

Interactive comment on “Nocturnal nitrogen oxides at a rural mountain-site in South-Western Germany” by J. N. Crowley et al.

Anonymous Referee #2

Received and published: 17 February 2010

This nicely and very clearly written paper describes measurements of nocturnal nitrogen oxides (NO, NO₂, NO₃, and N₂O₅) plus ozone, water vapour, and aerosol surface area at a mountainous location in the Taunus region near Frankfurt/Main. The major findings are significant in that include convincing evidence against the currently recommended rate coefficients for homogeneous hydrolysis of N₂O₅. I recommend acceptance of this paper after my (minor, I hope) comments below have been addressed.

pg 1, lines 18-19. Replace “A steady-state lifetime analysis showed that the nocturnal NO_x were generally dominated by reaction of NO₃ with volatile organic compounds...” with “A steady-state lifetime analysis is consistent with the nocturnal NO_x generally dominated by reaction of NO₃ with volatile organic compounds...”. In my opinion, a steady state analysis cannot “show” a cause; it can only “show” magnitudes of loss

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rates, and be consistent with an explanation.

pg 1, line 28. “... which is absent (or present ...)”. Consider rephrasing. Presence and absence are like black and white or being pregnant – it either is or is not.

pg 2, lines 8-10. Please state what rate coefficients were used (i.e., NASA-JPL or IUPAC).

pg 2, line 24. Heterogeneous uptake of N₂O₅ not only produces nitrate but also ClNO₂ (Behnke, W., et al. (1997), Production and decay of ClNO₂, from the reaction of gaseous N₂O₅ with NaCl solution: Bulk and aerosol experiments, Journal of Geophysical Research-Atmospheres, 102(D3), 3795-3804, and Osthoff, H. D., et al. (2008), High levels of nitryl chloride in the polluted subtropical marine boundary layer, Nature Geoscience, 1(5), 324-328). A fellow scientist, who is an expert on aerosol composition, transport and aging, told me at a conference that a group in Mainz claimed to have seen evidence for long-range transport of marine aerosol to the study region (near Mainz). I unfortunately do not remember who she had been talking to. Since I was born and grew up in Frankfurt/Main, I at first chuckled at the notion that the region would be strongly influenced by marine air, but then again, who is to argue with aerosol composition measurements. I was wondering what the authors' thoughts are on this, and if you could please add a short statement on whether the authors think chloride, from either marine or anthropogenic sources, could have been present in the aerosol phase at the Kleiner Feldberg location.

line 27. “... partitioning ... between the NO_x ... and NO_y families ...” Consider rephrasing as what happens is not really partitioning between NO_x and NO_y (NO_y includes NO_x, so NO_x can't partition to NO_y); suggestion: partitioning between various forms of NO_y, or NO_x to NO_z? Also, please define NO_y, and see comment on page 21.

pg 3, line 22. Give a reference for this equation. Suggestion: Fuchs, N. A., and A. G. Stagnin (1970), Highly Dispersed Aerosols, Ann Arbor, MI.

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pg 3, line 24 - pg 4, line 5. Homogeneous reaction of N₂O₅ with water vapour. The magnitudes of the rate coefficients for this reaction have been called into question by several field studies, e.g., Brown, S. S., et al. (2009), Reactive uptake coefficients for N₂O₅ determined from aircraft measurements during the Second Texas Air Quality Study: Comparison to current model parameterizations, *J. Geophys. Res.*, 114(D00), D00F10, doi:10.1029/2008JD011679, and Brown, S. S., et al. (2006), Variability in nocturnal nitrogen oxide processing and its role in regional air quality, *Science*, 311(5757), 67-70. Results presented in these two studies suggest that the rate coefficients for homogeneous are likely too large (as was concluded later in this manuscript). Please add a comment to this effect in the introduction.

pg 6, line 10. Please clarify what distance the 70 cm refers to (distance between ring-down mirrors, only the Teflon section, etc.).

pg 7, line 4 (and page 9, line 26). In the heated cell, N₂O₅ is measured as NO₃ at 85 C. Neither the Yokelson nor the Orphal study measured the NO₃ absorption cross-section in this temperature range. Please state what cross-section was used to determine N₂O₅. A useful reference might be Osthoff, H. D., et al. (2007), Temperature dependence of the NO₃ absorption cross-section above 298 K and determination of the equilibrium constant for NO₃+NO₂ <-> N₂O₅ at atmospherically relevant conditions, *Phys. Chem. Chem. Phys.*, 9(43), 5785-5793.

page 10, lines 2-3. Can you please comment on whether the blue light converter converts either NO₃ or N₂O₅ to NO, and whether that constitutes an interference/bias in the NO₂ measurement?

page 11, lines 4-6. Please state what typical aerosol surface area densities were observed, as the area is the more critical parameter rather than particle count.

page 15, line 24. Starting with: "poor agreement", consider starting a new subsection with a heading "inlet artifacts" or something similar.

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page 19, line 11. Please replace the word "figure" with "number" (I was wondering for a moment why the graph would shrink ...).

page 21, lines 15 and 17 (E12). This definition of NO_x is inconsistent with the definition of NO_x on page 2, line 27. Consider labeling the "NO_x" on page 21 as "Nocturnal NO_x" and the NO_x on page 2 as "daytime NO_x". Also, why are PAN and ClNO₂ not included in F(NO_x)?

line 27. There is also a minor NO₃ photolysis channel to NO. Orlando, J. J., et al. (1993), Quantum Yields for NO₃ Photolysis between 570 and 635 nm, *J. Phys. Chem.*, 97(42), 10996-11000. Please change "back to NO₂" to "back to NO₂ and NO".

pg 25 line 29. article number is missing from this citation.

pg 26, line 28. article number is missing from this citation.

pg 27, line 13. article number is missing from this citation.

pg 28, lines 14-23. I am not sure where/why evaluation #14 was cited. Please update and cite only #15.

line 25. Add subscripts to NO₃ and N₂O₅.

pg 31, Figure 2 caption. Looking at the Figure, it is unclear where the sample flow exits the sample cavities. Please add a sentence to the caption, or modify the Figure.

pg 33, Figure 4. [NO₂] increases by about 500 ppt after sunrise; before sunrise, there were 60 ppt of N₂O₅ and 20 ppt of NO₃, which would yield about ~140 ppt of NO_x. Can you please comment in the text (e.g., at the bottom of page 12) as to where you think the extra NO_x came from? The constant ozone mixing ratio suggests that boundary layer mixing / vertical transport at that time would have been minimal.

pg 35, Figure 6. Please state in the Figure caption what the dashed and solid black lines are conveying.

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pg 38, Figure 9. The red and blue line are identified as homogeneous and heterogeneous loss of N_2O_5 , but are defined differently in the text (page 18, line 21). The lifetime of NO_3 approaches the rate of photolysis after sunrise. Perhaps photolysis could be added to the figure? On the y-axis, please use U.S. notation (decimals and commas). I am not sure I “buy” the explanation of the gray trace. Consider rephrasing the explanation in the main text. At the levels of NO_3 observed here, both pinene and isoprene are rapidly oxidized by ozone and NO_3 . Unless there was a continuous weak nocturnal source of these compounds (I don't think there is), I'd expect their concentrations to approach zero rapidly. A more likely explanation is that there are other, unsaturated, hydrocarbons present that react with NO_3 and ozone more sluggishly than either alpha-pinene or isoprene. The net result would then be a curve similar to the grey line shown.

pg 39, Figure 10. I believe the y-axis title is incorrect (should it be lifetime, or “tau”?). Also, the labels for the blue and black line are unnecessarily confusing as one has to read the text on page 20 to understand the rationale behind those numbers. Since there is plenty of white space available on the Figure, consider labeling the blue line with something like “k_{homo} based on Wahner et al., 1998”. I am also not sure what the blue line is supposed to represent – is equivalency justified? Consider removing the blue line, as I find it very confusing.

Figure 11. If one integrates $k[\text{NO}_2][\text{O}_3]$, one can estimate $F(\text{NO}_x)$ plus the products of NO_3 and N_2O_5 reactions (presumably mostly HNO_3 , but also organic nitrates). Consider adding integral $k[\text{NO}_2][\text{O}_3]dt$ to (at least) the top panel.

Figure 12. The title of this Figure is misleading as I was expecting loss rates, not mixing ratios, to be shown. Since $[\text{OH}]$ was calculated using Ehhalt's parameterization, consider plotting $k_8[\text{NO}_2][\text{OH}]$ and the results of (E13) instead of showing the mixing ratios of NO_2 and N_2O_5 .

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 1309, 2010.