On the effectiveness of nitrogen oxide reductions as a control over ammonium nitrate aerosol

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Abstract

Nitrogen oxides (NO\textsubscript{x}) have fallen steadily across the U.S. over the last fifteen years. At the same time, NO\textsubscript{x} concentrations decrease on weekends relative to weekdays, largely without co-occurring changes in other gas-phase emissions, due to patterns diesel truck activities. These trends taken together provide two independent constraints on the role of NO\textsubscript{x} in the nonlinear chemistry of atmospheric oxidation. In this context, we interpret interannual trends in wintertime ammonium nitrate (NH\textsubscript{4}NO\textsubscript{3}) in the San Joaquin Valley of California, a location with the worst aerosol pollution in the U.S. and where a large portion of aerosol mass is NH\textsubscript{4}NO\textsubscript{3}. Here, we show that NO\textsubscript{x} reductions have simultaneously decreased nighttime and increased daytime NH\textsubscript{4}NO\textsubscript{3} production over the last decade. We find a substantial decrease in NH\textsubscript{4}NO\textsubscript{3} since 2000 and conclude that this decrease is due to reduced nitrate radical-initiated production at night in residual layers that are decoupled from fresh emissions at the surface. Further reductions in NO\textsubscript{x} are imminent in California, and nationwide, and we make a quantitative prediction of the response of NH\textsubscript{4}NO\textsubscript{3}. We show that the combination of rapid chemical production and efficient NH\textsubscript{4}NO\textsubscript{3} loss via deposition of gas-phase nitric acid implies high aerosol days in cities in the San Joaquin Valley air basin are responsive to local changes in NO\textsubscript{x} within those individual cities. Our calculations indicate that large decreases in NO\textsubscript{x} in the future will not only lower wintertime NH\textsubscript{4}NO\textsubscript{3} concentrations, they will also cause a transition in the dominant NH\textsubscript{4}NO\textsubscript{3} source from nighttime to daytime chemistry.
Aerosol abundances are decreasing across the U.S., improving air quality and affecting climate. These decreases have been broadly attributed to regulatory controls on the emissions of gas-phase precursors; however, it has proven difficult to link precursor reductions to observed changes in aerosol concentration via specific chemical mechanisms. Thus, there is limited knowledge of how impacts will scale in the future.

We present an analysis to identify driving chemical mechanisms and to quantify the effects of large reductions in nitrogen oxides (NO\textsubscript{x}) (e.g., Russell et al., 2012; McDonald et al., 2012) on secondary aerosol chemistry. We take advantage of decreased NO\textsubscript{x} emissions on weekends compared to weekdays, which occur mostly without changes in other gas-phase emissions (e.g., Dallmann et al., 2012), and couple these weekday-weekend patterns to long-term NO\textsubscript{x} reductions (Pusede and Cohen, 2012). The effect is that weekday NO\textsubscript{x} levels equal weekend NO\textsubscript{x} years earlier in the record (Fig. 1). We use this NO\textsubscript{x} constraint to interpret trends in observed wintertime ammonium nitrate (NH\textsubscript{4}NO\textsubscript{3}) concentrations over the last decade in the San Joaquin Valley (SJV) of California.

The SJV experiences the most severe aerosol pollution in the U.S. (American Lung Association, 2014). From 2001–2013 there were on average 44 exceedances each winter (November–March) of the 24-h National Ambient Air Quality Standard (NAAQS) of 35 µg m\textsuperscript{-3} in the cities of Bakersfield and Fresno, with as many as 70 per winter early in the record. High aerosol in the SJV is generally limited to the winter months, with few exceedances occurring in other seasons. In the SJV, 30–80% of wintertime aerosol mass is NH\textsubscript{4}NO\textsubscript{3} and the remaining portion is mostly organic material (Chow et al., 2006; Chen et al., 2007; Ge et al., 2012). Characteristics of the wintertime SJV that are conducive to high aerosol abundances include: shallow boundary layers (Bianco et al., 2011); prolonged periods of stagnation (Smith et al., 1981); and large emissions of NO\textsubscript{x} (NO\textsubscript{x} ≡ NO + NO\textsubscript{2}), ammonia (NH\textsubscript{3}) (Goebes et al., 2003; Clarisse et al., 2010), and organic aerosol (Ge et al., 2012). These conditions pose challenges to accurately simulating secondary aerosol in the region, as models need to represent bidirectional NH\textsubscript{3} exchange (Gilliland et al., 2006; Flechard et al., 2010; Pleim et al., 2013), variable local meteorology, complex airflows,
and vertical stratification in the rates of NO₂ oxidation to NO₃⁻ (Heald et al., 2012; Walker et al., 2012; Kelly et al., 2014; Schiferl et al., 2014; Markovic et al., 2014).

In this paper, we take an observational approach, combining the decade-long record of speciated aerosol concentrations and of gas-phase precursors in the region with detailed measurements collected during the DISCOVER-AQ experiment (Deriving Information on Surface Conditions from COlumn and VERtically resolved observations relevant to Air Quality, 14 January–14 February 2013). We show that wintertime NO₃⁻, which we treat as a measured surrogate for NH₄NO₃, has been dependent only on the NO₂ concentration over the last twelve years. We calculate observationally-constrained nighttime and photochemical NO₃⁻ production rates and show that measured trends in wintertime NO₃⁻ can be explained by decreased nitrate radical-initiated production in nocturnal residual layers, which are unmonitored layers of the atmosphere that are effectively separated from surface emissions at night. We test the impacts of forthcoming NOₓ emission controls on the probability of future NAAQS exceedances, showing that NOₓ reductions will not only decrease the frequency of high aerosol days, but will also shift both the timing and the oxidation mechanisms that drive NH₄NO₃ production.

2 Results from observations

Trends in wintertime (November–March) 24-h NO₃⁻ versus daytime (10 am–3 pm local time, LT) NO₂ are shown in Fig. 2 in the cities Fresno and Bakersfield on weekdays and weekends for the period 2001–2013. The source of these observations, the methods used for collection, and measurement biases are discussed in Appendix A. Weekdays are defined as Tuesday–Friday and weekends are Saturday–Sunday. We expect carryover to have an effect on the interpretation, as concentrations of NO₂ and aerosol are not only influenced by present day processes but also have some memory of processes occurring on the preceding day, especially in the winter when surface winds are slow and disorganized and horizontal transport is weak. We exclude Monday from weekdays for this reason but retain Saturdays to improve weekend statistics. As a result, weekend medians reported here might be slightly higher than would be observed due to weekend emissions alone. We define the day as beginning and ending at sunrise, since nighttime NO₃⁻ production builds from reactants present in the atmosphere during the preceding daytime hours.
In the wintertime SJV, persistent stagnant conditions are common and punctuated only by infrequent cold fronts accompanied by strong winds that remove accumulated pollution from the basin. Stagnation events are a few days to multiple weeks in duration, and, during these stable periods, surface winds are slow and disorganized, controlled largely by surface heating, with limited horizontal mixing (Smith et al., 1981). On any individual winter day, air stagnation and planetary boundary layer height are the dominant controls over gas and aerosol concentrations; however, considering the data separately by weekday and weekend and then comparing year-to-year changes, instead draws attention to the effects of emissions and subsequent chemistry.

By this method, the NO$_3^-$ mass concentration is observed to have depended on the previous day’s daytime NO$_2$ concentration with a sensitivity of 0.5 $\mu$g m$^{-3}$ ppb$^{-1}$ NO$_2$ in Fresno and 0.64 $\mu$g m$^{-3}$ ppb$^{-1}$ NO$_2$ in Bakersfield (slopes in Fig. 2). Uncertainties in the NO$_3^-$ concentration are computed as counting errors, with $N$ as the total number of wintertime data points (3-yr average), and are ±20% on weekdays and ±30% on weekends. Errors in NO$_2$ are computed in the same way and are less than ±9% on weekdays and ±13% on weekends in both Fresno and Bakersfield.

We interpret the positive $x$-intercept in Fig. 2 as consistent with the known low bias in NO$_3^-$ measurements (Appendix A) and the shorter wintertime atmospheric lifetime of NO$_3^-$ than NO$_2$ (Sect. 4). Uncertainty estimates, including a low NO$_3^-$ measurement bias of 25%, are ±$^{32\%}$ $\mu$g m$^{-3}$ ppb$^{-1}$ NO$_2$ on weekdays and ±$^{40\%}$ $\mu$g m$^{-3}$ ppb$^{-1}$ NO$_2$ on weekends. One ppb NO$_2$ corresponds to 2.56 $\mu$g m$^{-3}$ NO$_3^-$ after oxidation (at 25°C and 1 atm), thus the observed correlation corresponds to a decrease in NO$_3^-$ mass that is 20% of the NO$_2$ decrease. While, the full budget for wintertime NO$_x$ loss is beyond the scope of this paper, Fig. 2 implies that on average in the wintertime, 20% of each day’s NO$_x$ emissions are converted to NO$_3^-$ in 1–2 days.

The key idea is that present-day NO$_3^-$ concentrations on weekdays are equal to what were seen on weekends a decade ago, i.e. the NO$_2$ dependence of NO$_3^-$ has been unchanged with time. This suggests that in the wintertime average, the only source of NO$_3^-$ in the atmosphere has been oxidation of NO$_2$ and that NH$_4$NO$_3$ production has been nitrate rather than ammonium limited. Agreement of NO$_3^-$ in different years at identical NO$_2$ implies that there has been little change over time in the chemical mechanism producing NO$_3^-$, and hence NH$_4$NO$_3$. 

Additional evidence comes from observations made during DISCOVER-AQ, in which the sum of gas-phase nitric acid and aerosol-phase NO$_3^-$ (NO$_3^-$ (g+p)) was measured onboard the NASA P-3B on six research flights with almost identical flight patterns (Fig. 3a). See Appendix A for a description of the NO$_3^-$ (g+p) measurements and DISCOVER-AQ experiment. Comparing the spatial distribution of NO$_3^-$ (g+p) within the fully developed (afternoon) boundary layer (see Appendix A for the boundary layer filtering procedure) to NO$_2$ observed from the satellite (Fig. 1) and NO$_x$ from onboard the P3-B (Fig. 3b), suggests that NO$_3^-$ (g+p) better follows spatial patterns in NO$_2$ than gas-phase NH$_3$ (Fig. 3c), the precursor of particulate-phase NH$_4^+$. In Fig. 3a, urban-rural gradients in NO$_3^-$ (g+p) are steep. In Bakersfield, NO$_3^-$ (g+p) was on average 18–20 µg m$^{-3}$ near the city center, twice as high as just 20 km to the northeast. During DISCOVER-AQ, surface wind speeds were ~2–3 m s$^{-1}$ in the daytime (10 am–3 pm LT), ~1–2 m s$^{-1}$ in the morning (6 am–10 am LT), and typically < 1 m s$^{-1}$ at night. An air parcel moving within the surface layer at 3 m s$^{-1}$ would require approximately ~20 daytime h, equivalent to multiple days, to either reach Fresno from the upwind cities of Stockton or San Jose or to reach Bakersfield from Fresno. An additional transport mechanism is mixing by winds in nocturnal low-level jets, which are well documented in the SJV in the summertime (Bao et al., 2008). There are few measurements of these winds in the winter, but wind speeds of up to 1–8 m s$^{-1}$ have been observed at 0.1–2 km a.g.l. (3 days of data), which are fast enough to mix species valley wide in 1–2 days (Chow et al., 2006). However, the measured spatial heterogeneity in NO$_3^-$ (g+p) (Fig. 3a) indicates faster and/or more localized processes control a significant portion of the NO$_3^-$ concentration in each city.

We infer from Figs. 2 and 3 that the oxidation of locally emitted NO$_x$ is the largest term affecting the production of NH$_4$NO$_3$, that NH$_3$ is in excess, and that transport and mixing are too slow to fully homogenize the aerosol throughout the wintertime SJV.

3 Chemistry in the dynamic near-surface atmosphere

Under the abundant NH$_3$, low sulfur dioxide, high aerosol, and low temperature conditions found in the wintertime SJV, most NO$_3^-$ is aerosol bound in the 24-hour average and NH$_4$NO$_3$
abundances are driven by NO$_3^-$ production ($P$NO$_3^-$). $P$NO$_3^-$ occurs by distinct nighttime and daytime mechanisms, each of which is a nonlinear function of NO$_2$.

Nitrate radical (NO$_3$) is the most important nighttime oxidant (Brown and Stutz, 2012). It is formed via reaction of NO$_2$ with O$_3$ (Reaction 1).  

\[
1) \quad \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3
\]

NO$_3$-initiated chemistry occurs mainly at night because NO$_3$ photolyzes rapidly to NO$_2$. After sunset, large NO emissions can titrate O$_3$, altering the relative amounts of NO$_2$ and O$_3$, but conserving odd oxygen ($O_x \equiv \text{NO}_2 + \text{O}_3$). NO$_3$ radical production is a nonlinear function of NO$_2$ for a given O$_3$ concentration, increasing with NO$_2$ at low NO$_x$, maximizing when NO$_2$ is equal to O$_3$ at constant O$_x$, and decreasing at higher NO$_x$, shown as NO$_2$ (Appendix B, Fig. B1a).

In the evening, reduced sunlight diminishes the heating of the Earth’s surface, leading to strong suppression of vertical mixing and the formation of a shallow nocturnal boundary layer (NBL). Between the NBL and the free troposphere, in the nocturnal residual layer (NRL), mixing is weak and further layering may occur (Brown et al., 2007). The initial concentrations of species in the NRL are determined by the concentrations observed at the point in time when the residual layer decouples from the NBL, around sunset. Afterwards, the strong surface inversion keeps fresh emissions from entering the NRL, yet vertical chemical gradients have been observed within layers (Brown et al., 2007). The NRL is seen by surface monitors in the morning when solar heating and turbulent mixing reincorporate what was the NRL into the growing daytime boundary layer (Fig. 4), a process that also alters the NRL composition. On nights when NO$_3$ radical production in the NBL is zero due to high NO emissions, NO$_3$ chemistry may still be active in the dynamically decoupled NRL. Loss from the atmosphere is likewise affected by this vertical structuring, as deposition to the surface occurs during the daytime and during the night from the NBL, but not during the night from the NRL. Fig. 5 shows examples of enduring nocturnal structure seen via potential temperature, the vertical distribution of NO$_3^{-}(g+p)$, and O$_3$ during DISCOVER-AQ by the P-3B in the early mornings over Bakersfield. At least one NRL is apparent for each profile, evident in the potential temperature variability; however, due to a combination of extremely shallow surface inversions, intermittent NO$_3^{-}(g+p)$ sampling, and science flight timing, it is unclear that the P-3B ever captured NO$_3^{-}(g+p)$ concentrations in the
NBL prior to the second flight circuit in the late morning (not shown) when significant atmospheric mixing had already taken place.

Nitrate radical reacts with NO$_2$ to form dinitrogen pentoxide (N$_2$O$_5$) and generally under atmospheric conditions of high NO$_2$ and low temperature, N$_2$O$_5$ $\gg$ NO$_3$ (Brown et al., 2009; Brown and Stutz, 2012). The lifetime of N$_2$O$_5$ to thermal decomposition to NO$_2$ and NO$_3$ is ~10 minutes at 270 K. NO$_3$ is also lost to reaction with certain organic species, especially compounds with unsaturated carbon-carbon bonds and aldehydes. When reaction times are long, for example during long, dark winter nights, and when unsaturated hydrocarbon emissions are low, the most important loss of NO$_3$ is via N$_2$O$_5$ uptake onto aerosols (e.g., Dentener and Crutzen 1993; Macintyre and Evans 2010; Wagner et al., 2013), whereupon N$_2$O$_5$ reacts with aerosol-phase water to give either two NO$_3^-$ or, if NO$_2^+$ combines with Cl$^-$, ClNO$_2$ + NO$_3^-$. At sunrise, ClNO$_2$ photolyzes within a few hours (Nelson and Johnston, 1981), releasing NO$_2$ and Cl radical, the latter reacting rapidly with most gas-phase organic compounds. The heterogeneous loss rate of N$_2$O$_5$ is a function of the total aerosol surface area and of the fraction of gas-particle collisions resulting in N$_2$O$_5$ uptake. The latter is aerosol composition dependent, enhanced at higher aerosol water content (e.g., Hu and Abbatt, 1997; Hallquist et al., 2003; Thornton et al., 2003), reduced in the presence of organic coatings (e.g., Cosman and Bertram, 2008; McNeill et al., 2006), and inversely proportional to NO$_3^-$ (e.g., Wahner et al., 1998; Hallquist et al., 2003; Bertram and Thornton, 2009; Wagner et al., 2013).

During the daytime, nitric acid (HNO$_3$) is the gas-phase reaction product of the oxidation of NO$_2$ and the hydroxyl radical (OH) (Reaction 2).

$$\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$$

The production rate of HNO$_3$ increases rapidly with increasing NO$_x$ at low NO$_x$ and converges at a limit set by the primary HO$_x$ (HO$_x$ $\equiv$ OH + HO$_2$ + RO$_2$) production rate at higher NO$_x$. Major sources of HO$_x$ in the polluted troposphere are O($^1$D) + H$_2$O, formaldehyde (CH$_2$O), and nitrous acid (HONO). The functional form of the dependence of HNO$_3$ production on NO$_2$ (Fig. B1b) arises from the nonlinear effects of NO$_x$ on the OH abundance, as NO$_x$ both propagates and terminates the HO$_x$ catalytic cycle. Under the high NO$_x$ conditions of the wintertime SJV, HNO$_3$...
is the dominant daytime HOx termination product. Combined with excess NH3, partitioning to the aerosol phase is a function of ambient temperature and humidity.

Trends in calculated wintertime $PNO_3^-$ for the nighttime and daytime mechanisms, as constrained by the observations (calculations and data are described in Appendix B), suggest that $PNO_3^-$ in the NRL is the largest source of chemistry that matches trends in NO$_3^-$ (Fig. 2). Specifically, $PNO_3^-$ in the NRL exhibits identical NO$_2$ dependence as observed in the NO$_3^-$ measurements—both over time and from weekday to weekend. In Fig. 6, the calculated annual wintertime daily-integrated $PNO_3^-$ in the NRL is shown versus daytime NO$_2$ on weekdays and weekends in Fresno and Bakersfield. $PNO_3^-$ in the NRL has decreased by 0.9 $\mu$g m$^{-3}$ day$^{-1}$ ppb$^{-1}$ NO$_2$ in both cities, a rate approximately twice the trend observed in NO$_3^-$ versus NO$_2$. The total daytime $PNO_3^-$ (R2), equal to the sum of $PNO_3^-$ attributed to the HOx sources, O($^1$D) + H$_2$O, HONO, and CH$_2$O, has, by contrast, not significantly changed as a function of NO$_2$ over the last decade. In fact, $PNO_3^-$ linked to the HOx sources O($^1$D) + H$_2$O and CH$_2$O has increased by ~5% since 2001. $PNO_3^-$ attributed to HONO has decreased since 2001 (Appendix B, Fig. B2), displaying comparable NO$_2$ dependence to both measured NO$_3^-$ concentrations (Fig. 2) and calculated $PNO_3^-$ in the NRL (Fig. 6). However, we calculate that $PNO_3^-$ in the NRL is approximately five times greater than $PNO_3^-$ formed during the daytime from OH originating from HONO. In the NBL (not shown) $PNO_3^-$ has increased from <1 $\mu$g m$^{-3}$ day$^{-1}$ to 3–5 $\mu$g m$^{-3}$ day$^{-1}$ on weekdays and to 6–8 $\mu$g m$^{-3}$ day$^{-1}$ on weekends due to reduced NO$_x$ titration of O$_3$ at sunset. Increases in NBL $PNO_3^-$ are not reflected in Fig. 2, potentially because these changes have occurred within a small faction of the volume of the NRL and daytime boundary layer and because depositional loss from the NBL is not impeded. For example, for an NBL that is 10% the NRL height, $PNO_3^-$ in the NBL would need to exceed three times the NRL production in order to alter the daytime boundary layer concentration by 20%, even if zero deposition is assumed.

4 Discussion

4.1 Relating concentration and $PNO_3^-$
The concentration of NO$_3^{−}$ ($g+p$) is a function of $P$NO$_3^{−}$, as well as loss and mixing. While high aerosol days in the SJV are in part attributed to persistent and severe stagnation, controls over the portion of aerosol mass that is NH$_4$NO$_3$ are more dynamic (e.g., Pandis and Seinfeld, 1990; Vayenas et al., 2005). In this section we show that the effects of loss and mixing on the NO$_3^{−}$ concentration are consistent with observed NO$_3^{−}$ trends over time, differences by day-of-week, accumulation rates during stagnation, and differences between Fresno and Bakersfield.

On days when NH$_4$NO$_3$ exceeded 20–30 µg m$^{-3}$, typical during stagnation periods, the diurnal variability of surface NO$_3^{−}$ was characterized by a steep and substantial increase in NO$_3^{−}$ in the morning, a slow decline through midday, and a rapid decrease in the afternoon (Fig. 7). On these mornings, the rise rate of NO$_3^{−}$ was consistent with two $P$NO$_3^{−}$ pathways: reincorporation of high-NO$_3^{−}$ NRL air into the boundary layer and NO$_3^{−}$ formed by daytime chemistry with HONO as the OH source. By contrast, OH-initiated production attributed to O($^1$D) + H$_2$O and CH$_2$O increased gradually throughout the day. At midday, OH-initiated $P$NO$_3^{−}$, atmospheric loss, and mixing by winds all play upon [NO$_3^{−}$]. In the afternoon, OH-initiated $P$NO$_3^{−}$ was minimal due to attenuated evening radiation. On days exhibiting this pattern, the NO$_3^{−}$ concentration was observed to decrease at a rate equal to $3.0 \pm 1.3$ µg m$^{-3}$ h$^{-1}$ (1σ), with individual rates determined as the slopes of a linear fit through the magenta data and identified as periods of steady decrease at least three hours long. Time windows were allowed to vary and the average window was 1:25 pm–4:05 pm LT, spanning 10:30 am–6:30 pm LT. We use this afternoon rate of change, which is when loss dominates production and mixing, to derive the atmospheric NO$_3^{−}$ lifetime ($\tau_{NO_3}^{−}$).

The atmospheric lifetime of aerosol in the boundary layer is determined by wet and dry deposition of aerosol, the wet and dry deposition of gases in equilibrium with aerosol, and mixing to the free troposphere where concentrations are much lower. Wet deposition occurs by interaction with rain, which scavenges aerosol and soluble gases, and leaves the valley relatively clear. Multiday fog is common in the winter in the SJV (Holets and Swanson, 1981), enhancing NH$_4$NO$_3$ removal when fog leads to rain or drizzle (Jacob et al., 1986a; Jacob et al., 1986b), as inorganic ions readily partition into aqueous fog droplets (Waldman et al., 1982; Munger et al., 1983), but having little effect if fog dissipates. Fog has not been seen to accelerate the conversion of NO$_2$ to NO$_3^{−}$ in the SJV (Jacob et al., 1984).
There are few direct measurements of deposition rates of aerosol, HNO$_3$, and NH$_3$. HNO$_3$ is theorized to deposit at a transport-limited rate, NH$_3$ exchange is dependent on surface and meteorological conditions, and aerosol, especially smaller particles, to deposit slowly. PM$_1$ to PM$_{2.5}$ deposition velocities ($v_d$) have been reported to be 0.001 to 0.1 cm s$^{-1}$ (Sehmel, 1980; Slinn, 1982; Farmer et al., 2013), too slow to account for the observed afternoon loss rates in Fig. 7. To compute NO$_3^-$ loss by deposition of gas-phase HNO$_3$, HNO$_3^{(g)}$ was modeled with ISORROPIA II (Nenes et al., 1998; Fountoukis and Nenes, 2007) run in forward mode, an approximation that was reasonable because during the wintertime temperatures were low, humidities were high, and NH$_3$ was abundant. ISORROPIA II was initialized as $[\text{NO}_3^- + \text{HNO}_3] = [\text{NO}_3^-]_{\text{AMS}}$ and $[\text{NH}_4^+ + \text{NH}_3] = [\text{NH}_4^+]_{\text{AMS}}$. Calculated HNO$_3^{(g)}$ was added back to $[\text{NO}_3^- + \text{HNO}_3]$, while NH$_3^{(g)}$ was added as 1.1 HNO$_3^{(g)}$ (by mole) to ensure NH$_3$ was in excess because we found NH$_4$NO$_3$ to be NO$_3^-$-limited (Figs. 2 and 3). ISORROPIA II was solved iteratively until daytime HNO$_3^{(g)}$ changed by <2% by mass. The phase state was set as metastable (e.g., Rood et al., 1989; Zhang et al., 2003; Vayenas et al., 2005). We assume that gases and aerosol are in equilibrium, that aerosols are homogenous and internally mixed, and that unaccounted-for factors do not influence the thermodynamics of the system (Vayenas et al., 2005). Calculated HNO$_3^{(g)}$ mixing ratios were greatest in the afternoon (12–4 pm LT), at which time they were 2 ppb on average for the DISCOVER-AQ time period and up to 4–6 ppb on the warmest days only. In the 24-h average, HNO$_3^{(g)}$ was 15% of $[\text{NO}_3^- + \text{HNO}_3]$ by mass and was 40% (median) in the afternoon. High HNO$_3^{(g)}$ was generally simultaneous with the magenta-highlighted NO$_3^-$ data (Fig. 7). To compute the $v_d$ of HNO$_3$, the equation $\frac{\partial \text{NO}_3^-}{\partial t} = \frac{v_d}{h} C$ was solved, with $\frac{\partial \text{NO}_3^-}{\partial t}$ equal to the observed afternoon loss rate on designated (magenta) days, $C$ equal to the daily mean HNO$_3^{(g)}$ over the same time windows, and $h$ equal to the maximum boundary layer height (i.e. the afternoon height) visually identified according to aerosol backscatter estimates by a micro-pulse lidar (MPL) supplemented with a wide-field receiver system (Appendix A). In this way, we derived $v_d$ equal to 5 ± 2 cm s$^{-1}$, in line with previous direct measurements of 1–10 cm s$^{-1}$ (e.g., Huebert and Robert, 1985; Meyers et al., 1989; Sievering et al., 2001; Volpe Horii et al., 2005; Farmer et al., 2006) and constrained estimates of 6 cm s$^{-1}$ (Vayenas et al., 2005). Given a $v_d$ of 5 cm s$^{-1}$ (assumed constant), the hourly $\frac{\partial \text{NO}_3^-}{\partial t}$ was computed for every hour of the day, with $C$ equal to the time-varying HNO$_3^{(g)}$ and $h$ equal to the time-varying boundary layer height. We assume
losses are from the entire boundary layer, see Appendix C for our reasoning. For the daily time-varying $h$: the NBL was estimated as 10% the maximum daytime boundary layer height measured by MPL; the morning increase estimated as linear over 5 hours and fully developed at 11 am; and the evening (6 pm) collapse (also linear), estimated as occurring in 2 hours.

In this way and with respect to surface deposition alone, $\tau_{\text{NO}_3}$ was calculated to be 3 h (0.1 days) under daytime conditions. As a lower bound, if the true $v_d$ was at the slowest end of previous observations (1 cm s$^{-1}$), then $\tau_{\text{NO}_3}$ would be 14 h under daytime conditions. Lifetimes in this range are shorter than typical stagnation periods, observed to be $5 \pm 1.5$ days ($1\sigma$) in both Fresno and Bakersfield (decadal average). By comparison, PM$_{1-2.5}$ $v_d$ yield $\tau_{\text{NO}_3}$ of 6–58 days. Such long lifetimes indicate the frequency of frontal passages controls the PM lifetime. Because the loss of NH$_4$NO$_3$ via HNO$_3$ deposition is rapid and $P\text{NO}_3^-$ is relatively large, high aerosol days are expected to be more responsive to changes in emissions than expected when considering loss only through particle deposition.

There are other observational constraints that an account of aerosol NO$_3^-$ in the SJV should explain. Median NO$_3^-$ (2001–2013) is 25% higher in Bakersfield than Fresno (Fig. 2). However, the observationally-constrained calculated total $P\text{NO}_3^-$ (NRL plus OH-initiated) is 15% lower in Bakersfield than Fresno (Fig. 6). We find that wintertime stagnation events, defined as continuous days with increasing 24-h PM$_{2.5}$, are more severe in Bakersfield than in Fresno, meaning there is a greater increase in PM$_{2.5}$ day$^{-1}$ over each event. The median increase in PM$_{2.5}$ day$^{-1}$ event$^{-1}$ over the last decade was 15% greater in Bakersfield (7.9 µg m$^{-3}$ day$^{-1}$ event$^{-1}$) than Fresno (6.7 µg m$^{-3}$ day$^{-1}$ event$^{-1}$) leading to 23% larger increases in PM$_{2.5}$ event$^{-1}$ in Bakersfield (32.5 µg m$^{-3}$ event$^{-1}$) than Fresno (25.1 µg m$^{-3}$ event$^{-1}$). PM$_{2.5}$ on the first day of the event was also 20% higher in Bakersfield (8.6 µg m$^{-3}$ event$^{-1}$ versus 6.9 µg m$^{-3}$ event$^{-1}$). These differences between Bakersfield and Fresno may in part be attributed to the former’s location in the southern end of the SJV, where the city is enclosed on three sides by the mountains, resulting in reduced losses to advection and mixing than in Fresno. Likewise, transport may carry a portion of aerosol produced elsewhere in the valley to Bakersfield, either by advection in the surface-mixed layer or by a nocturnal low-level jet. Weaker correlations ($r^2$) in Fig. 2 in Bakersfield (0.6) than in
Fresno (0.9) serve as evidence for enhanced influences of mixing and transport processes over NO$_3^-$ concentrations in the southern SJV.

### 4.2 Impacts of future NO$_x$ reductions

California has committed to additional, sizable controls on NO$_x$ emissions, with decreases of at least 50%, and potentially up to 75% NO$_x$, imminent over the next decade. California has implemented a retrofit/replacement program to accelerate impacts of federal rules on diesel engines, affecting weekday NO$_x$ (Dallmann and Harley, 2010; California Air Resources Board, 2012), and has both tightened standards on gasoline-powered vehicles and required one in seven new cars sold in the state be zero-emission or plug-in hybrids for model years 2017–2025 (Environmental Protection Agency, 2012), affecting weekday and weekend NO$_x$.

Currently, average wintertime NO$_x$ concentrations are low enough that reductions of 50% and 75% are calculated to decrease $P_{NO_3^-}$ in the NRL in Bakersfield on weekends by 40% and 70%, respectively (Fig. 8a), with similar results in Fresno and Visalia. Recall, the NO$_3$ radical production is nonlinear versus NO$_2$ and, for a fixed O$_x$ concentration, production is described by a single curve in Fig. B1a. When O$_x$ is variable, NO$_3$ radical production is described by multiple curves, and is most sensitive to changes in O$_3$ at NO$_2$ concentrations which are at and/or greater than peak NO$_3$ radical production. At low NO$_x$ (and high NO$_x$), $P_{NO_3^-}$ that is limited by NO$_3$ radical production is more sensitive to changes in NO$_2$. Fig. 6 suggests that as a direct result of decreases in NO$_2$, the chemical sensitivity of $P_{NO_3^-}$ to NO$_2$ has been altered such that future NO$_x$ controls are poised to more effectively slow $P_{NO_3^-}$ in the NRL in the next decade than over the last, at least at weekend NO$_x$ levels.

We compute that NO$_x$ reductions of 50% and 75% are large enough that changes in the average wintertime NO$_3^-$ are quantified via 2.56:1 line (3.31 including molar equivalent NH$_4^+$), the stoichiometric NO$_3^-$ response to NO$_2$, meaning the O$_3$ feedback from reduced NO$_x$ on $P_{NO_3^-}$ is minimal. The highest NO$_x$ conditions in the SJV are present in the shallowest boundary layers of December and January; during DISCOVER-AQ, NO$_x$ concentrations were high enough that reduced weekend NO$_x$ (21 January–22 January) had the effect of increasing $P_{NO_3^-}$ in the NRL relative to the preceding weekdays, i.e. chemistry on these days was right of peak NO$_3$ radical production.
Our calculation implies greater decreases in $P_{NO_3^–}$ have occurred in lower-NOx rural environments than in cities since 2001 given the same relative NOx reductions. During a previous aerosol experiment, CRPAQS (California Regional PM10/PM2.5 Air Quality Study), conducted December 1999–February 2001 (Watson et al., 1998) with a wintertime intensive (15 December 2000–3 February 2001), it was generally observed that high NH$_4$NO$_3$ was a valley-wide phenomenon. CRPAQS measurements of 24-h NO$_3^–$ (November 2000–January 2001) were similar in rural locations and in Fresno and Bakersfield, while high organic aerosol concentrations were spatially correlated with the cities. From these data, it was hypothesized that nocturnal low-level currents efficiently transported NH$_4$NO$_3$ and NO$_3^–$ precursors, distributing NH$_4$NO$_3$ and NH$_4$NO$_3$ production throughout the SJV (Chow et al., 2006). On the contrary, during DISCOVER-AQ, NO$_3^–$ was observed to spatially correlate with cities. Long-term co-located NO$_3^–$ and NO$_2$ measurements do not exist at any rural location in the SJV; however, the discrepancy between spatial patterns during DISCOVER-AQ and during CRPAQS can be explained through a combination of NO$_x$ emission controls shrinking urban NO$_x$ plumes and low-NO$_x$ nighttime chemistry being more sensitive to changes in NO$_2$.

For NO$_x$ emission changes to affect daytime $P_{NO_3^–}$, they must be large enough to transition photochemistry into the NO$_x$-limited regime, less than a few ppb in the wintertime SJV (Fig. B1b). In Bakersfield (Fig. 8b), at ~50% NO$_x$ from current levels we predict an increase in daytime NH$_4$NO$_3$ production of 2 µg m$^{-3}$ day$^{-1}$ (~15%), but at ~75% NO$_x$, we predict a transition to low-NO$_x$ chemistry and a net decrease in NH$_4$NO$_3$ production of 1.5 µg m$^{-3}$ day$^{-1}$ (15%). Initial enhancements in NH$_4$NO$_3$ are caused by NO$_x$ feedbacks on the HO$_x$ precursors, O$_3$ and CH$_2$O, which are both predicted to increase in response to decreases in NO$_2$ (Fig. B2). In Fig. 7b, the gray line is the modeled NH$_4$NO$_3$ production day$^{-1}$ calculated for present day conditions. The modeled points show the results of the calculations, for which the influence of NO$_x$ decreases on PHO$_x$, and the subsequent feedbacks on NH$_4$NO$_3$ production, are accounted. Elevation of NH$_4$NO$_3$ production above the gray line is due to the NO$_2$-PHO$_x$ precursor feedback. In Fresno (not shown), we compute an increase of 0.5 µg m$^{-3}$ day$^{-1}$ (~5%) at ~50% NO$_x$ and a decrease in NH$_4$NO$_3$ production of ~3 µg m$^{-3}$ day$^{-1}$ (20%) at ~75% NO$_x$.

Combining our derived trends in NRL and daytime $P_{NO_3^–}$ (Table 1), we calculate impacts of past and future NO$_x$ controls on the frequency of wintertime 24-h PM$_{2.5}$ NAAQS exceedances.
Using data from a multi-year experiment in the early 2000s in Fresno (Appendix A), the 24-h NO$_3^-$ concentration was observed to be an almost constant fraction of 24-h PM$_{2.5}$ each winter when 24-h PM$_{2.5}$ was greater than 15 μg m$^{-3}$ and an even larger fraction at lower loadings, typically in March. During DISCOVER-AQ, surface aerosol in Fresno was 41% (median) and 39% (mean) NO$_3^-$ in PM$_{2.5}$, and 57% (median) and 53% (mean) NH$_4$NO$_3$ in PM$_{2.5}$. Previous work has shown that NH$_4$NO$_3$ is a smaller portion of total PM$_{2.5}$ in Fresno than in any other location in the SJV, including Bakersfield, with rural PM$_{2.5}$ dominated by NH$_4$NO$_3$ (Zhang et al., 2010). We applied our calculated changes in $P$NO$_3^-$ to 50% of wintertime PM$_{2.5}$ mass as a conservative estimate. We also assume that NH$_4$NO$_3$ has been and will continue to be 50% of the aerosol mass over the entire past and future record. This simplification implies there have and will be only small changes in the heterogeneous loss rate of N$_2$O$_5$, in the relative speciated NO$_3$ reactivity, and in the fractional product yields of N$_2$O$_5$ hydrolysis. Fig. 2 suggests these factors have not substantially affected the NO$_2$ dependence of NO$_3^-$ over time, at least in the wintertime average in this location. We find that over the last decade, the impact of NO$_x$ controls on $P$NO$_3^-$, and hence NH$_4$NO$_3$, has been to reduce the number of 24-h PM$_{2.5}$ exceedances by 18–46% (Table 1). The primary mechanism for these changes has been decreased $P$NO$_3^-$ in the NRL. Trends in $P$O$_3^-$ account for 32–90% of the total observed change. We hypothesize that controls on the organic portion of aerosol mass, for example district-level amendments to national home wood burning and fireplace rules (San Joaquin Valley Air Pollution Control Board, 2003), may have driven the other portion of reductions.

In the future, a 50% decrease in NO$_x$ is predicted to decrease $P$NO$_3^-$ in the NRL more efficiently and to the point where this source is approximately equal to OH-initiated $P$NO$_3^-$ on weekends. If reductions of 75% NO$_x$ are achieved, $P$NO$_3^-$ in the NRL will decrease sufficiently that daytime OH-initiated HNO$_3$ formation is anticipated to become the dominant source of wintertime NH$_4$NO$_3$ on all days of the week. We calculate that over the next decade the SJV will experience 7–16% fewer exceedance days with a 50% decrease in NO$_x$ and ~30% fewer exceedances with a 75% decrease in NO$_x$.

We have not considered the impact of NH$_3$ controls because our data indicate $P$NO$_3^-$ chemistry, not the NH$_3$ abundance, drives NH$_4$NO$_3$ (Figs. 2 and 3), and because it has been shown that NH$_3$ emissions in the SJV are too high for any reasonable NH$_3$ control to affect wintertime NH$_4$NO$_3$. 

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concentrations (Herner et al., 2006). While these NO\textsubscript{x} controls constitute a major improvement to the air quality in the SJV, it is evident that decreases in organic aerosol mass are also required to eliminate high aerosol days in the SJV. We have not quantified, but do expect, future NO\textsubscript{x} reductions to impact the portion of organic aerosol mass that is secondary (SOA). In the laboratory, it has consistently been observed that NO\textsubscript{x} concentrations, relative to gas-phase organic compounds, influence the molecular identity and volatility of oxidation products such that SOA yields are higher at low NO\textsubscript{x} and suppressed at high NO\textsubscript{x} (e.g., Presto et al., 2005; Ng et al., 2007; Kroll and Seinfeld, 2008; Chan et al., 2010). Recent summertime field measurements of aerosol-phase RONO\textsubscript{2} in Bakersfield (Rollins et al., 2012) and at a forested field site in Colorado (Fry et al., 2013) found that NO\textsubscript{3} radical-initiated SOA formation correlated with NO\textsubscript{3} production and was proportional to NO\textsubscript{x} at low to moderate NO\textsubscript{x} levels. In Fresno during DISCOVER-AQ, SOA constituted 40% of the organic fraction of PM\textsubscript{1}, or 22% of total PM\textsubscript{1} mass (Young et al., 2015). Reductions in NO\textsubscript{x} as large as 50% to 75% are expected to influence this portion of the aerosol mass, and likely in a way that affects the frequency of exceedances in the SJV; however, the magnitude and sign of the impact are beyond the scope of this work.

Additional benefits of NO\textsubscript{x} decreases include reductions in high summertime O\textsubscript{3} throughout the SJV (Pusede and Cohen, 2012; Pusede et al., 2014) and decreases in both summertime inorganic nitrate aerosol (Markovic et al., 2014) and NO\textsubscript{3}-radical initiated SOA (Rollins et al., 2012). Because the U.S. EPA has recently decided to strengthen the annual PM\textsubscript{2.5} standard of 12 µg m\textsuperscript{-3} (Environmental Protection Agency, 2013), compliance with this NAAQS in the SJV will require reductions in aerosol concentrations in all seasons. Generally speaking, regulatory policies of valley-wide inter-pollutant trading of NO\textsubscript{x} for PM\textsubscript{2.5} control aimed at wintertime NH\textsubscript{4}NO\textsubscript{3} must be designed with knowledge of each nonlinear PNO\textsubscript{3}~ mechanism versus NO\textsubscript{2}, instead of use of a single exchange rate, as urban (high-NO\textsubscript{x}) and rural (low-NO\textsubscript{x}) PNO\textsubscript{3}~ are differently responsive to changes in NO\textsubscript{2}. Finally, because NO\textsubscript{3}~ is concentrated over Fresno and Bakersfield, NO\textsubscript{x} reductions need to happen in those cities themselves, prioritizing localized interventions to maximize the public health benefit and probability of regulatory compliance.
5 Conclusions

We derived trends in the wintertime production of NO$_3^-$ ($P$NO$_3^-$) as calculated from measurements of gas-phase precursors over the last thirteen years. We used these $P$NO$_3^-$ trends to explain the observed NO$_3^-$ sensitivity to NO$_2$, which was $-0.5$ µg m$^{-3}$ ppb$^{-1}$ NO$_2$ and $-0.64$ µg m$^{-3}$ ppb$^{-1}$ NO$_2$ in the San Joaquin Valley (SJV) cities of Fresno in Bakersfield, respectively. We found that reductions in NO$_x$ have both decreased and increased NH$_4$NO$_3$ formation rates by the various chemical pathways, but that the net downward trend in NO$_3^-$ has been driven by local changes in nighttime chemistry in residual layers decoupled from fresh surface emissions. We showed that high NH$_4$NO$_3$ abundances were a combined function of active chemical $P$NO$_3^-$ and rapid atmospheric loss by deposition of gas-phase HNO$_3$ ($\tau_{NO_3^-} \sim 3$ daytime h); in contrast, the total aerosol mass lifetime was controlled by cold fronts that turnover valley air on average every $5 \pm 1.5$ days. We computed the impact of future NO$_x$ decreases on $P$NO$_3^-$ from both nighttime and daytime mechanisms, finding the sign and magnitude of the changes are dependent on oxidation pathway, oxidant precursor, NO$_2$ concentration, and, at night, altitude. We calculated that the SJV will experience $7$–$16\%$ fewer days in exceedance of the 24-h PM$_{2.5}$ standard with a 50% NO$_x$ reduction and $\sim$30% fewer 24-h PM$_{2.5}$ exceedance days with a 75% NO$_x$ reduction. As an additional consequence of anticipated NO$_x$ controls, daytime rather than nighttime chemistry will drive NH$_4$NO$_3$ production in the SJV in the future. The observations and calculations presented here offer improved insight into the chemistry imbedded in the wintertime NH$_4$NO$_3$ diurnal cycles and suggest such long-term measurements would inform the absolute and relative contributions by vertically stratified NO$_3$ chemistry and OH-initiated production, especially if a record that captured diurnal variability were put in place prior to the sizable NO$_x$ reductions that are forthcoming. The specific NO$_x$ constraints on NH$_4$NO$_3$ chemistry we described here likely inform the effects of NO$_x$ emission changes, both increases and decreases, on aerosol in other polluted cities.

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Appendix A: measurements

A1 Long-term records

The long-term aerosol NO$_3^-$ data are from 24-h integrated filter-based measurements of PM$_{10}$ collected once every three to six days as part of the U.S. EPA’s Chemical Speciation Network program. The data were downloaded from the California Air Resources Board (CARB) archive (http://www.arb.ca.gov/aqmis2/aqdselect.php). We used measurements at Fresno-First Street (36.782°N, 119.773°W) and Bakersfield-5558 California Avenue (35.357°N, 119.063°W), as the two stations had mostly uninterrupted records and co-located observations of NO$_2$ and O$_3$. In Fig. 2, Bakersfield NO$_3^-$ wintertime (November–March) medians include the years 2001–2013 with an average of 46 weekday and 18 weekend data points year$^{-1}$. The Fresno-First Street station was closed in 2012 and so the Fresno NO$_3^-$ wintertime medians include 2001–2012 with an average of 36 weekday and 17 weekend data points year$^{-1}$.

To make these NO$_3^-$ measurements, ambient air is sampled through a denuder and aerosol are collected on a quartz fiber filter for 24 h, midnight-to-midnight. Water-soluble ions are then quantified by ion chromatography. NH$_4$NO$_3$ is semi-volatile and exists in thermal equilibrium with gas-phase HNO$_3$ and NH$_3$. Long sample collection times (24 h) and the presence of a denuder result in low biases due to loss of NO$_3^-$ to the gas-phase (Appel et al., 1981; Shaw Jr et al., 1982; Hering and Cass 1999; Babich et al., 2000). This interference is well documented and observed to be large during summer months, when more than 80% of NH$_4$NO$_3$ may be lost, but is estimated to be ~20% when relative humidities are high and temperatures are cold (Appel et al., 1981; Shaw Jr et al., 1982; Hering and Cass 1999). If we assume ambient conditions, as opposed to conditions internal to the instrument, drive the equilibrium (Appel et al., 1981; Shaw Jr et al., 1982; Hering and Cass 1999; Babich et al., 2000), we are able to estimate the interference using surface AMS observations of NO$_3^-$, NH$_4^+$, Cl$^-$, and sulfate (SO$_4^{2-}$) and a particle into liquid sampler (PILS) of potassium (K$^+$) and magnesium (Mg$^+$) in Fresno during DISCOVER-AQ to constrain the thermodynamic model ISORROPIA II (Nenes et al., 1998; Fountoukis and Nenes 2007). To do this, we set the total gas plus particle concentration equal to the ion data, running ISORROPIA II in the forward mode to simulate the gas-aerosol partitioning after the air stream passed through a denuder, consistent with all gases being captured by the
denuder and all aerosol depositing on the filter. During DISCOVER-AQ, the daily average
temperature and relative humidity (RH) were 8.5°C and 70%, respectively. Median daytime (8
am–6 pm) wintertime temperatures were within ~1 °C and 1% RH in Bakersfield and Fresno.
When these conditions drive the interference, we predict that daily-integrated \( \text{NO}_3^- \) was biased
low by 25%, in line with other reports (Chow et al., 2005). The average wintertime (November–
March) temperature and RH at the USDA Shafter Station from 2000–2013 were 10°C and 79%,
respectively. Under these ambient conditions, we predict measurements of the daily-integrated
\( \text{NO}_3^- \) are biased low by 23%. Evaporative loss of \( \text{NO}_3^- \) of 25% implies the true slope is 20%
greater with respect to the measured value. The observed correlation between \( \text{NO}_3^- \) and \( \text{NO}_2 \)
indicates ~20% of \( \text{NO}_2 \) is oxidized to \( \text{NO}_3^- \) (Fig. 2), a 20% \( \text{NO}_3^- \) error implies that 25% of \( \text{NO}_2 \)
is oxidized to \( \text{NO}_3^- \).

Hourly \( \text{O}_3 \), 24-h total \( \text{PM}_{2.5} \), and \( \text{NO}_2 \) data are from the CARB archive at the following sites:
North Church Street (36.333°N, 119.291°W) (2000–2013), and Bakersfield-5558 California
Avenue (2000–2013). \( \text{NO}_2 \) measurements are made by chemiluminescence coupled to a heated
molybdenum catalyst and have a known but poorly quantified positive interference from higher
oxides of nitrogen (Winer et al., 1974; Williams et al., 1998; Dunlea et al., 2007). This
interference is largest in the summertime when weakly bound higher oxides are more abundant
relative to \( \text{NO}_x \) and minimal in the wintertime. These instruments sample ambient air through a
filter, removing \( \text{NO}_3^- \) and likely a considerable fraction of gas-phase \( \text{HNO}_3 \) and multifunctional
organic nitrates, reducing the positive artifact. \( \text{NO}_2 \) concentrations are decreasing across the
valley at a rate similar to that observed from space by OMI, an instrument selective for \( \text{NO}_2 \),
suggesting that relative trends in \( \text{NO}_2 \) are accurate (Russell et al., 2010).

Hourly solar radiation, temperature, and RH data were taken from the California Irrigation
Management Information System archive (http://wwwcimis.water.ca.gov/cimis/data.jsp) at the
Shafter U.S. Department of Agriculture (USDA) station (35.530°N, 119.280°W). Sunrise and
sunset times in Bakersfield (35.357°N, 119.063°W) were downloaded from the United States
Nitrate ion observations with 10-minute time resolution were available during select time periods and were used to determine the wintertime variability in the fraction of PM$_{2.5}$ that was NO$_3^-$.

There data were collected in Fresno in 2000–2001 and 2003–2005 (Watson et al., 2000) as part of the EPA PM Supersites program (http://www.epa.gov/tnamti1/supersites.html). These measurements were made by flash volatizing NH$_4$NO$_3$, reducing HNO$_3$ across a heated catalyst to nitric oxide (NO), and detecting NO by chemiluminescence (Stolzenburg et al., 2003; Chow et al., 2008). It was reported that 24-hour averages of these high-time resolution observations were well correlated with, but 20–40% lower than, 24-h PM$_{2.5}$ filter samples (annual averages). This effect has been attributed to incomplete volatization and/or incomplete catalytic conversion of NO$_3^-$ to NO. Two identical instruments at the Fresno supersite yielded data that were also well correlated but different by 10–55% in the annual average (Chow et al., 2008). As a result, we treat these observations as uncalibrated but internally consistent over time.

### A2 DISCOVER-AQ observations

The DISCOVER-AQ experiment synchronized multiple ground sites and aircraft sampling of in situ and column measurements, producing a dataset resolved in space, both horizontally and vertically, and in time. The DISCOVER-AQ sampling strategy was built on repeated sampling across urban-rural (horizontal) and vertical gradients and on connecting observations made from balloons, onboard aircraft, and from space to monitoring sites at the surface. The NASA P-3B aircraft flew only during daylight hours, completing 2–3 identical circuits day$^{-1}$, alternating low altitude (150 m a.g.l.), along the valley’s western edge, medium-low (300 m a.g.l.) and high altitude flight passes (2.6 km a.g.l.). Circuits included missed approaches at all cities and rural waypoints when visibility permitted. Missed approaches allowed the P-3B to reach altitudes as low as 20–40 m (a.g.l.) and were conducted over airstrips. Landing strips were often rural and little trafficked but may have experienced airport-related NO$_x$ enhancements in the cities of Fresno and Bakersfield.

The comprehensive suite of DISCOVER-AQ data is available to the public at: https://www-air.larc.nasa.gov/cgi-bin/ArcView/discover-aq.ca-2013. Table A1 lists the measurement accuracy, analytical technique, platform and location, and associated references of species key to this analysis.
The NO$_3$–(g+p) measurements were made by thermal dissociation laser induced fluorescence (TD-LIF). The TD-LIF operating principle is as follows: NO$_2$ is detected by laser-induced fluorescence (LIF) (Thornton et al., 1999). A tunable dye laser is pumped by a Q-switched, frequency doubled Nd$^{3+}$:YAG laser. The narrow band dye laser is etalon-tuned to a specific 585 nm rovibronic feature of NO$_2$, alternating between this feature and the weaker continuum absorption. The resulting red-shifted photons are imaged onto a photomultiplier tube and collected using time-gated counting. The LIF technique is spectroscopically specific and accurate (±5%). The system was calibrated in flight every ~30 minutes with an NO$_2$ reference standard added at the inlet. The higher oxides of nitrogen, peroxy nitrates (RO$_2$NO$_2$), alkyl nitrates (RONO$_2$), and HNO$_3$ were measured by thermal dissociation (TD) coupled to LIF (Day et al., 2002). Dissociation of thermally labile species into NO$_2$ and a companion radical occurs at characteristic temperatures due to differing N—O bond strengths. Ambient air is pulled through heated quartz tube ovens followed by PFA sampling lines before reaching the NO$_2$ detection cell. An unheated channel detects only NO$_2$, a second channel (180°C) measures NO$_2$ + RO$_2$NO$_2$, a third channel (400°C) measures NO$_2$ + RO$_2$NO$_2$ + RONO$_2$(g+p), and a fourth (600°C) measures NO$_2$ + RO$_2$NO$_2$ + RONO$_2$(g+p) + NO$_3$–(g+p). Mixing ratios of each species are determined as the difference between adjacent channels, i.e. NO$_3$–(g+p) equals the 600°C channel minus the signal in the 400°C channel. ClNO$_2$ is thought to appear primarily in the 400°C channel. Recent observations indicated that about 50% of ClNO$_2$ was observed in the 400°C channel and 50% in the 600°C channel. Residence times in the ovens are sufficient to volatize aerosol bound nitrates, which is reflected in the RONO$_2$(g+p) + NO$_3$–(g+p) subscripting (Day et al., 2004).

NO$_3$–(p) was measured onboard the P-3B by a PILS system sampling at 4-minute time resolution with a well characterized ~3 µm aerosol size cutoff. In Fig. A1, 4-minute averaged NO$_3$–(g+p) measured by TD-LIF is compared against PILS NO$_3$–(p) when the aircraft was below 0.5 km a.s.l. The data are fit using a linear least squares model that assumes equally weighted errors in both measurements. Reported uncertainties in the TD-LIF and PILS observations are 15% and 20%, respectively, and they correlate ($\gamma = 0.8x + 2.3$) within combined uncertainties of 25%. The TD-LIF is sensitive to HNO$_3$(g), while the PILS is not. Using ISORROPIA II (described in Sect. 4.2) HNO$_3$(g) is predicted to be up to a few ppb in the afternoon, corresponding to the highest
temperatures but not to the highest $\mathrm{NO}_3^-(p)$ (Fig. 7). Additional details on the TD-LIF aircraft inlet configuration are found in Perring et al. (2009) and Wooldridge et al. (2010).

A3 Data and filtering for boundary layer sampling

Occasionally the height of the daytime boundary layer was observed near the altitude of the P-3B’s low-level flight legs, requiring analysis to distinguish between free troposphere and boundary layer air. Within boundary layer sampling was identified using $1 \, \text{s}^{-1}$ measurements of NO and RH recorded by the aircraft data system, according to steep discontinuities in both tracers, being high in the boundary layer and low aloft. In some cases, $\mathrm{H}_2\mathrm{O}(v)$ measured by diode laser hygrometer (DLH) and $\mathrm{O}_3$ were also considered. In Fig. 3 in addition to filtering for within boundary layer sampling, data were only plotted when the pressure altitude (a.s.l.) was greater than zero.

For our derivation of $\tau_{\mathrm{NO}_3^-}$, boundary layer depth was estimated with data from a micro-pulse lidar (MPL) located in the town of Porterville during DISCOVER-AQ. The MPL was supplemented with a wide-field receiver system that allowed for improved near-range signal recovery of the 527 nm attenuated backscatter profiles that were recorded at 30-meter vertical and 1-minute time resolutions. For daytime mixed-layer conditions driven by convection, the aerosol gradient fall off and stable molecular scatter signal above the lowest mixed aerosol layer signal represents the boundary layer height. According to this aerosol gradient, boundary layer heights were observed to range from 300 to 700 m during DISCOVER-AQ.
Appendix B: calculating $P\text{NO}_3^-$

The chemistry producing NO$_3$ radical at night and HNO$_3$ in the daytime is shown in Fig. B1 as a function of NO$_2$. The production of NO$_3$ radical ($\mu$g m$^{-3}$ h$^{-1}$) is calculated at four initial O$_x$ (O$_x$ ≡ NO$_2$ + O$_3$) conditions: 50 ppb O$_x$ (black), 40 ppb O$_x$ (purple), 30 ppb O$_x$ (violet), and 20 ppb O$_x$ (gray). In Fig. B1b, the production of HNO$_3$ is shown for two $PHO_x$ conditions: 0.3 ppt s$^{-1}$ $PHO_x$ (orange) and 0.15 ppt s$^{-1}$ $PHO_x$ (golden). For the sake of the night-day comparison, in Fig. B1 NO$_3$ radical production is scaled by two, which assumes all NO$_3$ reacts with NO$_2$ and that N$_2$O$_5$ hydrolysis is rapid compared to NO$_2$ + O$_3$. In this analysis, we compute $P\text{NO}_3^-$ as NO$_3$ radical production scaled by the observationally constrained NO$_3$ radical reactivity yielding NO$_3$ (see text below).

B1 NO$_3$-initiated $P\text{NO}_3^-$ in the nocturnal residual layer (NRL)

Our time-dependent box model of NO$_3$ radical production was run separately for each day over the time period 2000–2013. The model was initialized with hourly O$_3$ measurements at the surface using the maximum O$_3$ concentration 1–3 hours before sunset and the median daytime (10 am–3 pm LT) NO$_x$. This window was determined based on the timing of steep afternoon O$_3$ titration observed in the hourly surface O$_3$ data, both during DISCOVER-AQ and throughout the interannual record. O$_3$ and NO$_x$ were treated as well mixed in the daytime boundary layer and $k_{NO_2+O_3}$ was calculated based on the mean surface temperature at 6–8 pm LT. NO$_3$ radical production was integrated from sunset to 1 hour prior to sunrise. Differences were insignificant using mean O$_3$ over this time window versus the daily maximum.

Although there is no long-term, vertically resolved measurement record of any species in the region, there is observational evidence that the rapid decline in afternoon O$_3$ corresponds to the stratification of the daytime boundary layer. First, as part of CRPAQS, measurements of NO, O$_3$, as well as NO$_3^-$, were made simultaneously atop a tower (90 m a.g.l.) and at a lower level (7 m a.g.l.) in the SJV town of Angiola. Winter average (December 2000–January 2001) NO and O$_3$ at the two sampling heights were comparable from 10 am–1 pm LT; however, by 2 pm LT the concentrations began to diverge, with O$_3$ at 7 m falling rapidly (~5 ppb h$^{-1}$), concurrent with increases in NO, while O$_3$ at 90 m remaining approximately constant until sunset, whereupon a decrease of ~2 ppb h$^{-1}$ was observed. NO at the 90 m level was near zero throughout the night.
7-day time series of $\text{NO}_3^-$ data at 90 m showed clear increases in $\text{NO}_3^-$ beginning at nightfall and persisting until sunrise of ~10 $\mu$g m$^{-3}$ (Brown et al., 2006). These diurnal patterns suggest that the NRL(s) decouple from the surface layer ~3 h prior to sunset and that initial concentrations of the nocturnal chemistry reactants, $\text{NO}_2$ and $\text{O}_3$, are also represented by surface concentrations 3 h prior to sunset. During DISCOVER-AQ, full vertical profiling by the P-3B (including a missed approach) concluded in Fresno at 2:30–3:30 pm, ~2–3 h prior to sunset. Profiles of $\text{O}_3$ and the conserved tracer $\text{O}_x$ suggest that stratification of the daytime boundary layer had begun by this time on multiple afternoons, although day-to-day variability was observed. A comparison of mean $\text{O}_3$ and $\text{O}_x$ concentrations in the top 100 m (~0.35–0.45 km a.s.l.) and bottom 100 m (~0.15–0.05 km a.s.l.) of the atmosphere below the height of the daytime boundary layer, found small differences in $\text{O}_x$ on all flight days, but, on some days, large differences in $\text{O}_3$. $\text{O}_3$ variations equaled 25–30% the mean $\text{O}_3$ profile concentration on two days, 18 January and 22 January 2013. At midday (12–1 pm) at the same altitudes, small absolute differences were observed in both $\text{O}_3$ and $\text{O}_x$.

Reaction fates of the $\text{NO}_3$ radicals calculated by the time-dependent box model described above were determined according to the mean proportional $\text{NO}_3$ reactivity contributions observed during DISCOVER-AQ. $\text{NO}_3$ reactions (R3–R5) are as follows:

(R3) $\text{NO}_3 + \text{NO}_2 + \text{M} \rightleftharpoons \text{N}_2\text{O}_5 + \text{M}

(R4) $\text{NO}_3 + \text{alkene} \rightarrow \text{RONO}_2

(R5) $\text{NO}_3 + \text{aldehyde or alcohol or dimethyl sulfide} \rightarrow \text{HNO}_3 + \text{products}

Each of the three pathways results in a different number of $\text{NO}_3^-$ produced per $\text{NO}_3$ radical. $\text{NO}_3$ reactivities are defined as: $k_{\text{N}_2\text{O}_5}\text{K}_{\text{eq}}(\text{T})[\text{NO}_2]$ (Brown et al., 2003; Brown et al., 2009),

$$\Sigma_i k_{\text{NO}_3 + \text{alkene}_i}[\text{alkene}_i],$$

and

$$\Sigma_i \left( k_{\text{NO}_3 + \text{alcohol}_i}[\text{alcohol}_i] + k_{\text{NO}_3 + \text{aldehyde}_i}[\text{aldehyde}_i] + k_{\text{NO}_3 + \text{DMS}}[\text{DMS}] \right),$$

for R3, R4, and R5, respectively. $k_{\text{N}_2\text{O}_5} = 0.25\bar{v}\gamma(\text{N}_2\text{O}_5)$ is the $\text{N}_2\text{O}_5$ uptake coefficient and $\text{K}_{\text{eq}}(\text{T})$ is R3 equilibrium constant. For $k_{\text{N}_2\text{O}_5}$, $\bar{v}$ is the $\text{N}_2\text{O}_5$ mean molecular speed, $A$ is the aerosol surface area density, and $\gamma(\text{N}_2\text{O}_5)$ is the $\text{N}_2\text{O}_5$ aerosol uptake coefficient. $A$ was determined as the
product of the dry surface area of particles 60–1000 nm in diameter measured by an ultra-high sensitivity aerosol spectrometer and the hygroscopic growth factor, f(RH), calculated from the signal difference of a two nephelometers, one sampling dried air (RH < 40%) and a second sampling after humidification to 80% RH (each measurement was made onboard the P-3B). During DISCOVER-AQ, below 0.4 km a.s.l., the mean dry surface area was 191.8 ± 75 µm$^2$ cm$^{-3}$ (1σ) and the mean f(RH) was 1.7 ± 0.2 (1σ). $\gamma$(N$_2$O$_5$) was set equal to 0.006 as estimated from the parameterization in Bertram and Thornton (2009) following Wagner et al. (2013): 30 M aerosol water and an aerosol system including only water, NH$_4^+$, and NO$_3^−$. Using the aerosol water, NH$_4^+$, and NO$_3^−$ that we computed by ISORROPIA II, NO$_3^−$ constituted 45% aerosol mass. We assume that all N$_2$O$_5$ was converted to 2NO$_3^−$. If ClNO$_2$ formation is an important N$_2$O$_5$ hydrolysis product in the SJV, we have overestimated the total NO$_3^−$ production. While there is limited observational insight into the extent of ClNO$_2$ formation, because ClNO$_2$ is predicted to thermally dissociate in the RONO$_2$ channel of the TD-LIF instrument (reviewed in Perring et al., 2013), in the early morning, a portion of the measured quantity RONO$_2$(g+p) is possibly due to ClNO$_2$. On all days, the P-3B flights began at ~8 am LT, which is early enough to capture at least portion of nocturnal ClNO$_2$ prior to photolysis. The mean RONO$_2$(g+p) before 10 am and below 0.4 m a.s.l is equivalent to 1.6 µg m$^{-3}$ NO$_3^−$, or 15% of measured NO$_3^−$(g+p). However, there is little discernable loss of RONO$_2$(g+p) in the late morning, which would be expected if the RONO$_2$(g+p) was due to ClNO$_2$, suggesting 15% is an upper limit.

NO$_3$ reactivities were computed using the DISCOVER-AQ dataset with daytime (1–5 pm LT) surface observations of NO$_2$, organic compounds (whole air canister sampling), and dimethyl sulfide (DMS) (whole air canister sampling). CH$_2$O measurements from onboard the P3-B were included in the speciated reactivity for R5. Little temporal variability was observed in the concentrations of organic compounds between 1–5 pm LT. If alkenes reactive with NO$_3$ in NRL are oxidized by OH or O$_3$ prior to nightfall, then $\sum_ik_{NO3+alkene_i}[alkene_i]$ represents an overestimate. This will alter the absolute value of the calculated change in $P$NO$_3^−$, but not the functional form of the dependence. To account for this, we decrease the concentrations of organic species by one e-fold prior to computing the NO$_3$ reactivity.

In Fresno and Bakersfield the reaction of NO$_2$ with NO$_3$ represented ~80% of total NO$_3$ reactivity, with negligible weekday-weekend differences. The mean NO$_3$ reactivity values used
in the model were: 0.005 s\(^{-1}\) for addition to double bonds, yielding 0 HNO\(_3\); <0.001 s\(^{-1}\) for hydrogen abstraction, yielding 1 HNO\(_3\); and 0.02 s\(^{-1}\) for reaction with NO\(_2\), which after heterogeneous conversion of N\(_2\)O\(_5\) yields 2 HNO\(_3\). This gives 1.5 NO\(_3^-\) produced per NO\(_3\) on average. The integrated \(PNO_3^-\) was taken as the NO\(_3\) radical production scaled by the NO\(_3\) reactivity to NO\(_2\), which assumed reactions with alkenes and DMS were instantaneous. This result is similar to that of the wintertime NACHTT experiment at comparable relative NO\(_2\) concentrations (Wagner et al., 2013). During NACHTT NO\(_3\) and N\(_2\)O\(_5\) were measured, the kinetics of N\(_2\)O\(_5\) explicitly included in the calculation of \(PNO_3^-\), and 1.6 HNO\(_3\) per NO\(_3\) radical produced was inferred.

**B2 NO\(_3^-\)-initiated \(PNO_3^-\) in the nocturnal boundary layer (NBL)**

The production of NO\(_3\) radical was directly computed from surface measurements of hourly O\(_3\), NO\(_2\), NO\(_3\), and temperature each day from 2000–2013. NO\(_3\) production was integrated between sunset and 1 hour prior to sunrise and scaled by 1.1 NO\(_3^-\) produced per NO\(_3\), which is the result from the NO\(_3\) reactivity calculation described above with no organic reactivity loss. There were times that under conditions of very high NO that nighttime O\(_3\) was observed to be positive and constant at nonphysical values of 1–10 ppb for multiple hours. This offset was interpreted as a measurement artifact as excess NO titrates O\(_3\) completely. To account for this, when NO\(_x\) was greater than five times the reported O\(_3\), O\(_3\) was set equal to zero prior to computing NO\(_3\) production. However, concentrations of DMS and organic emissions, largely anthropogenic in origin in the wintertime SJV, are predicted to be higher in the NBL than in the daytime boundary layer.

**B3 OH-initiated \(PNO_3^-\)**

The integrated daily production of HNO\(_3\) was calculated for each day from 2000–2013 separately for each of the three HO\(_x\) sources: O(\(^1\)D) + H\(_2\)O, HONO photolysis, and CH\(_2\)O photolysis (equation B1). \(PNO_3^-\) versus NO\(_2\) attributed to each HO\(_x\) source is plotted in Fig. B2. OH was modeled with an analytical model constrained to DISCOVER-AQ observations, built on the assumption that oxidizing radicals were in steady state (equation B2) and that RO\(_2\) and HO\(_2\) production are approximately equal, as are RO\(_2\) production and loss, giving equation B2 for both RO\(_2\) and HO\(_2\) (equation B3) (Murphy et al., 2007). The symbol \(\alpha\) is the RONO\(_2\) branching ratio.
RO$_2$NO$_2$ are considered to be in thermal equilibrium with NO$_2$ and peroxy radicals, and therefore not to contribute to net radical formation. Calculated wintertime OH values were ~$10^6$ molecules cm$^{-3}$ at noontime and exhibited reasonable nonlinear NO$_2$ dependence throughout the day. Observational inputs to the model were NO and NO$_2$, the total organic reactivity to OH (VOCR), $PHO_x$, $\alpha$, and temperature. VOCR was computed as equal to $\sum k_{OH+VOC}[VOC_i]$ using whole air samples of speciated organic molecules collected at the ground during DISCOVER-AQ and CH$_2$O data from onboard the P-3B, as VOCR equal to $\sum k_{OH+VOC}[VOC_i]$. The daytime average was ~$4$ s$^{-1}$, consistent with a recent analysis of the temperature dependence of total VOCR in Bakersfield (Pusede et al., 2014), giving confidence that the majority of the reactivity was accounted for. The $\alpha$ is set equal to 2%. Equations B2 and B3 are combined to solve for OH.

\[
PHO_x = 2j_{O_3 \rightarrow O_D}[O_3] \frac{k[H_2O]}{k[H_2O]+k[N_2+O_2]} + 2j_{CH_2O}[CH_2O] + j_{HONO}[HONO]
\]

(B1)

\[
PHO_x = LHO_x = 2k_{HO+HO}[HO_2]^2 + 2k_{HO+RO}[HO_2][RO_2] + 2k_{RO+RO}[RO_2]^2
\]

+ $k_{NO+OH}[NO_2][OH] + \alpha k_{NO+RO}[NO][RO_2]
\]

(B2)

\[
[RO_2] \sim [HO_2] = \frac{\text{VOCR}[OH]}{(1-\alpha)k_{NO+RO}[NO]}
\]

(B3)

Noontime $j_{O_3}$, $j_{HONO}$, and $j_{CH_2O}$ were computed with the TUV calculator, http://cprm.acd.ucar.edu/Models/TUV/Interactive_TUV (Madronich, 1987), on a clear-sky day (20 January, 2013), scaled by the ratio of the TUV $j_{NO_2}$ and a measurement of $j_{NO_2}$ made onboard the P-3B, and combined with the diurnally varying long-term record of solar radiation.

The trend in O($^1$D) + H$_2$O was calculated from the observational record of O$_3$, RH, and solar radiation.

No multi-year measurements of HONO have been reported in U.S. cities. HONO is formed at night by a mechanism functionally equivalent to the conversion of two NO$_2$ to one gas-phase HONO and one ground-surface adsorbed HNO$_3$ molecule (Finlayson-Pitts et al., 2003). We computed HONO as equal to 4% the nighttime (10 pm–6 am LT) mean NO$_2$ (Stutz et al., 2004), yielding one HONO data point for each day. This HONO initialized a calculation wherein
photolytic loss was computed, giving HONO concentrations at 1-hour time resolution. We have not accounted for daytime formation; however, in total, daytime source(s) are weekday-weekend independent (Pusede et al., 2015).

The interannual trend in CH$_2$O is also unconstrained with observations. In the winter, CH$_2$O is not monitored at the surface and cannot be quantified from space due to low column concentrations and shallow daytime boundary layers. CH$_2$O is a primary organic emission from agricultural activities associated with animal feeds (Howard et al., 2010), dairy cows (Shaw et al., 2007), and combustion. State inventories offer little insight into CH$_2$O trends, as it is unknown whether a priori accounts are complete. CH$_2$O is also the oxidation product of most organic molecules in the atmosphere. We calculated the CH$_2$O concentration using a 0-D chemical model constrained to the complete 1-minute DISCOVER-AQ dataset. All 95 organic molecules measured by whole air sampling at the ground level at the Fresno site were included after scaling by a fit to aircraft carbon monoxide. Within the boundary layer, modeled CH$_2$O typically captured 75% of the CH$_2$O measured on the P-3B, with the discrepancy most likely due to the local primary CH$_2$O emissions. We ran the model under four NO$_x$ reduction scenarios, –75% NO$_x$; –50% NO$_x$; +50% NO$_x$; and +75% NO$_x$ assuming the portion of CH$_2$O not captured by our model remained constant. At 50% higher NO$_x$, i.e. at the start of the record, secondary CH$_2$O was ~10% lower on weekdays and ~5% lower on weekends than in the base model (2013 conditions). At –50% and –75% NO$_x$, in the next decade, secondary CH$_2$O is predicted to increase by 15–25% from 2013 weekend NO$_x$ levels, as reductions in NO$_x$ increase OH.

The integrated wintertime 24-h NH$_4$NO$_3$ production for each of the three HO$_x$ sources is shown in Fig. B2, along with the projected response of to changes in NO$_x$ of –50% and –75% from weekend concentrations. PNO$_3^-$ attributed to O($^1$D) + H$_2$O is 2–3 µg m$^{-3}$ day$^{-1}$ (2000–2013) and has increased by ~0.1 µg m$^{-3}$ ppb$^{-1}$ NO$_2$ in all three SJV cities. It is an order of magnitude smaller than PNO$_3^-$ in the NRL in the wintertime average. NH$_4$NO$_3$ production attributed to HONO has decreased with reduced NO$_2$, i.e. the trend has the correct sign compared to NO$_3^-$ concentrations (Fig. 2). Declines in HONO have resulted in a decrease in NH$_4$NO$_3$ production of 3–6 µg m$^{-3}$ day$^{-1}$ over the entire NO$_2$ range. We find that CH$_2$O, observed to be 2.3 ±1.1 ppb (1σ) in Fresno and 2.0 ±0.9 ppb in Bakersfield, has been the largest contributor to photochemical production of NH$_4$NO$_3$ at ~6 µg m$^{-3}$ day$^{-1}$ NO$_3^-$.
Appendix C: additional details regarding $\tau_{\text{NO}_3^-}$

The timing of decoupling between the NBL and the NRL(s) has implications for our derivation of $\tau_{\text{NO}_3^-}$. Observed daily $\frac{\partial\text{NO}_3^-}{\partial t}$ are consistent with the majority of $\text{NO}_3^-$ lost via deposition of HNO$_3$(g) from most of the daytime boundary layer. If loss occurred from only the lowest 50 m of the daytime boundary layer, then the observationally derived HNO$_3$(g) $v_d$ would be only 0.4 cm s$^{-1}$, below direct measurements (e.g., Huebert and Robert, 1985; Meyers et al., 1989; Sievering et al., 2001; Volpe Horii et al., 2005; Farmer et al., 2006). Gaseous HNO$_3$ that does not deposit will repartition to the aerosol phase when temperatures fall and RH rises in the evening. Assuming an NBL height of 50–100 m, then a nighttime rise (black data in Fig. 7) of 10–5 fold is expected. An NO$_3^-$ concentration of 10 µg m$^{-3}$ shifted to the gas-phase would increase by 100–50 µg m$^{-3}$ at nightfall. By contrast, typical nighttime increases were 0–15 µg m$^{-3}$.

In Fig. C1 we show low altitude (20–350 m a.g.l.) observations from the P-3B colored by NO$_3^-$ concentration over the city of Visalia on five flight days as evidence that afternoon decreases are net HNO$_3$ + NO$_3^-$ loss and not a shift in partitioning between the two species. In each panel the left-hand flight track was at midday (12–1 pm LT) and the right-hand track, shifted in space by 0.02° longitude for visual clarity, was in afternoon (3–4 pm LT). On each of the 5 flights, ~two-fold higher concentrations of NO$_3^-$ (g+p) were observed at midday compared to a few hours later. Additionally, the reduction in NO$_3^-$ (g+p) is apparent at the higher altitudes, shown in the top and bottom third of each panel, suggesting the loss in NO$_3^-$ measured by AMS at the surface in Fresno does extend up to at least 300–350 m a.g.l.
References


Fig. 1. Wintertime (November–March) NO$_2$ columns (molecules cm$^{-2}$) in the SJV using the UC Berkeley OMI BEHR retrieval (Russell et al., 2011). The urban NO$_2$ plumes of Fresno, Visalia, and Bakersfield are labeled to the left of their respective cities in panel A. Panel A: 2005–2006 weekdays (Tuesday–Friday). Panel B: 2005–2006 weekends (Saturday–Sunday). Panel C: 2012–2013 weekdays. Panel D: 2012–2013 weekends.
Fig. 2. Observed NO$_3^-$ (µg m$^{-3}$) in PM$_{10}$ versus daytime (10 am–3 pm LT) NO$_2$ on weekdays (closed circles) and weekends (open diamonds). Data are 3-yr medians of wintertime (November–March) data in Fresno (A) (2001–2012) and Bakersfield (B) (2001–2013). There are an average of 41 weekday days and 18 weekend days point$^{-1}$. Uncertainties in NO$_3^-$ are ±32% µg m$^{-3}$ on weekdays and ±40% µg m$^{-3}$ on weekends for NO$_3^-$ and less than ±9% on weekdays and ±13% on weekends for NO$_2$ (see text for details). Slopes are 0.5 µg m$^{-3}$ NO$_3^-$ ppb$^{-1}$ NO$_2$ in Fresno and 0.64 µg m$^{-3}$ NO$_3^-$ ppb$^{-1}$ NO$_2$ in Bakersfield are calculated using a weighted linear least squares fit with errors assumed in both the $x$ and $y$; weights are computed as counting errors derived from the number of observations.
Fig. 3. NO$_3^{−}$(g+p) ($\mu$g m$^{-3}$) in PM$_{2.5}$ (A), NO$_x$ (ppb) (B), and NH$_3$ (ppb) (C) measured onboard the NASA P-3B below the fully formed afternoon boundary layer and at pressure altitude (a.s.l.) greater than zero on the same days and averaged to a 0.05° x 0.05° grid.
Fig. 4. Simplified illustration of the diurnal evolution of the near-surface atmosphere as it relates to $P\text{NO}_3^-$. Boundary layer dynamics schematic adapted from Stull (1988).
Fig. 5. Vertically resolved NO$_3^-(g+p)$ (blue) in PM$_{2.5}$ as a function of altitude (km a.g.l.) between 8–9 am LT over Bakersfield on four flights when visibility and air traffic permitted a missed approach. The O$_3$ (orange) and potential temperature (black) are also shown. The orange diamonds represent the mean O$_3$ measured at the surface (8–9 am LT).
Fig 6. Calculated wintertime median $P_{NO_3^-}$ ($\mu g m^{-3} day^{-1}$) in the NRL versus daytime (10 am–3 pm LT) NO$_2$ (ppb) on weekdays (closed circles) and weekends (open diamonds) in Fresno (A) for each year in 2001–2012 and in Bakersfield (B) in 2001–2013 (blue). There is no significant difference between medians and means. The light blue line has a slope of 2.56, expected for unit conversion of NO$_2$ to NO$_3^-$ (ppb to $\mu g m^{-3}$). The actual NO$_3^-$ versus NO$_2$ slope (gray line) is calculated using a weighted linear least squares fit with errors assumed in both the x and y and weights that are the counting errors derived from the number of observations. The direction of time can be inferred from the NO$_2$ trends, as NO$_2$ concentrations have generally decreased each year over the decade.
**Fig. 7.** Time series of $\mathrm{NO}_3^-$ (µg m$^{-3}$) in PM$_1$ measured at the ground in Fresno during DISCOVER-AQ. Days are in blue and nights are in black. Select afternoon data (magenta) were fit to derive $\tau_{\mathrm{NO}_3^-}$. 
Fig. 8. In Bakersfield, tethered 3-yr weekday (closed circles) and weekend (open diamonds) medians of calculated wintertime NH$_4$NO$_3$ production (µg m$^{-3}$ day$^{-1}$) in the NRL (A) and during the daytime (B) versus NO$_2$. Medians and means give the same result. Brighter data are observationally-constrained 3-yr medians at present (2010–2013). Pale points are observationally-constrained 3-yr medians at the start of the record (2001–2004). Predicted NH$_4$NO$_3$ production at −50% weekend NO$_x$ are black-filled diamonds and −75% weekend NO$_x$ are gray-filled diamonds. Weekend data were selected simply to expand the NO$_x$ range of individual curves; impacts on weekdays can be inferred. In panel A, the light blue line is stoichiometric and the gray line is a fit to the annual observations as in Fig. 5. In panel B, the gray line is the calculated HNO$_3$ production with PHO$_x$ and organic reactivity equal to present-day values.
Table 1. Effects of three NO\textsubscript{x} emission control scenarios on wintertime 24-h PM\textsubscript{2.5} NAAQS exceedances in Fresno, Visalia, and Bakersfield. Percentages are calculated according to days in which data exist, not total wintertime days. **Rows 1–2:** Average exceedances winter\textsuperscript{-1} (November–March) in the last 3 years of the record, rounded up, and percentage of days in violation. **Rows 3–9:** Number of exceedances predicted after a 50\% increase (back in time) and 50\% and 75\% reductions in NO\textsubscript{x}, including the calculated percent change from present day. In row 3, the number in parentheses is the actual number of exceedances averaged for 2001–2004. In row 5, the number of calculated exceedances was rounded down to compute the percent.

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<td>40 (53)</td>
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<td>% change in exceedances</td>
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Table A1. Species, measurement accuracy, analytical technique, time resolution, location/platform, and reference for select DISCOVER-AQ observation included in our analysis. Many compounds are measured with higher precision than accuracy. See original references for details.

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Fig. A1. P-3B TD-LIF NO$_3$\(^{(\text{g+p})}\) in ~PM$_{2.5}$ versus PILS NO$_3^-$ in PM$_3$ below 0.5 km a.s.l. The gray line is one-to-one and the black line is a least squares fit assuming equal weights in $x$ and $y$ data.
**Fig. B1. Panel A:** NO$_3$ radical production (µg m$^{-3}$ h$^{-1}$) versus NO$_2$ (ppb) under four O$_x$ conditions: 50 ppb O$_x$ (black), 40 ppb O$_x$ (purple), 30 ppb O$_x$ (violet), and 20 ppb O$_x$ (gray). The temperature is 282 K and NO$_3$ radical production is scaled by two, i.e. all NO$_3$ reacts with NO$_2$ and N$_2$O$_5$ hydrolysis is rapid compared to NO$_3$ formation. **Panel B:** Production of HNO$_3$ (µg m$^{-3}$ h$^{-1}$) as a function of NO$_2$ computed with an analytical model at NO:NO$_x$ = 0.3 and VOCR = 4 s$^{-1}$ at 0.3 ppt s$^{-1}$ PHO$_x$ (orange) and 0.15 ppt s$^{-1}$ PHO$_x$ (golden).
Fig. B2. Wintertime NH$_4$NO$_3^-$ production (µg m$^{-3}$ day$^{-1}$) by OH-initiated chemistry versus daytime (10 am–3 pm LT) NO$_2$ (ppb) for each individual HO$_x$ precursor: O($^{1}$D) + H$_2$O (red), HONO (turquoise), and CH$_2$O (green). Data are tethered present-day 3-yr medians on weekdays (closed circles) and weekends (open diamonds) in Fresno (A) and Bakersfield (B). Lighter tint data are tethered 3-yr medians at the start of the record (2001–2004). There is no significant difference between medians and means. Predicted NH$_4$NO$_3^-$ production calculated at –50% weekend NO$_x$ (NO$_x$ black-filled diamond) and –75% weekend NO$_x$ (gray-filled diamond) are also shown.
Fig. C1. NO$_3$\textsuperscript{(g+p)} (µg m$^{-3}$) in PM$_{2.5}$ measured during ten missed approaches on five days over Visalia. The left-hand flight track is the midday (12–1 pm LT) missed approach and the right-hand track, shifted east by 0.02°, is the afternoon (3–4 pm LT) missed approach.