Dear Steve,

Thank you for your careful review. Your feedback has improved our manuscript.

Best,

Sally and Ron

This paper uses a combination of data from long term monitoring at surface sites and from the recent DISCOVER campaign in the central valley of California to ascertain the chemical and dynamical mechanism responsible for winter NH_4NO_3 *aerosol formation. The paper further analyzes response of aerosol mass loading to past and predicted future changes in* NO_x *emissions.*

This is a highly valuable contribution. I recommend publication in ACP with attention to the following minor comments.

Page 27092, line 15: Does the 20% correlation between NO2 and NO3- imply that 20% of NOx emissions form ammonium nitrate? Some further reference to the overall NOx loss budget would be helpful at this stage of the manuscript.

We have changed the text to read:

> Page 6, lines 18–22: "One ppb NO_2 corresponds to 2.56 μg 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."

Page 27092, line 20: No error limits are given, only units.

We will ensure that these numbers appear in the final version.

Page 27093, line 15: Were there nighttime flight to measure the winds aloft, or is the "nighttime winds near zero" statement based on surface observations. Nocturnal low level jets are common in the SJV (e.g., Bao, J. Appl. Met. and Climat., 47, 2372, 2008), at least in summer. The authors should comment on the possibility for this transport mechanism to operate in winter.

There were no night flights conducted during DISCOVER-AQ, which we now state explicitly:

> Page 22, lines 18–19: "The NASA P-3B aircraft flew only during daylight hours, completing 2–3 identical circuits day^{-1}…"

We have changed the specific text from, "nighttime winds near zero" to:

Page 7, lines 11–12: "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."

We have also added discussion of transport by nocturnal low-level jets in two places in the text:

Page 7, lines 15–21: "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."

Page 15, lines 1–15: "Our calculation implies greater decreases in $P\mathrm{NO}_3^-$ have occurred in lower-NO_x rural environments than in cities since 2001 given the same relative NO_x reductions. During a previous aerosol experiment, CRPAQS (California Regional PM_{10}/$PM_{2.5}$ 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_4NO_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_4NO_3 and NO_3^- precursors, distributing NH_4NO_3 and NH_4NO_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. "

Page 27093, line 25: Whether or not NO3- is aerosol bound depends on the available ammonia in addition to temperature, correct?

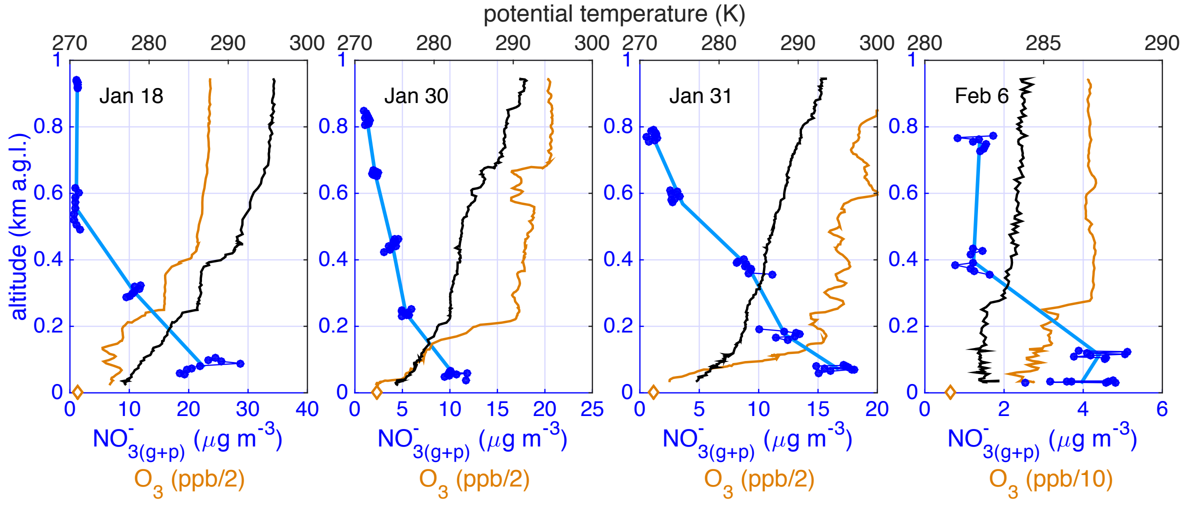
We have changed the test to read:

Pages 7–8, lines 27–2: “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_4NO_3 abundances are driven by NO_3^- production (PNO_3^-). PNO_3^- occurs by distinct nighttime and daytime mechanisms, each of which is a nonlinear function of NO_2.”

Page 27093, Figure A1: Residual layers are called out on the figure, which is shown as a time series, but without reference to the potential temperature structure. A plot of the chemical data (O3 and total nitrate) against height, with potential temperature included, would make a better case for the assignment of the residual layer structure.

We have updated the figure and added to/modified our discussion:

Pages 8–9, lines 24–2: “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.”



“**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)."

Page 27095, line 1-2: Statement that N_2O_5 » NO_3 is true for high NO_2 and low T, but is not general unless these conditions are met.

We have changed the statement to read:

Page 9, lines 3–4: "Nitrate radical reacts with NO_2 to form dinitrogen pentoxide (N_2O_5) and generally under atmospheric conditions of high NO_2 and low temperature, $N_2O_5 \gg NO_3$."

Page 27095, line 8: Should also reference reaction with Cl- to produce HNO3 + ClNO2 here. The paper as a whole lacks any other reference to this potential effect on the production rate of NO3- in the NRL. Similarly, the paper should reference the possibility for limitation of NO3- via the presence of aerosol nitrate (e.g., Wahner,et al, JGR, 103(D23), 31103-31112.)

We have added general information on both $ClNO_2$ formation and NO_3^- limitation in Section 3. Although we do not have observations to directly test the impact of either effect over time, we have added text speculating their influence on NO_3^- to the long-term trends. We have also used TD-LIF $RONO_2$ measurements to place an upper bound on the fraction of N_2O_5 hydrolyzed to NO_3^- + $ClNO_2$.

Page 9, lines 9–13: "…N_2O_5 uptake onto aerosols (e.g., Dentener and Crutzen 1993; Macintyre and Evans 2010; Wagner et al., 2013), whereupon N_2O_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_2O_5 is a function of the total aerosol surface area and of the fraction of gas-particle collisions resulting in N_2O_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)."

Page 27, lines 8–18: "We assume that all N_2O_5 was converted to $2NO_3^-$. If $ClNO_2$ formation is an important N_2O_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."

Page 27096, line 10: Check grammar – appears to be a run-on sentence.

The new text reads:

Page 10, lines 18–22: "In the NBL (not shown) PNO_3^- has increased from <1 μg m^{-3} day^{-1} to 3–5 μg m^{-3} day^{-1} on weekdays and to 6–8 μg 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."

Can a quantitative measure of the NBL vs NRL be given here? Data such as that in Figure A1 must provide some insight.

We have added this text to address the comment:

Pages 8–9, lines 27–2: "…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."

Page 10, lines 20–25: "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."

Page 27098, line 27: Where do the specified parameters for BL heights come from? Is this all measured using the micro pulsed lidar data?

We have changed the text to clarify:

Page 13, lines 1–4: "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."

Page 27099, lines 24-27: See comment above. If nighttime transport can occur via low level jet formation during wintertime, Bakersfield could be regarded as a receptor site.

We agree that Bakersfield is in part a receptor site and had intended to convey this in our original draft. We have modified the text so this it is now stated explicitly:

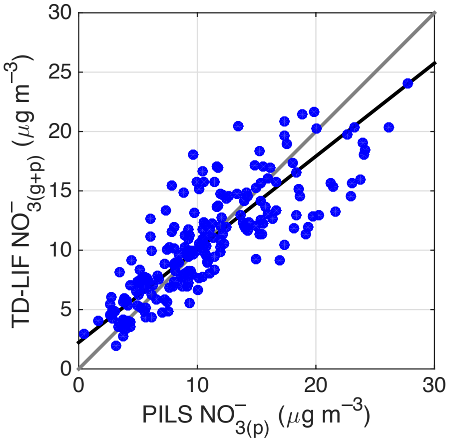
Pages 13–14, lines 23–2: "These differences between Bakersfield and Fresno may in part be attributed to the former's location in the southern end of the SJV, where the city is enclosed on three sides by the mountains, resulting in reduced losses to advection and mixing than in Fresno. Likewise, transport 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."

Page 27108, line 2-3: A figure showing the agreement between the TD-LIF and PiLS NO3- would be extremely helpful. Few if any such comparisons exist in the literature, and TD-LIF could be a very important method for this measurement if well validated.

We have added the Figure A1 (original Fig. A1 is now A2) and this text:

Pages 23–24, lines 22–2: "$NO_3^-{}_{(p)}$ 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 ($y = 0.8x + 2.3$) 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 $NO_3^-{}_{(p)}$ (Fig. 7). Additional details on the TD-LIF aircraft inlet configuration are found in Perring et al. (2009) and Wooldridge et al. (2010)."



"**Fig. A1.** P-3B TD-LIF $NO_3^-{}_{(g+p)}$ 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."

Figure B1. NO3 radical production rates are compared to photochemical HNO3 production. The figure would be more representative if nighttime HNO3 production, occurring at twice the nitrate radical production rate, were compared to photochemical HNO3. The former would assume hydrolysis rapid in comparison to the NO2 + O3 rate.

The text, figure, and caption have been updated. Text and caption below:

Page 25, lines 6–10: "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_2O_5 hydrolysis is rapid compared to NO_2 + O_3. In this analysis, we compute PNO_3^- as NO_3 radical production scaled by the observationally constrained NO_3 radical reactivity yielding NO_3^- (see text below)."

"**Fig. B1.** … 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_2O_5 hydrolysis is rapid compared to NO_3 formation."

Page 27109, line 15: Is NOx well mixed in the afternoon BL? The DISCOVER data should show this. DISCOVER data from the east coast shows that this is not a good approximation, so a comment on how well mixed NO2 is in the data is warranted here.

We had not intended to imply that NO_x is well mixed in the afternoon BL. We have clarified the text to this point. We have also added a discussion of the evidence that on average during the wintertime the daytime boundary layer begins to stratify 1–3 h prior to sunset, which in the winter in the SJV is 4:45–6:15 PST (November–March).

Page 25, line 13–17: "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…"

Pages 25–26, lines 21–13: "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 agl) and at a lower level (7 m agl) 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. A 7-day time series of NO_3^- data at 90 m showed clear increases in NO_3^- beginning at nightfall and persisting until sunrise of ~10 µg 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, NO_2 and 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 O_3 and the conserved tracer 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 O_3 and 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 O_x on all flight days, but, on some days, large differences in O_3. O_3 variations equaled 25–30% the mean 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 O_3 and O_x."

*Page 27110, lines 10-11: The statement implies that NO3 reactivity is calculated by comparing NO2 + NO3 to NO3 + VOC. This is not how standard NO3 budgets are calculated, since it neglects the back reaction of N2O5 to reform NO2 + NO3. Rather, NO3 + VOC is compared to the estimated heterogeneous uptake rate coefficient of N2O5, multiplied by the equilibrium ratio of N2O5/NO3 (given as K*NO2). Direct comparison of NO3 + VOC to NO3 + NO2 is incorrect, and should be modified accordingly if this is what the authors mean. See Brown et al., JGR 108(D17), D174539 for more details on this method. Use of daytime VOCs may not be appropriate for NRL calculations, since the reactive VOC content of the NRL is likely lower, and could be substantially lower, than the daytime BL.*

We have updated our work accordingly:

Pages 26–27, lines 20–8: "Each of the three pathways results in a different number of NO_3^- produced per NO_3 radical. NO_3 reactivities are defined as: $k_{N_2O_5}K_{eq}(T)[NO_2]$ (Brown et al., 2003; Brown et al., 2009), $\sum_i k_{NO_3+alkene_i}[alkene_i]$, and $\sum_i \left(k_{NO_3+alcohol_i}[alcohol_i]+k_{NO_3+aldehyde_i}[aldehyde_i]+k_{NO_3+DMS}[DMS]\right)$, for R3, R4, and R5, respectively. $k_{N_2O_5}=0.25\bar{v}A\gamma(N_2O_5)$ is the N_2O_5 uptake coefficient and $K_{eq}(T)$ is R3 equilibrium constant. For $k_{N_2O_5}$, $\bar{v}$ is the N_2O_5 mean molecular speed, A is the aerosol surface area density, and $\gamma(N_2O_5)$ is the N_2O_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 $\mu m^2\ cm^{-3}$ (1σ) and the mean f(RH) was 1.7 ± 0.2 (1σ). $\gamma(N_2O_5)$ 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."

This change in how we calculate NO_3 radical reactivity to NO_2 has caused a change in our numbers, which we have updated throughout the analysis and paper.

We do not have nocturnal VOC observations in either the NBL or NRL. We modified our approach as follows:

Pages 27–28, lines 22–3: “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 $\sum_i k_{\mathrm{NO_3+alkene_i}}[\mathrm{alkene}_i]$ represents an overestimate. This will alter the absolute value of the calculated change in $P\mathrm{NO_3^-}$, 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_2O_5 yields 2 HNO_3. This gives 1.5 NO_3^- produced per NO_3 on average.”

Page 28, lines 11–13: “[In the NBL] 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.”