Observations of ammonia, nitric acid, and fine particles in a rural gas production region


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HIGHLIGHTS
- Five years of measurements reveal low ammonia concentrations in western Wyoming.
- Ammonia and nitric acid concentrations show a strong seasonal variation.
- Ammonia concentrations peak in summer.
- Nitric acid concentrations peak in summer and winter.

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ABSTRACT
Continuous measurements of the atmospheric trace gases ammonia (NH₃) and nitric acid (HNO₃) and of fine particle (PM₂.₅) ammonium (NH₄⁺), nitrate (NO₃⁻) and sulfate (SO₄²⁻) were conducted using a denuder/filter system from December 2006 to December 2011 at Boulder, Wyoming, a region of active gas production. The average five year concentrations of NH₃, HNO₃, NH₄⁺, NO₃⁻ and SO₄²⁻ were 0.17, 0.19, 0.26, 0.32, and 0.48 µg m⁻³, respectively. Significant seasonal patterns were observed. The concentration of NH₃ was higher in the summer than in other seasons, consistent with increased NH₃ emissions and a shift in the ammonium nitrate (NH₄NO₃) equilibrium toward the gas phase at higher temperatures. High HNO₃ concentrations were observed both in the summer and the winter. Elevated wintertime HNO₃ production appeared to be due to active local photochemistry in a shallow boundary layer over a reflective, snow-covered surface. PM₂.₅ NH₄⁺ and SO₄²⁻ concentrations peaked in summer while NO₃⁻ concentrations peaked in winter. Cold winter temperatures drive the NH₃–HNO₃–NH₄NO₃ equilibrium toward particulate NH₄NO₃. A lack of NH₃, however, frequently results in substantial residual gas phase HNO₃ even under cold winter conditions.

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1. Introduction

Ammonia (NH₃) is the most abundant alkaline gas in the troposphere and is important for its ability to neutralize acidic components such as sulfuric acid (H₂SO₄) and nitric acid (HNO₃) which form, respectively, by oxidation of emissions of sulfur dioxide (SO₂) and nitrogen oxides (NOₓ). NH₃ is also an important contributor to nitrogen deposition (Beem et al., 2010; Benedict et al., 2013), which can cause eutrophication, soil acidification and biotic community changes (Cowell and Apsimon, 1998; Groot Koerkamp et al., 1998). It is widely recognized that important sources of NH₃ include agricultural activities such as fertilization and livestock emissions (Li et al., 2006; Mielke et al., 2000; Sutton et al., 2000). Reactions of HNO₃ and H₂SO₄ with ambient NH₃ generally form submicron ammonium nitrate (NH₄NO₃) and ammoniated sulfate (NH₄H₂SO₄, (NH₄)₂SO₄ or other forms) particles which can adversely impact human respiratory health and
impair atmospheric visibility through visible light scattering. In the United States (U.S.), a set of Class 1 areas (including National Parks and Wilderness Areas) has been identified for protection from visibility impairment through the Regional Haze Rule. Because oil and gas production regions of the western U.S. are often located near these visibility-protected areas, close attention is paid to their emissions of fine particle precursors. In order to reduce NO\textsubscript{x} emissions from natural gas drilling and production activities, for example, selective catalytic reduction (SCR) can be installed on drill rigs. While SCR can yield large reductions of NO\textsubscript{x} emissions; however, there is a risk of increased NH\textsubscript{3} emission into the atmosphere.

Western Wyoming is one region of active recent gas development where several air quality concerns have been raised (McMurray et al., 2013). Emissions of NO\textsubscript{x} have been of concern both because of possible impacts on regional haze and, especially, due to documented impacts on severe winter ozone episodes (Schnell et al., 2009). SCR implementation in the region has been active in recent years as one effort to limit winter ozone episodes. While these winter ozone episodes are believed to be local in nature, NO\textsubscript{x} emission impacts on regional haze may be more widespread. Unfortunately, few measurements exist in the region of NH\textsubscript{3} and haze impact assessments are generally forced to rely on an assumed background NH\textsubscript{3} concentration level. While a number of recent studies have considered the role NH\textsubscript{3} plays in the formation of fine particles across the United States in both urban and rural areas (Bari et al., 2003; Benedict et al., 2013; Edgerton et al., 2007; Gong et al., 2011; Heald et al., 2012; Lee et al., 2008; Nowak et al., 2010; Sather et al., 2008), knowledge of atmospheric concentrations of NH\textsubscript{3}, and their seasonal variability is still rather limited, especially in the interior western United States. Here we present five years of observations of concentrations of gaseous NH\textsubscript{3} and HNO\textsubscript{3} and fine particle concentrations of NH\textsubscript{4}, SO\textsubscript{4} and NO\textsubscript{3} from Boulder, Wyoming, a site in the heart of an active gas production region. These measurements provide the longest term record of NH\textsubscript{3} concentration measurements in this part of the U.S. and provide new insight into typical NH\textsubscript{3} concentrations in the region, their seasonal variability, and the gas-particle partitioning of the NH\textsubscript{3}−NH\textsubscript{4}−HNO\textsubscript{3}−NO\textsubscript{3}−SO\textsubscript{4} system that is one important contributor to regional haze.

2. Experimental methods

Measurements were made southwest of Boulder, Wyoming (42°43’7.9”N, 109°45’10.4”W) in the northwestern part of the Pinedale anticline area. Two visibility-protected areas, Bridger Wilderness Area and Fitzpatrick Wilderness Area, are located within 100 km. The Boulder area and nearby natural gas fields are situated on a high plateau between the Wind River Range to the east and the Wyoming Range to the west. Strong surface-based inversions, with inversion pools intersecting topography levels down to 50 m above ground (Schnell et al., 2009), are common in the region, especially during wintertime. The population density in Boulder, Wyoming is sparse with only 8.9 people per square km. The Jonah Gas Field and the Pinedale Anticline Gas Field, together representing one of the largest gas production regions in the U.S., are close to the sampling site with several active gas wells located approximately 3 km west of the sampling site. In 2008, there were more than 500 permits in the Jonah Gas Field and an additional 3100 wells are expected to be drilled in this field over the next 75 years. Total production in this region in 2011 was nearly 171 billion cubic feet of natural gas and 1.5 million barrels of oil (http://www.encana.com/pdf/communities/us/jonahField-FactSheet.pdf). NO\textsubscript{x} from the gas extraction operations and transportation emissions are the largest contributor to local NO\textsubscript{x} emissions (Fig. S1a). For NH\textsubscript{3} emissions, there are not many large sources in this immediate area. However, the Snake River Valley to the west of the measurement site is a large area of intense agricultural activity with elevated NH\textsubscript{3} emissions and concentrations (Clarisse et al., 2009) (Fig. S1b). Installation of more SCR systems in the Jonah-Pinedale region could elevate local NH\textsubscript{3} concentrations, contributing to more particle formation and visibility degradation.

Concentrations of gaseous NH\textsubscript{3} and HNO\textsubscript{3} and PM\textsubscript{2.5} (particles with an aerodynamic diameter less than 2.5 \(\mu\)m) inorganic ions (NH\textsubscript{4}, SO\textsubscript{4}\textsuperscript{−}, NO\textsubscript{3}, K\textsuperscript{+}, Mg\textsuperscript{2+} and Ca\textsuperscript{2+}) were sampled using a URG denuder/filter system (University Research Glassware, Inc., Model 3000CA), which was installed at 1.5 m height, followed by laboratory extraction and analysis by ion chromatography. The URG sampling system has been widely used because of its good performance in sampling acidic gaseous and volatile aerosols (Bari et al., 2003; Beem et al., 2010; Edgerton et al., 2007; Lee et al., 2004; Lin et al., 2006). Air was drawn through a Teflon-coated PM\textsubscript{2.5} cyclone followed by two 242 mm annular denuders connected in series, a 47-mm filter pack containing a nylon filter (Nylasorb, pore size 1\(\mu\)m, Pall Corporation) and another annular denuder (from Dec. 2006 through July 11th 2008, samples were collected used a backup coated filter rather than a 3rd denuder). Air flow was maintained at a constant mass flow rate by means of a mass flow-controlled pump (URG Inc.). The total flow rate through the system was nominally 10 L min\textsuperscript{−1} at ambient conditions. Actual sample volumes were determined using a sample pressure-compensated dry gas meter. The first denuder was coated with sodium chloride (NaCl) to collect gaseous HNO\textsubscript{3} and the second was coated with phosphorus acid (H\textsubscript{3}PO\textsubscript{4}) to collect gaseous NH\textsubscript{3}. The last denuder (or coated filter) was phosphorus acid-coated to collect any NH\textsubscript{3} re-volatilized from NH\textsubscript{4} salt particles collected on the filter. Nylon filters have been shown to retain volatilized HNO\textsubscript{3}, but loss of NH\textsubscript{4} can be significant (Yu et al., 2006). The sample trains were prepared in the lab at Colorado State University (CSU), and then shipped weekly and installed by a local site operator. Samples were typically collected twice a week (one 4 day sample and one 3 day sample). After sampling, the sample train was shipped back to the lab at CSU. The denuders were extracted with 10 ml deionized water, and the extracts refrigerated before analysis. Nylon filters were ultrasonically extracted for 55 min in 6 ml of high purity deionized water. Ion chromatography using a Dionex dual channel system was used to analyze the denuder and filter extracts. Cations (Na\textsuperscript{+}, NH\textsubscript{4}, K\textsuperscript{+}, Mg\textsuperscript{2+} and Ca\textsuperscript{2+}) in the samples were separated with a methanesulfonic acid eluent on a Dionex CG12A guard column and CS12A separation column followed by a CRS ULTRA II suppressor and detected by a Dionex conductivity detector. Anions (Cl\textsuperscript{−}, NO\textsubscript{3}, SO\textsubscript{4}\textsuperscript{2−}) in the samples were separated with a carbonate/bicarbonate eluent on a Dionex AG14A guard column and AS14A separation column followed by an ASRS ULTRA II suppressor and detected using a Dionex conductivity detector.

Meteorological data, including temperature, relative humidity and wind speed, were obtained from a co-located weather station (2 m height) operated by Air Resource Specialists, Inc.

Sample recovery was high, although there were occasional periods where samples could not be collected on the normal schedule (e.g., from bad weather affecting sampler shipment or operator access). Field and laboratory blanks were collected throughout the study and used to determine the method detection limit (MDL) and to blank-correct results. The MDLs for NH\textsubscript{3}, HNO\textsubscript{3}, NH\textsubscript{4}, SO\textsubscript{4}\textsuperscript{−}, NO\textsubscript{3}, K\textsuperscript{+}, Mg\textsuperscript{2+} and Ca\textsuperscript{2+} were determined as 0.012, 0.012, 0.002, 0.017, 0.001, 0.005, 0.007 and 0.025 \(\mu\)g m\textsuperscript{−3} respectively. Replicate extract analyses yielded measurement precisions of 5.4%, 3.8%, 3.5%, 0.8%, 2.1%, 4.9%, 7.6%, and 6.2% (relative standard deviation) for NH\textsubscript{3}, HNO\textsubscript{3}, NH\textsubscript{4}, SO\textsubscript{4}\textsuperscript{−}, NO\textsubscript{3}, K\textsuperscript{+}, Mg\textsuperscript{2+} and Ca\textsuperscript{2+}, respectively.
3. Results and discussion

From December 2006 through December 2011, 505 samples were collected. The summary of the annual and seasonal mean and standard deviation for all the trace gas concentrations, particulate species concentrations and meteorological parameter values are summarized in Table S1 in the supplement. Because of the high latitude of this continental sampling site and the monthly average temperatures, the following months were defined as representing specific seasons, for the purpose of discussing the analytical results below: April and May were defined as spring; June, July and August as summer; September and October as fall; and November through March as winter.

Fig. 1 shows time series of the concentrations of gaseous NH₃ and HNO₃ and PM₂.₅ NH₄⁺ and NO₃⁻ concentrations at Boulder, Wyoming. NH₃ concentrations peak in summer while NO₃⁻ concentrations peak in winter. HNO₃ exhibits a distinct bimodal seasonal concentration pattern with summer and winter maxima. As shown in Fig. 2, NH₄⁺, SO₄²⁻, and NO₃⁻ were the three most abundant inorganic ions in PM₂.₅ in all seasons. The concentration of NH₄⁺ varied least across seasons. During the warm season SO₄²⁻ was the most abundant inorganic anion in PM₂.₅, while during winter the concentration of NO₃⁻ was highest. More details concerning the trends of each of the trace gas and particulate species will be presented below.

3.1. Concentrations of major gas and fine particle species, their seasonal patterns, and gas-particle partitioning

Gaseous NH₃ exhibited a clear seasonal concentration pattern, ranging from an average concentration of 0.04 µg m⁻³ in winter to 0.39 µg m⁻³ in summer (Fig. 3a). The maximum quarterly NH₃ average concentration was 0.47 µg m⁻³ in summer 2008, 15 times higher than the winter 2008–2009 average of 0.03 µg m⁻³. The significantly higher summer concentration reflects a strong influence of temperature. Previous studies have reported similar phenomena (Edgerton et al., 2007; Gupta et al., 2003; Meng et al., 2011; Plessow et al., 2005; Walker et al., 2004). Higher levels of NH₃ in the summer are consistent with the positive influence of higher temperatures on NH₃ emissions (e.g., from natural soils, agricultural operations, and fires) and the decomposition of particulate NH₄NO₃ into gaseous NH₃ and HNO₃.

One potential local source of NH₃ is increased use of SCR for high-efficiency NOₓ control on drill rigs in the region. While use of SCR increased during the period of observation at Boulder, however, there is no clear increase in local NH₃ concentrations over the study. The annual mean concentration of NH₃ did not significantly increase during the study period. From 2007 to 2011, the annual NH₃ average concentrations in each year were 0.14, 0.20, 0.23, 0.15 and 0.13 µg m⁻³, respectively, suggesting that SCR emissions did not noticeably influence local concentrations of ambient NH₃.

Table S2 shows cross-correlation coefficients for measured trace gases, particle ions and meteorological parameters. Some
correlation was found between NH3 and K\(^+\) \((r^2 = 0.16)\). As illustrated by satellite fire-detect images (Fig. S2), there were more wild fires present around Boulder, Wyoming in 2007 and 2008; the correlation coefficients \((r^2)\) between NH3 and K\(^+\) in those two years were 0.33 and 0.40. As a marker of biomass burning, the correlation between NH3 and K\(^+\) may suggest a positive influence of fire emissions on NH3 concentrations (Anderson et al., 2003; Hegg et al., 1988; McMeeking et al., 2009; Sutton et al., 1995).

A background NH3 mixing ratio of 1 ppbv is often assumed when estimating impacts of NO\(_x\) emissions on visibility and regional haze in western regions of the U.S. where ambient NH3 concentration data are sparse or unavailable. Such estimates might be made, for example, through plume dispersion simulations using CALPUFF or other EPA-preferred models. The 5-year Boulder data records provide a better basis for choosing a representative background NH3 concentration for the Pinedale region. Fig. 4 reveals that seasonal mean NH3 mixing ratios ranged between a maximum of 0.85 ppbv (in summer 2008) and 0.03 ppbv (in winter 2010). The average for the full 5-year study period was 0.30 ppbv, less than one-third of the typically assumed background level. Even if PM\(_{2.5}\) NH\(_4\)\(^+\) (much of which certainly reacted with sulfuric and nitric acids upwind of the measurement region) and gaseous NH3 are combined, the average mixing ratio (0.63 ppbv) remains well below 1 ppbv. Assumption of a 1 ppbv NH3 background concentration in
model simulations, therefore, will lead to an overprediction of visibility impacts associated with local NOx emissions.

The five year average HNO3 mixing ratio was observed to be 0.03 ppbv, indicating typically low concentrations of HNO3 occur in this area. Seasonal mean HNO3 mixing ratios (Fig. 4) ranged between 0.13 ppbv (in summer 2007) and 0.01 ppbv (in spring 2008). As illustrated in Fig. 3b, HNO3 concentrations display a distinct bimodal seasonal pattern, with higher average concentrations in the summer (0.23 µg m⁻³) and in mid-winter (January/February average = 0.26 µg m⁻³) than in other seasons. One also can see in Fig. 4 that variability in observed HNO3 concentrations is quite high in January and February. Previous studies have generally shown that HNO3 peaks in summer with lower concentrations during winter (Adon et al., 2010; Gupta et al., 2003; Lee et al., 1999; Plessow et al., 2005). Increased concentrations of HNO3 are expected in the summer because of more intense and longer lasting photochemical activity associated with higher sun angles and longer days. Higher summer temperatures also promote dissociation of NH4NO3 back to gaseous NH3 and HNO3, as discussed above (Seinfeld and Pandis, 2006). The high winter concentrations observed at Boulder, by contrast, are quite unusual. The peak wintertime HNO3 concentration climbed as high as 1.40 µg m⁻³ for a single sample collected from February 22nd–25th in 2008. A closer look at the HNO3 timeline in Fig. 1 reveals frequent winter periods of elevated HNO3 concentrations. Other measurements at Boulder reveal that this area is frequently subject to periods of elevated winter ozone (Schnell et al., 2009) that occur during sunny winter periods when snow covers the ground. Strong nocturnal and morning temperature inversions that set up under these conditions trap local emissions of NOx and volatile organic compounds, associated largely with local energy production activities, in a shallow mixing layer while daytime photochemical activity is enhanced by strong reflectance from the bright snow surface. The photochemical reactions that generate ozone concentrations well in excess of the U.S. National Ambient Air Quality Standard can also lead to substantial oxidation of the locally emitted NOx to HNO3. While cold winter conditions favor reaction of HNO3 with NH3 to form fine particle NH4NO3 (as evidenced by the winter NH4NO3 spikes in Fig. 1), the Boulder observations reveal that all gaseous NH3 has often been consumed during these episodes leaving a substantial fraction of the HNO3 “trapped” in the gas phase.

Ambient NH4 concentrations at Boulder exhibited little seasonal pattern (Fig. 3c). The annual mean concentrations for 2007 to 2011 were also similar to each other at 0.29, 0.28, 0.23, 0.22 and 0.27 µg m⁻³, respectively. Formation of fine particle NH4 is influenced by a variety of factors, including the availability of gaseous NH3 and the availability of acidic sulfate aerosol and gaseous HNO3. Increases in NH3 and SO4²⁻ at Boulder during warmer months of the year will tend to increase NH4 concentrations as well. Formation of fine particle NH4NO3, however, is favored in winter. As previously discussed, the formation of NH4NO3 is thermodynamically favored by high relative humidity and low temperatures. During the winter in Boulder, the average temperature was −7.8 °C and average relative humidity was 72.5%. These offsetting seasonal patterns appear to result in an overall NH4 concentration pattern that shows little seasonality at Boulder.

Fig. 4. The seasonal variations of NH3 and HNO3 mixing ratios from 2007 to 2011. The plotted points are the seasonal mean values and the Y-error bars represent standard deviations.

![Fig. 4](image-url)

Fig. 5. Monthly variation of the ammonia conversion ratio (F_{NH3}) and nitric acid conversion ratio (F_{HNO3}). See text for details.

![Fig. 5](image-url)

Fig. 6. Comparison of the measured [NH3 (gas)[HNO3(gas)] product with the theoretical equilibrium constant for NH4NO3 as a function of temperature across the different seasons.

![Fig. 6](image-url)
The annual average concentrations of PM$_2.5$ NO$_3$ measured at Boulder were 0.30, 0.36, 0.29, 0.27 and 0.37 μg m$^{-3}$ in 2007 through 2011, respectively. The NO$_3$ concentrations exhibited a strong seasonality, with maximum values in winter and minimum values in summer (Fig. 3d). Because NH$_4$NO$_3$ formation is not favored under the warm, dry conditions of summer, the mean summer NO$_3$ concentration was only 0.11 μg m$^{-3}$. In winter, it increased to 0.60 μg m$^{-3}$, as NH$_4$NO$_3$ formation was more strongly favored. As indicated in Fig. 3d, considerable variability was also observed in winter NO$_3$ concentrations, similar to the pattern discussed above for HNO$_3$, with maximum observed concentrations exceeding 2.0 μg m$^{-3}$ in December, January, February, and March.

SO$_4^{2-}$ shows a seasonal cycle with maximum values in the warm season (Fig. 3e). This seasonal pattern is typical of SO$_4^{2-}$, due to enhanced photochemical activity and higher concentrations of hydroxyl radical, which can oxidize SO$_2$ to SO$_4^{2-}$ (Behera and Sharma, 2010). In-cloud oxidation of SO$_2$ to SO$_4^{2-}$ can also be enhanced in summer when hydrogen peroxide concentrations are typically higher. Annual average concentrations of SO$_4^{2-}$ at Boulder in 2007 through 2011 were 0.54, 0.53, 0.47, 0.38, and 0.47 μg m$^{-3}$.

In addition to anthropogenic emissions of nitrogen and sulfur species, wild and prescribed fires also contribute significantly to fine particle concentrations in the western U.S. (Jaffe et al., 2008; Malm et al., 2004). Water soluble potassium ion concentrations, one marker of biomass burning (Andreae, 1983; Duan et al., 2004), were elevated in summer (Fig. 3f). The average concentration of K$^+$ in the summer was 0.03 μg m$^{-3}$, which was nearly three times higher than the value in the winter (See Table S1). Not surprisingly, summer K$^+$ concentrations varied substantially; interannual variability in fire occurrence and the influence of emissions from fires that do occur on air quality at Boulder are expected. Across the sampling period, a number of wild fires occurred upwind of the site in summer.

Given the seasonally varying partitioning of NH$_3$/NH$_4$ and HNO$_3$/NO$_3$ between the gas and particle phases, it is useful to also examine seasonal changes in total reduced inorganic nitrogen in the −3 oxidation state [N(-III) = NH$_3$ + NH$_4$] and in total oxidized inorganic nitrogen in the +5 oxidation state [N(+V) = HNO$_3$ + NO$_3$]. As illustrated in Fig. 3g, N(-III) concentrations show a peak in the summer months, consistent with higher NH$_3$ emissions and greater SO$_4^{2-}$ concentrations at this time of year. N(+V) concentrations, by contrast, peak in the winter months. This winter peak reflects the formation of HNO$_3$ in a shallow boundary layer during winter ozone episodes as well as winter formation of fine particle NH$_4$NO$_3$, with its longer atmospheric residence time than HNO$_3$.

To investigate the seasonal phase changes of NH$_3$/NH$_4$ and HNO$_3$/NO$_3$, we define the ammonia gas fraction ($F_{NH_3}$ = the NH$_3$ gas concentration divided by the sum of the NH$_3$ gas and fine particle NH$_4$ concentrations) and the nitric acid gas fraction ($F_{HNO_3}$ = the HNO$_3$ gas concentration divided by the sum of the HNO$_3$ gas and fine particle NO$_3$ concentrations), where all concentrations are expressed in molar units. The monthly average partitioning for the reduced and oxidized inorganic nitrogen forms is plotted in Fig. 5. There was a gradual transition from the cooler months, when the particle phase was favored, to the warmer months, when the gas phase was favored, for both species. A maximum monthly average

![Fig. 7. Comparison of average levels of gases and aerosol species concentrations for this study and other sampling locations in the western U.S. There was no measurement of NH$_4$ and HNO$_3$ at Craters of the Moon National Monument, Idaho. Concentrations are in μg m$^{-3}$. More information about the comparison data can be found in Table S3.](image-url)
in the gas phase fraction of NH₃ occurred in July (0.64). This was more than 10 times higher than the minimum monthly average of 0.06 which occurred in January. Similarly, the HNO₃ gas fraction (F_{HNO₃}) was found to be highest in summer (0.73 in July) and lowest in winter (0.24 in January). The high summer level of F_{HNO₃} also reflects the tendency for NH₄NO₃ to dissociate to NH₃ and HNO₃ at high temperature. The high summer level of F_{HNO₃} reflects greater NH₃ emissions and the thermodynamic tendency for NH₄NO₃ to dissociate to NH₃ and HNO₃ at high temperature. The higher summer value of F_{HNO₃} also reflects the tendency for NH₄NO₃ to dissociate at higher temperatures. The still appreciable winter F_{HNO₃} level, which is not typical of previous results (Bari et al., 2003; Gupta et al., 2003; Sharma et al., 2007), reflects the continued photochemical production of HNO₃ at levels which exceed the amount of NH₃ available to participate in NH₄NO₃ formation.

Shifts in the equilibrium partitioning among gaseous NH₃ and HNO₃ and particulate NH₄NO₃ depend on relative humidity (RH), temperature (T), and the concentrations of NH₃ and HNO₃. Ambient relative humidity at the Boulder measurement site was usually less than the deliquescence relative humidity (DRH) of NH₄NO₃ so that we can simplify matters and consider here formation of solid NH₄NO₃. Under this condition, this reaction’s equilibrium constant (K_p) is the expected product of the NH₃ and HNO₃ concentrations and is given by the empirical formula (R1):

\[ \ln K_p = \frac{84.6 - \frac{24200}{T}}{6.1} - \frac{\ln T}{298} \]  

where \( K_p \) is in units of ppbv² and \( T \) is measured ambient temperature in Kelvin (Stelson and Seinfeld, 2007). The measured, apparent reaction constant (\( K_m \)) can be described as follows (R2):

\[ K_m = \frac{[\text{NH}_3] \times [\text{HNO}_3]}{[\text{NH}_4^+] \times [\text{NO}_3^-]} \]

where \([\text{NH}_3]\) is the gaseous NH₃ mixing ratio (ppbv) and \([\text{HNO}_3]\) is the gaseous HNO₃ mixing ratio (ppbv). NH₄NO₃ formation is favored when \( K_m \) exceeds \( K_p \). Fig. 6 shows the variation of both the theoretical equilibrium constant (shown as a solid line) and measured constant values (for each sample) with temperature (1000/T) across all seasons. This presentation of the data clearly illustrates that NH₄NO₃ formation is only favored during winter-time; even then, it is not favored during all sample periods. At warmer times of the year, the product of NH₃ and HNO₃ concentrations is insufficient to yield NH₄NO₃ formation at seasonal temperatures.

3.2. Comparison with other measurements

Fig. 7 presents a comparison of observations from this study with other observations from the Clean Air Status and Trends Network (CASTNET; http://www.epa.gov/castnet/), the Interagency Monitoring of Protected Visual Environments (IMPROVE; http://vista.cira.colostate.edu/improve), the National Atmospheric Deposition Program Ammonia Monitoring Network (AMoN; http://nadp.sws.uiuc.edu/amon/) and seven sets of ambient composition measurements completed by our lab at CSU in the western U.S. (Table S3). Concentrations of particle and gas phase species observed at Boulder were, overall, among the lower average concentrations measured across this set of western sites. Comparing mean values of NH₃ and HNO₃ and fine particle NH₄⁺, NO₃⁻, and SO₄²⁻ at Boulder with the other rural locations, the concentrations...
measured at Boulder were generally lower than those observed at sites further east such as Santee Sioux, South Dakota, Konza Prairie, Kansas, Cherokee Nation, Oklahoma, and Palo Duro, Texas. They were also significantly lower than concentrations measured closer to more populated areas, such as those at Sequoia National Park, California, Joshua Tree National Park, California, and Loveland, Colorado. Boulder, Wyoming NH₃ concentrations were substantially lower than NH₃ concentrations measured at sites more strongly impacted by regional agriculture/animal feeding operations, such as Brush, Colorado. Overall concentrations were fairly similar, however, between Boulder and other remote sites in central and western Colorado and in western Wyoming, suggesting some regional representativeness of the concentrations measured in Boulder (aside from the winter ozone episodes). Although the Boulder measurement site is only approximately 65 km from the Snake River Plain Valley, an area of intense agricultural activity with high NH₃ emissions (Clarisse et al., 2009), the low NH₃ concentrations observed at Boulder suggest that the Wyoming (Palisades) Mountain Range blocks at least the most direct transport of these emissions while other local NH₃ emissions are limited in their contributions to ambient NH₃ concentrations.

3.3. Interspecies correlations, the measured ion charge balance, and the importance of organic acids

Fig. 8 illustrates the correlation between fine particle NH₄⁺ and SO₄²⁻ in different seasons. Significant correlations were found in all seasons except in winter. The highest correlation ($r^2 = 0.84$) was in the fall and the lowest was in the winter ($r^2 = 0.15$). The weak correlation in winter results from substantial NH₄NO₃ formation during this time period. If one plots the excess NH₄⁺ (the amount beyond that needed to fully neutralize fine particle SO₄²⁻), one finds it to be strongly correlated with fine particle NO₃⁻ during winter ($r^2 = 0.76$; slope of 0.81), modestly correlated in fall ($r^2 = 0.31$; slope of 1.01), and showing almost no correlation in spring and summer (see Fig. S3).

Overall, on the basis of the seasonal variation of comparisons between NH₄⁺ and SO₄²⁻ and excess NH₄⁺ and NO₃⁻, one can conclude that most fine particle NH₄⁺ in summer exists as (NH₄)₂SO₄ while both (NH₄)₂SO₄ and NH₄NO₃ are found in fine particles in winter. An excess of NH₄⁺ in summer when NO₃⁻/C₀ concentrations are low, however, suggests that other unmeasured anionic species might also be important components of the

![Fig. 9. Seasonal charge balance, where the different colors represent the various sampling periods. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
fine particles. This pattern also appears in some fall and spring samples. This issue can be further evaluated by considering the overall ionic charge balance of measured fine particle anion (NO$_2^-$, NO$_3^-$, SO$_4^{2-}$) and cation (NH$_4^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$) concentrations. Fig. 9 presents the seasonal variation of the ionic charge balance. During spring and winter, the charge balance is very close to 1:1. During fall and, especially, summer, however, the charge balance generally indicates a deficiency of anions. Previous studies (Barsanti et al., 2009; Trebs et al., 2005) have reported that organic acids such as oxalic acid can be important contributors to the charge balance of fine mode aerosols. The warm season anion deficit observed here is consistent with higher organic acid concentrations during summer, coinciding with periods of enhanced photochemical production of secondary organic aerosols and increased biomass burning. Future measurements of summertime Boulder fine particle concentrations will include analysis of oxalate.

4. Conclusion

A five-year study of concentrations of gaseous NH$_3$ and HNO$_3$ and of fine particle inorganic ions was conducted in an active gas production region in Boulder, Wyoming. The five-year annual mean concentrations of NH$_3$, HNO$_3$, NH$_4$NO$_3$, NO$_2$, and SO$_2$ were 0.17, 0.19, 0.26, 0.32, and 0.48 $\mu$g m$^{-3}$, respectively. NH$_3$ exhibited a strong seasonal variation, with higher concentrations during the summer and lower concentrations during the winter. The low annual average NH$_3$ mixing ratio of 0.30 ppb suggests that the default value of 1 ppb often used in regional assessments of visibility impacts from NO$_x$ source emissions is higher than necessary.

Observed NH$_3$ concentrations correlated well with ambient temperature indicating the important influence of temperature on emissions and, likely, the greater long distance transport of those emissions during warmer times of year when mixing layers deepen. By contrast, higher concentrations of particulate NO$_2$ were observed in the winter when lower temperatures favor formation of NH$_4$NO$_3$. HNO$_3$ concentrations showed an unusual bimodal seasonal variation with higher levels both in summer (an expected result of active photochemical oxidation and a tendency for NH$_4$NO$_3$ to decompose at higher temperatures) and in winter. The unusual winter HNO$_3$ peak appears to be the result of active photochemical processing of local NO$_x$ emissions in a shallow boundary layer during periods of snow cover and a lack of NH$_3$ to fully tie up HNO$_3$ through fine particle NH$_4$NO$_3$ formation. Examination of the equilibrium thermodynamics of NH$_4$NO$_3$ formation, seasonal local temperatures, and available concentrations of gaseous NH$_3$ and HNO$_3$ indicates that NH$_4$NO$_3$ should be expected primarily in winter, as observed.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2013.10.007.


