Atmos. Chem. Phys. Discuss., 7, S2487–S2490, 2007
www.atmos-chem-phys-discuss.net/7/S2487/2007/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on “Observations of OH and HO_2 radicals in coastal Antarctica” *by* W. J. Bloss et al.

W. Sturges (Editor)

w.sturges@uea.ac.uk

Received and published: 19 June 2007

The following review is submitted on behalf of Nominated Referee Dr Ian C. Faloona, Department of Land, Air & Water Resources, University of California, Davis, USA

This paper presents a very interesting data set that should be published for the sake of ongoing OH/HO2 instrument & modeling efforts. Nevertheless, there is very little added value in the data analysis due to the lack of concrete constraints on the photochemical environment, which is not unusual in this field, but it makes one wonder why exactly there is an entirely separate modeling paper in preparation (ref. Bloss et al., 2007). Why include a cursory modeling effort here if there is a more thorough one to follow?

The main shortcoming I found in the modeling analysis is that it attempts to model the

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

OH levels alone, and then makes general conclusions about the entire HOx budget. I would recommend attempting to explain the HO2:OH ratio with a simple steady-state model, instead of the absolute OH concentrations. This ratio should be relatively independent of the overall HOx production rate and much less dependent on the overall OH loss rate (posited here to be a reaction with the perennial unmeasured hydrocarbon.) From the HO2:OH ratio, inferences about the relative importance of HOX should be more straightforward (e.g. because HONO is merely a HOx reservoir it should not perturb the ratio, unless there is an enormous source uncoupled from the gas phase chemistry.) At least you might consider trying to model the steady-state HOx levels as well as the OH.

Further, more specific, comments on the manuscript are listed below in the order in which they are encountered in the text: p.2908, l.7: I disagree with the statement that the HOx production is strongly related to the HOx levels "as a consequence of the short OH and HO2 lifetime." The same steady state assumption is applicable to many species with a broad range of chemical lifetimes.

p.2910, l.4: In mentioning the mean H2O2 reported by Walker et al. it might be helpful to include some measure of its variability to give an idea of how much that source might fluctuate (again, it should not influence the HO2:OH ratio.)

p.2911, l.4-6: These approximations would carry more weight if they were somewhat justified. Is that a reasonable aerosol surface area concentration seen by other Antarctic scientists? Is there a dominant mode that has been reported in the literature? Does making the "free molecular approximation" assume something about the dominant size of the aerosols (e.g. that it is much less than 1 micron in diameter)? Using your approximations, what was the average rate of the aerosol loss of HOI relative to photolysis (R13); that is, how significant is this highly uncertain aerosol loss estimate in your estimate of HOI's contribution to overall OH?

p.2912, l.24: It would help the reader to know what the time interval of the IO measure-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

ment was, how much the observations overlapped with the OH measurements, and what the r2 value is for the relationship reported in (5).

p.2913, l.1: The acetaldehyde value you assume in this model scenario (167 ppt) seems high given that the corresponding HCHO levels you report at Halley are only 130 ppt. It is not usual that the lightest, most common aldehyde should be present in inferior quantities. p.2913, l.16: There is no mention of the observed ABL heights at Halley during this experiment, so it is not really a supporting argument to simply refer to a "low mixed layer height" at the South Pole. The ABL heights were estimated to vary between 100 and 800 m during ISCAT2000, and it is not apparent why you suspect that those at Halley are drastically deeper.

p.2914, l.19: You mention that the NOx lifetime is principally controlled by heterogeneous hydrolysis of halogen nitrates, but earlier you mention that there is no data on aerosol surface area. How is it known, then, that the NOx is so strongly influenced by surfaces?

p.2915, l.23-25: From scrutinizing Fig. 7 it appears that the scenario 1 model-observed match that you label "reasonably well" is about a factor of 2. It seems the use of this term is arguable, especially considering that this is when the model is constrained by the observed HO2. Reporting a mean model:observation ratio might alleviate any ambiguity. p.2918, l.22: Insert "coastal" when referring to Antarctic boundary layer.

p.2919, l.19: It seems that discussing HONO measurements, which have not been through peer revision, so extensively distracts from the clarity of the paper. As it reads here, it seems unlikely that the HONO data is reliable.

p.2926, Table 1: Including the rough statistics of IO and BrO here would be helpful.

p.2928, Table 3: There are too many significant figures of this table. The last digit corresponds to 100s of molecules of OH per cubic centimeter!

p.2934, Fig. 6: I could not figure out what the p(OH) trace corresponds to in this plot, although I suspect it is the production from ozone photolysis.

Scientific Significance: Good Scientific Quality: Fair Presentation Quality: Good

---

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 2893, 2007.