Gas-phase reactive nitrogen near Grand Teton National Park: Impacts of transport, anthropogenic emissions, and biomass burning

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HIGHLIGHTS

- Gas phase reactive nitrogen species were measured near Grand Teton National Park.
- A diel cycle was observed in ambient reactive nitrogen concentrations.
- Ambient concentrations were driven, in part, by mountain-valley circulation.
- Biomass burning resulted in elevated concentrations of reactive nitrogen.

ARTICLE INFO

ABSTRACT

Excess inputs of reactive nitrogen can adversely affect terrestrial and aquatic ecosystems, particularly in sensitive ecosystems found at high elevations. Grand Teton National Park is home to such sensitive natural areas and is in proximity to potentially large reactive nitrogen sources. The Grand Teton Reactive Nitrogen Deposition Study (GrandTReNDS) was conducted in spring–summer 2011, with the aim of better understanding sources of reactive nitrogen influencing the region, spatial and temporal variability of reactive nitrogen in the atmosphere, and current levels of nitrogen deposition. Overall, NO_y was determined to be the most abundant class of ambient gas phase reactive nitrogen compounds, and ammonia was determined to be the most abundant individual nitrogen species. NO_x, NO_y and NH_3 concentrations all showed a diel cycle, with maximum concentrations during the day and minimum concentrations at night. This pattern appeared to be driven, in part, by mountain-valley circulation as well as long range transport, which brought air to the site from anthropogenic sources in the Snake River Valley and northern Utah. In addition to the nitrogen sources noted above, we found elevated concentrations of all measured nitrogen species during periods impacted by biomass burning.

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1. Introduction

Nitrogen emissions and deposition have been increasing in the western US (Fenn et al., 2003b), with increases in deposition especially evident at high elevations (Burns, 2003). Increased emissions are driven by anthropogenic sources, which have impacted even remote regions in the northern hemisphere since the beginning of the 20th century (Holtgrieve et al., 2011). Although large areas in the western US are exposed to low levels of atmospheric deposition (Fenn et al., 2003a), increases are sufficient to be detected and likely impact the biosphere at the hemispheric scale (Holtgrieve et al., 2011). Effects of excess nitrogen inputs are extensive, including impacts on water quality and nutrient cycling, nitrogen enrichment in soils and plants, eutrophication of lakes, decreased diversity of mycorrhizal communities, altered plant community composition, and impacts on drought, frost and pest tolerance (Bowman et al., 2006; Fenn et al., 2003a; Krupa, 2003). Ecosystems in the Rocky Mountains appear to be particularly sensitive to small increases in nitrogen (Bowman et al., 1993), where in some high elevation watersheds there has already been a shift from

nitrogen limited systems to ecosystems which are nitrogen saturated (Williams et al., 1996).

Reactive nitrogen sources are dominated by NO_x ($NO + NO_2$) and ammonia (NH_3) (Galloway et al., 2004). In the atmosphere, NO_x is typically converted to other NO_y species (NO_x plus other reactive oxidized nitrogen) such as HNO_3 in less than 1 day (Seinfeld and Pandis, 1998), which can then go on to influence the acidity of precipitation. There is substantial spatial and temporal variability in NO_x concentrations, which range from sub-ppb levels in remote environments to more than 100 ppb in urban areas (Seinfeld and Pandis, 1998). For ammonia, more than 80% of emissions are from agriculture in the U.S. (Reis et al., 2009), primarily from livestock wastes and volatilization of NH_3-based fertilizers, while biomass burning serves as an important natural source (Kopacek and Posch, 2011). Ammonia emissions in the US increased ~20% between 1990 and 2005 (Reis et al., 2009), and global emissions are expected to continue to rise (Galloway et al., 2004).

Although many studies have focused on wet nitrogen deposition, dry deposition of ammonia is also an important deposition pathway in the Rocky Mountains (Beem et al., 2010; Benedict et al., 2013a, 2013b; Burns, 2003; Day et al., 2012), particularly because it has been shown to drive plant species change faster than wet deposition of ammonium (Sheppard et al., 2011). Dry deposition of ammonia is most important close to the source (Asman et al., 1998), resulting in large spatial variability, with concentrations ranging from sub-ppb levels in remote environments (e.g. (Alkezweeny et al., 1986)) to hundreds of ppb near agricultural sources (e.g. (Sintermann et al., 2011)). Re-emission of deposited ammonia via bi-directional exchange with plant surfaces (Massad et al., 2010) can potentially expand the spatial extent of these emissions. There is also seasonal variability, with atmospheric NH_3 concentrations typically peaking in spring and summer (Krupa, 2003).

Satellite measurements have identified the Snake River Valley in Idaho as a U.S. hotspot for ammonia emissions (Clarisse et al., 2009), and modeling results suggest that areas near the border of WY and ID, on the western side of Grand Teton National Park (GRTE), are likely to have extensive nitrogen deposition (Fenn et al., 2003b). While agricultural areas may thrive on the enriched nitrogen, natural vegetation is more sensitive to NH_3 inputs (Krupa, 2003), and high elevation lakes within GRTE have been identified as being particularly sensitive to inputs of inorganic nitrogen (Nanus et al., 2009). The Greater Yellowstone Ecosystem, which includes GRTE, has already shown signs of changes triggered by increased nitrogen inputs (Saros et al., 2011). In this paper, we report atmospheric concentrations of several gas phase nitrogen species at a high elevation site near GRTE in spring-summer 2011, as part of the Grand Teton Reactive Nitrogen Deposition Study (GrandTReNDS).

2. Material and methods

The core measurement site for GrandTReNDS was located ~6 km from the west boundary of GRTE (Fig. 1 inset), on Peaked Mountain at Grand Targhee Resort (latitude 43.78 N; longitude 110.94 W; elevation 2722 m). The vegetative environment at Grand Targhee Resort is subalpine. The measurement site was located at the transition zone between forest and the tree line, with Douglas-fir, subalpine fir, Whitebark pine and Engelmann spruce being the dominant vegetation in the immediate vicinity, and stands of other species such as lodgepole pine and aspen being present within a few miles of the site. Real time measurements at the core site began August 1 and continued through September 22, 2011. Measurements were carried out in the National Park Service (NPS) mobile air sampling laboratory. The laboratory is temperature-controlled (~25 °C) and includes space and power for instrumentation.
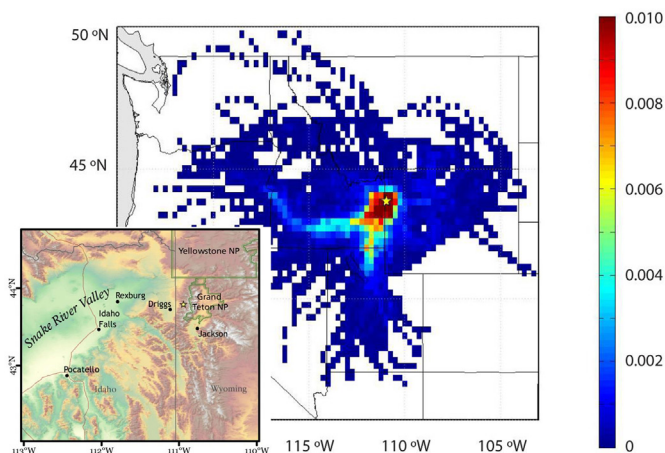

Fig. 1. Results from HYSPLIT 48 h back trajectory analysis for August 1, 2011–September 22, 2011. The location of the core site is shown as a star. Colors represent the fraction of time that a back-trajectory passed through a $0.2° \times 0.2°$ grid box. Inset shows regional topography for area surrounding the sampling site. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Back-trajectory residence time analysis using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT4) (Draxler, 1999; Draxler and Hess, 1998) with input from the NAM-12 meteorological data set provides insight regarding transport pathways of air masses impacting the site. Forty eight hour back trajectories initialized at 100 m AGL were run for every hour of the study period (August 1–September 22). Results from the study period show that the air masses came predominantly from the west, in the Snake River Valley, and the southwest, from northern Utah (Fig. 1).

2.1. Continuous gas measurements

Continuous gas measurements included ammonia (NH_3), NO_x, NO_y, carbon monoxide (CO), and an additional reactive nitrogen component described below. A schematic of the sampling strategy is summarized in Fig. 2. For NH_3, NO_x, CO and the additional reactive nitrogen component, sampling was from a common inlet ~3 m above ground level. The sampling line was ~1 m, 0.64 cm OD Teflon for NO_x, CO, NH_3 from the Air Sentry II Ion Mobility Spectrometer (IMS; Particle Measuring Systems), and the additional reactive nitrogen component. For these instruments, sample line residence time was <1 s. An additional ~1 m of sampling line was needed for NH_3 measured with a Picarro cavity ring down spectroscopy (CRDS) instrument; for the CRDS, residence time was ~2.5 s. This inlet included a PTFE filter with PFA housing (Mykrolis WGFG21KP3) upstream to remove particles. For NO_y, ambient air was sampled through a 6 m long, 0.64 cm OD Teflon sampling line, with an inlet ~2 m above ground level. Residence time in the sampling line was ~5 s. Calibrations for all instruments were performed prior to the study. All calibrations were done using certified, traceable standards provided by Airgas. Calibration gases were diluted using a Teledyne Zero Air Generator (Model 701) and Dynamic Dilution Calibrator (DDC, Teledyne Model 700). Every calibration included zero air and a span concentration, with calibration gases introduced at the sample inlets. For ammonia, sufficient time was allowed to ensure the calibration system was conditioned with ammonia (overnight). A separate line was added near the sample inlet to allow for collection and analysis of the calibration gas (NH_3) using a denuder. This method was used to account for any losses in the calibration system. For CO, NO_x, NO_y