

Reviewer 2:

Thank you for reviewing the paper and providing insightful and helpful feedback.

p 20129: "until the air parcel is removed from the upper troposphere by convective downdrafts." This is not a complete and accurate portrayal of the dynamics. A lot of downward transport occurs through large-scale descent, not part of convective events.

p 20130: "... and mixed with background upper tropospheric air until downdrafts associated with subsequent deep convection remove air parcels from the upper troposphere." Same point as above. I don't think this is true. Other scale downward motions play a huge role.

p 20135: "a distribution of time since convection defined by the frequency of frontal systems." How can this define the distribution? It certainly contributes, but other factors help define it, too. A parcel can go up in one frontal system. It needn't come down in the next. Large-scale subsidence processes also contribute.

The reviewer correctly points out that our description of air parcel removal from the upper troposphere is overly simplistic and leaves out larger scale processes. Although the description focuses on downdrafts, other removal processes are implicitly included in the back trajectory regression and in the conceptual model of our stochastic model framework. We have expanded the removal process description in the methods section, and now refer to "removal" more broadly in the rest of the paper.

p 20129 now reads: "After deep convection, air parcels undergo chemical processing that converts NO_x to HNO_3 , reducing the $\text{NO}_x:\text{HNO}_3$ ratio until the air parcel is removed from the upper troposphere by convective downdrafts or subsidence. Initial deep convection is identified by high $\text{NO}_x:\text{HNO}_3$ and subsequent removal is modeled stochastically."

p 20130 now reads: "After convection, the air parcel photochemically ages, converting NO_x to HNO_3 , and mixes with background upper tropospheric air until it is removed from the upper troposphere by convective downdrafts or subsidence."

p 20134-5 now reads: "Convective updrafts loft air parcels into the upper troposphere which are later removed by convective downdrafts or subsidence. The time between convective lofting and removal, hereafter air parcel lifetime τ_{air} , can be used to calculate the instantaneous or sampled distribution of time since convection $\text{Pr}(t)$ in the upper troposphere."

p 20134-5: "The time between convective lofting and subsequent subsidence, here- after air parcel lifetime ..." Isn't lifetime really just the time since convective lofting, even if subsidence has not occurred? Please clarify.

Time since convection and air parcel lifetime are distinct yet related properties. Time since convection is the time between lofting and some point in time, for instance at the time of sampling. Air parcel lifetime is the time since convection at the time the air parcel is removed from the upper troposphere. The distribution of air parcel lifetime and time since convection are mathematically identical if they have, as we assume, an exponential distribution. In that sense, a time since convection is independent of removal, but the distribution of sampled time since convection is dependent on the removal rate.

p 20134-5 now reads: "The time between convective lofting and removal, hereafter air parcel lifetime τ_{air} , can be used to calculate the instantaneous or sampling distribution of time since convection $\text{Pr}(t)$ in the upper troposphere."

p 20130: "Particle chemistry is most likely of limited importance in our study..." This claim is not supported in any quantitative manner. I am concerned that uptake of HNO₃ on particles could significantly effect the NO_x:HNO₃ ratio in ways ignored in the present analysis.

As the reviewer correctly points out, HNO₃ uptake on particles would influence the NO_x:HNO₃ and, so, was evaluated as a potential bias. As stated on p 20131 line 14, we minimize the influence of ice particles by excluding air parcels with cloud water droplets (LWC) or ice crystals (IWC). In clouds, the surface area of ice is very large and represents a large surface for HNO₃ adsorption. Our model is initialized immediately following cloud processing associated with convection. While our filtered air parcels exclude cloud droplets and cloud ice crystals, they do include other aerosols. These aerosols may have ice coatings, which would make them efficient surfaces for adsorption, though we note that the surface area is smaller than in clouds.

To examine the largest possible impact of HNO₃ uptake, and thus bound the influence, we evaluated the importance of aerosol uptake as if all aerosol surface area had uptake coefficients equal to ice. We then modeled HNO₃ uptake on particles using IUPAC recommendations for both a Langmuir isotherm (as in Marécal et al., 2010) and a kinetic process. In both cases, we have excluded trapping theory. Trapping theory would account for the transfer of adsorbed molecules from the surface into the bulk ice phase during ice growth. The ice growth would represent a refreshing surface that would potentially increase the fraction of HNO₃ in/on the ice at equilibrium. Marécal et al. (2010, p4997) find that, in clouds, trapping of HNO₃ is of the same order of magnitude as surface adsorption. If those cloud results can be extrapolated to our aerosol conditions, our surface adsorption equilibrium results can be doubled to estimate the combined effect of surface adsorption and trapping. In an attempt to counter-balance potential effects of ice growth or recoating, we make conservative assumptions for the uptake coefficient of aerosols and we assume that fractional coverage (θ) is unity with no surface site competition.

The results of our analysis showed that absorption is only significant for a short time and does not sequester a large amount of HNO₃. When we assume particle surfaces are coated

with ice and initially pristine and that fractional coverage (θ) is unity, aerosol uptake can be an important removal process for a short time (<15 min). Figure 13 shows HNO_3 uptake rates relative to HNO_3 formation rates, and the ratio of particle to gas-phase HNO_3 at equilibrium. After 15 minutes, the uptake process is small relative to HNO_3 formation and is unlikely to represent a major bias. Figure 14 shows the HNO_3 equilibrium given the observed aerosol surface area and temperature. At equilibrium, the total adsorbed HNO_3 is unlikely to strongly influence age categories because the total aerosol HNO_3 is a small fraction of total HNO_3 (always <3%). As a fraction of total HNO_3 within each age bin, particle phase HNO_3 is only more than 1% for a few outlier air parcels cases. These findings are also confirmed by the conservation of NO_y between age groups. If HNO_3 adsorption were a major loss of gas-phase nitrogen, our NO_y would also decrease with age.

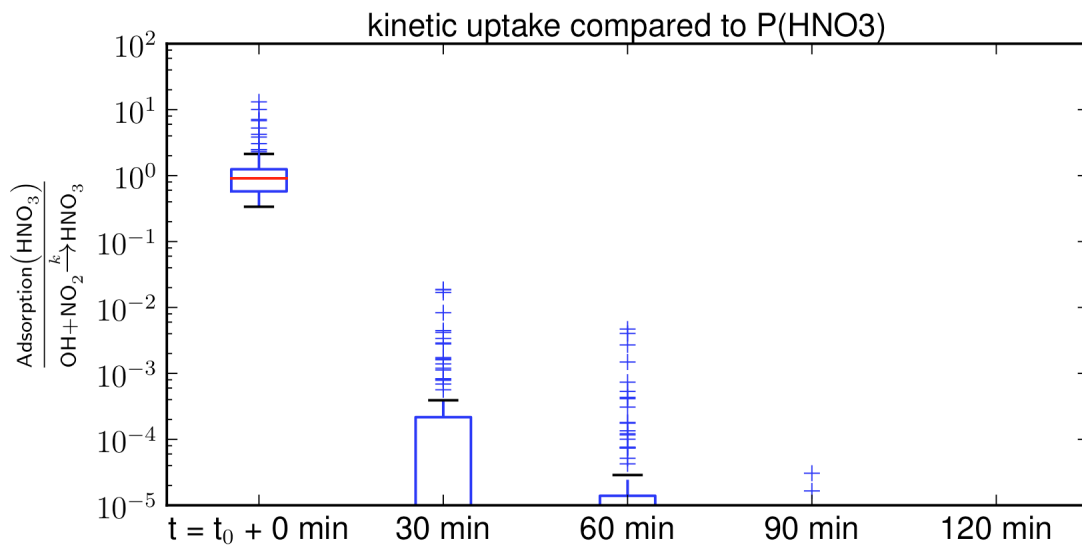


Fig. 13: Ratio of HNO_3 uptake to HNO_3 production as a function of time since convection.

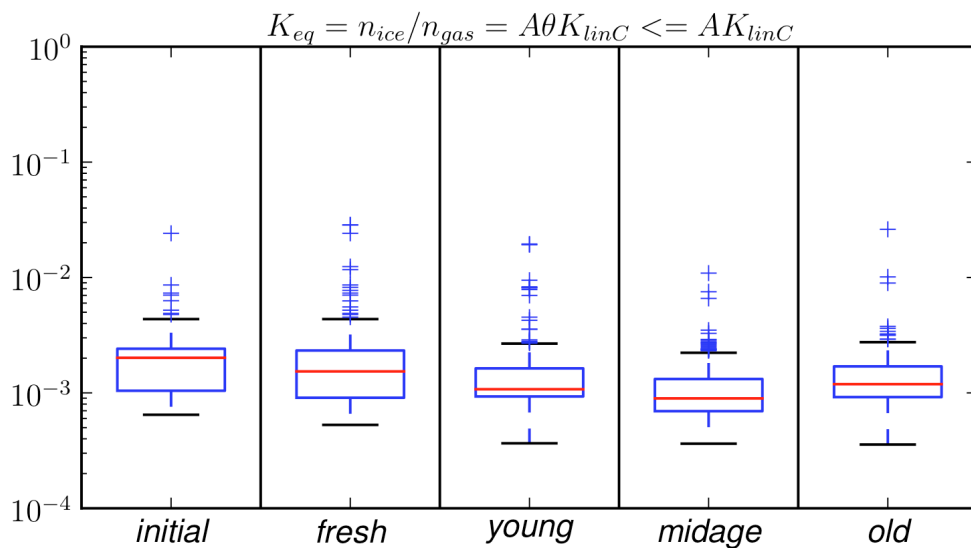


Fig 14: Upper bound ratio of particle to gas-phase HNO_3 binned by $\text{NO}_x:\text{HNO}_3$.

The results of this analysis were not included in this manuscript because of length concerns, but are planned for inclusion in a formal uncertainty analysis paper. That paper will include uptake of HNO₃ as well as N₂O₅, HO₂, and radical precursors. The broader influence of aerosols is unclear because of competing effects of various gas-phase species on the NO_x:HNO₃ ratio. While uptake of HNO₃ increases NO_x:HNO₃, uptake of radicals and precursors (e.g., HO₂, H₂O₂, CH₃C(O)OH) and N₂O₅ hydrolysis would decrease NO_x:HNO₃. Many aerosol adsorption rates have remaining uncertainty that we hope to help address with a directed scrutiny in a subsequent formal uncertainty analysis paper. Nitric acid, however, has a high uptake rate and direct influence on our aging metric, which makes it a good surrogate for assessing the influence of aerosols.

p 20130 now reads "Particle chemistry is most likely of limited importance in our study due to low particle surface area. In an initial analysis, less than 1% of HNO₃ is in the particle phase at equilibrium."

p 20132: "only NO_x and HNO₃ have age-dependent mixing ratios." To what extent does this result simply derive from the way in which the data are divided up? Using a NO:HNO₃ ratio helps to bring this about. Is too strong to say it guarantees it, but it sure pushes things in this direction. When NO_x:HNO₃ is high, NO_x tends to be high and HNO₃ tends to be low.

As the reviewer correctly points out, the binning approach used in this paper could bias this result. Our intention, was only to contrast other species and not to prove the NO_x:HNO₃ age-dependency demonstrated previously (Prather and Jacob, 1997; Jaeglé et al., 1998).

p 20132 now reads: "Figure 1 shows the total oxidized nitrogen (NO_y) partitioning of each age group and shows that pernitric acid, PANS, and organic nitrates did not show strong age-dependent mixing ratios."

p 20135: It is acknowledged that the aircraft sampling was biased toward young parcels. How does the doubling described compensate for this? This seems to be pulled out of thin air, but perhaps there is a justification.

p 20138: "bias-corrected" <- this is a potentially misleading phrase. Is it really correct? A doubling has been applied that is aimed to act in the direction of correcting, but does that really make it correct? Why a doubling and not some other factor?

The Fuelberg et al. (2008) and Bertram et al. (2007) papers cite a ~2x probability of sampling air parcels within the first 6 hours following convection. This study uses that result as the approximate basis for adjusting cumulative probability distribution function, which then allows us to derive the probability distribution function.

p 20135 now reads: “The INTEX-NA observations, however, preferentially sampled freshly convective air parcels. Bertram et al. (2007) showed that 21.4% of air parcels had time since convection less than 6 h, which is far greater than 12.5% of the sampling domain with convective activity during the INTEX-NA campaign. To approximately correct the sample bias, we increase the relative probability of sampling time since convection less than 6 h by a factor of 2.”

On the other hand, some things are dismissed rather casually, without quantification (see below – ... treatment of mixing [is given sensitivity check by varying the parameter, but is this adequate?])

The treatment of mixing in this paper is generally coarse, but sensitivity checks did go beyond varying the parameter. Using a single value will over-estimate mixing for some parcels, and under-estimate it for others, but the mean influence will be reasonable represented. A mean mixing parameter, while coarse, is consistent with treatment by other analyses (Ray et al., 2004; Bertram et al., 2007). In addition, we examined the effect of dynamic mixing. The Dynamic Mixing case (DynMix) shown in the appendix is a single instance of a larger dynamic mixing sensitivity analysis that we performed. We concluded that our results were robust with respect to a variety of treatments and decided to use the single parameter because it was most consistent with other literature.

p 20132 now reads: “The rate of mixing is assumed to be constant and set to 5% per day (Bertram, 2007). Sensitivity analysis using up to 10 times the mixing rate, and/or more complex dynamic background conditions and mixing rates did not yield meaningfully different results (see Fig. 10).”

p 20146, typo: “an test”

We thank the reviewer for catching this typo.

p 20146 now reads “a test”

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