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Key Points:
- Wintertime ammonium nitrate aerosol pollution is closely tied to photochemical ozone production through a common parameter, Ox,total.
- Box modeling reveals ammonium nitrate formation in the Salt Lake Valley is nitrate-limited but NOx-saturated.
- Mitigation strategies that focus on NOx control in some wintertime-polluted layers may initially increase ammonium nitrate.

Supporting Information:
- Supporting Information S1

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Abstract
Wintertime ammonium nitrate aerosol pollution is a severe air quality issue affecting both developed and rapidly urbanizing regions from Europe to East Asia. In the United States, it is acute in western basins subject to inversions that confine pollutants near the surface. Measurements and modeling of a wintertime pollution episode in Salt Lake Valley, Utah, demonstrate that ammonium nitrate is closely related to photochemical ozone through a common parameter, total odd oxygen, Ox,total. We show that the traditional nitrogen oxide and volatile organic compound (NOx-VOC) framework for evaluating ozone mitigation strategies also applies to ammonium nitrate. Despite being nitrate-limited, ammonium nitrate aerosol pollution in Salt Lake Valley is responsive to VOCs control and, counterintuitively, not initially responsive to NOx control. We demonstrate simultaneous nitrate limitation and NOx saturation and suggest this phenomenon may be general. This finding may identify an unrecognized control strategy to address a global public health issue in regions with severe winter aerosol pollution.

Plain Language Summary
Particulate matter (PM) is dangerous to human health and impacts visibility and climate. In the United States, Europe, and Asia, PM is severe in urban areas in the winter when ammonium nitrate, NH4NO3, comprises an appreciable fraction of the total PM mass. A key control strategy is to reduce emissions of the limiting reagent. Using measurements from a recent field campaign in the Salt Lake Valley, Utah, which experiences high PM levels in winter, we demonstrate that emission control strategies can be evaluated using the same framework commonly used to control ozone, another common pollutant that occurs at high levels in urban areas in the summer. We show that initial control of the NOx precursor is ineffective at reducing NH4NO3 aerosol in the Salt Lake Valley, while initial control of volatile organic compounds, which are not a direct precursor for either nitrate or ammonium, is effective due to their influence on oxidation cycles. This finding differs from many mitigation strategies in the western United States and may also be relevant to other regions in Europe and Asia which experience high wintertime PM.
1. Introduction

Air quality in most of the United States has been steadily improving for decades due to emissions control technologies and regulations (Hand et al., 2014). Ozone (O₃), which is a health hazard and greenhouse gas in the troposphere, has decreased markedly (Cooper et al., 2014) and is well understood in terms of its photochemical formation mechanism from nitrogen oxides (NOₓ = NO + NO₂) and volatile organic compounds (VOCs; Lin et al., 1988; Seinfeld, 1989). In contrast, many urban areas, such as the Salt Lake Valley (SLV) and San Joaquin Valley in the western United States, the Po Valley in Europe, and Beijing, China, in east Asia, experience severe wintertime pollution in the form of particulate matter smaller than 2.5 microns in diameter (PM₂.₅; Green et al., 2015; Figure 1). The SLV in northern Utah regularly experiences episodes of PM₂.₅ pollution (Silcox et al., 2012), exacerbated by the onset of persistent cold air pools (PCAPs; high-pressure systems that cap colder air within the basin), which prevent the vertical mixing of pollutants away from the surface (Whiteman et al., 2014). The trapped gas-phase pollutants, including NOₓ and VOCs from anthropogenic sources, undergo complex chemical oxidation reactions, forming nitric acid (HNO₃) that reacts with gas-phase ammonia (NH₃) to form ammonium nitrate aerosol (NH₄NO₃), which comprises ~75% of the PM₂.₅ composition in the SLV during pollution episodes (Baasandorj et al., 2017; Franchin et al., 2018; Kuprov et al., 2014).

\[
\text{NH}_3(g) + \text{HNO}_3(g) \rightleftharpoons \text{NH}_4\text{NO}_3(aq). \quad (R1)
\]

The SLV exceeds the 24-hr U.S. National Ambient Air Quality Standard for PM₂.₅ (35 μg/m³) on an average of 18 days/year (Whiteman et al., 2014), representing an important public health issue (Beard et al., 2012). A better understanding of the chemical processes that lead to the formation of ammonium nitrate and its precursors in the SLV and other polluted areas across the world is required to employ more effective control strategies.

Previous studies have demonstrated that during PCAP-induced pollution events, the valleys in the Salt Lake region typically have an excess of ammonia (Franchin et al., 2018; Kelly et al., 2013; Kuprov et al., 2014), and that the cold temperatures and high relative humidity drive the reversible reaction (R1) to form particulate ammonium nitrate (abbreviated pNO₃⁻; Blanchard et al., 2000; Franchin et al., 2018; Weber et al., 2016). The recent analysis of Franchin et al. (2018) demonstrates that the observed ratio between gas-phase nitric acid and total nitrate, HNO₃/(HNO₃ + pNO₃⁻), has a median value of <8% during PCAP episodes, and the calculated aerosol pH curve is insensitive to small changes in pH (supporting information Figure S1). Furthermore, Franchin et al. (2018) show that the initial response of total aerosol mass to reductions in total nitrate (HNO₃ + pNO₃⁻) is linear but substantially less than linear in its initial response to reductions in total reduced nitrogen (NH₃ + NH₄⁺). Therefore, the formation rate of pNO₃⁻ is mainly limited by the chemical formation rate of nitric acid (HNO₃) from oxidation of NOₓ, which is emitted from fossil fuel combustion. This HNO₃ limitation has led typical western U.S. control strategies to focus on emission reductions of NOₓ rather than NH₃ (Franchin et al., 2018; Kelly et al., 2018; Pusede et al., 2016). We demonstrate in this study that ammonium nitrate aerosol pollution may be treated in the same manner as O₃ pollution through a common parameter, O₅ totals, and may be most effectively reduced in the SLV by initially controlling VOC emissions rather than controlling emissions of NH₃ or NOₓ.

2. Methods

2.1. Observations of Wintertime Pollution Episodes in Northern Utah

The Utah Winter Fine Particulate Study (UWFPS) was a 4-week field campaign in the SLV region during the winter of 2016–2017 designed to observe the chemical processes that form ammonium nitrate aerosol during PCAPs (Baasandorj et al., 2018; Bares et al., 2018; Franchin et al., 2018). Ground sites made continuous surface-level measurements of trace gases (including O₃, NOₓ, and VOCs) and the chemical composition of PM₂.₅, while a Twin Otter light aircraft made periodic measurements aloft with a similar payload. This analysis primarily uses observations from the main SLV site at the University of Utah (UU), with auxiliary measurements from the Hawthorne site on the SLV floor and the Logan site in the nearby Cache Valley (Figure S2). Two major PCAP episodes occurred during the campaign, in which the 24-hr PM₂.₅ concentrations surpassed the National Ambient Air Quality Standard in at least one of the three major valleys for a
This analysis investigates the mechanisms for the PM$_{2.5}$ production that lead to the exceedance during one of the most intense pollution episodes of that winter, which occurred between 27 January and 4 February 2017 (Figure S2). These results are compared to observations of trace gas species from the recent Uintah Basin Winter Ozone Study, where a major PCAP in January 2013 led to elevated levels of O$_3$ (Ahmadov et al., 2015; Edwards et al., 2014). Measurement techniques for both campaigns are described in detail in Text S1 (Lee et al., 2014; Liao et al., 2017; Wild et al., 2014; Wild et al., 2016).

2.2. Ox$_{\text{total}}$ as a Parameter for Describing both HNO$_3$ and O$_3$ Formation

There are two mechanisms for HNO$_3$ formation: daytime production from the gas-phase reaction of OH + NO$_2$ and nighttime production from N$_2$O$_5$ uptake onto aerosol particles (Jones & Seinfeld, 1983). The full mechanistic details are listed in Text S2 and summarized here. In the daytime, VOCs are photolyzed or oxidized by the hydroxyl radical (OH) to form HO$_2$ or RO$_2$ radicals, collectively termed HOx radicals (HOx = OH + HO$_2$ + RO$_2$). Radical propagation reactions with NO generate an NO$_2$ molecule with each iteration, while the dominant radical termination reaction of OH with NO$_2$ generates HNO$_3$. The overall HNO$_3$ production efficiency of this cycle depends on (1) the availability of HOx radicals, which are generally less abundant in winter than in summer, and (2) the number of iterations each HOx radical makes prior to termination (i.e., chain length), which is determined by the relative abundance of VOC and NOx (Kleinman, 2005; Lin et al., 1988). During the day, NO$_2$ rapidly interconverts with NO and O$_3$, and therefore, the same HOx cycle that produces HNO$_3$ is also the dominant mechanism for O$_3$ production. At night, photolytic production of radicals and O$_3$ halts, and NO titrates the O$_3$ to NO$_2$, which then oxidizes to form N$_2$O$_5$, which further reacts heterogeneously with aerosol to form HNO$_3$ and ClNO$_2$ (Kelly et al., 2018).

The parameter Ox$_{\text{total}}$ (=O$_3$ + NO$_2$) has often been used to quantify the net photochemical formation of O$_3$ beyond its rapid daytime interconversion with NO$_2$ (Liu, 1977; Wood et al., 2009). Here we introduce an analogous parameter, Ox$_{\text{total}}$, which is equal to the sum of all gas- and particulate-phase species that contain an odd oxygen (O or O$_3$).

\[
\text{O}_x_{\text{total}} = \text{O}_3 + \text{NO}_2 + 2\times\text{NO}_3 + 3\times\text{N}_2\text{O}_5 + \text{CINO}_2 + \text{peroxyacyl nitrates} + 2\times\text{alkyl nitrates} + \text{OH} + 1.5\times(\text{HNO}_3 + \text{pNO}_3^{-}) \tag{R2}
\]

where the stoichiometric coefficients indicate the number of odd oxygen species it contains and are derived in Text S2. NH$_3$ is reduced nitrogen and is therefore not a component of Ox$_{\text{total}}$. The coefficient for the sum of gas-phase HNO$_3$ and pNO$_3^{-}$ is denoted here as 1.5 but may be as high as 2, depending on the mechanism that formed it, and therefore, Ox$_{\text{total}}$ as defined here should be considered a lower bound. Ox$_{\text{total}}$ may be more broadly defined than (R2) if one considers the products of the reactions of OH, O$_3$, and NO$_2$ with VOCs, for example, but for this analysis, we focus only on the propagation of odd oxygen through nitrogen chemistry.

The nighttime mechanism results in no net change in Ox$_{\text{total}}$, as those reactions represent only a repartitioning of its components. The daytime mechanism, on the other hand, generates one NO$_2$ molecule for each cycle without loss of an O$_3$ molecule and therefore represents an increase in Ox$_{\text{total}}$ before terminating in HNO$_3$ or alkyl nitrate production. Transport of air masses with background concentrations of O$_3$ and negligible concentrations of the other Ox$_{\text{total}}$ components into the SLV would deplete the other Ox$_{\text{total}}$ parameter, Ox$_{\text{total}}$, which is equal to the sum of all gas- and particulate-phase species that contain an odd oxygen (O or O$_3$).
components by their stoichiometric coefficients ($\geq 1$) for every O$_3$ molecule added, leading to a net decrease of O$_{x,\text{total}}$. Dry deposition of individual species to the surface is also a net loss process. Therefore, growth in O$_{x,\text{total}}$ beyond its background level in unpolluted air is a measure of the role that photochemistry plays in the net production of HNO$_3$ + pNO$_3^-$ during the PCAP.

2.3. Photochemical Box Modeling

The Dynamically Simple Model for Atmospheric Chemical Complexity (DSMACC) (Emmerson & Evans, 2009), a photochemical zero-dimensional box model, was used to characterize the growth of O$_{x,\text{total}}$ in the SLV during one of the most severe PCAPs sampled between 27 January and 4 February 2017. DSMACC utilizes the Master Chemical Mechanism (v3.3.1; Jenkin et al., 2015), a near-explicit mechanism to characterize the degradation of 143 VOCs by photochemistry and oxidation, using >15,000 reactions and >3,500 intermediate species. A subset of the Master Chemical Mechanism was used here, consisting of the 58 VOCs for which we had experimental constraints for the starting conditions. The Tropospheric Ultraviolet and Visible Radiation Model (v5.2; Madronich et al., 1998) was used to calculate the photolysis rate constants in the chemical mechanism. A zero-dimensional model treats the chemistry as a single system evolving in time and does not consider meteorology or boundary layer dynamics, but the relative simplicity of these models allows the use of a highly detailed chemical mechanism. The stagnant air and constrained meteorology in these valleys make this an appropriate technique for these conditions (Edwards et al., 2014). Further model details are described in Text S3 (de Gouw et al., 2017; Kurtenbach et al., 2001; McDuffie, 2018; Wesely & Hicks, 2000; Wild et al., 2017; Zhang et al., 2012).

3. Results

Figure 2a shows the most abundant components of O$_{x,\text{total}}$ observed at the UU sampling site during the UWFPS campaign. As the PCAP progressed, O$_{x,\text{total}}$ increased steadily at a rate of approximately 5.5 ppbv/day, and its composition quickly became dominated by NO$_2$ and pNO$_3^-$. A similar trend is observed in Twin Otter vertical profiles (Figure 2b). These observations of O$_{x,\text{total}}$ growth and partitioning are compared to a recent study in the nearby Uintah Basin that also experiences frequent wintertime PCAPs (Ahmadov et al., 2015). In contrast to SLV, the sparsely populated Uintah Basin in northeastern Utah experiences high wintertime levels of O$_3$ (UBWOS, 2014) due to photochemical oxidation of VOCs emitted in abundance from local oil and natural gas operations in a relatively NO$_x$-poor environment (Edwards et al., 2014). Figure 2c shows a similar growth rate of O$_{x,\text{total}}$ in the Uintah Basin in during a PCAP in January 2013, but unlike the SLV, O$_{x,\text{total}}$ in the Uintah Basin is partitioned nearly entirely to O$_3$. The SLV is densely populated and contains no oil and natural gas wells, though it does have significant agricultural and industrial sectors, and NO$_x$ and VOC emission profiles typical of U.S. urban areas (Figure S3a). The closely related O$_{x,\text{total}}$ growth in Figure 2 is reflective of the same photochemical mechanisms playing important roles in both valleys (Kleeman et al., 2005; Meng et al., 1997; Nguyen & Dabdub, 2002), and the widely divergent partitioning of its components to either pNO$_3^-$ in the SLV or O$_3$ in the Uintah Basin derives from their starkly different emission profiles (Figure S3b). The common parameter O$_{x,\text{total}}$ can therefore be used to evaluate mitigation strategies for controlling both criteria pollutants, as demonstrated below.

The production of tropospheric O$_3$, frequently the major component of O$_{x,\text{total}}$, is often evaluated in terms of its nonlinear sensitivity to NO$_x$ and VOC emissions (Lin et al., 1988; Milford et al., 1989; Seinfeld, 1989; Trainer et al., 1993). Because small changes in the availability of NO$_x$ can change the relative branching of the HO$_x$ radical reaction pathways, the O$_3$ production rate and yield may either increase or decrease with NO$_x$ availability, depending on the VOC concentration and composition (Lin et al., 1988), which often requires detailed modeling to characterize fully. Edwards et al. (2014) used a zero-dimensional box model to show that O$_3$ production in the Uintah Basin was close to its maximum efficiency with respect to NO$_x$ at the prevailing VOC concentrations in winter. Here we develop an analogous model to explain the growth of O$_{x,\text{total}}$ in the SLV. We modified the DSMACC box model to split into two concurrent boxes at night to model the residual layer (RL) and nocturnal boundary layer (NBL) separately, to more accurately model the vertical structure of the PCAP, as shown in Figure 3a.
Figure 3b shows the base case model compared with the observations. The base case was selected based on daytime agreement between modeled and observed $\text{O}_\text{x,total}$, VOCS, and $\text{NO}_3$, as detailed in Text S3. The model did not attempt to replicate the partitioning of HNO$_3$ between the gas and aerosol phase and simply treated the two as the lumped sum HNO$_3$ + pNO$_3$. Franchin et al. (2018) showed this partitioning to be >92% to the aerosol phase during UWFPS PCAP events. The UU site is located at slightly higher elevation.
on the side of the valley wall and may sample from either the NBL or RL at night at different times during the PCAP (see Text S3.1). Additionally, that site may be subject to upslope and downslope canyon flows along the basin walls (Baasandorj et al., 2017). Agreement between the model and UU observations was therefore only expected during daytime hours when the pollution layer is mixed. The split box model successfully captures the overall growth of Ox,total over the four model days, accurately predicts that there is O3 depletion in the NBL due to dilution and reaction with NO2 but not in the RL, and reproduces the observed partitioning of Ox,total (Figure S4).

The input emission rates may be adjusted from the model base case to determine the effect of various emission control strategies. Isopleths determined in this way are often used to predict the effect of emission controls on O3 production (Kleinman, 2005; Seinfeld, 1989). VOC controls on PM2.5 formation have been considered in the past in California (Kleeman et al., 2005; Nguyen & Dabdub, 2002; Pun & Seigneur, 2001). However, VOC controls in the context of the chemical equivalence of O3 and pNO3− in terms of Ox,total during weak photochemical environments, such as the SLV, have not been considered. Calculated isopleths of O3, Ox,total, and the sum of HNO3 + pNO3− are shown in Figure 4. They indicate that the SLV is in a NOx-saturated regime, where initial decreases in NOx emissions will increase O3, Ox,total, and HNO3 + pNO3−, absent concurrent VOC reductions.

NOx saturation in the SLV is attributed to the modeled average HOx chain length or the number of times a HOx radical undergoes a propagation reaction cycle generating NO2 before terminating (Jeffries & Tonnesen, 1994; Mao et al., 2010). The model predicts this value to be 1.07 in the SLV (Figure S5), so HOx is near its peak efficiency for HNO3 production, as over 99% of HOx radicals terminate in HNO3, rather than an alkyl nitrate or HOx self-reaction. This observation is also consistent with the low observed aerosol-phase organic nitrates (Franchin et al., 2018). NOx serves to quench the HOx-NOx cycle, and therefore, reductions in NOx increase the HOx chain length and drive more efficient production of O3 and HNO3. In the Uintah Basin, on the other hand, the average chain length is 4.3, indicating that HOx radicals are highly efficient in generating O3 before termination largely via self-reaction. The ratio of NOx to VOCs (Figure S3b) is a key parameter that dictates the ultimate fate of radicals: High NOx/VOCs yields high HNO3 in the SLV, whereas low NOx/VOC yields high O3 in Uintah Basin.

It is often assumed that when pNO3− production is HNO3-limited (as opposed to NH3-limited), HNO3 production must be NOx-limited (Guo et al., 2018; Wen et al., 2018), and previous studies in California’s San
Joaquin Valley have found that >50% NOx reductions would reduce pNO3\(^{-}\) (Kelly et al., 2018; Pusede et al., 2016). However, Figure 4 demonstrates that the SLV is HNO3-limited and NOx-saturated simultaneously (see also Pun & Seigneur, 2001). Our finding implies a counterintuitive control strategy to initially reduce VOC emissions could be more effective in controlling ammonium nitrate aerosol exceedances in the NOx-rich SLV, though a combination of NOx and VOC control will eventually be necessary for reduction below U.S. air quality standards. The model can also elucidate the relative roles of the daytime and nighttime chemical mechanisms for forming HNO3. We derive a 43% contribution to total HNO3 formation by nighttime N2O5 uptake on aerosol (Figure S6), with nighttime HNO3 production occurring primarily in the RL, where there are no NOx emissions.

4. Conclusions

Ox,total is a parameter that describes both O3 and pNO3\(^{-}\) production, demonstrating that they are different outcomes of the same chemical cycle, driven by different NOx/VOC emission ratios, and may be considered chemically equivalent. We have therefore modeled the predicted response of Ox,total to changes in NOx and VOC emissions in the same manner that O3 production is normally considered. Although this conceptual model is simplified, its conclusions are robust with respect to the underlying assumptions, as detailed in sensitivity tests in Text S4 (Li et al., 2014; Stemmler et al., 2006; Zhou et al., 2011). We find that this framework is an effective way of describing the response of ammonium nitrate aerosol to emission controls in an urban wintertime environment that is sensitive to HNO3. Furthermore, a more general three-component analysis which considers NOx, VOCs, and NH3 could describe ammonium nitrate formation under any conditions in the context of Ox,total. We find that the SLV is likely to be well within a NOx-saturated regime, and therefore, control strategies that initially focus on VOCs rather than NOx or NH3 would be most effective, contrary to the view that NOx reductions are most effective in HNO3 (rather than NH3) limited systems. The current understanding of U.S. VOC emissions and the cost and feasibility of their reduction continues to evolve (McDonald et al., 2018). Further detailed evaluation of the unique and changing biogenic and anthropogenic VOC profiles in the SLV and other valleys would be required to formulate an effective VOC emission control strategy.

Recent work has noted that summertime O3 and PM2.5 in the United States have steadily declined (Cooper et al., 2014; Hand et al., 2014) in response to emissions controls, but wintertime PM2.5, nitrate aerosol in particular, has not decreased as strongly (Green et al., 2015; Shah et al., 2018). Our analysis further suggests that these more gradual decreases in western U.S. PM2.5 may be attributable to recent reductions in VOC rather than NOx emissions and that NOx reductions may in fact have had the counterintuitive effect of slowing the rate of decrease of PM2.5 in areas dominated by ammonium nitrate. This analysis may also be relevant to both Europe and East Asia (Figure 1), where nitrate is increasingly a major component of wintertime PM2.5 (Xu et al., 2018), NOx concentrations are high (Guo et al., 2014; Wang et al., 2017, 2018; Wen et al., 2018), and ammonia is typically in excess (Guo et al., 2018). Mitigation strategies have normally focused on NOx control (Guo et al., 2018), though recent work has indicated that PM2.5 in northern China has a negative sensitivity to NOx (Zhao et al., 2017). Chinese emission inventories show recent reductions in NOx but increase in VOCs nationwide, a trend that could serve to exacerbate the severity of nitrate aerosol (Wang et al., 2017). Although the NOx and VOC emission profiles in European and Chinese cities may differ substantially from valleys in northern Utah, this framework for modeling aerosol suggests new and promising avenues for improved control strategies.

References


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