

## ***Interactive comment on “A photochemical model and sensitivity study of the triple-oxygen isotopic ( $\Delta^{17}\text{O}$ ) composition of $\text{NO}_y$ , $\text{HO}_x$ , and $\text{H}_2\text{O}_2$ in a polluted boundary layer” by G. Dominguez et al.***

**Anonymous Referee #2**

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*First of all, as I was offered the privilege (!) of reviewing an earlier version of this manuscript, I have to say I was extremely disappointed that many non-controversial scientific and technical corrections provided in my earlier review have not been taken into account by the authors before submitting a new version to Atmos. Chem. Phys. Discuss. I hope the authors will consider the comments below with more care and attention if they wish to revise their manuscript for potential publication in Atmos. Chem. Phys.*

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### **1 General comments**

Dominguez et al. propose an exploration of the factors controlling the isotope anomaly ( $\Delta^{17}\text{O}$ ) of atmospheric nitrate under polluted condition in the lower atmosphere, by means of computer-based simulation. This goal is useful and very timely since measurement-based studies have accumulated quickly in the recent years, providing the basis (and the need) for a thorough investigation of the causes of variability of this new atmospheric variable.

While the goal of this article is of great relevance to the current development of isotopic atmospheric chemistry, the manuscript in its current form suffers major shortcomings in the presentation of the method employed, the discussion of previous work on the topic, and the discussion of the results reached. **The presentation and the discussion of the results is at best superficial, and in many cases totally irrelevant to atmospheric chemistry. Most of the "results" provided by the authors seem to be driven more by mathematical curiosity than by the need to address atmospheric chemistry issues.**

I strongly suggest that the authors take the time to present and discuss their results more carefully, given the potentially high significance of their work. As it, the manuscript definitely does not meet any single criterium for publication in Atmos. Chem. Phys.

The first issue to be addressed is the structure of the manuscript. Many sentences throughout the text are introductory in nature, and should be put together in the introduction. Clearly assessing the goals of the paper in the introduction, as well as the potential relevance of the processes taken into account would help the reader (and quite possibly also the authors) to better understand how isotope measurements (and modeling) can be useful for atmospheric chemistry.

Before presenting the impact of variations of environmental factors on  $\Delta^{17}\text{O}$  of nitrate, the authors should stress why this study is useful, i.e. whether such variations in

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environmental factors can occur in the atmosphere, and why it is expected that it has an impact on the  $\text{NO}_x$  chemistry and the isotopic composition of atmospheric nitrate.

Very unfortunately, temporal and spatial scales are totally mixed-up in this article. In terms of temporal scales, one can spot that, even if the focus seems to be put on "polluted boundary layer" issues, which typically develop over time scales of hours to days maximum, references to the Vostok ice-core are provided to support a totally irrelevant sensitivity study to methane mixing ratios ... Another example of spatial inconsistency is that, although the work appears to be based on "polluted boundary layer" issues, some conclusions drawn are applied to Antarctic snow nitrate isotopic composition. The "latitude" test, performed on January 5 for a range of latitudes makes no sense at all, since the composition of the atmosphere varies latitudinally to a great extent (whether the air masses are marine, continental, close to pollution sources or not etc.).

Overall, the sensitivity studies presented in this article are in most case totally irrelevant, and their discussion is also flawed to a great extent. **It is strongly advised, to help the authors focus their work and anchor it to known atmospheric chemistry issues, to choose a geographical location where the simulations are performed, and to select a time scale for the study undertaken. A suggestion could be to choose the La Jolla site at the seasonal scale, where year-round isotope measurements are already available (Michalski et al., 2003) and direct comparison can be made.** Of course, the method can be applied at other locations, but at present the presentation of the results (and their relevance to atmospheric chemistry) is so poor that no sense can be made from the present paper. Once a location is fixed, then the authors can investigate the range of variability of the mixing ratio of the species involved (using previous publications, or measurements from local air quality institutions). This will avoid performing sensitivity studies in a range of variation totally inconsistent with basic atmospheric sciences (see details below). On the other hand, relevant sensitivity studies such as testing the value of  $\gamma(\text{N}_2\text{O}_5)$  could be presented in the paper and will be very useful for the community.

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Last, differences in  $\Delta^{17}\text{O}$  between submicron and supermicron aerosol nitrate are alluded to in the abstract, and in different places in the manuscript, but never quantitatively assessed, neither in the results or discussion section. This is a pity, as it constitutes one strong appeal to the manuscript, as inferred from the abstract. Published measurements of these differences can not only be found in Patris et al. (2007), but also in Morin et al. (2009).

The references are mostly referring to isotope geochemistry (sometime including atmospheric measurements) and almost never dealing with atmospheric chemistry issues. It is not sufficient to quote Seinfeld and Pandis. Also, in many occasions (see below), there is no reference supporting major assumptions made in this paper.

## 2 Specific comments

### 2.1 Introduction

The numbering of the sections at the beginning of the paper is particularly awkward, see below:

1. Introduction: triple oxygen isotopic composition of atmospheric species
- 1.1 Recent work on  $\Delta^{17}\text{O}$  of tropospheric nitrate and its precursors
2. Motivation for present work
3. Overview of present work
4. The origin of excess  $^{17}\text{O}$  in atmospheric nitrate
- 4.1 The conservative nature of mass-independent isotopic signatures

All of these sections appear to be introductory in nature, so they are treated together; however **they seem to be presented to the reader almost in random order**. The beginning of the introduction is extremely vague and general. As the focus here is on

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atmospheric chemistry, and given that the body of literature has grown considerably in recent years for atmospheric applications, there is no need to spend so many words on the history of oxygen isotopes measurements. Instead of focussing on isotope geochemistry (to little appeal to the ACP readership !), the authors could instead try to demonstrate how isotope measurements can help the isotopic chemistry community to solve problems that could not be solved without the help of isotopic measurements, i.e. what is the value of such an approach (not only to expand the number of things that are measured on Planet Earth). **I strongly suggest the introduction is totally rewritten and focused on atmospheric chemistry issues, not on isotope geochemistry, that constitutes only the tool, not the focus, of such a study.**

With this idea in mind, the authors may be able to write up an introduction that identifies the knowledge gaps in atmospheric chemistry problems, where isotopic measurements could be useful. This includes e.g.  $\text{NO}_x$  processing in the polluted boundary layer, of major relevance to air quality issues (e.g. Brown et al., 2006). An additional issues where isotopic measurements could help is to what extent halogen chemistry in polluted marine regions contributes to air quality deterioration and oxidative chemistry (ozone production or destruction), as recently demonstrated by Osthoff et al. (2008). These are simple examples to illustrate what could be appealing to the broader ACP readership and more useful to the atmospheric chemistry community.

Here is a suggestion for streamlining the introduction in a more consistent manner:

#### 1. Introduction

1.1 General atmospheric chemistry of  $\text{NO}_x$ , nitrate; impact on air quality; open issues (heterogeneous chemistry ...)

1.2 Isotopic approach (definition of  $\Delta^{17}\text{O}$ ); why measuring and studying  $\Delta^{17}\text{O}$  in atmospheric nitrate; why focus on  $\Delta^{17}\text{O}$  and not  $\delta$  values (conservativeness of  $\Delta^{17}\text{O}$ , "ease" to perform mass-transfer approaches rather than taking into individual fractionation constants associated to each single chemical reaction)

1.3 Overview of previous isotopic assessments of the chemistry of  $\text{NO}_x$ ; overview of

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the modeling approaches used so far.

1.4 Precise definition of the "explicit" approach taken by the authors; overview of the content of the study.

Other comments on the introduction:

Page 13357, line 18: please define what is "perchlortate". Is this a new chemical species ?

Page 13356, line 22 : the definition of  $\delta$  should not be relegated to an appendix. Note that the factor 1000 in the definition is extraneous and should be deleted.

Page 13357, line 12: if equation (1) gives the definition used by the authors, then the sign "=" should be used.

Page 13357, line 28: too long sentence, to be shortened.

Page 13358, line 4: "we briefly previous measurements" : what do the authors mean here ?

Section 1.1, Page 13358 : this "review" of recent work is useless since previous results are not confronted to scientific issues, but rather listed in chronological order. This should be shortened to a large extent.

Page 13359, line 14: The description of the work of Kunasek et al. (2008) is not correct. Geos-CHEM is not a "box model", and simulation were not performed "over three seasons".

Page 13359, line 16: I would be very interested to know what the authors mean by "modeled the data". To me, a model is a mathematical description of physical processes, which is used to perform simulations that are, in turn, confronted by data. "Modeling data" makes no sense.

Page 13359, line 27: the description of the modeling work by Morin et al. (2008) is not correct. It is nowhere cited in this publication that "a 0D Lagrangian box model [was used] to track the chemistry along the trajectory followed by air transiting to the sampling site". It is clearly stated in this paper that simulations were performed at  $40^\circ\text{N}$  and  $80^\circ\text{N}$ , during summer and winter.

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Page 13360, line 3: "several simplifying assumptions": please detail what are the simplifying assumptions. In which sense are they assumptions ? In which sense are they simplifying ? To what extent do the authors deviate from using these assumptions, and how ?

Page 13360, line 4: "The authors invoked BrO oxidation of NO to explain their isotopic measurements". First of all, this is only correct for springtime. Second, what explains the high  $\Delta^{17}\text{O}$  at this season is the role of  $\text{BrONO}_2$  hydrolysis.

Page 13360, line 17: Brothers et al. is not a published study. Dominguez et al. (2008) does not deal with  $\text{NO}_x$ -nitrate chemistry. In addition, a single paper cannot cover the whole chemistry from tropical rain forest to the polluted (marine) boundary layer. As suggested before, the authors are encouraged to select an atmospheric settings where to perform their sensitivity studies. Addressing global atmospheric chemistry in a single paper clearly is too ambitious at this stage ...

Page 13360, line 23: "explicitly". Please define explicitly what is meant here ...

Page 13361, line 25: Contrary to the claim of the authors, this work may be "significant" but it seems not at all "novel" in nature. Indeed, the authors simply seem to have extended to short (less than 1 hr) lifetime species ( $\text{HO}_x$ ,  $\text{NO}_x$ ) the **mass transfer approach** developed before for longer lifetime species (e.g. nitrate) by Michalski et al. (2003) and several following studies. In addition, the authors discuss (often inappropriately) the results of several papers mostly based on new measurements of  $\Delta^{17}\text{O}$  of atmospheric nitrate, including the development of modeling approaches to interpret them (Michalski et al., 2003; Morin et al., 2008; Kunasek et al., 2008), but they almost never mention modeling approaches developed in the recent past, dealing with shorter lifetime species: this includes the work of Lyons (2001), Zahn et al. (2006) - although the latter lacks tropospheric chemistry- and Liang and Yung (2007). Such studies have attacked the issue of simulating  $\Delta^{17}\text{O}$  of atmospheric  $\text{HO}_x$  and  $\text{NO}_x$ , and it cannot be avoided to compare the authors' results with prior work very similar in scope and nature.

Page 13362, line 10: Please change the syntax of this sentence. At present, "emis-

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sions" are "oxidized" ...

Page 13363, line 8: The authors seem to be doubtful that  $\text{NO}_x$  and  $\text{O}_3$  are photochemically interrelated. Where do these doubts come from ?

Page 13363, line 15: what does "not typically available" mean ?

Page 13364, true line 4 (pb in the numbering of this page): the authors seem to have misunderstood the study by Bhattacharya et al. (2008). Ozone made in the laboratory can have a very variable  $\Delta^{17}\text{O}$  (see Thieme and Heidenreich III, 1983 ...). So it is not correct so state that the  $\Delta^{17}\text{O}$  of lab-made ozone is 25 ‰. In contrast, it is true that Bhattacharya et al. (2008) quantified the degree of isotopic asymmetry of ozone in terms of  $\Delta^{17}\text{O}$ . Page 13364, true line 6 : "finding" → "findings"

Page 13364, true line 8: The link between the 3rd and 4th sentence of this paragraph can only be understood if the authors explain that the photolysis of ozone mostly produces  $\text{O}(^1\text{D})$  by expulsion of a terminal O atom. The proportion (on the order of 90 %) has been quantified by Sheppard and Walker (1983), which surprisingly misses from the reference list.

## 2.2 Section 5 - Photochemical modeling ...

First of all, note that the syntax of the title of the section is incorrect (missing "of", probably).

The description of the atmospheric chemistry model used is too short, in particular because very few other studies have used the model used by the authors. **It is absolutely needed that the authors provide a complete listing of all chemical reactions used in the model, with explicit references to the reaction rates used (both must be provided as an electronic supplement). This is standard practice for publication of atmospheric chemistry box-modeling.**

Page 13365, line 10: I believe concentrations (or mixing ratios), and not the species themselves (what would this mean ?), are calculated by the model.

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Page 13366, line 5: it is extremely surprising that ozone is an input parameter for a photochemical box model used in the polluted boundary layer. Apparently the authors ignore that the lifetime of ozone in a polluted boundary layer is only a few hours (because it is titrated by NO emissions, before it builds up due to photochemical ozone production). Thus it makes no sense, in a polluted boundary layer, to have ozone mixing ratios as a fixed input for a photochemical model. Here again, if the authors had chosen a specific situation where to apply their model, they could have realized that this approach is not consistent with a polluted boundary layer. A few lines below, one discovers that a polluted **marine** boundary layer is dealt with. What does this change in terms of ozone life time (up to a month in a clean marine boundary layer in the absence of local NO emissions) ? **This confusion must be solved before the authors can proceed with a revised article.**

Page 13366, line 15: the equation presented by the authors is problematic for a number of reasons. For of all, it is dimensionally not homogeneous (i.e., the units don't match). On the right hand side of the equation the little "d" ( $d[X_j(i)]$ ) doesn't match with the rest of the equation. It looks to me that this equation represents the numerical implementation of a general equation, in the "isotopic sub-model". Rather than providing this wrong equation (what is "i", by the way ???), the authors could explain better their approach by providing the general mass-balance equation. This is simply the mass-balance equation (standard in atmospheric chemistry), that includes the isotopic composition in terms of  $\Delta^{17}\text{O}$ , because no fractionation has to be taken into account.

Below is the general mass-balance equation for a given species X in the atmosphere:

$$\frac{d}{dt}[X] = \sum_j P_j - L \quad (1)$$

where  $P_j$  represents each production flux of the species X, and  $L$  represents the sum of each loss flux. When isotopes are taken into account, this mass-balance equation

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now reads:

$$\frac{d}{dt}([X] \times \Delta^{17}\text{O}(X)) = \sum_j (P_j \times \Delta^{17}\text{O}(X)_j) - L \times \Delta^{17}\text{O}(X) \quad (2)$$

In this equation,  $\Delta^{17}\text{O}(X)_j$  represents the isotope anomaly inherited by the species X through the production channel  $j$ . Note that this equation takes sinks into account, although they do not induce specific isotope anomalies (they are assumed to be mass-dependent). Thus they can be treated together and summed up before applying the equation above (contrary to the source reactions, which induce specific isotope anomalies because the mass-transfer rates are different). The authors are correct to state that individual sinks do not induce isotopic anomalies, but they should be included in the equation anyway, because sinks have a huge impact on the variability of  $\Delta^{17}\text{O}(X)$  (smoothing effect, discussed later by the authors in terms of nitrate, but this also applies to any other species). In summary, **I strongly suggest the authors to include the above paragraph in their article, because it makes the whole concept of mass-transfer much easier to understand. Also, I would like to be sure that the sinks are properly taken into account in the calculations, which seems not to be the case at the moment.**

Page 13367, line 10: the formatting of the equations is awkward. Please put them on the same line.

Page 13367, line 13: what is Y ???

Page 13367, line 19 : a reference clearly misses to support the value of 91 %.

Page 13368, line 8: what is the impact of neglecting mass-independent fractionation on the calculations ? The "explicit" treatment used by the authors should be able to quantify this.

Page 13368, line 10: why is the treatment of so OH specific ? Following the isotopic mass-balance equation above should make it straightforward for each species. Including isotopic exchange reactions should be straightforward. **This whole paragraph is very confusing a casts doubts on the whole approach.** Or it simply attempts to ex-

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plain what is the model doing at each time step, which is clearly not helping the reader at all. The discussion on the  $\Delta^{17}\text{O}$  of OH seems too quick, given that the complete framework (involving OH sinks and sources) was extensively detailed in Morin et al. (2007) and discussed by Kunasek et al. (2008).

Page 13369, line 3: what supports the lifetimes given here ? References are clearly missing. Such values could be tested during the sensitivity study (variable lifetimes).

Page 13369, line 7: how much for "your" aerosol nitrate ?

Page 13369, line 24: the presentation of the  $\gamma$  values is astoundingly short and does not take into account any of the recent literature on  $\gamma$  values for  $\text{N}_2\text{O}_5$  and  $\text{HNO}_3$ . The authors are encouraged to go read recent papers on such issues, such as Evans and Jacob (2005), Brown et al. (2006) and more recently by the Thornton group, the Brown group and so on. **It is unbelievable that such literature was apparently not read by the authors. This is a crucial issue in atmospheric chemistry at the moment, and the authors have, so far, missed the opportunity to demonstrate (or not) how isotopic approaches could be used to address this issue quantitatively.**

### 2.3 Section 6, Sensitivity study ...

The first paragraph is introductory in nature and has nothing to do here. In addition, in general sensitivity studies are only presented after a baseline case has been described in detail. This is clearly missing here. In addition, the "baseline" run provided in Figure 1 is done with a totally unrealistic mixing ratio for ozone (1 ppmv ...). It even does not correspond with the "baseline" conditions presented in Table 2 (where the ozone mixing ratio was set to 9.3 ppbv, which is also very surprising for a polluted boundary layer ...).

**This whole section on the sensitivity study is extremely disappointing on a scientific point of view. The relevant tests to be performed have not been presented. Instead, the reader is confronted with meaningless tests. Because of this, the**

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**review below is very short, and mostly identifies the most blatantly inconsistent "findings".**

#### 2.3.1 Sensitivity to RH

First of all, as noted by Greg Michalski (Reviewer comment),  $\gamma(\text{N}_2\text{O}_5)$  depends on RH. So changing only one variable makes little sense in atmospheric chemistry. In addition, a quick internet search revealed to me that the annual range of RH at La Jolla is 60 – 83 %. Page 13371, line 21, the authors indicate that the diurnal range of RH can be *mild or extreme*. Such statements should be replaced by quantitative assessments (NUMBERS !). In short, it is hard to find a place where tropospheric RH is lower than 30 %. So any discussion on model results below this value is irrelevant to atmospheric chemistry. In addition, what matters really is the specific humidity of the air, not is relative humidity, because results based on RH are only valid at one given temperature. Thus the authors are strongly advised to think deeply about the implications of changing RH, and how such changes translate in changes in  $\gamma$  for heterogeneous reactions and so on.

#### 2.3.2 Sensitivity to the ozone mixing ratio

As outlined above, it makes no sense to fix a constant value for the mixing ratio of ozone in a polluted environment. **In addition, the range chosen by the authors ( 0-5 ppbv for clean air, to 20 ppbv for polluted air), should simply have prevented this paper from appearing in ACPD. It simply is a pity to find such egregious numbers in a paper dealing with atmospheric photochemistry ....**

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### 2.3.3 Sensitivity to NO<sub>x</sub> fluxes

What is the chemical impact of such NO<sub>x</sub> fluxes ? Before assessing the isotopic implications, it is expected that the authors demonstrate whether this makes any sense chemically.

### 2.3.4 Sensitivity to methane

Simply irrelevant to tropospheric photochemistry at hours to days timescales.

### 2.3.5 Sensitivity to latitude

How can the authors think they can address such issues using a box model with fixed boundary conditions ? Latitudinal changes can only be approached using large scale chemistry/transport model (like GEOS-CHEM, Alexander et al., 2009), because boundary conditions vary very much from place to place. Also, **what is the relevance of choosing a single date in the year (January 5), when photochemistry is at its winter minimum ??**

### 2.3.6 Sensitivity to cloud albedo

It is not clear how cloud albedo is defined. Does this include cloud fraction ? Overall, this whole section makes no sense.

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### 2.3.7 Other sensitivities

Of course Julian Day has a measurable effect. This has been documents from Michalski et al. (2003) onwards. This is called **seasonal change in the intensity of photochemistry**.

## 3 Section 7, Comparison with ...

The authors have "discovered" that  $\Delta^{17}\text{O}$  of HO<sub>2</sub> can be high during the night. However, what is the concentrations at this time of the day ??? What effect can be expected on  $\Delta^{17}\text{O}$  of other species ?? The discussion lacks a clear assessment of the real impact of the findings, which are, in part, driven by the concentration levels.

Also, the authors find that the thermal dissociation of HNO<sub>4</sub> (pernitric acid, PNA) can yield a significant  $\Delta^{17}\text{O}$  in HO<sub>2</sub>. However, to support such a statement it must be demonstrated that there is an isotopic scrambling within HNO<sub>4</sub> before the dissociation. It appears from its structure that O atoms surrounding the central N atom are not equivalent (<http://www.chemindustry.com/chemicals/1230672.html>). Thus the thermal dissociation of HNO<sub>4</sub> does not necessarily lead to HO<sub>2</sub> with a different  $\Delta^{17}\text{O}$  than before HNO<sub>4</sub> is formed. Clearly this requires more investigation.

The discussion of  $\Delta^{17}\text{O}$  of NO<sub>2</sub> could have been interesting, as it was recently shown that the photochemical steady-state does not hold throughout the night, so that the "classical" formula for  $\Delta^{17}\text{O}$  of NO<sub>2</sub> does not always hold (see the recent interactive discussion on Alexander et al., 2009). It appears here that the authors want to include HO<sub>2</sub> as a species bearing a positive  $\Delta^{17}\text{O}$  in this equation, which could be interesting. However, it seems that HO<sub>2</sub> is not treated explicitly (see Page 13378, line 13). Also, it is not clear how the difference ( $\epsilon$ ) can be negative, and not positive for the baseline

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case. Maybe a confusion ? Last, the choice of  $\epsilon$  is very poor, as this generally refers to isotopic fractionation. Why is this plotted vs. total ozone column ? Here again, this has no relevance to polluted boundary layer issues.

There are again many problems in the typesetting here:

Page 13378, equation 8 : check the parentheses

Page 13378, line 17: what does "refsec:isotopesubmodel" mean ?

### 3.1 Conclusions

In the conclusion, the link with atmospheric processes in polar areas is not supported by solid evidence. In addition, the authors seem to ignore that atmospheric chemistry under polar conditions proceeds under very different conditions and that reactivity of nitrate after deposition on the snow has a major impact on the overlying  $\text{NO}_x$  budget (Davis et al., 2008). Thus drawing conclusions from the present study into the results presented by McCabe et al. (2007) is at least purely speculative, on the basis of the results presented here. Same with the reference to the work of Alexander et al. (2004). **Both should simply be removed, or the authors should undertake a specific study, dealing with polar regions.**

## 4 Plots

Almost all plots refer to an unknown chemical species ( $\text{NO}_3^{-1}$ ) ...

They all are very poor in design, not informative; the captions are useless. All of them should be redrawn, following up the entire revamping of the paper, with a much more focussed approach and the identification of atmospheric chemistry issues to be solved using stable isotope approaches.

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## 5 References

Many missing references (some indicated in the text above). In contrast, too many references from isotopic geochemistry; at least half of them should be eliminated from the reference list. This distracts the reader's attention and brings nothing to the discussion on atmospheric chemistry.

Many errors in authors names (e.g. Rockmann → Röckmann etc.), chemical formulae, wrong fromatting.

eg.

Page 13382, line 10: Please fix the extraneous "?".

Page 13383, line 2: fix the missing exponents

In addition, why is Morin et al. (2007) listed twice ?

## 6 References

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