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Discussions

Interactive comment on "Dimethylsulfoniopropionate (DMSP) and dimethylsulfide (DMS) cycling across contrasting biological hotspots of the New Zealand Subtropical Front" *by* Martine Lizotte et al.

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Response Reviewer 2. os-2017-32 Lizotte et al.

The manuscript reports on measurements of dimethyl sulfur compounds DMSC (DMS and DMSP) concentrations and their cycling rates on both sides of the Subtropical Front near New Zealand. The study is part of the SOAP experiment and intends to relate DMSPC dynamics to hydrographic and biological characteristics. To do so, measurements concentrate in three different areas that are investigated with a Lagrangian

approach. The DMSP availability hypothesis is used as the major driver for the interpretation of most of the data, yet with uneven fit. The authors conclude that, as previously suggested, oceanic fronts generate hotspots for the production and emission of dimethyl C1 sulfur. Even though no great advances in knowledge are provided that can be of applicability to a broad range of regions of the global ocean, the study is timely and the data valuable. The manuscript is well written and properly contextualized and referenced. I do not have major concerns towards publication but provide here below some questions and suggestions that may help improve the robustness and argumentation.

1. Methods, equation 1 and L206-213, also L541-550: SRD is calculated from dailyaveraged irradiance. Is it taken for the 24 hours prior to sampling? Or is it the 24 hours of the sampling day? The rationale of the SRD concept related to DMS (as from Vallina & Simó 2007) relies on the previous 24 hours, which is the time over which photobiological and photochemical processes led to the observed DMS concentration.

Answer ML. The calculations are indeed based on the daily irradiance averaged over the 24 hours prior to sampling. We made this clearer in the methodology by modifying the following sentence: "Solar radiation dose (SRD in W m-2) was calculated using Eq. (1) where I0 represents the daily-averaged irradiance (in W m-2) measured using an Eppley Precision Spectral Pyronometer (285-2800 nm), k (in m-1) are estimates of vertical diffuse attenuation coefficients based on Photosynthetically Active Radiation (PAR) offset between two depths (2 m and 10 m), MLD is the mixed layer depth defined as the point at which a 0.2oC difference from the sea surface temperature occurred and was calculated according to Kara et al. (2000).", and changing it to: "Solar radiation dose (SRD in W m-2) was calculated using Eq. (1) where I0 represents the daily-averaged irradiance of the 24 hours prior to sampling (in W m-2) measured using an Eppley Precision Spectral Pyronometer (285-2800 nm), k (in m-1) are estimates of vertical diffuse attenuation coefficients based on Photosynthetically Active Radiation (PAR) offset between two depths (2 m and 10 m), MLD is the mixed layer depth defined

as the point at which a 0.2oC difference from the sea surface temperature occurred and was calculated according to Kara et al. (2000).

2. L241-258: Provide details of how 35S-DMSPd loss was measured – I guess it was by removal of 35S-DMS, transformation of all the remaining 35S-DMSPd into 35S-DMS, which is trapped onto H2O2-soaked filter. Am I right?

Answer ML. The 35S-DMSPd loss rate is measured by the disappearance of dissolved 35S-DMSP over time: the loss of 35S-DMSPd reflecting what is being consumed. To add clarity to this part of the paper we included more information by modifying the following sentences: "The bottles were then incubated for 3 h at in situ temperature during which time subsamples were taken after 0, 30, 60, and 180 min to measure the loss of 35S-DMSPd over time. The kDMSPd was calculated as the slope of the natural log of the fraction of remaining 35S-DMSPd versus time." to these ones: "The bottles were then incubated for 3 h at in situ temperature during which time 1mL subsamples were taken after 0, 30, 60, and 180 min and transferred into 10-mL scintillation vials containing 5 mL EcolumeTM in order to measure the loss of 35S-DMSPd over time (the disappearance of 35S-DMSPd representing the consumption of this pool). The kDMSPd was then calculated as the slope of the natural log of the fraction of remaining 35S-DMSPd versus time." The "transformation of all the remaining 35S-DMSPd into 35S-DMS, which is trapped onto H2O2-soaked filter" mentioned by the reviewer is called the "unreacted or unconsumed dissolved 35S-DMSP" which was measured at the end of the incubation period. We discuss this around lines 279-283: "After the volatiles were trapped, a new stopper with H2O2-soaked filter was placed in the vial. Each vial was then injected with 0.2 mL NaOH (5N) through the stopper using a BD precision guide needle to quantitatively cleave remaining 35S-DMSPd into 35S-DMS. The 35S-DMS was trapped as described above." To make it clearer what this pool represents we modified the phrase which now reads as follows: "After the volatiles were trapped, a new stopper with H2O2-soaked filter was placed in the vial. Each vial was then injected with 0.2 mL NaOH (5N) through the stopper using a BD precision

guide needle to quantitatively cleave the remaining 35S-DMSPd into 35S-DMS (a pool known as the unconsumed 35S-DMSPd). The 35S-DMS was trapped as described above."

3. L341-342: How was the cryogenic trap cooled to -20âŰęC?

Answer ML. The trap was encased in a metal block that also contained a cold finger connected to an external cryo-cooling unit monitored and controlled automatically. The following phrase: "Briefly, calibrated volumes (5 mL) of seawater samples were purged with zero-grade nitrogen (99.9 % pure) and gas-phase DMS was cryogenically concentrated on 60/80 Tenax TA in a stainless steel trap at -20°C, then thermally desorbed at 100 °C for analysis by GC coupled with sulfur chemiluminescent detection.", was changed to: "Briefly, calibrated volumes (5 mL) of seawater samples were purged with zero-grade nitrogen (99.9 % pure) and gas-phase DMS was cryogenically concentrated on 60/80 Tenax TA in a stainless steel trap maintained at -20°C via a cold finger connected to a cryo-cooling unit, then thermally desorbed at 100 °C for analysis by GC coupled with sulfur chemiluminescent detection."

4. Results, L464-466: A bacterial DMS production rate (from DMSPd only) of 27 nmol/Ld is astonishingly high, more so when DMS concentration is 3 nmol/L and DMSPd is 10 μm, namely dinoflagellates.

Answer ML. We agree with the reviewer, this rate is quite high. Such high rates are rare but have been published before (Royer et al. 2010). We are confident however that this is not a problem with a specific incubation (or bottle effect) since all the incubations displayed the same results (even the duplicate dark-acclimated samples that we do not present in the paper, as mentioned in the methodology section, were extremely high and showed no significant differences with the light-acclimated samples that we discuss in the paper). We added the following phrases to this section in order to reflect potential reasons for this response: "These high rates reflect the very high DMSPd scavenging by the bacteria measured on this particular day. The fact that

concentrations of DMS remained low (ca. 3 nmol L-1) suggests that potential sinks, particularly bacterial DMS consumption, but not excluding DMS photo-oxidation and ventilation (Table 1) may have kept this pool in check."

5. Figure 5: Correlation between DMSPt and chlorophyll a is quite strong indeed. One would expect it even stronger with DMSPp, since it is better associated with algal cells. Perhaps it does not deserve another graph but some mention to the regression facts.

Answer ML. The strength of the regression between DMSPp and Chl a (r2 = 0.57) is very similar to the one between DMSPt and Chl a (r2 = 0.59). We added this information in the discussion section (starting at line 541): "A type II linear regression model suggests that 59% of the variance in pools of DMSPt can be explained by the variability in stocks of chl a (Fig. 5a), while the strength of the relationship between DMSPp and chl a is also strong (r2 = 0.57, data not shown)."

6. C3 Table 1: All variables are reported "in blooms" and in the vicinity (N or S of). But chlorophyll concentrations are not any lower in the vicinities. So, what is the definition of bloom?

Answer ML. This is discussed in detail by the SOAP overview paper (Law et al. also currently under review). However to add some precision to this aspect we added the following phrase to the methodology section (lines 204-209). "The SOAP blooms were coherent discrete areas of elevated ocean colour identified in satellite images characterized by a maximum of 1 mg/m3 chl a or higher. Sampling took place near the center of these blooms but also at stations on the periphery and outside the blooms (Table 1), as defined by the distance from the bloom centre and clear demarcation in surface biogeochemical variables (see Law et al., this issue)." In this paper, we separate the stations in "clusters" (see all figures and discussions ensuing), to account for the fact that stations are either directly "in" or "in the vicinity of" the blooms.

7. Same for nutrients and DMSP:Chla.

Answer ML. We are not certain what is being asked here, if possible, added information would help us address any concerns regarding this part of the paper. Thank you.

8. I like the data compilation in Table 3. Answer ML. We thank both reviewers for acknowledging this positive aspect of the paper.

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