

## TECHNICAL RESPONSE

## OCEAN CHEMISTRY

# Response to Comment on “Dissolved organic sulfur in the ocean: Biogeochemistry of a petagram inventory”

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Dittmar *et al.* proposed that mixing alone can explain our observed decrease in marine dissolved organic sulfur with age. However, their simple model lacks an explanation for the origin of sulfur-depleted organic matter in the deep ocean and cannot adequately reproduce our observed stoichiometric changes. Using radiocarbon age also implicitly models the preferential cycling of sulfur that they are disputing.

Dittmar and co-workers (1) claimed that the distribution of marine dissolved organic sulfur (DOS) reported in Ksionzek *et al.* (2) could be explained by simple water mass mixing alone. The authors calculated separate mixing models for the solid-phase extractable (SPE) fraction of dissolved organic carbon (DOC), nitrogen (DON), and DOS. They based their calculation on radiocarbon age and two end-members—deep and surface ocean water—that differed in concentration, elemental composition, and radiocarbon age of the dissolved organic matter (DOM).

We appreciate the interest in our publication; however, we disagree with their conclusions for three fundamental reasons: (i) Their mixing hypothesis considers deep-sea DOM as an independent end-member without reasoning for its origin or formation processes. (ii) Mixing without removal cannot adequately explain the stoichiometric changes that we observed. (iii) The authors mistakenly assumed that we exclusively addressed the removal of refractory DOS. Each of these aspects is addressed in detail below and rules out that mixing alone can explain the distribution of DOS and the depletion of nonlabile DOS.

We are well aware of the fact that the ocean consists of different water masses influenced by seasonal changes of the mixed-layer, deep-mixing, and circulation. Dittmar *et al.* outlined the accepted view that production in the ocean surface is the source for deep-sea DOM. Many previous stoichiometric studies [e.g., (3)] showed depletion of DON and dissolved organic phosphorus relative to DOC from surface to deep water, consistent with the DOS depletion and respective stoichiometric changes that we observed. Nonetheless, in their mixing model, Dittmar *et al.* treated surface and deep DOM as independent end-members (conservative mixing). Because the ultimate source of deep-ocean DOM is primary production, removal processes are fundamental to explain differences in concentration and stoichiometry (i.e.,  $\text{DOS}_{\text{SPE}}/\text{DOC}_{\text{SPE}}$  ratio), as well as the differing methionine-S yield between surface and deep DOM that we observed. Calculating the  $\text{DOS}_{\text{SPE}}$  removal exclusively for the meso- and epipelagic showed little effect on the rate coefficient (Fig. 1).

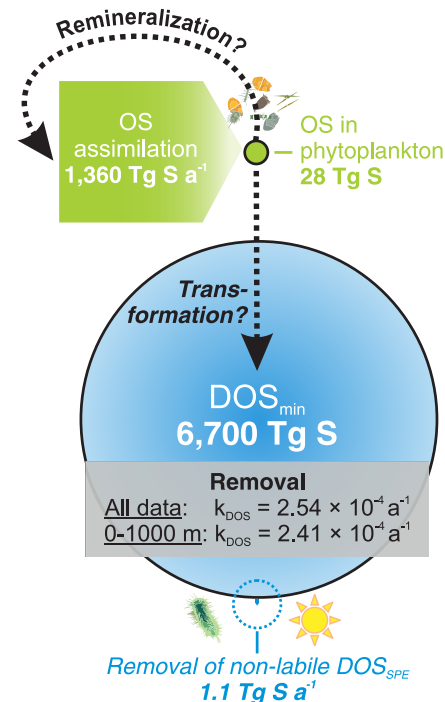
Our results are in agreement with many previous studies reporting microbial alteration of marine DOM composition (3–8). Dittmar and co-workers cited a recent study (9) that showed localized removal of refractory DOC in the deep Pacific. Hansell and Carlson conclude that the removal mechanisms are unknown and hypothesize that (i) the release of exoenzymes by microbial assemblages could lead to uptake of recalcitrant compounds, (ii) solubilization of sinking particles could support cometabolism, or (iii) sinking particles or gel formation could remove refractory DOC. Each of these processes would also contribute to our calculated DOS net removal.

By using radiocarbon age as a measure for mixing, Dittmar *et al.* introduced an inherent inconsistency: On the one hand, they correctly emphasized that bulk radiocarbon age is affected by preferential removal of labile DOM constituents above the pycnocline; on the other hand, they

used radiocarbon age to infer conservative mixing over the entire water column.

Although it is unclear how Dittmar *et al.* “fine-tuned” [caption, figure 2 of (1)] end-member values to match their exponents to our approach, they reproduced our gradients by their mixing models. However, the authors neglected to compare relative differences between their mixing models [see figure 2 of (1)] and the resulting changes in elemental stoichiometry; if it were truly conservative mixing alone, each element would be equally affected. A simple way to illustrate this is to compare relative differences between their end-member concentrations for deep and surface water. The concentrations of  $\text{DOS}_{\text{SPE}}$  ( $0.08 \mu\text{mol L}^{-1}$ ) and  $\text{DON}_{\text{SPE}}$  ( $0.7 \mu\text{mol L}^{-1}$ ) in the deep are 50% lower than surface concentrations ( $0.16$  and  $1.4 \mu\text{mol L}^{-1}$ , respectively), whereas  $\text{DOC}_{\text{SPE}}$  is only reduced by 39%.

Mass spectrometry data from this and previous studies (4, 5) provide independent measures



**Fig. 1. Scale representation of selected marine organic sulfur reservoirs and fluxes.** Circle sizes represent the global sulfur inventory in phytoplankton and the minimum inventory of marine DOS. Squares represent annual fluxes. Removal of nonlabile DOS (within the dotted circle) represents less than one per mil of the annual sulfur assimilation by primary production ( $1360 \text{ Tg S year}^{-1}$ ). Calculating the removal rate for DOS above the pycnocline ( $<1000 \text{ m}$ ), where existence of active removal is indisputable, only marginally reduces the coefficient compared with the calculation for the entire water column calculated in (2) (gray box). The major future scientific challenge is the unaddressed mineralization of organic sulfur derived from primary production and its conversion into nonlabile DOS (black dotted arrows).

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that mixing alone might model but cannot explain complex compositional DOM dynamics. In a mixing-only scenario with two end-members, one would expect a correlation of the peak magnitude for each observed mass with the mixing ratio (and age). Instead, we observed that only 65% of the total peak magnitude in the mass spectra correlated with radiocarbon age, whereas 35% was not correlated.

Although the SPE applied does not recover some of the most polar labile compounds, it does include molecules that are cycling on different time scales in the ocean, which led us to define the term “nonlabile”  $\text{DOS}_{\text{SPE}}$  (2). In the productive surface layer, this is reflected in higher methionine content, younger  $\text{DOM}_{\text{SPE}}$  radiocarbon age and unique sulfur-containing formulas. Thus our  $\text{DOS}_{\text{SPE}}$  removal rate encompasses degradable compounds and processes that are faster than those relevant for refractory DOM alone. It should be noted that in figure 3 of (1), the removal was assigned incorrectly as “refractory” and the sulfate reservoir should be  $1.2 \times 10^9$  Tg S. Most important, the rate demonstrates that 99.9% of the sulfur assimilated is subject to rapid cycling, whereas the nonlabile  $\text{DOS}_{\text{SPE}}$  removal discussed by Dittmar *et al.* only represents a very minor flux (Fig. 1).

Dittmar *et al.* also claimed that persistent sulfonates dominate the DOS pool and mix conservatively in the ocean, based on a previous study using a nonquantitative method in which steric hindrance was excluded a priori (10). Previous studies indeed identified relatively unreactive alkylsulfonates in marine DOM (11), which are potentially derived from anthropogenic surfactants (12). However, other studies, using independent methods, quantified additional reduced sulfur groups such as thioethers (identified as methionine in our data set) and thiols (13), consistent with the fact that the amino acids methionine and cysteine are primary biogenic precursors of DOS.

Dittmar *et al.* overlooked that we explicitly mentioned that the carbon in sulfur-containing compounds most likely cycles on different time scales than bulk DOC. We are well aware that changes in radiocarbon age are likely to be faster than the time elapsed, owing to the removal of the labile and young DOM fraction (5). Such a partitioning effect would have an effect on the absolute number for the net DOS removal (Fig. 1) but cannot support their mixing theory. On the contrary, the insight that DOS cycles faster than DOC supports the presence of a removal process.

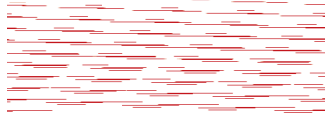
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