

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 #1

Received and published: 17 July 2011

The authors give an overview of nighttime chemistry during the DOMINO campaign. Since investigation of nighttime chemistry including direct measurements of N₂O₅ are sparse, this paper will contribute to a broader view on this topic. Unfortunately, direct NO₃ detection failed, but N₂O₅ concentration measurements are still valuable, because NO₃ concentrations could be calculated from the fast equilibrium between NO₃ and N₂O₅. The authors carefully analyze, if their analysis of the NO₃ lifetime can be applied for conditions encountered during the campaign. Overall the paper is well written and suitable for publication in ACP after addressing the following points.

p17826 l4-7: I would give a short hint that NO₃ concentrations were calculated from

C6495

N₂O₅ measurements. Otherwise the reader wonders, how the NO₃ lifetime can be analyzed from NO₂ and O₃.

p17826 l14: "... high NO₂ mixing ratios resulted in low NO₃ lifetimes...". As mentioned later in the manuscript, a correlation of high NO₂ and short NO₃ lifetime hints towards the importance of N₂O₅ uptake on aerosol and a low NO₃ lifetime is not a direct result of high NO₂. Therefore, I would suggest to rephrase this statement.

p17827 l1-3: I am not sure, if I understand the meaning of the latter part of the sentence. How does the interaction of NO₃ with VOCs can lead to radicals "via reactions of HO₂ with O₃ or NO₃"?

p17832 l21/22: After reading the entire section, it is not clear to me, what the limit of detection for NO₃ and N₂O₅ was. Do the number given here only refer to the uncertainty of the zeroing or do they give the real limit of detection including all noise sources? If they only refer to the zeroing please give the real limit of detection including the high loss of NO₃ in the cavity. Otherwise the reader cannot understand why NO₃ could not be detected at levels of more than 10ppt encountered e.g. during the first half of the night on 23-24 (Fig. 7).

p17832 l17/18: Please give numbers for the loss of NO₃ and N₂O₅ on the filter.

p17832 l25-26 and p17833 l1-2: I have the impression the reader is guided to the wrong direction at this point. Here, it is stated that NO₃ was not detected during the campaign and this might hint towards a deviation from equilibrium between NO₃ and N₂O₅. Later in the text it is clearly said that instrumental problems were most likely responsible for high NO₃ loss in the instrument and therefore NO₃ is calculated assuming equilibrium. Please rephrase this paragraph and clarify.

p17833 l24/25: How does the statement that the reactivity of the tubing could be reduced by passivation with high NO₃/O₃ fit the statement on l20 where the authors say that NO₃ loss increased after exposure of the cavity to NO₃/O₃/NO₂? Is there any idea

C6496

what caused the unexpected high NO₃ loss? Was this reproduced after the campaign in the lab?

section 4.1.1: A larger part of the discussion is more focussed on explaining small loss processes caused by local emissions rather than focussing on "clean air" as suggested by the title of the section. Maybe it would be better to restrict the discussion on that part of the night when clean air without local emissions was sampled. Otherwise the authors should be more clearly state the effects from local emissions. Please comment.

p17845/17846 and Fig 6/9/11: Eq. (5) gives an expression to calculate N₂O₅ concentrations from the production and destruction rates of NO₃ and N₂O₅. I have difficulties to see what can be learned from this. Isn't this just a difference representation of what is shown in the lower panels of Fig 6/9/11 where loss rates from individual loss channels are compared to the experimentally determined entire loss rate? For me the discussion of loss rates are intuitive and easy to interpret whereas the comparison of calculated and measured N₂O₅ mixing ratios are rather confusing. Please explain more clearly what additional information is given by this comparison.

p17847 l5-8: I do not agree with the statement that an artificially low NO₃ lifetime is derived in the presence of NO. The production term is not increased by the emission of NO, because as correctly said by the authors NO converts O₃ to NO₂. Therefore, the production rate ($k[\text{NO}_2][\text{O}_3]$) remains constant. The increase in NO₂ from the reaction of NO with NO₃ negligible since the NO₃ concentration is small compared to the NO₂ concentration. Please comment.

p17851: The section "unknown or undetermined reactions/loss processes" is relatively long without a clear conclusion. I would suggest to significantly shorten this part and to focus on the main points.

p17857 l23-28 and Figure 13: It is surprising that there is only a small difference between the continental sector and the clean air, because one may expect that the loss in clean air is much smaller than in the continental air. Please comment.

C6497

Technical corrections:

p17832 l9: There is an extra "." in the text.

p17839 l23: Please replace "had spend" with "had spent"

p17854 l17: Please replace "Novermber" with "November"

Figure 1: Please enlarge the numbers in the map and maybe change the red color for a better visibility.

Figure 9 and 11: In the lower panel the contributions of the different loss channels are hard to distinguish. It would be helpful if the y-scaling was reduced or the figure wwas larger in this direction.

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

C6498