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LETTER

Low-molecular-weight reduced sulfur substances: A major component of nonvolatile dissolved organic sulfur in the Pacific OceanPierre Fourier^{1,2}, Gabriel Dulaquais^{3*}¹Conservatoire National des Arts et Métiers, Intechmer, Cherbourg-en-Cotentin, France; ²LUSAC, Laboratoire Universitaire des Sciences Appliquées de Cherbourg, University Normandie, Cherbourg-en-Cotentin, France; ³Laboratoire des Sciences de l'Environnement Marin CNRS UMR 6539, Institut Universitaire Européen de la Mer, Université de Bretagne Occidentale, Plouzané, France**Scientific Significance Statement**

The role of sulfur (S) regarding the stability of marine dissolved organic matter remains unclear. Direct measurements of dissolved organic S (DOS) compounds are scarce in the ocean, making it difficult to decipher the bioavailability and dynamics of DOS. A combination of size exclusion chromatography and cathodic stripping voltammetry highlights the possibility of such quantification in a new way. Our results show that low-molecular-weight hydrophilic reduced sulfur substances (RSS) are major contributors to the DOS pool. RSS are produced by phytoplankton to prevent oxidative and metal stresses. These compounds are partly remineralized by microheterotrophs to fulfill their S requirement. This microbial alteration of DOM produces a very stable pool of secondary metabolites hydrophilic LMW DOS possibly composed of thioamidated RSS. In deep waters, the homogenous concentration of RSS highlights their recalcitrance to long-term mineralization.

Abstract

The low-molecular-weight (LMW) reduced sulfur substances (RSS) composition of dissolved organic matter (DOM) was examined along the GEOTRACES US-GP15 section in the Pacific Ocean. We demonstrate that LMW RSS constitutes a significant fraction of nonvolatile dissolved organic sulfur (DOS). While thiols such as glutathione were below our detection limit (300 pM), RSS containing two carbon (C) sulfur (S) bonds were present at concentrations in the hundreds of nM range. RSS accumulation was observed in subtropical waters. The most likely source of these RSS is microbial alteration of sulfurized DOM with production of secondary thioamidated metabolites. RSS are initially produced by cyanobacteria to mitigate copper and oxidative stress induced by UV-B irradiance. A preferential remineralization of RSS over dissolved organic carbon (DOC) in the upper 350 m suggests a partial lability of LMW DOS. Deeper, homogeneous concentrations and C : S ratio indicate increasing stability of this LMW DOS.

*Correspondence: gabriel.dulaquais@univ-brest.fr**Associate editor:** Sarah Fawcett**Author Contribution Statement:** Each of the authors contributed equally to the data processing and writing of this manuscript.**Data Availability Statement:** Size exclusion chromatography data and cathodic stripping voltammetry data from this project are available in Dryad (<https://doi.org/doi:10.5061/dryad.d51c5b0bq>).

Additional Supporting Information may be found in the online version of this article.

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Among the ~ 660 Gt of carbon (C) contained in marine dissolved organic matter (DOM), ~ 640 Gt are refractory to bacterial remineralization and persists for thousands of years in the ocean (Hansell et al. 2009). Several hypotheses explaining the high stability of DOM over time were proposed, notably the concept of intrinsic recalcitrance, which suggests that reactivity is determined by the molecular properties and composition of DOM (Jiao et al. 2010; Lechtenfeld et al. 2015; Baltar et al. 2021). It was shown that a low-molecular-weight C to nitrogen ratio reflects a high lability of DOM but it is still not clear regarding sulfur (S). In marine waters, dissolved S is mainly under its oxidized form: sulfate. However, several oceanic microheterotrophs cannot reduce sulfate (Tripp et al. 2008; Dupont et al. 2012), despite a high S demand (Matrai and Eppley 1989). These microorganisms depend on a pool of ~ 6.7 Gt of dissolved organic S (DOS, Ksionzek et al. 2016) to fulfill their metabolism. Consequently, microheterotrophs play a key role in controlling the dynamic of DOS in the ocean (Ksionzek et al. 2016; Levine 2016) and S content in DOM may reflect a certain level of lability. However, in the deep ocean, DOS seems refractory to microbial degradation and only scarce data suggest that S is selectively remineralized compare to C in refractory DOM (Koch et al. 2017; Longnecker et al. 2020; Ibrahim and Tremblay 2023). Abiotic sulfurization of DOM in sulfate-reducing sediments and its subsequent release into the ocean was proposed as a pathway of production of refractory DOS (Pohlabein and Dittmar 2015). During early diagenesis, in sulfide-bearing sediments, organic matter reacts abiotically (reactions additions during H and/or O removal/addition) with inorganic species (sulfides, polysulfides), forming organic S compounds (Damsté et al. 1989; Vairavamurthy et al. 1995; Schmidt et al. 2009). Abiotic sulfurization is a well-known process contributing to the protection of labile organic matter from microbes in fossil deposits (Sinninghe et al. 1998; Kok et al. 2000; Amrani et al. 2007; Bushnev and Burdel'Naya 2009). The release of refractory DOS from superficial sediments (Pohlabein and Dittmar 2015) could balance the slow and continuous mineralization of DOS in refractory DOM (Ksionzek et al. 2016) and induces a change in the chemical nature of DOS as observed by Longnecker et al. (2020). Phillips et al. (2022) indicate that the diffusion of sulfurized dissolved organic matter (DOM) plays a negligible role in the overall distribution of DOS. This is in line with the recent findings from Ibrahim and Tremblay (2023) that the primary origins of water-column and sedimentary DOS are distinct.

The above opposing hypotheses are based on a limited amount of data as the determination of organic S in DOM is complex. On the one hand, total organic S concentrations can be calculated as the difference between total S determined by reductive pyrolysis and sulfate seawater concentration (Cutter et al. 2004; Longnecker et al. 2020). On the other hand, solid-phase extractions (SPE) along with mass spectrometry also provide an estimation of DOS concentrations

(Ksionzek et al. 2016; Phillips et al. 2022). However, this may lead to a bias since SPE fractionate DOM and cannot access the fraction of LMW hydrophilic DOM (Dulaquais et al. 2023). Alternatively, direct determination of reduced sulfur substances (RSS), such as thiourea, cysteine and/or glutathione, can be assessed either directly using cathodic stripping voltammetry technics (Al-Farawati and van den Berg 1997, 2001; Laglera and van den Berg 2003; Pernet-Coudrier et al. 2013) or after SPE and subsequent derivitization in line with high-pressure liquid chromatography (HPLC, Swarr et al. 2016). These RSS are present in the environment at a wide range of concentrations (pM to μ M) and protect eukaryotic cells for from oxidative damage and exposure to toxic metals (Mopper and Kieber 1991; Leal and Van Den Berg 1998; Ercal et al. 2001; Rijstenbil 2002; Sunda et al. 2002; Jacob et al. 2003; Laglera and van den Berg 2003; Dupont et al. 2006; Dryden et al. 2007; Tilliette et al. 2023). RSS, especially thiols, may be exuded by phytoplankton (Leal et al. 1999; Swarr et al. 2016) but they seem mostly originate from heterotroph metabolism (Laglera and Tovar-Sánchez 2012; Mahanta et al. 2019; Moran and Durham 2019). Although RSS play a major role in biogeochemical interactions between S and marine microorganisms (autotrophs and heterotrophs) and have broader ecological roles such as for metal detoxification and microbial signaling (Moran and Durham 2019), their contribution to the pool of DOS in open ocean has, to our knowledge, been quantified only twice by Swarr et al. (2016) and Whitby et al. (2018).

The objective is to evaluate the spatial and vertical contribution of RSS detected by adsorptive cathodic stripping voltammetry (Ad-CSV) to the nonvolatile DOS pool in the Pacific. We study the sources and fate of thiols at large scale. A combination of Ad-CSV and size exclusion chromatography with organic carbon detection (SEC-OCD) datasets contributes to a better understanding of the role of low-molecular-weight (LMW) RSS in the oceanic DOS cycle.

Experimental section

Samples were collected during the cruise GEOTRACES US-GP15 (Fig. 1a). Bulk, high-molecular-weight (HMW) and LMW DOC concentrations were measured by SEC-OCD (DOC-Labor[®]) (Huber et al. 2011; Dulaquais et al. 2018; Fourrier et al. 2022a, 2022b). The analysis of RSS was performed on bulk samples by Ad-CSV at a deposition potential of 0 V (vs. Ag/AgCl) with a deposition time of 180 s (Pernet-Coudrier et al. 2013). Further details on the methods used in this study are provided in the Supporting Information.

Results and discussion

DOC concentrations and fractionation in the Eastern Pacific

Bulk DOC concentrations ranged from $34.9 \pm 1.0 \mu\text{MC}$ at 2633 m depth (20°S; 152°W) to $71.2 \pm 2.2 \mu\text{MC}$ in the

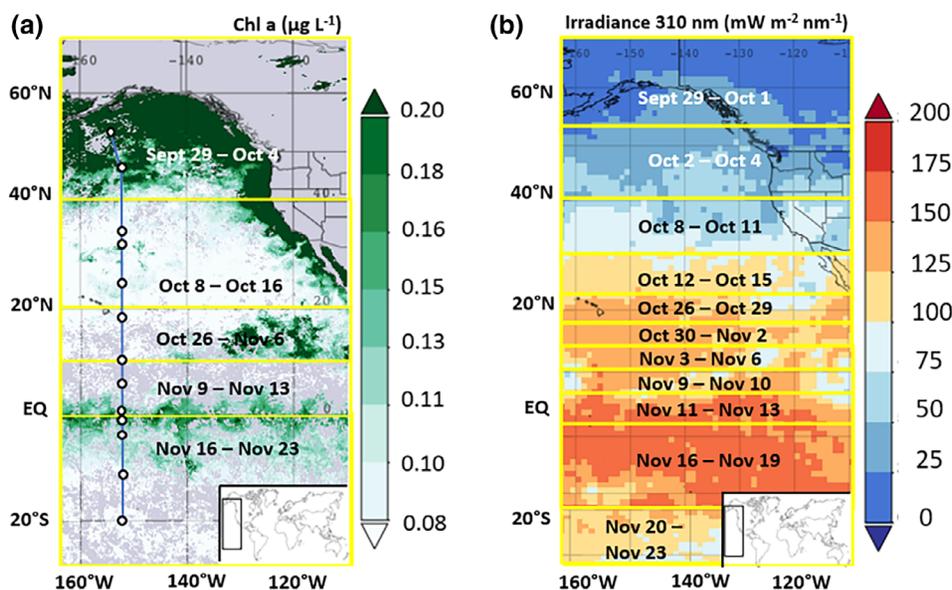


Fig. 1. (a) Location of the transect overlaid on a composite background map of chlorophyll *a* distribution (Chl *a*, $\mu\text{g L}^{-1}$; 8 daily 4-km over September–November 2018, MODIS-Aqua Satellite). Yellow boxes show Chl *a* data by week based on boat advance for the GEOTRACES US-GP15 cruise. (b) Time-averaged map of solar irradiance (310 nm) in the study area ($\text{mW m}^{-2} \text{nm}^{-1}$; daily 1°). Figure generated using Giovanni (giovanni.gsfc.nasa.gov).

euphotic layer at 55 m depth in the northern subtropical gyre (17.5°N ; 152°W). DOC concentrations measured in this study were compared with data from CLIVAR P16N cruise (150°W ; OCADS database, 2006). The vertical distributions of DOC concentrations as a function of depth (m) presented in Fig. 2 include data from the CLIVAR P16N cruise as well as data measured in this study (GEOTRACES transect US-GP15). Data were paired and the distribution clearly shows an overlap between the two datasets along the water column. The scatter plot of the paired data set ($n = 271$) shows a distribution along a 1 : 1 line taking into account the measurement uncertainties (Fig. 2b). A strong correlation ($p < 0.05$) with a R^2 equal to 0.93 between DOC from CLIVAR P16N and our measurements demonstrates that concentrations of DOC measured are consistent with the existing literature. Deviations from the 1 : 1 line mainly correspond to samples from surface waters (15–185 m) and mesopelagic waters (200–1000 m). These differences between the two datasets could be due to temporal changes in biological production or bacterial degradation (Cherrier et al. 1996; Thingstad et al. 1997; Morris et al. 2005; Carlson et al. 2007). This result confirms the relevance of using SEC for DOC determination in oceanic environment (Fourrier et al. 2022a). Preliminary results of DOC size fractionation along the section are presented Fig. 2a. It clearly shows that HMW DOC was only significant ($3\% \pm 2\%$ of bulk DOC) in the upper 100 m of the water columns. The LMW hydrophilic DOC, that mostly escapes SPE using styrene divinyl benzene polymer resin (PPL) sorbent (Dulaquais et al. 2023), accounted for $28.8\% \pm 5.8\%$ of bulk DOC all along the water column. All the RSS that can be detected by the Ad-CSV method we used (glutathione, cysteine, *N*-acetyl

cysteine, thioacetamide, thiourea) eluted in this fraction. These results imply that RSS are LMW hydrophilic compounds and may not be accurately recovered from seawater samples after SPE using PPL sorbent.

Reduced sulfur species in the Eastern Pacific

Electrochemical analyses of RSS using 180 s of deposition time revealed the systematic occurrence of a peak at -0.193 V (vs. Ag/AgCl) in all analyzed samples ($n = 395$). This peak is typical of the thioacetamide (TA) electrochemical response and can be related to thioamidated compounds with thioamide and thiocarbonyl functional groups. Quantification of this peak using TA as external standard (referred as TA-like in the next sections) revealed concentrations ranging from $117.6 \pm 14.1 \text{ nMeqTA}$ at 125 m in the equatorial area to $1140.4 \pm 136.8 \text{ nMeqTA}$ at 25 m in the north subtropical gyre (Fig. 3). The TA-like distribution showed high concentrations in the upper 100 m ($652 \pm 213 \text{ nMeqTA}$, $n = 48$), decreasing in the upper mesopelagic zone (343 ± 180 , $n = 95$ at depth deeper than 100 m) and reaching stable concentration ($235 \pm 41 \text{ nMeqTA}$; $n = 252$ at depths deeper than 600 m) (Fig. 3). In deep waters ($> 600 \text{ m}$), neither significant variation or correlation with hydrographic (e.g., temperature, salinity, O_2) nor biogeochemical (nutrients) parameters were observed. The distribution of TA-like compounds we report in this study suggests a biogenic production of these RSS in surface and particularly in oligotrophic waters (Fig. 3). The rapid decrease of TA-like at the 100-m horizon indicates a partial lability of freshly produced TA-like compounds. The homogenous concentration in the deep sea (Fig. 3) indicates that a fraction of the TA-like pool becomes refractory to long-term

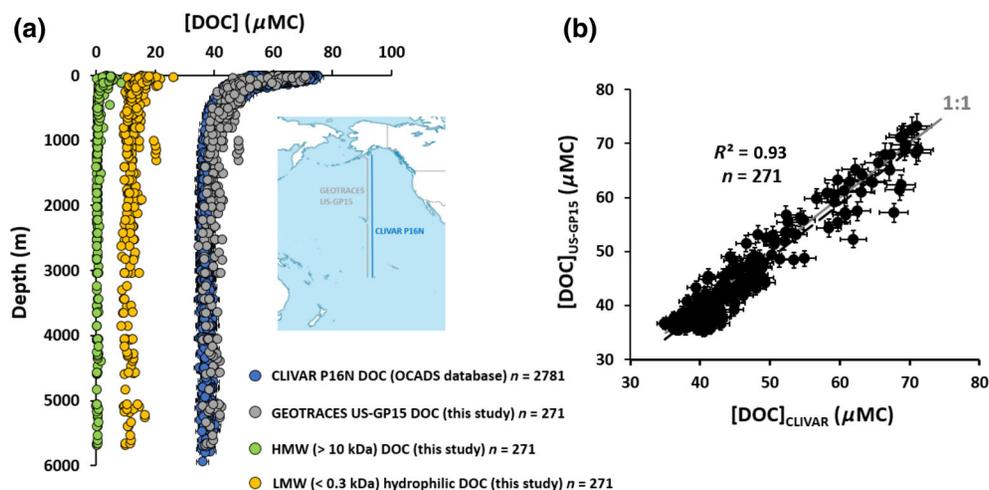


Fig. 2. (a) Vertical profiles of DOC (μMC) vs. depth (m) for the campaigns CLIVAR P16N (Swan et al., 2009; deep blue dots), and GEOTRACES USGP15 (this study; gray dots). High-molecular-weight (HMW) DOC (> 10 kDa; green dots) and low-molecular-weight (LMW) DOC (< 0.3 kDa; yellow dots) are also represented for this study. (b) Comparison between the two datasets for global DOC. The observed data were paired with historical data by station and depth.

remineralsation during microbial alteration of DOM in the mesopelagic zone. Biologic origin of TA-like compounds is in agreement with the previous work of Leal et al. (1999). Direct production/excretion may not be the main production pathway of TA-like compounds. These compounds are probably thioamidated secondary metabolites from S-containing molecules such as, but not restricted to, methanobactin (Kenney et al. 2018), thioholgamide (Kjaerulff et al. 2017), and thioalbamide (Frattaruolo et al. 2019).

Differently to TA-like compounds, electrochemical signal of cysteine-like and glutathione-like compounds were only detected one and three times at subnanomolar levels. The low-detection rate of these thiols may be related to their subnanomolar to picomolar concentrations in oceanic

waters (Swarr et al. 2016; Whitby et al. 2018) as our limit of detection was 0.3 nM at the deposition time we used (Pernet-Coudrier et al. 2013). The difference of abundance between TA-like and these thiols can be related to their specific reactivity and stability.

This difference may partly originate from the internal C–S bonds of these compounds with TA-like compounds having a double C–S bond (among others thioamide and thiocarbonyl functional groups), while cysteine-like and glutathione-like have single C–S bond. The stability of C–S single bonds ($< 300 \text{ kJ mol}^{-1}$) is low in oxygenated environments. Indeed, radical substitutions can lead to dissociation of the C–S bond within thiols (Rudyk and Eaton 2014). Among TA-like compounds, thioamide have a C–S double bond

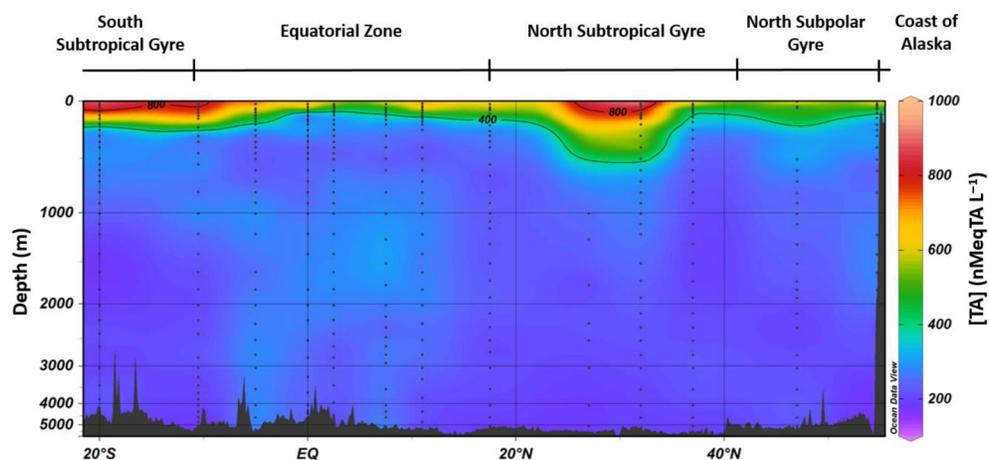


Fig. 3. Spatial and vertical distribution of sulfur compounds of thioacetamide type (TA; nMeqTA L^{-1}) along the GEOTRACES US-GP15 section (152°W).

conjugated to a nonbonding doublet of the nitrogen atom making them more stable, potentially explaining their detection in all the analyzed samples.

Surface waters (< 100 m) of the subtropical gyres and equatorial area showed RSS concentrations significantly higher than in the subpolar gyre displaying a north to south meridional gradient of concentration (Fig. 3). Subpolar, north subtropical, equatorial, and south subtropical surface waters displayed concentrations of 537 ± 168 ($n = 10$), 640 ± 256 ($n = 13$), 646 ± 199 ($n = 18$) and 853 ± 41 ($n = 7$) nMeqTA, respectively. The mean irradiance at 310 nm along the section during the cruise (Fig. 1b) shows a north to south gradient of surface waters exposition to UV-B. These observations are in line with the biological importance of RSS in the regulation of oxidative (Ercal et al. 2001; Rijstenbil 2002; Sunda et al. 2002) and copper (Whitby et al. 2018) stresses. Furthermore, it is likely that high levels of TA-like observed in the subtropical gyres reflect high production of RSS by cyanobacteria combined with continuous alteration and accumulation in these stratified domains.

Cellular oxidative damages on lipids, proteins, and DNA result from direct UV-B solar exposure or by indirect oxidative damages from reactive oxygen species (ROS) induced by UV-B irradiance (He and Häder 2002). Inside the phytoplankton cell, thiols can react with ROS lowering the intracellular concentration of hydroxyl, peroxy and superoxide radicals (Weiss 2005; Regoli and Giuliani 2014). Production of RSS compounds is a possible way for microorganisms to protect themselves from post-transcriptional oxidative modification of proteins (Rudyk and Eaton 2014). Large phytoplankton (diatoms) develop mostly in the subpolar gyre (Harrison et al. 1999) and the equatorial zone (Chavez et al. 1990) of the Pacific, while cyanobacteria (mainly *Prochlorococcus* and *Synechococcus*) dominate phytoplankton in the subtropical gyres (Winn et al. 1995; Ras et al. 2008). The surface gradient of RSS we measured from north to south (Fig. 3) may indicate the meridional variation in how the various phytoplankton communities respond to mitigating the production of ROS induced by UV-B radiation. On the one hand, for the subtropical gyres, increased sunlight exposure would lead to higher levels of ROS (Mopper and Kieber 2000). Consequently, there would be an increase in the biological production of RSS as a response to the induced oxidative stress (Latifi et al. 2009). This cellular response was observed in various thiol-related studies in the literature (Apel and Hirt 2004; Dupont et al. 2004; Bertini 2007; Fahey 2013). On the other hand, cloud cover and less sunlight in the subpolar gyre would not catalyze as much ROS production (Scully et al. 1996; Johannsson et al. 2017) resulting in a lower RSS production. Furthermore, diatoms that develop in the subpolar gyre and the equatorial zone may be less sensitive to these stresses compared to cyanobacteria from the subtropical gyres. These latter prokaryotic species have a single membrane that would make them more sensitive to oxidative stress and solar irradiation

compared to diatoms (Murphy 1983; Tyrrell 1991; Lesser 2006; Llabrés and Agustí 2006; Agustí and Llabrés 2007).

Cyanobacteria are also likely major producers of RSS for metal detoxification and acquisition (Singh et al. 1999; Tilliette et al. 2023). Among RSS, thiols are a major class of ligand particularly for the complexation of dissolved copper (dCu). Thiols limits the toxicity of this element to phytoplankton by lowering ambient copper ion (Cu^{2+}) concentrations (Florence and Stauber 1986; Rijstenbil et al. 1998; Morelli and Scarano 2004; Dulaquais et al. 2020). Alternatively, they can increase the bioavailability of dCu (Walsh et al. 2015). Thereby, thiols enhance acquisition or reduce toxicity of Cu^{2+} depending on phytoplankton species. The distribution of total dCu and labile dCu along GP15 section reported by Moriyasu et al. (2023) provides further perspective onto the links between RSS, Cu, and UV irradiation. According to authors, labile dCu (the more bioavailable fraction) accumulates in the stratified subtropical waters. This accumulation is probably induced by a continuous photochemical decomposition of an inert fraction of dCu. In these waters, cyanobacteria that have a low resistance to Cu toxicity (Brand et al. 1986) may enhance their production of RSS to keep Cu^{2+} at subpicomolar levels. This mechanism is in agreement with the high RSS concentrations we report in the subtropical domains. In addition, the previous works from Whitby et al. (2018) and Ruacho et al. (2020) in the Pacific showed higher dCu and Cu^{2+} in the surface waters of the subpolar gyre than in the equatorial waters. In these conditions, phytoplankton may experience a higher copper stress, in terms of scarcity, in the equatorial waters than in the subpolar waters. This would have induced the higher production of RSS for Cu^{2+} acquisition in the equatorial waters compared to the subpolar gyre resulting in the difference of concentration of RSS we observed (Fig. 3).

Contribution of RSS to DOS in the Eastern Pacific

To compare the DOS contained in RSS to bulk DOS, TA-like concentrations in nMeqTA were directly converted into nM of equivalent nonvolatile reduced DOS (RSS-DOS) by assuming $1 \text{ mol eq-TA} = 1 \text{ mol DOS}$. This assumption relies on the mechanism of TA quantification by the CSV method we used (see Supporting Information) and consider that almost all S functional groups in RSS are electroactive. Briefly during CSV analysis, the sulfur is adsorbed on the working electrode, forming a S-Hg complex. Then, during the voltammetric stripping scan, the complex is reduced creating a quantitative current proportional to the amount of electroactive S atoms adsorbed. A scheme is proposed in Supporting Information Fig. S2. The resulting TA-like DOS (117.6–1140.4 nM RSS-DOS, Fig. 4a) concentrations are lower than the scarce data reported in the literature for the West Atlantic total organic sulfur (43.8–1275.1 nM, TOS; Longnecker et al. 2020) and higher than DOS isolated by SPE using PPL (SPE-DOS) in the East Atlantic (59–201 nM-SPE-DOS; Ksionzek et al. 2016). Our

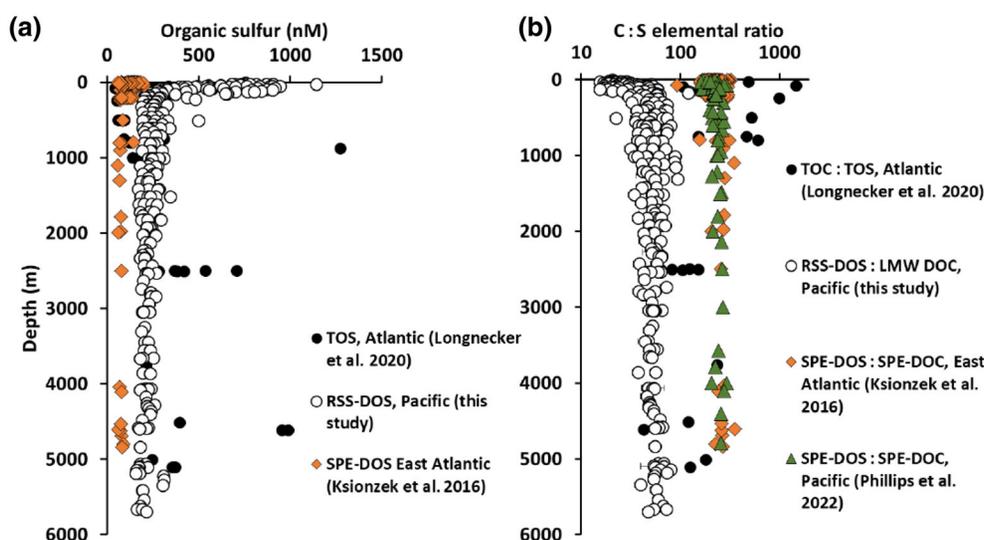


Fig. 4. Compiled data along with depth of (a) organic sulfur concentrations for total (black dots), LMW RSS (white dots) and SPE (orange diamonds) in the Atlantic and the Pacific. (b) Carbon : sulfur (C : S) elemental ratios for total (black dots), LMW RSS (white dots) and SPE (orange diamonds, green triangles) in the Atlantic and the Pacific.

result indicates that RSS-DOS (LMW hydrophilic) is a major contributor to bulk DOS and is at least as large as the SPE-DOS reservoir (LMW hydrophobic). The lower SPE-DOS concentrations than TA-like DOS is probably due to the incapacity of SPE using PPL to isolate LMW thiols and other RSS (Pohlabein and Dittmar 2015; Gomez-Saez et al. 2017), resulting in a low recovery of hydrophilic DOS by the SPE technic.

We then calculated the C : S ratios of LMW hydrophilic DOM (e.g., LMW DOC : RSS-DOS). Ratios ranged from 15 ± 10 to 121 ± 50 (Fig. 4b). These C : S are significantly lower than those reported for the West Atlantic TOS (38.0–1472.6, Longnecker et al. 2020) and DOM isolated by SPE (SPE-DOM) in the East Atlantic (92.7–351.4; Ksionzek et al. 2016) and the Pacific (160–303; Phillips et al. 2022) further suggesting LMW hydrophilic compounds as a major reservoir of DOS. The C : S ratios of LMW DOM were low in the shallowest waters and reached a threshold of 50 at 350 m. The sharp increase of C : S from the euphotic layer to the mid mesopelagic zone indicates a selective consumption of S compared to C in LMW DOM by microheterotrophs to fulfill their S requirement. Deeper C : S ratios kept a quasi-homogenous values of 56 ± 9 ($n = 240$) down to the most abyssal waters (Fig. 4). It indicates a strong stability of this DOS reservoir, without preferential remineralization of S over C with time at these depths. This apparent discrepancy with Ksionzek et al. (2016) and Longnecker et al. (2020) may indicate difference of lability between the DOS pools and oceanic basins. It could also reflect the long-term removal of nonlabile DOS (Ksionzek et al. 2016). According to size reactivity continuum, LMW DOM is often considered as less labile than high-molecular-weight compounds (Benner and Amon 2015; Walker et al. 2016). Our data suggest that LMW

hydrophilic DOS is an important pool of bioavailable DOS for microheterotrophs. This study suggests that the refractory nature of LMW DOM is not intrinsic but emerges from biological processes occurring in the mesopelagic zone in line with Dittmar et al. (2021).

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