Ocean Sci. Discuss., 6, C535–C541, 2009
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Ocean Science Discussions

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6, C535–C541, 2009

Interactive Comment

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.

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Author response to Anonymous Referee 1

Reviewer 1 raises a number of excellent points relating to the shipboard use of continuous flow equilibrators for DMS analysis. These include material incompatibilities, bubble purging, seawater residence times, and shear stress on DMS producing organisms. We agree with the reviewer's statement that: "... the authors should use their instrument for an intercalibration exercise using freshly collected, natural seawater or mixtures of DMS-producing organisms at typical biomass densities." The goal of this manuscript was to describe an instrument capable of serving as a real-time detector

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for seawater DMS in an equilibrated air stream. The manuscript does not demonstrate nor assert that the shipboard pumping system or membrane equilibrators used are free of artifacts. On the same point, the reviewer called for "a critical discussion of these issues". We reexamined the manuscript, and believe that this is treated as critically as possible (given the limited information available) in the Discussion section, as follows:

"This study focused primarily on the design and performance of the mini-CIMS itself, rather than on the equilibrator interface. The use of membrane equilibrators in this study is not meant to indicate that they are the only, or necessarily the best interface for unattended deployment. The greenhouse gas (CO_2, N_2O) and halocarbon communities have had considerable success with shower-head style equilibrators and similar devices should be examined for use with DMS (Johnson, 1999). The moderate solubility of DMS in seawater means that equilibrium with the gas phase is easily achieved. However, the biological issues associated with DMS analysis make equilibrator design more challenging. This is because of the potential for spurious DMS production in the equilibrator due to: 1) growth of DMS-producing organisms, or 2) rupture of phytoplankton cells and colonies as they pass through the scientific seawater system and equilibrator (Kiene and Slezak, 2006). The experience from this and prior studies (Marandino et al., 2007) suggests that the porous Teflon tube membrane equilibrator does not experience biofouling in oligotrophic conditions and certain bloom conditions. A rigorous comparison between the DMS levels in a ship's seawater pumping system and in discrete water samples has not yet been conducted. Similarly, intercomparison of membrane equilibrators, shower-type equilibrators and traditional purge/trap measurements are needed to validate these techniques under a variety of oceanographic conditions."

To further clarify, we will modify the Introduction as follows:

"This paper discusses the design and performance of a much smaller, lower-cost automated APCI-MS instrument specifically designed for measurements of surface ocean DMS from a seawater equilibrator. The design goals for this instrument (hereafter re-

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ferred to as the "mini-CIMS"), were to achieve a detection limit of 0.1 nM DMS in a relatively compact, low cost package with no moving parts and the potential for unattended operation. Although a membrane equilibrator was used in the testing of this instrument, this study did not critically evaluate the performance of the equilibrator."

The reviewer also raised a fair point about the high frequency variability in the field data, correctly stating that "The DMS data presented in Figure 6 appear to have a large 5 nM spread over approximately 10 min time intervals." The plot was inadvertently made from raw, 5 Hz data rather than 1 minute-averaged data. We have replotted the data with 1 minute averaged data (see figure below), and the resultant spread in the plot is consistent with the stated noise characteristics of the instrument (Figure 6 below). We discovered the same issue with Figure 4, which had been plotted with 1 Hz data. A revised Figure with 1 minute data is shown below.

The technical corrections requested to Figures 1, 2, and 4 are addressed in the revised Figures accompanying this comment.

We thank the reviewer for these comments and we certainly agree that "A thorough intercomparison with existing purge and trap techniques is clearly the next step." We are working to arrange such a study in the near future.

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

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Figure 1

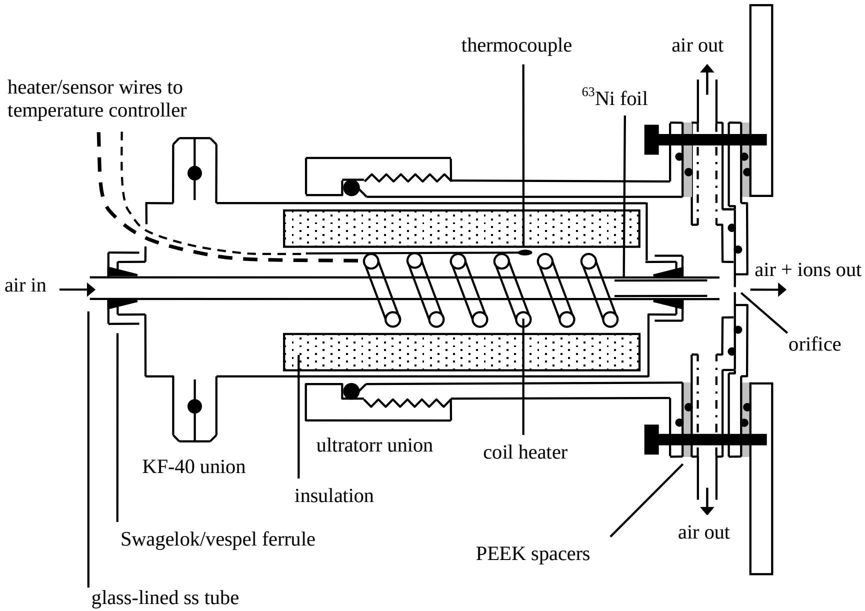

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Figure 2

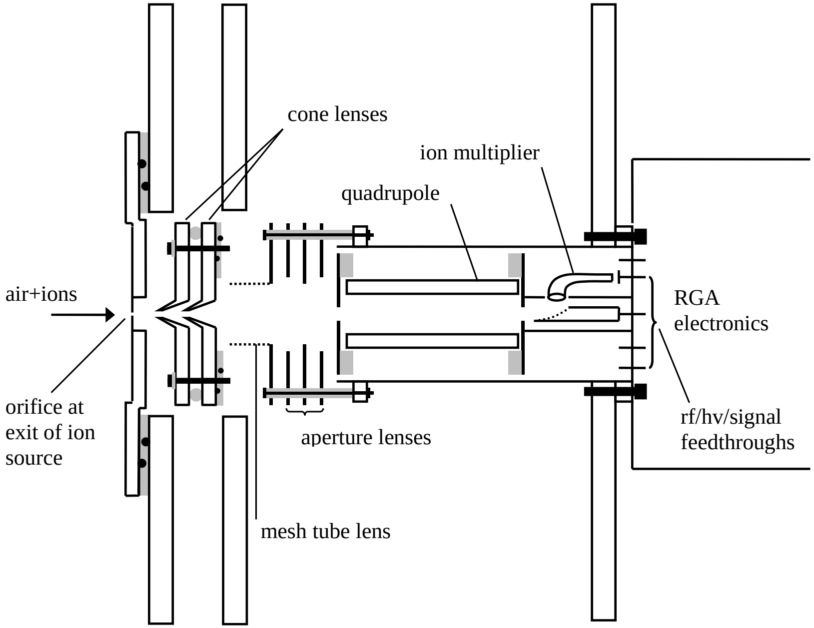

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Figure 4

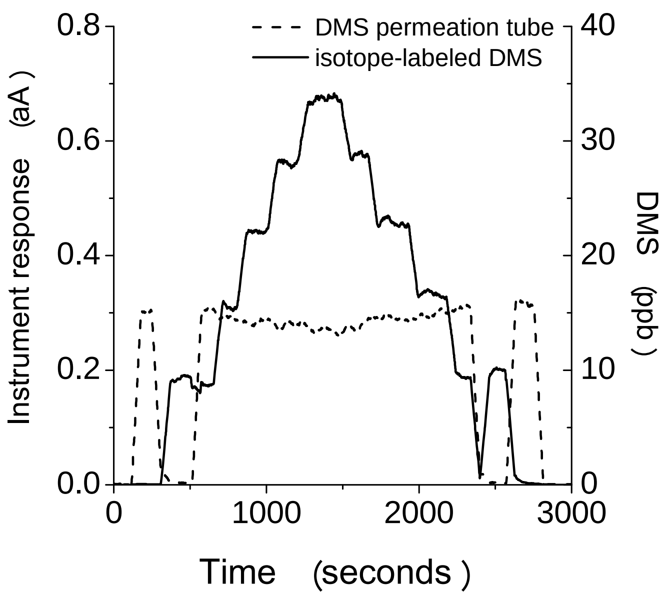
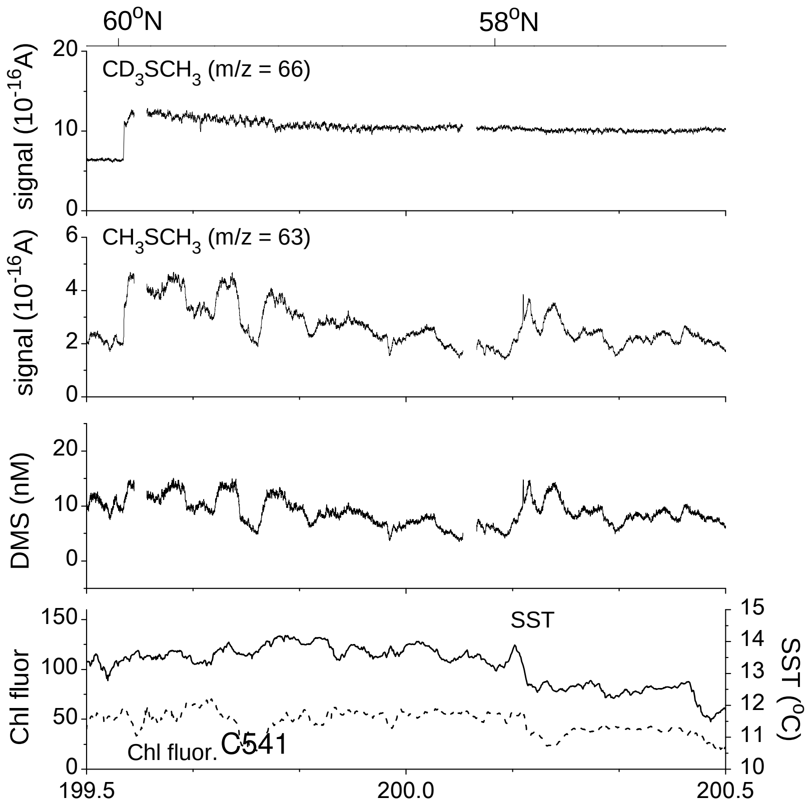


Figure 6



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