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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 #1

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General Comments

This is an interesting paper that describes the use of a counter flow membrane equilibrator in combination with a chemical ionization mass spectrometer for the continuous quantification of the marine trace gas dimethylsulfide (DMS) in seawater. The existing global dataset for DMS is very limited and new methods and technologies are urgently needed to improve the coverage and frequency of data in the near future.

Specific Comments

I have reservations about using an onboard pumped seawater supply system for measurements of DMS. These systems are often constructed of materials that are incom-

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patible with such analyses. Also, such systems frequently include a large bubble tank that removes bubbles from the seawater before it is being pumped to the onboard laboratories and efficiently purges trace gases from the sample water. Flushing rates and retention times of seawater in such systems are often not described but may affect the production and removal of DMS. Whether this was the case on the described cruise is of secondary relevance, since the presented method should aim for a wider usage on all sort of different research and non-research platforms. It is unfortunate that the authors do not compare their measurements with bucket or Niskin samples of freshly collected seawater. Only such measurements would confirm (or reject) the suggested new method for continuous measurements of DMS.

The equilibrator requires a seawater flow of 2 L/min through a gap of approximately 5 mm between the inner and the outer tubes. This presents another problem for the analysis of DMS in seawater. It can be expected that under these conditions DMS-producing organisms will experience significant shear stress, a parameter that has previously been shown to increase DMS production by microbial organisms.

I appreciate that these issues are not specific to the methodologies presented here and similar attempts to monitor DMS on-line will suffer from comparable shortcomings. However, I believe that a critical discussion of these issues is necessary. Ultimately, 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. This will likely assist in establishing the true utility of the new instrument.

The DMS data presented in Figure 6 appear to have a large 5 nM spread over approximately 10 min time intervals. Although more conservative DMS quantification methods (e.g. cryogenic enrichment coupled to GC-FPD) have a sampling frequency of only about 20 min, such spread of DMS concentrations is not frequently encountered in open ocean environments. Hence, the presented data casts some doubt over the utility of the method without averaging out this apparent “error”.

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Technical Corrections

Page 1572, line 1: add space between “automated” and “APCI-MS”.

Figures 1 and 2: Direction of sample flow in Fig 2 and how both components are put together is unclear.

Figure 4: Difference between grey and black lines is unclear. What is the arrow indicating - a time point or the grey line?

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