

Interactive comment on “Variable lifetimes and loss mechanisms for NO₃ and N₂O₅ during the DOMINO campaign: contrasts between marine, urban and continental air” by J. N. Crowley et al.

Anonymous Referee #3

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General Comments

This paper presents in-situ measurements of N₂O₅ at a fixed height (7–12 m above ground level) and related trace gases during the DOMINO campaign in southern Spain. Direct measurements of NO₃ were apparently compromised by analytical difficulties, but NO₃ was derived from the N₂O₅ and co-located NO₂ measurements using equilibrium. These derived NO₃ measurements compare well with an open path DOAS measurement. The paper primarily interprets the NO₃ measurements to determine the losses for this compound using a steady state approach. The validity of the steady state approximation is considered and justified. The analysis is presented as 3 case

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studies for different nights with air masses from different sectors: marine, industrial and continentally influenced.

The consideration of loss processes is comprehensive, with a generally good review of the relevant literature for each process considered. The principal conclusion is that losses should be dominated by direct losses of NO₃, rather than heterogeneous losses of N₂O₅ (or heterogeneous loss of NO₃, which is also considered), but that the measurements of additional gas-phase compounds frequently does not account for the observed, very short lifetimes of NO₃. The authors provide speculation on the potential role of some unmeasured compounds, including reduced sulfur compounds and alkenes from the industrial sector. They are careful to indicate which conclusions are speculative, so that the overall discussion is useful within the limits of the measured gas-phase compounds.

The paper does not discuss the potential for halogen activation through formation of ClNO₂ upon N₂O₅ hydrolysis, even for the marine-influenced air masses. Some mention of this loss process, and the potential for chloride in the aerosol to regulate the loss of N₂O₅ (see papers by Bertram and Thornton on this subject) would be a useful addition to this paper.

The authors should probably also make some additional mention of the effect of vertical stratification on the analysis. While this is covered in the referenced Theiser paper, there is potential for vertical transport effects to influence the steady-state lifetimes that are principally used in this analysis. See papers by Stutz and coworkers on this topic.

Specific comments

Page 17829, line 6: Was the surface area really dominated by such small particles (< 100 nm)? Possibly the authors mean 1000 nm (1 micron)?

Page 17829, line 27: The term $k_2[\text{NO}_2][\text{O}_3]$ should probably read $k_2[\text{NO}_2][\text{NO}_3]$

Page 17839, top. NO₃ production rates were “low” but not quantified. It would be useful

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to have a number or a range in pptv or ppbv hr⁻¹, possibly as an addition to Figure 4.

Page 17844, top: Isoprene reacts relatively rapidly with NO₃ and would be more appropriately grouped with pinene or NO than with formaldehyde, whose reaction is negligible.

Page 17844, bottom: Reaction of NO₃ with NO can dominate at a level of 5 pptv of NO, but the stated detection limit for the NO instrument was 6 pptv (section 3.2). Is it possible to put a constraint on the NO₃ consumption by a local (e.g., soil based) NO source? There would likely be a large uncertainty associated with this calculation since the required NO levels are so small.

Page 17846, line 17: Although it is very likely that DMS contributed to NO₃ loss in marine influence air masses, a mixing ratio of 200 pptv would be atypically large, unless the site was rather close a known hot spot for DMS. Do the authors have any information about local DMS sources?

Related to the same discussion – can the authors speculate on second-generation oxidation products of the biogenics (either DMS or monoterpenes) with NO₃? Can these contribute to the missing reactivity?

Page 17848, line 12: “large NO₃ production rates” – again, how large?

Page 17851, line 20-21. Does H₂S react with NO₃?

Page 17857, line 25: Figure 13 gives an absolute, but not a relative, NO_x loss. What was the total NO₂ present, and what fraction of NO_x was consumed by nighttime reactions?

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 17825, 2011.