Interactive comment on “Variable lifetimes and loss mechanisms for \( \text{NO}_3 \) and \( \text{N}_2\text{O}_5 \) during the DOMINO campaign: contrasts between marine, urban and continental air” by J. N. Crowley et al.

Anonymous Referee #1

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The authors give an overview of nighttime chemistry during the DOMINO campaign. Since investigation of nighttime chemistry including direct measurements of \( \text{N}_2\text{O}_5 \) are sparse, this paper will contribute to a broader view on this topic. Unfortunately, direct \( \text{NO}_3 \) detection failed, but \( \text{N}_2\text{O}_5 \) concentration measurements are still valuable, because \( \text{NO}_3 \) concentrations could be calculated from the fast equilibrium between \( \text{NO}_3 \) and \( \text{N}_2\text{O}_5 \). The authors carefully analyze, if their analysis of the \( \text{NO}_3 \) 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 \( \text{NO}_3 \) concentrations were calculated from \( \text{N}_2\text{O}_5 \) measurements. Otherwise the reader wonders, how the \( \text{NO}_3 \) lifetime can be analyzed from \( \text{NO}_2 \) and \( \text{O}_3 \).

p17826 l14: "... high \( \text{NO}_2 \) mixing ratios resulted in low \( \text{NO}_3 \) lifetimes...". As mentioned later in the manuscript, a correlation of high \( \text{NO}_2 \) and short \( \text{NO}_3 \) lifetime hints towards the importance of \( \text{N}_2\text{O}_5 \) uptake on aerosol and a low \( \text{NO}_3 \) lifetime is not a direct result of high \( \text{NO}_2 \). 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 \( \text{NO}_3 \) with VOCs can lead to radicals "via reactions of HO2 with O3 or NO3"?

p17832 l17/18: Please give numbers for the loss of \( \text{NO}_3 \) and \( \text{N}_2\text{O}_5 \) 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 \( \text{NO}_3 \) was not detected during the campaign and this might hint towards a deviation from equilibrium between \( \text{NO}_3 \) and \( \text{N}_2\text{O}_5 \). Later in the text it is clearly said that instrumental problems were most likely responsible for high \( \text{NO}_3 \) loss in the instrument and therefore \( \text{NO}_3 \) 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 \( \text{NO}_3/\text{O}_3 \) fit the statement on l20 where the authors say that \( \text{NO}_3 \) loss increased after exposure of the cavity to \( \text{NO}_3/\text{O}_3/\text{NO}_2 \)? Is there any idea...
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[NO2][O3]) 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.

Technical corrections:
p17832 l9: There is an extra "." in the text.
p17839 l23: Please replace "had spend" with "had spent"
p17854 l17: Please replace "November" 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 was larger in this direction.

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