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Supplementary Information for

Novel sulfur isotope analyses constrain sulfurized porewater fluxes as a minor component of marine dissolved organic matter.

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Other supplementary materials for this manuscript include the following:

Datasets S1

Station Specific Methods

N Atlantic Gyre. Samples (*n* = 12) of 10 L were collected aboard the *R/V Atlantic Explorer* at BATS Station (31° 40'N, 64° 10'W) during the October 2020 leg of the Bermuda Atlantic Time Series (BATS) cruise (Figure S1). Nutrient and DOC* concentrations were provided by the Bermuda Atlantic Time Series, with details available online: http://bats.bios.edu/. *Note: the BATS protocols measure total organic carbon, which (due to low particulate organic matter in the gyre) are indistinguishable from dissolved organic carbon. We therefore use DOC, rather than TOC, for consistency with the rest of the manuscript.

NE Pacific OMZ Samples were collected aboard the *R/V Oceanus* on two cruises to the NE Pacific oxygen minimum zone (OMZ) region off the coast of Mexico in April 2017 and June 2018 (Figure S2). Samples were collected from five sites across the two cruises: Station 2 (16° 30'N, 107° 12'W; *n*=10), Station 3 (16° 00'N, 110° 00'W; *n*=7), Station 4 (21° 30'N, 109° 30'W; *n*=5), Station 5 (24° 41'N, 113° 17'W; *n*=7), and Station 6 (27° 23'N, 117° 30'W; *n*=1). Station 6 was only sampled in 2017. Stations 3 and 4 were only sampled in 2018. Stations 2 and 5 were sampled in both years. 20 L of seawater was extracted per depth on the 2017 cruise, and 5 L of seawater per sample on the 2018 cruises. One additional sample was collected in April 2018 aboard the *R/V Western Flyer* at Station M (34° 30'N, 123° 00'W; *n*=1): this 15L sample was collected by ROV *Doc Ricketts* 1 m above the seafloor. Details on nutrients and DOC measurements are detailed elsewhere (1).

NE Pacific and NE Pacific Shelf Seawater samples for DOM_{SPE} analysis were collected aboard the *R/V Sally Ride* at two stations in the NE Pacific off the coast of Southern California in November 2020 (Figure S3): on the shelf (33° 11'N, 118° 37'W; *n* = 7) and offshore (32° 33'N, 120° 31'W; *n* = 12). ~7-9 L of seawater was collected per sample. No nutrient or DOC data are reported from these cruises.

N Pacific Gyre Samples (*n* = 12) were collected aboard the *R/V Kilo Moana* at Station ALOHA (22° 45'N, 158° 00'W) during the November 2020 leg of the Hawaii Ocean Time-series (HOT; Figure S4). 10 L seawater samples were collected for DOM_{SPE} analysis. Metadata was provided by the Hawaii Ocean Time-series, which are available publicly or by request. Details on methodology can be accessed online: https://hahana.soest.hawaii.edu/hot/protocols/protocols.html.

San Pedro Basin Samples (*n*=9) were collected aboard the *R/V Yellowfin* on the February 2021 leg of the San Pedro Ocean Time-series (SPOT) cruise off the coast of Southern California to one station (33° 33'N, 118° 24'W; Figure S5). ~7-9 L seawater were collected for DOM_{SPE} analysis per sample. Nutrient data was provided by the San Pedro Ocean Time-series and is available online or by request. Details on methodology can be accessed online: https://dornsife.usc.edu/spot/methods/.

S Pacific Gyre Seawater samples (*n*=7) of 5-7 L were collected aboard the *R/V Ronald Brown* during the first leg of the P18 GO-SHIP (US Global Ocean Ship-based Hydrographics Investigations Program) cruise at a single station (12° 59'S, 103° 00'W) in November to December 2016 off the coast of Peru (Figure S6). Nutrient data from this cruise is available online at https://cchdo.ucsd.edu/ while DOC measurements followed the same protocols as the NE Pacific OMZ samples (1).

Caeté Estuary and Caeté Estuary Porewater Water samples were collected by boat in the dry season of October 2018 along a 35 km salinity transect from riverine (1° 1'S, 46° 45'W) to marine (0° 54'S, 46° 36'W), ending at the Amazonian mangrove-fringed estuary near Bragança City (Pará State, Brazil) in the Caeté Estuary (2). Porewater samples (~3-6 L) were taken in a tidal creek close to the marine end of the transect, at the mangrove-fringed estuary. Water samples were filtered using a thoroughly pre-rinsed 1.0 µm Causapure filter cartridge (CPR-001-09-DOX, PP, Infiltec). DOC and nutrient data are not reported for these stations.

North Sea Porewater Porewater from an anoxic intertidal flat was collected in the Northern German Wadden Sea at the Janssand site close to the barrier island Spiekeroog in 2010 (3). Samples were collected in 10 L acid-cleaned polycarbonate carboys after digging a hole and scooping porewater out of the holes. The samples were filtered through pre-combusted (450°C, 4 hours) glass fiber filters (Whatman 1 µm GMF and 0.7 µm GFF) and solid phase extracted (4). DOC and nutrient data are not reported for these stations.

Station Specific Results

N Atlantic Gyre. Samples were analyzed between 5 and 4800 m water depth (Figure S8). $\delta^{34}S$ values decreased with depth from a maximum of 18.9‰ in the surface (5 m) to a minimum value of 14.9‰ below the photic zone. C:S ratios generally increased with depth, from a surface minimum of 191 to a maximum value of 303 in the deep ocean (2000 m). DOM_{SPE} $\delta^{13}C$ values were constant with depth, averaging -22.3 ± 0.1‰.

NE Pacific OMZ Samples were collected at six stations largely within the upper 150 m of the water column (Figure S9). DOM_{SPE} $\delta^{34}S$ values showed no change with depth in the upper 150 m, averaging 19.0 ± 0.5‰. Deeper samples were limited, but within error, averaging 18.0 ± 1.0‰. DOM_{SPE} $\delta^{13}C$ values were also constant with depth, averaging -22.2 ± 0.3‰. C:S values generally decreased with depth but had a large range in the surface ocean (< 150m), between 166 and 291. Variations in C:S values and $\delta^{34}S$ values were not related to station number or sampling year. NE Pacific OMZ samples displayed no correlation with dissolved oxygen concentrations, which ranged from ~0 to 250 µM across the sample set (Figure S10). However, samples did show a significant negative correlation between $\delta^{34}S$ values and C:S ratios (R^2 = 0.47, P<.001).

NE Pacific and NE Pacific Shelf Samples were analyzed from between 5 and 1275 m on the shelf and between 5 and 3790 m in the coastal ocean (Figure S11). Carbon isotopes were similar across stations, with lower DOM_{SPE} $\delta^{13}C$ values in the upper 150 m (-22.6 ± 0.3‰) than below the photic zone (-22.1 ± 0.1‰). $\delta^{34}S$ values were largely constant in the NE Pacific, averaging 17.9 ± 0.5‰ throughout the water column. Meanwhile, $\delta^{34}S$ values from the NE Pacific shelf decreased from a maximum of 19.1 ± 0.2‰ to 15.0 ± 0.2‰ from surface to deep. DOM_{SPE} C:S ratios fluctuated, with a minimum of 160 ± 4 to a maximum of 275 ± 3.

N Pacific Gyre Samples were analyzed between 5 and 4800 m (n =12; Figure S12). DOM_{SPE} $\delta^{13}C$ values were constant throughout the water column, averaging -22.7 ± 0.1‰. DOM_{SPE} $\delta^{34}S$ values were also fairly constant, with an average of 18.1 ± 0.8‰, but with higher variability. C:S ratios were similarly variable, with an average of 230 ± 25. $\delta^{34}S$ values were also negatively correlated with C:S ratios (R^2 = 0.47, P<.05).

San Pedro Basin Samples were analyzed between 2 and 880 m (Figure S13). San Pedro is a persistently hypoxic (<1 mL/L dissolved oxygen) restricted basin off the coast of Los Angeles, Southern California. DOM_{SPE} samples showed no change in $\delta^{13}C$ values, averaging -22.5 ± 0.2‰. In contrast, C:S ratios and $\delta^{34}S$ values were strongly dependent on depth. C:S ratios increased from 153 ± 3 in the surface (2 m) to 287 ± 6 at depth (880 m) while $\delta^{34}S$ values from the same depths decreased from 18.6 ± 0.2‰ to 16.7 ± 0.3‰. C:S and $\delta^{34}S$ values were also significantly negatively correlated (R^2 = 0.71, P<.01).

S Pacific Gyre Samples were analyzed between 435 and 4411 m (Figure S14). DOM_{SPE} $\delta^{13}C$ values fluctuated between a minimum of -22.7 ± 0.1‰ and a maximum of -21.5 ± 0.1‰, although without depth dependence. DOM_{SPE} $\delta^{34}S$ values decreased from 18.1 ± 0.2‰ to 16.7 ± 0.2‰ with depth while C:S ratios increased from 235 ± 3 to 277 ± 3.

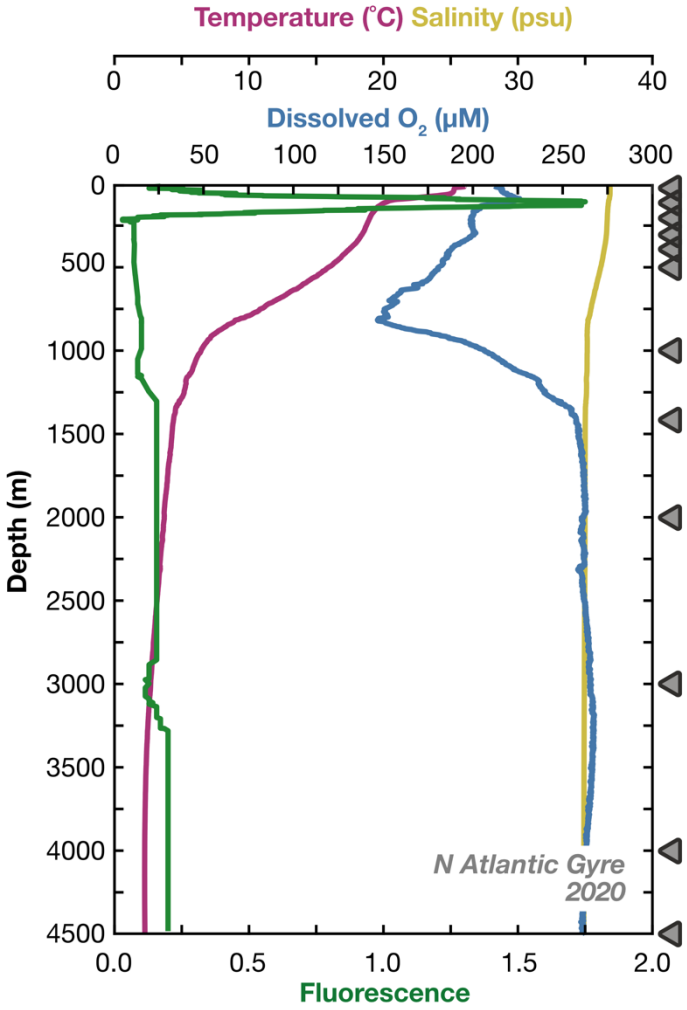

Fig. S1. CTD profile from October 2020 Bermuda Atlantic Time Series cruise at BATS station in the N Atlantic Gyre. Profiles of salinity (psu, yellow line) and temperature (˚C, magenta line) are plotted on the upper x-axis, dissolved oxygen concentration (µM, blue line) on the second upper x-axis and fluorescence (relative fluorescence units) in green on the lower x-axis. Sampling depths for DOM are marked on the right side of the y-axis with grey triangles.

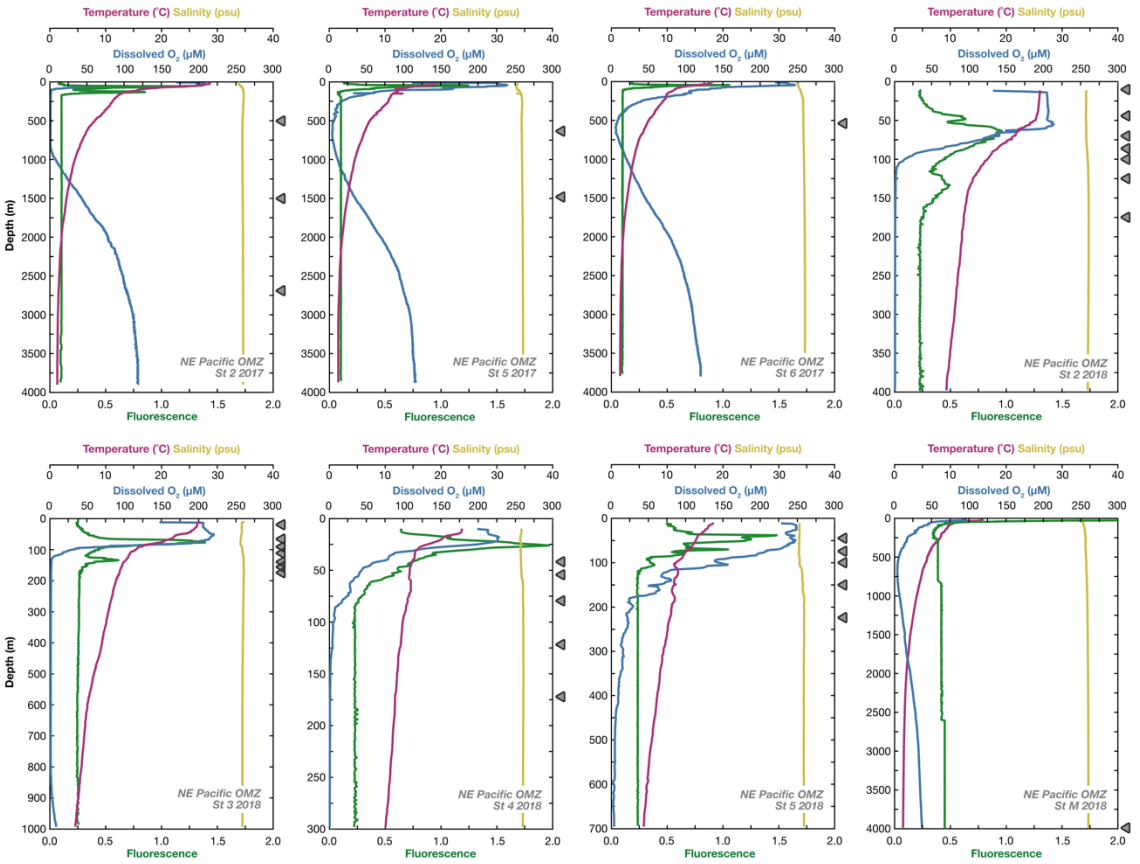

Fig. S2. Physical properties from stations sampled in the NE Pacific OMZ from 2017-2018. Note that while x-axes are constant for each subplot, y-axes are not. Colors and units are the same as Figure S1. Sampling depths for DOM are marked on the right side of the y-axis with grey triangles.

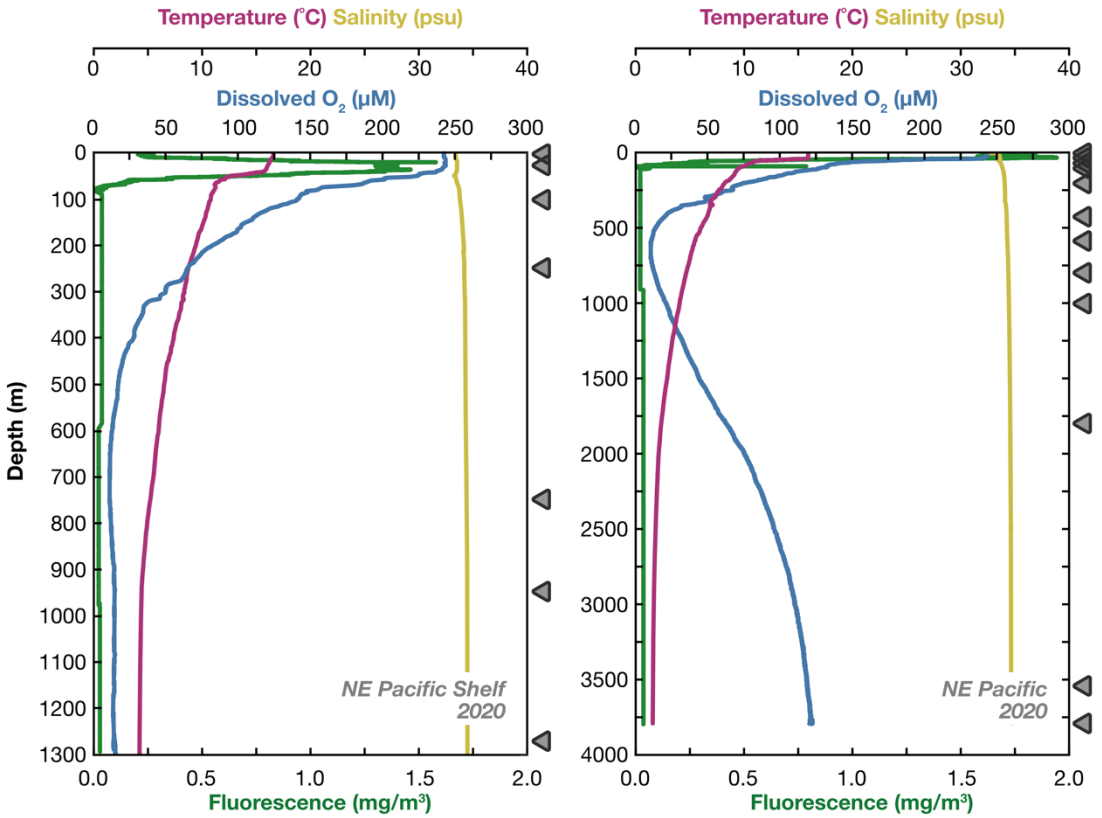

Fig. S3. CTD profile from November 2020 cruise to the NE Pacific and NE Pacific shelf. Note the change of scale in the y axis. Colors and units are the same as Figure S1. Sampling depths for DOM are marked on the right side of the y-axis with grey triangles.

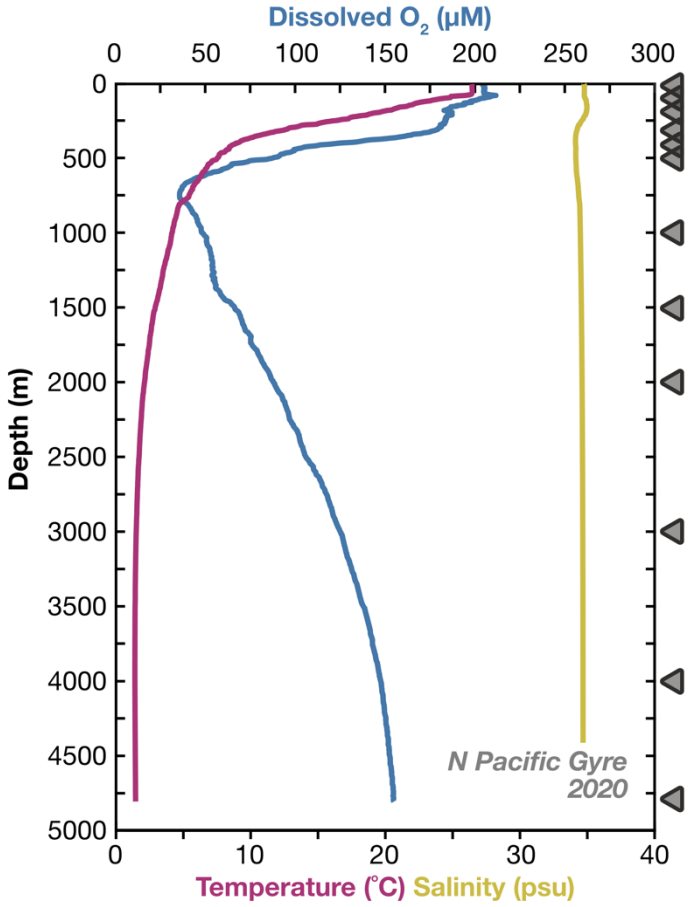

Fig. S4. CTD profile from November 2020 Hawaii Ocean Timeseries cruise at Aloha station in the N Pacific Gyre. Colors and units are the same as Figure S1. Sampling depths for DOM are marked on the right side of the y-axis with grey triangles.

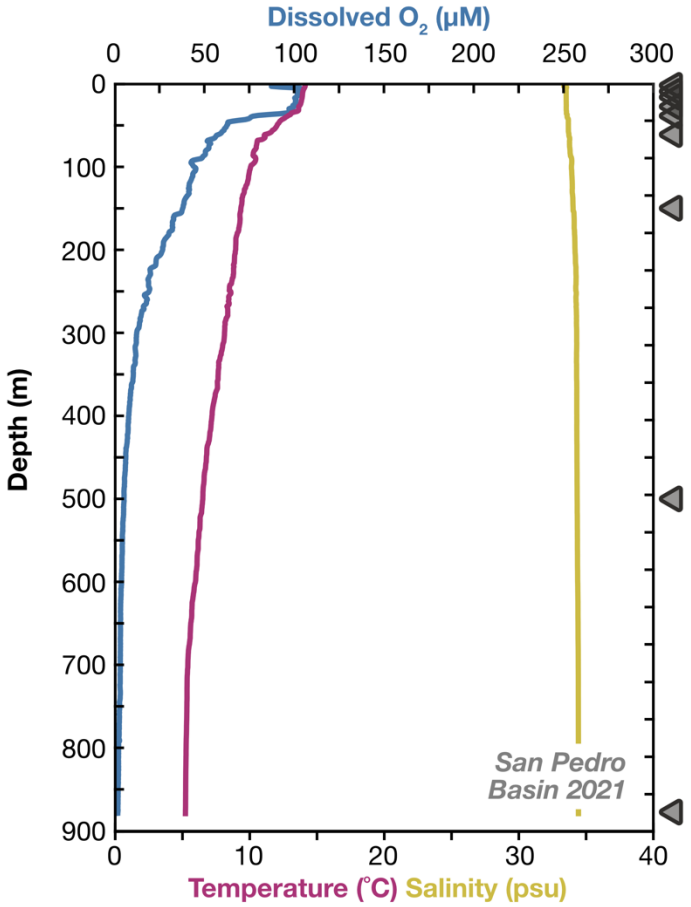

Fig. S5. CTD profile from San Pedro Basin during the February 2021 SPOT cruise. Colors and units are the same as Figure S1. Sampling depths for DOM are marked on the right side of the y-axis with grey triangles.

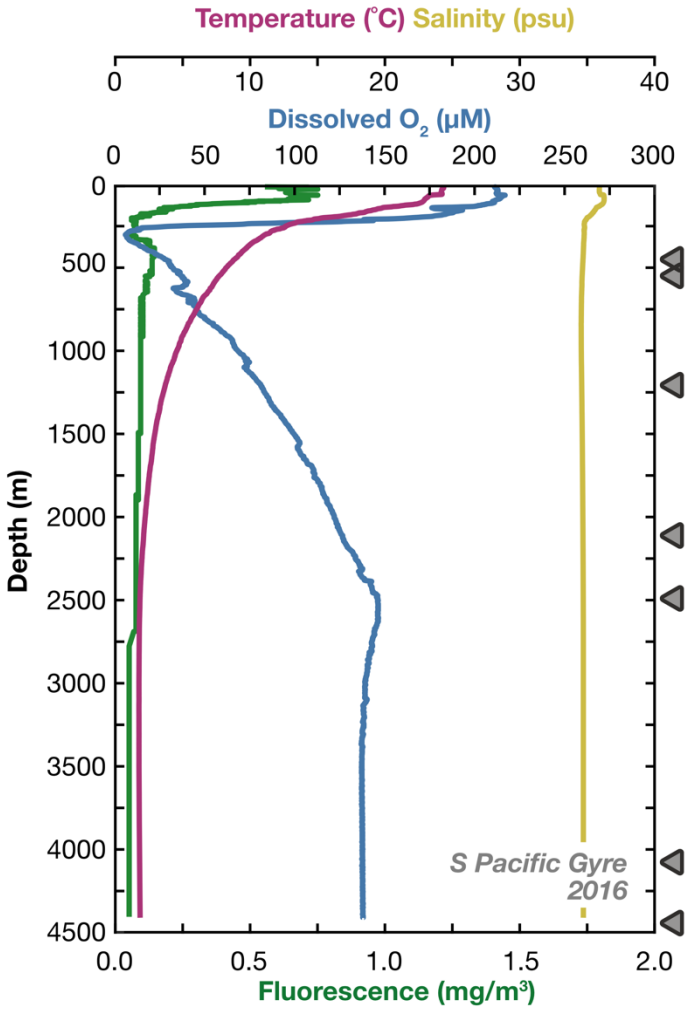

Fig. S6. CTD profile from November 2016 GO-SHIP cruise to the S Pacific Gyre. Colors and units are the same as Figure S1. Sampling depths for DOM are marked on the right side of the y-axis with grey triangles.

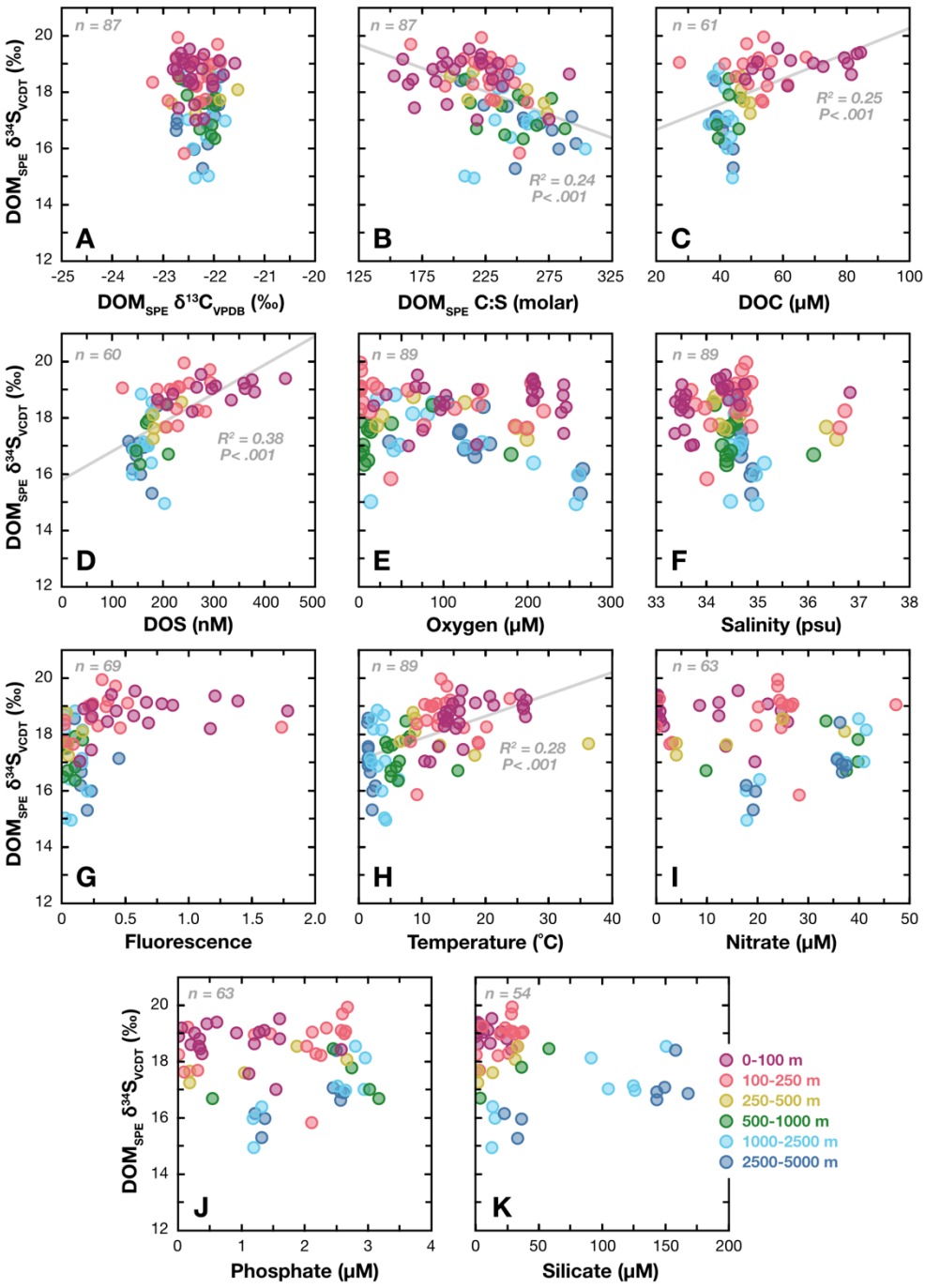

Fig. S7. Metadata analysis of potential correlations between DOM$_{SPE}$ δ^{34}S values against (A) δ^{13}C values, (B) C:S ratios (C) DOC (D) DOS calculated from DOS (apparent DOS) and DOM$_{SPE}$ C:S (E) oxygen (F) salinity (G) CTD fluorescence (a proxy for chlorophyll a) (H) temperature (I) nitrate (J) phosphate and (K) silicate. Only C:S ratios had a significant negative correlation with δ^{34}S values. Temperature and DOC were positively correlated. However, C:S ratios, δ^{34}S values, temperature, and DOC concentration all also vary with depth. Samples from different depths were binned into 0-100 m (magenta), 100-250 m (pink), 250-500 m (yellow), 500-1000 m (green), 1000-2500 m (light blue), and 2500-5000 m (dark blue).

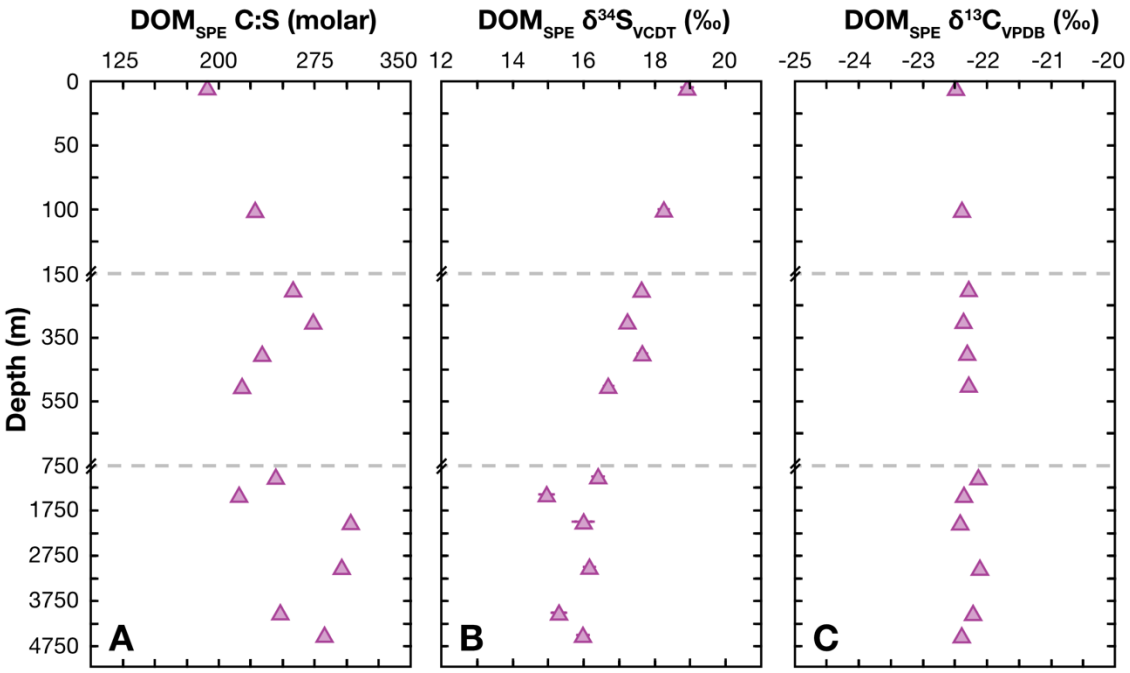

Fig. S8. DOM samples from the N Atlantic Gyre against depth for (A) C:S ratios, (B) $\delta^{34}S$ values (C) $\delta^{13}C$ values. Note the scale breaks at 150 m 750 m on the y-axis. 1σ standard errors are shown for $\delta^{34}S$ values, but error bars for C:S and $\delta^{13}C$ values are within the size of the symbol.

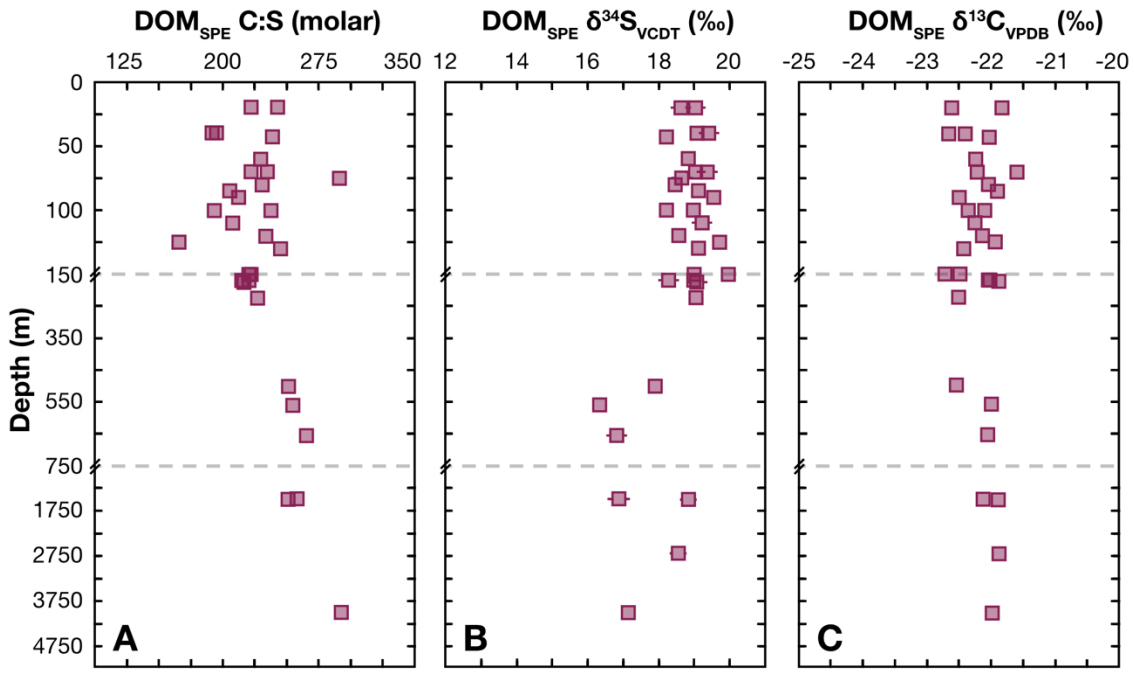

Fig. S9. DOM samples from the NE Pacific OMZ against depth for (A) C:S ratios, (B) $\delta^{34}S$ values (C) $\delta^{13}C$ values. Note the scale breaks at 150 m 750 m on the y-axis. 1σ standard errors are shown for $\delta^{34}S$ values, but error bars for C:S and $\delta^{13}C$ values are within the size of the symbol.

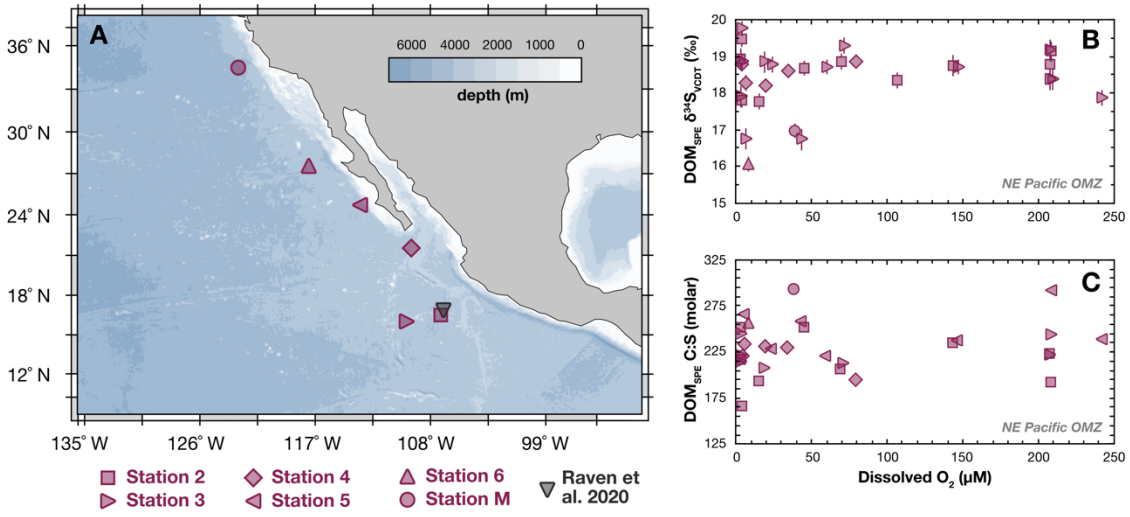

Fig. S10. Map (A) of NE Pacific OMZ sampling locations in this study (magenta shapes), with the sampling site from Raven et al. 2020 (5) marked with a dark grey inverted triangle. Oxygen concentration is plotted against DOM_{SPE} (B) $\delta^{34}S$ values and (C) C:S ratios.

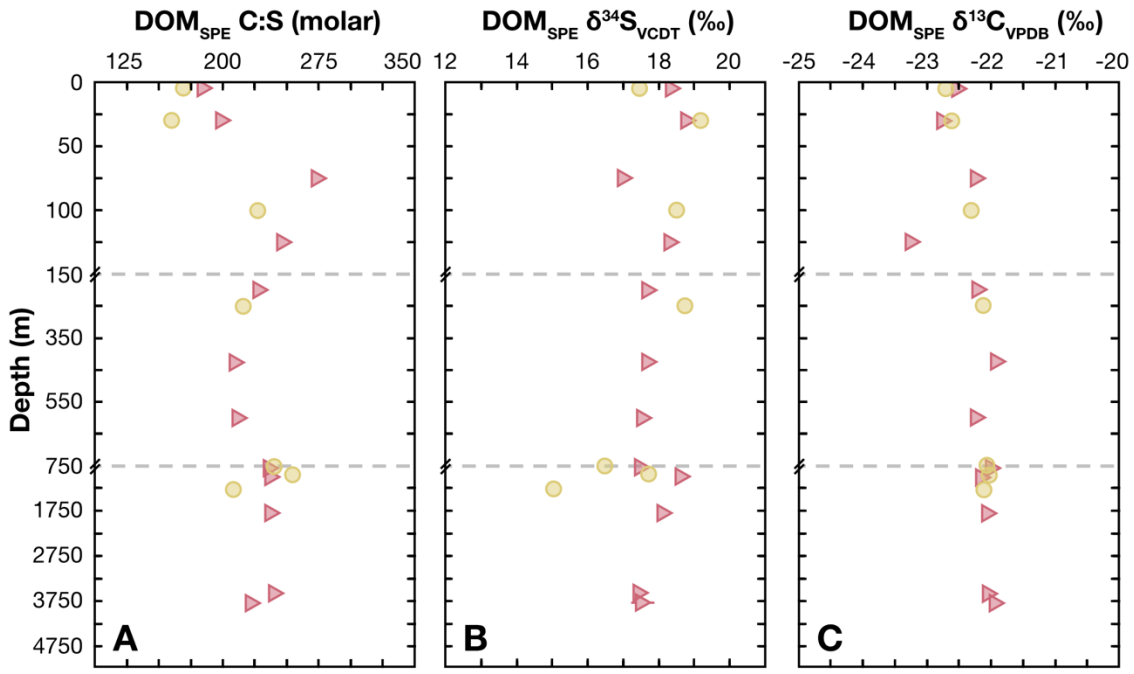

Fig. S11. DOM samples from the NE Pacific (light pink right-facing triangles) and NE Pacific Shelf (yellow circles) against depth for (A) C:S ratios, (B) $\delta^{34}S$ values (C) $\delta^{13}C$ values. Note the scale breaks at 150 m 750 m on the y-axis. 1σ standard errors are shown for $\delta^{34}S$ values, but error bars for C:S and $\delta^{13}C$ values are within the size of the symbol.

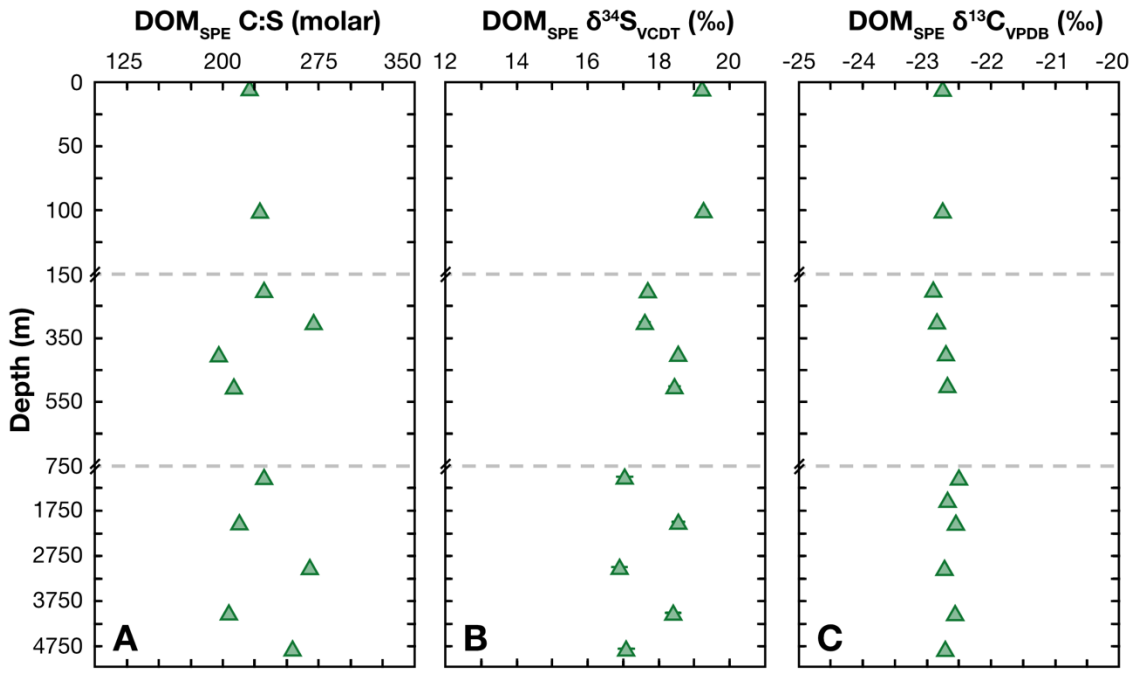

Fig. S12. DOM samples from the N Pacific Gyre against depth for (A) C:S ratios, (B) $\delta^{34}S$ values (C) $\delta^{13}C$ values. Note the scale breaks at 150 m 750 m on the y-axis. 1σ standard errors are shown for $\delta^{34}S$ values, but error bars for C:S and $\delta^{13}C$ values are within the size of the symbol.

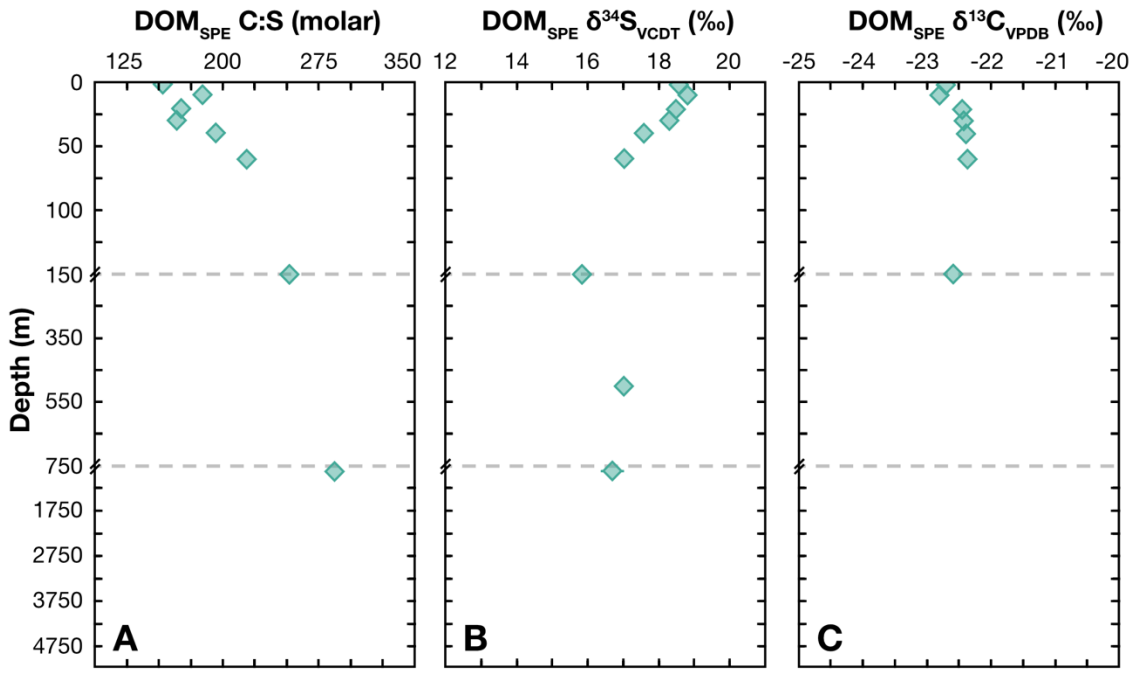

Fig. S13. DOM samples from the San Pedro Basin against depth for (A) C:S ratios, (B) $\delta^{34}S$ values (C) $\delta^{13}C$ values. Note the scale breaks at 150 m 750 m on the y-axis. 1σ standard errors are shown for $\delta^{34}S$ values, but error bars for C:S and $\delta^{13}C$ values are within the size of the symbol.

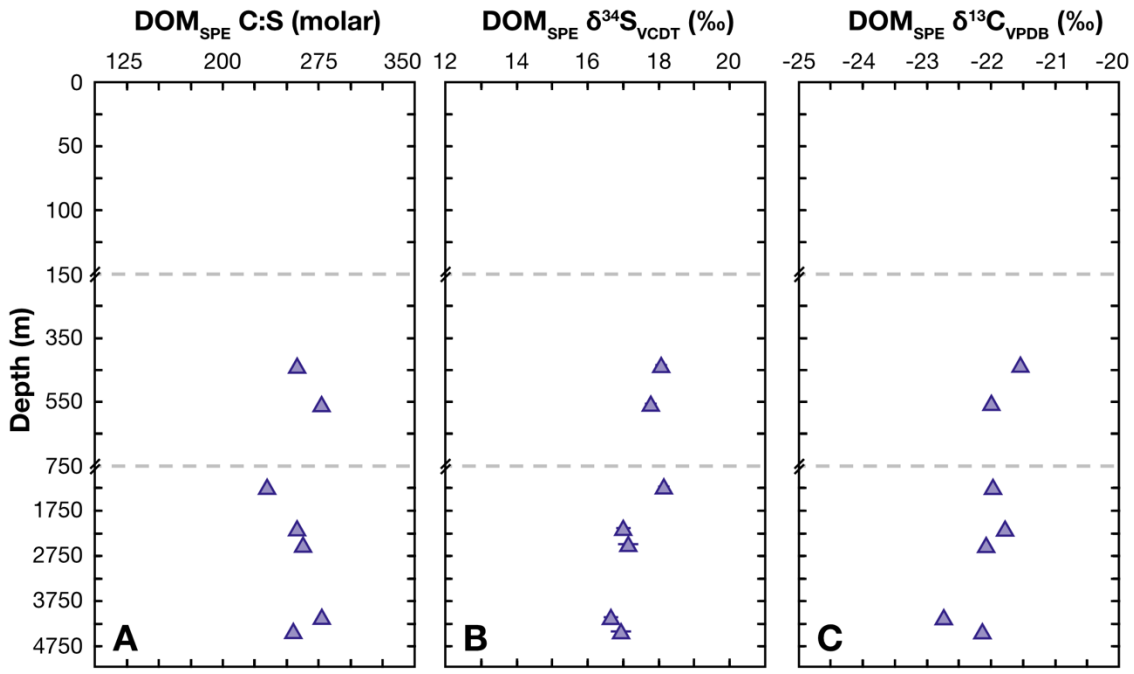

Fig. S14. DOM samples from the S Pacific Gyre against depth for (A) C:S ratios, (B) $\delta^{34}S$ values (C) $\delta^{13}C$ values. Note the scale breaks at 150 m 750 m on the y-axis. 1σ standard errors are shown for $\delta^{34}S$ values, but error bars for C:S and $\delta^{13}C$ values are within the size of the symbol.

Table S1. Ranges of parameters measured by this study on DOM_{SPE} samples from water columns and porewater, by station. Note that there is only one sample from the North Sea porewater.

Station	DOM_{SPE} C:S (molar)	DOM_{SPE} $\delta^{34}S$ (‰)	DOM_{SPE} $\delta^{13}C$ (‰)
North Sea Porewater	18	-0.2	-23.3
Caeté Porewater	40 – 45	-2.7 – 0.7	-27.1 – -26.7
Caeté Estuary	73 – 117	4.2 – 8.7	-28.6 – -24.2
N Atlantic Gyre	191 – 303	14.9 – 18.9	-22.4 – -22.1
NE Pacific OMZ	166 – 293	16.4 – 19.9	-22.7 – -21.6
NE Pacific	186 – 275	17.1 – 18.8	-23.2 – -21.9
NE Pacific Shelf	160 – 255	15.0 – 19.1	-22.7 – -22.0
N Pacific Gyre	197 – 271	16.9 – 19.3	-22.9 – -22.5
San Pedro Basin	153 – 287	15.8 – 18.8	-22.8 – -22.4
S Pacific Gyre	235 – 277	16.7 – 18.1	-22.7 – -21.5

Dataset S1. Supplementary excel data file with all collected EA-IRMS data (DOM_{SPE} $\delta^{34}S$, DOM_{SPE} $\delta^{13}C$, DOM_{SPE} C:S), physical parameters (from CTD casts at each station), and chemical data, sorted by location.

SI References

1. M. E. White, “Studies of Nitrogen and Organic Carbon Cycling in the Eastern Pacific Ocean Using Natural Abundance Isotopes,” UC San Diego. (2021) (January 19, 2022).

2. M. Call, *et al.*, High pore-water derived CO2 and CH4 emissions from a macro-tidal mangrove creek in the Amazon region. *Geochimica et Cosmochimica Acta* **247**, 106–120 (2019).

3. M. Seidel, *et al.*, Biogeochemistry of dissolved organic matter in an anoxic intertidal creek bank. *Geochimica et Cosmochimica Acta* **140**, 418–434 (2014).

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5. M. R. Raven, R. G. Keil, S. M. Webb, Microbial sulfate reduction and organic sulfur formation in sinking marine particles. *Science* (2020) https:/doi.org/10.1126/science.abc6035 (December 18, 2020).