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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Fast heterogeneous N_2O_5 uptake and $ClNO_2$ production in power plant plumes observed in the nocturnal residual layer over the North China Plain” *by* Zhe Wang et al.

Anonymous Referee #1

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Wang et al. report measurements of N2O5 and ClNO2 at a mountain site on the North China Plain. The data contain occasional coal power plant plumes in which ClNO2 mixing ratios were enhanced. N2O5 uptake parameters and ClNO2 yields were calculated from a steady state model and found to be fast (i.e., large gamma and high phi) compared to other regions. Calculated uptake parameters were rationalized in terms of aerosol ionic composition (nitrate, chloride, and water calculated using a thermodynamic model). Overall the manuscript reads well and would be of interest to the community. Some of the methodology (such as the calculations of uptake parameters, equations 6 and 8,) require some clarification and may need refinement.

Specific comments

pg 3 line 11 Consider citing Tham, Y., C. Yan, L. Xue, Q. Zha, X. Wang, and T. Wang (2014), Presence of high nitryl chloride in Asian coastal environment and its impact on atmospheric photochemistry, Chin. Sci. Bull., 59(4), 356-359, doi: 10.1007/s11434-013-0063-y.

pg 3, line 12 "such as Colorado, Hessen and Canada" Hessen and Colorado are States of Germany and of the U.S.A. To be consistent, please list the third one as Alberta (a province in Canada).

pg, line 13. The Faxon et al 2015 study was in SE Texas and close to the coast and shouldn't be cited here. Instead consider citing Mielke, L. H., A. Furgeson, C. A. Odame-Ankrah, and H. D. Osthoff (2016), Ubiquity of ClNO2 in the nocturnal boundary layer of Calgary, AB, Canada, Canadian Journal of Chemistry, 94(4), 414-423, doi: 10.1139/cjc-2015-0426.

pg 3 line 14. Following " Anthropogenic sources of chlorine including coal combustion in power plants, industries, and biomass burning may potentially facilitate ClNO2 production" cite Riedel, T. P., et al. (2013), Chlorine activation within urban or power plant plumes: Vertically resolved ClNO2 and Cl2 measurements from a tall tower in a polluted continental setting, J. Geophys. Res., 118(15), 8702-8715, doi: 10.1002/jgrd.50637.

pg 3, line 15 Please state the uncertainty of this number (4.7 ppbv +/- ?)

pg 3, line 26. For readers not familiar with the NCP – please indicate the relative locations of Wangdu and Jinan – perhaps as dots in Figure 1?

pg 3, line 31 "In the present study, we measured the concentrations of N2O5, ClNO2, and related species at a mountaintop site in the NCP and characterized the nighttime nitrogen chemistry within the residual layer over a polluted region of northern China. " please state month or season and the year here as the season (i.e., temperatures) are relevant for N2O5 chemistry

pg 4 line 14 " the measurement site is located in an area that is not frequently visited and therefore, should not be significantly affected by local anthropogenic emissions" Since Mt. Tai has been the site of other studies, the data ought to exist to definitively say whether the site IS or IS NOT affected by local emissions.

pg 4, line 17. Along the same lines, since a dozen power plants are mentioned, do the data from the earlier suggest that the site is impact by coal power plant emissions (e.g., high SO2, black carbon, or sulfate levels)?

Is this site sufficiently close or far enough to the coast to be impacted (or not) by sea salt aerosol?

pg 4 line 24 " .... which was replaced daily and washed in the ultrasonic bath to minimize wall loss caused by deposited particles (Wang et al., 2016)." Was there any change in signal levels after the line was washed? What time of day was the tubing changed?

pg 4 line 27 "Manual calibrations of N2O5 and ClNO2 were conducted daily to monitor the instrument sensitivity and background." Please state what the CIMS response factors and associated uncertainties and background levels for each of the ions monitored were.

pg 4, line 28 " The N2O5 standard was synthesized on-line from the reaction between NO2 and O3, and the ClNO2 was produced by passing a known concentration of N2O5 through a NaCl slurry " Please state how the N2O5 and ClNO2 concentrations of this source were quantified or what assumptions were made (e.g., ClNO2 yield from NaCl + N2O5).

pg 5, line 10 " Water soluble ionic compositions of PM2.5... were measured hourly... " It would be great to show a time series of these data. Were chloride concentrations higher in power plant plumes?

pg 5 line 26 and Figure 2. There is a lot of sustained N2O5 during daytime which is unusual especially since temperatures frequently were >20C during the day. Is this a real signal? I am a bit doubtful. In any case, it warrants discussion that N2O5 at 3 pm was in greater abundance than at 3 am (Figure 3).

I am also suspicious about the relatively low levels at night. Was the N2O5 transmission efficiency monitored? If so, please show those data. If not, please state that it was not.

It also looks like there is a hardly any NO during the day which is consistent with there being N2O5, but is strange also as NO2 should photo-dissociate and sustain NO. Perhaps the O3 levels are high enough and photolysis rates low enough for this to happen. In my opinion, this warrants a bit of analysis & discussion – are the levels consistent with a simple photostationary analysis, or is the pss severely perturbed (i.e., too much NO2 relative to NO)?

pg 6 "The elevated ClNO2 levels observed at Mt. Tai are similar to recent measurements at a surface rural site (Wangdu) in northern China (Tham et al., 2016) and a mountain site (Tai Mo Shan) in southern China (Wang et al., 2016), but are slightly higher than previous measurements conducted in coastal (e.g., Osthoff et al., 2008; Riedel et al., 2012; Mielke et al., 2013) and inland sites (e.g., Thornton et al., 2010; Phillips et al., 2012; Riedel et al., 2013) in other regions of the world." This is an interesting comparison though more information is needed to put this particular study site and the above comparisons in context. Is the study site affected by sea salt aerosol from the Pacific Ocean? Based on that information, what levels of ClNO2 would have been expected?

pg 6 line 13 "88.6 ppbv" and "24.4 ppbv" - are these averages? If so, also state the range of values (or standard error).

pg 6, line 16 "16.4 ppbv" same comment as above

pg 6, line 23 – section 3.2 This plume is very interesting. It may be that all the SO2 has generated enough sulfate to make the aerosol quite acidic. Was Cl2 monitored by any chance?

pg 8, line 20 " Because of the lack of concurrent VOCs measurements in the present study, we used the average VOC speciations measured before sunrise and in the evening at Mt. Tai during our previous study in 2007 ". Would these VOC levels be sustained in the power plant plume, where the P(NO3) is greater than in surrounding air? Consider adding a statement that this estimate is likely an upper limit.

pg 9, lines 19-20. "the observed γ values in the present study are significantly higher". This could also be indicatative of a measurement bias such as N2O5 inlet losses (see earlier comment). Considering that the authors claim very large gamma values, attention should be paid to biases introduced by measurement uncertainties. Please add a couple of sentences about this potential issue to the manuscript.

pg 10, line 1. There a multiple versions of the E-AIM model. Please be specific as to what was used (inputs & model).

pg 10, line 21 "nitrate can suppress the N2O5 uptake (Bertram and Thornton, 2009)" The nitrate effect is well documented and goes back to Mentel, T. F., M. Sohn, and A. Wahner (1999), Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols, Phys. Chem. Chem. Phys., 1(24), 5451-5457, doi: 10.1039/a905338g, and not Bertram and Thornton. In general, gamma scales inversely with nitrate as the reaction of NO2+ with nitrate reverses N2O5 uptake and is consistent with Figure S1 shows. The paragraph on lines 17-25 is unnecessarily confusing in that the discussion here neglects the simultaneous effects of other ions (e.g., chloride – discussed in next paragraph). Consider tightening this paragraph.

pg 11, equation 6. The math here is not sound – it should not be dN2O5/dt in the denominator (if N2O5 achieves steady state, as argued earlier, this quantity would be zero). Please remove the first 2 terms.

The assumption here is that ClNO2 is conserved and is not produced by other sources (such as Cl + NO2) – please state these assumptions.

The paragraph that follows equation 6 does not provide enough information. How was the yield of ClNO2 actually calculated? Was the N2O5 uptake loss truly integrated using a time-integrated box-model? Or was it approximated using the ratio of observed mixing ratios (as suggested by the first term in eqn 6)? Note that rates change from the point of emission to the point of observation.

pg 12, line 5 "The parameterized ÏŢ values exhibit positive dependence on the aerosol chloride concentration and the Cl-/H2O ratio. " I am assuming this is based on the colors shown in Figure 10? How good is the water estimate?

Also, if concentrations of N2O5 are underestimated due to a measurement bias and real concentrations of N2O5 were higher, things fall into place ... (see earlier comments)

pg 12, line 2. Please state that the chloride concentration was measured and the water content is based on a thermodynamical model and perform an error estimate (so that appropriate error bars can be added to Figure 10).

pg 12, eqn 8. This equation is not correct. It ought to be the loss rate of N2O5, not its rate of change (d[N2O5]/dt) which would be zero at steady state. There are major assumptions made here – that aerosol nitrate is conserved, i.e., absence of aerosol deposition and volatilization via NH4NO3 formation etc. These assumptions should be clearly stated.

pg 12, line 31. "The NO3 formation was predicted by integrating each derived formation rate over the corresponding ..." the formation rate of nitrate changes from the point emission to the point of observation, which was not taken into account here.

pg 13, line 16. Wang et al., 2016 is not the best reference. Please cite Behnke, W., C. George, V. Scheer, and C. Zetzsch (1997), Production and decay of ClNO2, from the reaction of gaseous N2O5 with NaCl solution: Bulk and aerosol experiments, J. Geophys. Res., 102(D3), 3795-3804, doi: 10.1029/96JD03057 instead.

pg 13, lines 16/17 "For simplicity, the reactions of NO3 with VOCs can be assumed to result in the complete removal of reactive nitrogen (Wagner et al., 2013)". This is likely not true in this study, where NO3 primarily reacts with terpenes. Wangberg et al. (1997), Product and mechanistic study of the reaction of NO3 radicals with alpha-pinene, Environm. Sci. Technol., 31(7), 2130-2135, and others since have showed that a significant fraction of NO2 is ultimately released again.

pg 13, line 22. "The NOx removal rate varied from 0.19 to 2.34 ppb h-1, with a mean of 1.12 ± 0.63 ppb h-1. This loss rate is higher than that determined from tower measurements during wintertime in Colorado, with integrated nocturnal NO2 loss ranging from 2.2 to 4.4 ppbv (Wagner et al., 2013)" Comparing absolute loss rates may not be meaningful since the overall NOx levels may be different – consider normalizing, for example, through division of average nocturnal NOx mixing ratios at both locations to derive a pseudo-first order loss rate coefficient.

pg 14, line 21 " The results demonstrate the significance of heterogeneous N2O5-ClNO2 chemistry in the polluted residual layer over the NCP, ..." Are these rates significant? Perhaps. The question is: significant in what sense or compared to what? Consider adding more context (e.g., daytime nitrate formation rates, rates of other locations, etc.)

pg 19, Figure 1. Please indicate the scales of Fig. 1a (lat/long) and 1b (km/km)

pg 19, Figure 2 Please give a vertical scale for jNO2

pg 21 Figure 4c – is the triangle the measurement location? If so, indicate in the caption.

Figure 4b and 5b – state the fit uncertainties (-1.77+/-?; -1.44+/-?) on the figure

pg 22 Figure 7 - state the fit uncertainties (0.011+/-? and 0.040+/-?) on the figure pg 22 Figure 8 – show the error bars for the experimental values

pg 24 Figure 10 is there a difference between phi(N2O5) in Figure 10a and phi(ClNO2) in Figure 10b (and Tables 1 and 2)? The main manuscript defines only phi without subscript.

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Discussion paper