

Interactive
Comment

***Interactive comment on “Mass tracking for
chemical analysis: the causes of ozone formation
in southern Ontario during BAQS-Met 2007” by
P. A. Makar et al.***

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We thank Dr. Stockwell for his kind words on our original manuscript. Reading the manuscript afresh, we agree with the criticism regarding the situational detail – the manuscript tended to focus at length on individual case studies (the “situational detail” Dr. Stockwell noted) rather than the underlying principles. The message, on the manner in which ozone formation occurs in the unique region that we were studying, was getting lost in excessive detail.

We’ve therefore condensed the original manuscript considerably, with 7 fewer pages of text, and 11 less figures. A revised version of the manuscript, along with a version

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showing the modifications are attached as a supplemental zip file for the reviewer and the editor's consideration.

We've also changed the focus somewhat, away from the model evaluation and more towards the analysis of ozone formation in the study region. We are not, in this particular paper, trying to improve the regional model. Rather, we are using it as an analysis tool, to attempt to understand the formation of ozone in a region with multiple lake breeze fronts and the resulting very complex meteorology. With this goal in mind, we have described how the lakes act as photochemical ovens, with each lake having a different circulation pattern and depth of the ozone forming region. We find that the lake breeze circulation concentrates precursors and ozone itself in convergence lines, and these lines are capable of transporting the ozone very long distances. The comparisons to observations (both the formal statistical evaluation and the time series comparisons to observations) suggest that the model can predict ozone concentrations with sufficient skill that the model-predicted causes for ozone formation in this region are likely to be correct.

A very important part of this work has been to show that the complexity of the system is not solely the result of atmospheric chemistry, rather, the local circulation has a controlling influence on the chemistry that can take place.

With regards to Dr. Stockwell's concerns on the broader issue of the desire for new principles that can improve air-quality models, some thoughts: (1) While we agree with Dr. Stockwell that one of the key aspects of modelling research is to ->improve<- the models, we also feel that an important part of modelling research is to ->apply<- the models, in order to synthesize and integrate observations. That second role is the focus of the work under consideration here. That is, we feel that the models have progressed sufficiently far that they may now provide real insight into predicting the causes of ozone formation in a very complex environment – and that sort of analysis is a necessary and useful part of modelling research. (2) The application of a model to a new and complex domain may have the additional benefit of leading to model improvements.

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While we here make use of the model as a tool for analysis, the same project has also led to an extensive study on methodologies for applying climatological ozone boundary conditions, recently accepted as a separate paper in ACP. Even when we “just” analyse and integrate observations, we often end up with model improvements as well.

With regards to the role of the HOx radical and the paper by Chen et al (2010): we’re grateful for that reference, and we’ve included both it and Kuhn et al 1999 into an additional paragraph in the revised conclusions, as a caveat on our conclusions. Both of these references suggest that ozone is one of the chemical species that are less sensitive to the details of the reaction mechanism, particularly as the precursor concentrations become high (as they are in the polluted region we are studying). However, both papers also note that the ability to capture the HOx / H₂O₂ cycle is one of the key differences between different chemical mechanisms. The Chen et al (2010) reference is quite important, in that it also implies a systematic failing of the existing reaction mechanisms to correctly predict HOx levels. They also note that their results may indicate measurement error, rather than a problem with the model chemistry. We therefore feel that the issue is not crucial to conclusions of our analysis, but one that’s worth bringing to the attention of the wider community, in accord with Dr. Stockwell.

We can think of studies which could address the HOx deficit issue, beyond the scope of the current work, which we mention here as a suggestion to the community. One such study would make use of the new HOx measurement instrumentation in a repetition of some of the classic smog chamber experiments (single VOC and mixture of VOCs), to determine whether the ambient observations of an HOx deficit in simulations are also present in the laboratory. This strikes us as being a necessary first step in understanding the causes of the deficit, and determining the extent to which it may be remedied by changes in the gas-phase mechanisms. The oxidation rate of those species which are oxidized only by OH could be used as a check on the directly measured HOx concentrations, to reduce the possibility of HOx measurement error in the form of a positive bias. If, on the other hand, the chamber results of such studies

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are in accord with the HO_x produced by the mechanisms (i.e. the chamber shows no deficit), then either a chamber dependant process is missing from the ambient atmosphere (e.g. HO_x loss on the chamber walls) or an additional process, absent in the chambers, is present in the real atmosphere.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/10/C7384/2010/acpd-10-C7384-2010-supplement.zip>

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 14241, 2010.

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