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

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Ksionzek et al. (Reports. 28 October 2016, p. 456) provide important data describing the distribution of dissolved organic sulfur (DOS) in the Atlantic Ocean. Here, we show that mixing between water masses is sufficient to explain the observed distribution of DOS, concluding that the turnover time of refractory DOS that Ksionzek et al. present cannot be deduced from their data.

Ksionzek et al. (1) identified dissolved organic sulfur (DOS) as the second-largest pool of sulfur in the ocean. Sulfate is the largest. The surface mixed layer appears to be a site of active production and turnover of semilabile DOS, whereas the deep ocean contains a large pool of refractory DOS. These findings are important contributions to our understanding of the global sulfur cycle.

Ksionzek et al. also estimate that 1.1 Tg of refractory DOS is annually removed from seawater and that the average lifetime of this refractory DOS is more than 2500 years shorter than that of refractory dissolved organic carbon (DOC). Such estimates are potentially of major relevance because they imply that the long-term stability of dissolved organic matter (DOM), still a major conundrum in marine science, is dependent on its elemental composition. Ksionzek et al. also conclude that “DOS degradation kinetics...are determined by a continuum of reactivities...rather than discrete degradation stages.” Unfortunately, Ksionzek et al.’s turnover estimate and associated interpretations are not supported by their data, owing to a conceptual oversight.

In the laboratory, decomposition rates are assessed by incubations in constrained environments (e.g., a bottle) and by fitting kinetic functions to observed changes in concentration versus time (Fig. 1A). It is analogous to the loss of substrate in a Lagrangian water parcel without the effect of ocean mixing. Ksionzek et al. sampled depth profiles in the Atlantic Ocean. They used the estimated radiocarbon age of DOC in these samples as a proxy for incubation time. They then plotted DOC, DOS, and dissolved organic nitrogen (DON) concentrations against DOC radiocarbon age and fitted first-order decay terms to estimate degradation rates (figure S1 in (1)). This approach is problematic because the Atlantic Ocean is not a well-mixed, self-contained volume (Fig. 1A); it is a stratified fluid (Fig. 1B) composed of water masses formed in different regions that are influenced by ocean circulation and mixing processes. Consequently, interpretation of observed profiles requires careful consideration of ocean transport and mixing in addition to the in situ decomposition.

It is a well-established observation that a small fraction of DOM accumulates over decades to form a considerably sized pool of semilabile DOM in the upper ocean (2). Owing to this addition of newly produced DOC, the radiocarbon age of DOC is much lower in the surface mixed layer than in the deeper meso- and bathypelagic ocean (3, 4). Large amounts of semilabile DOM are exported via the “mixed-layer pump” from the surface to mesopelagic depths by the seasonal deepening and shoaling of the mixed layer (5), but because this semilabile pool turns over within decades, it does not contribute to observed gradients in refractory DOC in the bathypelagic (2). In the deep ocean, DOC is on average much longer-lived than in the upper ocean but also represents a range of components with apparent radiocarbon ages from modern to >10,000 years (4, 6, 7).

If decomposition is slower than mixing, then tracer properties in physical systems are largely controlled by the effect of mixing. This is the case for refractory and semilabile DOM, the degradation of which is slower than the mixed-layer pump, suggesting that conservative mixing of DOM between deep and upper ocean waters can explain the vertical distribution of DOC concentrations and radiocarbon ages (4). Also, below the main pycnocline, trends in refractory DOC concentration in the deep Pacific (8) and DOM molecular composition in the deep Atlantic (9) can be explained by conservative mixing without the need for in situ decomposition.

To investigate whether mixing may also explain the trends reported by Ksionzek et al., we modeled...
Fig. 2. A conservative two-source mixing model of surface and deep waters explains the distributions observed by Ksionzek et al. For the mixing calculations, we considered two end-members (gray circles: surface mixed layer and deep ocean), which by themselves are mixtures of multiple constituents. The water of these two end-members was conservatively mixed in our model. The white circles represent 5% mixing increments, from 100% surface water (left) to 100% deep ocean water (right). Despite the linear mixing of water, nonlinear trends emerge if concentrations are plotted versus a property (4). The values of the two end-members match observations and were fine-tuned so that the exponential fits to the mixing curves are identical to the equations provided by Ksionzek et al. for apparent first-order decay. Consequently, the observed preferential accumulation of semilabile DOS in the surface mixed layer cannot be interpreted in the context of long-term DOS turnover in the deep ocean. The slopes (exponents) of the exponential fits vary between DOC, DON, and DOS. This is not a shortcoming of the mixing model but is due to different stoichiometries of semilabile and refractory DOM in the surface and deep ocean, respectively.

Ksionzek et al. made two further untested assumptions for their calculations of DOS turnover rates. First, they assumed that their estimated radiocarbon age for DOC is also representative of DOS age. If DOS cycled faster than DOC, then this would not be the case. Second, they assumed that the time of degradation can be estimated from the radiocarbon age of bulk DOC. However, many labile constituents of marine DOM are young in radiocarbon age (7, 12), and the radiocarbon age of DOC is expected to increase more than the actual time that has elapsed. Thus, DOM decomposition time cannot be derived directly from bulk radiocarbon ages.

Of course, there is likely a sink of refractory DOS in the ocean, but Ksionzek et al.’s estimates of the turnover rate of refractory, deep-ocean DOS are premature and not supported by their data. Specifically, the short time scales of mixing relative to DOM degradation rates void their key assumptions. Mixing has also been neglected in other studies (13), suggesting that other deep-sea DOM gradients may have been misinterpreted (8). As stated previously (4), major observational efforts are required to properly address the uncertainty in water-mediated transport of DOM. Recent work is promising in this context (5), and Ksionzek et al.’s data may be reanalyzed in future coupled reaction-transport models.

REFERENCES

15 December 2016; accepted 7 April 2017 10.1126/science.aan6039
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Science 356 (6340), 813.
DOI: 10.1126/science.aam6039

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