

Interactive comment on “Efficient N₂O₅ Uptake and NO₃ Oxidation in the Outflow of Urban Beijing” by Haichao Wang et al.

Anonymous Referee #2

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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, NO_x 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, NO_x 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

C1

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, NO_x, or air mass-age) is clearly a poor assumption given that the NO_x to NO_y 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) if 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 calculate 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 (HYSPPLIT) 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, $\delta \dot{Z}_c \times f$, 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

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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 is 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 the 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.

C4

L403 This section deals with oxidation of VOCs and loss of NO_x 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 α -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 NO_x 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 NO_x.

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.

L305which 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.

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C6