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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 #3

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General comments:

This paper presents measurement of N2O5 and ClNO2 from a polluted mountaintop site in the North China Plain during summer 2014. Measurements of these nighttime reactive nitrogen species in the polluted residual layer of China are novel and a valuable contribution to the literature. The authors attribute several of the plumes encountered at the mountaintop site to emissions from regional coal fired power plants. They further use several standard analysis metrics to interpret the data and provide estimates of N2O5 uptake coefficients and ClNO2 yields, along with the overall influence of nighttime chemistry on aerosol nitrate formation in the region.

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Discussion paper

Results for N2O5 uptake coefficients are generally larger and ClNO2 yields are generally smaller than previous literature determinations. These observations may not be unrelated. If the analysis method biases the N2O5 uptake coefficient to large values, then the same analysis will tend to predict lower ClNO2 yields. The authors should be careful to consider uncertainties that could lead to such a bias, especially in the aerosol size distribution measurement and in the assessment of NO3-VOC reactivity. Alternatively, the very high relative humidity at this site could lead to exactly the effect that is found here, producing faster N2O5 reactivity but also a larger fraction tending toward HNO3 rather than ClNO2. The paper could make this point explicitly in its comparison to previous work (e.g. Phillips, et al., Wagner et al.).

The paper should be published subject to these comments and the minor comments below.

Specific comments.

Page 4, line 16-17. Is there a database showing the location of major coal fired power plants that could be included with the map in Figure 1? This would help to clarify the number of sources and their distance from the observatory.

Page 4, line 27. What were the results of the manual calibrations for N2O5 and ClNO2? Give some sense for reproducibility, and lack of either N2O5 loss or ClNO2 generation on the inlets.

Page 6, line 5. Elevated CO is not normally associated with coal fired power plant emissions, at least in the U.S and Europe.

Page 6, line 26. What are the slopes of correlation plots of SO2 vs NOy, SO2 vs CO and CO vs NOy? This information is important in the attribution of this plume to a coal fired plant, since coal typically has larger SO2/NOy and lower CO/NOy than that from urban emission. These values could be included in Table 1.

For comparison, what was the overall relationship between CO and NOy or SO2 and

NOy for the entire campaign? If most of the NOy is urban, then the global relationships might define the urban numbers so that the power plants could be more easily distinguished.

Page 7, line 17. Authors probably mean a slope steeper than -1 (rather than +1).

Page 8, line 25. The determination of N2O5 reactivity is not quite clear. Text implies that equation 3 is used, and that k(NO3)/Keq[NO2] is subtracted from this number based on the measured VOCs from a different year. Correct? If so, this should be stated explicitly, possibly with an equation.

If the above is correct, then for the sake of clarity, the NO3 loss rates quoted in line 23 should be divided by Keq[NO2] to make it obvious how the budget was done.

What is not given here is a sense for the uncertainty (e.g., N2O5 contributions of 80% and 71% given to two significant figures with no uncertainty). Since VOC measurements from a separate year are used, and since the NO3 reactivity is dominated by reaction with monoterpenes, which are variable and quite temperature dependent, there could be substantial year to year variability and thus considerable uncertainty in this budget. At the very least, this uncertainty should be qualitatively noted. If the authors have data that would quantify year to year or night to night variability in the NO3 losses, then those numbers should be used to formulate a quantitative error budget.

Is there any potential for unmeasured VOC that contributes more to the NO3 reactivity budget? Have the authors considered reaction of NO3 with peroxy radicals?

Page 9, line 14. Similar comment regarding error analysis in Table 2. The authors should provide error bars for the determined gamma and phi values based on measurement uncertainties. Especially important, but not discussed, is the uncertainty in the aerosol size distribution measurement to determine Sa in equation (5). Such measurements often have considerable uncertainty that can be limiting for the gamma determinations.

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Page 10, line 17. What does a plot of gamma vs. NO3-/H2O or Cl-/H2O look like? Especially for the nitrate effect, the dependence against the nitrate to liquid water ratio should give the most information.

Page 11, equation (6). The analysis measured ClNO2 production relative to N2O5 loss. The denominator is difficult to determine with certainty, and especially if the N2O5 loss rates are too large (see concerns about aerosol surface area and NO3 loss to VOC above), the analysis will produce too small a value for phi(ClNO2). These caveats should be noted. There should be production of aerosol nitrate or nitric acid together with the N2O5 loss. Are any trends in aerosol nitrate or NOz (=NOy-NOx) during the periods of ClNO2 increase available to corroborate the analysis? This approach could be more quantitative than one based on N2O5 loss.

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