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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.

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We thank reviewer 1 for her/his critical review of our work and for deeming it to be of substantial interest to many researchers.

The comments of reviewer 1 are addressed in detail below, however, at the outset it is useful to re-iterate the key aspects of the mesocosm design since the central concern expressed by reviewer 1, is the applicability of the mesocosm in examining VOC fluxes at the air-sea interface.

From the point of view of trace gas exchange, the mesocosm is a transparent tent, set over an area of ocean surface (circa 3 m^2) and extending from 1.5 m over the surface to 9.5 m below. The tent contains a pocket of gas which is ventilated with ambient air at a constant flow (residence time of the air is 191 minutes for mesocosm 7 and 170 minutes for mesocosm 8). The mesocosm experiment differs markedly from the static chamber flux experiments often conducted in soil and plant science. Most importantly, the uppermost 5 m of seawater in the mesocosm is kept well mixed by use of an aquarium pump (constant flow) and it is from this volume that chlorophyll and DOC measurements are made. In the "real" world many physical parameters may affect the sea-air flux of a given species. For example the wind speed (as was shown by Carpenter et al. 2004) and mixing down from the ocean uppermost mixed layer. The beauty of the mesocosm experiment is that the wind speed and the downward mixing are kept as constant as possible by means of a constant air flow and the constant effective mixing of the 0-5 m seawater layer, thus allowing other potentially controlling parameters to be investigated. Particularly suited for investigation in the mesocosm system is the significance of: a) ocean biology producing or consuming organic trace species in the seawater, b) organic chemicals in the seawater (either directly or indirectly produced by the biology) which may be photochemically degraded abiologically to organic gases and which subsequently escape to the air. A considerable advantage of the mesocosm experiment over laboratory studies of single plankton species is that the plankton ecosystem is investigated as a whole, and possible interactions between plankton species (community dynamics) can occur. Moreover within the mesocosm experiment the biology can be monitored, as opposed to "real world" aircraft studies (e.g. Singh et al 2004) or coastal studies (e.g. Carpenter et al. 2004). Reviewer 1 has raised three key questions which need to be examined in more detail when interpreting the data namely friction velocity, the effect of changing temperature on the mesocosm and the possibility of slow saturation. We agree with reviewer 1 that these issues should have been discussed in more detail. They are discussed below and included in the revised version of this paper.

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Paragraph 2 and 3.

Reviewer 1 is correct that a very relevant reference regarding this work was omitted, that of Carpenter at al. 2004. This will be incorporated in the revised ACP version of this work. A comparison of the deposition velocity found by Carpenter et al. 2004 (0.02-0.33 cm s^{-1}; best estimate = 0.09 cm s^{-1}) to that observed in this mesocosm (circa 0.05 cm s^{-1}) shows reasonable agreement. We note that methanol is an alcohol rather than a carbonyl as stated by reviewer 1. Moreover we also interpret the deposition velocity of methanol found by Carpenter et al. 2004 as not indicating an uptake entirely dominated by aerodynamic resistance (interpreted as the turbulent resistance in the atmosphere) as stated by reviewer 1 even at the reasonably high wind speeds of 8 m s^{-1}. If this were the case (i.e. surface resistance is unimportant) then deposition velocities would be higher (similar to those of HNO_3 ca. 0.5-1 cm s^{-1}. The comparison of modeled and measured values for methanol wind speed dependencies given by Carpenter et al.2004 do not show a particularly good match, especially at low wind speeds despite being described a good agreement (see Fig 6 in Carpenter et al. 2004), perhaps because the model is not fully describing the processes in play ? As reviewer 1 rightly states, global model parameterization of the air-sea exchange must take into account friction velocity, atmospheric and ocean column depths, temperatures, mixing etc. However in the mesocosm system the influence of any dynamic parameter (e.g. friction velocity) on the VOC fluxes can be assumed to be constant because the air flow through and the mixing in the system is not changing and the water in the first 5 m is constantly mixed (page 9911 lines 21-28 and lines 14-15). Thus the observed variation in the VOC fluxes cannot be accounted for, in terms of such dynamic parameters. On the other hand, results from the mesocosm must be interpreted bearing in mind that the air flow through the system was constant and that the water in the first 5m was constantly mixed, both of which are normally not the case under “natural” conditions.

Paragraph 4

Reviewer 1 sees no relation between the air-sea trace gas fluxes of methanol and ace-

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tone, and photosynthetically active radiation (PAR). Our premise here is that ocean biology can potentially play a role in air-sea exchange by either, consuming a dissolved gas from the surface mixed layer to maintain an undersaturation (e.g. CO_2 or methanol), or by directly releasing organic species into the water as a byproduct of photosynthesis (e.g. isoprene) or as a photoproduct of biogenic precursors (as has been reported for acetone). Therefore, since PAR drives most biological activity in the surface ocean (via photosynthesis), it is reasonable to investigate potential links between light and ocean VOC fluxes.

We agree with reviewer 1 that the potential effect of temperature in our set-up must be discussed in more detail. The maximum and minimum temperature of the ambient air during the period of our study (and thus a good approximation for the mesocosm air temperature) was 283 °K (minima at 00:00 - 07:00 hrs local time) and 289 °K (maxima at 10:00 - 20:00 hrs local time)(source: http://web2.gfi.uib.no/veret/ ; http://www.wordtravels.com/Cities/Norway/Bergen/Climate). Thus, the difference between the maximum and minimum temperature on any given day during our study was never more than 6 degrees for the ambient air. The temperature in the water of mesocosm 8 (the upper 5m layer) was monitored daily and the minimum and maximum temperatures during the period of study was 282 K and 284.5 K respectively, the water temperature tending to gradually increase during the experiment.

1) In order to ascertain the maximum possible influence of temperature on the emissions, let us assume that the temperature change in the mesocosm water is 6°K (a generous upper limit, bearing in mind the high specific heat capacity of water). A simple calculation of how the trace gas partitioning would change between the aqueous and gas phase according to Henry's law from 283 K to 289 °K for the oxygenates methanol, acetone ,acetaldehyde is given below (Calculations performed using values given at - Sander, R: Compilation of Henry's law constant for inorganic and organic species of potential importance in environmental chemistry http://www.henrys-law.org, 1999,8191,8200)

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Compound	Henry's law constant (Cwater/Cair)	Temperature (K)
Methanol	13003	283
Methanol	9067	289
Acetone	1430	283
Acetone	1027	289
Acetaldehyde	969	283
Acetaldehyde	686	289

These results clearly show that the maximum temperature effect would cause a 43.4 % relative concentration change for methanol, 39.2 % relative concentration change for acetone and 41.2 % relative concentration change for acetaldehyde concentrations in the gas phase based on the change in the Henry's law partitioning for the temperature difference of 6 degrees. The relative change in the mixing ratios, between a diel minima and maxima is however much greater, varying between 500 % - 1500 % depending on the VOC and the biological phase. Moreover a diel variation time series generated purely by the temperature effect should show no marked difference throughout the experiment. In fact, as stated previously the water temperature increased slowly during the campaign. If temperature were the controlling parameter for emissions we would have observed an increase in emissions. This was not observed, rather the emission rate generally decreased. Thus the temperature effect on the solubility of these gases cannot solely account for the observed mixing ratio variations.

A further temperature effect has occurred to us when considering this response which could potentially occur within the mesocosm air. If during the day a heat induced stratification occurred in the mesocosm air restricting turbulence then this could indeed affect the flux. However the ventilating mechanism (30 L min^{-1} of air being removed from near the mesocosm top) would limit any heat induced stratification. Furthermore,

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buffeting of the plastic walls of the mesocosms by surface waves and winds aided mixing within the mesocosm.

Paragraph 5

Reviewer 1 is skeptical that biological mediation of the deposition rate can occur. She/he suggests that the methanol uptake might have decreased simply because the water was under saturated in the beginning and became gradually more saturated towards the end of the experiment. This is clearly not the case since the same trend would also have been seen in the acetone profiles (see Fig 3 and 4). Let us nonetheless consider this suggestion further. The well mixed mesocosm water volume is 15 m^3 . In order to saturate this volume of water at 283 °K, and assuming there is absolutely no methanol in the water to start with; one would need 214 mg of methanol(Taking H= 10000 and Cair =1 nmol mol^{-1}). Using an uptake flux of 1 ng m^{-2} s^{-1} (a generous value as can be seen from Fig 3 and Fig 4), during the period 17th till 30th May, we calculate that 1.2 mg methanol would have been available for dissolution in this 14 day period, indicating that based on this criteria alone, the mesocosm water would still be significantly under saturated before we commenced our measurements with the PTRMS on the 31st of May. Now, if the mesocosm water's under saturation was just a function of 'physically driven' under saturation then there should have been a constant decrease in the uptake flux of methanol over time, because the degree of under saturation would decrease. What we see however is that on the afternoon of 2nd June and 9th June, even for similar mixing ratios of methanol in the ambient air of around 2 nmol mol^{-1}, the uptake flux of methanol is in fact more than 1.6 times higher on the 9th of June. Clearly this is inconsistent with the notion of an undersaturation driven solely by physical parameters and suggests a possible biological contribution to the maintenance of undersaturation in the mesocosm water. What we are suggesting in the paper is that surface waters in the mesocosm are in fact close to equilibrium and that the undersaturation was driven by the biological uptake.

Paragraph 6

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Reviewer 1 questions whether we believe that species with a positive flux (to the atmosphere) and apparent covariance with PAR are directly released by phytoplankton or a product of DOC, particularly because of concerns relating to the role of the microlayer. We believe that the issue of the microlayer has arisen because it was not initially clear in our paper that the first 5m of water (approx.15000 L) were effectively mixed. If the surface water is stagnant and transport between the liquid bulk and liquid surface is inhibited, then as rightly pointed out by the reviewer, a constant surfactant layer can form which might be more enriched in DOM compared to the bulk water due to inefficient transport and inhibited mixing. However the entire upper 5 m water layer 's mixing precludes such a possibility and the result is a homogeneous 5 m water column. The efficiency of the mixing can be gauged by the way acetone, acetaldehyde and isoprene emissions mirror PAR profiles with no time- phase shift. Thus as described in the manuscript, since DOC and DOM values do not change significantly but the emissions decrease in the second phase of the study, coupled with the fact that isoprene (a compound that is not produced by photo-degradation of DOM but only as a by-product of photosynthesis) correlates so strongly with acetaldehyde (r = 0.86), it indicates that the production of oxygenates like acetaldehyde and acetone is possibly linked to a biological mechanism as well. Unfortunately we are not able to distinguish emissions produced directly from biology (e.g. isoprene) and those produced indirectly through photochemistry of ocean emitted precursors.

In conclusion we appreciate the candid views of reviewer 1. We will make it clearer in the revised version that we are investigating the potential effect of biology and PAR on trace gas fluxes and that the fluxes derived from the mesocosm studies should be interpreted with caution because the physical parameters are clearly different to the open ocean. Nonetheless we still maintain that the data shown in the paper do point to a significant role for oceanic biology and PAR in trace gas fluxes and that the mesocosm approach is a valuable new method for research in this area. From the comments of reviewer 1 it is clear that in future studies both aqueous and gas phase concentrations should be monitored, and to ensure thorough mixing in the gas phase

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the mesocosm air should be actively circulated with a fan. Finally we believe that the results have revealed interesting new aspects of the biogeochemical cycling of VOCs in the marine environment.

References

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2) Singh, H., Salas, L., Chatfield, R., Czech, E., Fried, A., Walega, J., Evans, M., Field, B., Jacob, D., Blake, D., Heikes, B., Talbot, R., Sachse, G., Crawford, J., Avery, M., Sandholm, S., and Fuelberg, H.: Analysis of the atmospheric distribution, sources, and sinks of oxygenated volatile organic chemicals based on measurements over the Pacific during TRACE-P, J. Geophys. Res.-Atmos., 109(D15), D15S07-D15S20, 2004

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