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Correspondence to:

Y. Xiang,
yaxiang@uw.edu

Subtropical Gyre Nutrient Cycling in the Upper Ocean: Insights From a Nutrient-Ratio Budget Method

Yang Xiang[1,2,3] ⓘ, Paul D. Quay[2] ⓘ, Rolf E. Sonnerup[1,3], and Andrea J. Fassbender[3] ⓘ

[1]Cooperative Institute for Climate, Ocean, and Ecosystem Studies, University of Washington, Seattle, WA, USA, [2]School of Oceanography, University of Washington, Seattle, WA, USA, [3]NOAA/OAR Pacific Marine Environmental Laboratory, Seattle, WA, USA

Abstract We use a nutrient-ratio budget method to investigate the relative importance of different nutrient source and sink terms at time-series Station ALOHA and Bermuda Atlantic Time-series Study (BATS) in the North Pacific and North Atlantic subtropical gyres, respectively. At mean state conditions over annual and multi-year time scales, vertical phosphate (PO_4^{3-}) supply from the subsurface accounts for ~60% of the total phosphorus supply at both sites. Dissolved organic matter transport and zooplankton excretion are more important phosphorous export pathways than sinking particles at Station ALOHA and BATS. The nutrient-ratio budget approach provides quantitative, observation-based constraints on nutrient sources and sinks in the surface ocean, which helps improve our understanding of the biological carbon pump in oligotrophic oceans.

Plain Language Summary In this study, we explore the cycling of nutrients that support primary production in the surface ocean and its subsequent export to depth using observed elemental ratios of nitrogen to phosphorus for various nutrient sources and sinks. We use nutrient observations from long-term oceanographic time-series studies at Station ALOHA near Hawaii and the Bermuda Atlantic Time-series Study near Bermuda. We assume that both stations are under conditions of steady state in which nutrient concentrations are not changing over long time periods, and therefore, that the nitrogen-to-phosphorus ratio between inputs and outputs should be balanced. We apply a mathematical model to estimate the relative contribution of each input and output term. Our results suggest that nutrient input is driven primarily by the vertical transport of subsurface water at both study sites. Nutrient output (loss) is driven by the gravitational sinking of large particles, the downward mixing of dissolved constituents, and the active transport of migrant animals. The loss due to the latter two processes is more important in magnitude. Our simple methodology provides quantitative, observational constraints of nutrient sources and sinks to the upper ocean, contributing improved understanding of the biological carbon pump in the oligotrophic subtropical ocean.

1. Introduction

The transfer of organic matter produced by phytoplankton in the surface ocean to the ocean interior exerts a strong control on the surface ocean carbon dioxide gas (CO_2) concentration, which in turn has a significant impact on the atmospheric CO_2 level (Kwon et al., 2009; Volk & Hoffert, 1985). Despite the importance of this vertical transfer process, termed the ocean's biological carbon pump, regional variations in its strength and sensitivity to environmental changes are poorly characterized (Quay et al., 2020). Our understanding of organic matter elemental composition has long been based on the Redfield ratio (Redfield, 1958), a constant carbon/nitrogen/phosphorus (C/N/P) ratio of 106/16/1, which is commonly used to link marine nutrient and carbon fluxes. Over the past 20 years, however, many laboratory (e.g., Geider & La Roche, 2002), field (Karl et al., 2001; Lomas et al., 2022; Martiny, Pham, et al., 2013; Martiny, Vrugt, et al., 2013), and modeling studies (Deutsch & Weber, 2012; Teng et al., 2014; Wang et al., 2019; Weber & Deutsch, 2010) have indicated that the C/N/P stoichiometry of organic matter is significantly more variable both in time and space.

In the subtropical gyres, sinking particles collected by sediment traps near the surface exhibit N/P ratios generally >25 at time-series Station ALOHA and BATS (Karl et al., 2001; Lomas et al., 2022; Singh et al., 2015), located in the North Pacific Subtropical Gyre (NPSTG) and the North Atlantic Subtropical Gyre (NASTG), respectively. Nitrogen fixation is required to support the export flux and high N/P of sinking particles at Station ALOHA (Karl et al., 1997; Quay, 2021). In addition to nitrogen fixation, lateral supply of both inorganic (nitrate + nitrite (NO_3^-)) and phosphate (PO_4^{3-})) and organic (dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP))
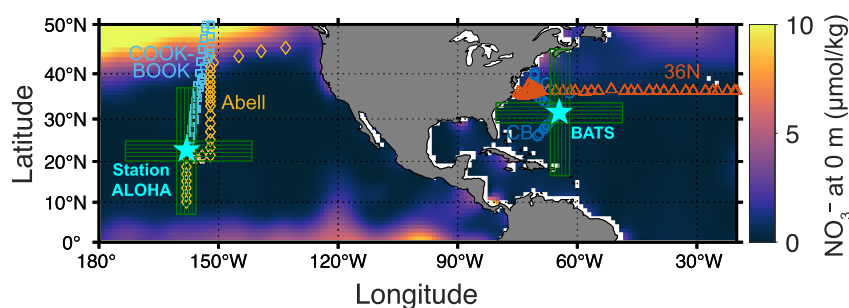
Figure 1. Location of Station ALOHA and BATS (cyan pentagrams) and cruise tracks of dissolved organic nutrients measurements superimposed on surface nitrate concentrations from the WOA18 annual climatology (Garcia et al., 2018). Coordinates in the North Pacific are from Abell et al. (2000) (diamonds) and COOK-BOOK cruises (Church et al., 2008) (squares). North Atlantic data are from Cavender-Bares et al. (2001) (CB; circles) and Torres-Valdés et al. (2009) (36N; triangles). Regions of WOA18 nutrient data used to calculate surface lateral supply ratios are highlighted with four green boxes that are $30° \times 5°$ and twenty 1-degree latitude or longitude bands.

nutrients has been proposed as another important supply mechanism in the oligotrophic subtropical gyres (e.g., Abell et al., 2000; Letscher et al., 2016; Lomas et al., 2010; Mahaffey et al., 2004; Reynolds et al., 2014). The relative importance of each nutrient supply mechanism and the associated impact on exported matter N/P has been difficult to quantify observationally, however.

A budget method, based on ratios of inorganic nutrient (PO_4^{3-}, NO_3^- and dissolved inorganic carbon) supply, has been used to estimate the C/N/P ratio of organic matter exported from the surface ocean in the Pacific Ocean (Quay, 2021). We expand on this work by including the input and output of dissolved organic nutrients (e.g., Abell et al., 2000; Hopkinson & Vallino, 2005) and the export of dissolved nutrients (inorganic and organic) through zooplankton excretion (Hannides et al., 2009; Steinberg et al., 2002). The steady state framework of our budget method dictates that the N/P ratio of all dissolved nutrient sources to the mixed layer ($\Delta NO_3/\Delta PO_4$, $\Delta DON/\Delta DOP$), supplied either vertically or laterally, should equal the N/P ratio of all nutrient sinks (sinking particles, dissolved organic matter (DOM) transport, zooplankton excretion) from the mixed layer. In the subtropical gyres, nitrogen fixation is an important source of nitrogen (Böttjer et al., 2017; Karl et al., 1997) and needs to be incorporated into the budget method. The advantage of a "ratio" budget is that it does not require nutrient flux estimates, which typically carry large uncertainties. The nutrient-ratio budget method provides quantitative constraint on the relative importance of nutrient sources and sinks when the source or sink terms are characterized by a distinct N/P ratio.

2. Materials and Methods

2.1. Nutrient Data

Nutrient observations (dissolved, particulate, and sediment trap) used in this study come from time-series Station ALOHA (22.8°N, 158.0°W) and the Bermuda Atlantic Time-series Study (BATS; 31.6°N, 64.2°W) (Figure 1) (Karl et al., 2021; Lomas et al., 2013). The annual mean N/P ratio of sinking particles (excluding N/P ≥ 100) from the shallowest sediment trap (150 m) at Station ALOHA and BATS is calculated as an integrated N/P ratio over the course of each year, weighted by the particulate P flux. The multi-year mean N/P ratio of sinking particles (Sinking N/P) is computed as the mean of all annual mean N/P ratios, weighted by the number of sediment trap flux observations in each year. Likewise, the multi-year mean surface N/P ratio of suspended particles (Suspended N/P) is calculated as the mean of all annual mean N/P ratios (0–150 m), weighted by the number of suspended particle observations in each year. Additional data sources include NO_3^- and PO_4^{3-} data from World Ocean Atlas (WOA18) monthly climatology (Garcia et al., 2018), and DON and DOP observations from cruises near Station ALOHA and BATS (Abell et al., 2000; Cavender-Bares et al., 2001; Church et al., 2008; Torres-Valdés et al., 2009) (Figure 1).
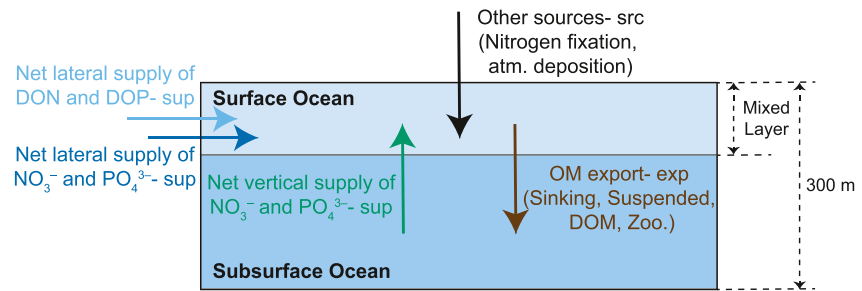
Figure 2. Surface ocean N and P budgets. Nutrient supply (sup) and external N source (src) terms: vertical and lateral supply of dissolved inorganic and organic N and P; nitrogen fixation and atmospheric (atm.) deposition. Nutrient export (exp) terms: sinking (Sinking) and suspended (Suspended) particles; exported dissolved organic matter (DOM); and zooplankton (Zoo.) excretion.

2.2. Nutrient-Ratio Budget Method

The relative importance of external N sources (N_{src}) to the N export flux (N_{exp}) can be estimated by combining the N and P budgets for the surface ocean (Quay, 2021) (Figure 2):

$$\frac{N_{src}}{N_{exp}} = 1 - \left(\frac{N}{P}\right)_{sup} \Big/ \left(\frac{N}{P}\right)_{exp} \tag{1}$$

where N_{src}/N_{exp} is the fraction of exported organic nitrogen supported by external N sources to the surface ocean, $(N/P)_{sup}$ is the dissolved N and P nutrient supply ratio to the surface ocean, and $(N/P)_{exp}$ is the N/P ratio of exported organic matter from the surface ocean.

The dissolved nutrient supply term is further decomposed into vertical (v) and lateral (l) components. As in Quay (2021), the vertical nutrient supply (flux) ratio from the subsurface, $(\Delta NO_3/\Delta PO_4)_v$, is estimated from the slope of NO_3^- to PO_4^{3-} data between the mean mixed layer depth (MLD) and 300 m for each year of observations at Station ALOHA and BATS. Robust regression is used to minimize the influence of outliers (*robustfit* in MATLAB). The vertical nutrient supply ratio incorporates the influence of preferential P remineralization in the subsurface. The multi-year mean $(\Delta NO_3/\Delta PO_4)_v$ between 1988 and 2020 is averaged from the annual vertical inorganic supply ratios (Figure S1 in Supporting Information S1). The sensitivity of $(\Delta NO_3/\Delta PO_4)_v$ to the depth interval used for the regression is discussed in Text S1 in Supporting Information S1. The steady-state assumption is supported by the lack of significant changes in the N/P of annual vertical supply and sinking particles with time using all data available in the past 30 years at Station ALOHA and BATS ($p > 0.05$; Figure S1 in Supporting Information S1). The mean lateral nutrient supply ratio, $(\Delta NO_3/\Delta PO_4)_l$, is calculated from the slope of NO_3^- to PO_4^{3-} within the annual mean MLD using WOA18 monthly climatology data (Garcia et al., 2018) across specified meridional (30° latitude × 5° longitude) and zonal (5° latitude × 30° longitude) transects centered at Station ALOHA and BATS (Figure S2 in Supporting Information S1). Each transect is divided into five 1-degree longitude or latitude bands to estimate the variability of lateral supply ratios meridionally or zonally, respectively.

Concurrent DON and DOP measurements near the time-series stations are limited (Hansell et al., 2021; Knapp et al., 2021). In the North Atlantic, we use observations from individual cruises ($N = 5$) to calculate the slope of the DON to DOP within the annual mean MLD across meridional (26–41°N and 62–71°W; Cavender-Bares et al., 2001) and zonal (35–38°N and 8–75°W; Torres-Valdés et al., 2009) transects to estimate lateral supply ratios, $(\Delta DON/\Delta DOP)_l$, at BATS (Figure 1). In the North Pacific, we use DON and DOP observations from three cruises between 10 and 45°N along 152–158°W (Abell et al., 2000), and between 24–55°N along 152–157°W (Church et al., 2008) to estimate the meridional lateral organic nutrient supply ratio at Station ALOHA (Figure 1). We were unable to find cruise data appropriate for determining the zonal $(\Delta DON/\Delta DOP)_l$ ratio for Station ALOHA. The vertical supply of semilabile DON and DOP from the subsurface is minimal (Lomas et al., 2010; Mahaffey et al., 2004) and not considered in our budgets.
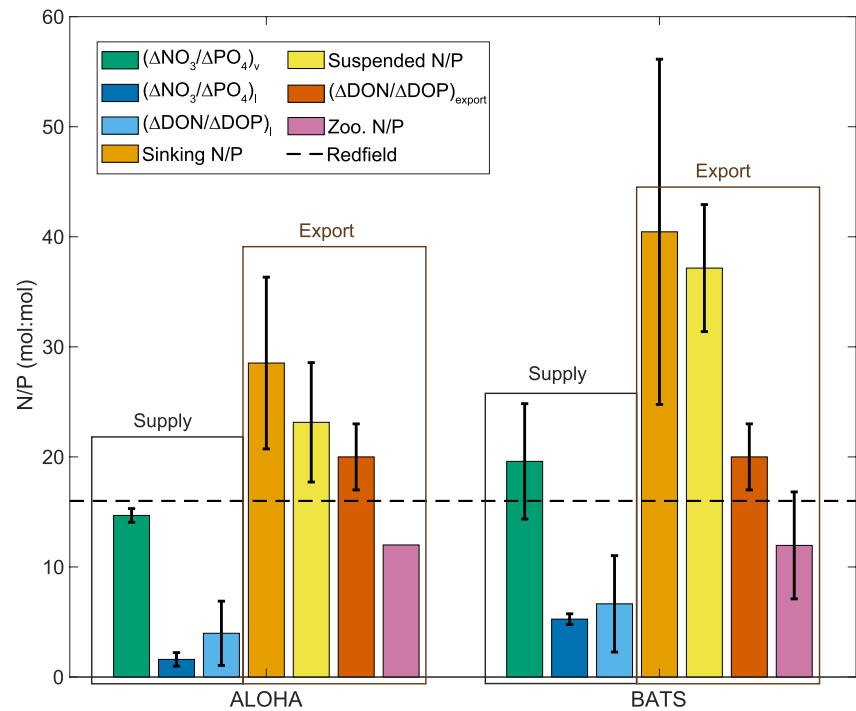
Figure 3. All N/P supply $(N/P)_{sup}$ and export $(N/P)_{exp}$ terms in the surface ocean at Station ALOHA and BATS. Error bars represent ± 1 standard deviations. "Supply" and "Export" boxes represent all nutrient supply and export terms, respectively.

3. Results and Discussion

3.1. N/P Ratios at Station ALOHA and BATS

3.1.1. N/P of Nutrient Supply

The mean vertical inorganic nutrient supply ratios $(\Delta NO_3/\Delta PO_4)_v$ at Station ALOHA and BATS are 14.7 ± 0.6 and 19.6 ± 5.2, respectively (Figure 3 and Figure S1 in Supporting Information S1). The lateral inorganic nutrient supply ratios $(\Delta NO_3/\Delta PO_4)_l$ are much smaller than the vertical ratios (Figure S2 in Supporting Information S1). Near Station ALOHA, the lateral surface transport comes mainly from the equatorial region to the north (Abell et al., 2000; Quay & Stutsman, 2003). A meridional $(\Delta NO_3/\Delta PO_4)_l$ of 1.6 ± 0.6 is estimated using WOA18 nutrient data between 7–22.5°N and 155.5–160.5°W (Figure S3 in Supporting Information S1). Near BATS, the largest lateral surface transport comes from the north (Palter et al., 2011; Siegel & Deuser, 1997; Williams & Follows, 1998). A meridional $(\Delta NO_3/\Delta PO_4)_l$ of 5.3 ± 0.5 is estimated between 15–45°N and 62–67°W (Figure S2 in Supporting Information S1). We hereafter refer to the lateral supply ratio as that estimated from meridional $(\Delta NO_3/\Delta PO_4)_l$ terms at both locations. These estimates are likely an upper limit of $(\Delta NO_3/\Delta PO_4)_l$ since lateral gradients into the subtropics are generally largest near the coastal margins (McGillicuddy Jr. et al., 2003; Williams & Follows, 1998; Williams et al., 2011) and PO_4^{3-} concentrations in the subtropical gyre compiled by the World Ocean Atlas are higher compared to observations derived from high-sensitivity methods (Martiny et al., 2019).

Semilabile DON and DOP transported from coastal regions into the interior ocean has been identified as a potential nutrient source for the oligotrophic gyres (e.g., Abell et al., 2000; Letscher et al., 2016; Lomas et al., 2010; Mahaffey et al., 2004; Reynolds et al., 2014). Abell et al. (2000) estimated the net supply flux of DON and DOP into the NPSTG to be 20 ± 2 mmol N and 4.4 ± 1.0 mmol P m^{-2} yr^{-1}, respectively, which yields a meridional $(\Delta DON/\Delta DOP)_l$ supply ratio of 4.5 ± 2.4 from the Equatorial region to Station ALOHA. The meridional ratio is 3.4 ± 1.6 estimated using DON and DOP data from the COOK-BOOK cruises (Church et al., 2008). We therefore use the average meridional ratio of 4.0 ± 2.9 for Station ALOHA. Near BATS, the lateral $(\Delta DON/\Delta DOP)_l$ supply ratio is 6.7 ± 4.4 meridionally (Cavender-Bares et al., 2001) and 6.9 ± 1.9 zonally (Torres-Valdés et al., 2009) (Figure S4 in Supporting Information S1).

3.1.2. N/P of Nutrient Export

Export of organic matter is categorized into three primary pathways, that is, the gravitational pump, mixing pump, and migrant pump (Siegel et al., 2023). The N/P representing the gravitational pump is determined from sinking particles collected in the 150-m sediment trap (Sinking N/P) which yield mean ± s.d. of 28.5 ± 7.8 and 40.5 ± 15.7 at Station ALOHA and BATS, respectively. Sinking N/P at both time-series stations are much higher than the Redfield ratio as well as the vertical and lateral supply ratios (Figure 3 and Tables S1 and S2 in Supporting Information S1).

The "mixing pump" represents the downward transport of both suspended particulate and DOM by various physical mechanisms (Dall'Olmo et al., 2016; Hansell et al., 2009; Levy et al., 2013; Omand et al., 2015; Roshan & DeVries, 2017; Resplandy et al., 2019). The multi-year weighted mean N/P ratios of suspended particles in the upper 150 m (Suspended N/P) are 23.1 ± 5.4 at Station ALOHA and 37.2 ± 5.8 at BATS, consistent with previous estimates (Karl et al., 2001; Singh et al., 2015) and higher than the Redfield ratio. The lifetime of refractory DON and DOP (>4,000 years; Letscher et al., 2015) far exceeds the ventilation timescale of waters at 300 m (≥4–10 years; Bullister et al., 2006; Stanley et al., 2012), so we only consider the export of semilabile DON and DOP. The N/P ratio used to represent transport of semilabile DON and DOP export at both Station ALOHA and BATS (20 ± 3; $(\Delta DON/\Delta DOP)_{exp}$) comes from the mean of incubation experiments at Station ALOHA, Georges Bank, and the Mid-Atlantic Bight (Hopkinson & Vallino, 2005). This value aligns with the global mean N/P ratio of ∼20 for semilabile DON and DOP export in a modeling study (Letscher & Moore, 2015). Depth gradients of suspended particle concentrations are on average ∼10%–20% of the depth DOM concentration gradients at Station ALOHA and BATS (Figure S5 in Supporting Information S1) so we ignore the transport of suspended particles in this study.

The "migrant pump" represents dissolved (in)organic nutrients actively transported by migrating zooplankton. At Station ALOHA, Hannides et al. (2009) found that migrant excretions of dissolved nutrients (organic + inorganic) are characterized by a mean N/P ratio of 12. Steinberg et al. (2002) measured the dissolved inorganic N/P excretion ratios averaging 12.0 ± 4.9 for a few zooplankton species at BATS. The N/P ratios associated with migrant excretion (Zoo. N/P) in the NPSTG and NASTG are very similar, and are P-rich compared to sinking N/P.

## 3.2. Nutrient-Ratio Budgets at Station ALOHA and BATS

3.2.1. Role of Nitrogen Fixation in the Subtropical Nutrient Budget

At both Station ALOHA and BATS, the significantly greater N/P of exported organic matter than N/P of dissolved nutrient supply is due, in part, to external N supplied from nitrogen fixation. Given small atmospheric nitrogen deposition rates at Station ALOHA (Duce et al., 2008; Kim et al., 2014), the external N source must primarily be nitrogen fixation. Nitrogen fixation was previously estimated to supply about 30%–50% of exported organic N based on $\delta^{15}N$ measurements at Station ALOHA (Böttjer et al., 2017; Karl et al., 1997). Using a simplified version of the nutrient-ratio budget method discussed here, Quay (2021) estimated that nitrogen fixation could support 33%–43% of the exported organic N (i.e., N_{src}/N_{exp}).

At BATS, the difference in N/P between the dissolved nutrient supply and exported particles is even greater than at Station ALOHA (Figure 3 and Tables S1 and S2 in Supporting Information S1). Unlike at Station ALOHA, however, nitrogen fixation at BATS likely accounts for <10% of export flux based on $\delta^{15}N$ measurements (Altabet, 1988; Knapp et al., 2005), N budgets (Helmke et al., 2010; Jenkins & Doney, 2003; Stanley et al., 2015; Tang et al., 2019), and models (Wang et al., 2019). Rate estimates of atmospheric nitrogen deposition are approximately half the nitrogen fixation at BATS (Knapp et al., 2010; Singh et al., 2013; Zamora et al., 2010). Thus N_{src}/N_{exp} is likely <15% at BATS, which is significantly lower than the >50% fraction needed to balance the N/P budget. Therefore, additional nutrient sources with higher N/P, and/or nutrient sinks with lower N/P ratios are needed to balance the N and P budgets at BATS.

3.2.2. Using N/P to Estimate the Relative Importance of Nutrient Sources and Sinks

We use the observed N/P of the nutrient sources and sinks coupled with observed constraints on N_{src}/N_{exp} at Station ALOHA and BATS to quantitatively estimate the relative importance of specific nutrient sources and sinks for the surface ocean. Using a Monte Carlo method, we randomly assign an N/P value for each of the three dissolved nutrient source terms ($(\Delta NO_3/\Delta PO_4)_v$, meridional $(\Delta NO_3/\Delta PO_4)_l$, and meridional $(\Delta DON/\Delta DOP)_l$)
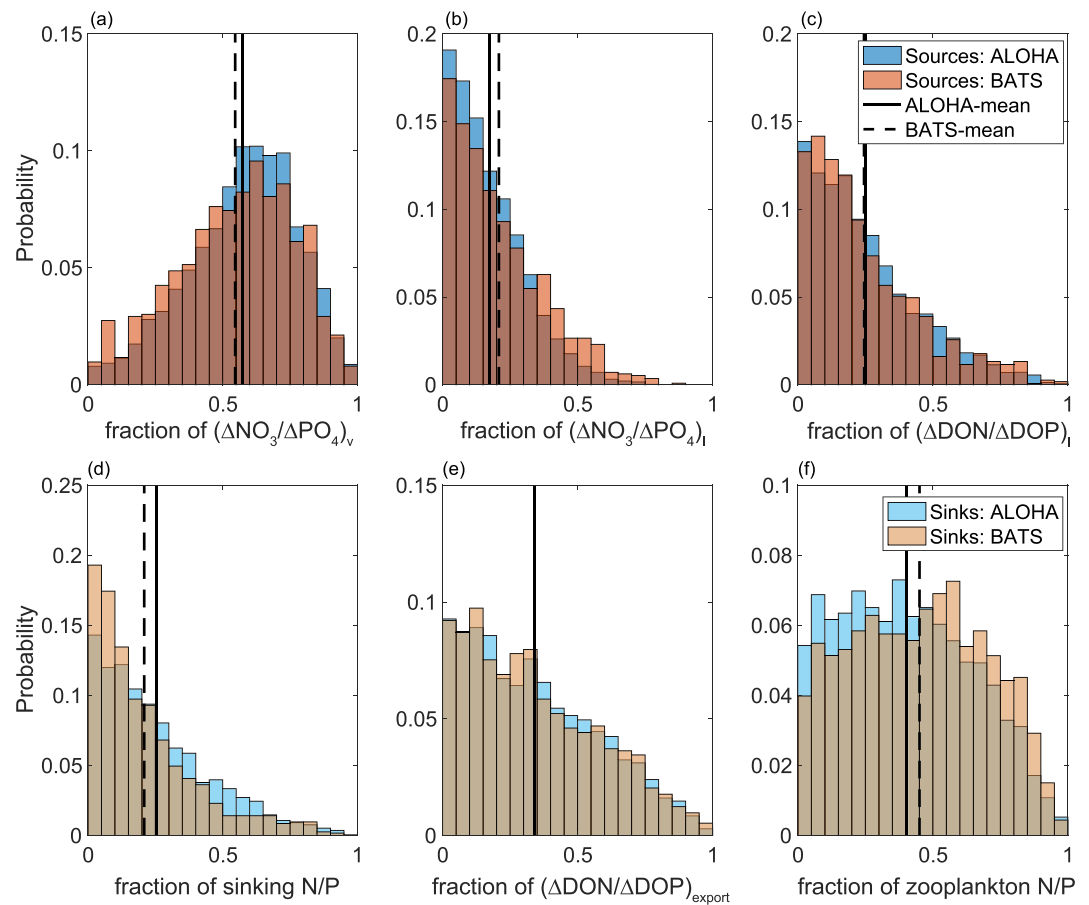
Figure 4. Histograms of the fraction of various nutrient sources (a-c) and sinks (d-f) at Station ALOHA and BATS, determined from the Monte Carlo simulations. The y axis is the probability of occurrence which sums to 1 for all fractions. The x axis represents the fraction of various sources and sinks. Panels illustrate the fractions of (a) vertical inorganic nutrient supply, (b) lateral inorganic nutrient supply, (c) lateral organic nutrient supply, and nutrient export through (d) sinking particles, (e) semilabile DOM export, and (f) zooplankton excretion. Vertical solid and dashed lines show the mean fractional contributions for Station ALOHA and BATS, respectively.

and the three nutrient sink terms (Sinking N/P, transported DOM N/P, and Zoo. N/P) based on their observed means and standard deviations assuming normal distributions (Tables S1 and S2 in Supporting Information S1). Input values for the fractional contributions of each nutrient source (supply) and sink (export) term are assumed to be independent and are randomly selected, but are forced to sum to 1 in each case. The N/P of total nutrient supply $(N/P)_{sup}$ and export $(N/P)_{exp}$ is determined and used to calculate N_{src}/N_{exp} based on Equation 1. The process is repeated 100,000 times. The subset of these scenarios that yield N_{src}/N_{exp} values within the observed ranges (0.3–0.5 at Station ALOHA and 0–0.15 at BATS, as discussed above) are used for interpretation. The mean, median, and interquartile range of each subset is used to determine the likely fraction of each nutrient source and sink term (Tables S1 and S2 in Supporting Information S1). Fractions of all nutrient terms are not normally distributed (Lilliefors test; $p \ll 0.05$) and are better described by medians and interquartile ranges than means and standard deviations (Sainani, 2012). However, medians of the total nutrient source or sink do not sum to 100% whereas the means do. Therefore, we present both means and medians in the following discussion.

At Station ALOHA, histograms of the fractional contributions of lateral inorganic and organic nutrient supply are similar and both positively skewed (Figures 4b and 4c), whereas the vertical inorganic nutrient supply histogram is negatively skewed (Figure 4a). The mean (median; interquartile range) of $(\Delta NO_3/\Delta PO_4)_v$, $(\Delta NO_3/\Delta PO_4)_l$, and $(\Delta DON/\Delta DOP)_l$ fractions at Station ALOHA are 0.58 (0.60; 0.45–0.72), 0.17 (0.14; 0.07–0.25), and 0.25 (0.20; 0.10–0.36), respectively (Table S1 in Supporting Information S1). The fractional contribution to $(N/P)_{sup}$ from vertical inorganic supply is significantly greater than the total lateral nutrient supply (Mann-Whitey

U test; $p \ll 0.05$). For (N/P)$_{exp}$, all three fractions are positively skewed (Figures 4d–4f). The mean (median; interquartile range) of sinking particles, semilabile DOM export, and zooplankton excretion fractions are 0.25 (0.21; 0.09–0.37), 0.34 (0.31; 0.14–0.51), and 0.40 (0.39; 0.20–0.59), respectively (Table S1 in Supporting Information S1).

At BATS, similar nutrient supply patterns emerge with the fractions of lateral inorganic and organic nutrient supply being positively skewed, and the vertical inorganic nutrient supply being slightly negatively skewed (Figures 4a–4c). The mean (median; interquartile range) of $(\Delta NO_3/\Delta PO_4)_v$, $(\Delta NO_3/\Delta PO_4)_l$, and $(\Delta DON/\Delta DOP)_l$ fractions are 0.55 (0.57; 0.40–0.72), 0.21 (0.17; 0.07–0.31), and 0.25 (0.19; 0.09–0.35), respectively (Table S2 in Supporting Information S1). The fractional contribution to (N/P)$_{sup}$ from the vertical inorganic nutrient supply at BATS is also significantly higher than the total lateral nutrient fraction ($p \ll 0.05$). The distribution of export fractions due to zooplankton excretion is almost symmetrical at BATS (skewness = 0.04) (Figure 4f). The mean (median; interquartile range) of sinking particles, semilabile DOM export, and zooplankton excretion fractions are 0.21 (0.15; 0.07–0.29), 0.34 (0.30; 0.13–0.52), and 0.45 (0.46; 0.24–0.65), respectively (Table S2 in Supporting Information S1).

The vertical inorganic nutrient supply term that dominates the total supply in our Monte Carlo analysis represents all processes contributing to the vertical nutrient flux, such as turbulent diffusion below the base of the surface layer or episodic eddy events as observed by Johnson et al. (2010) at Station ALOHA. The skewness of histograms of fractional contributions is caused by the different N/P ratios of the individual nutrient sources and sinks, and the imposed range of N_{src}/N_{exp} (Figures S6 and S7 in Supporting Information S1). The N/P of nutrient sinks (Station ALOHA: 12.0–28.5; BATS: 12.0–40.5) differs greatly from the N/P of lateral $(\Delta NO_3/\Delta PO_4)_l$ and $(\Delta DON/\Delta DOP)_l$ supply (1.6–6.7), while the N/P of vertical $(\Delta NO_3/\Delta PO_4)_v$ supply (14.7–19.6) falls within the range of sink term N/P ratios (Figure 3 and Tables S1 and S2 in Supporting Information S1). The strong positive skewness for fractions of lateral inorganic and organic supply occurs because increasing the fraction of lateral supply decreases overall (N/P)$_{sup}$ ratio which severely diminishes the number of scenarios that can yield a balance N/P budget constrained by the upper bound of N_{src}/N_{exp} constraints (Station ALOHA: 0.5; BATS: 0.15). Likewise, most of the scenarios with a higher fraction of sinking particles (with highest N/P of ∼30–40) are filtered out because they require an external N source that exceed the imposed upper bound of N_{src}/N_{exp}.

To identify which N/P terms contribute the most uncertainty to the mean fractions of different nutrient sources and sinks, we repeated our Monte Carlo simulation while excluding the standard deviation on each N/P source or sink term, one at a time. Based on this sensitivity analysis (Table S3 in Supporting Information S1), the N/P terms that yield the most uncertainty in the estimated mean fractional contributions are lateral organic nutrient supply, sinking particles, and zooplankton excretion at both Station ALOHA and BATS, which suggests that better constraining N/P ratios of these terms should be a focus of future research efforts.

Note that the fractions of different N/P terms represent the relative contributions of different P sources and sinks to the surface P budget. The vertical supply of inorganic PO_4^{3-} is the dominant dissolved P source and almost identical at Station ALOHA (mean: 58%) and BATS (55%). The combined export of semilabile DOP and zooplankton excretion far exceed (∼3 folds) the export by sinking particles at Station ALOHA (25 vs. 75%) and BATS (21 vs. 79%). The significant P fluxes from DOM export and zooplankton excretion may explain why oxygen and dissolved inorganic carbon budget based estimates of total organic matter export (Emerson, 2014; Quay, 2021; Stanley et al., 2015) consistently exceed sediment trap fluxes at 150 m at Station ALOHA and BATS (Church et al., 2013; Karl et al., 2021; Lomas et al., 2013, 2022).

4. Conclusions

A nutrient budget method leveraging distinct elemental N/P ratios at Station ALOHA and BATS in the oligotrophic subtropical gyres was used to estimate the importance of different nutrient supply and export pathways in the surface layer at these two time-series stations. We found that vertically supplied PO_4^{3-} from below is the dominant nutrient source at both stations, accounting for ∼60% of the total phosphorus supply. At both stations, the combined export of organic matter via DOM transport and zooplankton migration and excretion is more important than export via sinking particles, which supports previously observed discrepancies between chemical tracer-budget estimates of export and sediment trap fluxes at these sites.

Elemental stoichiometry (e.g., N/P) is a powerful tool to study nutrient cycling in the ocean, because it avoids the need to estimate rates of nutrient supply and organic matter export which are difficult to make. To the best of our knowledge, these budgets provide the first observation-based constraints on the fractional contributions of multiple nutrient source and sink processes associated with organic matter export from the surface ocean. Contemporaneous measurements of the C/N/P elemental stoichiometry of particles, DOM, and zooplankton excretion across additional ocean biomes would improve characterization of nutrient cycling and the biological carbon pump at a global scale.

Data Availability Statement

The nutrient data used for estimating N/P ratios of vertical nutrient supply, sinking and suspended particles in the study are available at the home pages of the Hawaii Ocean Time-series (HOT) Project and Bermuda Atlantic Time-series Study. Station ALOHA data were obtained via the Hawaii Ocean Time-series HOT-DOGS application (https://hahana.soest.hawaii.edu/hot/hot-dogs/interface.html) from the University of Hawai'i at Mānoa under National Science Foundation Award # 1756517. The BATS data were obtained from the Bermuda Atlantic Time-series Study (http://bats.bios.edu/data/) supported by the NSF Chemical and Biological Oceanography Programs. The WOA18 nutrient data used to estimate horizontal nutrient supply ratios were obtained from the National Centers for Environmental Information website (https://www.ncei.noaa.gov/access/world-ocean-atlas-2018/). This study also uses data from the cruise RRS Charles Darwin CD171, provided by the British Oceanographic Data Centre and funded by the Natural Environment Research Council. DOP and DON data from the COOK-BOOK cruises can be found at https://hahana.soest.hawaii.edu/cookbook/cookbook.html. The code for the Monte Carlo approach used in this study can be found at https://doi.org/10.5281/zenodo.7568622.

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