

Referee Comment on “Can we trust simple marine DMS parameterizations within complex climate models?” by P.R. Halloran, T.G. Bell and I.J. Totterdell

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The paper by Halloran et al. makes the point that simple correlations which account in part for the present day DMS distribution may not have fidelity into the future. Although this has been strongly foreshadowed in several works (e.g. IPCC, 1996; Gunson et al. 2006), Halloran and company make the first clear exposition and demonstration of the problem. I find that I am in complete agreement with their major conclusions. In fact our group is now working with a combination of high profile correlations (e.g. Vallina and Simo, 2007) and process models of varying complexity (e.g. Chu et al. 2003; Elliott 2009) to formulate similar statements. Thus we hope soon to provide further modeling evidence for a lack of “trust”. But given an opportunity here in the present review, I would like to propose ahead of time that the arguments be extended in several ways.

The authors expose and adopt two well known correlations for the global surface ocean dimethyl sulfide distribution, against major oceanographic state variables or combinations thereof (Anderson et al. 2001; Simo and Dachs, 2002). They then show that while the relationships work reasonably well for the recent period of observations, results diverge moving into a future Earth System Modeling context (ESM). This is with regard to both magnitude and sign, underscoring and recalling twenty five years later the seminal work of CLAW (Charlson et al., 1987) –which can be viewed as discouraging. Obviously the results sets cannot both be correct. In fact much of the difficulty is evident from a brief inspection of the equations involved. They contain hinges and fixed concentration points that cannot evolve with the biogeochemistry of the ocean. The correlations are thus necessarily and partially static.

In the real ocean, DMS concentrations are controlled in any given location by a complex web of interactions between the metabolisms of various autotrophic producers,

heterotrophic consumers of dissolved carbon and chemoautotrophic oxidizers of DMS itself. Physical mixing within, below and from the mixed layer are superimposed. Roughly speaking, the following processes are involved –1) some phytoplankton upregulate synthesis of the DMS precursor dimethylsulfoniopropionate (DMSP), to deal with various sorts of local stresses including oxidative, osmotic, nutritional and cryological, 2) different classes perform this process to different degrees in different locations, reaching variable cell internal maxima of the precursor, 3) senescence and mortality lead to cell leakage while zooplanktonic or viral attack spill contents directly, 4) the major sulfur compound released into the water column is DMSP, which is then sought by bacteria either for its carbon or sulfur, 5) yield of DMS given bacterial action on the propionate is determined by local sulfur demand of the microbial system and varies over an order of magnitude, 6) any DMS freed during the process is subject to several competing removal mechanisms including sea-air transfer but dominated by microbial consumption, 7) the primary consumers may or may not be specialist chemoautotrophs whose cell densities will be determined by the strength of the sulfur cycle itself, 8) all the bacteria in the list are subject to ultraviolet and other types of stress which will influence their growth and uptake rates, 9) some phytoplankton may recycle the sulfur compounds via uptake...

This list should already appear daunting but could be multiplied many times based on the research programs and literature which have followed in the wake of CLAW. All major features of the sulfur cycle depend on depth, season and location across the entire globe. In an ocean of change, evolution is possible at both systems and Darwinian levels. I recommend that interested readers consult the review by Stefels and company (2007) to obtain a feeling for how complex this situation actually is. A citation search on Charlson et al. (1987) may also be instructive. The fundamental explanation for all the intricacy is simple -biology of an entire planet is involved in distributing this one small molecule we have come to know and love. Any prediction strategy relying on fixed baseline concentrations and a few state variables must also somehow account for major features of the total mechanism. It is surprising that so many of the one-line models have been attempted...or perhaps not. CLAW constitutes a strong climate change lever which lies

almost entirely under the control of microscopic organisms. This is of course the climatologist's nightmare -Gaia. In some sense it is thus natural that more optimistic approaches are among the first tested.

Halloran et al. make the point that process based models may offer a remedy, but here is where I will add a bit of my own spin. The sequence listed above includes at least three critical steps which will dictate future DMS concentrations and fluxes at the regional level. The tropical cyanobacteria produce very little reduced sulfur and are likely to increase in dominance as the ocean stratifies under global warming. The sulfur demand of heterotrophs is a complex function of both their abundance and DOC availability, so that yield is difficult to predict. The ice algae produce extremely concentrated DMSP/DMS injections at high latitudes and seed a diatomaceous follow-on population in the marginal ice zone. This in turn will be relatively weak in DMS production. The major process models, which include Vogt et al. (2010) as mentioned by the authors plus a handful of others (Le Clainche et al. 2010) do not have reliable treatments for these channels. As they begin to evolve and take the stage in the next decade we will be faced with problems analogous to those discussed in the paper under review here. For example, suppose Vogt et al. choose to represent sulfur demand as a proportion to bacterial cell densities, while groups such as ours opt for a relation to inverse DOS. Divergent answers could well be obtained over large areas of the surface ocean where the yield of the process is currently low. We are back to Figure 5 of the paper under review.

In fact the arguments extend readily to the entire remainder of the biogeochemosphere. Halloran et al. cast their work as a demonstration that the marine sulfur cycle must be sorted out before the systems models will be reliable. This may be true, but with DMS measurements being adjusted continually downward in surface waters it also seems possible that a certain amount of control over CCN must be acknowledged for other substances. The case has been advanced courageously for several decades by a small cadre of researchers (Leck and Bigg, 2005). Recently the albedo community is starting to show considerable interest (Simo and Lana, 2010). I like to think of this option as Super-CLAW. Not only dimethyl sulfide but a variety of organic compounds and forms in the

surface ocean can influence cloud droplet numbers. Vapors which become secondary organics, surfactant microlayers and even pieces of organisms may be involved. Details of the Kohler curve effects are nicely explained in the textbook Seinfeld and Pandis (1998). The community will find itself in the same predicament as we begin to link general mixed layer organic chemistry with cloud properties –it will not be possible to construct high fidelity simulators for future effects because reaction pathways of the surface ocean will be largely unknown.

And from the clouds it is logical to extend further, to the greenhouse gases whether direct or indirect, to multiphase linkages with the chemistry of the atmosphere, and then ultimately back to nutrient supplies. Methane clathrates hidden along the Arctic continental shelf are currently destabilizing (Westbrook et al. 2009). We do not know if the major methanotrophic consumers have sufficient trace metal available to them in seawater to synthesize mono-oxygenase enzyme and oxidize the compound. If they fall short, an ultra strong greenhouse gas reaches the atmosphere (Archer, 2007). If they succeed, hypoxia may set in and nitrous oxide is generated instead (Codispoti, 2010). As a greenhouse gas it is ten times stronger still. The ecosystems of the surface ocean which control DMS levels also set those of the major form of recycled nitrogen, which is ammonia. It fluxes across the interface and basifies the aerosol throughout the marine troposphere. The pH of hydrometeors in turn exerts control over the bioavailability of iron in dust (Zhuang et al. 1992; Meskhidze et al. 2006). Iron controls the productivity of ecosystems over the Southern Ocean and elsewhere.

All of these cycles are problematic at the systems modeling level in ways which are related to those implied by the Halloran et al. work for DMS –the keys are held by marine organisms/ecosystems which cannot yet be simulated with fidelity. All could be substantial contributors to either exacerbating or ameliorating global change. It would seem critical at the very least to perform some sort of organized assessment of the matrix of effects. But sometimes it appears that the ESM community is hoping all these problems will just go away. Or at least that they will wait to make themselves apparent until the appropriate research has been done to support model development. But the bugs

are not likely to defer. They will choose their own time and place to exert their planetary scale influence. Water and the ocean cover the vast majority of Earth's surface. If we pretend the aqueous phase is inert or acts merely as a sink for CO₂, we are living on a fantasy planet. It may be very stimulating scientifically to some portions of the community, but it is a fantasy nonetheless.

What is to be done about this? The current default strategy is a scattered but persistent set of individual efforts at model improvement. This can't hurt the situation. But it will probably also fail to yield full comprehension of the role of biota on the time scale required. What we CAN do are many more of the sorts of experiments pioneered in the present paper. In my view, the chief contribution of the authors is to set this example. The community must apply process models systematically to show policy makers how the biogeochemical uncertainties interweave. This will constitute a service to human society at large, which currently labors under a very dangerous misconception -that all we need to know is fossil CO₂ emission.

There are only a few minor editing problems I can point up for the Halloran et al paper. The most important is consistency of the referencing style. The authors have tended to cite the same work in several ways. The original Kettle climatology offers the best example. It occurs as Kettle et al. (1999) in some cases -which is correct- or as Kettle 2000 in others -which is not. My assumption is that when the latter appears the authors likely mean Kettle and Andreae (2000), an update of the original that in fact demonstrates clearly what are the uncertainty levels. Halloran et al. emphasize the ability of the simple equations to outperform the Kettle interpolations-extrapolations in a synthetic experiment involving new data. My take is that this is understandable, not critical and probably fortuitous to a large degree. Kettle tuned carefully to the older values, which now appear to be incorrect. Simo and Dachs (2002) is biased low and as the measurements come down it appears to work better. Consider again the extreme over-simplicity of the equations -fixed concentrations over much of the sea, entire ecosystem structures determined by the depth of the mixed layer. The authors mention the related relationship of Vallina and Simo (2007), which attempts to link DMS to the solar radiation dose as an

exclusive controlling variable. This is perhaps the very best example of the sort of issues the authors have raised. Our group is now adopting this equation as a demonstration. It works fairly well in the contemporary. This is probably because phytoplankton demand light for growth everywhere in the ocean while sunlit zones tend to support stronger producers. But in the future, ecosystem structure/stresses will shift not only among the autotrophs but also for processor/consumer bacteria of several stripes...and some entirely new Vallina/Simo correlation may take its place.

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