 2001). The abundance of sulfuric acid and sulfur deposition in general have declined since 1990 due to regulation of sulfur dioxide emissions, largely from coal-burning power plants. Nitrogen deposition (total wet and dry), however, has remained approximately constant over the same period (Baumgardner et al., 2002). If these trends continue,  $\text{HNO}_3$  may become an even more important contributor to acid deposition. Weekly  $\text{HNO}_3$  dry deposition estimates from the Clean Air Status and Trends Network (CASTNet) suggest that dry and wet  $\text{HNO}_3$  deposition contribute nearly equally to the total (U.S. EPA, 2001).

Because the distribution of total atmospheric reactive nitrogen among individual species has implications for both atmospheric chemistry and ecosystem conditions, it is important to measure the concentrations and fluxes of the individual species. Comparisons between the sum of atmospheric concentrations of individual  $\text{NO}_y$  species,  $\sum[\text{NO}_y]_i$ , and total  $[\text{NO}_y]$ , measured by catalytic conversion (on hot gold or molybdenum) to  $\text{NO}$ , have been conducted at continental rural sites (e.g. Parrish et al., 1993; Aneja et al., 1996; Thornberry et al., 2001; Hayden et al., 2003), at coastal sites (e.g. Harrison et al., 1999), and in the remote free troposphere (e.g. Bradshaw et al., 2000). Differences sometimes observed between  $[\text{NO}_y]$  and  $\sum[\text{NO}_y]_i$  could be due in part to interference of reduced nitrogen species (e.g.  $\text{NH}_3$ ,  $\text{HCN}$ , and other organic

molecules with direct C–N bonds) with the  $\text{NO}_y$  measurements (Kliner et al., 1997; Bradshaw et al., 1998; Harrison et al., 1999), but unmeasured species, such as alkyl and hydroxyalkyl nitrates, have also been implicated (Day et al., 2003; Rosen et al., 2004).

Few studies have attempted to speciate the reactive nitrogen deposition budget, and consequently, considerable uncertainty attaches to the importance of processes controlling the fluxes of individual species. Munger et al. (1996, 1998) observed concentrations and eddy covariance fluxes of  $\text{NO}_y$  and  $\text{NO}_x$ , showing that  $\text{NO}_x$  was not a major contributor to deposition, and implying that nearly all dry deposition of  $\text{NO}_y$  occurs in the form of rapidly depositing species such as  $\text{HNO}_3$ . They indirectly inferred a summertime contribution due to organic hydroxyalkyl nitrates formed during the oxidation of biogenic hydrocarbons (isoprene and monoterpenes). Recently, we confirmed through eddy covariance flux measurements that net deposition of  $\text{NO}_x$  is small compared to  $\text{NO}_y$  fluxes (Horii et al., 2004). Recent measurements suggest that PAN deposition to vegetation is controlled by leaf stomatal aperture, varying with species and leaf internal PAN concentration (Sparks et al., 2003). Though Sparks et al. suggest that PAN deposition may play a more important role in the nitrogen flux budget than indicated by previous estimates (Shepson et al., 1992; Schrimpf et al., 1996; McFadyen and Neil Cape, 1999), the measured PAN deposition rates were slower and more variable than those of  $\text{HNO}_3$ .

Due in part to its tendency to adsorb onto surfaces,  $\text{HNO}_3$  measurement techniques with demonstrated accuracy, high precision, and a lack of interference have taken decades to develop. Increasingly reliable methods have appeared over the last several years. Filter packs and denuders of various designs are employed for routine monitoring (e.g. Harrison et al., 1999; Rosman et al., 2001; Clarke et al., 1997). These techniques often require collection times on the order of hours to days, after which the filter or denuder is removed, extracted, and processed to detect  $\text{NO}_3^-$  in solution by ion chromatography. Mist chamber techniques rely on capture and dissolution of  $\text{HNO}_3$  and detection by ion chromatography; recent implementations have the advantage of much shorter integration times (minutes) and thorough calibration procedures, which have greatly reduced the uncertainties associated with the measurements (cf. Talbot et al., 1997; Bradshaw et al., 1998). Day et al. (2003) employ thermal dissociation of  $\text{NO}_y$  compounds at calibrated temperatures followed by laser-induced fluorescence detection of  $\text{NO}_2$  to measure  $\text{HNO}_3$ , peroxy nitrates, and alkyl nitrates. Chemical

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