

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

**Anonymous Referee #1**

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The paper by Sinha et al addresses some very important uncertainties in the fluxes and indeed direction of exchange of oxygenated compounds. From this perspective the work is likely to be of substantial interest to many researchers.

I have however some very major reservations about the experimental methodology used and some of the conclusions that are drawn. Most of my concern relates to the use of a simple ‘by-difference’ flux estimation method for this system. The exchange of polar and soluble compounds between sea and air is more complex than, for example, irreversible emissions from plant to atmosphere where this technique is used widely. An

Interactive  
Comment

ocean atmosphere flux of a gas is the product of chemical partial pressure difference and the gas transport velocity, and subsequently this flux becomes strongly dependant on the functionality of the compound in question, - essentially differing regimes dominate depending on whether a gas is soluble or not within seawater.

The authors do not make reference to a work by Carpenter et al 2004 (GBC, 18, 4027) which is particular of relevance here. For a soluble carbonyl (eg methanol) there is no chemical resistance to its transfer between phases, rather the resistance is entirely aerodynamic. Where aerodynamic resistance is the controlling factor, then friction velocity above sea surface defines the magnitude of the flux. The exact flux under any given conditions requires a treatment of friction velocity, atmospheric and ocean column depths and turnover rates, temperature, and concentration gradient. It is simply not one which may be expressed as a uniform mass per unit surface area emission.

Throughout the paper PAR is reported as being a major environmental factor in determining organic compound exchange rates. This makes no sense at all to me, and there is really no convincing mechanisms proposed as to why for example methanol deposition or acetone emission should be in any way related to specifically to PAR. Temperature must be investigated as an influential parameter within this mesocosm. Surely within the sealed bag there will have been temperature fluctuations during the day, in line one assumes with the profiles generated by PAR? If this was suggested as a controlling factor I could believe it, - enhancing gas phase transfer rates and mixing when warmer. What comment would the authors make on this?

There is further comment with respect to methanol that there is biological mediation of the deposition rate inferred from pre and post bloom measurements. This can only be the case if firstly biological consumption is very fast (much quicker than anything previously reported which is of the order of days to weeks half-life) and that the water is close to or at saturation in methanol. Since this isn't measured we won't know. The latter point is an important one however. Since the water is not exchanged in the chamber, it would seem appropriate to assume that over time the water, although initially sub satu-

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Comment

rated, may ultimately approach saturation and the uptake rate reduce of its own accord. The covariance with phytoplankton could therefore be entirely coincidence? Models of methanol uptake all indicate that mixing down is a key parameter in determining the ocean / atmosphere budget since it prevents surface saturation occurring.

For those species with a positive flux and an apparent covariance with PAR, - is the hypothesis that these are released by phytoplankton here or a product of DOC photolysis? With no winds, the transport in the liquid bulk and the liquid phase gas exchange will be very inhibited and yet the gas phase composition mirrors PAR exactly with no time-phase shift. How is this possible, unless for example all production was proposed to occur within the microlayer? The Zhou and Mopper paper referred to in the references is relevant only to microlayer. Is that therefore the source of acetone /acetaldehyde in this study? If it is then DOC values in the bulk water are of little use in interpretation, rather DOC in the microlayer is the parameter that needs to be reported.

I appreciate that this may appear a rather negative review. I am without doubt that the PTR observations will have been carefully made, and that substantial effort will have been put into this study. However I must stress again my substantial unease at the applicability of the methodology used here to derive a meaningful flux. The assignment of so much of the observed behaviour to PAR when other key variables are untested is poor science. I would in this case refrain however from an outright rejection without giving an opportunity of reply.

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