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SPATIOTEMPORAL PATTERNS OF DISSOLVED ORGANIC NUTRIENT LABILITY ACROSS THE SUBTROPICAL NORTH PACIFIC

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SPATIOTEMPORAL PATTERNS OF DISSOLVED ORGANIC NUTRIENT LABILITY ACROSS THE SUBTROPICAL NORTH PACIFIC

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THESIS

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ABSTRACT

Net biologically produced organic matter integrated over an annual cycle in the euphotic zone of the global ocean is equal to annual net community production (ANCP). ANCP is limited by the rate of delivery of essential nutrients (nitrogen (N), phosphorus (P), and iron (Fe)) to the sunlit surface ocean and the efficiency with which these nutrients are either metabolized or returned to the ocean's interior. In subtropical oceans, which are regions of large-scale downwelling and consequently characteristic of nutrient-depleted surface waters, ANCP remains comparable to more nutrient replete ecosystems (~2 – 5 mol C m^{-2} yr^{-1}). To understand what may fuel this productivity, analyses of dissolved organic matter (DOM) within the upper 500 meters of the subtropical North Pacific gyre were performed. Observed meridional gradients suggest the consumption of dissolved organic phosphorus (DOP) and bioavailable dissolved organic nitrogen (bDON) may contribute bioavailable P and N on the order of 8.8 ± 2.2 mmol P m^{-2} y^{-1} and 14.3 ± 3.7 mmol N m^{-2} y^{-1} along the northward transit of waters from the southern edge towards the gyre core.

Additionally, bioassay incubation experiments were performed within two vertically distinct layers of the euphotic zone to quantify the magnitude and rate of heterotrophic DOP remineralization in surface waters (5 m) and the deep chlorophyll maximum (DCM) (125 m) at two stations in the subtropical North Pacific; Station ALOHA (22.75°N) and 31°N along a transect on 158°W, north of Oahu, HI. Evidence for a measurable pool of labile DOP present in surface waters on the order of 25 – 60 nM was found to be consumed in ~5 days near the southern edge of the gyre at Station ALOHA. This consumption was ~1/3 of the latitudinal gradient in surface waters to 31°N, the core of the gyre. Additionally, a new method was deployed to estimate the fraction of the bulk dissolved organic nitrogen (DON) pool composed of bioavailable DON

(bDON). A similar meridional gradient in surface ocean bDON was observed on the order of 230 nM N across the gyre, with a DON pool that was comprised of ~13.3 ± 3.5% bDON. The meridional gradients observed in the size of the surface ocean labile DOP and DON pools found in this study largely affirms the importance of upper-ocean lateral organic nutrient transport on supplying North Pacific subtropical gyre surface waters with bioavailable phosphorus and nitrogen and provides important observational data to validate existing models of marine organic nutrient cycling.

1. INTRODUCTION

1.1 Subtropical ocean deserts

As a major regulator of climate, atmospheric CO_2 plays an integral role in biological, chemical, and physical processes across the Earth's surface, particularly in the era of climate change. Approximately one-quarter of annual anthropogenic CO_2 emissions are taken up by and stored in the oceans, representing the largest exchangeable carbon pool in the global carbon system (Lomas et al., 2013). The ocean's ability to assimilate CO_2 depends on a variety of factors: hydrography, circulation of water masses, mixed-layer dynamics, wind stresses, solubility effects, and biological production (Bates et al., 1996). Each play a role in oceanic uptake of CO_2, thus stimulating the solubility pump or the biological carbon pump and eventually sequestering carbon deep within the ocean's interior through the export of particles from the euphotic zone. Historically, the incorporation of these mechanisms into general ocean circulation models has served as a primary tool for quantifying the flux of carbon to the deep ocean, revealing the importance of the biological carbon pump which dominates over the solubility pump, ~12 vs. 2.8 Pg C yr^{-1}, respectively (e.g. Emerson, 2014; Friedlingstein et al., 2021). An inherent assumption underlying the representation of the biological pump in these models is that the stoichiometry of carbon to the major plant nutrients nitrate (NO_3^-) and phosphate (PO_4^{3-}) is fixed at 106C:16N:1P, defined as the 'Redfield Ratio' (Redfield et al., 1934; 1958). Over the past few decades, however, correlating organic carbon production with Redfield nutrient-carbon relationships has proven increasingly difficult, as more recent publications have observed inorganic carbon drawdown without measurable nutrients present to support subsequent production (Bates et al., 1996; Michaels et al., 1994; Lomas et al., 2013), and marine plankton biomass with elevated carbon-nutrient stoichiometry (e.g. Martiny et al., 2013). These observations largely focus on the

oligotrophic ocean, indicating biogeochemical processes in nutrient-depleted oceanic surface waters cannot accurately be explained by the classic description of the biological carbon pump (Ducklow et al., 1995).

Subtropical gyre regions, spanning ~15° – 40° N & S (Bates et al., 1996), cover ~40% of the Earth's surface. Moreover, these oligotrophic waters are thought to be responsible for upwards of 50% of the net carbon export from the ocean's euphotic zones (Emmerson et al. 1997), a process key for sustaining the ocean's role as a sink for atmospheric carbon dioxide CO_2. Over the past decade, analysis of surface chlorophyll data detected by earth-orbiting satellites has revealed the spatial extent of oligotrophic gyre regions is expanding (Polovina et al., 2008). With increasing areal coverage of these 'biological ocean deserts', characterized by high nutrient stress to resident phytoplankton, investigating the biogeochemical cycling of what little nutrients are present is critical to understanding the mechanisms driving atmospheric carbon drawdown in these vast spatial regions across the Earth's surface.

Within the ocean's subtropical gyres, a multitude of dynamic factors result in oligotrophic surface waters with depressed standing stocks of phytoplankton and primary productivity rates as compared to more nutrient replete ocean biomes. In the coming years of global warming, vertical stratification is expected to intensify, particularly in the subtropics where waters are already characterized by strong stratification (Sarmiento et al., 2004). Upper ocean stratification inhibits the vertical mixing of nutrients, an important mechanism for resupplying nutrients to the biologically productive upper ocean. Primarily due to the reduction of the turbulent mixing supply of nutrients to the upper ocean via enhanced stratification, projections suggest that the overall net primary productivity of the ocean will likely decrease by 4 – 11% by 2100 (Bindoff et al., 2019).

Another critical factor in nutrient depleted surface waters of the subtropics results from the rotational force of the earth deflecting the net movement of surface currents. The vertical motion in subtropical gyre regions is believed to be dominated by large-scale sinking, or downwelling, due to Ekman pumping (Doddridge et al., 2016) as surface waters are forced to sink due to the net deflection of anticyclonic circulation towards the center of the gyre. This central convergence of the Ekman layer generates a region of subtropical high pressure at the center of the gyre and a subsequent downward flux of surface water, further impeding delivery of new nutrients into the euphotic zone (Williams & Follows, 1998).

Despite these physical processes inhibiting nutrient resupply, the extant field observations suggest subtropical gyre ecosystems support annual rates of net community production (ANCP) (equivalent to carbon export at steady-state) comparable to more nutrient replete ecosystems, in the range ~2 – 5 mol C m^{-2} yr^{-1} (Emerson, 2014). Often this ANCP occurs in the absence of measurable nutrients in the productive surface layer, (e.g. Michaels et al., 1994; Keeling et al., 2004; Johnson et al., 2010), leading to a vigorous, decades long quest by marine biogeochemists to account for all of the potential nutrient sources sustaining ocean desert fertility and carbon export (e.g. Lomas et al., 2013). The consideration of these factors in comparison to the export flux of carbon from the euphotic zone suggests subtropical surface-dwelling phytoplankton are dependent on alternative methods of nutrient delivery to sustain growth, which may include nitrogen fixation (Dore et al., 2002), eddy movements (McGillicuddy et al., 2003; Johnson et al., 2010), atmospheric deposition (Baker et al., 2003), and lateral inputs of inorganic (Williams & Follows, 1998) and organic (Torres-Valdes et al., 2009; Letscher et al., 2016) nutrients.

1.2 The role of phosphorus

Of the major nutrients, phosphate (PO_4^{3-}) is widely known to be limiting in the North Atlantic basin, where sensitive analytical methods have found nM level surface phosphate concentrations (Karl & Tien, 1992). However, less is understood about spatial PO_4^{3-} patterns within the oligotrophic waters of other basins, as surface concentrations are commonly below the detection limit for standard methods. Because the North Atlantic is uniformly depleted in PO_4^{3-} concentrations across its entire basin (Fig. 1) much of the phosphorus (P) cycling studies have been conducted specific to this region. In standard methodology, an autoanalyzer combined with a spectrophotometer yields high variance and low interlaboratory accuracy below ~100 nM. This methodology is commonly used for many oceanographic research programs and results in low-sensitivity data which get propagated into the World Ocean Atlas (Garcia et al., 2013) which is used widely to calibrate and validate Earth system models. Inevitably, the geographic distribution of PO_4^{3-} in oligotrophic waters around the global ocean is potentially being misrepresented and thus the role for phosphate limitation outside the North Atlantic is overlooked. It wasn't until recently that a global assessment of ocean PO_4^{3-} concentrations based on high-sensitivity measurements (yielding a detection limit as low as ~0.5 nM) has been compiled, revealing that the

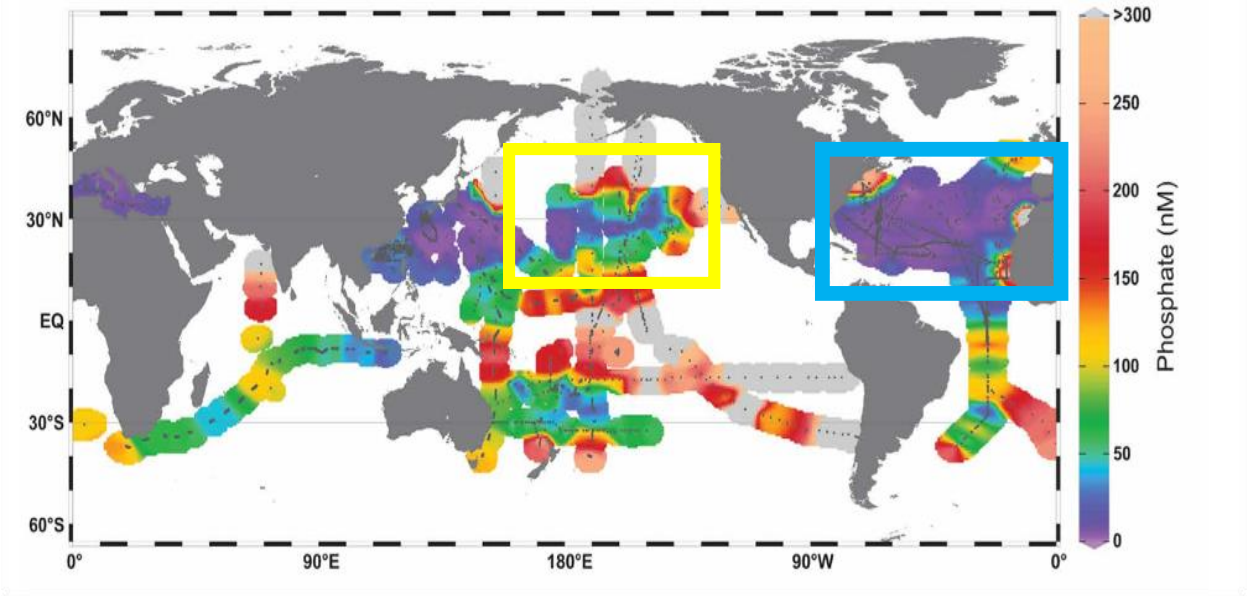

Fig. 1. Global distribution of surface DIP observed using high-sensitivity techniques (adapted from Martiny et al. 2019). The blue box represents the North Atlantic basin, and the yellow box represents the North Pacific basin.

same depleted surface ocean concentrations of PO_4^{3-} that have been observed in the North Atlantic Basin are now identified in the North Pacific (Martiny et al. 2019) (Fig.1).

Decades of research have focused on the biogeochemical cycling and availability of dissolved inorganic phosphorus in seawater, dominated by the phosphate ion (PO_4^{3-}) and its associated protonated forms, to both infer and predict spatiotemporal patterns of marine biomass production and its subsequent turnover by heterotrophic microbes. However, in recent years other pools of P present in seawater have increasingly gained appreciation as potential sources of P supporting marine biological productivity collectively termed dissolved organic phosphorus (DOP). Many major lineages of marine phytoplankton are known to harbor enzymes capable of accessing these organic forms of P including cyanobacteria (Dyhrman et al., 2006; Su et al., 2007) and diatoms (Lin et al., 2013), with numerous field and laboratory studies having documented the ability of these algal taxa to use DOP to supplement and/or satisfy their cellular P requirements (e.g. Björkman & Karl, 2003; Dyhrman & Ruttenberg, 2006; Orchard et al., 2010).

Prior studies suggest when PO_4^{3-} concentrations are scarce, typically on the order of ~10 - 300 nM (Martiny et al., 2019), subtropical nutrient budgets shift to a dependence on bioavailable dissolved organic phosphorus (DOP). In the low-latitude oligotrophic gyres of both the North Atlantic and North Pacific, DOP concentrations greatly exceed PO_4^{3-} and pose potential to support a large fraction of the microbial community's P demand. Because dissolved organic nutrients comprise the bulk of the total dissolved nutrient pools in the oligotrophic surface ocean (200 m), and these oligotrophic regions are thought to be responsible for a surprisingly large percentage of net export production from euphotic zones, dissolved organic P may play a larger role in autotrophic nutrition than traditionally thought.

1.3 Lateral DOP gradients in surface waters of subtropical gyres

Lateral supply of organic nutrients including DOP and dissolved organic nitrogen (DON) to gyres from the more productive equatorial, eastern, and poleward boundaries have been suggested to supplement subtropical ocean nutrient budgets (Roussenov et al., 2006; Charria et al., 2008; Torres-Valdes et al., 2009; Reynolds et al., 2014; Letscher et al., 2016). This process is best characterized for the North Atlantic subtropical gyre where surface PO_4^3 concentrations are at or near the global minima (~1-10 nM; Martiny et al., 2019), leading to P limitation of NPP and ANCP (Ammerman et al., 2003; Lomas et al., 2010), for which lateral supply of DOP may provide a nutritional subsidy to marine phytoplankton (Reynolds et al., 2014; Duhamel et al., 2021). Mather et al. (2008) reported on the latitudinal and longitudinal gradients in DOP, PO_4^3, and alkaline phosphatase activity (APA), a common enzyme used by marine plankton to access P in DOP across the Atlantic basin, finding strong observational support for the microbial utilization of surface marine DOP when surface PO_4^3 dropped below ~100 – 200 nM. Many major lineages of marine phytoplankton are known to harbor enzymes such as these, capable of accessing these organic

forms of P including cyanobacteria (Dyhrman et al., 2006; Su et al., 2007), diatoms (Lin et al., 2013), and other eukaryotic algae (Shaked et al., 2006; Li et al., 2018), with numerous field and laboratory studies having documented the ability of these algal taxa to use DOP to supplement and/or satisfy their cellular P requirements (e.g. Björkman & Karl, 2003; Dyhrman & Ruttenberg, 2006; Orchard et al., 2010).

Abell et al. (2000) were among the first and only to collect observational data regarding DOM concentration gradients in the North Pacific subtropics and assess the contribution its autotrophic consumption and degradation makes towards nutrient regeneration. Figure 2 illustrates the observed lateral DOP gradient within the upper 50 m (encompassing the depth of the wind driven Ekman layer) decreasing northwards across the gyre from a high of 0.35 µM at 14°N to a low of 0.1 µM at 35°N while PO_4^{3-} concentrations remained near detection limit (0.02 µM). The decreasing meridional DOP concentration gradient coupled with the northwards Ekman transport across the subtropical gyre was suggested to supply bioavailable P at a rate capable of supporting 40 – 80% of the export productivity. Similar organic nutrient gradients and inferred contributions to subtropical nutrient budgets have been diagnosed from coupled ocean physics-biogeochemistry models, e.g. the results from Letscher et al., 2016 reproduced in Figure 3a, where the physical flux

of DOP supplied by lateral transport appears highest at the southern edge of the North Pacific subtropical gyre and decreases with an increase in latitude (towards the gyre center).

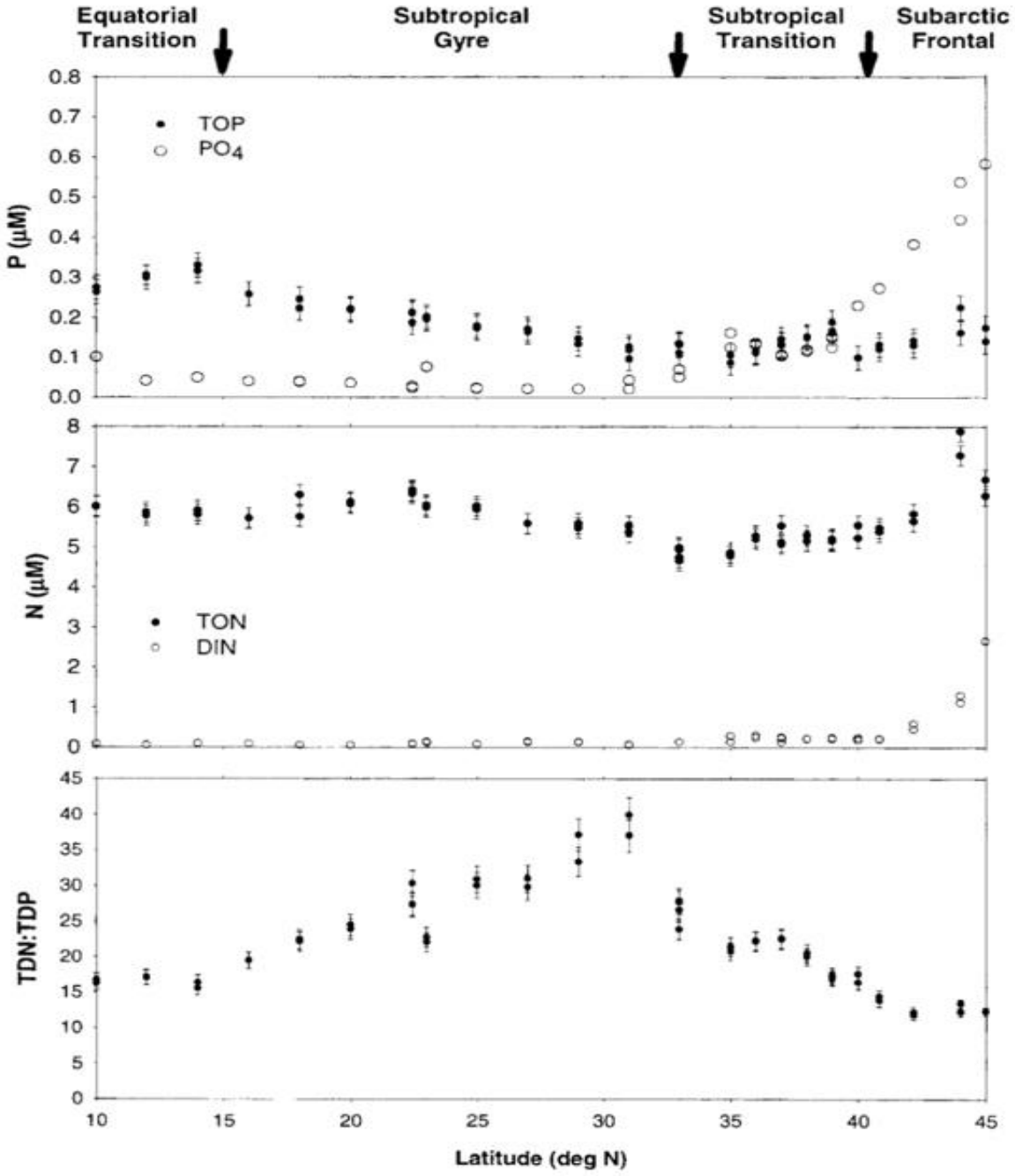

Fig. 2. Total organic phosphorus (TOP; TOP ≅ DOP), PO4, total organic nitrogen (TON; TON ≅ DON), dissolved inorganic nitrogen (DIN), and TDN:TDP ratios for samples in the upper 50 m of the surface ocean. Error bars represent the maximum standard deviation associated with the TOP and TON measurement For TDN:TDP. The error bars are propagated from the maximum standard deviation for the TDN and TDP

1.4 Vertical partitioning of microbial ecosystems within the euphotic zone

Previous work has centered around the vertical partitioning of microbial ecosystems within the euphotic zone and the unique bioavailable pools of nutrients supplied to these communities.

There are thought to be two biologically distinct communities within the euphotic zone of marine ecosystems: the surface-dwelling planktonic community relies on the plentiful sunlight but must adapt to nutrient depletion, while the deeper waters are inhabited by a community which is spatially closer to the top of the nutricline and therefore has better access to remineralized nutrients. However, this deeper community is forced to make the tradeoff to adapt to low light conditions as the majority of the light energy has attenuated and therefore the deep chlorophyll maximum (DCM) is roughly observed as phytoplankton increase their cellular chlorophyll to carbon ratio.

Previous studies have compared dissolved organic carbon (DOC) and DON consumption between these two communities, finding these pools of organic matter may be recalcitrant to the surface community but labile to that of the DCM. Therefore, a portion of the DOC and DON pool has been observed to preferentially get consumed by the DCM community (and deeper into the upper mesopelagic; Carlson et al., 2004; Letscher et al., 2013; Letscher et al., 2015) that is not consumed by the surface community. However, a similar assessment for DOP is currently lacking.

1.5 Bioavailable dissolved organic nitrogen

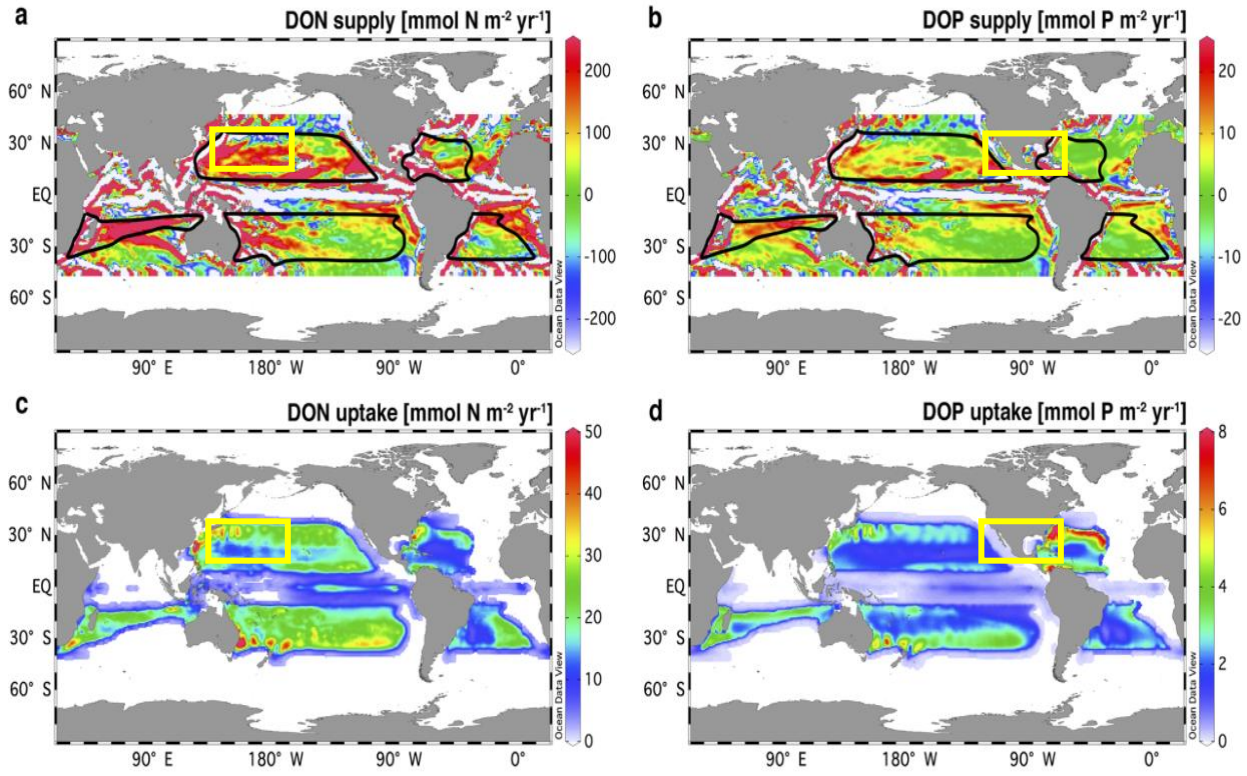

Fig. 3. The physical flux of DON (a) and DOP (b) and the biological uptake flux of DON (c) and DOP (d) supplied by lateral transport integrated over the euphotic depth across the global ocean (adapted from Letscher et al., 2016). A steady decrease (~15 mmol P m^{-2} yr^{-1} and ~150 mmol N m^{-2} yr^{-1}) in DOP and DON supply, respectively, is observed from the southern edge of the North Pacific subtropical gyre (~20°N) to ~30°N (yellow box).

Much like P, the majority of the standing stock of fixed nitrogen (N) takes the form of DON within the global surface ocean (Letscher et al., 2013). Thus, the transport of DON from gyre margins into the interior of nutrient-scarce subtropical gyre regions may also provide an important source of new nutrients to gyre euphotic zones, sustaining observed export production. Abell et al. (2000) observed a slight decrease (~1 µM) in surface [TON] across the NPSG from a high of 6 µM at 14°N to a low of 5 µM at 33°N while the inorganic N pool was consistently measured at its detection limit of 0.1 µM throughout the subtropical region (Fig. 2). Figure 2 also illustrates the overall DOM pool was steadily enriched in N with respect to P as the TDN: TDP ratio increases across the gyre region, cited to primarily be driven by the decrease in TOP across the gyre. The biogeochemical model results from Letscher et al., 2016 (Fig. 3a) inferred similar

results where the physical flux of DON supplied by lateral transport appears highest at the southern edge of the NPSG and decreases with an increase in latitude (towards the gyre center).

Unlike the DOP pool which is generally thought to be mostly comprised of bioavailable phosphate esters and phosphonates (Duhamel et al., 2021), within the marine DON pool, a significant contribution of biologically recalcitrant material may accumulate via direct production by autotrophs (McCarthy et al., 2004) or heterotrophic microbial alteration of the molecular structure (Sipler & Bronk, 2015). Because recently produced or fresh material has been observed to be the most bioavailable (Aluwihare et al., 2005; Broek et al., 2019; Walker et al., 2016), the major pathway of organic matter degradation is a continuous change from bioavailable organic particles and macromolecules to small refractory organic molecules, e.g. the size-age-reactivity continuum. (Amon & Benner, 1996). Two major classes of organic molecules have been shown to populate the bioavailable, high molecular weight fraction of marine DON including dissolved proteins and N-acetyl aminopolysaccharides (NAAP, e.g. peptidoglycan and chitin) (Aluwihare et al., 2005). Unlike the phosphate esters and phosphonates populating marine DOP for which many marine autotrophic taxa possess the necessary enzymes for their direct utilization as a P source, the proteins and NAAP populating marine DON are thought to require breakdown and remineralization by heterotrophic microbes to release inorganic N before the external supply of DON could potentially support export production in oligotrophic gyre regions as a source of new N (Letscher et al., 2013).

Previous work has focused on spatiotemporal analyses of the bulk DON concentration gradients across regional to global scales to assess its potential importance as a laterally supplied new nutrient source in the upper ocean, similar to DOP (Letscher et al., 2013; 2016; Knapp et al., 2018). However, the study of biogeochemical cycling of DON in seawater has been hindered by

extant analytical methods. Separate determinations of multiple N species are currently required to determine DON by difference which results in substantial analytical error, on the order of ±0.5 µM or ~10-25%. Given that the portion of the marine DON pool that is produced in surface waters and subsequently removed with depth can be deemed 'bioavailable,' and is thought to be comprised of dissolved proteins and NAAP, Letscher, Gray, Aluwihare (in prep.; LGA22) have developed a targeted chemical method for the quantification of bioavailable amide N found in marine DON utilizing mild acid hydrolysis (6M HCl) to convert amide N to primary amine. This liberated amine can be measured using a highly sensitive (nanomolar range) fluorometric technique with the addition of o-phthaldialdehyde (OPA) for the quantification of dissolved primary amines (Josefsson et al., 1977). Using this new method to measure acid labile or bioavailable dissolved organic nitrogen (bDON) in marine samples, bDON can be estimated with a precision of 100 nM and detection limit of 16 nM (LGA22). Through the deployment of this new method, the contribution of DON to upper ocean nutrient cycling can be more accurately assessed for its ability to support net community production. This is particularly important in the oligotrophic subtropical ocean where inorganic nutrient fluxes (i.e. nitrate (NO_3^-)) into the euphotic zone are subdued. Further, model-based estimates have suggested 15-40% of net community production may be supported by the lateral delivery of DON (Torres-Valdes et al., 2009; Letscher et al., 2016) which will be further explored here via field observations of bDON.

1.6 Study site and research questions

The North Pacific subtropical gyre (NPSG) is formed by the clockwise circular pattern of four prevailing ocean currents: the North Equatorial Current (south), Kuroshio and Kuroshio Extension (west), North Pacific Current (north), and California current (east) (Kubota, 1994). With a surface area spanning ~2 x 10^7 km^2 and extending from 15 – 35° N and 135°E – 135°W, the

NPSG is often cited as the largest of the open ocean habitats and Earth's overall largest contiguous biome (Karl et al., 2002). Towards the southern flank of the NPSG region, a circle of six-mile radius defines Station ALOHA (A Long-term Oligotrophic Habitat Assessment) (Fig. 4). Located at 22° 45 0 N, 158° 00 0 W, approximately 100 km north of Oahu, Hawaii, Station ALOHA has served as a focal point for a range of oceanographic research since 1988. The research questions of this thesis include those derived from field-observational data specific to the NPSG:

(1) Is there an observed lateral gradient of DOP concentration in surface waters across the subtropical North Pacific gyre suggestive of its role as an organic nutrient sustaining a portion of ANCP?

(2) Is there evidence for DOP consumption (i.e. a labile DOP pool) within surface waters of the NPSG?

(3) Is there evidence for preferential DOP consumption between surface waters and the shallow surfaces of the ocean interior of the NPSG?

(4) Similarly for DON, is there an observed gradient in bDON concentration in surface waters across the NPSG suggestive of its role as an organic nutrient sustaining a portion of ANCP?

In June 2021, a 12-day oceanographic cruise was performed in the NPSG waters north of Oahu, HI (Figure 4). Questions 1 and 4 are assessed with data collected on ten CTD/Rosette casts performed down to depths of 500 meters. Questions 2 and 3 are assessed with biological incubations (bioassays) performed at Station ALOHA and at a station at 31ºN.

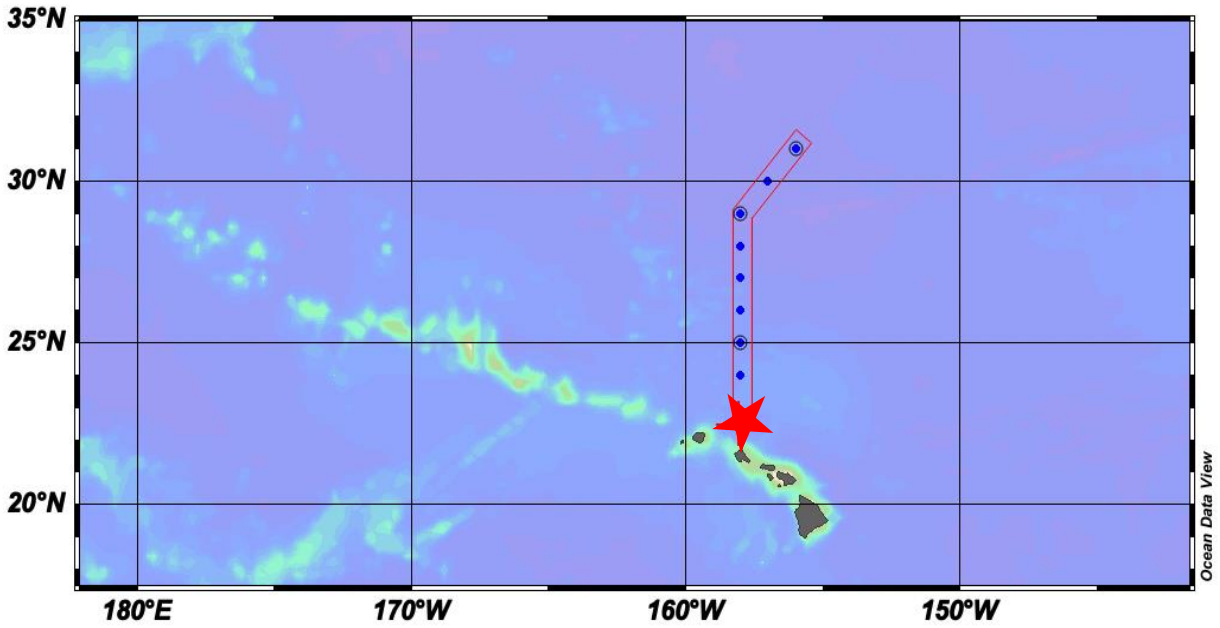

Fig. 4. Regional map of the cruise track study site beginning at St. ALOHA (22.75°N) (red star) and ending closer to the center of the NPSG at 31°N.

2. METHODOLOGY

2.1 Sample Collection

During a 12-day cruise aboard the R/V Kilo Moana (Figure 5) in June of 2021, samples were collected along a transect which extended along 158°W (with the exception of the two northernmost stations which were sampled at 157 and 156°W, respectively) from 22.75°N to 31°N. For the purposes of this study, Station ALOHA marked the

Fig. 5. The R/V Kilo Moana oceanographic research vessel used to travel to the study site and collect samples from 22.75° - 31° N.

Southern edge of the NPSG region as the following stations sampled approached the core of the gyre region. As portrayed in Table 1, ten stations were occupied including Station ALOHA which was sampled twice: at the beginning of the research cruise (June 6th, 2021) and at the end (June 16th, 2021) marking Station 1 and 10, respectively.

Table 1. Geographic coordinate locations and respective mixed layer depth (MLD) at the time of sampling for each of the ten stations sampled.

Station	Latitude (°N)	Longitude (°W)	MLD (m)
1	22.75	158	35
2	25	158	40
3	27	158	30
4	29	158	20
5	30	157	35
6	31	156	30
7	28	156	30
8	26	158	40
9	24	158	20
10	22.75	158	40

At every station, ~100 mL of 0.7 um-filtered (GF/F) water was drawn from 24 L Niskin bottles attached to a conductivity, temperature, and depth (CTD) rosette and collected in 60 mL acid-washed HDPE bottles. These bottles were immediately frozen at sea (-20ºC) for later analysis of total dissolved phosphorus (TDP), PO_4^{3-}, total dissolved nitrogen (TDN), NO_3^-, and bioavailable DON (bDON), back at the shore-based laboratory at UNH.

2.2 TDP and PO_4^{3-}

A modified version of the Solórzano & Sharpe (1980b) ash hydrolysis method was employed to measure TDP. With this method, seawater samples are dried with the presence of added magnesium sulfate. The resulting residue is baked at high temperature (450ºC, 5 hours) to oxidize organic phosphorus compounds and the polyphosphates are hydrolyzed to orthophosphate. This subsequent ash hydrolysate was measured using the standard colorimetric molybdenum blue method, adapted from Strickland and Parsons (1968). It is important to note the TDP samples were first analytically measured directly from the HDPE bottles after having been stored frozen for

approximately two to three months. The results yielded lower concentrations than expected, leading to a second round of analytical measurements incorporating an acidification step prior to dehydration via magnesium sulfate. Recent analyses (Liang et al., submitted) suggests the addition of 50 µL of 6M HCl (pH ≈ 1) to each HDPE sample bottle to ensure the release of all TDP from the plastic walls of the bottle. Traditionally, this step has only been cited necessary for samples stored on the order of years, however, elevated concentrations of TDP were found upon the analysis of samples incorporating this initial step suggesting initial acidification was necessary for accurate measurements.

Procedures presented for separate analyses of total dissolved P and total particulate P in seawater give midrange precision of ±1% (Solórzano & Sharpe, 1980b). Using these results, DOP is determined by subtracting the ambient soluble reactive P concentration ($[PO_4^{3-}]$) from the measured total dissolved P concentration ([TDP]) (Equation 1).

$$[DOP] = [TDP] - [PO_4^{3-}] \quad (1)$$

2.3 TDN and NO_3^-

The nature of all DON measurement procedures involves oxidizing organic nitrogen compounds to an inorganic form to produce a measure of the total dissolved nitrogen present within a given sample. The persulfate oxidation method (Solórzano & Sharp, 1980a) was used to measure the TDN pool in seawater samples, with the resulting nitrate measured by the chemiluminescent method using an acidic vanadium (III) solution (Braman & Hendrix, 1989). The same chemiluminescent method was used to determine the separately analyzed ambient $[NO_3^-]$ of the sample, allowing for estimation of DON (mean precision of ± 0.3 µM or 5 – 10%) by subtracting the measured concentration of inorganic concentration N ($[NO_3^-]$) from the total dissolved N concentration ([TDN]) (Equation 2).

$$[DON] = [TDN] - [NO_3^-] \quad (2)$$

2.4 bDON

Bottle samples were measured in triplicate for the concentration of bDON ([bDON]) using the new method of LGA22 to liberate primary amines from the acid hydrolysis of the naturally occurring dissolved proteins/peptides and NAAP in seawater. The analytical day precision estimated from the average standard deviation of triplicate analyses of the blank was ± 0.1 µM-N. The primary amine content of seawater samples was assessed by fluorometric detection using a Turner Trilogy benchtop fluorometer (Turner Designs, USA). Excitation is in the UV at 350 nm and emission recorded at 410-450 nm using the Turner 'Ammonium' module (7200-067) in a 1 cm acrylic cuvette.

2.5 Bioassay incubation experiments

At either end of the transect (22.75°N and 31°N) the magnitude of heterotrophic DOP remineralization was quantified via bioassay incubation experiments targeting two vertically distinct microbial communities: those residing within the sunlit surface waters (5 m) and those dwelling in the lower-lit waters in and around the DCM (125 m). Seawater was collected into 20 L amber polycarbonate carboys which were acid-washed and rinsed in triplicate with Millipore Q (Milli-Q) water prior to use. The carboys were then incubated within two separate environmental chambers in the dark (Figure 6). Since these cultures include measurable photoautotrophic bacteria and pico-eukaryote biomass, incubation in the dark was conducted with the intention of eradicating autotrophic activity. The incubation baths were kept at respective *in situ* temperatures in relation to the depth they were collected at-approximately 22.5°C for surface samples and 15.2°C for the

DCM depth at Station ALOHA. All experiments were performed in the summer, albeit early, so the physical separation of distinct nutrient fields and biological community structures through stratification was assumed.

Fig. 6. The shipboard incubators where the incubation experiment carboys were held over the course of the experiment.

The experimental design included two separate treatments to each sample collected from 5 m and 125 m at both 22.75°N and 31°N. The first (Whole) treatment simply contained 100% whole (unfiltered) seawater and the second (Mixed) treatment contained a mixture of 20% whole seawater and 80% 0.2 µm-filtered seawater. Preparation of each treatment initiated within a few hours of sample collection and CTD recovery. The Mixed treatment was deployed to release natural assemblages of bacterioplankton from grazer predation, allowing enhanced growth on naturally occurring substrates (Ammerman et al., 1984). All waters were collected in Niskin bottles on dedicated CTD casts to 5 m or 125 m and transferred directly to 50 L HDPE carboys without manipulation. Gravity filtration was used through an in-line Pall Acropak 1000 (0.8/0.2 µm) filter attached directly to the 50 L HDPE carboy spigot, collecting the filtrate in 50 L HDPE carboys.

After obtaining initial samples representative of time point zero, each treatment was sampled at unintentionally varying additional time points ranging from 110 – 132 hours total anywhere from 21 – 44 hours apart (Table 2). Over the course of the incubation experiment, four time points were sampled for all treatments with the exception of samples collected at 125 m depth at Station ALOHA where only three time points were sampled. Similar to bottle samples collected on casts, ~100 mL incubation samples were collected via gravity filtration (0.7 µm, GF/F) and immediately stored in 60 mL HDPE bottles at -20°C until future analysis on shore. A total of four

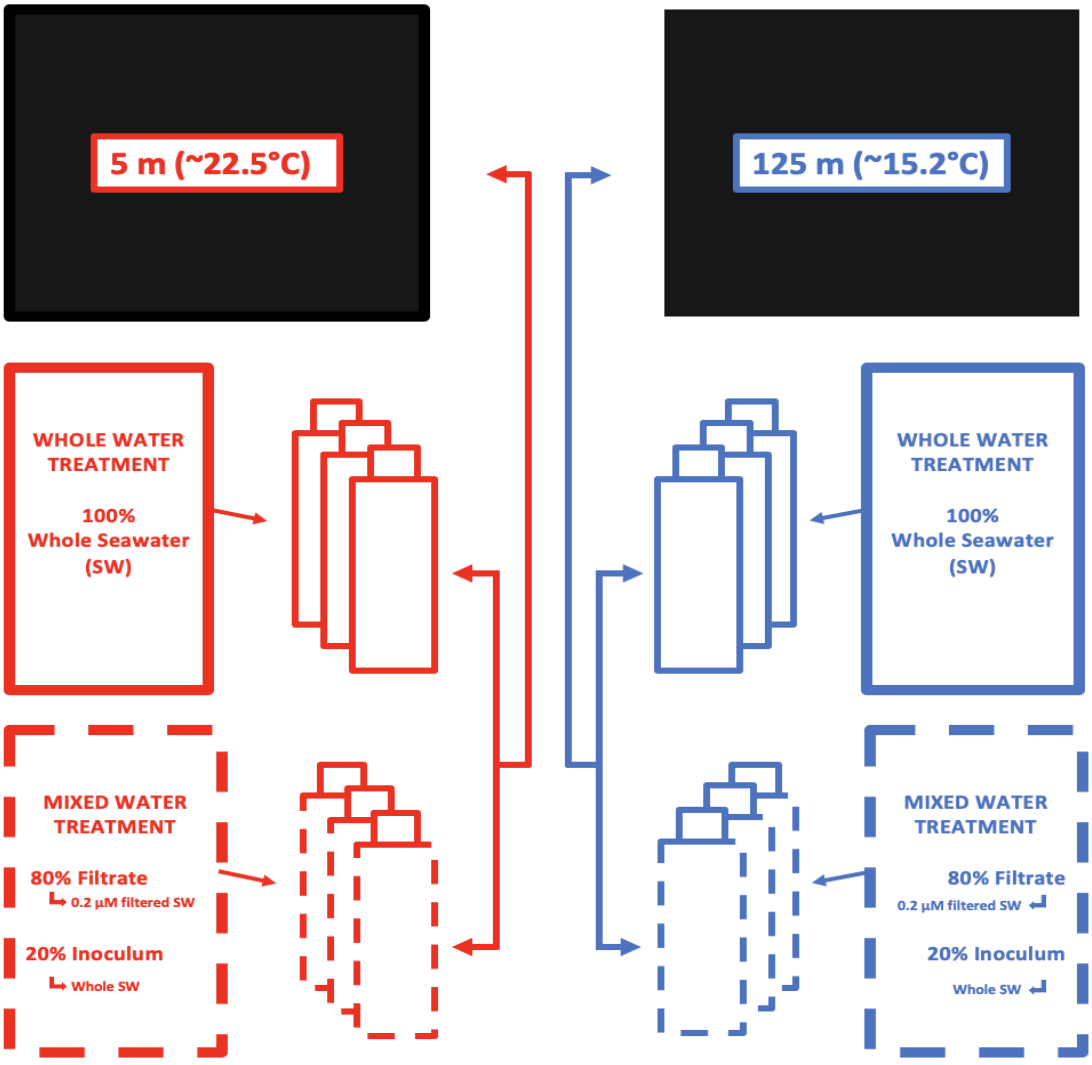

Fig. 7. The incubation set up containing samples collected at both Station ALOHA (22.75°N) and 31°N. Each incubator contained triplicate incubation treatments for both whole (solid) and mixed (dashed) water treatments collected at 5 m (red) and 125 m (blue).

Table 2. Time point sampling for incubation experiments conducted at Station ALOHA (22.75°N) and 31°N for both surface waters (5 m) and the DCM (125 m).

	Time Point	Date (local)	Time elapsed (hrs)
22.75°N 5 m	0	6/7/21	0
	1	6/8/21	33
	2	6/9/21	57
	3	6/10/21	88
	4	6/12/21	132
22.75°N 125 m	0	6/7/21	0
	1	6/8/21	29
	2	6/9/21	53
	3	6/11/21	92
	4	6/12/21	113
31°N 5 m	0	6/12/21	0
	1	6/14/21	42
	2	6/15/21	70
	3	6/17/21	110
31°N 125 m	0	6/12/21	0
	1	6/13/21	28
	2	6/15/21	69
	3	6/16/21	95
	4	6/17/21	120

treatments, 5 m Whole and Mixed and 125 m Whole and Mixed, were performed at each of two stations, Station ALOHA (22.75ºN 158ºW) and at 31ºN 156ºW. The 5 m and 125 m treatments at Station ALOHA were terminated after 132 and 113 hours, respectively. The 5 m and 125 m treatments at 31ºN were terminated after 110 and 120 hours, respectively. Lastly, a two-way ANOVA was conducted for these data with both sample location (i.e., 22.75°N or 31°N) and depth (i.e., 5 m or 125 m) as factors to determine significance.

2.6 Sea surface height as a proxy for mesoscale eddies

To aid in the interpretation of our results, sea surface height (SSH) information was extracted from Mercator Ocean International as part of the Copernicus Programme to investigate the potential presence/absence of mesoscale eddies impacting our study region at the time of the cruise. The Operational Mercator global ocean analysis and forecast system dataset provides three-dimensional global ocean forecasts updated daily. The time series product includes daily mean output of sea surface heigh above the geoid at a spatial resolution of 0.083 degree latitude x 0.083 degree longitude and with global geographic coverage. The global ocean output files are displayed with regular longitude/latitude equirectangular projection and available to the public at https://doi.org/10.48670/moi-00016. Daily mean data was extracted from June 01, 2021 through

June 20, 2021 from ~18 – 32°N, 162 – 154°W and individual days were analyzed to diagnose spatial patterns in SSH.

3. RESULTS

3.1 DOP and DON variability across the NPSG

From the ten sample stations along the cruise track, both DOP and PO_4^{3-} surface concentration measurements were averaged within the upper 50 m and plotted across the latitudinal transect. Figure 8 demonstrates a decrease in both DOP and PO_4^{3-} concentrations with increasing latitude (ΔDOP = -141 nM and ΔPO4 = -34 nM) which largely agrees with prior observation and modelling predictions (Abell et al., 2000; Letscher et al., 2016). Figure 9 depicts the latitudinal gradient of both [DON] and [NO_3^-] across the surface waters (<50 m) at the ten stations sampled.

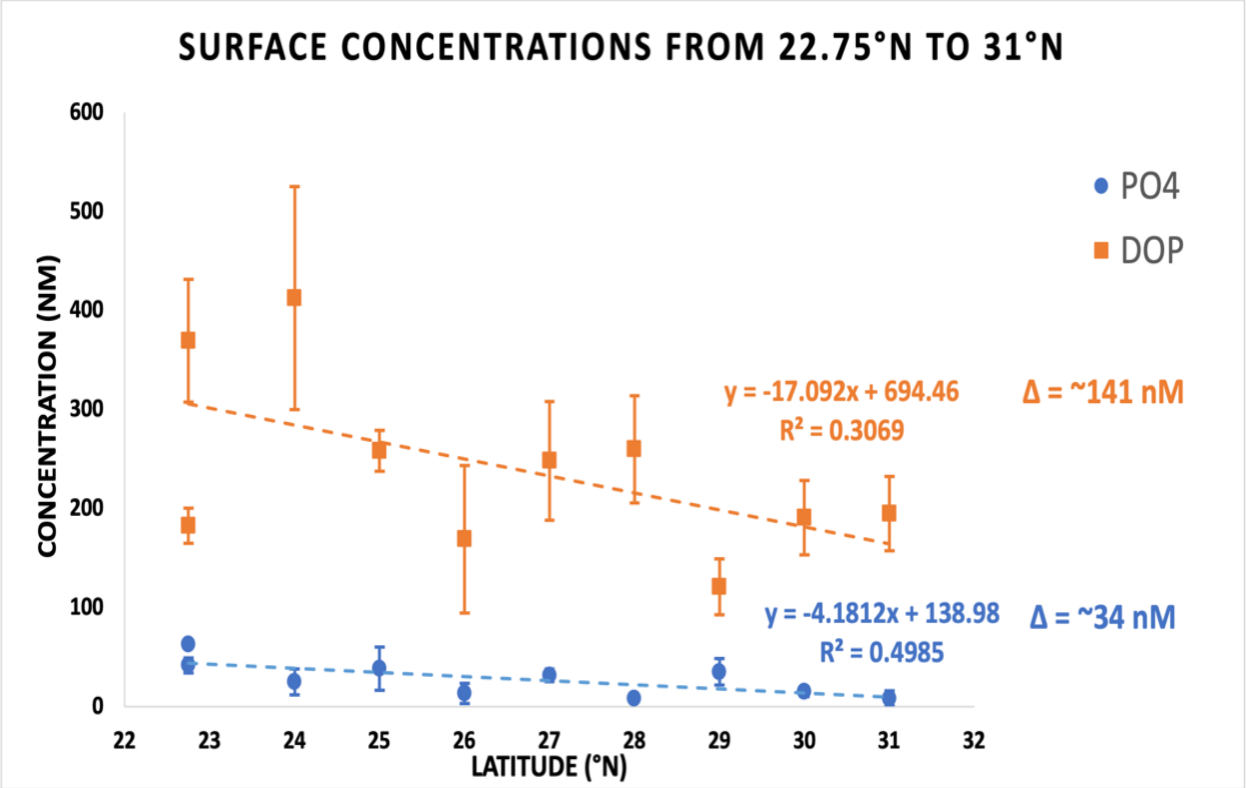

Fig. 8. Surface (upper 50 m) averaged concentrations of DOP (orange) and PO_4^{3-} (blue) from 22.75 – 31°N. Error bars represent the standard deviation of triplicate analyses across three depths.

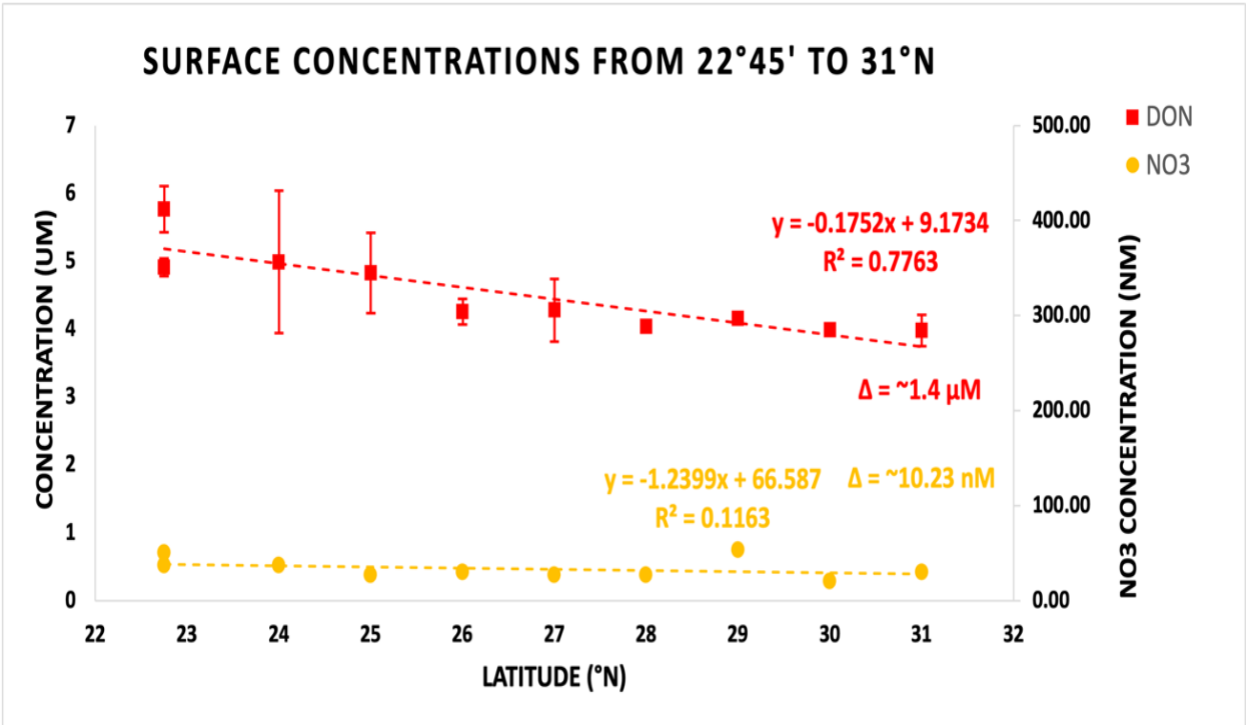

Fig. 9. Surface (upper 50 m) averaged concentrations of DON (red) and NO_3^- (yellow) from 22.75 – 31°N. Error bars represent the standard deviation of triplicate analyses across three depths.

A decrease in both the dissolved organic and inorganic N pools was observed (ΔDON = -1.4 µM

and ΔNO3 = -10.2 nM) with increasing latitude. Interestingly, between the two casts at Station ALOHA (22.75°N) obtained ten days apart, both the size of the DOP and DON pool appeared to increase significantly; a doubling of DOP; 380 nM (Sta. 10) vs. 190 nM (Sta. 1) ($p=0.002$) and a 20% increase for DON; 5.9 µM (Sta. 10) vs. 4.9 µM (Sta. 1) ($p=0.03$).

The vertical distribution of [DOP] (Fig. 10a) depicts elevated concentrations at ~24°N (~0.3 – 0.5 µM) spanning from surface waters to approximately 200 m depth. Notably, at ~29°N <0.05 µM [DOP] was observed throughout the vertical water column. Further, the vertical thickness to which detectable DOP concentrations were observed roughly decreased moving towards the core of the gyre region. By identifying the depth at which temperature and salinity decrease by 0.1°C and 0.01 kg m^{-3}, respectively, the mixed layer depth (MLD) was interpolated at each station along the latitudinal transect. The MLD remains relatively static within the spatial extent of the transect at an average of 32 ± 7.5 m, reaching its shallowest at 24 and 29°N (20 m) and its deepest at both 25 and 26°N (40 m). The DCM, identified as the depth of maximum fluorescence from CTD casts at each station (interpolated between each station) was observed to slightly decrease in depth moving towards the core of the gyre (Fig. 10).

The vertical distribution of [DON] (Fig. 10b) indicates elevated concentrations from the surface waters at Station ALOHA to a depth of approximately 300 m (4 – 6 µM). However, this vertical thickness decreased across the latitudinal transect from 22.75° - 31° N. While surface concentrations were observed to range between 3.5 – 4.5 µM at each station, from 25 – 31°N these elevated concentrations were only observed to a depth of ~150 m.

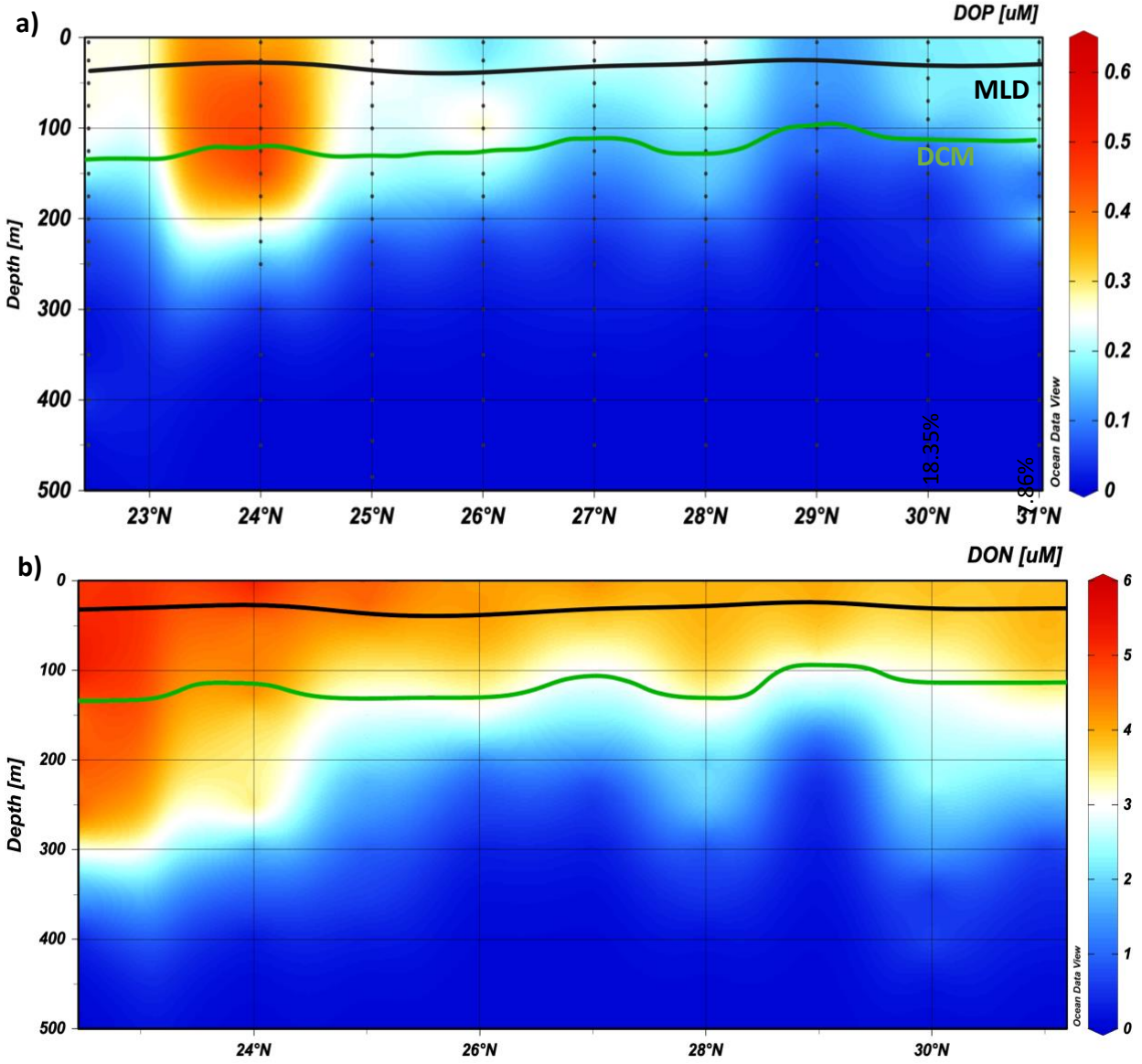

Fig. 10. DOP (a) and DON (b) concentrations within the upper 500 m of the water column across the latitudinal cruise track from 22.75°N – 31°N.

Within the DON pool, the portion of N available to biological utilization [bDON] is graphically portrayed alongside the total [DON] (Fig. 11). Both [bDON] and [DOP] were observed to decrease across the NPSG at comparable magnitudes (Fig. 12). The upper 50 m of the water column at 22.75°N and that of 31°N were observed to differ in surface [bDON] by ~228 µM and ~141 µM in surface [DOP]. Similar to DOP and DON trends, the pool of bDON at Station ALOHA

was significantly elevated in concentration (~+0.47 µM) (p=0.001) when measured a second time, ten days after sampling Station 1.

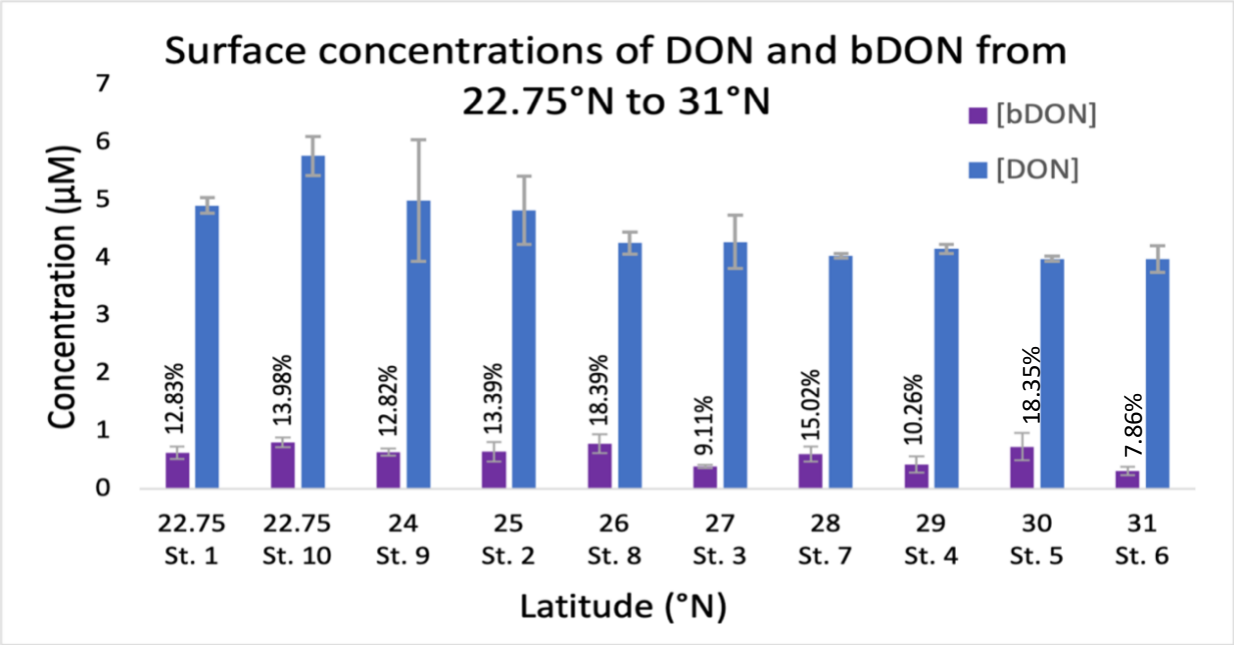

Fig. 11. [DON] (blue) and [bDON] (purple) averaged within the upper 50 m of the water column across the latitudinal cruise track from 22.75°N – 31°N. Error bars represent the standard deviation of triplicate analyses across three depths. The fraction of the total DON pool comprised of acid labile DON is indicated by the percentages above [bDON].

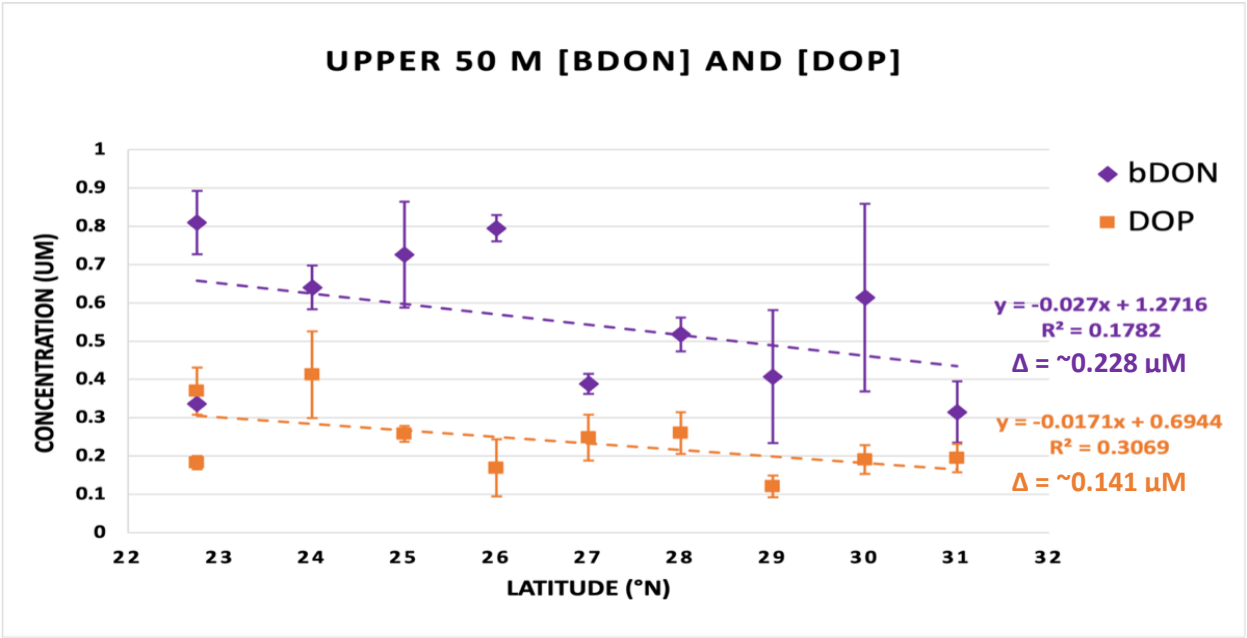

Fig. 12. [bDON] (purple) and [DOP] (orange) averaged within the upper 50 m of the water column across the latitudinal cruise track from 22.75°N – 31°N. Error bars represent the standard deviation of triplicate analyses across three depths.

3.2 Incubation data

Significantly more DOP consumption activity was observed at the southern edge of the gyre than at the gyre core. Figure 13 summarizes the magnitude of DOP consumed within each of the incubation experiment treatment types, depths, and locations. Appreciable DOP consumption was observed within the DCM microbial community in both the whole (~59 ± 22 nM) and mixed (~46 ± 16 nM) water treatments at St. ALOHA after 132 hours of incubation. Incubation experiments containing surface-dwelling heterotrophic communities also consumed DOP in the whole water treatment (~38 ± 5 nM) and more appreciable consumption was observed in the mixed water treatment (~44 ± 5 nM) after 132 hours of incubation. The overlapping error bars preclude a statistically significant difference in DOP consumption when comparing the communities at 5 m and 125 m ($p=0.7591$). There was a lack of any DOP consumption activity within the DCM microbial community closer to the gyre core at 31°N, and in the surface waters there was minimal consumption over the course of the 110-hour incubation period for both the whole water treatment (~12 ± 7 nM) and the mixed (~7 ± 3 nM).

In surface waters (5 m) towards the southern edge of the gyre at St. ALOHA (22.75 °N), the heterotrophic community (averaged across both the mixed and whole water treatments) were observed to consume a significantly larger amount of DOP (38.1 ± 6.7 nM) than the surface-dwelling heterotrophic community sampled at 31°N (9.1 ± 6.7 nM) ($p<0.0001$) (Fig. 14). These findings are inconsistent with previous model predictions (Letscher et al. 2016) which depicted an

increase in biological uptake flux moving from the southern edge of the gyre towards the gyre core (Fig. 3).

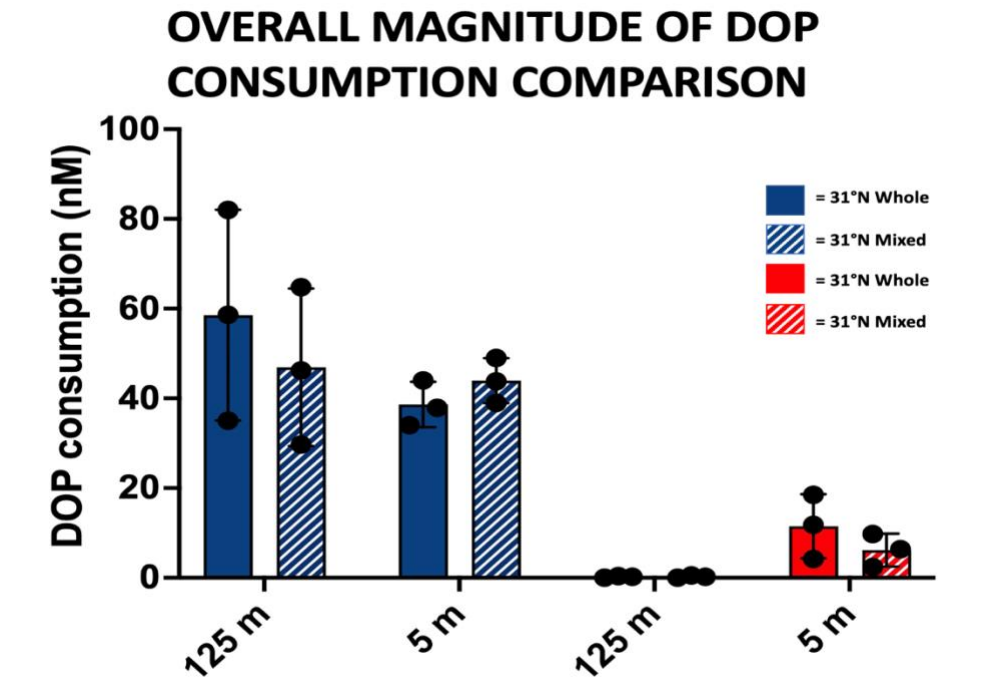

Fig. 13. DOP consumption in whole water (solid) and mixed water (dashed) incubation experiments at St. ALOHA (blue) and 31°N (red). Error bars represent the standard deviation of triplicate analyses for each measurement and black data points indicate the observed DOP consumption for each individual experimental replicate.

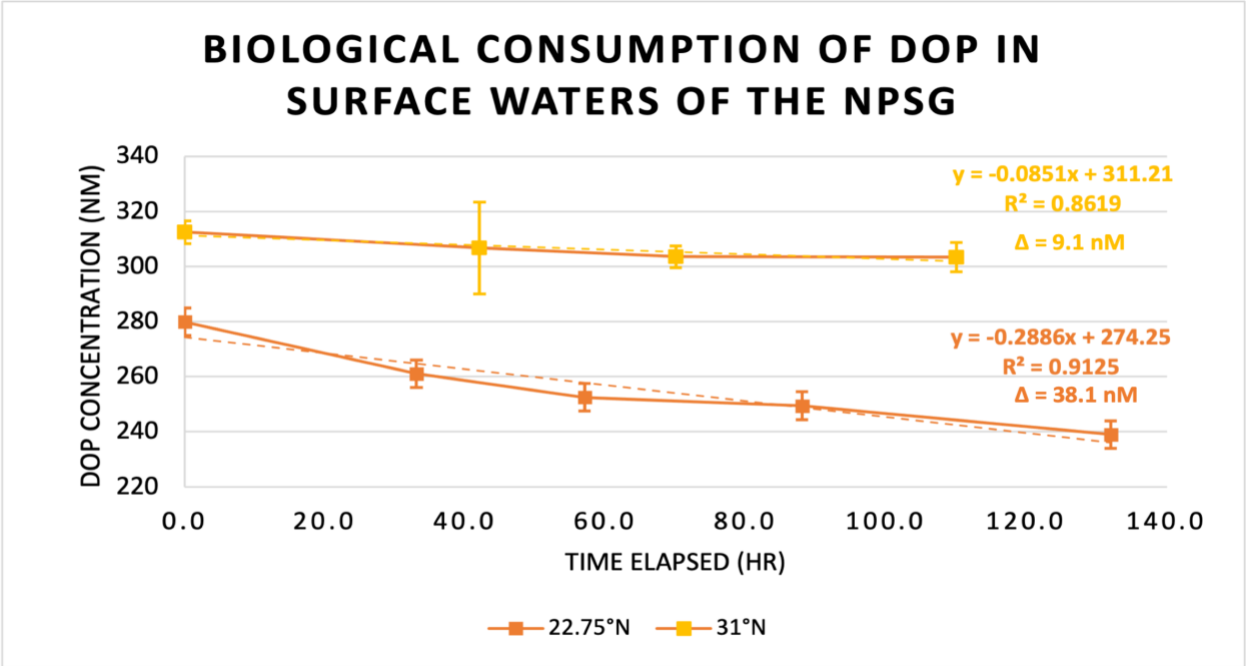

Fig. 14. DOP consumption in surface (5m) water bioassay incubation experiments at St. ALOHA (22.75°N) (orange) and 31°N (yellow). Error bars represent standard deviation of triplicate analyses for each measurement.

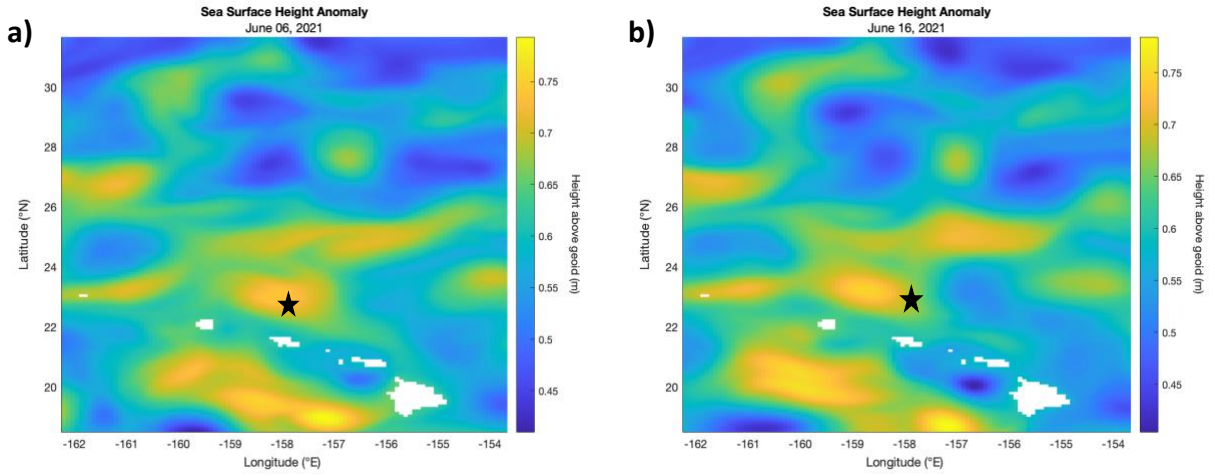

Fig. 15. Sea surface height for June 06, 2021, the date of Station 1 occupation (a) and June 16, 2021, the date of Station 10 occupation (b). The black star indicates the location of sampling (Station ALOHA) at 22.75°N, 158°W.

3.3 Sea surface height

Sea surface height products using The Operational Mercator Ocean biogeochemical global ocean analysis and forecast system were utilized to analyze the spatiotemporal fluctuation of mesoscale eddies around Station ALOHA. Two casts were made at Station ALOHA (22.75°N, 158°W) the first on June 06, 2021, and the second on June 16, 2021. Upon visualization, a region of convergence created an elevated sea surface height (~ +0.75 m) that centered around Station ALOHA when Station 1 was sampled. Over the ten-day period of the cruise, this mesoscale eddy moved increasingly to the northwest away from Station ALOHA; thus, the eddy's eastern edge was sampled upon return.

4. DISCUSSION

Decades of research and the consequential traditional scientific thinking have focused on the biogeochemical cycling and availability of dissolved inorganic nutrients in seawater to both infer and predict spatiotemporal patterns of net community export production and its subsequent remineralization by heterotrophic microbial bacteria. Although the indispensable role of these inorganic nutrients for biological life has long been recognized, scientific understanding of the

way in which nutrients are cycling throughout the marine ecosystem has markedly changed over recent years. With the realization that marine plankton are capable of harnessing multiple metabolic strategies to cope with varying nutrient availability came plentiful research aimed at identifying the primary mechanisms controlling export production from the ocean's euphotic zone (Lin et al., 2016). This study targeted four questions with the intention of enhancing modern understanding of the biogeochemical cycling of nutrients in the upper oligotrophic ocean. These research questions are discussed below in greater detail along with suggestions for future research central to observations made here.

4.1 *Is there an observed lateral gradient of DOP concentration in surface waters across the subtropical North Pacific gyre suggestive of its role as an organic nutrient sustaining a portion of ANCP?*

The observed latitudinal gradient of DOP from 22.75° - 31°N exhibits an overall relatively replete pool within the surface waters at Station ALOHA and depleted concentrations closer to the core of the gyre (Fig. 10a). Using linear regression analysis, the net decrease of [DOP] in the upper 50 m of the water column was approximated as 141 nM (R^2 = 0.307). Prior studies surrounding this region of the global ocean have discussed the net consumption rates for DOM and compared its contribution to existing rates of particulate export. Abell et al. 2000 found a strikingly similar latitudinal gradient in upper ocean DOP, 130 nM, along a path slightly to the east of our cruise. Coupling this gradient with the mean Ekman transport rates for this region, Abell et al. (2000) estimated an annual mean consumption of 4.4 ± 1.0 mmol DOP m^{-2} y^{-1} from surface waters within the gyre using a mass balance established from 15°N to 30°N. Notably, this consumption could result from biological conversion to PO_4^{3-} or incorporation into sinking particulate matter. However, no increase in [PO_4^{3-}] was observed across the gyre, in fact, Fig. 10a illustrates a slight

decrease (~34 nM) from 22.75°N – 31°N (R^2 = 0.50). Thus, the removal of DOP is likely attributable to either direct phytoplankton utilization of DOP or its remineralized PO_4^{3-} released by heterotrophic consumption, ultimately leading to sinking particulate P. Hansell and Waterhouse (1997) have interpreted a decrease in surface DOM across the southern Pacific gyre in an analogous fashion. Our data and its interpretation support a similar supply of DOP sustaining export production along an Ekman transport path northwards from Station ALOHA towards the NPSG core. Estimates result from using mean northward Ekman velocity calculated from 0.25° ensemble-mean velocities of drifters drogued at 15-m depth between 1979 – 2007 (smoothed to 1°) (Maximenko et al., 2009). Extracting a mean northward Ekman velocity of 4 cm/s ± 25%, the rate of DOP consumption (DOP_{cons}) spanning the nine degrees of latitude (~999 km) studied was estimated at 8.8 ± 2.2 mmol DOP m^{-2} y^{-1} (Equation 3).

$$DOP_{cons} = \frac{(\Delta DOP)(D_{Ek})}{T_{22°-31°N}} \qquad (3)$$

Where ΔDOP = 0.141 µM (Fig. 8), the approximate time it took surface water to move nine degrees of latitude at 4 cm/s ($T_{22°-31°}$) = 0.80 yr, and the depth of the Ekman layer which DOP consumption was integrated over (D_{ek}) = 50 m. This calculated magnitude is nearly quadrupole the predicted magnitude for the region by an earlier modeling study (Letscher et al., 2016; Fig. 3a) and double previous consumption rates approximated across similar gradients (Abell et al., 2000). Variability in the consumption of DOP across this latitudinal gradient may be associated with both seasonality in upper 50 m DOP concentrations (19.7%) at Station ALOHA (estimated from Hawaii Ocean Time-series observations) and drifter velocity data estimation (± 25%). The latter was chosen as a more conservative estimate for the reported uncertainty in our estimation of DOP_{cons}.

At Station ALOHA, particulate export of P approximated via sediment traps ranges from 4.2 – 5.4 mmol P m^{-2} yr^{-1} (Karl et al., 1995). The consumption of DOP determined by Abell et al.

(2000), and reaffirmed by this study, within the NPSG could supply upwards of 80% of this export. Additional estimates of new production at Station ALOHA have suggested that 2 mol C m^{-2} yr^{-1} are exported from the euphotic zone (Emerson et al., 1997). Karl et al., 1995 assumes 60% of this carbon (C) export is comprised of sinking particles with a C:P ratio between 112:1 and 136:1. Therefore, the export of P would fall within the range of 8.8 – 10.7 mmol P m^{-2} yr^{-1}. This estimate results in a meridional advection of DOP supplying approximately 40% of the particulate P export at Station ALOHA. In addition to field-based observations, model distributions for particulate P export with and without semilabile DOP included have approximated <16 mmol P m^{-2} yr^{-1} and <8 mmol P m^{-2} yr^{-1}, respectively, over subtropical gyre regions. The DOP input within these model estimates was reported to account for ~70% of the P supply over the subtropical gyre (Roussenov et al., 2006).

Consequently, among both field- and model-based data, as well as the observational data obtained within this study, corroborating evidence largely suggests that the cycling and transport of DOP within the NPSG plays a central role in providing the P required for export production over the subtropical gyre region. The focus of future research should seek to narrow the percentage estimate for DOP's contribution to particulate P export in order to more accurately address its effects on nutrient budgets for the subtropics.

4.2 *Is there evidence for DOP consumption (i.e. a labile DOP pool within surface waters of the NPSG?*

A long-standing challenge within the realm of marine biogeochemistry and ecology has been to obtain accurate estimates of nutrient fluxes through the microbial community due to the required knowledge of the lability of the nutrient pool. To date, the knowledge of the chemical composition of the DOM pool remains limited, thus no readily available methods to ascertain the

bioavailability of the DOM pool have risen to prominence. However, a variety of approaches have been made to address said challenges. In the case of P contained within the DOM pool, Björkman & Karl (2003) employed methods determining the size of the biologically available P pool by assessing the total radioactivity of the sample after ^{32}P tracer addition and the measured intracellular activity of the terminal P group within incubated samples. Dyhrman and Ruttenberg (2006) used the enzyme alkaline phosphatase and its subsequent activity as a metric of DOP bioavailability, as alkaline phosphatase can hydrolyze phosphomonoesters into bioavailable phosphate. Through these techniques, past studies have documented the ability phytoplankton to utilize DOP to satisfy their cellular P requirements.

This study employed incubation experiments to determine heterotrophic DOP consumption at the edge of the gyre region and closer to its center. While ultimately our interest lies in the ability of DOP to serve as an organic nutrient source sustaining algal growth, performing incubations in the light to allow for autotrophic activity complicates the interpretation of DOP dynamics since DOP is also produced by autotrophs during the incubation. Thus, by interpreting DOP bioavailability from heterotrophic consumption incubations, we are making the assumption that heterotrophic DOP lability approximates autotrophic DOP lability, not unreasonable since the main enzyme responsible for DOP utilization, alkaline phosphatase, is widely distributed across the domains of life (Sharma et al., 2013). Results yielded significantly more DOP consumption overall within the surface water samples at the southern edge of the gyre (22.75°N) than those closer to the core of the gyre (31°N). Interestingly, initial DOP concentrations for incubation experiments within the surface waters at 31ºN were approximately double those found in situ, (~380 nM and ~190 ± 1 nM, respectively). In theory, initial [DOP] should measure nearly equivalent, however, a doubling suggests external contamination in the process of establishing the

mixed treatment incubation samples. Filtrate for the mixed water samples was collected via gravity filtration using 0.2 µm-filters. As the majority (80%) of these samples consisted of the filtrate, it is possible that the cells were lysed during filtration leaching organic P from the cell's interior into the DOP pool. However, we observe that this apparent contamination process did not appreciably augment the size of the bioavailable DOP pool over the course of the incubation as evidenced by the small ~10 nM of consumed DOP (Fig. 14).

Because significantly greater DOP consumption was observed within surface waters where [DOP] was elevated, biological uptake may be interpreted to increase in regions where DOP is more readily available. This observation is inconsistent with prior modeling results of Letscher et al. (2016) (Fig. 3b) which predict inverse behavior of biological supply and uptake fluxes within the NPSG. Letscher et al.'s (2016) global modeling study extended estimates for the fraction of subtropical ANCP supported by lateral DOP utilization within the NPSG region, finding a significant role for DOP in export production. However, another potentially important (but overlooked) biogeochemical factor in determining the biogeochemical context in which marine DOP accumulates or is utilized as an additional autotrophic P source within surface waters is the availability of dissolved iron (Fe) and/or ecosystem Fe stress, revealed by a recent global analysis (Liang et al., 2022). The prior modeling study (Letscher et al., 2016) did not consider the role of iron stress on DOP use and it is observed that surface ocean dissolved iron concentrations exhibit a decreasing south to north gradient across the NPSG (GEOTRACES, 2021), which may help explain the discordance between the model predictions and the observed/inferred DOP lability and consumption. Future modeling work should aim to explicitly couple the marine P and Fe cycles to investigate the nexus of iron and DOP supply and their subsequent contribution to marine ANCP.

4.3 *Is there evidence for preferential DOP consumption between surface waters and the shallow surfaces of the ocean interior of the NPSG?*

The bulk pools of DOM contain both a fraction that is refractory and homogenously mixed throughout the water column, and a nonrefractory fraction which is labile on some timescale relevant to the timescale of ocean ventilation and overturning circulation (Carlson, 2002). Because the two fractions have unique stoichiometry and lifetimes, prior research has examined these specific stoichiometric ratios of DOM to assess if preferential P remineralization is a global phenomenon and its implication on the magnitude and spatial distribution of marine primary productivity and the biological pump. When direct utilization of DOP by phytoplankton and preferential DOP remineralization by heterotrophic remineralization are included in a coupled physical-biogeochemical ocean model, these processes are found to increase the strength of marine net primary productivity and the biological pump by ~10% and ~9%, respectively versus the case of Redfield DOM cycling and no autotrophic DOP uptake (Letscher & Moore, 2015).

Field-based observations from this study found appreciable DOP consumption in the DCM microbial community at Station ALOHA (Fig. 13), consistent with findings from Clark et al., (1998) who observed dramatic increase in C:P and N:P ratios with depth. However, when comparing the magnitude of DOP consumption carried out by the DCM microbial communities at 125 m with those resident within surface waters (5 m), the substantial overlap in error bars limit the ability to conclude a statistically significant greater amount of DOP consumption at one depth versus the other. This observation is contrary to numerous incubation and field studies investigating the euphotic vs. disphotic zone lability of the marine DOC and DON pools, which find evidence for a larger and more rapid consumption of surface accumulated DOC and DON when exposed to subsurface mesopelagic microbial communities (Hansell & Carlson, 2001;

Carlson et al., 2004; Letscher et al., 2013; 2015). Instead, our study identifies the primary axis of DOP consumption variability to be horizontal across the NPSG from Station ALOHA in the south (~45 nM DOP consumption at both 5 and 125 m) to the gyre core at 31ºN (nil to ~10 nM DOP consumption at 5 and 125 m). Although this study did not present significant evidence for preferential consumption of DOP by depth in the ocean, future research should continue to explore the selective removal of P from DOM as a proxy for the nutrient demand of marine microorganisms.

4.4 *Similarly for DON, is there an observed gradient in bDON concentration in surface waters across the NPSG suggestive of its role as an organic nutrient sustaining a portion of ANCP?*

Surface (<50 m) [DON] distributions across the NPSG were observed to decrease ~1.4 µM (R^2 = 0.78) from 22.75°N – 31°N (Figs. 9 and 10b). Although this decrease was slight within surface waters, the mesopelagic (~200 m) [DON] exhibited a sharp decrease across the latitudinal gradient where concentrations decreased from ~4.5 to 1.5 µM. In other words, the vertical distribution of the DON pool reached greater depths around 22.75°N compared to 31°N. Within gyre regions and transition zones, the vertical distributions of DOM result primarily from degradation along isopycnals (Abell et al. 2000). This degradation returns nutrients and inorganic C to the upper thermocline, ultimately feeding primary production in the euphotic zone. Future research could explore the fraction of organic matter remineralization due to DOM degradation on each isopycnal to further quantify the contribution this DOM degradation makes toward nutrient regeneration.

With ambient [NO_3^-] in the oligotrophic North Pacific surface waters observed as <50 nM, it is critical to consider alternate sources of N and their potential to contribute to marine export production. DON is known to be consumed by marine heterotrophs with the liberated inorganic N

in turn available for phytoplankton and has thus been invoked as a source of N fueling export production in oligotrophic gyres when lateral surface ocean DON gradients have been observed (Letscher et al., 2016; Torres-Valdes et al., 2009). In particular, field and bioassay results from Letscher et al. (2013) suggest DON consumption occurs as waters transit from productive gyre margins to the interior of gyres. Here, the fraction of DON deemed bioavailable (by a novel acid hydrolysis method) was assessed alongside the total bulk DON pool to provide insight to the potential for organic N to stimulate productivity. On average, 13.3 ± 3.5% of the surface DON pool was comprised of bDON across the latitudinal transect sampled in this study, aligning with previous research within the North Pacific subtropics where [bDON] represented 15-25% of the bulk DON pool (LGA22). Further, an overall gradient of this bioavailable pool of DON was observed across the latitudinal transect from 22.75°N – 31°N indicating ~228 nM of bDON consumption (Fig. 12). This suggests DON consumption is largely occurring as waters are laterally advected towards the center of gyre regions and surface waters become increasingly scarce of inorganic nutrients. If a similar northwards Ekman transport rate is applied to the bDON surface ocean gradient as was applied to the DOP gradient, we estimate a flux of 14.3 ± 3.7 mmol m^{-2} y^{-1}, potentially fueling export production across the southern half of the NPSG, comparable to that predicted by the modeling study of Letscher et al. (2016). Future work should continue to utilize targeted methods for the quantification of bioavailable amide N found in marine DON to accurately measure the bioavailable DON pool and infer spatiotemporal changes within the marine ecosystem.

4.5 *Mesoscale eddy effect on surface DOM at Station ALOHA*

Eddy-driven sources and sinks of nutrients in the upper ocean have proven an important vehicle for nutrient transport in the world's oceans (McGillicuddy et al., 2003). Particularly in

oligotrophic gyre systems where largescale convergence results in a net downward flux of surface waters at the rotating center, mesoscale eddies (of the order 10^2 km) can provide critical pockets of upwelling (new production) or amplified downwelling depending on their direction of rotation and geographical location (McGillicuddy et al., 1998).

The research conducted from this cruise posed the unique opportunity to sample Station ALOHA at higher temporal resolution than traditional timeseries studies. Station ALOHA (22.75°N) was sampled on June 06, 2021 (St. 1) and June 16, 2021 (St. 10) where dramatically different surface concentrations of [DOP], [DON], and [bDON] were observed. Upon returning to 22.75°N ten days after sampling Station 1, surface [DOM] increased roughly by a factor of two. Upon visual analysis of SSH, Station 1 was sampled during a period of mesoscale convergence where SSH was ~0.75 m higher than the historical average. This eddy appeared to move increasingly northwest over the course of the ten days between sampling Station ALOHA, and in contrast, Station 10 sampled the eddy's eastern edge where SSH was ~10 cm lower and therefore closer to the average height of the geoid. These results largely agree with the notion that anticyclonic eddies with elevated SSH in the Northern Hemisphere are associated with downwelling and consequently depressed biological activity (McGillicuddy et al., 1998).

5. CONCLUSIONS

In spite of low euphotic zone inorganic nutrient concentrations, oligotrophic gyres contribute significantly to global marine export production. To understand the processes controlling this export, it is crucial to identify the primary mechanisms leading to nutrient supply to the surface ocean. Analyses of DOM measurements performed here within the surface and DCM communities suggest the consumption of DOP and DON are important additional controls on nutrient cycling within the subtropical NPSG region. The distributions of DOP and bDON across

the surface of the NPSG suggest that both pools may contribute bioavailable P and N on the order of 8.8 ± 2.2 mmol P m^{-2} y^{-1} and 14.3 ± 3.7 mmol N m^{-2} y^{-1}, along the northward transit of waters from the southern edge towards the gyre core. To address the question of bioavailability, bioassay incubation experiments were performed to quantify the magnitude and rate of heterotrophic DOP remineralization in both the upper euphotic (5m) and lower euphotic (125m; DCM) zones at two stations in the subtropical North Pacific; Station ALOHA (22.75°N) and 31°N along a transect on 158°W, north of Oahu, HI.

Experimental results found evidence for the existence of a measurable pool of labile DOP present in surface waters on the order of 25 – 60 nM that was consumed in ~5 days near the southern edge of the gyre at Station ALOHA. This consumption was ~1/3 of the latitudinal gradient in surface waters to 31°N, the core of the gyre. However, both approaches found little evidence for labile DOP present at 31°N. DOP consumption was greatest in surface waters and in treatments where the heterotrophic bacteria were released from grazer control, with evidence of DOP consumption by the DCM microbial community present at Station ALOHA.

The new methods of LGA22 allowed for targeted quantification of bioavailable amide N found in marine DON to estimate the fraction of the bulk DON pool composed of labile N. Results provided evidence for a lateral gradient decreasing northwards in bDON present in surface waters across the latitudinal transect. A similar gradient in the percentage of the DON pool measured as bDON was not observed, averaging ~13.3 ± 3.5% bDON in DON across the transect. Analytical uncertainties in measured DON and bDON concentrations on the order of ~5-10% may preclude a robust estimation of the percentage of bDON in DON at the observed range of ~10-15%. Future research should continue to target the assessment of the labile DON pool in oligotrophic surface waters and its contribution to overall export production. The latitudinal gradients observed in the

surface ocean DOM pool and its vertical lability to heterotrophic microbes found in this study largely affirms the importance of upper-ocean lateral organic nutrient transport on supplying North Pacific subtropical gyre surface waters with bioavailable N and P. This study provides valuable in situ observational data and experimental results from the subtropical North Pacific to test the hypotheses of a global modeling study (Letscher et al., 2016) examining organic nutrient contributions to oligotrophic nutrient budgets that was largely calibrated against Atlantic basin DOP data.

LIST OF REFERENCES

Abell, J., Emerson, S., & Renaud, P. (2000). Distributions of TOP, TON and TOC in the North Pacific subtropical gyre: Implications for nutrient supply in the surface ocean and remineralization in the upper thermocline. *Journal of Marine Research, 58*(2), 203-222.

Aluwihare, L. I., Repeta, D. J., Pantoja, S., & Johnson, C. G. (2005). Two chemically distinct pools of organic nitrogen accumulate in the Ocean. *Science, 308*(5724), 1007–1010. https://doi.org/10.1126/science.1108925

Ammerman, J. W., Hood, R. R., Case, D. A., & Cotner, J. B. (2003). Phosphorus deficiency in the Atlantic: An emerging paradigm in oceanography. *Eos, Transactions American Geophysical Union, 84*(18), 165-170.

Amon, R. M., & Benner, R. (1996). Bacterial utilization of different size classes of dissolved organic matter. *Limnology and Oceanography, 41*(1), 41–51. https://doi.org/10.4319/lo.1996.41.1.0041

Baker, A. R., Kelly, S. D., Biswas, K. F., Witt, M., & Jickells, T. D. (2003). Atmospheric deposition of nutrients to the Atlantic Ocean. *Geophysical Research Letters, 30*(24).

Bates, N. R., Michaels, A. F., & Knap, A. H. (1996). Seasonal and interannual variability of oceanic carbon dioxide species at the US JGOFS Bermuda Atlantic Time-series Study (BATS) site. *Deep Sea Research Part II: Topical Studies in Oceanography*, *43*(2-3), 347-383.

Björkman, K. M., & Karl, D. M. (2003). Bioavailability of dissolved organic phosphorus in the euphotic zone at Station ALOHA, North Pacific Subtropical Gyre. *Limnology and Oceanography*, *48*(3), 1049-1057.

Braman, R. S., & Hendrix, S. A. (1989). Nanogram nitrite and nitrate determination in environmental and biological materials by vanadium (III) reduction with chemiluminescence detection. *Analytical chemistry, 61*(24), 2715-2718.

Broek, T. A., Bour, A. L., Ianiri, H. L., Guilderson, T. P., & McCarthy, M. D. (2019). Amino acid enantiomers in old and young dissolved organic matter: implications for a microbial nitrogen pump. *Geochimica et Cosmochimica Acta*, *247*, 207-219.

Carlson, C. A. (2002), Production and removal processes, in *Biogeochemistry of Marine Dissolved Organic Matter*, 1st ed., edited by D. A. Hansell and C. A. Carlson, pp. 91–151, Academic Press, San Diego, Calif., doi:10.1016/B978-012323841-2/50007-5.

Carlson, C. A., & Ducklow, H. W. (1996). Growth of bacterioplankton and consumption of dissolved organic carbon in the Sargasso Sea. *Aquatic Microbial Ecology*, *10*(1), 69-85.

Carlson, C. A., Giovannoni, S. J., Hansell, D. A., Goldberg, S. J., Parsons, R., & Vergin, K. (2004). Interactions among dissolved organic carbon, microbial processes, and community structure in the mesopelagic zone of the northwestern Sargasso Sea. *Limnology and Oceanography*, *49*(4), 1073-1083.

Charria, G., Dadou, I., Llido, J., Drevillon, M., & Garcon, V. (2008). Importance of dissolved organic nitrogen in the north Atlantic Ocean in sustaining primary production: a 3-D modelling approach. *Biogeosciences*, *5*(5), 1437-1455.

Clark, L. L., Ingall, E. D., & Benner, R. (1998). Marine phosphorus is selectively remineralized. *Nature*, *393*(6684), 426-426.

Dore, J. E., Brum, J. R., Tupas, L. M., & Karl, D. M. (2002). Seasonal and interannual variability in sources of nitrogen supporting export in the oligotrophic subtropical North Pacific Ocean. *Limnology and Oceanography*, *47*(6), 1595-1607.

Doddridge, E. W., Marshall, D. P., & Hogg, A. M. (2016). Eddy Cancellation of the Ekman Cell in Subtropical Gyres, *Journal of Physical Oceanography*, *46*(10), 2995-3010.

Ducklow, H. W., Carlson, C. A., Bates, N. R., Knap, A. H., & Michaels, A. F. (1995). Dissolved organic carbon as a component of the biological pump in the North Atlantic Ocean. *Philosophical Transactions of the Royal Society of London. Series B: Biological Sciences*, *348*(1324), 161–167. https://doi.org/10.1098/rstb.1995.0058

Duhamel, S., Diaz, J. M., Adams, J. C., Djaoudi, K., Steck, V., & Waggoner, E. M. (2021). Phosphorus as an integral component of global marine biogeochemistry. *Nature Geoscience*, *14*(6), 359-368.

Dyhrman, S., Chappell, P. D., Haley, S., Moffett, J., Orchard, E., Waterbury, J., & Webb, E. (2006). Molecular Evidence of Phosphonate Utilization in Trichodesmium. *EOS, Transactions, American Geophysical Union*, *87*(36).

Dyhrman, S. T., & Ruttenberg, K. C. (2006). Presence and regulation of alkaline phosphatase activity in eukaryotic phytoplankton from the coastal ocean: Implications for dissolved organic phosphorus remineralization. *Limnology and Oceanography*, *51*(3), 1381-1390.

Emerson, S. (2014). Annual net community production and the biological carbon flux in the ocean. *Global Biogeochemical Cycles*, *28*(1), 14-28.

Emerson, S., Quay, P., Karl, D. *et al.* Experimental determination of the organic carbon flux from open-ocean surface waters. *Nature* **389**, 951–954 (1997). https://doi.org/10.1038/40111

Flombaum, P., Gallegos, J. L., Gordillo, R. A., Rincón, J., Zabala, L. L., Jiao, N., Karl, D. M., Li, W. K., Lomas, M. W., Veneziano, D., Vera, C. S., Vrugt, J. A., & Martiny, A. C. (2013). Present and future global distributions of the marine

cyanobacteria prochlorococcus and synechococcus. *Proceedings of the National Academy of Sciences*, *110*(24), 9824–9829. https://doi.org/10.1073/pnas.1307701110

Friedlingstein, P., Jones, M. W., O'Sullivan, M., Andrew, R. M., Bakker, D. C., Hauck, J., ... & Zeng, J. (2022). Global carbon budget 2021. *Earth System Science Data*, *14*(4), 1917-2005.

Garcia, H. E., Locarnini, R. A., Boyer, T. P., Antonov, J. I., Baranova, O. K., Zweng, M. M., ... & Levitus, S. (2013). World ocean atlas 2013. Volume 4, Dissolved inorganic nutrients (phosphate, nitrate, silicate).

GEOTRACES Intermediate Data Product Group (2021). The GEOTRACES Intermediate Data Product 2021 (IDP2021). NERC EDS British Oceanographic Data Centre NOC. DOI: 10.5285/cf2d9ba9-d51d-3b7c-e053-8486abc0f5fd .

Hansell, D. A., & Carlson, C. A. (2001). Biogeochemistry of total organic carbon and nitrogen in the Sargasso Sea: control by convective overturn. *Deep Sea Research Part II: Topical Studies in Oceanography*, *48*(8-9), 1649-1667.

Hansell, D. A., & Waterhouse, T. Y. (1997). Controls on the distributions of organic carbon and nitrogen in the eastern Pacific Ocean. *Deep Sea Research Part I: Oceanographic Research Papers*, *44*(5), 843-857.

Johnson, K. S., Riser, S. C., & Karl, D. M. (2010). Nitrate supply from deep to near-surface waters of the North Pacific subtropical gyre. *Nature*, *465*(7301), 1062-1065.

Josefsson, B., Lindroth, P., & Östling, G. (1977). An automated fluorescence method for the determination of total amino acids in natural waters. *Analytica Chimica Acta*, *89*(1), 21-28.

Karl, D. M., R. Letelier, D. Hebel, L. Tupas, J. Dore, J. Christian and C. Winn. 1995. Ecosystem changes in the North Paci□ c subtropical gyre attributed to the 1991–1992 El Nino. Nature, 373, 230–234.

Karl, D. M., & Tien, G. (1992). Magic: A sensitive and precise method for measuring dissolved phosphorus in Aquatic Environments. *Limnology and Oceanography*, *37*(1), 105–116. https://doi.org/10.4319/lo.1992.37.1.0105

Keeling, C. D., Brix, H., & Gruber, N. (2004). Seasonal and long-term dynamics of the upper ocean carbon cycle at Station ALOHA near Hawaii. *Global Biogeochemical Cycles*, *18*(4).

Knapp, A. N., Casciotti, K. L. & Prokopenko, M. G. Dissolved Organic Nitrogen Production and Consumption in Eastern Tropical South Pacific Surface Waters. *Glob. Biogeochem. Cycles* **32**, 769–783 (2018).

Kubota, M. (1994). A mechanism for the accumulation of floating marine debris north of Hawaii. *Journal of Physical Oceanography*, *24*(5), 1059–1064. https://doi.org/10.1175/1520-0485(1994)024<1059:amftao>2.0.co;2

Letscher, R.T., Gray, J. & Aluwihare L. (2022). A simple method for the quantification of bioavailable dissolved organic nitrogen in seawater, in prep. for *L&O Methods*.

Letscher, R. T., Hansell, D. A., Carlson, C. A., Lumpkin, R., & Knapp, A. N. (2013). Dissolved organic nitrogen in the global surface ocean: Distribution and fate. *Global Biogeochemical Cycles*, *27*(1), 141-153.

Letscher, R. T., Knapp, A. N., James, A. K., Carlson, C. A., Santoro, A. E., & Hansell, D. A. (2015). Microbial community composition and nitrogen availability influence DOC remineralization in the South Pacific Gyre. *Marine Chemistry*, *177*, 325-334.

Letscher, R. T., & Moore, J. K. (2015). Preferential remineralization of dissolved organic phosphorus and non-Redfield DOM dynamics in the global ocean: Impacts on marine productivity, nitrogen fixation, and carbon export. *Global Biogeochemical Cycles*, *29*(3), 325-340.

Letscher, R. T., Primeau, F., & Moore, J. K. (2016). Nutrient budgets in the subtropical ocean gyres dominated by lateral transport. *Nature Geoscience*, *9*(11), 815-819.

Li, T., Guo, C., Zhang, Y., Wang, C., Lin, X., & Lin, S. (2018). Identification and expression analysis of an atypical alkaline phosphatase in Emiliania huxleyi. *Frontiers in microbiology*, *9*, *2156.*

Liang, Z., Letscher, R. T., & Knapp, A. N. (2022). Dissolved organic phosphorus concentrations in the surface ocean controlled by both phosphate and iron stress. *Nature Geoscience*, *15*(8), 651-657.

Liang, Z., McCabe, K., Fawcett, S.E., Forrer, H.J., Jeandel, C., Marconi, D., Planquette, H., Saito, M.A., Sohm, J.A., Thomas, R.K., Letscher, R.T., & Knapp, A.N. (2022). A global ocean dissolved organic phosphorus (DOP) concentration database (DOPv2021), in revision for *Scientific Data*.

Lin, H. Y., Shih, C. Y., Liu, H. C., Chang, J., Chen, Y. L., Chen, Y. R., ... & Lin, H. J. (2013). Identification and characterization of an extracellular alkaline phosphatase in the marine diatom Phaeodactylum tricornutum. *Marine biotechnology*, *15*(4), 425-436.

Lomas, M. W., Bates, N. R., Johnson, R. J., Knap, A. H., Steinberg, D. K., & Carlson, C. A. (2013). Two decades and counting: 24-years of sustained open ocean biogeochemical measurements in the Sargasso Sea. *Deep Sea Research Part II: Topical Studies in Oceanography*, *93*, 16-32.

Lomas, M. W., Burke, A. L., Lomas, D. A., Bell, D. W., Shen, C., Dyhrman, S. T., & Ammerman, J. W. (2010). Sargasso Sea phosphorus biogeochemistry: an important role for dissolved organic phosphorus (DOP). *Biogeosciences*, *7*(2), 695-710.

Martiny, A. C., Lomas, M. W., Fu, W., Boyd, P. W., Chen, Y.-ling L., Cutter, G. A., Ellwood, M. J., Furuya, K., Hashihama, F., Kanda, J., Karl, D. M., Kodama, T., Li, Q. P., Ma, J., Moutin, T., Woodward, E. M., & Moore, J. K. (2019). Biogeochemical controls of surface ocean phosphate. *Science Advances*, *5*(8).

Martiny, A. C., Pham, C. T., Primeau, F. W., Vrugt, J. A., Moore, J. K., Levin, S. A., & Lomas, M. W. (2013). Strong latitudinal patterns in the elemental ratios of marine plankton and organic matter. *Nature Geoscience*, *6*(4), 279-283.

Maximenko, N., Niiler, P., Centurioni, L., Rio, M. H., Melnichenko, O., Chambers, D., ... & Galperin, B. (2009). Mean dynamic topography of the ocean derived from satellite and drifting buoy data using three different techniques. Journal of Atmospheric and Oceanic Technology, 26(9), 1910-1919.

Mather, R. L., Reynolds, S. E., Wolff, G. A., Williams, R. G., Torres-Valdes, S., Woodward, E. M. S., ... & Achterberg, E. P. (2008). Phosphorus cycling in the North and South Atlantic Ocean subtropical gyres. *Nature Geoscience*, *1*(7), 439-443.

McCarthy, M. D., Benner, R., Lee, C., Hedges, J. I., & Fogel, M. L. (2004). Amino acid carbon isotopic fractionation patterns in oceanic dissolved organic matter: an unaltered photoautotrophic source for dissolved organic nitrogen in the ocean?. *Marine Chemistry*, *92*(1-4), 123-134.

McGillicuddy Jr, D. J., Anderson, L. A., Doney, S. C., & Maltrud, M. E. (2003). Eddy-driven sources and sinks of nutrients in the upper ocean: Results from a 0.1 resolution model of the North Atlantic. *Global Biogeochemical Cycles*, *17*(2).

McGillicuddy, D. J., Robinson, A. R., Siegel, D. A., Jannasch, H. W., Johnson, R., Dickey, T. D., ... & Knap, A. H. (1998). Influence of mesoscale eddies on new production in the Sargasso Sea. *Nature*, *394*(6690), 263-266.

Melet, A. V., Hallberg, R., & Marshall, D. P. (2022). The role of ocean mixing in the climate system. *Ocean Mixing*, 5–34. https://doi.org/10.1016/b978-0-12-821512-8.00009-8

Michaels, A. F., Knap, A. H., Dow, R. L., Gundersen, K., Johnson, R. J., Sorensen, J., ... & Bidigare, R. (1994). Seasonal patterns of ocean biogeochemistry at the US JGOFS Bermuda Atlantic Time-series Study site. *Deep Sea Research Part I: Oceanographic Research Papers*, *41*(7), 1013-1038.

Orchard, E.D., Ammerman, J.W., Lomas, M.W., & Dyrhman, S.T. (2010). Dissolved inorganic and organic phosphorus uptake in Trichodemium and the microbial community The importance of phosphorus ester in the Sargasso Sea. *Limnology and Oceanography, 55*(2), 1390-1399.

Polovina, J. J., Howell, E. A., & Abecassis, M. (2008). Ocean's least productive waters are expanding. *Geophysical Research Letters*, *35*(3).

Redfield, A. C. (1934). *On the proportions of organic derivatives in sea water and their relation to the composition of plankton* (Vol. 1). Liverpool: university press of liverpool.

Redfield, A. C. (1958). The biological control of chemical factors in the environment. *American scientist*, *46*(3), 230A-221.

Reynolds, S., Mahaffey, C., Roussenov, V., & Williams, R. G. (2014). Evidence for production and lateral transport of dissolved organic phosphorus in the eastern subtropical North Atlantic. *Global Biogeochemical Cycles*, *28*(8), 805-824.

Roussenov, V., Williams, R. G., Mahaffey, C., & Wolff, G. A. (2006). Does the transport of dissolved organic nutrients affect export production in the Atlantic Ocean? *Global Biogeochemical Cycles*, *20*(3). https://doi.org/10.1029/2005gb002510

Sarmiento, J. L., Slater, R., Barber, R., Bopp, L., Doney, S. C., Hirst, A. C., Kleypas, J., Matear, R., Mikolajewicz, U., Monfray, P., Soldatov, V., Spall, S. A., & Stouffer, R. (2004). Response of ocean ecosystems to climate warming. *Global Biogeochemical Cycles*, *18*(3). https://doi.org/10.1029/2003gb002134

Sipler, R. E., & Bronk, D. A. (2015). Dynamics of dissolved organic nitrogen. *Biogeochemistry of marine dissolved organic matter*, 127-232.

Shaked, Y., Xu, Y., Leblanc, K., & Morel, F. M. (2006). Zinc availability and alkaline phosphatase activity in Emiliania huxleyi: Implications for Zn-P co-limitation in the ocean. *Limnology and Oceanography*, *51*(1), 299-309.

Sharma, U., Pal, D., & Prasad, R. (2014). Alkaline phosphatase: an overview. *Indian Journal of Clinical Biochemistry*, *29*(3), 269-278.

Solórzano, L., & Sharp, J. H. (1980a). Determination of total dissolved nitrogen in natural waters 1. *Limnology and Oceanography*, *25*(4), 751-754.

Solórzano, L., & Sharp, J. H. (1980b). Determination of total dissolved phosphorus and particulate phosphorus in natural waters1. *Limnol. Oceanogr.*, *25*(4), 754–758.

Strickland, J.D.H. and Parsons, T.R. (1968) A Practical Handbook of Seawater Analysis. Bulletin of Fisheries Research Board of Canada, 167, 1-311.

Su, Z., Olman, V., & Xu, Y. (2007). Computational prediction of Pho regulons in cyanobacteria. *Bmc Genomics*, *8*(1), 1-12.

Torres-Valdés, S., Roussenov, V. M., Sanders, R., Reynolds, S., Pan, X., Mather, R., ... & Williams, R. G. (2009). Distribution of dissolved organic nutrients and their effect on export production over the Atlantic Ocean. *Global Biogeochemical Cycles*, *23*(4).

Walker, B. D., Beaupré, S. R., Guilderson, T. P., McCarthy, M. D., & Druffel, E. R. M. (2016). Pacific carbon cycling constrained by organic matter size, age and composition relationships. *Nature Geoscience, 9*(12), 888–891. https://doi.org/10.1038/ngeo2830

Williams, R. G., & Follows, M. J. (1998). The Ekman transfer of nutrients and maintenance of new production over the North Atlantic. *Deep Sea Research Part I: Oceanographic Research Papers, 45*(2-3), 461-489.