

Interactive comment on “Assessment of the reduction methods used to develop chemical schemes: building of a new chemical scheme for VOC oxidation suited to three-dimensional multiscale HO_x-NO_x-VOC chemistry simulations” by S. Szopa et al.

S. Szopa et al.

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Reply to Anonymous referee 1

We thank referee 1 for the helpful comments.

a) abstract, I(ine)3: What is meant by " different scales"

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"at different scales" means suited to questions relevant to global modelling (characterised by low to middle NO_x concentrations) as well as questions relevant to regional modelling (characterised by high levels of chemical precursors and, hence, high NO_x chemical regime).

In the revised version (I.3 p 756) "at different scales" is replaced by "for various NO_x levels from remote tropospheric conditions to highly polluted areas".

b) The abstract should already make reference to the preceding article by Aumont et al., where the method is presented, by which the detailed mechanism (reference mechanism) is generated.

Yes. In the revised version (I.5 p 756) "(i) the development of a tool for writing the fully explicit schemes for VOC oxidation" is replaced by "(i) the development of a tool for writing the fully explicit schemes for VOC oxidation (see companion paper Aumont et al. 2005)".

c) p 758, l 5; "...at different scales" To be useful in CTMs the reaction mechanism must be applicable to ALL chemical regimes encountered in the model domain (in space and time).

Yes. In the revised version (I6 p 758) "The objective of this work was to develop and assess a reduced chemical scheme suited to the study of gaseous photo-oxidant pollution at different scales, i.e. to different chemical regimes." is replaced by "The objective of this work was to develop and assess a reduced chemical scheme suited to the study of gaseous photo-oxidant pollution at different scales, meaning applicable to all chemical regimes encountered in the model domains for global climate chemistry modelling as well as regional air quality modelling."

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d) p 758, l 7: "No attempt has been made in this study to keep in the reduced scheme the chemical information that may be required to deal with other aspect related to organic oxidation in the atmosphere (e.g. secondary organic aerosol formation or cloud chemistry)." This is a very severe limitation, which is often simply forgotten by the users of the reduced model. Since the latter contains reaction of aldehydes, ketones peroxides, etc, model results for these compounds are interpreted as meaningful output of the model simulation. It would be helpful in this matter, to clarify with help of the simulations for the scenarios of the paper to what extend mixing ratios of those compounds are quantitatively modelled. Without such a statement the reduced scheme has a very limited range of application.

"No attempt..." means that we lumped secondary products keeping qualitatively the quantity of each secondary function but not the explicit structures of each one. Hence, aldehydes, ketones and peroxides can be interpreted as meaningful outputs (e.g. HOx production is due to VOC photolysis) but saturated vapour pressure or Henry constants can not be EXPLICITLY determined for explicit modelling of secondary aerosols formation.

Consequently, in the revised manuscript (l7 p 758) "No attempt has been made in this study to keep in the reduced scheme the chemical information that may be required to deal with other aspect related to organic oxidation in the atmosphere (e.g. secondary organic aerosol formation or cloud chemistry)." is replaced by "Attention was paid to representing the chemistry of secondary organics to the extent that it influences the HOx, NOx, and Ox cycles. However, other aspects of organic photooxidation, such as the specific identity of compounds that could contribute to secondary organic aerosols formation or cloud chemistry, are not included here. "

Furthermore, was added in the revised version l.18 p.776:

"Regarding the organic functions (aldehydes, ketones, PAN, nitrates, alcohols, car-

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boxylic acids), a fairly good agreement is found between explicit and reduced chemical schemes with a difference of less than 10% for highly polluted scenarios. For moderately polluted scenarios, organic functionalities are reproduced with a bias lesser than 10% except nitrates in summer (up to 15% deviation), alcohols in winter (up to 50% deviation), ketones in winter (up to 25% deviation) and carboxylic acids in winter (up to 20% deviation). Note that the fairly good results in simulating PAN and nitrates are of particular interest here since these species are key reservoir compounds transporting NO_x from polluted to remote areas.

For the scenarios representing the free relaxation of air masses, the differences between the explicit and the reduced scheme never exceed 55% (being systematically lesser than 30% for winter and free tropospheric conditions) for the organic functions."

e) p 759, l 22: "Modifications.." Please, be more specific. How does the program decide what a "closest structure" is.

In the current version of the generator, the lumping of primary species must be done manually by the modeller. Regarding the species having ten or more carbon atoms, the emission inventory of Derwent and Jenkin (1991) contain either n-alkanes or methyl-nonanes. The emissions of n-alkanes are reported on n-nonane while emissions of methyl-nonanes are reported on methyl-octanes.

In the revised manuscript, "closest structure" is replaced by "closest structure (i.e. n-nonane for n-alkanes having ten or more carbon atoms and methyl-octanes for methyl-nonanes)."

f) p 759, l 25: "mass conservation"? Does this imply "C-conservation"

Yes. In the revised version, p759 l.25, "mass conservation" is replaced by "carbon conservation"

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g) p 760,l 14: "Correlation" Here one needs a statement about agreement or discrepancy in absolute terms (for example slope, correlation, and offset) The description of the pre-reduction is rather brief and needs to be extended in order to be understandable.

The slope is 1.0 and the offset 0.0. The text was change consequently:

p760, l8 "Only isomers containing the same number of carbon atoms and bearing the same functional groups were grouped together. Attention was paid on the possible resonance between the functional groups, which implies different chemistry. The best compromise between bias and reduction efficiency was found when the species of third or higher generation of stable products were replaced." will be replaced by "Every secondary species produced after three generation of stable products (VOCprim → VOCsec → VOC**third**) is compared with already treated species. Replacement of a product by another is done if (i) it bears the same number of carbon atoms (ii) it contains the same functional groups and (iii) the respective position of functional groups in the species does not induce a particular reactivity for the molecule or its products. For example, a C-C=C-CO- structure cannot be replaced by a C=C-C-CO- structure, these two isomers having distinct behaviour (electron delocalisation).

p760, l14 "Correlation coefficients were found to be greater than 0.9999 for O3, NOx, H2O2, OH and HO2 when using this pre-reduction for these two species." is replaced by "Correlation coefficients were found to be greater than 0.9999 (slope=1.0 and offset being 0.0) for O3, NOx, H2O2, OH and HO2 when using this pre-reduction for these two species.

h) p 761,l 26: *In the presence of long-lived compounds like methane, CO and small alkanes the system cannot reach a stationary state within several days.*

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Consequently, in the revised version, "Simulations were run over five days, corresponding to the time required to reach a steady state over a full diurnal cycle." is replaced by "Simulations were run over five days, corresponding to the time required to reach two quasi identical successive diurnal cycles for the key species (e.g. O₃, NO_x, H₂O₂, OH, HO₂)."

i) p 762, section 4: Comparison of simulations with the full and the reduced scheme are necessary to assess the validity of the reduction. Comparison with field data are questionable, because disagreement can always be attributed to the use of an inadequate meteorological model. It is not clear to me what one can learn about the reduction of reaction mechanisms from such a comparison.

As specified in the paper, the objective of these tests was to test the chemistry in realistic and various environmental conditions rather than representing any particular location or time period. Such comparisons with measured data have thus to be viewed as a verification of the realism of the scenario as being typical of urban or regional conditions but in no case as a "validation". In the revised version, p762 l16, "to test the basic realism of the model" is replaced by "to test the basic realism of the scenario".

j) p 764, l 10-20: Does the grouping into classes conserve carbon? If not, how large is the violation?

As described in Madronich and Calvert (1990) and Laval-Szopa (2003), the counter method inherently conserves all atoms (C,H, etc.). The peroxy radicals are not lumped in this reduction step, and each peroxy radical is still individually considered. The self and cross reactions are not explicitly written and each peroxy radical reacts with "fictive" species (i.e. the counter species). Counter concentrations are computed at each time step by summing the concentrations of the various peroxy radicals. Three counter species (i.e. of distinct class of RO₂) are considered, instead of 9 in the

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explicit scheme and thus decrease the number of reactions. Consequently, the carbon conservation is not at all affected by this reduction.

k) p 765, l 12: What is the inorganic imbalance?

In order to clarify, in the revised manuscript "the inorganic balances are redundant for various species in spite of their structural differences, except the organic nitrate yields" is replaced by "the inorganic budgets (NO to NO₂ conversion, HO₂ radical regeneration, NO consumption during formation of nitrate, HO₂ consumption, etc.) are redundant for various species in spite of their structural differences, except the organic nitrate yields".

l) p 766, l 5-p 767, l 14: I have difficulties to understand what has be done.

The operator approach is not an original work. A complete description of the method can be found in Carter (1990, 2000), Bey (2001). The description done in this paper aims at giving to the reader already accustomed to this method the tracks to understand what is significantly new in our approach (completely described in Laval-Szopa (2003)).

m) p 771, section 6: Before comparing simulations with the full and the reduced scheme, one would like to learn more about the impact of the inorganic chemistry including the reactions of CO, methane, and HCHO. These compounds are not directly influenced by the reduction. What is their influence on the OH-reactivity, the burden of RO_x, the formation of ozone In other words, how large is the remaining contribution of the other organic chemistry that underwent reduction? This information for all scenarios would set the frame with respect to which the deviations between full and reduced scheme should be assessed. For example, I presume that for the clean air cases (relaxation scenarios) the contributions of the latter are only minor and negligible

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differences between the full and reduced scheme are to be expected independent of the reduction method.

Yes, some key results regarding the role of C1 chemistry are added to the paper:

p771, end of line 10: "As stated above, the inorganic and organic C1 chemistry is not affected by the reduction. Its role in the OH-reactivity and in the burden of ROx was therefore systematically quantified to help in the interpretation of the results."

p773, line 20: "Furthermore, secondary VOC chemistry is a major contributor to the total OH reactivity in these scenarios (respectively 30% and 60% for summer and winter cases). These tests thus remain highly sensitive to the reduction of secondary species. We point out that in these scenarios, C1 chemistry also plays a major role in OH reactivity, i.e. growing from 30% to 60% during the 5-days summer simulation but remaining below 20% in the winter scenario."

p774, line 16: "The role played by one-carbon species in this scenario does not exceed 25% after 5 days. The impact of the reductions can thus be examined without being masked by the C1 chemistry."

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 755, 2005.

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