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Passive sampling capabilities for ultra-trace quantitation of atmospheric nitric acid (HNO_3) in remote environments

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ABSTRACT

Custom-built $HNO_{3(g)}$ passive diffusion-based samplers employing nylon filters were comprehensively quality assurance and quality control (QA/QC) tested, including analysis of the PTFE protective filters for potential bias. The passive samplers routinely quantified $HNO_{3(g)}$ mixing ratios in the Canadian boreal up to a factor of 20 lower compared to previous passive sampling dose-response determination and measurements. The use of appropriate blanks alongside field collections resulted in the detection of time-weighted mixing ratios as low as 5 parts per trillion by volume (pptv) over a monthly sampling period or 121 pptv over a 24-h sampling period. The nylon filters were tested for a single reuse to reduce resources required and no statistical difference between the measured mean value of reused and new filters between five replicates across four intercomparisons was found. This showed that a single nylon filter reuse in remote regions is sound as long as replicates are employed. The custom-built passive samplers were installed along the Newfoundland and Labrador – Boreal Ecosystem Latitudinal Transect (NL-BELT) to quantify mixing ratios of $HNO_{3(g)}$ in these forests. Samples generated monthly time-weighted average mixing ratios at the NL-BELT field regions. Samples were collected monthly across 15 months from the summer of 2015 through to the fall of 2016 on the order of tens to a hundred pptv. Across this time period the $HNO_{3(g)}$ mixing ratios ranged from 9 to 200 pptv – after incorporation of comprehensive field QA/QC – with seasonal maxima occurring during the early summer months. No consistent latitudinal trends were observed along the transect, except that the most northern region always corresponded to the lowest mixing ratios of $HNO_{3(g)}$ for a given observation period. Extracts of the protective PTFE filter and collocated measurements of temperature and humidity determined that previously uncertain effects on sampling accuracy likely result in a negative sampling bias of 10–30%. These unpowered devices are now demonstrated to be sensitive, affordable, simple, and redeployable for the continuous ultra-trace detection of $HNO_{3(g)}$ in regions such as the remote Canadian boreal forest.

1. Introduction

As a result of anthropogenic activity, mixing ratios of reactive nitrogen (N_r) in the global atmosphere have increased over the past century (Lamarque et al., 2010). Field measurements and chemistry-climate models have shown that N_r impacts rural and remote ecosystems when it deposits in high amounts (Canfield et al., 2010; Robertson and Vitousek, 2009; Sutton, 2011; USEPA, 2011). Large inputs of N_r, particularly nitrogenous acids, can be toxic to vegetation, lead to soil acidification, and lower ecosystem biodiversity (Bobbink et al., 2010; Cisneros et al., 2010). In terrestrial ecosystems that are N-limited, such as those in high-latitude regions, nitrogen inputs may stimulate vegetation and forest growth (Bedison and McNeil, 2009; Bobbink et al., 2010). Thus, a N-fertilization effect impacts the carbon cycle and Earth's climate (Bedison and McNeil, 2009; Ollinger et al., 2008; Sokolov et al., 2008). Feedbacks are complex and depend on N-deposition magnitude in relation to climate change impacts, but they can change rates of within-ecosystem N cycling, which is typically the major source of available N in N-limited ecosystems (Cleveland et al., 1999). Atmospheric nitric acid ($HNO_{3(g)}$) has been shown to dry deposit

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significant quantities of N in rural and remote environments and thus has the capability to influence the productivity and function of ecosystems. Potential interactive effects of $HNO_{3(g)}$ via N-deposition and climate change in N-limited remote regions (e.g. Arctic and boreal) require quantification of $HNO_{3(g)}$ inputs to constrain its ecosystem-level role. Accurate ultra-trace quantitation of the oxidized nitrogenous acids nitric acid ($HNO_{3(g)}$) and nitrous acid ($HONO_{(g)}$), in conjunction with biogeochemical and ecosystem ecological research on the N-cycle, therefore, will enable a better capacity for prediction of atmosphere-biosphere linkages between external inputs and ecosystem responses to climate change.

Precursor gases for $HNO_{3(g)}$ and $HONO_{(g)}$ are emitted into the atmosphere primarily through anthropogenic fuel combustion processes, which account for approximately 60% of global emissions (Finlayson-Pitts and Pitts, 2000; Müller, 1992). The major species emitted are nitrogen monoxide (NO) and nitrogen dioxide (NO_2), which summed, are termed NO_x due to their rapid photochemical interconversion in the atmosphere. Other sources of atmospheric NO_x are biomass-burning, lightning and denitrifying bacteria (Denman et al., 2007; Müller, 1992). $HNO_{3(g)}$ formation in the daytime atmosphere occurs by reaction of hydroxyl radical ($OH_{(g)}$) with $NO_{2(g)}$ from direct emissions or oxidation of $NO_{(g)}$, while $HNO_{3(surf)}$ and $HONO_{(g)}$ are formed from surface reduction of $NO_{2(g)}$ in the presence of water (R1, R2). At night, dinitrogen pentoxide ($N_2O_{5(g)}$) hydrolyses to form two $HNO_{3(surf)}$ in the condensed phase (R3), which can partition to the gas phase under the appropriate thermodynamic conditions. Hydrogen abstraction by the nitrate radical ($NO_{3(g)}$) can also produce $HNO_{3(g)}$ at night (R4).

(R1) $OH_{(g)} + NO_{2(g)} + M \rightarrow HNO_{3(g)} + M$

(R2) $2\ NO_{2(g)} + H_2O_{(surf)} \rightarrow HONO_{(g)} + HNO_{3(surf)}$

(R3) $N_2O_{5(g)} + H_2O_{(surf)} \rightarrow 2\ HNO_{3(surf)} \rightleftharpoons HNO_{3(g)}$

(R4) $\cdot NO_{3(g)} + RH_{(g)} \rightarrow HNO_{3(g)} + \cdot R'_{(g)}$

Once formed, $HNO_{3(g)}$ is rapidly wet deposited due to its water soluble ($K_H = 3.26 \times 10^6\ M^2\,atm^{-1}$, (Levine and Schwartz, 1982)) strong acid nature and dry deposited from the atmosphere due to its 'stickiness' (Schwartz and White, 1983) downwind of its source location with deposition velocities of $3 \pm 1\ cm\,s^{-1}$ in boreal regions (Flechard et al., 2011; Hicks and Liss, 1976; Wesely and Hicks, 2000). Precursor nitrogen oxides can also react with volatile organics or with atmospheric bases and undergo long-range transport to remote ecosystems as peroxyacetyl nitrates (PANs), alkylnitrates (ANs), or as fine ammonium nitrate aerosol (Browne and Cohen, 2012; Browne et al., 2013, 2014; Min et al., 2012; Seinfeld and Pandis, 2006; Singh and Hanst, 1981) (R5-R8). PANs are thermally stable in when transported into the upper troposphere. They can remain stable there for months, reaching remote regions on a global scale before thermally decomposing to release $NO_{2(g)}$ under common surface temperatures (Atkinson, 1997). ANs represent a significant sink of NO_x and can produce $HNO_{3(g)}$ or particulate nitrate upon reaction downwind of source regions (Browne et al., 2013). Particulate nitrate can release $HNO_{3(g)}$ through changes in thermodynamic equilibrium partitioning and chemistry (Seinfeld and Pandis, 2006). Conversely, $HONO_{(g)}$ is a short-lived locally-produced species that is present at low pptv to part per quadrillion (ppqv) levels in remote regions. It is not considered an important source of new nitrogen in biogeochemical processes as its production is local and levels are assumed to be much lower than $HNO_{3(g)}$ (Cisneros et al., 2010; Flechard et al., 2011; Geddes and Martin, 2017; Zhang et al., 2009), although significant soil $HONO_{(g)}$ emissions, as a loss of nitrogen, have been recently proposed or measured in some environments (Oswald et al., 2013; Scharko et al., 2015; Su et al., 2011; Weber et al., 2015). Thus, an accurate measure of $HNO_{3(g)}$ provides insight into regional and long-range pollutant transport to remote regions and subsequent impacts of N_r on biogeochemical systems.

(R5) $NO_{2(g)} + RO_{2(g)} + M \rightleftharpoons ROONO_{2(g)} + M$

(R6) $NO_{3(g)} + Alkene_{(g)} \rightarrow RONO_{2(g)} \rightleftharpoons RONO_{2(particle)}$

(R7) $NO_{(g)} + RO_{2(g)} \rightarrow RONO_{2(g)} \rightleftharpoons RONO_{2(particle)}$

(R8) $HNO_{3(g)} + NH_{3(g)} \rightleftharpoons NH_4NO_{3(particle)}$

In rural and remote ecosystems $HNO_{3(g)}$ mixing ratios in air can be as low as 10 parts per trillion by volume (pptv), requiring a sensitive measurement technique for quantification. For example, Flechard et al. (2011) and Zhang et al. (2009) sampled $HNO_{3(g)}$ at rural and remote forests by pumping samples through coated annular denuders. Chemical ionization mass spectrometers have also obtained rural measurements with high spatial resolution via aircraft campaigns (Le Breton et al., 2014). However, active sampling techniques are limited to areas with access to powered infrastructure, reducing their ability to continuously quantify deposition in remote environments.

Constraining the inputs and cycling of $HNO_{3(g)}$ with measurements in remote ecosystems therefore remains a challenge, with chemical transport models providing best estimates from known emissions and chemistry. Global atmospheric $HNO_{3(g)}$ mixing ratios were recently modeled by Verbeke et al. (2015) by incorporating current atmospheric $HNO_{3(g)}$ formation and loss mechanisms into a global chemistry-climate model. Production of $HNO_{3(g)}$ was found to be driven by anthropogenic urban point source emissions over biomass burning in North America and Europe. The model did not include soil biogenic or lightning emissions of NO_x (Lamarque et al., 2010), which is a concern because soil is estimated to contribute up to 25% of global NO_x emissions, and consequently $HNO_{3(g)}$, in rural and remote ecosystems (Butterbach-Bahl et al., 2009; Molina-Herrera et al., 2017; Müller, 1992). Such unrepresented emissions will impact estimates of deposited quantities and regional biogeochemical recycling of these reactive nitrogen species. This motivates a need for measurements of $HNO_{3(g)}$ in remote environments to constrain or validate model-derived deposition estimates, but in situ $HNO_{3(g)}$ measurements in remote ecosystems without power are logistically and analytically challenging. Therefore, a simple and reliable technique capable of monitoring $HNO_{3(g)}$ inputs to rural and remote ecosystems is critical in fully understanding the fate of anthropogenic nitrogen in the atmosphere and its biogeochemical impacts.

Passive diffusion sampling of $HNO_{3(g)}$ overcomes the power-availability limitation of active sampling and was developed using nylon membrane filters as sorption media for $HNO_{3(g)}$ in remote areas and has been applied to polluted Class I National Park forests in California, U.S.A. (Bytnerowicz et al., 2002a, 2002b; Cisneros et al., 2010) and boreal forest areas near the Oil Sands in Alberta, Canada (Bytnerowicz et al., 2010). Passive nylon filter sampling has the advantages of low costs, low maintenance, reduced field-personnel training, and the potential to obtain large spatial scale measurements (Krupa and Legge, 2000). However, this technique has rarely quantified $HNO_{3(g)}$ in remote ecosystems where $HNO_{3(g)}$ mixing ratios are expected to be below 100 pptv and calibration dose-response values have not been validated at these levels (Bytnerowicz et al., 2002a, 2002b, 2005, 2010; Cisneros et al., 2010). The potential detection limits of these devices have not been determined in previous work and neither have the performance of true field and method blanks in quantitative analysis. Potential biases of temperature, humidity, and particulate matter in nylon membrane $HNO_{3(g)}$ sampling have been suggested for nylon media (Bytnerowicz et al., 2005) and characterized for filter pack sampling (Padgett, 2010). These variables likely affect a passive nylon approach, but have not yet been explored by experiment or from real samples. Previous works have proposed that the best way to correct for all passive sampling uncertainties is by intercomparson with collocated – and powered – denuder systems to derive the passive dose-response slope (Bytnerowicz et al., 2005, 2010; Cisneros et al., 2010; Koutrakis et al., 1993a, 1993b; Krupa and Legge, 2000), which is not viable for truly remote locations.