NH₃ Monitoring in the Upper Green River Basin, Wyoming

Extended Abstract #70

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INTRODUCTION

A long term ammonia air monitoring study was initiated in December, 2006 at Boulder, Wyoming, by Shell Exploration & Production Company. The monitoring site is located in the Upper Green River Basin of western Wyoming southwest of the Bridger Wilderness, a Class I area with an IMPROVE monitoring site. This region is experiencing rapid development of natural gas resources with possible consequences of air quality and visibility impacts in the Bridger Wilderness. Only very limited short-term ammonia measurements were previously available for this region. Thus, the primary objective of this study is to characterize the local airborne nitrogen budget and, specifically, ammonia concentrations and concentrations of related gases and particles in the basin for at least one year. Gaseous and particulate samples were collected twice per week (integrated 3-day and 4-day samples) beginning December 15, 2006 and will continue through May, 2008. Samples were collected using coated annular denuders and stacked filters in a University Research Glassworks (URG) sampler. The Colorado State University Atmospheric Science Department provided laboratory-prepared sample media and laboratory analysis for gas and particle concentrations. Standard operating procedures, technical instructions, and a QAPP for instrument installation, operation and maintenance, field sampling, filter handling, and laboratory analyses were developed and submitted to Wyoming Department of Environmental Quality – Air Quality Division.
MONITORING AND LABORATORY PROCEDURES

Table 1 lists the instrumentation used and parameters monitored for the Boulder station ammonia study. Scheduled denuder and filter changes were performed twice per week, providing three- to four-day integrated samples for the duration of the study period. Ammonia concentrations and the concentrations of related gases and particles were measured using coated annular denuders and stacked filters in a University Research Glassworks (URG) sampler. The Colorado State University Atmospheric Science Department provided laboratory-prepared sample media and laboratory analysis for gas and particle concentrations. The two-channel sampler operated continuously, the air flow being controlled by a programmable pump with a mass flow sensor, and subsequent volumetric gas flow meters. The sampling method requires that metered air is drawn through a PM$_{2.5}$ size selective cyclone inlet, then through a series of annular denuders and filters. The denuders are coated with an acid-based substrate to collect ammonia gas. A second denuder is coated with NaCl to collect gaseous nitric acid. A subsequent stack of two filters is utilized to collect particles. A nylon filter collects particles, and a second, acid-coated filter collects any ammonia volatilized from collected, semi-volatile ammonium nitrate particles. The nylon filter retains any nitric acid volatilized from particulate ammonium nitrate. Following field exposure, the denuders, filters, and field data logs are sent to the CSU lab for chemical extraction and analysis. Total sampler air volume from the data sheet is then used to calculate concentrations.

Table 1: Instrumentation and Monitored Parameters Boulder, Wyoming Air Quality Station

<table>
<thead>
<tr>
<th>Component</th>
<th>Instrumentation</th>
<th>Height</th>
<th>Frequency</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>GASEOUS</td>
<td>URG denuders</td>
<td>1.5m</td>
<td>3-day and 4-day integrated samples</td>
<td>Ammonia, NH$_3$, Nitric Acid, HNO$_3$</td>
</tr>
<tr>
<td>PARTICULATE</td>
<td>URG stacked filters</td>
<td>1.5m</td>
<td>3-day and 4-day integrated samples</td>
<td>Ammonium, NH$_4^+$, Nitrate, NO$_3^-$, Sulfate, SO$_4^{2-}$</td>
</tr>
</tbody>
</table>

RESULTS

Figure 1 shows a timeline of gaseous and particulate concentrations from December, 2006 – January, 2008. Figure 2 plots the monthly mean, standard deviation, minimum, and maximum NH$_3$ concentrations. NH$_3$ concentrations are below 1 ppbv for most of the monitoring period, peaking in August, 2007 at 1.55 ppbv. Elevated NH$_3$ concentrations here coincide with warmer summer months. A shift in ammonium nitrate equilibrium toward the gas phase might be responsible for some of this increase, although an increase in total reduced nitrogen (ammonium + ammonia) during the summer suggests that changes in emissions and or transport patterns are likely also important contributors.
Three events stand out: high particulate NO\(_3^-\) in January, 2007; high particulate NO\(_3^-\) in December, 2007 – January, 2008; and high particulate SO\(_4^{2-}\) in May, 2007. The winter nitrate events are interesting as all reduced nitrogen is present as particle phase ammonium while considerable nitric acid remains in the gas phase. Sufficient increases in ammonia emissions during this period could have substantially increased PM\(_{2.5}\) concentrations by further ammonium nitrate formation.

Figure 3 displays a timeline of the gas/particle partitioning of the measured species for the same time period. Particulate sulfate (red) dominates throughout most of the year. Reduced nitrogen (green bars) shows an increased partitioning into the gas phase.
(ammonium to ammonia). Increased particulate nitrate in late winter is consistent with thermodynamic expectations: ammonium nitrate formation is favored at lower temperatures and higher relative humidities.

**Figure 3:** Timeline of gas-particle partitioning. Concentrations in μg/m³, top bar stack for particles, bottom bar stack for gases.

RESIDENCE TIME ANALYSIS

Ammonia weighted back trajectories were used to identify the geographic source areas most likely to contribute to the highest measured ammonia days. Back trajectory analyses use interpolated measured or modeled meteorological fields to estimate the most likely central path over geographical areas that provided air to a receptor at a given time. The method essentially follows a parcel of air backward in hourly steps for a specified length of time. Back trajectories account for the impact of wind direction and wind speed on delivery of emissions to the receptor, but do not account for chemical transformation, dispersion and deposition of emissions.

Trajectories were generated using the Hybrid-Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model developed by the National Oceanic and Atmospheric Administration’s (NOAA) Air Resources Laboratory (ARL). Detailed information regarding the trajectory model and these data sets can be found on NOAA’s Web site (http://www.arl.noaa.gov/ready/hysplit4.html).

Three back trajectories were generated per day, including end times of 0400, 1200 and 2000 MST and end heights of 100 m. Each hourly point along a 72-hour back trajectory paths was weighted with measured ammonia concentration corresponding to the end date of each trajectory. The ammonia values associated with each hourly point were then summed and normalized into 1/4 degree horizontal grid cells of latitude and longitude.

Figure 4 presents a map of the ammonia weighted residence time for 2007. One path of influence follows the Snake River from Idaho to the Columbia River. This is a significant
agriculture region. Another distinct path is from the South-Southwest along I-15 to Nevada then along the Colorado River. In addition to the major urban areas of Salt Lake City and Las Vegas, this pathway includes the agriculture regions of Star Valley north of Salt Lake City, the Wasatch front in Utah, and the Colorado River Basin.

**Figure 4:** NH$_3$ weighted residence time analysis for 2007.

### SUMMARY
A 15 month study in the Upper Green River Basin of Wyoming measuring ammonia and nitric acid gasses and ammonium, nitrate, and sulfate particles has been completed. The results of the study show that in the Upper Green River Basin of Wyoming 2007 ammonia concentrations are (1) quite variable throughout the year, (2) are below or near detectable limits from December through late February, (3) peak in August at 1.55 ppbv, and (4) have a yearly mean value of 0.24 ppbv. NH$_3$ weighted Residence time analysis indicates that much of the NH$_3$ present is transported into the region from agriculture and urban areas to the West and Southwest.