**Ocean Science
Discussions**

Interactive comment on "A chemical ionization mass spectrometer for continuous underway shipboard analysis of dimethylsulfide in near-surface seawater" *by* E. S. Saltzman et al.

Anonymous Referee #2

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General comments

DMS is an important climate-active gas, mainly produced in marine areas. Complex ecosystem processes affect its concentration in surface waters. The main source of DMS is dimethylsulfoniopropionate (DMSP) which is a compatible solute produced by several phytoplankton taxa. The mini-CIMS method described here, measures one product (DMS) of the complex sulfur cycle. Although this gives limited information on the ecosystem processes leading to DMS, it is invaluable for validation of the new-generation climate models. Since the publication of a DMS database by Kettle et al (1999), it is possible to develop climate models that include DMS. However, Kettle et

al. (1999) also revealed that global DMS-data coverage is very poor, both in space and in time. Updates of the "Kettle database" are currently underway and will certainly improve the potential for model validation, but the bottom line is that there is still not enough data to get a complete overview of DMS patterns in the various ocean provinces. The instrument described in the paper by Saltzman et al. is able to make a big step forward in gathering DMS data: it is a relatively low-cost, easy to handle instrument and has the potential to be deployed unattended for continuous measurements on board of research vessels, ships of opportunity or on measuring platforms. This will greatly improve both spatial and temporal coverage of DMS data. The paper is well written and the method is described extensively.

Specific comments

p. 1574: DMS seawater concentrations are calculated from the mixing ratio measurements multiplied with ambient atmospheric pressure and the Henry's Law constant for DMS as determined by Dacey et al (1984). Although I agree Dacey et al is the best reference in this respect, it has been determined with a different system. Given the fact that there is some variation in the literature for H, that may be related to differences in methods used, this may also be true for the current set-up. For instance: Are there potential issues with temperature-sensitive solubility of DMS in the porous membrane, which might have an effect on the diffusion across the membrane? Did you try to determine an "instrument-specific H" with the current system, e.g. by immersing the porous membrane in a solution with know DMS concentrations, at different temperature and/or salinity and measuring the DMS mixing ratio in equilibrated air?

p. 1574-6: There is no description of the site of protonation (Ni-foil?) in the section on instrument design. Please add.

p. 1577: The membrane equilibrator used here is a very elegant and non-disruptive way of establishing equilibrium between water and gas phase. This is especially important for compounds easily affected by disturbed biological processes, such as DMS.

I noticed that the manufacturer of the used membrane has tubing of three different porosities. Since there are potential problems with bubble breakthrough, did you experiment with different porosities? Which porosity was used here and what was the wall thickness of the tubing you used?

p. 1580: It is estimated that the instruments detection limit under field conditions is 170 ppt. However, in figure 4 a signal noise of ~5 ppb is observed during a calibration run. When looking at the instrument's signal, the same range in noise is measured during the field trip, presented in Figure 6. This related to a noise in the DMS water concentration of 3-5 nM, which is not trivial. With such an instrument noise, how can you get a detection limit of 170 ppt? (I just read in your reply to ref #1, that these figures display raw instrument data, but taking 1-minute means will smooth 170 ppt differences.)

p. 1580: With lower temperature, the detection limit of water samples increases. A 50% increase of the detection limit is found when going from 25 to 15°C. I presume this results from the computed Henry's Law constant used in the calculation of the DMS water concentration. However, when going down in temperature the humidity of the sample gas flow will reduce. The subsequent reduction in primary ions will influence the instruments response to DMS. Although on p.1582 it is argued that this does not affect the measurements since both ambient DMS and internal standard are affected similarly, I would think it will affect the detection limit. Given the fact that large ocean areas have much lower temperatures than the tested 15°C, the question is how well the instrument functions in e.g. polar areas. If my reasoning is correct, can't you overcome this problem by supplying a fixed amount of water vapour to the instrument, e.g. by humidifying the dilution airflow at a fixed temperature?

Technical corrections:

p. 1572: To both sides of formula 1 "N2" is added. I presume this should have been "Ni", to indicate the site of protonation?

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p. 1579, last line: Shouldn't the "63/66 ratio" be changed in: "66/63 ratio" as in figure 5?

Interactive comment on Ocean Sci. Discuss., 6, 1569, 2009.