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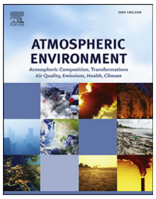

Enhanced concentrations of reactive nitrogen species in wildfire smoke

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HIGHLIGHTS

- NH_3, NO_x, HTC-RN, NO_3^-, and NH_4^+ were measured in fresh smoke from two wildfires.
- Enhanced concentrations of all reactive nitrogen species except NH_4^+ were observed.
- Ammonia during smoke-impacted periods was enhanced by a factor of 20.
- Excess mixing ratios NH_3 relative to excess CO were found to be 0.027 ± 0.002.
- Excess mixing ratios NO_x relative to excess CO were found to be 0.057 ± 0007.

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ABSTRACT

During the summer of 2012 the Hewlett Gulch and High Park wildfires burned an area of 400 km^2 northwest of Fort Collins, Colorado. These fires both came within 20 km of the Department of Atmospheric Science at Colorado State University, allowing for extensive measurements of smoke-impacted air masses over the course of several weeks. In total, smoke plumes were observed at the measurement site for approximately 125 h. During this time, measurements were made of multiple reactive nitrogen compounds, including gas phase species NH_3, NO_x, and HNO_3, and particle phase species NO_3^- and NH_4^+, plus an additional, unspeciated reactive nitrogen component that is measured by high temperature conversion over a catalyst to NO. Concurrent measurements of CO, levoglucosan and $PM_{2.5}$ served to confirm the presence of smoke at the monitoring site. Significant enhancements were observed for all of the reactive nitrogen species measured in the plumes, except for NH_4^+ which did not show enhancements, likely due to the fresh nature of the plume, the presence of sufficient regional ammonia to have already neutralized upwind sulfate, and the warm conditions of the summer measurement period which tend to limit ammonium nitrate formation. Excess mixing ratios for NH_3 and NO_x relative to excess mixing ratios of CO in the smoke plumes, $\Delta NH_3/\Delta CO$ (ppb/ppb) and $\Delta NO_x/\Delta CO$ (ppb/ppb), were determined to be 0.027 ± 0.002 and 0.0057 ± 0.0007, respectively. These ratios suggest that smoldering combustion was the dominant source of smoke during our plume interceptions. Observations from prior relevant laboratory and field measurements of reactive nitrogen species are also briefly summarized to help create a more comprehensive picture of reactive nitrogen and fire.

1. Introduction

Biomass burning represents an important source of particles and trace gases to the global atmosphere, with 33–43 million km^2 burned annually (Giglio et al., 2010). Although global burn area is dominated by savanna fires in Africa (Giglio et al., 2010; van der Werf et al., 2006), fire carbon emissions largely track burning of forested areas (van der Werf et al., 2006). In temperate North America, approximately 1.5 Mha are burned annually. Large

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wildfires (>400 ha or 4 km^2) in the western US increased significantly in the mid-1980s (Westerling et al., 2006), and more recent data demonstrate that wildfires are becoming larger in size relative to 20th century fires (www.nifc.gov). Such increases may be tied to a warming climate (Moritz et al., 2012). In the Greater Yellowstone ecosystem, Westerling et al. (2011) showed that a difference in average summer and spring temperature of only ~0.5 °C is sufficient to distinguish extreme fire years from most other years. With a warmer future climate predicted, fire activity is expected to increase in the US (Flannigan et al., 2000; Moritz et al., 2012; Spracklen et al., 2007), including fires caused by lightning (Price and Rind, 1994).

During years of large acreage burned from wildfires, biomass burning emissions can account for up to 65% of $PM_{2.5}$ organic carbon (OC) emissions in the western US (Spracklen et al., 2007). Regional variability in OC concentrations throughout the continental US can, in part, be explained by western US wildfire emissions. Additionally transport of air masses across international boundaries in some regions results in significant increases in OC mass with implications for ambient air quality standards, visibility, and cloud radiative properties (Ge et al., 2014; Park et al., 2003; Targino et al., 2013). In addition to carbon, nitrogen compounds are abundant in biomass burning emissions (Yokelson et al., 2008; Wiedinmyer et al., 2006, 2011; Akagi et al., 2011; Andreae and Merlet, 2001). In fact, global anthropogenic reactive nitrogen emissions were dominated by biomass burning until the middle of the 20th century (Kopáček and Posch, 2011). Ammonia (NH_3) and nitrogen oxides (NO_x) emissions can account for 20–50% of the nitrogen consumed during burns, with lesser contributions from nitric acid (HNO_3) and particulate nitrogen species (McMeeking et al., 2009). Additionally, nitrous acid (HONO), hydrogen cyanide (HCN), and acetonitrile (CH_3CN) are important N-containing compounds emitted by biomass burning (Akagi et al., 2011). Emissions ratios (ER) to CO (mol/mol) for a variety of fuel types are reported in Stockwell et al. (2015) for a number of nitrogen containing gases including NH_3 (max ER 0.194), HCN (0.022), NO (0.0893), NO_2 (0.0588), HONO (0.0119), CH_3CN (0.0073), dimethylamine and ethylamine (C_2H_7N; 0.0024), acetamide (C_2H_5NO; 0.00998), triethylamine (C_3H_9N; 0.0028), assorted amides (C_4H_9NO; 0.000797), assorted amines ($C_4H_{11}NO$; 0.00023), benzonitrile (C_7H_5N; 0.00022). Additional N-containing compounds were observed but were unable to be quantified, including acrylonitrile, propanenitrile, pyrrole, and pyridine.

Observation of many of these nitrogen-containing organic compounds are few but the results from Stockwell et al. (2015) indicate that together they may account for 0.1–8.7% of fuel nitrogen. The ratio of NH_3 to NO_x has been shown to be strongly related to modified combustion efficiency (MCE), where a higher ratio of NH_3 to NO_x is associated with a lower MCE (Goode et al., 2000, 1999; McMeeking et al., 2009; Yokelson et al., 1996), suggesting a tradeoff in the form of nitrogen depending on combustion conditions. An average of measurements from more than 19 wildfires suggest that emissions of ammonia are 2% of carbon monoxide (CO) emissions in nitrogen limited environments (Goode et al., 2000; Nance et al., 1993) such as those found in the Rockies (Baron et al., 2000). However, there is evidence that fire environment (e.g. atmospheric conditions, soil moisture content) plays an important factor in the $\Delta NH_3/\Delta CO$ emission ratio (Hegg et al., 1988). Ammonia concentrations tend to decrease as a plume ages (Goode et al., 2000), relative to CO concentrations, likely due to deposition and conversion to particulate NH_4^+, while particulate nitrate concentrations generally increase (Hobbs, 2003) from chemical reactions in the plume such as nitric acid conversion to nitrate. The formation of submicron particulate ammonium nitrate can move both gaseous ammonia and gaseous nitric acid into the particle phase. Ammonium nitrate formation, which is reversible, is favored when temperatures are low and relative humidities are high.

In US emission inventories, agricultural practices such as livestock manure management and application of chemical fertilizers contribute 80% to national ammonia emissions, while emissions from vehicles that have catalytic converters contribute 7% (Reis et al., 2009). Biofuels also may be a significant source of ammonia to the atmosphere in regions such as Africa, India, and the Amazon (Bertschi, 2003; Christian et al., 2007). Because emissions inventories are designed from regulatory data, wildfire emissions are often not included, and for those inventories that include wildfire emissions of ammonia, attempts to validate them do not always show consistent results (Whitburn et al., 2015). Globally, biomass burning is thought to account for emission of 5.9–10.3 Tg yr^{-1} of NH_3 (Andreae and Merlet, 2001; Bouwman et al., 1997; Hegg et al., 1988), with burning in natural ecosystems accounting for 3.2 Tg N yr^{-1} (Asman et al., 1998). In the US the 2011 EPA National Emissions Inventory (NEI) lists wildfires as the third largest source of ammonia nationally, contributing ~5% of ammonia emissions; when all fires (wildfires, prescribed burns, and agricultural fires) are considered, fires make up nearly 9% of total ammonia emissions. Increases in ambient NH_3 and other reactive nitrogen species concentrations due to fires have been observed in the laboratory (Christian et al., 2007; Levin et al., 2010; McMeeking et al., 2009; Yokelson et al., 2008, 1996), from ground-based (Benedict et al., 2013a; Prenni et al., 2014) and aircraft-based field studies (Andreae et al., 1988; Goode et al., 2000; Hegg et al., 1988; Hobbs, 2003), from monitoring networks (Chen et al., 2014) and from satellite observations (Coheur et al., 2009; R'Honi et al., 2013; Van Damme et al., 2014; Whitburn et al., 2015).

Here we report measurements of ammonia and other reactive nitrogen species during smoke impacts from two wildfires in northern Colorado, the Hewlett Gulch and High Park fires. We also summarize laboratory and field measurements of unspeciated reactive nitrogen species collected from biomass burning events from previous studies by our research group.

2. Experimental

2.1. Colorado wildfires

The Hewlett Gulch fire began on May 14, 2012 and was human caused. The fire was approximately 20 km northwest of Fort Collins, CO and ultimately grew to 3100 ha (inciweb.nwcg.gov/incident/2863/). Grasses and shrubs (mountain mahogany and bitter brush) were the dominant fuels on the southerly facing slopes while fuels on the north facing slopes were timber, primarily Ponderosa pine with some Douglas fir and white fir at higher elevation (Richardson, 2012). Measurements at our laboratory at Colorado State University began May 17 and continued through June 4, well after the fire was contained and when smoke impacts were no longer observed. The High Park fire (inciweb.nwcg.gov/incident/2904/) was significantly larger, covering 35,300 ha (Walker et al., 2012), and contributing significantly to aerosol loading over a large vertical extent in northern Colorado (Val Martin et al., 2013). The lightning-caused fire began in earnest on June 9, and this fire came within 4 km of our laboratory. Measurements from the High Park fire were carried out from June 9 through June 30. At lower elevations during the High Park fire, fuels included lodge pole pine, ponderosa pine, and Douglas-fir (Walker et al., 2012). Upper elevations consisted of forests transitioning to Engelmann spruce and subalpine fir. Pockets of aspen existed throughout forested areas.