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# *Interactive comment on* "Efficient $N_2O_5$ Uptake and $NO_3$ Oxidation in the Outflow of Urban Beijing" *by* Haichao Wang et al.

## Anonymous Referee #2

Received and published: 14 March 2018

Wang et al present measurements of N2O5, ClNO2 and ancillary species in the urban outflow of Beijing and thereby analyze nocturnal rates of oxidation of VOCS, NOx lifetimes and chlorine activation via heterogeneous reaction of N2O5 on chloride containing particles. N2O5 uptake coefficients were in the "usual" range and ClNO2 yields were high, implying abundant sources of chlorine. The authors use established expressions to analyze their data and the manuscript contributes to the growing literature on nighttime VOC oxidation, NOX loss and ClNO2 formation without providing significant new insight. Detracting from this work, much of the referencing seems to be an arbitrary selection (often self-citation) of related work and the estimation (or presentation) of uncertainties in derived parameters is largely missing.

The following points should be addressed (some are major) and the English language

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Discussion paper

corrected (some suggestions are listed below) before re-review.

L61 State how the yield of SOA (23.8 % or 174 %) is defined.

L70 kN2O5 is not a rate coefficient. Its best to call it a pseudo-first order loss rate constant to avoid confusing it with rate constants for gas-phase reactions

L70 Eq. (1) was certainly not derived by Tang et al in 2017. Use an appropriate (earlier) reference.

L175 The correction factor of 0.6 (independent of time of day, day of campaign, NOx, or air mass-age) is clearly a poor assumption given that the NOx to NOy ratio is highly variable in time and space. The assumption that the correction factor in Wangdu is the same as in Changping is without real basis. Note also that the photo-stationary state between NO,NO2 and O3 will break down in the presence of other oxidants (e.g. RO2) so that measurement of NO and O3 (and j-NO2) cannot replace NO2 measurements. The authors must estimate the uncertainty related to this correction factor (and thus with the NO2 measurements) is they wish to use NO2 data in any quantitative sense. This applies to section 4.2 where they calculate N2O5 lifetimes in steady state via calculation of the N2O5 production term, which requires NO2 mixing ratios. It also applies to the calculation of NO3 from the N2O5 and NO2 measurements and the equilibrium constant and this impacts on the results of section 4.2 where NO3 concentrations are used to calculated oxidation rates of VOCs. In principal, the lack of accurate NO2 measurements during this campaign reduces many conclusions of this paper to a qualitative level.

L191 "Figure 2 shows the calculated backward trajectories using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model". As far as I can tell, this is the first and last mention of air-mass trajectories. I would suggest that the Figure can be relegated to the SI.

L235 "The single peak (in N2O5) occurred near 20:00 and then gradually decreased".

C2

Is this a reproducible feature of the campaign or a bias of the mean due to one or two events. Taking the median rather than the mean would resolve this. Also, why (line 236) does the N2O5 increase before sunrise (or do the authors mean "at sunrise") ?

L243-246 "ClNO2 accumulated corresponding to N2O5 after sunset but ClNO2 peaked in the middle or the second half of the night since the nocturnal sinks of ClNO2 were negligible to our knowledge." I'm not sure what the authors are trying to say here. There are many examples that show great variability in the N2O5–to-ClNO2 ratio. The interesting part of this section (lines 243 to 267) is the discussion of the sources of chloride needed to drive the ClNO2 formation in this continental region. In principal, the chloride content of the aerosol can be calculated from the yield of ClNO2 and the appropriate expression that defines the parameter "f". I suggest the authors do this.

L249 and promoted the N2O5 conversion to ClNO2 (e.g., Roberts et al., 2009). Why this citation ? The formation of ClNO2 from N2O5 was known (and quantified) long before 2009. Cite the appropriate literature.

L279 In lines 280-290 It is not clear whether we are dealing with ratios of the concentrations of ClNO2 and N2O5 or ratios in their production rates (L282). If relative rates are calculated we need to know over which period they were derived.

L295 A composite term, ðİŻ¿ × f, was used to evaluate the overall ClNO2 yield (f)......

L296 How and over what period was the production rate of ClNO2 determined ? How stable were N2O5 and Sa in this period ?

L296 the term was estimated by considering..... Give the expression used to derive the composite term from the observables.

L300 and 301 (and Table 3) The average values need to be listed with standard deviations to enable comparison. The same applies to Table 4.

L313 uptake coefficients are derived from analysis of particulate nitrate and ClNO2 concentrations. Only those nights were chosen when a clear covariance between

these parameters was observed. The authors should explain how they define "clear covariance" and why, on other nights, covariance did not exist. Surely the formation of ClNO2 must always be accompanied by formation of particle nitrate ? A major issue in this analysis is the assumption that the particulate nitrate id only formed from N2O5 uptake and not influenced by (temperature dependent) HNO3 repartitioning. It appears that there were no measurements of gas-phase HNO3 or ammonia to support the contentions that this was not important. The authors must assess this rigorously and state how he uptake coefficients would be influenced by HNO3 uptake.

L327 "the most rigorous analysis was used in this study". I do not understand what this implies. Most rigorous compared to what ?

L330 Figure 6 would be improved by adding the result of a calculation with lower (factor two ?) and higher (factor two ?) uptake coefficients to test the sensitivity of the data to the derived parameter. Also, what is the source of the offset in the particle nitrate ? How does the particle nitrate look over the diel period. This is essential information when trying to understand the effects of HNO3 re-partitioning (see comment above). .

L331 "the predicted N2O5 uptake coefficient and ClNO2 yield were 0.017 and 1.0, respectively." What are the uncertainties ?

L334 "The errors from each derivation were 30% - 50% and came from the field measurements of Sa, N2O5, pNO3- and ClNO2." Using the uncertainties listed in Table 1 results in total uncertainty (propagated in quadrature) of > 50 %. I do not understand how the quoted 30-50 % was derived.

L369 "The time periods with NO concentration larger than 0.1 ppbv were excluded". Why was this threshold chosen. The lifetime of NO3 at 0.1 ppbv of NO is about 10-20 s.

L389 The uncertainties in the N2O5 loss rate need to be calculated. As this involves NO2 measurements, the uncertainty will be very large.

L403 This section deals with oxidation of VOCs and loss of NOx to nitrates (inorganic and organic). NO3 was not measured but calculated from N2O5 and NO2 (the latter also not measured properly). The NO3 concentrations derived are therefore associated with great uncertainty. This needs to be assessed and used in the subsequent discussion and comparison with O3-induced oxidation.

L416 Similar to k(OH). . . . . . I'm not sure why OH is being mentioned here.

L422 Terpenes were measured using PTRMS, i.e. no speciation. What is the basis for assuming that ïĄą-pinene can be used as surrogate for NO3 + terpene reactivity in these air masses ?

Figure 9 Needs uncertainties on the two terms being compared.

Some (certainly not exhaustive) suggestions for improvement of the English.

L18 Nocturnal reactive nitrogen compounds play an important role in regional air pollution

L27 The concentration of the nitrate radical (NO3) was calculated assuming that. . ..

L34 which indicates that reduction of NOx emissions cannot help reduce the nocturnal formation of ONs.

L42 NO3 can initiate the removal of many kind of anthropogenic

L58 The reactions of NO3 with several BVOCs produce considerable amounts of organic nitrates

L207 . . .nocturnal nitrate radical production rate, P(NO3), was large, with an average. . .

L61 The reaction of NO3 with isoprene has a SOA yield of 23.8% (Ng et al., 2008). For the reaction with a monoterpene, such as limonene, the yield can reach 174% at ambient temperatures (Boyd et al., 2017).

L97 the reaction also contributed significantly to NOX. . . . . .

C5

L259 by acid displacement

L260 "however, the photolysis with profound ClNO2 was still maintained until noon". I think the authors are trying to say that ClNO2 survived until noon ? In this context the should mention the J-values of ClNO2.

L273-276 This needs rewriting. I think the gist if this is that that the N2O5 concentration depends on the NO2 level more than on the O3 concentration. If so, please explain why.

L305 . . ..which implies that the ClNO2 formation efficiency. . ...

L403 The title of this section is misleading. NO3 is not oxidized, but the VOCs. I suggest "NO3-induced nocturnal oxidation of VOCs" or similar.

L429 For calculating nocturnal ONs production from NO3 oxidation of isoprene and monoterpene, as well as inorganic nitrate production via N2O5 heterogeneous uptake over the same period. . ...