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Atmospheric
Chemistry
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Discussions

Interactive comment on “The chemistry of OH and HO_2 radicals in the boundary layer over the tropical Atlantic Ocean” *by* L. K. Whalley et al.

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Many thanks to the reviewer for helpful comments to improve the paper. The specific comments of the reviewer are addressed below:

Referee comment: On page 15963, line 28 the authors note that the measurement site "CVAO is thought to be representative of the open ocean tropical MBL". The authors should provide convincing arguments for that statement and discuss more thoroughly this assumption as it is crucially important for the general conclusions of the paper.

Author reply: To support this statement, the manuscript now refers to the Read et al (2008) paper and Lee et al (this issue) where a fully discussion on the measurement site and how it is representative of the open ocean can be found. Ship and Aircraft mea-

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surements have demonstrated that the measurements at the CVAO are representative of the surrounding area. These measurements are discussed in detail by both Read et al and Lee et al and are also now referred to in the manuscript: 'CVAO is thought to be representative of the open ocean tropical MBL; ship and aircraft measurements confirm that the measurements at the site are representative of the surrounding area (Read et al., 2008; Lee et al., 2009a) and hence these observations suggest a potentially global presence of halogen oxides.'

Referee comment: In this context, I wonder where acetaldehyde is coming from, making it the second most important sink of OH? If it is produced from alkenes, where do these VOCs come from and would this source be representative for global oceans?

Author reply: Lewis et al ACP (2005) have demonstrated that up to 200 pptv acetaldehyde may be formed as a secondary product from the oxidation of VOCs (propene, n-butane, iso-pentane). In the Lewis study the concentration of these VOCs were much higher than is typically observed at the CVAO, so secondary formation of acetaldehyde is unlikely to contribute significantly to the observed acetaldehyde concentrations. We now suggest in the paper that the oceans are acting as a net source of acetaldehyde: 'The source of acetaldehyde at remote marine locations, such as Cape Verde, has not been determined conclusively and remains subject to debate. Acetaldehyde is formed by the oxidation of primary hydrocarbons, it may derive from direct terrestrial emissions or from the photochemical degradation of organic matter in the oceans (Singh et al., 2001 and references therein). Singh et al., (2003) have inferred from aircraft measurements of acetaldehyde that the surface waters of the Pacific are greatly supersaturated with acetaldehyde and may act as a large oceanic source. Read et al., (in preparation) suggest that an oceanic flux of acetaldehyde is a likely source of the observed acetaldehyde concentrations in the Cape Verde region also.'

Referee comment: The PAN concentration of 100 ppt also appears to be quite high indicating the influence of aged anthropogenic emissions. In their discussion the authors should also pay attention to PAN measurements on the open Atlantic by Muller and Rudolph (J. Atmos. Chem. 15, 361, 1992) who report values significantly below 10ppt along 30W at latitudes between 35N and 30S.

Author reply: The Muller and Rudolph study is now included in the nighttime results section (3.2). We agree that a [PAN] of 100 pptv is high for this region. The nighttime [HO2] data was taken when the site was influenced by air originating over North America, however, and there is evidence, for example from the CO data, that this airmass contained aged anthropogenic emissions. This airmass type is somewhat atypical of the usual airmass that is intercepted at the site but to replicate the nighttime [HO2] during this time we have found that increasing the [PAN] helps. We agree though that it is unlikely that [PAN] would be this high in other airmass types.

Referee comment: Another important question is the source of reactive halogen compounds at CVAO. If it is related to algae, it may be enhanced at CVAO due to upwelling ocean water near the African continent.

Author reply: We agree with the referee's comments that it is important to determine the source of the halogen compounds at the observatory – the exact source of the halogen oxides is still uncertain, however, but the most recent literature does not suggest that the upwelling region is causing an enhancement of halogen containing compounds at the site. Carpenter et al (this issue) have found that although upwelling regions are regional hop-spots of bromocarbons, globally they supply at most a few percent of the total emissions. Furthermore, modelling studies, e.g. Vogt et al., 1999, that incorporate acid catalysed activation of bromine from seasalt, predict [BrO] similar to those observed at the CVAO – indicating that the [BrO] present at the site is likely representative of the open ocean [BrO] in general. The source of IO at the site is more uncertain, given the relatively short atmospheric lifetime of the IO precursors and proximity of the site relative to the upwelling region, however, it is unlikely that emissions from the upwelling can account for the [IO] observed at the site. Recent work by Reeser et al (J. Phys. Chem. A, 2009) have demonstrated a novel route for gas-phase halogenated species from irradiation of chlorophyll in the sea surface

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microlayer to form a chl+ cations that are able to oxidise halide anions to form halogen atoms and so the presence of photoactive organic compounds in sea water may act as an important source of IO.

Referee comment: I agree with the other referee that the paper would benefit from some reorganization of the manuscript. Author reply: The manuscript has been reorganised in accord with the referee's suggestions.

Referee comment: In addition it would be helpful for the reader if some of the figures were newly drawn (see minor comments). Author reply: The figures have been redrawn as suggested.

Referee comment: Minor comments All figures and text: specify the time used in the paper (local time?) and the relevant time zone. Tic mark spacings should be changed to give integral rather than fractional hours. Fig. 1: the figure has a poor graphical quality; lines are too thin and the chemical labels are difficult to read. Fig.1: what is the meaning of the red arrow going from OH to XO and what does the red label (+X) mean ? Fig. 3: color code of CO is not correct. Figs. 4 - 7: the overall size of the figures and the font size should be increased for better readability. Fig. 5: the color code 'white' has twofold meanings in some of the pie charts; use unambiguous color assignments! Fig. 6: typing error: dirunal. Fig. 8: more intense colors and a legend would greatly help to read the figure! page 15965, line 8: change "Torr" to SI units. page 15977, line 3: typing error: photoylsis.

Author reply: All minor comments raised by the referee have been addressed. In response to the comments regarding figure 1 specifically, the purpose of figure 1 was to show pictorially the sources and sinks of O3, OH and HO2, (the red 'X' was attempting to demonstrate that 'X' is only formed via the photolysis of HOX (this reaction pathway was highlighted in red also) as opposed to other OH formation routes. Owing to comments by referee 1 and 2, however, we have decided to redraw figure 1 and focus just on OH and HO2 and their relevant formation and loss pathways for simplicity.

The ozone destruction reactions (including surface deposition) are now listed in the introduction section of the manuscript instead.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 15959, 2009.

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