Factors contributing to elevated concentrations of PM$_{2.5}$ during wintertime near Boise, Idaho

George Ruchathi Mwaniki$^{1,2}$, Chelsea Rosenkranz$^{3,4}$, H. Will Wallace$^{1,5}$, B. Tom Jobson$^1$, Mathew H. Erickson$^1$, Brian K. Lamb$^1$, Rick J. Hardy$^1$, Rasa Zalakeviciute$^{1,7}$, Timothy M. VanReken$^1$

$^1$ Laboratory for Atmospheric Research, Department of Civil & Environmental Engineering, Washington State University, Pullman, Washington, USA
$^2$ Now at National Environment Trust Fund, Nairobi, Kenya
$^3$ Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, Washington, USA
$^4$ Now at Washington River Protection Solutions, LLC, Richland, Washington, USA
$^5$ Now at Department of Civil & Environmental Engineering, Rice University, Houston, Texas, USA
$^6$ Idaho Department of Environmental Quality, Boise, Idaho, USA
$^7$ Now at Department of Ecology & Evolutionary Biology, Cornell University, Ithaca, New York, USA

ABSTRACT

Wintertime chemical composition of water–soluble particulate matter with aerodynamic diameter less than 2.5 µm (PM$_{2.5}$) was monitored in the Treasure Valley region near Boise, Idaho. Aerosol was sampled using a Particle Into Liquid Sampler (PILS) and subsequently analyzed using ion exchange chromatography and a total organic carbon analyzer. During the two–month sampling campaign, the region experienced varying meteorological regimes, with an extended atmospheric stagnation event towards the end of the study. For all of the weather regimes, water–soluble PM$_{2.5}$ was dominated by organic material, but particulate nitrate showed the greatest variation over time. These variations in particulate nitrate concentration were found to be dependent on the time of day, nitrogen oxides (NO$_x$) concentrations, and relative humidity. The increases in particulate nitrate did not correlate with an equivalent molar increase of ammonium concentration, ruling out solid ammonium nitrate formation as the dominant source. Instead, our analysis using an online aerosol thermodynamic model suggests that the condensation of gas phase nitric acid was possible within the meteorological conditions experienced during the study. In running this model, atmospheric chemical and physical parameters close to those observed during the study were used as model input. The simulation was run for three different scenarios, representing the different meteorological regimes experienced during the study. From the simulation particulate nitrate concentration was highest during cold and humid nights. Currently this region is in attainment with the National Ambient Air Quality Standards (NAAQS) for PM$_{2.5}$; however, with the projected increase in population and economic growth, and the subsequent increase in NO$_x$ emissions, these episodic increases in particulate nitrate have the potential of pushing the area to non–attainment status.

Keywords: Atmospheric inversion, Boise, Treasure Valley, particulate material, nitrate

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1. Introduction

Exposure to ambient PM$_{2.5}$ has been found to correlate with an enhanced risk of cardio–respiratory diseases (Pope et al., 2004). The adverse health effects associated with fine particulates even at low concentrations prompted the United States Environmental Protection Agency (U.S. EPA, 2012) to lower the 24–hr PM$_{2.5}$ standard from 65 µg m$^{-3}$ to 35 µg m$^{-3}$. This new standard is expected to increase the number of areas classified as being in non–attainment for PM$_{2.5}$. This anticipated reclassification would likely include portions of the Treasure Valley, a region that extends from the low–lying areas of southeastern Oregon into southern Idaho and encompasses the Boise metropolitan area. Currently the Treasure Valley is in attainment for PM$_{2.5}$, but this status is at risk due to the lowered standard and the rapid economic and population growth in the area surrounding Boise.

Wintertime stagnation periods are of particular importance in the Treasure Valley since historical data suggest that the region experiences its worst particulate concentrations during this time of the year. Episodes of increased PM$_{2.5}$ concentrations are common in this region during winter months and they can last several days or more. These events are driven by a combination of topography, meteorological factors, and chemical emissions. The most salient feature of these events is the presence of stagnant air. During winter at high latitudes, long nights and short days with low solar angle significantly reduce surface heating. Enhanced surface reflectivity due to the presence of snow can further decrease radiative heating at the surface. These conditions often lead to a persistent surface temperature inversion, and the resultant stable boundary layer strongly inhibits vertical mixing. When a high pressure condition exists in this area, horizontal winds are greatly reduced, and valley topography can further inhibit horizontal mixing. Combined, these effects result in a situation where emissions can remain close to the surface near their source location for extended periods of time, allowing pollution to build up to hazardous levels. These so–called wintertime stagnation events have not been as thoroughly studied as warm–weather smog conditions, but they have been observed in many locations around the world, including the mid–western United States (Katzman, 2010; Stanier et al., 2012), the western United States (Chen et al., 2012), Utah’s Cache Valley (Silva et al., 2007), London (Bower et al., 1994), the Chamonix Valley in the French Alps (Chazette et al., 2005), and near Shanghai, China (Shan et al., 2010). In 2004, using data from the EPA’s Speciation Trends Network (STN), Chu (2004) found these stagnation events to be a

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frequent cause of elevated wintertime particulate matter (PM) concentrations in the continental United States.

Wintertime stagnation events have also been observed in Idaho’s Treasure Valley, in Boise and the surrounding areas (Wolyn and McKee, 1989). This area’s topography can be characterized as a U-shaped valley with a relatively flat bottom; Figure 1 shows a topographic map of the region. Previous studies have found that particulate levels in the Treasure Valley are highest between December and February (Kuhns et al., 2003; Stockwell et al., 2003). The region is already a maintenance area for CO and PM$_{10}$, and recent revisions to the NAAQS are expected to lead to an increase in PM$_{2.5}$ exceedances.

In anticipation of this possible outcome, a two–month observational study, called Treasure Valley PM$_{2.5}$ Precursor Study, was conducted within an urbanized part of the Treasure Valley during the winter of 2008–09. This study was aimed at characterizing and understanding the processes that lead to the elevated wintertime PM$_{2.5}$ concentrations in the region. While the fundamental meteorological drivers of the pollution events are generally understood, the specific chemical drivers for PM$_{2.5}$ loadings during the events are not, making it difficult to forecast when PM$_{2.5}$ levels would exceed the air quality standards.

During the study, the region experienced several dry and several wet periods as well as an extended atmospheric stagnation event, allowing for the characterization of the PM$_{2.5}$ and its precursors under different atmospheric conditions. In this manuscript we discuss the aerosol measurements collected during the study. The data reveal several periods where significant production of particulate nitrate occurred; our analysis explores possible pathways that could lead to such production and evaluates whether the observations are consistent with this proposed pathways.

2. Experimental Methods

2.1. Site description

The experiment was based at the Idaho Department of Environmental Quality’s (IDEQ) regional air quality monitoring site in Meridian, Idaho (the “St. Luke’s” site, latitude 43.6008 N, longitude 116.3484 W, and elevation 811 meters), approximately 11 km west of central Boise. Measurements occurred from December 1, 2008 until January 31, 2009. During the study, instruments were located in a temporary trailer in a flat, empty field behind St. Luke’s Hospital near the intersection of Interstate Highway 84 and Eagle Road. Except for equipment transport, there was no vehicle traffic within 100 m of the measurement site. Interstate 84, the most heavily traveled road in the region, was located approximately 300 m to the south running in an east–west direction.

2.2. Methodology and instrumentation

Instruments were housed in a climate–controlled trailer at the sampling site. Sample inlet lines for particle measurements were mounted to the outside of the trailer and consisted of vertically oriented 15 mm internal diameter copper tubes. The particle inlets were approximately 3 m above the ground level, roughly equal in height to the trailer’s roof. The lines were mildly heated to prevent ice formation within the tube. Aerosol size distribution and chemical composition were monitored during the study. In addition, ambient concentrations of nitrogen dioxide (NO$_2$), nitrogen oxide (NO), NO$_x$ (NO+NO$_2$+other oxidized species), ozone (O$_3$), and selected volatile organic compounds were also monitored, as were local boundary layer meteorological conditions. This manuscript will only concentrate on measurements most relevant to the current analysis, primarily the ambient particulate measurements.

![Figure 1. Treasure Valley topographical map showing the major roads and cities in the region. The sampling site was located in Meridian.](image-url)
Particle size distribution. Particle size distributions between 13 and 820 nm were monitored using a custom-built scanning mobility particle sizer (SMPS) with major components from TSI Inc. (Shoreview, MN). This SMPS, herein referred to as the long–SMPS, consisted of a long differential mobility analyzer (DMA, TSI Model 308100) and a TSI Model 3771 condensation particle counter (CPC). During the last three weeks of the study (beginning on January 7, 2009), an aerodynamic particle sizer (APS, TSI Model 3321) was used to monitor larger particles with aerodynamic diameters between 505 nm and 20 μm. These two instruments employ different principles in sizing the particles and as a result, single particle spectrum from these two instruments is usually estimated by considering the SMPS up to a certain diameter and then beyond this diameter the APS is used (Shen et al., 2002). In estimating PM$_{2.5}$ mass from the particle size distribution data, these two instruments were used with the following size ranges: 20 nm to 820 nm for the long–SMPS and 820 nm to 2.45 μm for the APS.

Additional particle data were collected by IDEQ using tapered element oscillating microbalances (TEOM, Model 1400A, Thermo Fisher Inc., Waltham, MA). One of the TEOMs was located at the St Luke’s sampling site and another at the Nampa monitoring site, located approximately 17 km to the southwest of the St Luke’s site. The Nampa TEOM was operational from the start of the study period until January 20, 2009, while the St Luke’s TEOM was operational from January 2, 2009, until the end of the study.

Water–soluble PM$_{2.5}$ composition. Water–soluble PM$_{2.5}$ samples were collected at one–hour sampling intervals using a particle–into–liquid sampler (PILS, Brechtel Manufacturing Inc., Hayward, CA) from December 21, 2008 to January 17, 2009. The PILS was developed for continuous sampling of ambient water–soluble particulate material (Orsini et al., 2003; Sullivan et al., 2004). The instrument employs an impactor at the sample inlet for particle size selection; in this study an impactor with a size cut of 2.5 μm was employed. The PILS samples were collected at a volumetric flow rate of 15 liters per minute (lpm), controlled by an internal critical orifice. From the inlet the sampled air passes through a series of denuders that are designed to minimize gas–phase sampling artifacts by removing organic vapors and acidic and basic water–soluble gases. After the soluble gases are removed the sample passes into the condensation chamber where it is mixed with steam at +100°C. The mixing between the steam and the relatively cold ambient air induces a supersaturation condition in the chamber, which enables the condensational growth of the particles to collectable size. The grown, wet particles are then impacted onto a wetted surface and transported out of the condenser by a continuous wash of ultra high–purity water. The wash is spiked with a known concentration of lithium (Li$^+$) fluoride (F$^–$); Li$^+$ and F$^–$ are non–interfering ions that help quantify the sample dilution. Syringe pumps next transfer the solution containing the aerosol sample to one of a series of vials held in a rotating carousel atop the PILS. The carousel is capable of holding up to 38 vials, allowing for at most 36 hours of continuous sampling. During this study the carousel was usually changed after every 26 hours of sampling, which included 24 samples of ambient particles and two field blanks. Field blanks were collected to monitor the sampling method artifacts; they were obtained by routing the PILS sample flow through a particle filter immediately after the instrument’s inlet impactor and keeping all other instrument parameters unchanged.

Once a PILS run cycle was complete the samples were labeled and stored in a refrigerator at 5°C, and another carousel was loaded with empty vials for the next PILS run cycle. At the end of the field study all samples were transported to the Laboratory for Atmospheric Research at Washington State University where they were analyzed for bulk water–soluble organic carbon (WSOC) using a total organic carbon (TOC) analyzer (Sievers 5310C, Boulder CO), and for inorganic ions using dual ion chromatographs (Compact IC 761, Metrohm–Peak, Herisau, Switzerland).

Supporting meteorological and trace gas measurements. Surface level (10 m) meteorological data were collected at one–minute time resolution using a WXT510 weather transmitter (Vaisala, Finland). Ozone ($O_3$) concentration was monitored using a UV–absorption $O_3$ monitor (Dasibi, Glendale, CA). Nitrogen oxide (NO) and nitrogen dioxide (NO$_2$) were measured using a high–sensitivity NO$_2$/NO$_x$ instrument (Air Quality Design Inc., Wheat Ridge, CO). Carbon monoxide (CO) concentration was measured using vacuum–ultra–violet (VUV) fluorescence analyzer (Aerolaser GmbH., Germany). The weather station and trace gas inlets were mounted on a 10 m tower erected adjacent to the instrument trailer. A detailed description of the NO$_x$ and CO measurements during the study and their relationship to vehicle emissions are presented by Wallace et al. (2012).

Aerosol thermodynamic model. The online Extended Aerosol Inorganic Model II (E–AIM) (Clegg et al., 1998; UEA, 2013) was used during data analysis to evaluate possible pathways for aerosols formation during the study. This model is an online aerosol thermodynamic model which offers an interactive tool for calculating equilibrium in a gas–liquid–solid system containing the following ions, H$^+$, NH$_4^+$, SO$_4^{2–}$, NO$_3^{–}$, and H$_2$O. In this system the user has the liberty to define, add or remove any of the ions in calculating the equilibrium. This model works within the temperature range of 200 to 330 K. In running this model input parameters derived from the Treasure Valley study were used and only the following ions were considered: H$^+$, NH$_4^+$, SO$_4^{2–}$, NO$_3^{–}$, and H$_2$O.

3. Results

A summary of the major boundary layer meteorological variables are presented in Figure S1 (see the Supporting Material, SM). During the study, the region experienced varied boundary layer meteorological conditions, characterized by fluctuating temperature and relative humidity. In the last two weeks of the study, from January 13 to January 25, 2009, the local boundary layer meteorological conditions were characterized by persistent fog, low temperatures below freezing, mild winds mainly from the southeast, high relative humidity, and low incoming solar radiation.

3.1. Particle size distribution

An overview of the particle number concentration of the aerosol samples using the long–SMPS is summarized in Figure S2 (see the SM). The particle number concentration was generally high, and dominated by ultrafine particles (0.1–100 nm). Particle concentrations showed a distinct dependence on wind direction, with the highest particle concentrations being recorded when winds were blowing from the southeast (the most commonly observed wind direction during the study). The proximity of the interstate highway south of the study site suggests that vehicular activities may be the source of the enhanced particle concentrations. This conclusion is similar to what was observed in the NO$_x$ (NO+NO$_2$) and CO concentrations, where roadways nearby the sampling site were found to have a substantial influence (Wallace et al., 2012).

3.2. Water–soluble PM$_{2.5}$ composition

The dominant components in the PM$_{2.5}$ mass were organics, nitrate (NO$_3^{–}$), ammonium (NH$_4^+$) and sulfate (SO$_4^{2–}$), with NO$_x$ showing the greatest temporal variation. The Mass LOQ for each ion was calculated as the 95% confidence interval from the field blanks collected during the study. The LOQ for all the ions monitored during the study are shown in Table S1 (see the SM), along with a summary of the zero air statistics and the IC’s LOQ for monitored ions. Organics field blank concentrations are not included in Table S1 as these concentrations varied
considerably between PILS run cycles, presumably due to variability in the organic carbon concentration of the ultrahigh purity water used during field sampling.

Figure S3 (see the SM) shows the speciated water–soluble PM$_{2.5}$ mass concentrations as well as a time series of the relative humidity, temperature and the estimated PM$_{2.5}$ mass from particle size distribution data (long SMPS+APS) obtained during the sampling period. The estimated mass concentration of PM$_{2.5}$ from the size distribution data and the water–soluble mass as sampled by the PILS showed the same general temporal trends. During periods where the particulate concentrations are elevated, organics and nitrate are the dominant aerosol components, with nitrate showing the greatest temporal variability. The NO$_3^-$ variability corresponded closely to variations in the relative humidity, with the highest concentrations being observed during cold and humid periods. Even though the organics contribution to the PM$_{2.5}$ was the most significant, the focus here will be on particulate nitrate as it was the most unexpected result. In addition, the particulate organics data available from this study represents the bulk water–soluble organics, and therefore a complete characterization of the total organic aerosol is not possible.

Owing to the varied boundary layer meteorological conditions experienced during the study, the data set was divided into three categories to match the prevailing meteorological conditions. These were (1) low RH periods; (2) high RH periods before the stagnation event; and (3) the stagnation event. Even though NO$_3^-$ was not the only major driver of elevated PM$_{2.5}$ its wide concentration variability raises interesting questions about its atmospheric drivers, thus we have focused our analysis on its most probable formation pathways with respect to these three meteorological conditions.

In general the observed increase in NO$_3^-$ during humid periods did not correspond to similar increases in sulfate and ammonium. Consequently a molar imbalance in the speciated water–soluble PM$_{2.5}$ was observed frequently during the study. This suggested that at least part of the NO$_3^-$ observed during this study cannot be explained by the heterogeneous reaction between ammonia (NH$_3$) and nitric acid (HNO$_3$). The amount of NO$_3^-$ present beyond what can be neutralized by the available ammonium may be defined as the excess particulate NO$_3^-$ (ExNO$_3$). ExNO$_3$ was calculated following the approach of Pathak et al. (2008):

$$\text{ExNO}_3 = \text{NO}_3^- - \text{ExNH}_4^+$$  \hspace{1cm} (1)

$$\text{ExNH}_4^+ = \text{NH}_4^+ - 1.5 \text{SO}_4^{2-}$$  \hspace{1cm} (2)

For Equations (1) and (2), all concentrations are in molar units (i.e., nmol m$^{-3}$). Excess ammonium (ExNH$_4^+$) was defined assuming that sulfate was partially neutralized and that 1.5 moles of NH$_4^+$ are sufficient to partially neutralize each available mole of SO$_4^{2-}$ forming a mixture of ammonium sulfate and ammonium bisulfate aerosol (Pathak and Chan, 2005). This leads to a conservative estimate of ExNO$_3$; if a higher NH$_4^+$/SO$_4^{2-}$ ratio is used (e.g., NH$_4^+$/SO$_4^{2-}$=2.0), then the values of ExNO$_3$ would be greater than those reported here. Comparing the unneutralized nitrate directly to relative humidity reveals a strong relationship (see the SM, Figure S4). There were virtually no instances of unneutralized nitrate when the relative humidity was lower than 67%.

4. Discussion

The results indicate that during the study period organic matter dominated the PM$_{2.5}$ mass, followed by particulate nitrate; both of which showed significant temporal variability, making them the most important drivers of wintertime PM$_{2.5}$ in the region.

In the atmosphere, particulate NO$_3^-$ can be formed through several pathways that are each highly dependent on the local boundary layer meteorological conditions. One of the best understood and presumed dominant pathway is the heterogeneous neutralization of gaseous HNO$_3$ by gaseous NH$_3$ to form ammonium nitrate aerosol (NH$_4$NO$_3$). Particulate nitrate can also be formed through the nighttime chemistry of NO$_2$ as illustrated by reactions R1 to R3. The production of particulate nitrate through this mechanism is likely to contribute to the observed excess nitrate in the Treasure Valley. However, due to the limited data obtained during this study we are not able to conclusively assign the excess nitrate to this mechanism, and more research on this mechanism is needed.

$$\text{NO}_2(g) + \text{O}_3(g) \rightarrow \text{NO}_3(g) + \text{O}_2(g)$$ \hspace{1cm} (R1)

$$\text{NO}_3(g) + \text{NO}_2(g) \rightarrow 2\text{N}_2\text{O}_3(g)$$ \hspace{1cm} (R2)

$$\text{N}_2\text{O}_3(g) + \text{H}_2\text{O}(p) \rightarrow 2\text{HNO}_3(p)$$ \hspace{1cm} (R3)

Ambient particulate nitrate can also be formed through the condensation of gases HNO$_3$ into particle phase. This process is usually favored by low temperature and high relative humidity (Schlager et al., 1990) and it is reversible with reduced relative humidity and/or increased temperature. This process is further discussed in the aerosol thermodynamics model section of this manuscript.

4.1. Meteorological effects

Meteorological conditions appeared to have a direct effect on the amount of ExNO$_3$ observed in the samples. As a result, the study period was classified into three regimes as defined above. Table 1 presents a summary of the major aerosol and meteorological properties observed within each of these regimes. In the table, long–SMPS estimated mass is presented as representative of the aerosol mass loading because it was operational throughout the study. A one–hour average relative humidity of 67% was chosen as the boundary between the low and high relative humidity regimes, based on our comparison of the percentage of neutralized particulate nitrate by the available ammonium to the relative humidity (see the SM, Figure S4). Throughout the stagnation event the relative humidity remained above 67% and therefore this entire period was classified as high relative humidity.

Low relative humidity periods. These periods exhibited much lower aerosol mass loadings compared to the other two meteorological regimes. Water–soluble PM$_{2.5}$ mass during this period featured contributions by organics, NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$. Organics and NH$_4^+$ were the largest measured mass components, though their combined mass was generally less than 5.0 μg m$^{-3}$. Throughout this period, virtually no instances of ExNO$_3$ were observed. This suggests that under low RH conditions the dominant aerosol nitrate production mechanism was via the solid NH$_4$NO$_3$ formation pathway.

High relative humidity periods. All major water–soluble aerosol species were elevated within this regime relative to the low RH regime. The increase in PM$_{2.5}$ mass was predominantly a result of increases in the organics and nitrate concentrations. The increase in nitrate averaged over this regime was more than six–fold compared to the low RH periods, while the increase in organics was approximately two–fold. However, the organics temporal variability was much higher relative to nitrate, suggesting that RH was not the only significant contributor to the variability in organics. The observed increase in nitrate did not correspond to similar increases in other ion concentrations; most notably, NH$_4^+$ exhibited a much smaller change relative to the low RH period. The presence of unneutralized nitrate indicates that the dominant formation pathway for the observed nitrate was not the neutralization of HNO$_3$ by NH$_3$ to form solid ammonium nitrate.
**Table 1. Summary of the water soluble PM$_{2.5}$ ions for the different sampling periods during the study. Values below the limit of quantitation are marked as BLOQ.** In the table 'N' is the number of data points, 'Avg' is the average value, 'Max' is the maximum value, 'Min' is the minimum value, 'StdDev' is the standard deviation, 'WSO' is the water soluble organic mass, 'RH' is the relative humidity and 'TWS' is the total water soluble PM$_{2.5}$

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<th>Chloride$^a$</th>
<th>Nitrate$^a$</th>
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<th>Ammonium$^a$</th>
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<th>TWS PM$_{2.5}$$^a$</th>
<th>Mass estimate$^a$</th>
<th>Long-SMPS dN$^b$</th>
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<td>22.3</td>
<td>7</td>
<td>7 500</td>
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<td>0.1</td>
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<td>0.1</td>
<td>0.1</td>
<td>4.6</td>
<td>2.9</td>
<td>6</td>
<td>5 600</td>
</tr>
</tbody>
</table>

$^a$ Units are µg m$^{-3}$

$^b$ Units are cm$^{-3}$

$^c$ Units are °C

$^d$ Units are %

$^e$ Represents values as monitored by the long–SMPS only

A typical period representing this regime spanning from January 5 to January 6, 2009 is shown in Figure 2a. The average temperature and relative humidity for this representative two–day period were $-1.4±2.4$ °C and 92.0±1.5%, respectively. PILS mass averaged 14.3±11.2 µg m$^{-3}$. During this ~24–hour period, ExNO$_3^-$ exhibited a diurnal pattern, where it increased gradually during the night and decreased during the day. The increase in the NO$_3^-$ (and ExNO$_3^-$) did not correspond with an increase in the particle number concentration.

**The stagnation event.** From January 13 to 25, 2009 the Treasure Valley experienced an extended atmospheric stagnation event; a representation of the speciated water–soluble PM$_{2.5}$ for a portion of this event is presented in Figure 2b. Speciated PM$_{2.5}$ samples were only collected during the first few days of the stagnation event, and therefore the aerosol composition data presented here is not necessarily representative of the entire event. During the portion of the stagnation event when the PILS was operational, organics accounted for more than 65% of the total water–soluble PM$_{2.5}$ mass. Nitrate was the second largest contributor of PM$_{2.5}$ mass. The ExNO$_3^-$ concentrations during this period were lower than those during the high RH periods before the stagnation event, but remained positive. The aerosol number concentration during this period was also relatively smaller than for the other two regimes. However, during this period we observed an increase in aerosol number concentrations monitored by the APS, which meant there was a shift in the aerosol number concentration from smaller particles to bigger particles. During the selected analysis period (January 14–15, 2009, Figure 3b) the average mass of PM$_{2.5}$ as monitored by the PILS was 13.9±11.4 µg m$^{-3}$. ExNO$_3^-$ was positive for the selected analysis period, as it was in general for this regime, but its magnitude was smaller than it was during the high RH period before the stagnation.

![Figure 2](image-url)
5. Results Interpretation

To help interpret the results observed in the different meteorological regimes, we examined the time series of the particle data in conjunction with the coincident gas phase measurements and meteorological data. When the individual aerosol nitrate formation events were examined, several patterns emerged.

Figure 3a shows an example of a nighttime sampling period when an increase in NO$_3^-$ concentration was observed. This episode occurred concurrently with an increase in NO$_2$ concentrations from <5 ppbv to >30 ppbv starting at around 5 pm. At the start of this episode NO concentration was low (<5 ppbv) and remained low for ~3 hours from the start of the episode. At the start of this episode temperature was below freezing at −5 °C and an abrupt increase in RH from 55% to 73% was observed. The initial hours of this episode inconveniently coincided with the collection of blank samples by the PLS instrument, so the nitrate formation during the first two hours of this episode was not measured. However, when the PLS returned to normal sampling at approximately 7 pm, a considerable increase in NO$_3^-$ was observed; the large jump in nitrate concentration is highly suggestive that its buildup began during the period between 6 pm and 7 pm when PLS data are not available. This assumption is also corroborated by the considerable increase in aerosol surface area, which started at around 6 pm. Ammonium concentrations remained below the LOQ throughout this period, a strong indicator that homogeneous gas phase reaction between NH$_3$ and HNO$_3$ was not the source of this nitrate. Concurrent with the presumed rise in aerosol nitrate concentration between 6 pm and 7 pm, a peak in the NO$_2$ concentration was also observed. Later, beginning around 8 pm, an increase in the NO concentration from <5 ppbv to above 50 ppbv was observed, which coincided with the start of a gradual decrease in the aerosol nitrate concentration.

Figure 3b illustrates another nitrate formation event that occurred before the stagnation period. Here, nitrate concentrations were observed to increase beginning on the evening of January 5, 2009. At this time, NO concentrations were well below 5 ppbv, while NO$_2$ was ~20 ppbv, RH was ~91%. The aerosol nitrate concentration continued to build throughout the night, and then started to drop after sunrise on January 6 before reaching a minimum concentration around midday. This drop in particulate nitrate concentration during the morning hours coincided with an increase in NO concentration from 5 ppbv to more than 50 ppbv. A slight increase in temperature from −3 °C to 2 °C was also observed.

Increased NO$_3^-$ production was also observed during the stagnation event (Figure 3c). During the event, the observed concentration of NO$_3^-$ did not show as much variation as during the high RH period before the event. During the period highlighted in Figure 3c, we also observed an increase in ammonium concentration, but the aerosol nitrate concentration remained above what the available ammonium could neutralize. The major difference between the high relative humidity period before the stagnation and during the stagnation period is the relatively smaller increase in EnNO$_3^-$ in the latter case. During the high RH period before the stagnation, a much greater increase in NO$_3^-$ was observed than during the stagnation event.

5.1. Aerosol thermodynamics model

One of the possible sources of the observed excess particulate nitrate is the partitioning of gas phase nitric acid to particulate nitrate. The partitioning of nitrate between gas, solid, and aqueous phases is determined by evaporation and condensational processes. For submicron particles these thermodynamic processes (condensation/evaporation) can be fast enough to achieve thermodynamic equilibrium within atmospherically relevant timescales (Dassios and Pandis, 1999; Cruz et al., 2000). This partitioning is usually highly dependent on meteorological conditions, in particular on ambient RH and temperature. To investigate whether this mechanism was capable of producing the amount of observed excess particulate nitrate, we used the online Extended Aerosol Inorganic Model II [E–AIM] (Clegg et al., 1998; UEA, 2013). We also calculated the aerosol water content for an H$^+$, NH$_4^+$, SO$_4^{2-}$, NO$_3^-$ and H$_2$O system, for conditions similar to those during our study. The model results indicated that the aerosol water content was very low when the RH was below ~67%, with an average value of 2.5 μm$^{-3}$. For RH values above 67% the water content increased to an average value of 21.4 μm$^{-3}$. The model was simulated for three scenarios. These scenarios were differentiated by the model input, where these inputs were selected to match the scenarios shown by Figure 3a–3c.

In the first simulation we evaluated whether the particulate nitrate observed in Figure 3a could have been generated by the condensation of nitric acid. In this run concentrations corresponding to the concentrations observed during the episode shown in Figure 3a were used as model inputs. The following concentrations were used, 40 nmol m$^{-3}$, 5 nmol m$^{-3}$, 10 nmol m$^{-3}$ and 40 nmol m$^{-3}$ for NO$_3^-$, SO$_4^{2-}$, NH$_4^+$, and H$^+$, respectively. The
model was run by varying RH between 60 and 78%, while temperature was held constant at 270 K. In addition to these inputs, ice formation was suppressed. Results from this model run are shown in Figure 4a. In this run the condensation of gas phase nitric acid contributed \(-0.11\) nmol m\(^{-3}\) (\(-0.01\) µg m\(^{-3}\)) to the particulate nitrate concentration. This was very low compared to the observed excess nitrate during this period (24 nmol m\(^{-3}\)), which suggests that the condensation of nitric acid was not the sole source of the observed excess nitrate during this episode. The coincident increase in excess nitrate and NO\(_2\) suggests that N\(_2\)O\(_5\) chemistry might have played a bigger role in the observed excess nitrate during this period. However, the data obtained during this study are inadequate to address this.

In the second simulation we evaluated the effects of temperature on the observed excess nitrate, in this run concentrations of NO\(_3^–\), SO\(_4^{2–}\), NH\(_4^+\), and H\(^+\) corresponding to the values observed in the episode represented by Figure 3b were used as model inputs. These concentrations were: 300 nmol, 15 nmol, 170 nmol and 140 nmol for NO\(_3^–\), SO\(_4^{2–}\), NH\(_4^+\), and H\(^+\) respectively. During this run RH was held constant at 91%, while temperature was varied between 270 and 278 K. Ice formation was also suppressed during this run. Results from this run are shown in Figure 4b. In this run the partition of particulate nitrate back to nitric acid offers a partial explanation for the observed drop in particulate nitrate with temperature rise as in Figure 3b. This partitioning accounted for 10 nmol m\(^{-3}\) (0.62 µg m\(^{-3}\)) reduction in particulate nitrate concentration. However, the observed drop in particulate nitrate during this episode was \(\approx\)250 nmol m\(^{-3}\) (15.5 µg m\(^{-3}\)). This discrepancy between what the model predicts and what was observed can possibly be explained by other boundary layer dynamics associated with increases in temperature, such as the increase in mixing height. On the other hand, this run did not offer an explanation for the observed rise in particulate nitrate during the first half of the episode represented by Figure 3b. This suggests that other particulate nitrate forming mechanism other than the condensation of nitric acid was responsible for the observed rise in particulate nitrate during this episode.

Figure 4c shows the results obtained by simulating the case presented by Figure 3c. In simulating this episode, concentrations corresponding to the concentrations observed during the episode were used as model inputs. The following concentrations were used, 230 nmol, 40 nmol, 160 nmol, and 150 nmol for NO\(_3^–\), SO\(_4^{2–}\), NH\(_4^+\), and H\(^+\), respectively. During this run temperature was held constant at 270 K and relative humidity was varied between 75% and 99%. As in the other two runs ice formation was also suppressed. From this simulation, condensation of nitric acid into particulate nitrate offered the best explanation for the observed excess nitrate during this episode. From the model condensation of nitric acid accounted for 123 nmol m\(^{-3}\) (7.81 µg m\(^{-3}\)) of the observed excess nitrate, while from the field observation the excess nitrate during this period peaked at 150 nmol m\(^{-3}\) (9.30 µg m\(^{-3}\)). These two values are within the measurement uncertainty and therefore it is reasonable to postulate that the observed excess nitrate during this episode was more likely to be as a result of nitric acid condensation.

From these three model simulations condensation of nitric acid only offers a partial explanation for the observed excess nitrate. It is important to mention that the first two episodes where condensation of nitric acid did not explain the observed excess nitrate were observed during night time hours. While the episode where nitric acid condensation explained the observed excess nitrate occurred during daytime hours. This difference in time between the episodes suggests that nighttime chemistry between NO\(_2\) and O\(_3\) as illustrated in reactions R1 to R3 could be a leading cause of the observed excess nitrate during nighttime hours. However, due to the limited data obtained during this study, it is not possible to evaluate the role this mechanism played in the observed particulate nitrate increases and therefore we recommend a more focused study to evaluate this proposition.

6. Conclusion

Wintertime chemical and physical characterization of PM\(_{2.5}\) was carried out for Idaho’s Treasure Valley. Particulate organic matter and particulate nitrate were found to be the major contributors to the PM\(_{2.5}\) mass loading in this region, with their concentration depending in large part on the local boundary layer meteorological conditions. During the study period, the region experienced different boundary layer meteorological regimes, which included an atmospheric stagnation event. To better characterize the meteorological impacts on the speciated PM\(_{2.5}\) mass loading, the data obtained during the study period were divided into three sets in accordance with the local meteorological conditions. Water–soluble PM\(_{2.5}\) mass concentrations were lowest during the low RH periods and highest during the stagnation event. The high RH periods were characterized by a significant increase in particulate NO\(_3^–\) concentration especially if the high RH condition existed during nighttime hours. This NO\(_3^–\) concentration increase did not correspond to an equivalent increase in ammonium, leading to the presence of so-called excess nitrate. An increase in NO\(_3^–\) was also observed during the stagnation event, although
during this period the PM$_{2.5}$ mass loading was dominated by organic materials. The increase in particulate nitrate concentration for the high RH period and the stagnation event was found to be episodic and highly dependent on the RH and NO$_x$ concentration. Evidence during these two periods suggests that this episodic particulate nitrate concentration could have resulted from two mechanisms: the heterogeneous hydrolysis of N$_2$O$_5$ onto hydrated aerosols, or the shift in aerosol thermodynamics favoring the condensation of gas phase nitric acid to particle phase or a combination of the two mechanisms. The condensation of nitric acid was found to be more active during daytime hours, while the heterogeneous hydrolysis of N$_2$O$_5$ was postulated to be the leading mechanism in the observed nighttime increases in particulate nitrate.

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Supporting Material Available

Summary of the meteorological conditions (Figure S1), Summary of aerosol size distribution (Figure S2), Percentage neutralized nitrate (Figure S3), Scatter plot comparing the PM$_{2.5}$ mass loading obtained using the TEOM (Figure S4).

References


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