

Interactive comment on “Radical budget analysis in a suburban European site during the MEGAPOLI summer field campaign” by V. Michoud et al.

V. Michoud et al.

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First, we would like to thank the reviewers for their valuable comments on the manuscript. We answer to the comments addressed by each referee and summarize the changes made to the revised manuscript in the following document.

Response to referee #1:

> *The paper is quite long, and I would encourage the authors to consider if section 4.4*

C7750

in particular could be shortened.

In agreement with the first referee we have shortened the section 4.4 of the paper in the revised manuscript as he suggested. However, since additional information have been requested elsewhere in the revised manuscript, this revision of section 4.4 does not lead to a reduction of the paper.

>*Problems with the PSS approach A PSS approach is presented to calculate OH levels for comparison with measurements. However, the approach used mixes OH and HO₂/RO₂ sources and sinks, and neglects partitioning between OH, HO₂ and RO₂. As presented, combining equations 1 and 2/3 would determine the sum of [OH] + [HO₂] + [RO₂], not [OH] (if it is assumed that HO_x loss is dominated by OH + NO₂). Equations 4 and 5 are therefore not correct, and the quantity Pr/Lr should be compared with [OH]+[HO₂]+[RO₂], if this approach is to be followed. In practice the much longer lifetime of HO₂ and RO₂, compared with OH, begins to make such an analysis, using point observations, problematic. To obtain a steady state level for OH, you need to consider OH sources and sinks - this will need to include HO₂+NO and probably HO₂+O₃, from either measured or calculated HO₂. Total radical (HO_x) termination may be dominated by OH + NO₂, but OH removal is dominated by OH + VOC (ca. 80 %, as shown by your radical budget analysis, section 4.4), so this term should feature in any PSS calculation for comparison with observed OH.*

It must be indicated here that this approach is not so uncommon as it has been already used in recent papers, for example in [Holland et al., 2003; Elshorbany et al., 2009]. The basic idea is that we considered fast interconversion between radical species which are in a stationary state. Its validity can be demonstrated as follow:

C7751

Considering a cycle between OH, RO2 and HO2 which is initiated only by the three following reactions: Ozone photolysis, HONO photolysis and HCHO photolysis; which is terminated only by reactions between OH and NO and between OH and NO2 and which propagation reactions are reaction between OH and VOC, RO2 and NO and HO2 and NO. If the three species (considering RO2 as a unique species) are at a stationary state (sources=losses), it leads to the following equations:

Considering RO2 species:

$$k_{OH+COV}[OH][COV] = k_{RO_2+NO}[RO_2][NO] \quad (1)$$

Considering HO2 species:

$$k_{RO_2+NO}[RO_2][NO] + 2J(HCHO_rad)[HCHO] = k_{HO_2+NO}[HO_2][NO] \quad (2)$$

If we replace equation (1) in equation (2), it leads to:

$$k_{OH+COV}[OH][COV] + 2J(HCHO_rad)[HCHO] = k_{HO_2+NO}[HO_2][NO] \quad (3)$$

Considering OH species:

$$k_{HO_2+NO}[HO_2][NO] + J(HONO)[HONO] + 2\Phi_{OH}J(O^1D)[O_3] =$$

$$k_{OH+COV}[OH][COV] + k_{OH+NO}[OH][NO] + k_{OH+NO_2}[OH][NO_2] \quad (4)$$

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If we replace equation (3) in equation (4), it leads to:

$$k_{OH+COV}[OH][COV] + 2J(HCHO_rad)[HCHO] + J(HONO)[HONO] + 2\Phi_{OH}J(O^1D)[O_3] =$$

$$k_{OH+COV}[OH][COV] + k_{OH+NO}[OH][NO] + k_{OH+NO_2}[OH][NO_2] \quad (5)$$

Finally, the equation (5) gives us the following equation, which corresponds to the equation (4) of the article:

$$OH_{PSS} = \frac{2J(HCHO_rad)[HCHO] + J(HONO)[HONO] + 2\Phi_{OH}J(O^1D)[O_3]}{k_{OH+NO}[OH][NO] + k_{OH+NO_2}[OH][NO_2]} \quad (6)$$

As noticed by the second referee, this approach is valid as long as some assumptions are fulfilled: 1) total initiation and termination rates of ROx radicals balance each others, 2) radical losses other than reaction between OH and NOx are negligible, 3) all main radical formation pathway, including HONO photolysis, are included in the radical initiation rate.

> *Model mechanism. This is something of a matter of opinion but it may not be desirable to construct "hybrid" mechanisms (as has been done here, mixing reactions from the MCM and from SAPRC), rather than using a single, well-defined, auditable, mechanism to facilitate comparison with other work. Does the new mechanism reproduce e.g. chamber data to a similar level to the original mechanisms? If so, why bother with the change - if not, what are the consequences for confidence in the model simulations? (There is also the issue that some mechanisms, such as SAPRC, are tuned to chamber datasets, so while reactions may look like fundamental processes, other dependencies within the mechanism mean that direct changes to single parameters are not, strictly, valid - without re-tuning the whole mechanism. This*

C7753

does not however apply for the near-explicit MCM).

In this study we did not build any "hybrid" mechanism. In fact, we keep all MCM reactions and we do not add any other reaction. We have only updated the kinetic data (e.g. the reaction rates) for the inorganic part of the model with the SAPRC07 data which are more recent. The aim of this study was to assess if our current knowledge allow understanding the oxidation chemistry in this kind of environment. The update of kinetic data for the inorganic part of the model with more recent data was hence almost unavoidable.

> *Abstract, minor points: Clarify if RO2 includes HO2, and ensure this usage is consistent with the rest of the manuscript. "Various modelling procedures" and "two extremes" both undefined are not very helpful here - these either need to be specified, or this section re-worded more generally. Give % contributions for the various "significant" pathways mentioned.*

In the abstract, the RO2 term means (HO2 + RO2) when it refers to the measurements and the only organic peroxy radicals (RO2) when it refers to the radical budget. We agree that it can be confusing and "RO2" have been replaced by "(HO2 + RO2)" when necessary in the abstract of the revised manuscript. The section concerning the different versions of the model in the abstract has been reworded. The % contributions for the different pathways mentioned have also been added in the revised manuscript.

> *Introduction: NO3 reactions represent another HOx initiation route*

This initiation pathway has been mentioned in the second paragraph of the introduction

C7754

in the revised manuscript.

> *p.15888 L5 need to specify the rate constant for X with RO2, HO2. Include Fuchs et al. (AMT 2011) reference for the HO2 - RO2 interference.*

The rate constant used by Hofzumahaus et al. (2009) for the reactions between X and the radicals RO2 and HO2 are the same than the reaction between NO and the radicals RO2 and HO2 as it is said in the manuscript (p.15888 L4). The reference to the study made by Fuchs et al. (2011) has been added to the revised manuscript concerning RO2 interferences to the HO2 measurements.

> *p.15889 L19: The other cause for model-observation discrepancy is of course error in the measurements. This should be considered, for example with reference to the recent papers by Mao et al (ACPD 2012) and Fuchs et al. (AMT 2012) - especially given that in this work a different technique (CIMS) is used for the OH measurements.*

Some words have been added concerning the model-observation discrepancies due to errors in the measurements in the introduction of the revised manuscript.

> *p.15891 L8 please ensure consistent usage of RO2, to include or exclude HO2 throughout the paper - it would be better to refer to "HO2 + RO2" for clarity. The term "ROx" appears later in the paper - is this OH+HO2+RO2??*

C7755

In the paper, as previously said "RO2" means (HO2 + RO2) when it refers to the measurements and the only organic peroxy radicals (RO2) when it refers to the radical budget. As it can be confusing "RO2" have been replaced by "(HO2 + RO2)" when necessary in the revised manuscript. The term "ROx" appearing later in the paper refers to the sum of radicals (OH+HO2+RO2).

> p.15891 L25 Would it be useful to estimate the systematic uncertainty in the mean OH and HO2+RO2 levels also - e.g. the uncertainty that might be expected in the mean diurnal profiles shown in figs 5, 11 ?

As it is described in the text and in the Supplementary material, the systematic uncertainty is determined mostly by the calibration uncertainty: 30% (2s) for OH and 40% (2s) for HO2+RO2 measurements. The systematic uncertainty for the mean levels will be the same. Additional uncertainty for the mean values comes from the natural day to day variability which is not related to the systematic uncertainty. The standard deviation for the day to day variability is presented on the Figures 3, 5 and 11 with error bars.

> p.15892 the description of the albedo treatment is not clear, what values were used for e.g. JHONO or JHCHO ? Is the 25% uncertainty in JHONO 2 s.d. ? This seems rather high.

C7756

No measurements of J(HCHO) was made during the campaign. Furthermore, the actinic fluxes measured by the spectroradiometer is corrected with the measurements of J(NO2) from the filterradiometer owning two sensors: one looking upwards and one looking downwards. The albedo issue is thus integrated in the correction of the spectroradiometer e.g. J(HONO) measurements. The 25% uncertainty in J(HONO) is 2 sigma which we agree is rather high. This can be explain by the fact mentioned above that this measurement is corrected using J(NO2) measurements. Its uncertainty includes, thus, both uncertainty in J(NO2) measurement and uncertainty in spectroradiometer measurement.

> p.15893 Please specify if the NO2 measurement used a thermal (heated Mo catalyst) or photolytic NO2 converter.

Indeed, NO2 measurements using ozone chemiluminescence is an indirect measurement which requires a conversion of NO2 into NO. During this conversion, others nitrogen species, such as, PAN or organic nitrate are also converted into NO and act as interferences. To avoid these problems, we performed NO2 measurements with a commercial analyser (NOxTOy- MetAir) which uses luminol chemiluminescence [Hasel et al., 2005]. This technique is direct for NO2 and, thus, does no need any NO2 converter. Indeed, the luminol (3-aminophthalhydrazine) is an aqueous solution which reacts with NO2 forming an excited compounds which then emits a photon while returning to a non-excited state. These photons are counted by a photomultiplier giving direct NO2 measurement. The NOxTOy allow measuring other nitrogen species such as PAN or total odd nitrogen (NOy) thanks to various converters. However, during MEGAPOLI campaign, we only used the NO2 measurement channel. In short,

C7757

a very special care was taken to insure the quality NO_x measurement and all possible interferences were carefully quantified before the campaign.

> Equation 4 $k(\text{OH}+\text{NO}_2)$ not $k(\text{NO}+\text{NO}_2)$

"kNO+NO₂" has been replaced by the term "kOH+NO₂" in the equation 4 in the revised manuscript.

> p.15896 You say that all alkenes except methylpropene were below DL, but then that measurements of isoprene, a/b-pinene, limonene were made ??

Indeed, measurements of isoprene, a/b-pinene, limonene and methylpropene were performed. Thus, all alkenes were not under the detection limit of the instrument. The expression "alkenes" has, therefore, been replaced by "alkenes of anthropogenic origin" in the revised manuscript, to describe the alkenes species which were under the detection limit of our instrument.

> p.15898 the description of the spin-up process is a little confusing.

The description of the spin-up process has been reworded to minimize possible confusion.

C7758

> p.15899 would a dilution loss with 1-2 hours timescale be expected, in a well-mixed boundary layer ?

These corresponding time of 1 and 2 h for the loss by dilution have been selected arbitrarily. These timescales of 1 and 2 h are consistent with the timescale of the vertical transport in a well-mixed boundary layer and are thus consistent with a vertical dilution. This loss by dilution has been added to avoid any accumulation of secondary organics in the model which would reach unrealistically high concentrations if they were not eliminated from the model. A higher residence time for the dilution loss process led to similar results than simulations performed using a residence time of 2h for the dilution loss process. This indicates that the majority of secondary compounds formed in the model have a chemical lifetime lower than 2h.

> p.15095 It would be useful to refer back to the observational uncertainty for NO₂, in particular considering the type of NO₂ converter used and potential for retrieval of other NO_y as NO₂.

As previously said, NO₂ measurements were performed using a direct measurement technique: the luminol chemiluminescence. As it is a direct NO₂ measurement, no converter is needed. For our own experience, no significant interference from other NO_y is expected. The only interference reported is a small interference to ozone which is corrected in the data treatment. Furthermore, uncertainties in NO₂ measurements are given in Tab 1.

C7759

> p.15907 please include (briefly) the quantitative outcome (ie. % change in HOx) of the aerosol loss sensitivity runs.

The quantitative outcome of the aerosol loss sensitivity runs has been included to the revised manuscript.

> p.15910 Do the calculated role of alkenes relate to the observed alkene concentrations, or the runs in which 100 ppt was assumed for various species, or ?? Similarly, for the overall budget figures presented on p.15911.

The calculated role of alkenes given in the radical budget part refers to the observed alkenes concentrations only. It is the same for the overall budget presented on p. 15911.

> Graphs, several subscripts missing in captions and legends.

The graphs where captions and legends were missing have been corrected in the revised manuscript.

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Response to referee #2:

> I agree with anonymous referee #1 that the approach used to calculate steady state concentrations of OH is not usual. However, I think that Eqs. 4 and 5 are valid as long as the following assumptions are fulfilled: (1) total initiation and termination rates of ROx radicals balance each other, (2) radical losses other than OH+NO₂ and OH+NO are negligible, and (3) the gross formation rate of OH from HONO photolysis is included in the ROx initiation rate.

As the referee #2 noticed, this approach can be applied if some assumptions are fulfilled. These assumptions pointed out by the second referee have been, furthermore, included in the answer to the first referee together with the demonstration of the formula used. In fact, the comparison between the OH concentrations measured and calculated by the PSS aimed to verify if these assumptions were fulfilled in Palaiseau's environment and therefore if the PSS was appropriate to explain observed OH levels. It appears that it was not the case, mainly because the second assumption was not correct. Indeed, other radical losses such as reaction between RO₂ and NO_x are not negligible during MEGAPOLI summer campaign.

Such an approach is not so uncommon as it has been already used in recent papers (see for example in [Holland et al., 2003; Elshorbany et al., 2009]).

> P15895: Eq. 2: " $J(O1D) \times [O3] \times FOH$ " should read " $2 \times J(O1D) \times [O3] \times FOH$ " since each O1D atom react with water to form 2 OH radicals. Was the right equation used in the

C7761

calculations?

Indeed, Eq. 2 should include a factor 2. This factor was applied in the calculation of the FOH term and therefore does not appear in Eq. 2. However, to clarify we have added this factor 2 to the Eq. 2 in the revised manuscript.

> P15895: Eq. 2: " $J(\text{HCHO})[\text{HCHO}]$ " suggests that both photolytic pathways of HCHO, one leading to H+HCO and one leading to H₂+CO, were used in the PSS calculations. Only the pathway leading to the formation of H+HCO should be used since it is the only one to contribute to the formation of HO₂. What did you use in the PSS calculations? I recommend to use the notation " $J(\text{HCHO_Rad})$ " in Eq. 2.

In the calculation, we used the $J(\text{HCHO})$ which leads to the formation of H+HCO. We replace " $J(\text{HCHO})$ " by " $J(\text{HCHO_Rad})$ " in Eq. 2 in the revised manuscript.

> P15890 L3: "a box model containing the Master Chemical Mechanism (MCM) and constrained with all the species and the parameters measured during MEGAPOLI." Please indicate what types of constraints were used. How many VOCs, J-values...?

An indication of what constraints were used has been added in the revised manuscript.

C7762

> P 15891 L10: "radical quencher" should read "radical scavenger"

"radical quencher" has been replaced by "radical scavenger" in the revised manuscript.

> P15891 L23: Were the instrumental sensitivities for OH and HO₂+RO₂ measured periodically during MEGAPOLI? If so, how variable were they?

The following correction has been added to the page 3, line 19 of the Supplementary material:

Accounting for the measurement precision and the calibration uncertainty estimated from the calibration measurements performed 4 times during the MEGAPOLI campaign, the overall (2s) uncertainty of the 10 min averaged measurements of OH and RO₂ is estimated to be 35% and 45%, respectively.

> P15892 L25: The uncertainty of 20% stated for $J(\text{O1D})$ is similar to that stated on L8 for $J(\text{NO2})$. I would have expected a larger uncertainty for $J(\text{O1D})$ values compared to $J(\text{NO2})$ since the $J(\text{O1D})$ filterradiometer response factor was derived from an intercomparison to the TUV model while the $J(\text{NO2})$ filterradiometer was calibrated. Could the authors comment on this point?

C7763

The uncertainty of J(NO₂) measurements has been calculated taking into account the observed uncertainty for the calibration made using the spectroradiometer of the "Institut für Energie und Klimaforschung" at the Forschungszentrum Jülich GmbH. Moreover, another campaign took place at the same site (SIRTA site) and during the same period of year (July) two years after the MEGAPOLI campaign. During this campaign, J(NO₂) were measured using the same spectroradiometer of the "Institut für Energie und Klimaforschung" than during our instrument calibration. Differences between J(NO₂) measured on clear sky days for these two campaigns have been observed, and thus have, also, been included in the calculation of J(NO₂) measurement uncertainty for MEGAPOLI campaign. Considering that, we obtained a 20% uncertainty for J(NO₂) measurements, which is, we agree, a bit high for calibrated measurements. The uncertainty of J(O₁D) has been calculated by varying separately the different parameters used in the TUV calculation, e.g. albedo, ozone column, aerosol column in the uncertainty range of each parameters and from uncertainty in the slope of the intercomparison. This calculation leads to an uncertainty of 20% which is the same than the J(NO₂) uncertainty.

> P15896 Eq. 4: "kNO+NO₂" should read "kOH+NO₂"

The term "kNO+NO₂" has been replaced by the term "kOH+NO₂" in the revised manuscript.

> P15896 Eq. 5: "kOH+NO₂" should read "kOH+NO₂ [NO₂]"

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We agree and the term "kOH+NO₂" has been replaced by "kOH+NO₂ [NO₂]" in the revised manuscript.

> P15898 L6-7: "loss cycles" should read "termination rates"

"Loss cycles" has been replaced by "termination rates" in the revised paper.

> P15899 L10-11: How did you choose dilution losses of 1 and 2 hours for the unmeasured oxidation products?

As said in the answer to the first referee, these corresponding time of 1 and 2h for the loss by dilution have been selected arbitrarily. They are, however, consistent with the timescale of the vertical transport in a well-mixed boundary layer and are thus consistent with a vertical dilution. Moreover, the loss by dilution has been added to avoid any accumulation of secondary organics in the model which would reach unrealistically high concentrations if they were not eliminated from the model. Furthermore, sensitivity tests have been performed applying a higher corresponding time for the loss by dilution terms leading to similar results than with a corresponding time of 2h.

> P15900 L9-10: "For the multifunctional species, the highest deposition velocity by function was adopted". What is "the deposition velocity by function"? Please clarify.

C7765

This means that if a species own several functions, the deposition velocity applied to this species is the one of the functions which has the highest deposition velocity. For example, if a species contained a function aldehyde and a function PAN, the deposition velocity applied to this species is the one of the function aldehyde, e.g. 0.33cm.s⁻¹ because the deposition velocity of the PAN function is 0.2cm.s⁻¹ and thus lower than the one of the aldehyde function. Clarification has, also, been given in the revised manuscript concerning this point.

> P15902 L23-25: *"The PSS approach appears to be sufficient to explain OH concentrations in polluted environments, as it has been already shown in the highly polluted urban area of Santiago, Chile (Elshorbany et al., 2009)." It should be clearly stated that Elshorbany et al. did not compare calculated OH concentrations to field measurements since OH was not measured in Santiago. These authors compared the PSS calculations to the outputs of a box model.*

Indeed, as OH was not monitored during the Santiago campaign, Elshorbany et al. (2009) were not able to compare calculated OH concentrations to field measurements; we believe in addition that this is one of the originality of the present work. Nevertheless, since the two calculations (PSS and boxmodel) leads to the same OH concentrations during daytime, it can be conclude that in the work of Elshorbany et al. (2009) the sources and sinks included in the PSS approach were sufficient to explain the radical chemistry in the polluted environments of Santiago.

For clarity, it is now indicated in the revised manuscript that Elshorbany et al. (2009)

C7766

did not compared calculated OH concentrations to measurements as suggested.

> P15903 L16-17: *"The model is in pretty good agreement with the observations for several days of the campaign (07/09; 07/11; 07/13; 07/15; 07/19; 07/20; 07/21), the difference being within the measurements uncertainties" and "On some other days, the model largely overestimates OH measurements:" Please state quantitatively how the measured and modeled concentrations agree.*

A more quantitative statement describing the agreement between measured and modelled concentrations has been added to the revised manuscript.

> P15904 L3-5: *"Thus, the model including a detailed description of radical sources and sinks enables to represent the processes involved in OH budget under intermediate and low NO_x levels better than the PSS calculations." It would be interesting to briefly discuss the main sinks that were not included in the PSS calculations and their contributions to the total loss rate of radicals.*

This point is discussed elsewhere in the article, e.g. in the section dealing with the radical budget: p15911 l23-26 : "The importance of termination reactions between RO₂ and NO or NO₂, not taken into account in PSS calculations, can explain the poor ability of PSS calculations to reproduce OH concentrations while better results are observed for model calculations, where these reactions are included".

C7767

> P 15904 L9-11: "both versions of the model overestimate measured RO₂ concentrations on 7/20 and 7/24 and underestimate the measurements on 7/16." And "The NO_x levels were quite low on 7/20 and 7/24 and quite high on 7/26." Please be quantitative.

Quantitative information are now given in the revised manuscript concerning the model and measurement disagreement and the NO_x levels on those three days.

> P15905 L16: "These simulations lead to a rise of radical concentrations in the model, with a larger impact of alkene ozonolysis on radical concentrations (OH, HO₂ and RO₂) during the night than during daytime, as expected." Please indicate why it is expected.

The addition of alkene concentrations in the model constraints leads to a rise in radical concentrations. The impact of these sensitivity tests is expected to be higher at night when other sources than alkenes ozonolysis, mainly photolytic, have a lower influence on radical budget.

> P15906 L6 and Line 9: Was the HCHO concentration changed by +-25 or +- 10%

The HCHO concentrations were changed by +25%. The sentence: "when HCHO

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concentrations are decreased or raised by 10 %" (p 15906 L8-9) is, thus, wrong and have been replaced by "when HCHO concentrations are decreased or raised by 25" in the revised manuscript.

> P15908 L12-13: "These reactions act as propagation reactions, leading mainly to RO₂ formation but also directly to HO₂ formation at a non negligible fraction." Please be quantitative

Quantitative information has been given in the revised manuscript concerning the fraction of OH+VOC reactions which leads to HO₂ formation compared to the fraction of these reactions leading to RO₂ formation.

> P15909 L11-27 and P15910 L18-21: The radical budget of HO₂ and RO₂ radicals are discussed in detail. However, there is no information about HO₂+RO₂ concentrations at night in Figs.10 and 11. It would be interesting for the reader to display the night-time modeled concentrations of RO₂+HO₂ as it was done for OH in Figs. 5 and 8.

The nighttime RO₂+HO₂ modelled concentrations are quite high (a second spike appears at night) and have not been plotted in the Figs 10 and 11 because of the non-compatibility of the vertical scale (daytime concentrations would then be very difficult to read). Furthermore, the comparisons between simulated and measured concentrations of RO₂+HO₂ concern only daily concentrations since no measurements were

C7769

performed at night. An analysis of modelled night-time radical concentrations would, furthermore, make the article longer which is not desirable.

> P15914 Lines 27-29: *"The total initiation and termination rates were in balance and similar to other ones found during previous studies in suburban or remote areas but far lower than other ones found in previous urban field campaigns."* Please be quantitative

Quantitative information has been added in the revised manuscript concerning this conclusion.

> P15927 Table 3: *Please indicate the time period used to perform these sensitivity tests*

Sensitivity tests have been performed over the full campaign. This information has been added in the caption of Tab.3 in the revised manuscript.

> P15932 Fig.5: *Wrong caption*

This error did not appear in the document which was initially submitted to ACP (obviously this caption come from another article). Thank you for having noticed this

C7770

mistake, it has not been corrected in the revised manuscript but we hope that it will not happen again.

> P15937 Fig. 10 and P15938 Fig. 11: *The labels of the vertical axes indicate ROx radicals. Did you really plot OH+HO2+RO2? Or did you plot RO2+HO2?*

The labels of vertical axes are wrong; the data plotted are (RO2+HO2). The modifications of the vertical axes and of the legends have been made in the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 15883, 2012.

C7771