

Review of

"Consistent increase in dimethyl sulphide (DMS) in response to high CO₂ in five shipboard bioassays from contrasting NW European waters."

by F.E. Hopkins and S.D. Archer, manuscript number **bg-2013-656**

1. General comments

This manuscript presents valuable data on CO₂ induced changes to DMSP and DMS cycling during bottle incubations of samples from NW European shelf waters and the Bay of Biscay. This area of research is highly topical and timely in view of recent findings on ocean acidification. The particular strength of this manuscript is that it provides a near synoptic view of DMS cycling as it covers rates of DMSP production as well as rates of DMS production and consumption. Much of the data are transparently shown, by and large clearly support the authors' main conclusions, and apparently based on sound, up-to-date methodology. However, I do have concerns regarding various matters concerning context and presentation, and also regarding some aspects of data evaluation and interpretation.

Firstly, the MS reports DMSP production rates obtained with the mass ratio progress method by Stefels et al 2009. In this method, a stable isotopic tracer is added to the sample, and subsequent changes in the ratio of labelled versus non-labelled product are monitored. As I understand, these data are then fitted to a linearised form of the logistic growth model to obtain a first order rate constant with the inverse of time as its unit (e.g. d⁻¹). Unfortunately, the manuscript does not mention any of the underlying theory and assumptions, and merely points the reader to Stefels et al 2009. Furthermore, I could not find any example data illustrating the goodness of fit of observations to the logistic growth model used. I trust that some appropriate background and example data can be readily provided by the authors, perhaps complemented by some statistical measure of the goodness of fit. I would also appreciate it if the authors could be more careful with their use of terminology in their manuscript: their ' μ DMSP' [d⁻¹] is a rate constant, not a rate as stated e.g. at the top of section 3.4.

Secondly, the manuscript reports biological consumption rates and on p 2276 lines 11 ff states that "*Rates [...] were estimated from the slope of the linear decrease in ¹³C-DMS concentrations over the 10–12 h incubation period.*" While DMS consumption rates, i.e. $\delta(\text{DMS})/\delta t$, may be estimated from linear decreases over very short (yet not quite infinitesimal) time intervals with little error, I am less certain that this can be done over a 10-12 h period given that these processes are not linear with time. Perhaps the authors could demonstrate the validity of this approach by showing some example data that allow readers to assess if ¹³C-DMS decrease over time is approximately linear?

Biological consumption rates are then corrected for changes in substrate concentrations from tracer additions (see equation 1). I entirely agree with this approach. However, application of equation 1 requires knowledge of the half

saturation constant, K_s . Unfortunately, details on experimental determinations of K_s are tucked away in the paper's supplement with no critical discussion. On closer inspection, one can see that K_s were determined for stations (and possibly conditions) different to those used for the bottle incubation studies. This may warrant at least some discussion in the manuscript itself (how representative are these data?). The finding that values for K_s varied 5-fold should also be discussed briefly. I perfectly understand the experimental constraints which dictate corrections for changes in substrate levels, and I suspect that it was not possible to conduct bottle incubations and K_s determinations simultaneously. However, it is possible to provide at least some brief transparent discussion of the above together with an assessment of the uncertainties involved: how large were the applied corrections and how do they change with your choice of K_s ?

Thirdly, section 3.2 and figures 3A & B illustrate changes of DMS:DMSPt ratios with hydrogen ion concentration. The figures show what looks like a polynomial fit. However, no fit model is described nor is there any rationale given for model choice. I believe the authors should either remove best fit lines and statistics or provide details and rationale in the accompanying text.

Finally, the discussion section (4.1, p 2284 ff) refers to UV-induced responses from previous work without making it sufficiently clear that the author's experimental setup very likely excluded UV (see section 2.1.: use of LED panels and polycarbonate bottles which are known to cut off UV). It remains unclear to me how this relates to the authors' acidification experiments, unless they can provide some information (or even informed speculation) that there may be a reason to assume similarities between UV-stress responses and response to enhanced CO_2 .

Recommendation:

I believe this MS tells a very interesting story which is well supported by a comprehensive and novel data set. Despite the issues raised by my comments above, I believe that thorough revision can produce a high quality manuscript that merits publication in BG.

Further specific and editorial comments are detailed below.

2. Specific and editorial comments

Abstract:

- * Some tangible information should be added to the abstract, for example study area, dates, what was measured and some quantitative information.

Introduction:

- * Some references are missing or have incorrect in-text citations, e.g. page 2269 ff: Andreae 1990 (not in references), Kiene and Linn 2000 (should be Kiene et al 2000), Kim et al 201?. Please check references throughout.
- * Page 2270, “turn-of-the-century levels of CO₂”: did you mean 2100? Please clarify.

Materials and Methods

- * Page 2276, lines 17 ff “[Gross production] was estimated as the difference between net DMS production and BC”. Is gross production not equal to the sum of net P plus BC? Please clarify.
- * Also: no information is given on ancillary data, including pH, CO₂, nutrients etc. How were these obtained? Can data sources be referenced? I also wondered why Table 1 gives 'TON' but not dissolved inorganic N (DIN) or nitrate, which would in my view be more useful for characterising the study sites. Is TON = DON + PON? If the authors have DON, which is obtained by subtracting DIN from TN, why is it not in Table 1?,

Results

- * P 2278 line 26 ff. Please report coefficients of determination as per convention (values between 0 and 1) and not as percentages. See also Figure 3.
- * P 2280 lines 8 ff: the authors state that variations in DMSP production rates are caused by physiological rather than taxonomic changes. Can this statement be made in the absence of any taxonomic data? Please clarify.

Discussion

- * P 2283, line 11 ff: “*As a result of this general reduction in phytoplankton biomass and productivity, ratios of DMSP t : chl a were predominantly lower under high CO₂.*” As far as I can see, the manuscript does only report cell number concentrations for phytoplankton below 10 μm, and does not report data on biomass changes during incubations. Also: if biomass and hence chl a decrease, then DMSP : chl a ratios should increase and not decrease. Please clarify.
- * P 2286, line 26 ff: “... *saturation of consumption kinetics was exceeded*”. Please rephrase; saturation cannot be exceeded.
- * P2287 line 8. Text refers to a missing Figure (Fig. 7). Please correct.

- * Section 4.3 Exploring the regional variability. This section arbitrarily discusses only data from stations E01 (Mingulay Reef) and E04 (SE North Sea) which are arguably the least representative for the shelf waters studied here. I recommend including all stations in this discussion.

End of review