Atmos. Chem. Phys. Discuss., 6, S5866–S5869, 2007
www.atmos-chem-phys-discuss.net/6/S5866/2007/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Air-sea fluxes of methanol, acetone, acetaldehyde, isoprene and DMS from a Norwegianfjord following a phytoplankton bloom in a mesocosm experiment" *by* V. Sinha et al.

V. Sinha et al.

Received and published: 2 January 2007

Reply to reviewer 2 We thank reviewer 2 for her/his positive comments and for recommending that the work be published in ACP. We also thank both reviewers for their constructive comments that have helped to improve the paper further. Reviewer 2 has raised some interesting points which we believe we have addressed comprehensively in this response.

Paragraph 2 Although the reviewer agrees with the methodology employed for calculating the VOC fluxes in this study, the reviewer raises valid concerns with regard to the conditions in the mesocosm being different from conditions in the open oceans

and that the mesocosm-derived fluxes should regarded as a lower limit for DMS and upper limit for methanol. The latter is now duly stated in the revised manuscript. As mentioned in the manuscript, the mesocosm is an artificial set up with low and almost constant wind speed, possible wall losses and subdued wave activity, conditions that may represent significant deviation from 'natural' oceanic conditions. Wall losses in the mesocosm cannot be ruled out although our experience of methanol and acetone measurement through similar materials has not indicated significant losses. Indeed, if wall losses were the dominant factor, one would have seen uptake all the time, i.e. ambient air would be stripped of the compound in the mesocosm by the walls and not the sea. The two most polar compounds we examine are methanol and acetone. While we do observe uptake with methanol, acetone clearly shows emission as well. Moreover, the wall loss cannot account for the flux changes relating to biology or light. Stratification and mixing of the water column in the mesocosms is designed to simulate open ocean conditions. Stratification prevents re- introduction of sedimented material into the surface sea layer and mixing ensures efficient transport between the bulk and surface waters. However, we agree with the reviewer that in the mesocosm system, physical parameters are not favourable for sea-air gas exchange. Consequently, they are not the dominant factors controlling the VOC fluxes in the mesocosm, rather ocean biology and PAR are the primary driving forces of the sea-air fluxes in the mesocosms. Thus, the flux derived from the mesocosms gives an idea of how important ocean biology and PAR can be for the marine emissions and / or uptake of different VOCs. All the oceanic VOC budget estimates, except perhaps DMS, are based on the few measurements conducted in the "open" oceans in "selected" oceanic regions which have been extrapolated to the global oceans (see references in Table 5 of revised version), although conditions vary widely and vastly from one part of the global ocean to another. Given this current uncertainty in VOC fluxes from / to the ocean (as highlighted in Table 5) we argue that our measured fluxes can be used to "tentatively extrapolate" for an "indication of the possible global flux". Keeping in mind the advice of both the reviewers, the associated uncertainties of this approach will be more strongly stressed

ACPD

6, S5866–S5869, 2007

upon in the revised version. We argue these values should be retained in the paper as they translate the fluxes into values relating to the potential effect on the global budget which is more familiar to most readers.

Paragraph 3 We find the reviewer's suggestion to correlate the day and night time fluxes of the trace gas species quite useful. Doing so, has revealed a very good correlation between day time fluxes of acetone and acetaldehyde and acetone and isoprene (r = 0.96 and 0.85 respectively). A new table with all the day time and night time correlation coefficients has been incorporated in the revised version along with a discussion of the possible implications. Inter-correlation of the different trace gas species between the two biological phases does not yield new insights and so we have not included this part in the new table.

Paragraph 4 We thank the reviewer for drawing our attention to Nguyen et al.1988.This work is relevant to the DMS measurements reported in our work and has been considered for interpretation in the revised version.

Paragraph 5 We have acted on the reviewer's suggestion to correlate the flux of each VOC with each of the measured biological parameters by doing a linear regression analysis of the daily averaged VOC flux against the measured biological parameters in both the mesocosms. For acetone, the daily emission flux and daily uptake flux have been treated individually. However, we would like to point out that since some of the measured biological parameters are individual species such as Emilania huxleyi and Synechococuss sp.and the others like nano plankton (size class), pico plankton (size class) and heterotrophic bacteria are bulk parameters that comprise of more than one species, appropriate care should be taken while interpreting the significance of the correlations. Moreover, the chlorophyll content and hence photosynthetic activity depends to considerable degree on the cell size of the autotrophic species, so one cell of Emiliania huxleyi will be more potent in producing isoprene (a byproduct of photosynthesis) that one cell of the other smaller autotrophic species. It should also be borne in mind that at different stages in their life cycle, biological organisms can exhibit different re-

ACPD

6, S5866–S5869, 2007

sponses and community dynamics can cause coincidental correlations. Nevertheless, appreciating the reviewer's comment that such data may stimulate future studies that seek to identify specific species involved in the emission / uptake of OVOCs , isoprene and dimethyl sulphide, an additional plot with all the regression lines and associated 'r' values has been included in the revised manuscript as Figure 7.

Paragraph 6 The sentence has been rephrased to be more specific in the revised version.

Paragraph 7 It is not possible to quantify contributions due to possibly different compounds in an unknown air sample using a PTR-MS. We base our premise of isoprene being the major contributor to mass 69 and acetaldehyde being the major contributor to mass 45 in the PTR-MS on previous open ocean studies and GC-PTRMS comparative studies.

Paragraph 8 The ambient marine air was sampled outside the mesocosm enclosures and so our ambient air measurements represent direct atmospheric measurements. Thus, comparisons with previous ambient air studies in the marine environment are certainly valid.

Paragraph 9 The point that the reviewer makes about the fluxes of isoprene and DMS being twice that of the fluxes of the OVOCs is an interesting one. We have rephrased the text (page 13, second paragraph) to include this point, that is, when fluxes rather than mixing ratios are considered, isoprene and DMS are two times higher.

Paragraph 10 The conclusion has been rewritten to include a summary of some of the major findings in the work along with suggestions for future research in this relatively unexplored field.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 9907, 2006.