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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Variable lifetimes and loss mechanisms for NO_3 and N_2O_5 during the DOMINO campaign: contrasts between marine, urban and continental air" *by* J. N. Crowley et al.

Anonymous Referee #2

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Review of "Variable lifetimes and loss mechanisms for NO3 and N2O5 during the DOMINO campaign: contrasts between marine, urban and continental air" by Crowley et al.

This paper describes the results of a measurement campaign focusing on the nocturnal nitrogen oxides NO3 and N2O5 in Southern Spain. New data and a NO3 loss frequency analysis, sorted by local wind direction, based on an assumed steady state in NO3 and N2O5 are presented.

Unfortunately, I cannot recommend this paper to be accepted for publication in its present form and unless the authors make considerable revisions. Unlike reviewer

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Interactive Discussion
Discussion Paper

#1 I don't think the paper is written well at all.

The introduction (including title + abstract) does not adequately describe what the paper is about (I had to read through the whole manuscript very carefully to figure that out). I would like to see an introduction that describes what is novel and states the objectives and methods of the present study and highlights why the study was needed and worthwhile.

The discussion of validity of the steady state assumption (page 17830) could be considerably shortened as these concepts are already well established in the literature (e.g., Brown et al., 2003a) but should really appear in the analysis section.

On the measurement side, the authors describe having considerable problems observing NO3 using CRD. The performance of the CRD instrument in this campaign is disappointing, considering that the authors reported field measurements of NO3 and N2O5 in the past. To be fair, the observed inlet losses suggest very polluted air likely containing semi-volatile and unsaturated VOCs. The authors should have anticipated such losses, and I am now a bit concerned about the accuracy of some of the author's earlier reported field measurements of NO3 and N2O5 and how well inlet losses have been characterized in the past.

Further, the analysis seems rather tentative and often appears to be more a description of time series without providing any significant new insight into nocturnal nitrogen oxide chemistry.

The paper in its present form also fails to include an analysis of nocturnal loss of NOx and Ox and fails to even mention the possibility that ClNO2 might be formed nocturnally at this site. ClNO2 formation should be substantial at a site that experiences mixed marine and continental air such as this one.

The analysis shorts 3 short sections of data, but I was not very clear as to what guided the choice of sections. The authors should also discuss for these sections if the steady

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state assumption is valid (as it was used).

A big can of worms that the authors chose to omit is the vertical structure of the boundary layer and vertical mixing. For this data set, the authors have the luxury of having this information (LP-DOAS) and it should be included in the analysis here.

The conclusion that the factor n in equation (6) can be 1 is somewhat of a surprise statement is the concept of n is not even introduced until the conclusion. Perhaps some restructuring and focusing the loss rate analysis on issues such nocturnal NOx and Ox loss early on would do some good.

In summary, the paper appears to be rather hastily written and not very well thought out. Given the depth of the data set, the paper could be considerably improved by deepening the analysis and rephrasing of considerable portions of the text. The data appear to be interesting, but as a whole the manuscript requires a considerable amount of additional work.

Below I provide some more comments to the authors that may help in their revisions of this manuscript.

Abstract. The acronym DOMINO should be defined and the measurement location and dates of the measurements should be given here.

The phrase "Observation of N2O5 was intermittent" could be misunderstood and implies that measurements were made only intermittently.

pg 17827, line 5 replace "ozone" with "O3" for consistency with the remainder of the manuscript

pg 17828 line 5. Some of the terms given here are negligible, such as fH2O (as discussed later) and the heterogeneous uptake of NO3. It is curious as the authors' previous work concluded this yet the earlier conclusions are not implemented here.

pg 17829 line 10-11. γ(NO3) values of 0.5 are highly unrealistic. Yes, there are some

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recent lab studies that show on certain types of aerosol gamma values may be high, but that has yet to be shown in field studies.

pg 17829 lines 14-15 "the right-hand term in the denominator of Eq. (2)" Consider calling it fss(NO3) or "loss frequency of NO3" for clarity

pg 17830, line 2 "k'(NO3) and k"(N2O5) are first order loss rate constants ..." insert the words "sum of the" between "are" and "first"

pg 17830 lines 6-15. This paragraph somehow seems out of place. Is it meant to describe what is being done in the paper?

The last sentence of this paragraph, " The low N2O5 and NO3 concentrations observed (implying short lifetimes) meant that stationary state was achieved within 1–2 h after dusk and within the time of transport from the major source of NOx (e.g. Huelva)." sounds like a result of a piece of analysis (that is incidentally, missing) and probably should not be in the introduction.

pg 17832, line 3. Replace "Figure 1" with "Fig. 1" for consistency

pg 17832, line 17-18 " The losses of NO3 and N2O5 to the filter were characterised prior to and after the campaign. Loss rates in the cavities were also measured during the campaign."

It would be helpful if it was described how the losses were characterized.

Line 21-22. Are the noise levels given with 1 or 2 sigma standard deviation?

In either case, the noise levels appear to be considerably higher than the authors' previous own work and that is perhaps worthwhile to comment on.

pg 17832. The CRD sampled "through a few meters of ... PFA tubing" (line 13) and "NO3 was not observed directly during the campaign even when N2O5 levels of several hundred pptv were present" (line 25). Given that the measurement location was in Spain and the nights were warm, the above statements suggest that there losses of

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NO3 through the inlet were considerable and may have also affected the N2O5 measurement (as it is converted to NO3 in the instrument). The authors should discuss why they still believe their N2O5 measurements to be accurate under these conditions. Out of curiosity: Did the authors try to improve their inlet's NO3 transmission efficiency by replacing or washing the inlet? In light of this, I'd suggest that section 3.1 not be started with "NO3 and N2O5 mixing ratios were measured using " (OA-CRD) as clearly no NO3 measurements could be made by CRD.

pg 17834, line 14 "... in good agreement ". Please add a scatter plot of NO3 mixing ratios calculated using equation (4) against LP-DOAS and give a correlation coefficient (r2 value).

pp 17834-17837. A table summarizing the various instruments present during the study would be useful.

pg 17835. Please describe how accurate the NO instrument is at low mixing ratios, in particular in regard to zero drifts. A lot of the analysis depends crucially on the accuracy of this measurement.

pg 17836 line 7 please define the acronym TD-GC-MSD. Section 3.5 "Aerosol Measurements" There are known issues with the accuracy of FMPS measurements (e.g., Jeong and Evans, Aerosol Sci. Technol. 43, 364, 2009). Please comment on how this instrument was calibrated and how accurate the authors think the resulting aerosol surface area is.

pg 17839 line 10. Please clarify if only nighttime or day and night NO3 lifetimes were plotted.

pg 17840 Is it possible that the small mixing ratios of NO are an instrumental artifact (baseline drift)?

pg 17841, line 24. The formula NH3HSO4 does not make sense.

pg 17841. The kinetics of the N2O5 uptake is also affected by aerosol chloride (see

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Bertram & Thornton, 2009).

pg 17843. Please justify the choice of a 100 m boundary layer height as this a major assumption (and I personally would not think is valid for this particular location). line 17. k2 should be K2

pg 17845. The very large uptake coefficients observed for NO3 are for very specific aerosol types and is probably not applicable in most situations, as aerosols containing such unsaturated groups likely is oxidized/modified rather rapidly (by any of the atmospheric oxidants). It's interesting that the authors include this in this analysis, but I highly doubt these processes to be significant.

pg 17846 " Considering that this air mass had spent several days over the ocean, it is conceivable that CH3SCH3 ... " I would argue that this is almost certain, not just conceivable.

pg 17848 lines 1-10 This section is rather descriptive. Is there a conclusion?

pg 17849 line 10. I do not think that low gamma values as reported in the Zaveri paper are applicable here as at this site the aerosol likely also contained aerosol chloride and was deliquesced.

pg 17851. It may be helpful to the reader if there is a statement at the beginning of this paragraph what unmeasured NO3 losses the authors consider, e.g., reduced sulfur compounds, peroxy radicals, olefins, etc.

pg 17854 line 17 "23 Novermber" Please correct.

line 19. The charge on the ammonium is incorrect.

General comment on Figures. In a well-written paper, one should be able to capture the main points (or tell the story) of the paper by simply looking at the Figures (and maybe reading the captures). Unfortunately, the Figures in the current manuscript are not clear as to what point(s) the authors were trying to make (if any). I also strongly

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encourage the authors to redo all of their time series plots as they are generally too condensed and unnecessarily confusing.

pg. 17865, Fig. 1. It is not clear from the Figure where the measurement site is located. Consider making it more obvious by enlarging the dot.

pg 17866, Fig 2. Consider reorganizing the figure. Combine NO2, ozone, and Ox (=O3+NO2) in row 1 on a single y-axis. Combine the two NO3 data sets and N2O5 (divided by 10) on the second row (all 3 on same axis). Show temperature and relative humidity (the latter is relevant to gamma) on row 3. Show the aerosol surface area on a separate row. I would also choose additional colors rather than having 3 traces appear in red and another 3 in black. Avoid time series that go off-scale.

pg 17867 Fig 3. 3 sectors are discussed in the manuscript and 4 are shown here. Consider dividing lines to identify the sectors. Also, by plotting each and every data point, the reader does not get a good feel as to how many data points the plot contains. Consider making a rose plot that identifies what fraction of the data are below certain thresholds (e.g., pie charts that identify the 10, 25, 50, 75, and 90th percentile in each sector). Also, I would restrict this analysis to nighttime measurements only.

pg 17868, Fig. 4. See comments under Fig 2. Also, the AMS community generally uses a standard color scheme (blue for nitrate, red for sulfate, etc.). This scheme was implemented mainly to make plots and Figures more readily accessible to other users and it'd be great if the authors adopted this scheme as well in their presentations and manuscript figures.

pg 17869, Fig 5. By definition, the lifetime is inversely proportional to NO2, so I am not really sure what scientific point (other than the obvious one) is being made. The caption should also mention that temperature and K2 was used in the calculation.

pg 17870 Fig. 6. This sector is labeled as "Atlantic air" with is inconsistent with the presence of monoterpenes which are generally derived from vegetation. Also, the

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homogeneous hydrolysis of water should be removed unless the authors doubt their own published work.

pg 17871 Fig 7. See my earlier comments regarding organization of time series and time series going off-scale. The caption should state the month. Fig. 8 and 12 These graphs are puzzling as I have no idea what they are meant to convey. The lifetime of NO3 is inversely related to NO2 by definition, and neither NO3 nor N2O5 are known to react with SO2. To compare NO3 lifetime with aerosol surface area also does not make any sense as the latter should be weighted by the N2O5:NO3 ratio (K2[NO2]).

Scientific Significance: Good (2)

Scientific Quality: Fair (3)

Presentation Quality: Fair (3)

Are the scientific results and conclusions presented in a clear, concise, and well-structured way (number and quality of figures/tables, appropriate use of English language)? no

Does the paper address relevant scientific questions within the scope of ACP? yes

Does the paper present novel concepts, ideas, tools, or data? yes

Are substantial conclusions reached? yes

Are the scientific methods and assumptions valid and clearly outlined? Yes

Are the results sufficient to support the interpretations and conclusions? Yes

Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? yes

Do the authors give proper credit to related work and clearly indicate their own new/original contribution? yes

Does the title clearly reflect the contents of the paper? Yes

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Does the abstract provide a concise and complete summary? No

Is the overall presentation well structured and clear? No

Is the language fluent and precise? Yes

Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? Yes

Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? Yes

Are the number and quality of references appropriate? Yes

Is the amount and quality of supplementary material appropriate? n/a

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