

## Referee 1

### Comment.

The authors give an overview of nighttime chemistry during the DOMINO campaign. Since investigation of nighttime chemistry including direct measurements of N<sub>2</sub>O<sub>5</sub> are sparse, this paper will contribute to a broader view on this topic. Unfortunately, direct NO<sub>3</sub> detection failed, but N<sub>2</sub>O<sub>5</sub> concentration measurements are still valuable, because NO<sub>3</sub> concentrations could be calculated from the fast equilibrium between NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>. The authors carefully analyze, if their analysis of the NO<sub>3</sub> 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.

### Reply

No reply required.

### Comment.

p17826 14-7: I would give a short hint that NO<sub>3</sub> concentrations were calculated from N<sub>2</sub>O<sub>5</sub> measurements. Otherwise the reader wonders, how the NO<sub>3</sub> lifetime can be analyzed from NO<sub>2</sub> and O<sub>3</sub>.

### Reply

We now state “a steady state analysis constrained by measured mixing ratios of N<sub>2</sub>O<sub>5</sub>, NO<sub>2</sub> and O<sub>3</sub> ....etc

### Comment.

p17826 114: "... high NO<sub>2</sub> mixing ratios resulted in low NO<sub>3</sub> lifetimes...". As mentioned later in the manuscript, a correlation of high NO<sub>2</sub> and short NO<sub>3</sub> lifetime hints towards the importance of N<sub>2</sub>O<sub>5</sub> uptake on aerosol and a low NO<sub>3</sub> lifetime is not a direct result of high NO<sub>2</sub>. Therefore, I would suggest to rephrase this statement.

### Reply

We now state “high NO<sub>2</sub> mixing ratios were associated with low NO<sub>3</sub> lifetimes”

### Comment.

p17827 11-3: I am not sure, if I understand the meaning of the latter part of the sentence. How does the interaction of NO<sub>3</sub> with VOCs can lead to radicals "via reactions of HO<sub>2</sub> with O<sub>3</sub> or NO<sub>3</sub>"?

### Reply

The sentence has been simplified and now reads: The interaction of NO<sub>3</sub> with VOCs leads to the formation of organic peroxy radicals, and via secondary reactions to HO<sub>2</sub> and OH (Platt et al., 1990; Sommariva et al., 2009).

### Comment.

p17832 121/22: After reading the entire section, it is not clear to me, what the limit of detection for NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> 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 NO<sub>3</sub> in the cavity. Otherwise the reader cannot understand why NO<sub>3</sub> 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).

### Reply

The limit of detection includes all noise sources and corrections for cavity losses (about 20 %). It does however not include the (unexpected) complete loss of NO<sub>3</sub> in the inlet line, which is described in detail in the subsequent text. This unexpected loss is the reason for not

observing NO<sub>3</sub>. We have modified the text to include this fact. “The detection limit is partly defined by accuracy of the chemical zero (measured by adding NO as described in detail previously (Schuster et al., 2009)) and was between 2 and 3 pptv for NO<sub>3</sub> and 5-7 pptv for N<sub>2</sub>O<sub>5</sub> (both assuming zero losses in the inlet tubing).” However, NO<sub>3</sub> was not observed directly during the campaign even when N<sub>2</sub>O<sub>5</sub> levels of several hundred pptv were present....etc

**Comment.**

p17832 117/18: Please give numbers for the loss of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> on the filter.

**Reply**

The text now reads: The losses of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> to the filter ( $15 \pm 3$  % and  $<2$  %, respectively) were characterised prior to and after the campaign.

**Comment.**

p17832 125-26 and p17833 11-2: I have the impression the reader is guided to the wrong direction at this point. Here, it is stated that NO<sub>3</sub> was not detected during the campaign and this might hint towards a deviation from equilibrium between NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>. Later in the text it is clearly said that instrumental problems were most likely responsible for high NO<sub>3</sub> loss in the instrument and therefore NO<sub>3</sub> is calculated assuming equilibrium. Please rephrase this paragraph and clarify.

**Reply**

The two realities are not incompatible. A potential cause for low NO<sub>3</sub> (below the detection limit) is high NO<sub>2</sub> and low temperatures pushing the equilibrium towards N<sub>2</sub>O<sub>5</sub>. The deviation from equilibrium (at low NO<sub>2</sub> and high temperatures) indicate loss of NO<sub>3</sub> on the inlet (the instrument problem) on the timescale of seconds. The text has been modified and now reads: **A potential cause of disequilibrium between NO<sub>2</sub>, O<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> is the loss of NO<sub>3</sub> in the PFA inlet.** This had not been anticipated as it was not encountered on a previous campaign at a rural location (Crowley et al., 2010) in which a similar sampling strategy (**long PFA line with 1 s residence time**) had been periodically deployed in place of the normally used, FEP-coated high-volume flow glass sampling line.

**Comment.**

p17833 124/25: How does the statement that the reactivity of the tubing could be reduced by passivation with high NO<sub>3</sub>/O<sub>3</sub> fit the statement on 120 where the authors say that NO<sub>3</sub> loss increased after exposure of the cavity to NO<sub>3</sub>/O<sub>3</sub>/NO<sub>2</sub>? Is there any idea what caused the unexpected high NO<sub>3</sub> loss? Was this reproduced after the campaign in the lab?

**Reply**

**We do not state that the NO<sub>3</sub> loss increased** after exposure of the cavity to NO<sub>3</sub>/O<sub>3</sub>/NO<sub>2</sub>. We rather state that the **transmission** of NO<sub>3</sub> increased after exposure of the cavity to NO<sub>3</sub>/O<sub>3</sub>/NO<sub>2</sub>. Post campaign tests in the lab also revealed high initial reactivity of the inlet lines to NO<sub>3</sub>, which we now mention in the text: “These observations indicate that the PFA tubing rapidly became reactive to NO<sub>3</sub> when exposed to the air and this reactivity could be reduced by extended passivation with high NO<sub>3</sub> / O<sub>3</sub> concentrations or by heating to 90 °C. **Post-campaign tests of the inlets used also revealed high (initial) reactivity to NO<sub>3</sub>.**”

**Comment.**

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 to 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.

**Reply**

We now emphasise the fact that “clean, maritime air” was encountered only between 02:30 and 04:30. We write: The observation of a decrease in a biogenic trace gas (pinene) from 10-20 pptv before 02:30 to 2-3 pptv after 02:30 supports a change in air-mass origin at this time. **An increase in NO after 04:30 indicated weak local emissions. The cleanest, maritime air was thus sampled between 02:30 and 04:30 on this night.**

**Comment.**

p17845/17846 and Fig 6/9/11: Eq. (5) gives an expression to calculate N<sub>2</sub>O<sub>5</sub> concentrations from the production and destruction rates of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>. 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 N<sub>2</sub>O<sub>5</sub> mixing ratios are rather confusing. Please explain more clearly what additional information is given by this comparison.

**Reply**

**No additional information is contained in the upper panel, which has been removed from Figures 6, 9 and 11.**

**Comment.**

p17847 15-8: I do not agree with the statement that an artificially low NO<sub>3</sub> 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 O<sub>3</sub> to NO<sub>2</sub>. Therefore, the production rate ( $k[\text{NO}_2][\text{O}_3]$ ) remains constant. The increase in NO<sub>2</sub> from the reaction of NO with NO<sub>3</sub> negligible since the NO<sub>3</sub> concentration is small compared to the NO<sub>2</sub> concentration. Please comment.

**Reply**

**This is correct. This text has been deleted.**

**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.

**Reply**

In this section two potential causes for the large loss rates of NO<sub>3</sub> are introduced for the first time (reduced sulphur chemistry or unsaturated HC). It is true that we make no hard conclusion concerning the source of high reactivity, but in the absence of constraining measurements this is not possible. It is not obvious how this could be shortened.

**Comment.**

p17857 123-28 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.

**Reply**

As written in equation 6, if the lifetime of NO<sub>3</sub> (or N<sub>2</sub>O<sub>5</sub>) is short, the loss of NO<sub>x</sub> depends only on the NO<sub>2</sub> and O<sub>3</sub> concentrations. An examination of Figures 4 and 10 shows that NO<sub>2</sub> and O<sub>3</sub> concentrations were similar on these two nights, hence the losses of NO<sub>x</sub> are similar.

**Technical corrections:**

p17832 19: There is an extra "." in the text.

p17839 123: Please replace "had spend" with "had spent"

p17854 117: 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 was larger in this direction.

### Reply

All technical corrections have been made as suggested. Figures 9 and 11 have been expanded in the vertical as suggested (also in line with the comment of reviewer 1).

## Referee 2

### Comment.

This paper describes the results of a measurement campaign focusing on the nocturnal nitrogen oxides NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> in Southern Spain. New data and a NO<sub>3</sub> loss frequency analysis, sorted by local wind direction, based on an assumed steady state in NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> 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 #1 I don't think the paper is written well at all.

### Reply

Significant modifications have been made.

### Comment.

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.

### Reply

The objectives of the present study were to examine the role of NO<sub>3</sub>- and N<sub>2</sub>O<sub>5</sub>-driven nocturnal chemistry at the DOMINO site during different chemical regimes (urban, continental and maritime air masses). These objectives are clearly reflected in the title but were not clearly outlined in the introduction. Text (see below) has now been added to describe these objectives at the beginning of the introduction (after reactions R1-R-2).

“The impacts of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> on nighttime chemistry depends on their relative rates of loss via gas-phase and heterogeneous reactions. Whereas NO<sub>3</sub> is lost mainly via gas-phase reactions with e.g. VOCs (see above), N<sub>2</sub>O<sub>5</sub> is removed predominantly by heterogeneous hydrolysis on aqueous aerosol, which can substantially modify the amount of reactive nitrogen available for daytime photochemistry. In the polluted boundary layer, this process influences the fate of NO<sub>x</sub> emissions and their potential for photochemical ozone formation and also (via heterogeneous chemistry on sulphate particles) links O<sub>3</sub> production rates to emissions of SO<sub>2</sub> from e.g. power plants or shipping (Brown et al., 2006). It has recently been suggested that heterogeneous reactions of N<sub>2</sub>O<sub>5</sub> with chloride containing particles can also represent a significant source of photolabile chlorine (in the form of ClNO<sub>2</sub> and Cl<sub>2</sub>) (Roberts et al., 2009; Thornton et al., 2010).

The objectives of this study were to examine the roles and relative importance of gas phase and heterogeneous processing of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> in chemically distinct air masses: urban (strong anthropogenic influence), continental (mainly biogenic emissions) and maritime. In

order to achieve these objectives the NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> measurements were accompanied by instrumentation for trace gas and aerosol characterisation (see later).”

The section outlining how NO<sub>3</sub> lifetimes are calculated is also separated by its own subsection (1.1 NO<sub>3</sub> lifetimes).

**Comment.**

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.

**Reply**

The text dealing with steady state calculations has been moved to its own section (see above). A reader familiar with these concepts can now choose to skip this section. However, as the following discussion of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> chemistry requires the concepts introduced here, it seems reasonable to maintain its present length.

**Comment.**

On the measurement side, the authors describe having considerable problems observing NO<sub>3</sub> using CRD. The performance of the CRD instrument in this campaign is disappointing, considering that the authors reported field measurements of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> 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 NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> and how well inlet losses have been characterized in the past.

**Reply**

We agree that the inlet losses may relate to the presence of very reactive organics in the air masses. The extrapolation of this problem to our previous measurements (Crowley et al., 2008) is however unjustified, as neither the inlet strategy nor pollution levels are comparable. In Crowley et al 2010, we used a high volume flow, wide bore (10 cm) FEP coated glass tube (2m long) with a residence time of 0.1 s. In Crowley et al 2010, we also report the periodic use of a long piece of PFA tubing to sample the air. In the latter case we found that 20 % of the NO<sub>3</sub> was lost, in line with residence times and measured loss rates on PFA tubing. The glass-tubing was not an option at the DOMINO campaign as we needed to get the inlet to the similar height as the other instruments. The text on page 17833 has been modified to remove any confusion. It now reads: “This (total loss of NO<sub>3</sub>) had not been anticipated as it was not encountered on a previous campaign at a rural location (Crowley et al., 2010) in which a similar sampling strategy (long PFA line with 1 s residence time) had been periodically deployed in place of the normally used high-volume, FEP-coated flow glass sampling line.”

**Comment.**

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.

**Reply**

There is indeed some qualitative description of the conditions during the three nights discussed in detail. This is necessary to describe the distinct chemical environments encountered. The great majority of the analysis is however based on NO<sub>3</sub> lifetime calculations with an assessment of individual contributions (gas-phase, heterogeneous) to the NO<sub>3</sub> loss rate. As an example, for the night 6-7 December (section 4.1.1) there are ~ 25 lines of text describing the conditions followed by ~150 lines of detailed analysis of loss processes.

**Comment.**

The paper in its present form also fails to include an analysis of nocturnal loss of NO<sub>x</sub> and Ox and fails to even mention the possibility that ClNO<sub>2</sub> might be formed nocturnally at this site. ClNO<sub>2</sub> formation should be substantial at a site that experiences mixed marine and continental air such as this one.

**Reply**

Section 5 deals with nocturnal NO<sub>x</sub> losses, which are summarized in Figure 13. **We now mention (in the introduction, with references) that ClNO<sub>2</sub> can be formed from N<sub>2</sub>O<sub>5</sub> uptake.** However, as in DOMINO NO<sub>x</sub> was lost mainly via NO<sub>3</sub> reactions, the formation of ClNO<sub>2</sub> (or HNO<sub>3</sub>) from N<sub>2</sub>O<sub>5</sub> uptake will not influence the nocturnal losses of NO<sub>x</sub> significantly.

**Comment.**

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 state assumption is valid (as it was used).

**Reply**

The choice of sections was guided by the different air masses encountered. **The introduction has been modified to clarify this (see reply to the second comment of this reviewer).** The validity of applying a steady-state analysis is discussed in detail in the new section 1.1 and is redressed at the end of section 4.1.1

**Comment.**

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.

**Reply**

Whilst recognizing (and indicating) that vertical mixing plays an important role, we do not have height resolved mixing ratios of NO, reactive organics or aerosol surface areas to conduct the same detailed analysis of NO<sub>3</sub> lifetimes at any height other than ground level. This paper intentionally focuses on NO<sub>3</sub> reactivity in different chemical regimes and we feel that the DOAS measurements of NO<sub>3</sub> gradients are better treated in a separate paper, as proposed (Thieser et al.).

**Comment.**

The conclusion that the factor n in equation (6) can be 1 is somewhat of a surprise statement as the concept of n is not even introduced until the conclusion. Perhaps some restructuring and focusing the loss rate analysis on issues such nocturnal NO<sub>x</sub> and Ox loss early on would do some good.

**Reply**

**A new section has been added (4.1) dealing with the nocturnal losses of NO<sub>x</sub>.**

**Comment.**

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.

**Reply**

**The paper has been restructured by adding two new sections (see above).**

**Comment.**

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

**Reply**

Done

**Comment.**

The phrase "Observation of N<sub>2</sub>O<sub>5</sub> was intermittent" could be misunderstood and implies that measurements were made only intermittently.

**Reply**

The word intermittent has been removed. We now state simply that "N<sub>2</sub>O<sub>5</sub> mixing ratios ranged from below the detection limit (~ 5 ppt) to ~ 500 ppt."

**Comment.**

pg 17827, line 5 replace "ozone" with "O<sub>3</sub>" for consistency with the remainder of the manuscript

**Reply**

done

**Comment.**

pg 17828 line 5. Some of the terms given here are negligible, such as fH<sub>2</sub>O (as discussed later) and the heterogeneous uptake of NO<sub>3</sub>. It is curious as the authors' previous work concluded this yet the earlier conclusions are not implemented here.

**Reply**

In our previous work we concluded that the rate constant for a gas-phase reaction between N<sub>2</sub>O<sub>5</sub> and water-vapour was a factor ~three less than that derived from laboratory studies. This does not imply that we can rule out a very slow reaction, which under some circumstances may reduce N<sub>2</sub>O<sub>5</sub> lifetimes. In our subsequent analysis in this paper we use an even lower upper limit (~factor 10) for this rate coefficient derived from the work of Brown et al. There is no disparity between our previous analysis and conclusions and the use of the full expression (2) to describe NO<sub>3</sub> losses.

**Comment.**

pg 17829 line 10-11. (NO<sub>3</sub>) values of 0.5 are highly unrealistic. Yes, there are some 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.

**Reply**

We do not imply that these uptake coefficients are realistic. As should be clear from the foregoing text, they are simply upper limits based on diffusion limited uptake. As already stated, realistic values (from lab and field studies are discussed in detail later).

**Comment.**

pg 17829 lines 14-15 "the right-hand term in the denominator of Eq. (2)" Consider calling it f<sub>ss</sub>(NO<sub>3</sub>) or "loss frequency of NO<sub>3</sub>" for clarity

**Reply**

We actually refer to the losses of N<sub>2</sub>O<sub>5</sub> only. To clarify, we now state: At low aerosol loading (or low values of  $\gamma$ ) and negligible dry deposition the term

$$\left(0.25\bar{c}\gamma(N_2O_5)A + f_{dd}(N_2O_5) + f_{H_2O}\right)K_2[NO_2]$$

becomes diminishingly small and  $\text{NO}_3$  lifetimes are largely independent of  $\text{NO}_2$  concentrations.

**Comment.**

pg 17830, line 2 " $k'$ ( $\text{NO}_3$ ) and  $k$ "( $\text{N}_2\text{O}_5$ ) are first order loss rate constants ..." insert the words "sum of the" between "are" and "first"

**Reply**

Done

**Comment.**

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

**Reply**

It describes how use of the steady-state analysis was validated. This text is now in the new section " $\text{NO}_3$  Lifetimes 1.1" We have also shortened the text somewhat.

**Comment.**

The last sentence of this paragraph, "The low  $\text{N}_2\text{O}_5$  and  $\text{NO}_3$  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  $\text{NO}_x$  (e.g. Huelva)." sounds like a result of a piece of analysis (that is incidentally, missing) and probably should not be in the introduction.

**Reply**

Correct, this text is now in the new section " $\text{NO}_3$  Lifetimes 1.1" We have also shortened the text somewhat.

**Comment.**

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

**Reply**

We had in fact consistently used "Figure" in the submitted article. This will be remedied during final editing.

**Comment.**

pg 17832, line 17-18 " The losses of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  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.

**Reply**

This is described in detail in our previous paper (already cited) describing the same instrument. It is not useful or appropriate to repeat this.

**Comment.**

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.

**Reply**

The noise levels varied during the campaign (3-7 ppt for  $\text{N}_2\text{O}_5$  and 2-5 ppt for  $\text{NO}_3$ ) and, at some times, were indeed worse than reported in Crowley et al., 1010 (4-5 ppt for  $\text{N}_2\text{O}_5$  and 1-2ppt for  $\text{NO}_3$ ). The performance of a field instrument can be influenced by the direct environment (electrical, mechanical and thermal stability etc) so such fluctuations in performance are not unexpected. We have added a line of text to indicate this.



**Comment.**

pg 17832. The CRD sampled "through a few meters of ... PFA tubing" (line 13) and "NO<sub>3</sub> was not observed directly during the campaign even when N<sub>2</sub>O<sub>5</sub> 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 NO<sub>3</sub> through the inlet were considerable and may have also affected the N<sub>2</sub>O<sub>5</sub> measurement (as it is converted to NO<sub>3</sub> in the instrument). The authors should discuss why they still believe their N<sub>2</sub>O<sub>5</sub> measurements to be accurate under these conditions.

**Reply**

This point is already discussed in detail. Inlet losses of NO<sub>3</sub> cannot lead to N<sub>2</sub>O<sub>5</sub> loss as the thermal decomposition rate of N<sub>2</sub>O<sub>5</sub> is too low. The nights were not warm.

**Comment.**

Out of curiosity: Did the authors try to improve their inlet's NO<sub>3</sub> transmission efficiency by replacing or washing the inlet? In light of this, I'd suggest that section 3.1 not be started with "NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> mixing ratios were measured using " (OA-CRD) as clearly no NO<sub>3</sub> measurements could be made by CRD.

**Reply**

We already state (P17833, Line 9) that use of new inlet lines did not result in observation of NO<sub>3</sub>". The methods section outlines the methods for measurement of both NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>. and to change the title in inappropriate.

**Comment.**

pg 17834, line 14 "... in good agreement ". Please add a scatter plot of NO<sub>3</sub> mixing ratios calculated using equation (4) against LP-DOAS and give a correlation coefficient (r<sup>2</sup> value).

**Reply**

DOAS measurements over an extended light-path and a point measurement of NO<sub>3</sub> cannot be analysed so simply. A statistical analysis is not warranted.

**Comment.**

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

**Reply**

There were several instruments in use which are not relevant to this manuscript and which are not discussed here. This sort of information would be more useful in a campaign overview paper. A Table with just the instruments cited here would be redundant as all are described in sections 3.1 to 3.6.

**Comment.**

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.

**Reply**

We have added the text: "The drift in instrument zero was less than ~2 ppt over the duration of one night."

**Comment.**

pg 17836 line 7 please define the acronym TD-GC-MSD. Section 3.5 "Aerosol Measurements"

**Reply**

The TD-GC-MS is now written in full (Thermal Desorption-Gas-Chromatograph-Mass Spectrometer.)

**Comment.**

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.

**Reply**

The FMPS is known to significantly underestimate the concentration of particles below about 30 nm by up to 30% (e.g. Jeong and Evans, Aerosol Sci. Technol. 43, 364, 2009). However, since only about 10-20% of the total aerosol surface area is found in this particle size range (Diesch et al., 2011) this under-measurement results in an underestimate of the total aerosol surface area in the order of less than 5% which is probably smaller than other uncertainties in the measurement. We estimate the total uncertainty of the aerosol surface area measurement to be in the order of 10%.

**Comment.**

pg 17839 line 10. Please clarify if only nighttime or day and night NO<sub>3</sub> lifetimes were plotted.

**Reply**

Only nighttime. This information is now added to the Caption of the Figure

**Comment.**

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

**Reply**

Drift is too small (see above). The coincident, gradual increase in NO<sub>2</sub> and the gradual change in wind direction strongly suggest that the increase in NO from 0 to ~5 ppt is real.

**Comment.**

pg 17841, line 24. The formula NH<sub>3</sub>HSO<sub>4</sub> does not make sense.

**Reply**

This has been corrected to NH<sub>4</sub>HSO<sub>4</sub>

**Comment.**

pg 17841. The kinetics of the N<sub>2</sub>O<sub>5</sub> uptake is also affected by aerosol chloride (see Bertram & Thornton, 2009).

**Reply**

Yes. The chloride content can offset the nitrate effect. The sentence referring to this has been modified: "Both laboratory and field work indicate that N<sub>2</sub>O<sub>5</sub> uptake coefficients can be significantly lower in the presence of organic components or nitrate, although the presence of chloride can offset the nitrate effect (see e.g. (Mentel et al., 1999; Anttila et al., 2006; Bertram and Thornton, 2009; Griffiths et al., 2009; Riemer et al., 2009))."

**Comment.**

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. k<sub>2</sub> should be K<sub>2</sub>

**Reply**

Calculating with a nocturnal boundary layer height of 50 or 200m will have no impact on the Conclusion, that dry deposition is insignificant. We now write “Assuming of a factor two lower or higher boundary layer would not alter this conclusion.”  $k_2$  has been changed to  $K_2$ .

**Comment.**

pg 17845. The very large uptake coefficients observed for  $\text{NO}_3$  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.

**Reply**

We agree. We state that even using these large uptake coefficients does not result in significant loss of  $\text{NO}_3$  via heterogeneous processes.

**Comment.**

pg 17846 " Considering that this air mass had spent several days over the ocean, it is conceivable that  $\text{CH}_3\text{SCH}_3$  ... " I would argue that this is almost certain, not just conceivable.

**Reply**

Agreed. The text now reads: “Considering that this air mass had spent several days over the ocean,  $\text{CH}_3\text{SCH}_3$  (not measured) is a likely contributor to  $\text{NO}_3$  reactivity.

**Comment.**

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

**Reply**

These 10 lines are indeed descriptive. There is no conclusion.

**Comment.**

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.

**Reply**

The reference to the Zaveri paper was not central to the discussion and has been removed.

**Comment.**

pg 17851. It may be helpful to the reader if there is a statement at the beginning of this paragraph what unmeasured  $\text{NO}_3$  losses the authors consider, e.g., reduced sulfur compounds, peroxy radicals, olefins, etc.

**Reply**

This is done in the second paragraph.

**Comment.**

pg 17854 line 17 "23 Novermber" Please correct.

**Reply**

Done

**Comment.**

line 19. The charge on the ammonium is incorrect.

**Reply**

Corrected

**Comment.**

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

**Reply**

The specific comments on the Figures are addressed below.

**Comment.**

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.

**Reply**

We feel that the location of the site (where all the back trajectories come together) is already quite obvious.

**Comment.**

pg 17866, Fig 2. Consider reorganizing the figure. Combine NO<sub>2</sub>, ozone, and O<sub>x</sub> (=O<sub>3</sub>+NO<sub>2</sub>) in row 1 on a single y-axis. Combine the two NO<sub>3</sub> data sets and N<sub>2</sub>O<sub>5</sub> (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.

**Reply**

Figure 2 has been redrawn. There are now 4 rows. RH has been added, NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> are plotted together. The caption has been suitably modified.

**Comment.**

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.

**Reply**

The analysis is already restricted to nighttime periods only. This is now mentioned in the caption.

**Comment.**

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.

**Reply**

The plot has been modified to adopt the AMS community's colour preferences.

**Comment.**

pg 17869, Fig 5. By definition, the lifetime is inversely proportional to  $\text{NO}_2$ , 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  $K_2$  was used in the calculation.

**Reply**

This statement is not entirely correct. The  $\text{NO}_3$  lifetime will be inversely proportional to  $\text{NO}_2$  only if indirect losses dominate. If only direct processes lead to  $\text{NO}_3$  loss, then there is no dependence on  $\text{NO}_2$ . The point we are making is that an observed dependence of  $\tau \text{NO}_3$  on  $\text{NO}_2$  does not necessarily mean that heterogeneous losses are important, as is frequently assumed. In this study, they are not dominant.

**Comment.**

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

**Reply**

As we describe in the text the portion of this night with "Atlantic Air" starts at about 02:30. We mention that the reduction in monoterpenes after this is consistent with the observed shift in wind direction. The reviewer presumably refers to the homogeneous hydrolysis of  $\text{N}_2\text{O}_5$  (not water). We have never stated that there is no gas-phase reaction between  $\text{N}_2\text{O}_5$  and  $\text{H}_2\text{O}$  and we do not doubt our own work on this. We have simply taken a better upper limit to the rate coefficient from the data of Brown. See our reply above to the **comment** related to pg 17828 line 5.

**Comment.**

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.

**Reply**

**The plot has been redrawn to address off scale data-points.** The month is stated in the x-axis.

**Comment.**

Fig. 8 and 12 These graphs are puzzling as I have no idea what they are meant to convey. The lifetime of  $\text{NO}_3$  is inversely related to  $\text{NO}_2$  by definition, and neither  $\text{NO}_3$  nor  $\text{N}_2\text{O}_5$  are known to react with  $\text{SO}_2$ . To compare  $\text{NO}_3$  lifetime with aerosol surface area also does not make any sense as the latter should be weighted by the  $\text{N}_2\text{O}_5:\text{NO}_3$  ratio ( $K_2[\text{NO}_2]$ ).

**Reply**

The referee's comment "The lifetime of  $\text{NO}_3$  is inversely related to  $\text{NO}_2$  by definition" is based on the (wrong) assumption that  $\text{NO}_3$  losses are indirect (via  $\text{N}_2\text{O}_5$  hydrolysis). We have clearly shown in this manuscript that this is not the case. We are fully aware that  $\text{SO}_2$  does not react with  $\text{NO}_3$ . The point we make in Figures 8 and 12 (now 13) is that large  $\text{SO}_2$  mixing ratios are associated with very low  $\text{NO}_3$  lifetimes.  $\text{SO}_2$  is then used as a proxy for possible reactive traces gases as described in the text.

**Summary.**

Scientific Significance: Good (2)

Scientific Quality: Fair (3)

Presentation Quality: Fair (3)

Are the scientific results and conclusions presented in a clear, concise, and wellstructured 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

### Referee 3

#### Comment.

This paper presents in-situ measurements of N<sub>2</sub>O<sub>5</sub> at a fixed height (7-12 m above ground level) and related trace gases during the DOMINO campaign in southern Spain. Direct measurements of NO<sub>3</sub> were apparently compromised by analytical difficulties, but NO<sub>3</sub> was derived from the N<sub>2</sub>O<sub>5</sub> and co-located NO<sub>2</sub> measurements using equilibrium. These derived NO<sub>3</sub> measurements compare well with an open path DOAS measurement. The paper primarily interprets the NO<sub>3</sub> 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 studies for different nights with air masses from different sectors: marine, industrial and continentally influenced.

#### Reply

No reply required

#### Comment.

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 NO<sub>3</sub>, rather than heterogeneous losses of N<sub>2</sub>O<sub>5</sub> (or heterogeneous loss of NO<sub>3</sub>, which is also considered), but that the measurements of additional gas-phase compounds frequently does not account for the observed, very short lifetimes of NO<sub>3</sub>. 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.

#### Reply

No reply required

#### Comment.

The paper does not discuss the potential for halogen activation through formation of ClNO<sub>2</sub> upon N<sub>2</sub>O<sub>5</sub> 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 N<sub>2</sub>O<sub>5</sub> (see papers by Bertram and Thornton on this subject) would be a useful addition to this paper.

#### Reply

We have added the text: “It has recently been suggested that heterogeneous reactions of N<sub>2</sub>O<sub>5</sub> with chloride containing particles can also represent a significant source of photolabile chlorine (in the form of ClNO<sub>2</sub> and Cl<sub>2</sub>) (Roberts et al., 2009; Thornton et al., 2010).”

**Comment.**

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.

**Reply**

We are aware of the excellent analyses of Stutz and co-workers on this subject, and we shall certainly make use of them when preparing the manuscript by Thieser et al. See our reply to referee 2 on this matter.

**Comment.**

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

**Reply**

In fact 200 nm is more appropriate. This has been changed.

**Comment.**

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

**Reply**

Correct. This change has been made.

**Comment.**

Page 17840, top.  $\text{NO}_3$  production rates were “low” but not quantified. It would be useful to have a number or a range in pptv or ppbv  $\text{hr}^{-1}$ , possibly as an addition to Figure 4.

**Reply**

We have added this information to the text: After 02:30,  $\text{O}_3$  levels were between 25 and 35 ppb, with  $\text{NO}_2$  close to 1 ppbv, resulting in comparatively low  $\text{NO}_3$  production rates ( $\sim 2 \times 10^{-2} \text{ ppt s}^{-1}$ ).

**Comment.**

Page 17844, top: Isoprene reacts relatively rapidly with  $\text{NO}_3$  and would be more appropriately grouped with pinene or NO than with formaldehyde, whose reaction is negligible.

**Reply**

We have modified the text and now write: “The reactions of  $\text{NO}_3$  with both NO and  $\alpha$ -pinene have large rate coefficients ( $k_4 = 2.6 \times 10^{-11}$ ,  $k_5 = 6.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) whereas HCHO reacts much more slowly ( $k_7 = 5.6 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). Isoprene is an intermediate case with  $k_6 = 7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson et al., 2004; Atkinson et al., 2006).”

**Comment.**

Page 17844, bottom: Reaction of  $\text{NO}_3$  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  $\text{NO}_3$  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.

**Reply**

The detection limit (6 ppt) includes uncertainty in the zero measurement. The trend in NO observed during this night (from 0 to 5 ppt) is however greater than instrument drift over this

period and can be regarded as real even though the maximum value is less than the detection limit. As the referee points out, the uncertainty in this calculation is large, yet the increase in NO<sub>3</sub> loss rate is indeed consistent with the observed trend in NO.

**Comment.**

Page 17846, line 17: Although it is very likely that DMS contributed to NO<sub>3</sub> loss in marine influence air masses, a mixing ratio of 200 pptv would be atypically large, unless the site was rather close to a known hot spot for DMS. Do the authors have any information about local DMS sources?

**Reply**

Unfortunately, we have no information about local CH<sub>3</sub>SCH<sub>3</sub> sources at this or any other time of year at this location.

**Comment.**

Related to the same discussion – can the authors speculate on second-generation oxidation products of the biogenics (either DMS or monoterpenes) with NO<sub>3</sub>? Can these contribute to the missing reactivity?

**Reply**

In general, second-generation products of the reaction of NO<sub>3</sub> with biogenics all tend to react more slowly than the initial step. Having said this, we cannot rule out a contribution to reactivity of e.g. the partially nitrated, unsaturated organics, which could be formed. However, given that the identity of the primary biogenic was generally unknown, an analysis of the evolution of the air mass reactivity towards NO<sub>3</sub> is not possible.

**Comment.**

Page 17848, line 12: “large NO<sub>3</sub> production rates” – again, how large?

**Reply**

We have added this information to the text: “Prior to midnight, NO<sub>2</sub> mixing ratios between ~1 and 6 ppbv and ozone levels of > 25 ppbv resulted in large NO<sub>3</sub> production rates (up to ~0.12 pt s<sup>-1</sup>) and the highest N<sub>2</sub>O<sub>5</sub> concentrations in the entire campaign (~500 ppt) were measured.”

**Comment.**

Page 17851, line 20-21. Does H<sub>2</sub>S react with NO<sub>3</sub>?

**Reply**

No, a reaction has not been observed and the rate coefficient is estimated as  $< 8 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

**Comment.**

Page 17857, line 25: Figure 13 gives an absolute, but not a relative, NO<sub>x</sub> loss. What was the total NO<sub>2</sub> present, and what fraction of NO<sub>x</sub> was consumed by nighttime reactions?

**Reply**

The mean concentration of NO<sub>2</sub> on the three nights is now listed in the caption: “Mean NO<sub>2</sub> concentrations on these nights (18:00 till 06:30) were 2,7, 1,3 and 1,2 ppbv, for the 23-24th, 26-27th and 06-17th, respectively.”

Text has also been added to (new) section 4.1 (nocturnal loss of NO<sub>x</sub>): “These calculations indicate that over the course of a 12 hour night, 0.8, 1.0 and 1.8 ppbv of NO<sub>x</sub> were removed from the boundary layer on the 23-24<sup>th</sup>, 26-27<sup>th</sup> and 06-07<sup>th</sup>, respectively. This is equivalent to ~ 70 % of NO<sub>2</sub> as mean mixing ratios were 1,2, 2,7 and 1,3 ppbv on these nights.”