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Export stoichiometry and migrant-mediated flux of phosphorus in the North Pacific Subtropical Gyre

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ABSTRACT

Export processes play a major role in regulating global marine primary production by reducing the efficiency of nutrient cycling and turnover in surface waters. Most studies of euphotic zone export focus on passive fluxes, that is, sinking particles. However, active transport, the vertical transfer of material by migrating zooplankton, can also be an important component of carbon (C) and nitrogen (N) removal from the surface ocean. Here we demonstrate that active transport is an especially important mechanism for phosphorus (P) removal from the euphotic zone at Station ALOHA (Hawaii Ocean Time-series program; 22°45′N, 158°W), a P-stressed site in the North Pacific Subtropical Gyre. Migrant excretions in this region are P-rich (C_{51}:N_{12}:P_1) relative to sinking particles (C_{250}:N_{31}:P_1), and migrant-mediated P fluxes are almost equal in magnitude (82%) to P fluxes from sediment traps. Migrant zooplankton biomass and therefore the importance of this P removal pathway relative to sinking fluxes has increased significantly over the past 12 years, suggesting that active transport may be a major driving force for enhanced P-limitation of biological production in the NPSG. We further assess the C:N:P composition of zooplankton size fractions at Station ALOHA (C_{88}:N_{18}:P_1, on average) and discuss migrant-mediated P export in light of the balance between zooplankton and suspended particle stoichiometries. We conclude that, because active transport is such a large component of the total P flux and significantly impacts ecosystem stoichiometry, export processes involving migrant zooplankton must be included in large-scale efforts to understand biogeochemical cycles.

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1. Introduction

Biological production in oligotrophic open-ocean systems depends mostly on intense nutrient recycling within the euphotic zone, with only a small fraction supported by the input of "new" nutrients from atmospheric deposition or deep-water entrainment (e.g., Falkowski et al., 1998). In a steady-state ocean, the input of bio-limiting nutrients such as nitrogen (N) and phosphorus (P) must be offset by corresponding fluxes of material from surface waters, e.g., export (Eppley and Peterson, 1979). These processes are often considered to be stoichiometrically balanced with carbon (C) fluxes, occurring at typical plankton C:N:P ratios of 106:16:1 (the "Redfield" ratio; Redfield, 1958). However, long-term variations in the stoichiometries of

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particulate export, remineralization and re-supply processes may lead to decadal oscillations in N- vs. P-limitation of marine primary production (Karl, 2002). Thus, the magnitude and stoichiometry of euphotic zone export have important implications for understanding global ocean productivity and plankton community structure.

The vast majority of studies on euphotic zone export emphasize the passive flux of sinking particles (Ittekkot et al., 1996; Buesseler et al., 2007a). However, vertically migrating zooplankton can also actively transport material inter-zonally, feeding in surface waters at night and releasing metabolic by-products (CO_2, NH_4^+, HPO_4^{2-} and dissolved organic substances) in midwaters during the day (Longhurst, 1991). Faecal production beneath the euphotic zone and mortality at depth also contribute to migrant-mediated export of surface-derived material (Zhang and Dam, 1997; Schnetzer and Steinberg, 2002). Although active transport affects all essential major elements (C, N and P), previous studies of migrant-mediated fluxes in marine systems have typically considered only C and N (Longhurst et al., 1989, 1990; Dam et al., 1995; Hays et al., 1997, 2001; Zhang and Dam, 1997; Steinberg et al., 2000, 2008; Al-Mutairi and Landry, 2001). Only one study to date has evaluated migrant-mediated export of P (Le Borgne and Rodier, 1997), and none has compared active P transport with simultaneously measured sinking fluxes of particulate P. The traditional focus on C and N export, and relatively small number of observations of P flux (Karl, 2007), derives from the tenet that P only limits marine production on geologically relevant time scales (>1000 yr; Codispoti, 1989). However new evidence indicates that P may limit biological production in several low-latitude marine systems (Benitez-Nelson, 2000) and can limit specific populations of N_2-fixing plankton (Sañudo-Wilhelmy et al., 2001; Moutin et al., 2005), thus significantly impacting biogeochemical cycles in the subtropical open ocean (Karl et al., 1997). In sum, a potentially major route for P removal from the surface ocean, with important consequences for ecosystem stoichiometry, has largely been ignored.

In this study we examine the stoichiometry of zooplankton C, N and P at Station ALOHA, a P-stressed (Karl et al., 2001; Karl, 2002, 2007) time-series site in the North Pacific Subtropical Gyre (NPSG; Karl and Lukas, 1996). We calculate active transport of P at Station ALOHA for the first time and demonstrate its importance relative to passive particulate P fluxes. We further place our results in the context of NPSG ecosystem stoichiometry by considering the balance between zooplankton and suspended particle C:N:P ratios and its implications for migrant-mediated P fluxes.

2. Methods

2.1. Zooplankton sampling and biomass analyses

Zooplankton samples were collected at Station ALOHA (22°45′N, 158°W) on approximately monthly Hawaii Ocean Time-series (HOT) cruises from 1994 to 2005. Plankton were collected on each cruise with a 1-m^2, 200-μm mesh net towed obliquely through the euphotic zone, as described by Landry et al. (2001). Zooplankton collected from three day (1000–1300) and three night (2200–0100) plankton tows on each cruise were size fractionated using 0.2, 0.5, 1, 2 and 5-mm sieves, filtered onto pre-weighed 0.2-mm Nitex filters and frozen in liquid N. This procedure yielded the following size fractions: f_5 (>5 mm), f_2 (2–5 mm), f_1 (1–2 mm), $f_{0.5}$ (0.5–1 mm) and $f_{0.2}$ (0.2–0.5 mm). For each size-fraction sample, dry weight (DW) biomass was determined after thawing and oven drying (60 °C, 5 d). The biomass of diel vertical migrators, or "migrant" biomass, is defined as the difference in DW biomass between mean day ($n=3$) and mean night ($n=3$) tows for each size fraction (f_5–$f_{0.2}$) or for total zooplankton biomass (Σf).

Zooplankton C, N and P were analyzed for all size fractions (f_5–$f_{0.2}$) from one day and one night tow on each cruise from 1998 to 2001 (40 cruises in total). C and N values were determined using a Perkin-Elmer Model 2400 CHN Elemental Analyzer or an elemental analyzer interfaced to a Micromass Optima Isotope Ratio Mass Spectrometer. Each analytical run included a series of elemental (acetanilide) standards. Zooplankton P values were determined using acid digestion and colorimetric analysis, following Karl and Björkman (2001). Briefly, ~0.01 g of dried plankton from each filter was combusted (500 °C for 4.5 h), acid leached (0.15 N HCl at 60 °C for 1 h) and analyzed using the molybdenum blue spectrophotometric technique. Replicate P samples agreed within $<2\%$, and analyses of NIST Tomato Leaves standard reference material were within 5% of certified P values. In this study, we refer to soluble reactive phosphorus (SRP) as dissolved inorganic phosphorus (DIP) and soluble non-reactive P (= total dissolved P−SRP) as dissolved organic phosphorus (DOP).

The passive flux of particulate material from the euphotic zone was measured with free-floating particle interceptor traps at 150-m depth. The traps were deployed for 3 d on each cruise to Station ALOHA from 1994 to 2005. Flux estimates from traps positioned at 300- and 500-m depth were also available for 1994 and 1995. Details of the collections are described in Karl et al. (1996) and at http://hahana.soest.hawaii.edu/hot/hot_jgofs.html, the HOT website. Particulate material collected in the traps was analyzed for C and N using a Perkin-Elmer Model 2400 CN analyzer or an elemental analyzer coupled to a Finnigan Delta Plus mass spectrometer. P values were determined by combustion, acid leaching and colorimetric analysis (Karl et al., 1996). Trap fluxes (PC, PN, and PP) are expressed as mmol C, N and P m^{-2} d^{-1}.

2.2. Excretion rates

Inorganic excretion rates of diel migrating zooplankton were calculated from migrant DW biomass using empirical allometric relationships following Al-Mutairi and Landry (2001). The allometric relationships were compiled from a dataset of 2641 respiration and excretion measurements of 56–143 zooplankton species from eight

phyla at temperatures ranging from −1.4 to 30 °C (Ikeda, 1985). For each cruise, rates of respiration (R_O: μl O_2 consumed indiv^{-1} h^{-1}), ammonia excretion (E_N: μg N in div^{-1} h^{-1}) and phosphate excretion (E_P: μg P indiv^{-1} h^{-1}) were calculated as

$$\ln R_O = -0.2512 + 0.7886 \ln \mathrm{DW} + 0.0490T \quad (r^2 = 0.939) \tag{1}$$

$$\ln E_{DIN} = -2.8900 + 0.7616 \ln \mathrm{DW} + 0.0511T \quad (r^2 = 0.854) \tag{2}$$

$$\ln E_{DIP} = -4.3489 + 0.7983 \ln \mathrm{DW} + 0.0285T \quad (r^2 = 0.864) \tag{3}$$

Oxygen consumption rates (Eq. (1)) were converted to respiratory C equivalents (R_C: μg CO_2 evolved indiv^{-1} h^{-1}) assuming a respiratory quotient of 0.8, i.e., a protein-based diet (Hayward, 1980). All hourly rates were converted to daily rates assuming that migrators metabolize at their daytime resting depth (300–500 m) for 12 h at temperatures (T) of 8.6–12.1 °C (average ± s.d.: 9.9 ± 0.60 °C for 300–500, $n = 117$). For each cruise, daily rates were converted to molar fluxes for the entire migratory community using mean estimates of the biomass per individual and the number of migrants m^{-2} in each size fraction, giving respiration (R_C) in units of mmol CO_2 m^{-2} d^{-1}, inorganic N excretion (E_{DIN}) in units of mmol N m^{-2} d^{-1} and inorganic P excretion (E_{DIP}) in units of mmol P m^{-2} d^{-1}. Results using these established metabolic relationships have been shown to be equivalent to those calculated by more direct methods, e.g., measurement of individual migrator N and C content before and after their daily transit to midwater depths (Hays et al., 1997, 2001).

Organic excretion by diel migrant zooplankton was calculated assuming organic moieties represent a constant fraction of the total amount of waste by-products released by migrant zooplankton at depth. For organic C this fraction is 0.24 (Steinberg et al., 2000), for organic N 0.53 (Le Borgne and Rodier, 1997) and for organic P 0.47 (Pomeroy et al., 1963). Thus excretion of dissolved organic C, N and P (E_{DOC}, E_{DON} or E_{DOP}: mmol C, N or P released m^{-2} d^{-1}) can be calculated as

$$E_{DOC} = \frac{0.24}{(1-0.24)} R_{DIC} \tag{4}$$

$$E_{DON} = \frac{0.53}{(1-0.53)} E_{DIN} \tag{5}$$

$$E_{DOP} = \frac{0.47}{(1-0.47)} E_{DIP}. \tag{6}$$

3. Results

3.1. Migrant zooplankton time-series

The biomass of migrant zooplankton, defined as the difference between night and day estimates of DW biomass in the upper 160 m at Station ALOHA, varied from 0.04 to 1.1 g DW m^{-2} over our 12 years of measurement and was significantly greater than zero (one-sample Student's t-test, $p < 0.001$, $n = 113$; Fig. 1). Negative "migrant" biomasses were observed twice due to phytoplankton blooms (e.g., the *Hemiaulus hauckii* bloom in October 2001; Sheridan and Landry, 2004), but these anomalous numbers were not included in calculations. Over an annual cycle, migrant biomass was highest in the spring (March–May, mean: 0.51 g DW m^{-2}) and lowest in the fall (September–November, mean: 0.33 g DW m^{-2}), with a significant difference found between these two seasons (*post-hoc* Scheffé test, $p < 0.05$). From 1994 to 2005, the biomass of vertically migrating zooplankton increased significantly at a mean rate of 12.4 mg DW m^{-2} yr^{-1} (linear regression, $p < 0.05$, $n = 112$). This change was

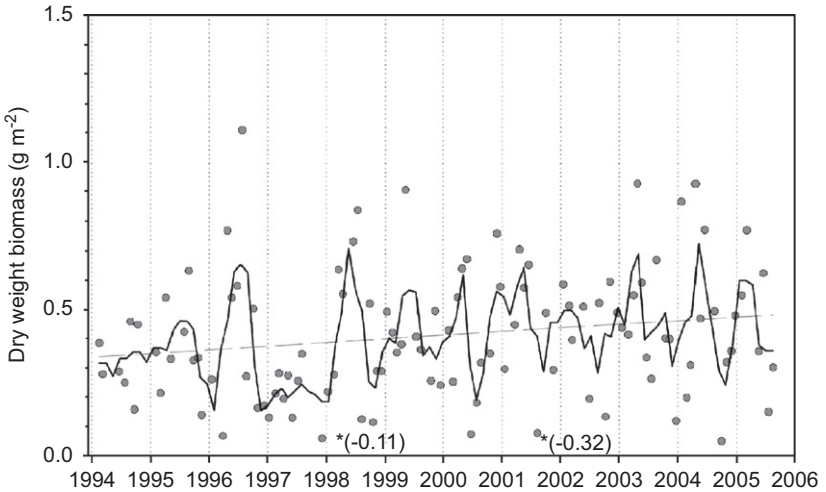


Fig. 1. Migrant zooplankton biomass from 1994 to 2005 at Station ALOHA, as determined by the difference between mean night and mean day tows in the euphotic zone. Asterisks indicate two cruises where anomalous negative migrant biomasses were observed. The solid line is the three-point running mean. Migrant biomass has increased significantly over the 12-yr period (regression on data points: dashed line, mg DW m^{-2} = 0.035 [95% C.I.: 0.0013, 0.068](time in days)+266 [121, 411], $r^2 = 0.04$, $p < 0.05$, $n = 112$).

driven primarily by animals in the 0.5–1.0 mm ($p<0.025$) and >5.0 mm ($p<0.005$) size fractions.

3.2. Zooplankton elemental stoichiometry

C and N contents of zooplankton at Station ALOHA were generally uniform with size (Table 1 and Fig. 2), as noted by Landry et al. (2001). Only the f_5 size fraction had significantly lower DW ratios than smaller plankton (*post-hoc* Scheffé test, $p<0.02$). In contrast, P:DW decreased with size (Table 1), with P:DW significantly greater for larger size fractions than for the small size fractions, e.g., $f_5>(f_1, f_{0.5}, f_{0.2})$, $f_2>(f_{0.5}, f_{0.2})$ and $f_1>f_{0.2}$ (night collections, *post-hoc* Scheffé test, $p<0.05$). Elemental contents did not differ between night and daytime collections except for f_2 (Fig. 2). DW ratios for this size fraction (and P:DW for f_5) were always higher during the night than during the day (*t*-test, $p>0.05$). On average (±s.d.), elemental compositions as %DW for all zooplankton size fractions were 35.44±0.03% for C, 8.76±0.01% for N and 1.007±0.002% for P (weighted by the biomass contributions of f_5–$f_{0.2}$; $n=37$–40 cruises).

Among the zooplankton size fractions, C, N and P stoichiometries were more variable than elemental compositions (Table 1), largely because of differences in P contents (Fig. 2). C:N ratios (mol:mol) did not differ much with size (Fig. 3), although C:N for $f_{0.2}>f_1$ and f_2 (*post-hoc* Scheffé test, $p<0.05$). On average, C:N was 4.66±0.33 (mean±s.d., weighted by f_5–$f_{0.2}$ biomass, $n=37$–40 cruises). C:P and N:P molar ratios increased with decreasing size (Table 1) and were significantly larger for the 0.2–0.5 mm ($f_{0.2}>f_1$, f_2 and f_5) and 0.5–1 mm ($f_{0.5}>f_2$ and f_5) size fractions (*post-hoc* Scheffé test, $p<0.05$). The size-fractionated C:N, C:P and N:P ratios did not differ significantly by season or year (ANOVA, $p\gg0.05$), with the exception of C:N ratios for $f_{0.2}$, which were higher in the summer (June–August) than in the spring (March–May; *post-hoc* Scheffé test, $p<0.05$). Average zooplankton C:N, C:P and N:P molar ratios (±s.d.) were 4.66±0.33, 87.6±14.3 and 18.4±2.3, respectively (weighted by f_5–$f_{0.2}$ biomass, $n=37$–40 cruises).

3.3. Active transport by migrant zooplankton

Active fluxes of dissolved inorganic C and N due to the respiration (R_C) or excretion (E_{DIN}) of migrant zooplankton at depth (300–500 m) varied significantly from 1994 to 2005 (CV~60%; Figs. 4 and 5). On average, however, R_C (0.31±0.19 [s.d.] mmol C m^{-2} d^{-1}, $n=113$) and E_{DIN} (0.049±0.030 mmol N m^{-2} d^{-1}) were similar to those reported by Al-Mutairi and Landry (2001) for the subset of this data from 1994 to 1996. Active transport of dissolved inorganic P (E_{DIP}) due to migrant zooplankton P excretion at depth was also variable (CV~60%), averaging 0.0038±0.0023 mmol P m^{-2} d^{-1} (Fig. 6). Despite the significant increase in migrant zooplankton biomass from 1994 to 2005 (see Results above), calculated estimates of R_C, E_{DIN} and E_{DIP} did not increase significantly with time (regression, $p>0.05$). Annual fluxes for migrant-mediated export of inorganic C, N and P, on average (±s.d., $n=11$) 108±23 mmol C m^{-2} yr^{-1} (R_C), 14.4±3.2 mmol N m^{-2} yr^{-1} (E_{DIN}) and 1.30±0.29 mmol P m^{-2} yr^{-1} (E_{DIP}), also did not increase with time (ANOVA, $p\gg0.05$). The relative constancy of the active transport fluxes was due to a decrease in the ambient water temperature experienced by migrant zooplankton at their daytime resting depths. Thus the increase in migrant community metabolic rates due to greater zooplankton biomass was offset by the significant decline in ambient water temperatures from 1994 (10.4 °C) to 2005 (9.8 °C, regression, $p<0.03$).

Migrant-mediated export of C, N and P due to respiration and excretion at depth averaged 14%, 18% and 41% (median: 14%, 17% and 32%) of trap-collected PC, PN and PP at 150 m, respectively (Fig. 7). If excretion of dissolved organic C, N and P (E_{DOC}, E_{DON}, E_{DOP}) by migrant zooplankton at depth was also taken into account, total active transport accounted for 19%, 38% and 78% (median: 18%, 36%, and 61%) of trap PC, PN and PP at 150 m, respectively (Fig. 7). Considerable variation in the relative contributions of active and passive fluxes to total export was observed over the 12-yr time-series (CV = 60–84% for C, N and P). Total active transport of C, N and P (R_C+E_{DOC}, $E_{DIN+DON}$ and $E_{DIP+DOP}$) ranged from 0.23–63% of trap PC

Table 1
Dry weight and stoichiometric ratios of carbon (C), nitrogen (N) and phosphorus (P) for zooplankton collected at Station ALOHA from 1998 to 2001. Elemental content and stoichiometry is presented for zooplankton size fractions

	C:DW (mg:g)	N:DW (mg:g)	*n*[a]	P:DW (mg:g)	*n*	C:N (mol:mol)	*n*	C:P (mol:mol)	N:P (mol:mol)	*n*
Zooplankton-day										
f_5 (>5 mm)	287±14[b]	70±4	32	8.8±1.3	18	4.70±0.34	17	83±10	16.4±1.8	12
f_2 (2–5 mm)	328±7	81±2	38	10.4±0.4	27	4.69±0.07	37	83±2	17.3±0.5	26
f_1 (1–2 mm)	362±6	92±2	38	10.8±0.2	38	4.57±0.05	38	87±2	18.9±0.4	38
$f_{0.5}$ (0.5–1 mm)	353±5	87±2	38	9.6±0.2	38	4.69±0.05	38	95±2	20.2±0.4	38
$f_{0.2}$ (0.2–0.5 mm)	352±6	82±2	38	8.6±0.3	37	5.00±0.08	38	108±4	21.4±0.5	37
Zooplankton-night										
f_5 (>5 mm)	307±11	77±3	39	13.0±0.8	34	4.72±0.10	29	72±5	15.3±1.0	25
f_2 (2–5 mm)	349±4	90±1	40	12.5±0.3	37	4.54±0.04	40	73±2	16.1±0.3	37
f_1 (1–2 mm)	372±3	95±1	40	11.2±0.1	40	4.59±0.04	40	85±1	18.6±0.3	40
$F_{0.5}$ (0.5–1 mm)	361±4	88±1	40	10.0±0.2	39	4.77±0.04	40	96±4	20.0±0.9	39
$F_{0.2}$ (0.2–0.5 mm)	363±6	87±2	40	9.2±0.2	39	4.92±0.06	40	105±4	21.3±0.5	39

[a] Number of samples (*n*) used to calculate C:DW & N:DW and C:P & N:P ratios were the same.
[b] Mean±standard error of the mean.

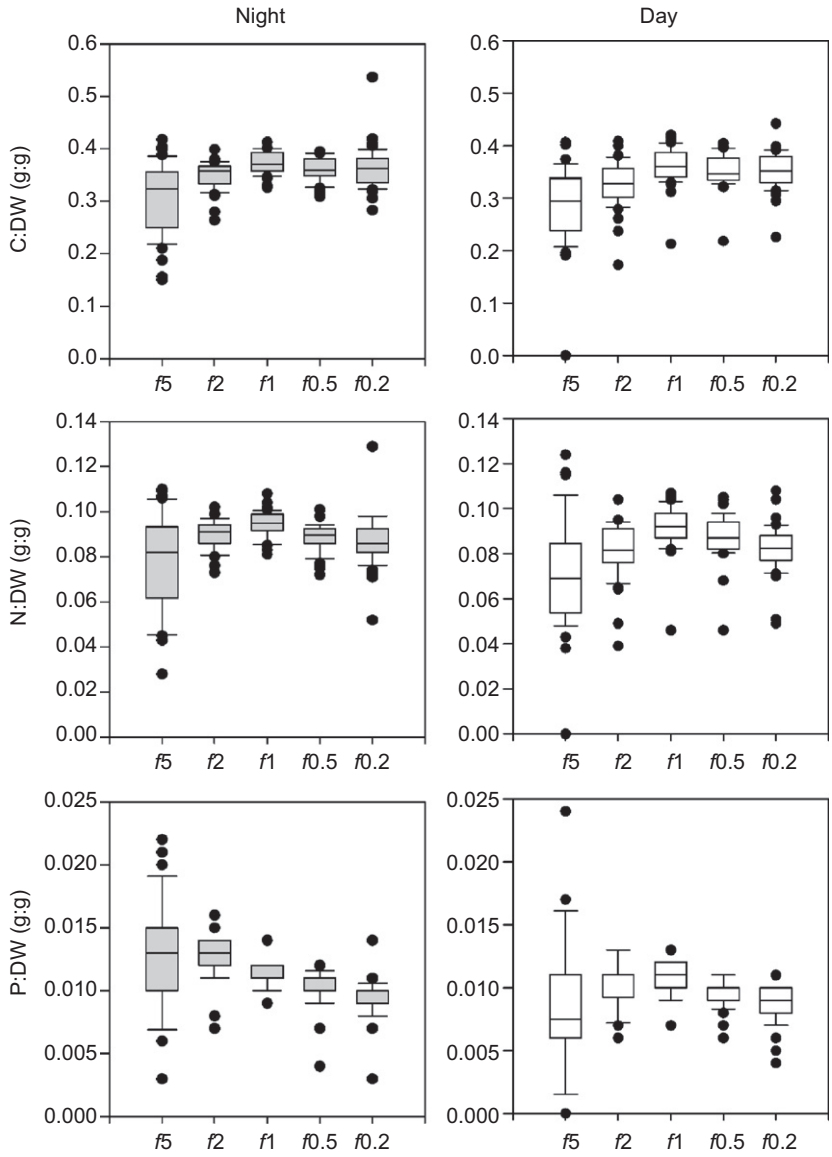


Fig. 2. Zooplankton carbon (C), nitrogen (N) and phosphorus (P) contents in the North Pacific Subtropical Gyre. Elemental composition as a fraction dry weight is shown for size fractions of zooplankton collected from 1998 to 2001 at Station ALOHA (night: $n = 34$–40; day: $n = 19$–37). Size fractions (on the x-axis) are f_5 (>5 mm), f_2 (2–5 mm), f_1 (1–2 mm), $f_{0.5}$ (0.5–1 mm) and $f_{0.2}$ (0.2–0.5 mm). Boxes and whiskers delineate the 25–75th, 10th and 90th percentiles, respectively, and outliers are denoted as circles.

(Fig. 4), 1.7–117% of trap PN (Fig. 5) and 2.4–441% of trap PP (Fig. 6). For C and N, no trends in the relative amounts of active export to trap fluxes were observed (regression, $p \gg 0.05$). The average % contributions of migrant-mediated fluxes to total C and N export for the whole time-series (1994–2005) are thus similar to those calculated by Al-Mutairi and Landry (2001) for 1994–1996. However, active P export as a % of trap PP increased significantly with time (Fig. 6; regression, $p < 0.02$), and this increase was significant even when the data was log-transformed to account for deviations from normality (regression, $p < 0.01$). Active P export as a % of trap PP increased largely because of a weak increase in active P export (regression, $p = 0.077$) and a weak decrease in trap PP (regression, $p = 0.078$). Thus the end result of these small temporal trends was a significant change in the relative contributions of passive and active processes to total P export.

The calculations above compare migrant-mediated export fluxes with particulate material settling out of the euphotic zone (i.e., trap-collected PC, PN and PP) at the sediment trap depth that provides the longest time-series of data, i.e., 150 m. However, migrant zooplankton rest at depths of 300–500 m, or greater, during the day, and thus much of the migrant C, N and P release occurs deep in the midwater region of the world's oceans. Consumption and microbial utilization of particulate material exiting the euphotic zone causes a rapid decay in particulate fluxes

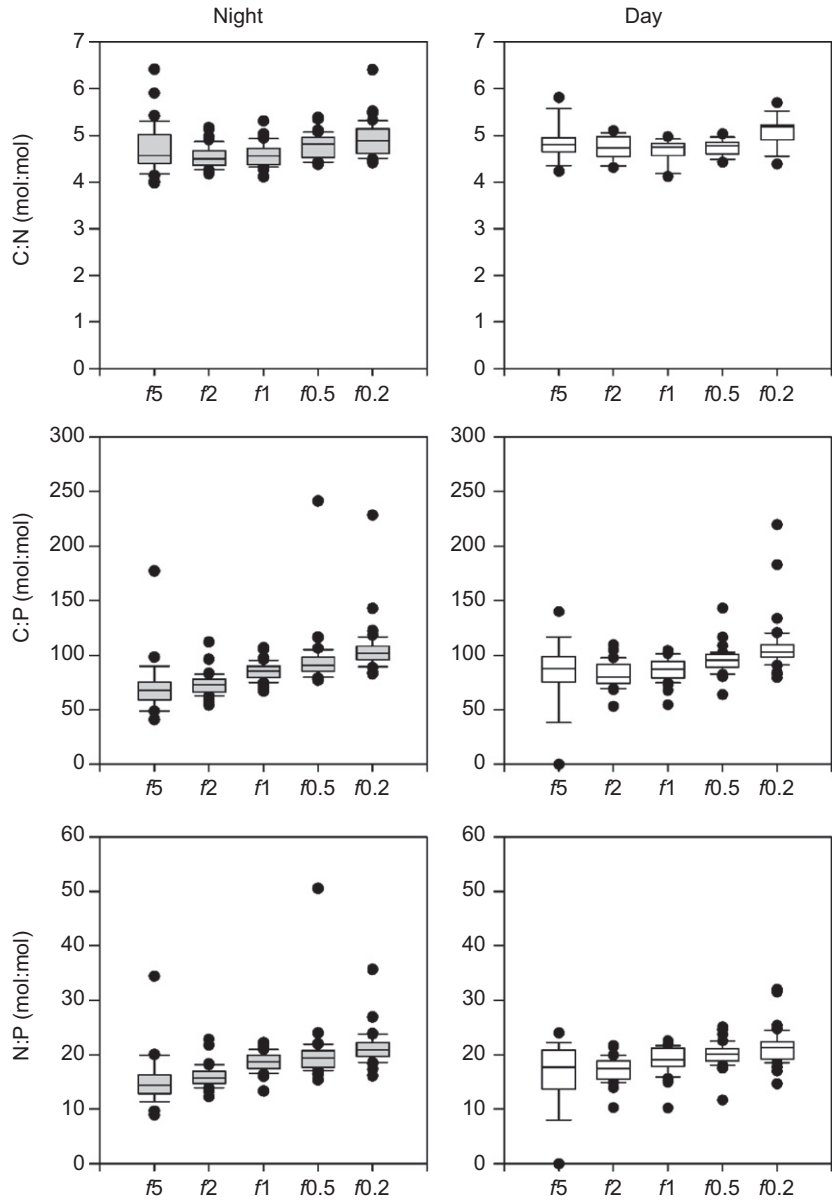


Fig. 3. Carbon (C), nitrogen (N) and phosphorus (P) stoichiometries of zooplankton in the North Pacific Subtropical Gyre. Elemental ratios are shown for size fractions of zooplankton collected from 1998 to 2001 at Station ALOHA (night: $n = 25$–40; day: $n = 12$–37). Size fractions (on the x-axis), boxes, whiskers and outliers as in Fig. 2.

(Suess, 1980; Martin et al., 1987), especially for P (Karl et al., 1996). Sinking particle fluxes at 500 m (1994–1995) are only 32%, 18% and 22% of C, N and P fluxes at 150 m, respectively. Thus, because of the exponential decay in particulate C, N and P fluxes with depth, estimates of migrant export (R_C+E_{DOC}, $E_{DIN+DON}$, $E_{DIP+DOP}$) amount to 39%, 184% and 179%, respectively, of the particulate fluxes measured at 300 m (1994–1995), and 44%, 189% and 292%, respectively, of the fluxes measured at 500 m.

We note finally that the migrant-mediated export fluxes we have calculated assume that zooplankton migrators spend approximately 12 h of the day resting at depths of 300–500 m. However a portion of migrant excretion likely occurs en-route to their daytime resting depth, and some migrants may rest at depths greater than 500 m (Steinberg et al., 2008). The sensitivity of our active flux estimates to these uncertainties can be examined by assuming that migrators swim at $\sim$100 m h^{-1} (Wiebe et al., 1992; Heywood, 1996) through the relatively warm waters between 150 and 300 m (average $\pm$ s.d.: 17.0 $\pm$ 1.1 °C, $n = 117$), for a total of $\sim$3 h d^{-1}, spending the remaining 9 h at 300–750 m. This analysis indicates that our previous active flux estimates relative to the base of the euphotic zone (150 m) are conservative, with zooplankton migrants transporting up to 0.42 $\pm$ 0.26 mmol C m^{-2} d^{-1} (R_C+E_{DOC}), 0.105 $\pm$ 0.065 mmol N m^{-2} d^{-1}

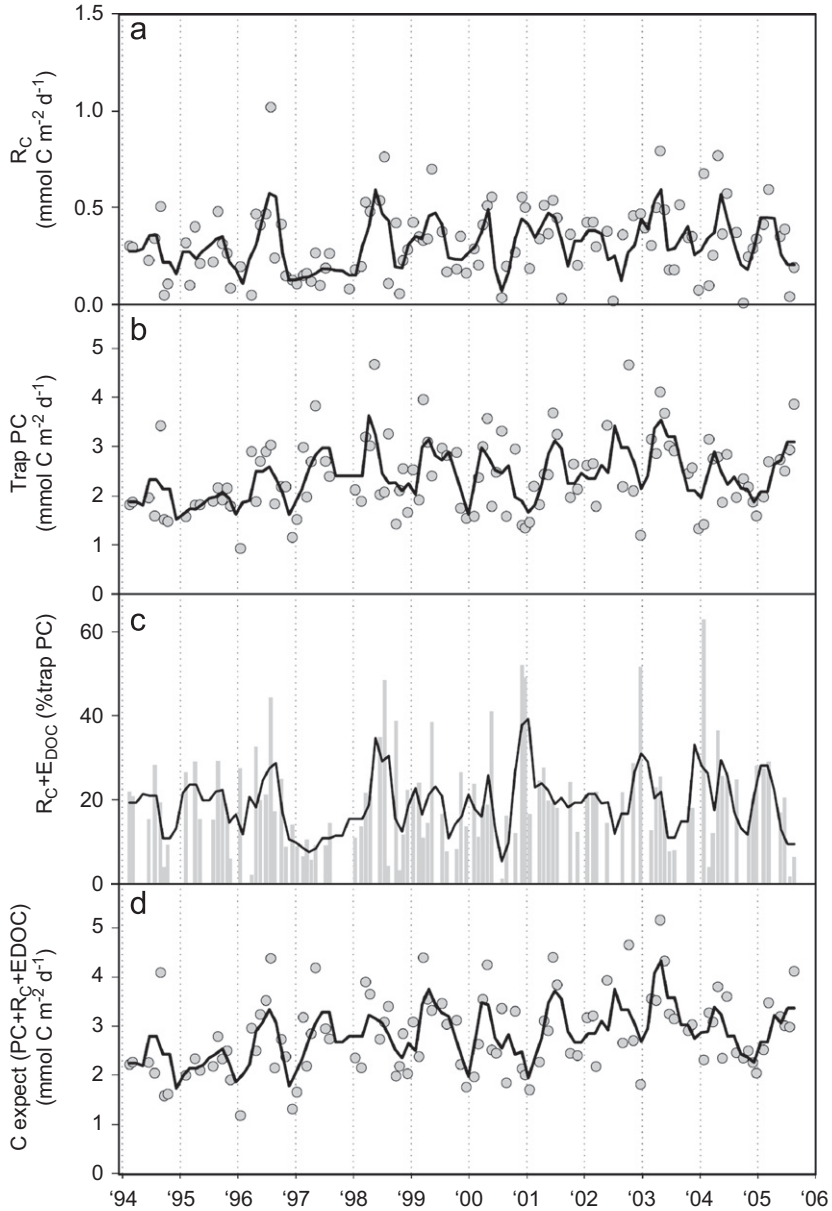


Fig. 4. Active and passive export flux of carbon from the euphotic zone at Station ALOHA from 1994 to 2005. Included are the active transport due to migrant zooplankton respiration (R_C; a), the passive particulate flux of C (PC; b), total active export of C (R_C+E_{DOC}) as a percentage of trap-collected PC (c) and the total (active+passive) export of C from the euphotic zone (d). Solid lines are three-point running means.

(E_{DIN}+E_{DON}) and 0.0071 ±0.0043 mmol P m^{-2} d^{-1} (E_{DIP}+E_{DOP}), i.e., potentially accounting for 19%, 39% and 79% of trap-collected PC, PN and PP at 150 m. On the other hand, this analysis also indicates that migrant export (R_C+E_{DOC}, $E_{DIN+DON}$, $E_{DIP+DOP}$) may amount to only 29%, 85% and 94%, respectively, of the particulate fluxes measured at 300 m because a portion of migrant excretion (~3 h) occurs above this depth. Despite this restriction, the minimum contribution of migrant-mediated P transport to total (active+passive) P fluxes below 300 m remains large (45%). Midwater plankton community dynamics are poorly characterized, despite recent large-scale programs examining the ocean's "twilight zone" (Buesseler et al., 2007b; Steinberg et al., 2008). In light of the multiple unknowns, we focus the remainder of this study on our initial, conservative estimates of active export fluxes.

4. Discussion

4.1. C:N:P stoichiometry of zooplankton at Station ALOHA

Average C, N and P compositions for zooplankton in the NPSG are within the ranges found by Båmstedt (1986) and Mauchline (1998) for calanoid copepods, i.e., C: 28–68% DW, N: 5.2–15% DW and P: 0.3–1.8% DW. Mean C:DW is

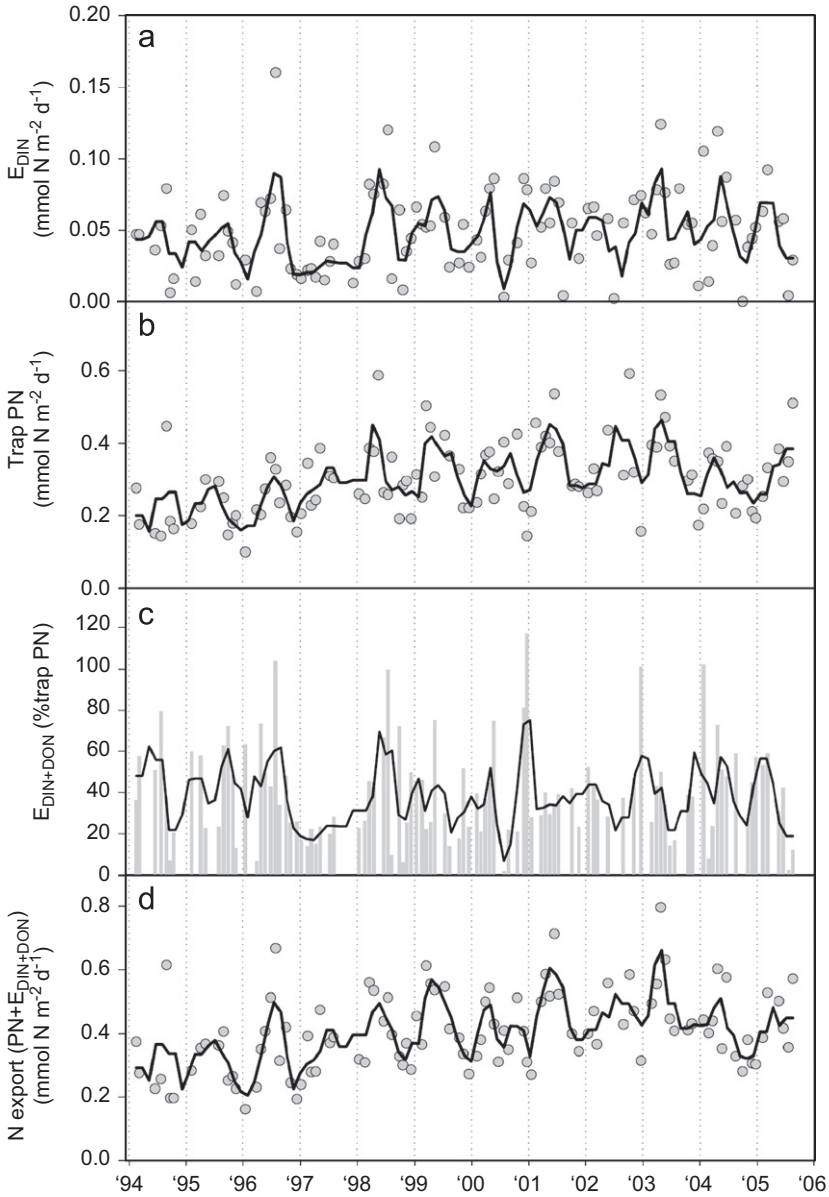


Fig. 5. Active and passive export fluxes of nitrogen (N) from the euphotic zone at Station ALOHA from 1994 to 2005. Shown are the active transport due to migrant zooplankton excretion of ammonia (E_{DIN}; a), the passive particulate flux of N (PN; b), the total active export of N ($E_{DIN+DON}$) as a percentage of trap-collected PN (c) and the total (active+passive) export of N from the euphotic zone (d). Solid lines are three-point running means.

the same as that found by Landry et al. (2001), i.e., 36.5% for zooplankton collected at Station ALOHA from 1994–1996. Thus, average C, N and P contents for zooplankton at Station ALOHA (36%, 9% and 1% DW, respectively) are reasonable relative to previous studies. Although C:DW and N:DW ratios were fairly constant among different size fractions, zooplankton P:DW increased in the larger size classes (>2 mm) at night. C:DW and N:DW were also higher for large (2–5 mm) zooplankton collected at night than those collected during the day. The increase in elemental content was likely due to diel changes in the community structure of large zooplankton at Station ALOHA. Chaetognaths and gelatinous predators make up a greater fraction of the 2–5 mm zooplankton size fraction during the day, whereas higher crustacea are more abundant at night (Landry et al., 2001) because of the nocturnal migration of euphausiids and shrimps into the euphotic zone (Al-Mutairi and Landry, 2001). Euphausiids, mysids and other large crustaceans have higher relative P contents than chaetognaths and, particularly, gelatinous zooplankton (Beers, 1966). For example, Postel et al. (2000) found euphausiid C:P molar ratios of 84:1, whereas chaetognath C:P averaged 137:1 and gelatinous C:P$\geqslant$149:1. Thus, the changes in elemental contents of the larger size classes, particularly in P content, may reflect a shift in community structure from

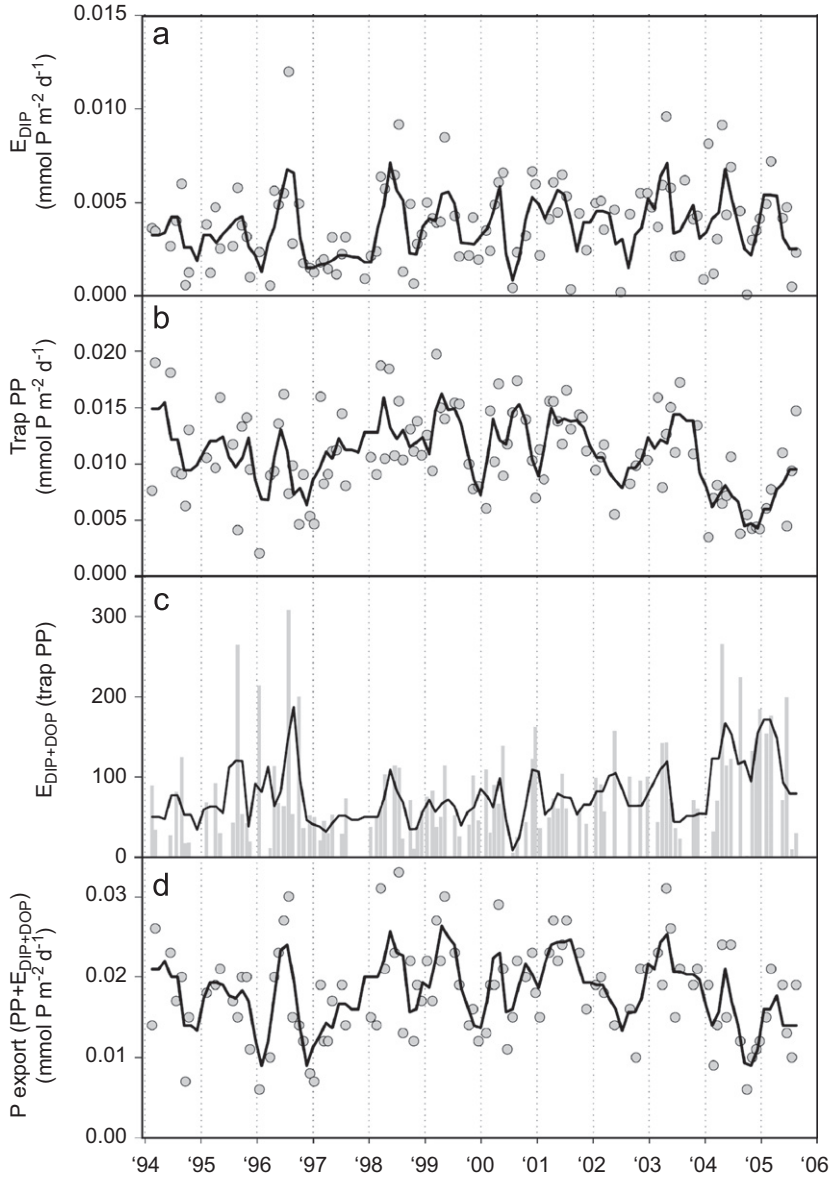


Fig. 6. Active and passive export flux of phosphorus (P) from the euphotic zone at Station ALOHA from 1994 to 2005. Shown are the active transport due to migrant zooplankton excretion of dissolved inorganic phosphorus (E_{DIP}; a), the passive particulate flux of P (PP; b), the total active export of P ($E_{DIP+DOP}$) as a percentage of trap-collected PP (c) and the total (active+passive) export of P from the euphotic zone (d). Solid lines are three-point running means.

more gelatinous or semi-gelatinous plankton during the day to more crustaceans at night.

Zooplankton C:N stoichiometry at Station ALOHA was relatively stable; that is, most diel or size-class changes in C:N molar ratios were not significant. Average zooplankton C:N (4.7:1) was within the range found for tropical and subtropical copepods (C:N = 3.0–5.2; Mauchline, 1998) and analogous to that found for zooplankton collected at Station ALOHA from 1994 to 1996 (C:N = 4.8–5.3; Landry et al., 2001). Båmstedt (1986) found that C:N molar ratios for subtropical copepods were low and invariant relative to higher latitude species, and Beers (1966) observed similar C:N among subtropical copepods (5.0), euphausiids (4.8) and chaetognaths (4.2), which dominate the NPSG community (Landry et al., 2001). Thus, despite the diversity of zooplankton in different size fractions at Station ALOHA, the relative constancy of zooplankton C:N is unsurprising.

The mean molar stoichiometries of C:P and N:P for NPSG zooplankton (88:1 and 18:1, respectively) are similar to those found previously for tropical zooplankton (e.g., N:P: 18.5–24.6; Le Borgne, 1982). Zooplankton C:P and N:P molar ratios at Station ALOHA were much more variable than zooplankton C:N because of size-class differences in P content (Fig. 2). Similarly, Gismervik (1997) found that C:P varied more than C:N for different copepod species in a Norwegian fjord, with species-specific C:N:P molar ratios ranging from 348:38:1 for

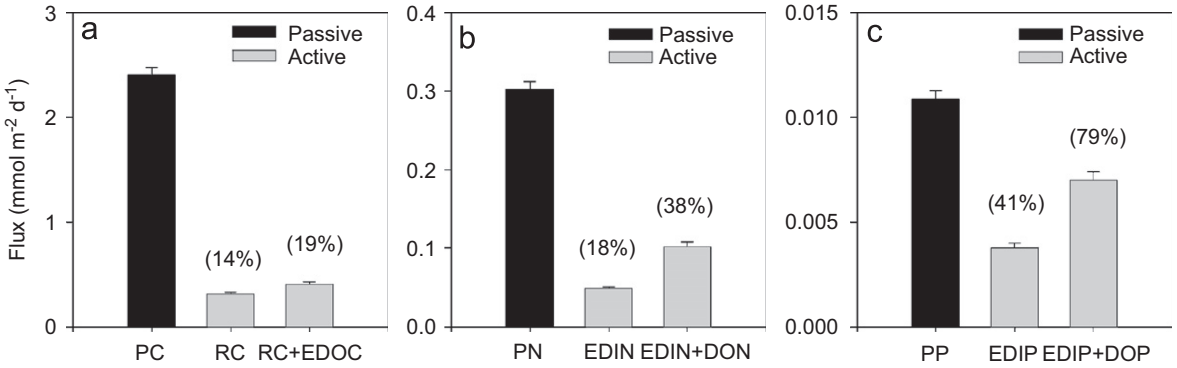


Fig. 7. Mean estimates of passive and active export fluxes of carbon (a), nitrogen (b) and phosphorus (c) from the euphotic zone at Station ALOHA. Passive export is from sediment trap collections at 150 m (1994–2004, $n = 103$: PC, PN and PP). Active inorganic fluxes are from migrant zooplankton respiration and inorganic excretion (1994–2005, $n = 113$: R_C, E_{DIN} and E_{DIP}). Active inorganic+organic fluxes additionally include migrant zooplankton organic excretion (1994–2005, $n = 113$: R_C+E_{DOC}, $E_{DIN+DON}$ and $E_{DIP+DOP}$). Percentages above active flux estimates are active fluxes as mean percentage of passive particle fluxes. Error bars are standard errors of the means.

Table 2
Standing stocks, fluxes and stoichiometry for carbon (C), nitrogen (N) and phosphorus (P) in the NPSG ecosystem

	Carbon	Nitrogen	Phosphorus	C:N:P[a]
Standing stock (mmol m^{-2})				
Suspended particles	299±4[b]	45.1±0.6	1.94±0.03	158:24.0:1 [0.10;3;0.5][c]
Zooplankton[d]	364±13	88±3	13.9±0.6	88:18.0:1 [0.02;2;0.3]
Fluxes (mmol m^{-2} d^{-1})				
Passive[e]	2.4±0.1	0.30±0.01	0.0109±0.0004	250:31.3:1 [0.14;10;1.3]
Active				
Inorganic excretion & respiration	0.31±0.02	0.049±0.003	0.0038±0.0002	84:13.2:1 [0.06;1;0.4]
Organic excretion	0.099±0.006	0.055±0.003	0.0034±0.0002	29.8:16.7:1 [0.02;0.2;0.5]
% of Passive Flux				
Inorganic excretion & respiration	14±1%	18±1%	42±3%	
Σ excretion	19±1%	38±2%	79±6%	

[a] C:N:P molar ratios.
[b] Mean±standard error of the mean.
[c] Brackets contain the standard error for mean C:N, mean C:P and mean N:P, respectively.
[d] Standing stock and molar ratios given for night-collected zooplankton only.
[e] Sediment-trap collected particulate flux measured at 150 m.

Calanus spp. to 63:8:1 for *Acartia clausi*. Pertola et al. (2002) also observed a large range in C:N:P for copepod species in the Baltic Sea (from 41:7:1 for *Acartia* spp. to 144:24:1 for *Limnocalanus macrurus*) but less variable zooplankton C:N in comparison to zooplankton C:P. High variability in C:P and N:P but more stable C:N molar ratios has been noted for many animals and is consistent with the large variability in P content but relatively small range in N content observed in most biochemicals and organelles (Sterner and Elser, 2002). These observations suggest that inter-taxon differences in biochemical composition, such as RNA content or lipids (e.g., Sterner and Elser, 2002), contribute to the large range in zooplankton C:P and N:P stoichiometries observed at Station ALOHA.

4.2. NPSG ecosystem stoichiometry and zooplankton P excretion

On average, zooplankton at Station ALOHA are P- and N-rich compared to suspended particulate material in the euphotic zone (Table 2). Zooplankton and other animals typically demonstrate stoichiometric homeostasis; that is, their C:N:P composition does not vary as a function of the stoichiometry of their food sources (Sterner and Elser, 2002). Marine zooplankton appear to maintain homeostasis of body elemental content by altering the amount of nutrients they release (e.g., Liu et al., 2006). Thus bulk zooplankton C:N:P molar ratios should always fall close to 88:18:1, with some deviation among different size fractions due to changes in community composition. In line with this theory, zooplankton elemental stoichiometry at Station ALOHA did not vary significantly by season or by year, despite temporal changes in zooplankton biomass (Landry et al., 2001; Sheridan and Landry, 2004). In contrast to the strict stoichiometric homeostasis observed for many zooplankton (e.g., Andersen and Hessen, 1991), autotroph C:N:P ratios vary with changes in resource availability (Sterner and Elser, 2002). At Station ALOHA the N:P of suspended material has increased significantly over the past two decades, largely because of the

biological fixation of atmospheric N_2 and consequent drawdown of P (Karl, 2002). Thus, the autotrophic community at Station ALOHA may be P-limited, which could contribute to their greater-than-Redfield (106:16:1; Redfield, 1958) C:N:P ratios (Karl et al., 2001; Karl, 2007).

Zooplankton at Station ALOHA must grow at C:N:P ratios of ~ 88:18:1 while feeding on relatively N- and P-deficient suspended material and organisms in a system that has become increasingly P-limited. How, then, can migrant zooplankton contribute to export through excretion of waste N and P at depth? According to models by Urabe and Watanabe (1992) and Olsen et al. (1986), zooplankton excrete less N or P as they become progressively more N or P stressed. These models suggest that zooplankton excretion will reach zero at a food source "threshold elemental ratio" (TER). Andersen and Hessen (1995) further developed this model by assuming that assimilation efficiencies (and thus gross growth efficiencies) can be <100%. Thus, following Andersen and Hessen (1995), we can define a conservative TER for P as

$$TER_P = [(C:P)_Z\, AE_P]/GGE_C$$

where $(C:P)_Z$ is the molar ratio for zooplankton (i.e., 88:1), GGE_C is the C-specific gross growth efficiency (Urabe and Watanabe, 1992) and AE_P is the P-specific assimilation efficiency (72%; Reinfelder and Fisher, 1991). Assuming an average GGE_C for copepods of 33% (Båmstedt et al., 2000), the TER for P-limited growth (TER_P) is 191. That is, the growth of zooplankton consuming food with C:P lower than 191 will not be P-limited, and P will be released by excretion and egestion processes rather than retained for growth. Other compilations of literature estimates suggest a mean and median copepod GGE_C of 26% and 22%, respectively (Straile, 1997). TER_P calculated for these alternate estimates are 287 and 243, respectively. All of these TER_P are much higher than the average C:P of suspended particles (158:1 ±3 (s.e.m.) $n = 117$, 1994–2005), indicating that omnivorous zooplankton at Station ALOHA are not P-limited and will excrete P rather than retain all ingested P for growth. Migrant zooplankton derive much of their nutrition from animal sources (Petipa, 1978; Schnetzer and Steinberg, 2002), thus the difference between TER_P and their food (C:P ⩽ 108, Table 1) is even greater and P should be readily excreted.

Our comparison of ecosystem stoichiometry at Station ALOHA indicates that migrant zooplankton are C-limited and will not retain all ingested P for growth. C-limitation is also supported by our calculation of zooplankton TER_N, which were all much higher (10–29) than suspended particle C:N (6.7:1 ±0.10 (s.e.m.) $n = 117$, 1994–2005) at Station ALOHA. Similarly, Andersen and Hessen (1995) found that marine zooplankton growth was C-limited (as opposed to N-limited), suggesting that "C-limitation" (or limitation by specific biochemicals, Tang and Dam, 1999) is a common characteristic of marine zooplankton growth. In general, marine zooplankton have high assimilation efficiencies for C, N and P (>70%; Landry et al., 1984; Hassett and Landry, 1988; Reinfelder and Fisher, 1991) but a low net production efficiency for C (Le Borgne, 1982). Thus metabolic costs force marine zooplankton to respire much of their ingested C and, consequently, to release much of the co-ingested N and P to maintain stoichiometric homeostasis. P release will only be restricted (e.g., Olsen et al., 1986) if P-rich zooplankton, for example *Acartia* spp. (Gismervik, 1997), become P-limited when feeding on suspended particles with low assimilation efficiencies (e.g., Liu et al., 2006). P release by zooplankton feeding on microplankton may be affected by increasing P depletion in the euphotic zone at Station ALOHA (Karl, 2007), as recent suspended C:P molar ratios (236:1 ±15 (s.e.m.), $n = 12$, 2006) are higher than the long-term average (Table 2). However, this is not likely to affect migrant P excretion at depth because migrant zooplankton largely consume animal material (Petipa, 1978; Schnetzer and Steinberg, 2002) and their TER_P is greater than the C:P of their prey (e.g., Table 1). Moreover, migrant zooplankton will continue to excrete nutrients when food is N- or P-deficient (Sterner and Elser, 2002) because of catabolic loss processes that cause N or P release when zooplankton growth is zero (Tang and Dam, 1999). That is, migrant zooplankton respire while maintaining basal metabolic rates at depth, and thus must excrete N and P to maintain stoichiometric homeostasis (Liu et al., 2006). In summary, whether growing or simply maintaining basal metabolic rates, vertically migrating zooplankton contribute to C, N and P export in the NPSG by releasing dissolved nutrients in midwaters (Longhurst and Harrison, 1988).

4.3. Migrant-mediated export of C, N and P

Zooplankton that migrate on a diel cycle in the NPSG export significant amounts of C, N and P from the euphotic zone by respiring and excreting at midwater depths. Migrant zooplankton are particularly important for mediating N and P export because, in part, C:N:P stoichiometries of active fluxes are relatively N- and P-rich (Table 2). Our empirical estimates of excretion stoichiometry agree with direct measurements of excreted N:P by Gaudy and Boucher (1983) for *Pleuromamma xiphias* (N:P = 13.4) and *Pleuromamma abdominalis* (N:P = 17.8), common migrators at Station ALOHA (Al-Mutairi and Landry, 2001). In contrast to the stoichiometry of migrant excretion, particulate export from the euphotic zone at Station ALOHA is deplete in N and P relative to C (Table 2). Sinking particles are readily utilized by metazoa and microbes and subject to disaggregation–reaggregation processes (Wakeham and Lee, 1993; Sheridan et al., 2002), which alter their organic composition (Lee et al., 2004) and preferentially remove N and P relative to C (Knauer et al., 1979; Karl et al., 1996; Christian et al., 1997). Export stoichiometry therefore implies that inter-zonal migrant excretion has the potential to transport significant amounts of N and P from the euphotic zone relative to the passive flux of sinking particles.

Comparison of active vertical transport estimates with concurrent measures of passive particle flux supports the hypothesis that vertically migrating zooplankton are important mediators of C, N and especially P export in the NPSG. Fluxes of C, N and P due to migrant respiration and inorganic excretion are equivalent to 14%, 18% and 42%

of sediment trap PC, PN and PP fluxes at the base of the euphotic zone (150 m), respectively (Table 2). If the excretion of dissolved organic material by vertically migrating zooplankton is taken into consideration, migrant-mediated fluxes approximately double for N and P (Table 2). Thus, active vertical transport fluxes are three-quarters of the trap-collected P fluxes on average (Table 2), and periodically much higher (Fig. 6). Zooplankton-mediated export processes clearly contribute significantly to P cycling in the subtropical Pacific Ocean.

Our study estimated organic excretion of migrating zooplankton as a constant percentage of total C, N and P release. However, in reality, organic moieties make up a variable fraction of the total waste by-products released by marine zooplankton. For example, Steinberg et al. (2000) found that DOC accounted for 5–42% of the total C excreted by different taxa in the subtropical North Atlantic Ocean, and Le Borgne and Rodier (1997) found that DON makes up 46–59% of the total N excreted by mesozooplankton in the tropical Pacific Ocean. Corner and Davies (1971) noted that the percentage of total P excreted as DOP varied from 47% to 74% (Pomeroy et al., 1963; Satomi and Pomeroy, 1965; Hargrave and Geen, 1968). These earlier studies measured P excretion by large assemblages of zooplankton, not by a limited number of animals as in Steinberg et al. (2000) and Le Borgne and Rodier (1997). Although the resultant crowding of container vessels may increase metabolic rates (e.g., Zeiss, 1963; Nival et al., 1974), P excretion can decrease with overcrowding (Hargrave and Geen, 1968), likely because of the negative effects of capture and storage stressors on zooplankton metabolism (Ikeda et al., 2000). Another study found that 52% of total P excretion was in an organic form (Le Borgne, 1973). Thus the values chosen in this study represent an average estimate for the contributions of dissolved organic substances to total C and N release and, for P, the most conservative estimate available.

All of the active fluxes presented thus far are conservative because they do not include excretion by under-sampled micronekton migrants and the consumption of migrants by midwater predators. Both of these processes enhance the net vertical flux of C, N and P from the euphotic zone to depth (Le Borgne and Rodier, 1997; Zhang and Dam, 1997). In accordance with the results of Al-Mutairi and Landry (2001), if these additional processes are included here, total NPSG migrant C and N export increase to 24% and 42% of the trap-collected PC and PN flux at 150 m, respectively. For P, including micronekton and midwater grazing contributions increases the active P flux estimate to 101% of the sediment trap PP flux at 150 m. Thus, even if literature estimates of organic P excretion are too high by a factor of 2, the total active migratory P flux would still be substantial, e.g.: 73% of trap PP. Active vs. passive flux comparisons will also be affected by methodological issues, such as sediment trap undercollection or the loss of P to trap supernatants. However our estimates of total active transport remain high (60%) relative to the total passive P flux at 150 m if we include potential P losses to formalin-poisoned supernatants (30% of total trap P; O'Neill et al., 2005). Another issue that could affect the balance between active and passive export fluxes is trap undercollection (e.g., discrepancies between trap and ^{234}Th-derived export fluxes). Trap undercollection can be substantial during episodic high export events (Benitez-Nelson et al., 2001), e.g., following summer phytoplankton blooms (Dore et al., 2008), and it is likely that the contribution of migrant-mediated export fluxes is small at these times. On average, however, total migrant P flux in the NPSG (0.0051 mmol P m^{-2} d^{-1}: Table 2+micronekton+grazing) is clearly a large component of total P export.

The significance of active transport relative to passive particle flux has been examined by several researchers, beginning with Longhurst and Harrison (1988). These studies have found migrator-mediated C and N fluxes to be appreciable relative to passive fluxes measured in sediment traps or calculated using flux-production models (Longhurst et al., 1989, 1990; Dam et al., 1995; Rodier and Le Borgne, 1997; Zhang and Dam, 1997; Steinberg et al., 2000; Al-Mutairi and Landry, 2001). Migrant-mediated export of C and N appears to be most important in oligotrophic tropical and subtropical regions, where particle fluxes are small (e.g., Le Borgne and Rodier, 1997). Of the studies listed above, only Le Borgne and Rodier (1997) have considered migrant-mediated export of P. Interestingly, our rates of total P export (~0.007 mmol P m^{-2} d^{-1}) closely match those of Le Borgne and Rodier (1997) at an oligotrophic tropical station, although migrator biomass at Station ALOHA is larger (410 DW m^{-2}) than in the equatorial Pacific warm pool (118 mg DW m^{-2}; Le Borgne and Rodier, 1997). These differences can be attributed to different methodologies. The present estimates are based on established metabolic equations for DIP excretion (Ikeda, 1985) and a conservative estimate for %DOP excretion (Pomeroy et al., 1963) to migrator biomass. In contrast, Le Borgne and Rodier (1997) directly measured weight-specific rates of total P (DIP+DOP) excretion and applied them to station estimates of migrator biomass. Because our total P excretion estimates are similar to those of Le Borgne and Rodier (1997) while migrator biomass is ~4 × higher, this comparison suggests that the contribution of DOP to total P excretion in the NPSG may actually be higher than that estimated by Pomeroy et al. (1963). Other uncertainties in the export calculations include seasonal or body size-dependant changes in the amount of time migrators spend beneath the thermocline (Hays, 1995), or the fact that plankton nets can under-sample gelatinous plankton, which may be strong vertical migrators. Clearly, many questions remain to be resolved concerning migrant zooplankton and P excretion. For the present analysis, we will focus on our conservative estimates of migrant-mediated C, N and P flux, i.e., active transport due to migrant respiration, inorganic excretion and organic excretion (Table 2).

The above discussion only considers active transport by vertically migrating zooplankton and particle fluxes exiting the euphotic zone. This comparison is significant in that it estimates how much export production (the "e-ratio") may be underestimated if only passive particle fluxes are considered. In the case of P-specific export production, this discrepancy is very large (Table 2, Fig. 7). However migrant zooplankton rest at depths of

300–500 m (or greater) during the day, and thus much of migrant C, N and P release occurs deep in the midwater region of the world's oceans. Suspended material and sinking particles at these depths are very altered in quantity (Suess, 1980; Martin et al., 1987; Benitez-Nelson et al., 2001) and biochemical composition (Wakeham and Lee, 1993; Sheridan et al., 2002; Lee et al., 2004) compared to suspended material in the upper 150 m and particles exiting the euphotic zone. The elemental content of particulate material also changes, with sinking particles increasingly enriched in C and depleted in N and P at midwater depths (Karl et al., 1996; Christian et al., 1997). At Station ALOHA, the exponential reduction in passive particle fluxes and concurrent change in their stoichiometry indicates that migrant zooplankton are a major source of N and P to microbial communities inhabiting the midwater "twilight zone" (Buesseler et al., 2007b; Steinberg et al., 2008). For example, migrant zooplankton P excretion was much larger than passive particle fluxes measured at 300 and 500 m for the portion of our time-series when sediment trap data at these depths were available (nine cruises in 1994–1995; Fig. 8). Moreover, this P release is likely to be labile and readily available to the midwater microbial community. Turnover of P in marine zooplankton is high (Liu et al., 2006), and excreted organic P compounds are likely derived from rapidly cycling metabolic pools (e.g., ATP, RNA). Björkman et al. (2000) found that dissolved ATP and nucleic acids were highly bio-available compared to other DOP compounds, a finding consistent with the highly variable residence times of DOP that track upper ocean primary production in NPSG surface waters (Benitez-Nelson and Karl, 2002). It is unknown how similar metabolic P-containing compounds are used by bacteria and archaea at midwater depths (Karner et al., 2001); however, the quantity and quality of migrant excretory products (Fig. 8) suggest that they may be important in stimulating microbial production in the NPSG "twilight zone".

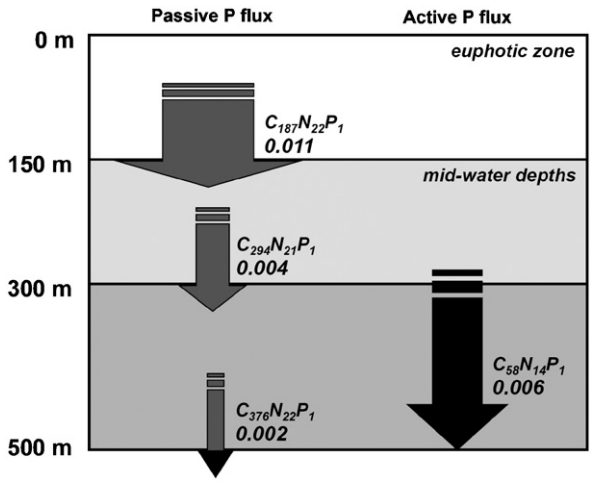


Fig. 8. Passive particulate P flux and migrant-mediated P flux in the NPSG from 1994 to 1995 ($n = 9$ cruises). Arrow widths indicate passive P fluxes (mmol P m^{-2} d^{-1}) measured by sediment trap collections at 150, 300 and 500 m depths and the active P fluxes due to excretion by vertically migrating zooplankton at $\geqslant$300 m depth. At each depth, the average P flux (in italics beside each arrow) and the C:N:P stoichiometry are shown.

4.4. Temporal trends in N:P stoichiometry in the NPSG

The NPSG zooplankton community is not static, but exhibits significant changes in biomass on seasonal and interannual time-scales (Landry et al., 2001; Sheridan and Landry, 2004). How do these dynamic alterations affect C, N and P export? The most significant temporal change to the migrant community has been the slow increase in migrant zooplankton biomass over the past decade. This was not observed by Al-Mutairi and Landry (2001) or Sheridan and Landry (2004). However, our longer 12 years of time-series sampling indicates that the change in migrant biomass may have occurred in response to climate oscillation reversals in 1998 (Keeling et al., 2004) and concurrent shifts in plankton community structure (Corno et al., 2007). The increasing trend was driven by 0.5–1 and $>$5 mm zooplankton, e.g., higher crustacea and copepods from the Metridinidae family, such as *P. xiphias* (Al-Mutairi and Landry, 2001). Although the increase in migrant biomass over the past decade was significant, active transport of C, N and P increased only slightly from 1994 to 2005 because ambient water temperatures experienced by the migrators at depth, and thus metabolic rates, declined. Over the same time period, particulate P export decreased systematically (Karl, 2007). Thus, the net result of the interannual changes in migrator biomass and particulate export from 1994 to 2005 was a significant increase in the proportion of total P export due to active transport. Moreover, because migrant excretory products are relatively P-rich, decoupling between N and P was less over the past decade than if only the N:P of passive particle fluxes had been considered.

The magnitude of migrant-mediated P fluxes at Station ALOHA and its importance in altering export stoichiometry imply that active transport should be explicitly included in P budgets for the NPSG. Numerous lines of evidence support the notion that biogeochemical cycling of P is dynamic and may cyclically limit productivity in this region (Karl, 2002). For example, surface pools of dissolved and particulate material at Station ALOHA have C:P and N:P ratios much greater than the Redfield ratio (C_{106}:N_{16}:P_1; 1958; e.g., Table 2), and inventories of DIP in the upper ocean (0–100 m) have systematically decreased over the duration of the time-series program (Karl, 2007). Thus the NPSG may have become more P-limited, as discussed by Karl et al. (2001) and Karl (2002). These changes are thought to result from the enhanced activity of diazotrophs such as *Trichodesmium* spp. (Karl et al., 1997), which fix CO_2 and N_2 from the atmosphere while using phosphate and other bio-available forms of P from the surface ocean (Dyhrman et al., 2006). Because migrant excretory products are P-rich relative to sinking particles (Table 2) and active P transport has become more important in the past decade, migrant zooplankton have likely exacerbated the euphotic zone P-deficit attributed to N_2-fixation. That is, the N:P of the total (active+passive)

export flux (24:1, on average) is closer to Redfield, or "bulk plankton", ratios than the N:P of sinking particle flux. Thus, as migrant-mediated export has increased in importance, relatively less fixed N in "excess" of biological N:P ratios has been removed from the surface ocean and the system has been more quickly driven into a P-limited state.

P-limitation of the NPSG ecosystem is affected by several processes whose impact on euphotic zone macronutrient budgets remains difficult to constrain. Large export events following summer phytoplankton blooms occur every year in the NPSG (Dore et al., 2008) but can be missed by sediment traps (Benitez-Nelson et al., 2001), and thus may represent an important but poorly studied P removal mechanism. The net export of dissolved organic material from the euphotic zone may also be important in the NPSG (e.g., Emerson et al., 1997); however, the contribution of this pathway to P removal remains unresolved. An intriguing but unsatisfactorily constrained P flux into the euphotic zone in the NPSG is phosphacline "mining" by vertically migrating phytoplankton. White et al. (2006) have shown that migrating colonies of *Trichodesmium* spp. could import up to 10% of trap-measured P export fluxes at Station ALOHA, and "P-mining" by phytoplankton may be enhanced by phosphacline shoaling during the passage of mesoscale features (Dore et al., 2008). Another potentially important P source is the vertical migration of *Rhizosolenia* mats (Wilson et al., 2008), which are known to contribute significantly to new N fluxes in the northeast Pacific gyre (Villareal et al., 1999). Clearly a more comprehensive analysis of P sources and sinks (e.g., surface ocean entrainment, sinking particle fluxes, active transport and P-mining) is needed to understand decadal-scale trends in surface ocean P inventories and biological variability in the NPSG.

Active transport of P is likely to be an important regulator of ecosystem processes in low-latitude, oligotrophic systems, where particle fluxes are low. Migrant zooplankton may be particularly important in influencing C sequestration because active processes export so little C per unit N and P (C_{51}:N_{12}:P_1, on average). Previous studies indicate the net export of C from the surface ocean is driven by preferential remineralization of N and P relative to C from sinking particles (e.g., Christian et al., 1997; Schaffer et al., 1999; Michaels et al., 2001). However active transport substantially modifies total export stoichiometries. For example, our total (passive+active) export stoichiometries at 150 m (C_{168}:N_{24}:P_1, 1994–2005 average) and 500 m at Station ALOHA (C_{141}:N_{16}:P_1, 1994–1995 average) are much closer to organic matter remineralization ratios (Anderson and Sarmiento, 1994) than those considering only passive fluxes (Fig. 8). Thus, given the activities of vertical migrators, the ability of the marine biological pump to sequester C in low-latitude, oligotrophic systems may be less than has been previously considered. In summary, because active transport is such a large component of the total P flux and can significantly impact total export stoichiometries, processes involving migrant zooplankton must be included in large-scale efforts to understand marine biogeochemical cycles.

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References

Al-Mutairi, H., Landry, M.R., 2001. Active export of carbon and nitrogen at Station ALOHA by diel migrant zooplankton. Deep-Sea Research II 48, 2083–2103.

Andersen, T., Hessen, D.O., 1991. Carbon, nitrogen and phosphorus content of freshwater zooplankton. Limnology and Oceanography 36, 807–814.

Andersen, T., Hessen, D.O., 1995. Carbon or nitrogen limitation in marine copepods? Journal of Plankton Research 17, 317–331.

Anderson, L.A., Sarmiento, J.L., 1994. Redfield ratios of remineralization determined by nutrient data analysis. Global Biogeochemical Cycles 8, 65–80.

Båmstedt, U., 1986. Chemical composition and energy content. In: Corner, E.D.S., O'Hara, S.C.M. (Eds.), The Biological Chemistry of Marine Copepods. Clarendon Press, Oxford, pp. 1–58.

Båmstedt, U., Gifford, D.J., Irigoien, X., Atkinson, A., Roman, M., 2000. Feeding. In: Harris, R.P., Wiebe, P.H., Lenz, J., Skjoldal, H.R., Huntley, M. (Eds.), ICES Zooplankton Methodology Manual. Academic Press, San Diego, p. 684.

Beers, J.R., 1966. Studies on the chemical composition of the major zooplankton groups in the Sargasso Sea off Bermuda. Limnology and Oceanography 11, 520–528.

Benitez-Nelson, C.R., 2000. The biogeochemical cycling of phosphorus in marine systems. Earth-Science Reviews 51, 109–135.

Benitez-Nelson, C.R., Karl, D.M., 2002. Phosphorus cycling in the North Pacific Subtropical Gyre using cosmogenic ^{32}P and ^{33}P. Limnology and Oceanography 47, 762–770.

Benitez-Nelson, C.R., Buesseler, K.O., Karl, D.M., Andrews, J., 2001. A time-series study of particulate matter export in the North Pacific Subtropical Gyre based on ^{234}Th:^{238}U disequilibrium. Deep-Sea Research I 48, 2595–2611.

Björkman, K.M., Thomson-Bulldis, A.L., Karl, D.M., 2000. Phosphorus dynamics in the North Pacific subtropical gyre. Aquatic Microbial Ecology 22, 185–198.

Buesseler, K.O., Antia, A.N., Chen, M., Fowler, S.W., Gardner, W.D., Gustafsson, O., Harada, K., Michaels, A.F., van der Loeff'o, M.R., Sarin, M., Steinberg, D.K., Trull, T., 2007a. An assessment of the use of sediment traps for estimating upper ocean particle fluxes. Journal of Marine Research 65 (3), 345–416.

Buesseler, K.O., Lamborg, C.H., Boyd, P.W., Lam, P.J., Trull, T.W., Bidigare, R.R., Bishop, J.K.B., Casciotti, K.L., Dehairs, F., Elskens, M., Honda, M., Karl, D.M., Siegel, D.A., Silver, M.W., Steinberg, D.K., Valdes, J., Van Mooy, B., Wilson, S., 2007b. Revisiting carbon flux through the ocean's twilight zone. Science 316 (5824), 567–570.

Christian, J.R., Lewis, M.R., Karl, D.M., 1997. Vertical fluxes of carbon, nitrogen and phosphorus in the North Pacific Subtropical Gyre near Hawaii. Journal of Geophysical Research 102 (C7), 15667–15677.

Codispoti, L.A., 1989. Phosphorus vs. nitrogen limitation in new and export production. In: Berger, W.H., Smetacek, V.S., Wefer, G. (Eds.), Productivity of the Oceans: Present and Past. Wiley, Chichester, pp. 372–394.

Corner, E.D.S., Davies, A.G., 1971. Plankton as a factor in the nitrogen and phosphorus cycles in the sea. Advances in Marine Biology 9, 101–204.
Corno, G., Karl, D.M., Church, M.J., Letelier, R.M., Lukas, R., Bidigare, R.R., Abbott, M.R., 2007. Impact of climate forcing on ecosystem processes in the North Pacific Subtropical Gyre. Journal of Geophysical Research 112, C04021, doi:10.1029/2006JC003730.
Dam, H.G., Roman, M.R., Youngbluth, M.J., 1995. Downward export of respiratory carbon and dissolved inorganic nitrogen by diel-migrant mesozooplankton at the JGOFS Bermuda time-series station. Deep-Sea Research I 42 (7), 1187–1197.
Dore, J.E., Letelier, R.M., Church, M.J., Lukas, R., Karl, D.M., 2008. Summer phytoplankton blooms in the oligotrophic North Pacific Subtropical Gyre: historical perspective and recent observations. Progress in Oceanography 76, 2–38.
Dyhrman, S.T., Chappell, P.D., Haley, S.T., Moffett, J.W., Orchard, E.D., Waterbury, J.B., Webb, E.A., 2006. Phosphonate utilization by the globally important marine diazotroph *Trichodesmium*. Nature 439, 68–71.
Emerson, S., Quay, P., Karl, D., Winn, C., Tupas, L., 1997. Experimental determination of the organic carbon flux from open-ocean surface waters. Nature 389, 951–954.
Eppley, R.W., Peterson, B.J., 1979. Particulate organic matter flux and planktonic new production in the deep ocean. Nature 282, 677–680.
Falkowski, P.G., Barber, R.T., Smetacek, V., 1998. Biogeochemical controls and feedback on ocean primary production. Science 281, 200–206.
Gaudy, R., Boucher, J., 1983. Relation between respiration, excretion (ammonia and inorganic phosphorus) and activity of amylase and trypsin in different species of pelagic copepods from an Indian Ocean equatorial area. Marine Biology 75, 37–45.
Gismervik, I., 1997. Stoichiometry of some marine planktonic crustaceans. Journal of Plankton Research 19 (2), 279–285.
Hargrave, B.T., Geen, G.H., 1968. Phosphorus excretion by zooplankton. Limnology and Oceanography 13, 332–342.
Hassett, R.P., Landry, M.R., 1988. Short-term changes in feeding and digestion by the copepod *Calanus pacificus*. Marine Biology 99, 63–74.
Hays, G.C., 1995. Ontogenetic and seasonal variation in the diel vertical migration of the copepods *Metridia lucens* and *Metridia longa*. Limnology and Oceanography 40, 1461–1465.
Hays, G.C., Harris, R.P., Head, R.N., 1997. The vertical nitrogen flux caused by zooplankton diel vertical migration. Marine Ecology Progress Series 160, 57–62.
Hays, G.C., Harris, R.P., Head, R.N., 2001. Diel changes in the near-surface biomass of zooplankton and the carbon content of vertical migrants. Deep-Sea Research II 48, 1063–1068.
Hayward, T.L., 1980. Spatial and temporal feeding patterns of copepods from the North Pacific Central Gyre. Marine Biology 58, 295–309.
Heywood, K.J., 1996. Diel vertical migration of zooplankton in the Northeast Atlantic. Journal of Plankton Research 18, 163–184.
Ikeda, T., 1985. Metabolic rates of epipelagic marine zooplankton as a function of body mass and temperature. Marine Biology 85, 1–11.
Ikeda, T., Torres, J.J., Hernández-Léon, S., Geiger, S.P., 2000. Metabolism. In: Harris, R.P., Wiebe, P., Lenz, J., Skjoldal, H.R., Huntley, M. (Eds.), ICES Zooplankton Methodology Manual. Academic Press, San Diego, p. 684.
Ittekkot, V., Schäfer, P., Honjo, S., Depetris, P.J., 1996. Particle Flux in the Ocean. Wiley, New York.
Karl, D.M., 2002. Nutrient dynamics in the deep blue sea. Trends in Microbiology 10 (9), 410–418.
Karl, D.M., 2007. The marine phosphorus cycle. In: Hurst, C.J., Crawford, R.L., Garland, J.L., Lipson, D.A., Mills, A.L., Stetzenbach, L.D. (Eds.), Manual of Environmental Microbiology. American Society of Microbiology, Washington, DC, pp. 523–539.
Karl, D.M., Björkman, K.M., 2001. Phosphorus cycle in seawater: dissolved and particulate pool inventories and selected phosphorus fluxes. Methods in Microbiology 30, 239–270.
Karl, D.M., Lukas, R., 1996. The Hawaii Ocean Time-series (HOT) program: background, rationale, and field implementation. Deep-Sea Research II 43 (2–3), 129–156.
Karl, D.M., Christian, J.R., Dore, J.E., Hebel, D.V., Letelier, R.M., Tupas, L.M., Winn, C.D., 1996. Seasonal and interannual variability in primary production and particle flux at Station ALOHA. Deep-Sea Research II 43 (2–3), 539–569.
Karl, D.M., Letelier, R., Tupas, L., Dore, J., Christian, J., Hebel, D., 1997. The role of nitrogen fixation in biogeochemical cycling in the subtropical North Pacific Ocean. Nature 388, 533–538.
Karl, D.M., Bjorkman, K.M., Dore, J.E., Fujieki, L., Hebel, D.V., Houlihan, T., Letelier, R.M., Tupas, L.M., 2001. Ecological nitrogen-to-phosphorus stoichiometry at station ALOHA. Deep-Sea Research II 48 (8–9), 1529–1566.
Karner, M.B., DeLong, E.F., Karl, D.M., 2001. Archaeal dominance in the mesopelagic zone of the Pacific Ocean. Nature 409 (6819), 507–510.
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), GB4006, doi:10.1029/2004GB002227.
Knauer, G.A., Martin, J.H., Bruland, K.W., 1979. Fluxes of particulate carbon, nitrogen, and phosphorus in the upper water column of the northeast Pacific. Deep-Sea Research 26A, 97–108.
Landry, M.R., Hassett, R.P., Fagerness, V., Downs, J., Lorenzen, C.J., 1984. Effect of food acclimation on assimilation efficiency of *Calanus pacificus*. Limnology and Oceanography 29 (2), 361–364.
Landry, M.R., Al-Mutairi, H., Selph, K.E., Christensen, S., Nunnery, S., 2001. Seasonal patterns of mesozooplankton abundance and biomass at Station ALOHA. Deep-Sea Research II 48, 2037–2061.
Le Borgne, R.P., 1973. Etude de la respiration et de l'excrétion d'azote et de phosphore des populations zooplanctoniques de l'upwelling mauritanien (mars-avril, 1972). Marine Biology 19, 249–257.
Le Borgne, R., 1982. Zooplankton production in the eastern tropical Atlantic Ocean: net growth efficiency and P:B in terms of carbon, nitrogen and phosphorus. Limnology and Oceanography 27 (4), 681–698.
Le Borgne, R., Rodier, M., 1997. Net zooplankton and the biological pump: a comparison between the oligotrophic and mesotrophic equatorial Pacific. Deep-Sea Research II 44 (9–10), 2003–2023.
Lee, C., Wakeham, S., Arnosti, C., 2004. Particulate organic matter in the sea: the composition conundrum. Ambio 33 (8), 565–575.
Liu, S., Wang, W.X., Huang, L.M., 2006. Phosphorus dietary assimilation and efflux in the marine copepod *Acartia erythraea*. Marine Ecology-Progress Series 321, 193–202.
Longhurst, A.R., 1991. Role of the marine biosphere in the global carbon cycle. Limnology and Oceanography 36 (8), 1507–1526.
Longhurst, A.R., Harrison, W.G., 1988. Vertical nitrogen flux from the oceanic photic zone by diel migrant zooplankton and nekton. Deep-Sea Research I 35, 881–889.
Longhurst, A.R., Bedo, A., Harrison, W.G., Head, E.J.H., Horne, E.P., Irwin, B., Morales, C., 1989. NFLUX: a test of vertical nitrogen flux by diel migrant biota. Deep-Sea Research I 36 (11), 1705–1719.
Longhurst, A.R., Bedo, A.W., Harrison, W.G., Head, E.J.H., Sameoto, D.D., 1990. Vertical flux of repiratory carbon by oceanic diel migrant biota. Deep-Sea Research I 37 (4), 685–694.
Martin, J.H., Knauer, G.A., Karl, D.M., Broenkow, W.W., 1987. VERTEX: carbon cycling in the northeast Pacific. Deep-Sea Research 34 (2), 267–285.
Mauchline, J. (Ed.), 1998. The Biology of Calanoid Copepods. Elsevier, San Diego.
Michaels, A.F., Karl, D.M., Capone, D.G., 2001. Element stoichiometry, new production, and nitrogen fixation. Oceanography 14 (4), 68–77.
Moutin, T., Van Den Broeck, N., Beker, B., Dupouy, C., Rimmelin, P., Le Bouteiller, A., 2005. Phosphate availability controls *Trichodesmium* spp. biomass in the SW Pacific Ocean. Marine Ecology-Progress Series 297, 15–21.
Nival, P., Malara, G., Charra, R., Palazzoli, I., Nival, S., 1974. Etude de la respiration et de l'excretion de quelques copepodes planktonique (Crustacea) dans la zone de remontee d'eau profonde de cotes Marocaines. Journal of Experimental Marine Biology and Ecology 15, 231–260.
Olsen, Y., Jensen, A., Reinertsen, H., Børsheim, K.Y., Heldal, M., Langeland, A., 1986. Dependence of the rate of release of phosphorus by zooplankton on the P:C ratio in the food supply, as calculated by a recycling model. Limnology and Oceanography 31 (1), 34–44.
O'Neill, L.P., Benitez-Nelson, C.R., Styles, R.M., Tappa, E., Thunell, R.C., 2005. Diagenetic effects on particulate phosphorus samples collected using formalin-poisoned sediment traps. Limnology and Oceanography: Methods 3, 308–317.
Pertola, S., Koski, M., Viitasalo, M., 2002. Stoichiometry of mesozooplankton in N- and P-limited areas of the Baltic Sea. Marine Biology 140, 425–434.
Petipa, T.S., 1978. Matter accumulation and energy expenditure in planktonic ecosystems at different trophic levels. Marine Biology 49, 285–293.
Pomeroy, L.R., Mathews, H.M., Min, H.S., 1963. Excretion of phosphate and soluble organic phosphorus compounds by zooplankton. Limnology and Oceanography 8, 50–55.
Postel, L., Fock, H., Hagen, W., 2000. Biomass and abundance. In: Harris, R.P., Wiebe, P.H., Lenz, J., Skjoldal, H.R., Huntley, M. (Eds.), ICES

Zooplankton Methodology Manual. Academic Press, San Diego, pp. 83–192.
Redfield, A.C., 1958. The biological control of chemical factors in the environment. American Scientist 46, 205–221.
Reinfelder, J., Fisher, N., 1991. The assimilation of elements ingested by marine copepods. Science 251, 794–796.
Rodier, M., Le Borgne, R., 1997. Export flux of particles at the equator in the western and central Pacific ocean. Deep-Sea Research II 44 (9–10), 2085–2113.
Sañudo-Wilhelmy, S.A., Kustka, A.B., Gobler, C.J., Hutchins, D.A., Yang, M., Lwiza, K., Burns, J., Capone, D.G., Raven, J.A., Carpenter, E.J., 2001. Phosphorus limitation of nitrogen fixation by *Trichodesmium* in the central Atlantic Ocean. Nature 411, 66–69.
Satomi, M., Pomeroy, L.R., 1965. Respiration and phosphorus excretion in some marine populations. Ecology 46 (6), 877–881.
Schaffer, G., Bendtsen, J., Ulloa, O., 1999. Fractionation during remineralization of organic matter in the ocean. Deep-Sea Research I 46, 185–204.
Schnetzer, A., Steinberg, D.K., 2002. Active transport of particulate organic carbon and nitrogen by vertically migrating zooplankton in the Sargasso Sea. Marine Ecology-Progress Series 234, 71–84.
Sheridan, C.C., Landry, M.R., 2004. A 9-year increasing trend in mesozooplankton biomass at the Hawaii Ocean Time-series Station ALOHA. ICES Journal of Marine Science 61 (4), 457–463.
Sheridan, C.C., Lee, C., Wakeham, S.G., Bishop, J.K.B., 2002. Suspended particle organic composition and cycling in surface and midwaters of the equatorial Pacific Ocean. Deep-Sea Research I 49, 1983–2008.
Steinberg, D.K., Carlson, C.A., Bates, N.R., Goldthwait, S.A., Madin, L.P., Michaels, A.F., 2000. Zooplankton vertical migration and the active transport of dissolved organic and inorganic carbon in the Sargasso Sea. Deep-Sea Research I 47, 137–158.
Steinberg, D.K., Steinberg, D.K., van Mooy, B.A.S., Buesseler, K.O., Boyd, P.W., Kobari, T., Karl, D.M., 2008. Bacterial vs. zooplankton control of sinking particle flux in the ocean's twilight zone. Limnology and Oceanography 53 (4), 1327–1338.
Sterner, R.W., Elser, J.J., 2002. Ecological Stoichiometry: The Biology of Elements from Molecules to the Biosphere. Princeton University Press, Princeton.
Straile, D., 1997. Gross growth efficiencies of protozoan and metazoan zooplankton and their dependence on food concentration, predator–prey weight ratio, and taxonomic group. Limnology and Oceanography 42 (6), 1375–1385.
Suess, E., 1980. Particulate organic carbon flux in the oceans—surface productivity and oxygen utilization. Nature 288, 260–263.
Tang, K.W., Dam, H.G., 1999. Limitation of zooplankton production: beyond stoichiometry. Oikos 84 (3), 537–542.
Urabe, J., Watanabe, Y., 1992. Possibility of N or P limitation for planktonic cladocerans: an experimental test. Limnology and Oceanography 37 (2), 244–251.
Villareal, T.A., Pilskaln, C., Brzezinski, M., Lipschultz, F., Dennett, M., Gardner, G.B., 1999. Upward transport of oceanic nitrate by migrating diatom mats. Nature 397, 423–425.
Wakeham, S.G., Lee, C., 1993. Production, transport, and alteration of particulate organic matter in the marine water column. In: Engel, M.H., Macko, S.A. (Eds.), Organic Geochemistry. Plenum Press, New York, pp. 145–169.
White, A.E., Spitz, Y.H., Letelier, R.M., 2006. Modeling carbohydrate ballasting by *Trichodesmium* spp. Marine Ecology-Progress Series 323, 35–45.
Wiebe, P.H., Copley, N.J., Boyd, S.H., 1992. Coarse-scale horizontal patchiness and vertical migration of zooplankton in Gulf Stream warm-core ring 82-H. Deep-Sea Research 39 (Suppl. 1), S247–S278.
Wilson, C., Villareal, T.A., Maximenko, N., Bograd, S.J., Montoya, J.P., Schoenbaechler, C.A., 2008. Biological and physical forcings of late summer chlorophyll blooms at 30°N in the oligotrophic Pacific. Journal of Marine Systems 69 (3–4), 164–176.
Zeiss, F.R., 1963. Effects on population densities on zooplankton respiration rates. Limnology and Oceanography 8, 110–115.
Zhang, X., Dam, H.G., 1997. Downward export of carbon by diel migrant mesozooplankton in the central equatorial Pacific. Deep-Sea Research II 44 (9–10), 2191–2202.