Undetected blooms in Prince William Sound: using multiple techniques to elucidate the base of the summer food web

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Key Words: Prince William Sound, *Noctiluca* sp., HPLC, bloom, phytoplankton, food web

Abstract

Prince William Sound supports many commercially and culturally important species. The phytoplankton community dynamics which support and sustain the high biomass and diversity of this ecosystem are largely unknown. The aim of this study was to describe the phytoplankton community composition during the summer, the time at which this system supports many additional migrants and commercially important fisheries. Phytoplankton community composition (pigments), dissolved nutrients, secchi depth, total and particulate organic carbon and nitrogen, and export to deep water were measured during the summers of 2008-2010. In addition, natural abundance stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) of particulate organic matter (POM) and faunal samples were measured in 2010. Analysis of the phytoplankton community composition using multivariate statistics showed that changes over the summer were driven by changes in proportion of the dominant groups: diatoms, dinoflagellates, cyanobacteria, cryptophytes, chlorophytes and prasinophytes. These changes were driven by changes in nutrients including an organic nitrogen source, phosphate, and silica and correspond to shifts in particulate concentrations. A consistent pattern was observed each year: a large *Noctiluca* sp. bloom in June concurrent with low nutrients, low diversity, and high POC concentrations was followed by a shift in the phytoplankton community to a more diverse smaller size class community in July and equilibrating in August. This annual summer bloom could be an important contributor to the energy and nutrient inputs at the base of the regional marine food web.

Introduction

Prince William Sound (PWS), Alaska, has many commercially important fisheries (including five species of salmon, Pacific halibut, Pacific cod and many shellfish species), abundant marine mammal populations (including humpback, sei, fin, minke, and killer whales, sea otters, harbor seals, and Steller sea lions), and a high diversity of birds (220 species); (Alaska Department of Fish and Game). The biological base supporting these populations is not completely understood. While it has been well documented that fisheries yields are tied to primary productivity on regional and global scales (Chassot et al. 2010; Ware and Thomson 2005; Chassot et al. 2007), few studies have looked at the phytoplankton dynamics in this region. Nutrient and plankton dynamics are tightly coupled to the physical conditions in PWS (Eslinger et al. 2001; Childers 2005; Quigg et al. 2013), which is downwelling dominated (Childers 2005). The system is well mixed in the fall and winter, replenishing the surface water with nutrients. The water column begins to stratify in the spring from inflow of freshwater and surface warming. Short, intense spring blooms occur during calmer spring seasons, while stormier years lead to increased mixing and delayed stratification, resulting in a longer, less intense bloom, with the majority of the primary production transferred up the food chain (Eslinger et al. 2001).

Phytoplankton biomass in Simpson Bay, one of the fjords on the southeastern side of PWS, ranges from 0.5-12 μg L^{-1} during the summer and is co-limited by N and P or N and Si (Quigg et al. 2013). While understanding of the autotrophic group dynamic as a whole is imperative, phytoplankton communities are composed of a wide range of functional groups and size classes; the composition of which is determined by bottom-up (nutrient availability and light) and top-down (grazing pressures) controls. Because phytoplankton range over 10 orders of magnitude in volume (Irwin et al. 2006) the composition of this dynamic group at the base of the food web determines the quantity energy flow within the ecosystem. Beyond the amount of production available to a system, phytoplankton (through community composition) determine: length of food web, transfer efficiency, and interconnectivity/resilience (Finkel 2007). There exists a strong relationship between taxonomic class of phytoplankton and size (Irwin et al. 2006). Taxonomic groups can be identified by their accessory pigment composition (Table 1; Jeffrey et al. 1997). This has been used as a mechanism for understanding of the phytoplankton community composition and ecology through analysis of marker pigments (e.g., Aiken et al. 2009; Dorado et al. 2012).

This study investigated the summer phytoplankton community composition and production in an effort to understand the base of the food web which supports the high biological productivity in this system beyond the spring bloom. We hypothesized that more production occurs more in this region than is estimated using chlorophyll *a* alone. We determined the variability in the phytoplankton community (using 17 pigments as biomarkers), dissolved nutrients, secchi depth, total and particulate organic carbon and nitrogen (POC/N), and export (total particulate reaching 20 m and 40 m) in the summers of 2008-2010, plus particulate organic matter (POM) and faunal samples for stable isotope ($\delta^{13}C$ and $\delta^{15}N$) analysis in 2010. By using a multifaceted approach we were able to detect increases in biomass that were previously missed using chlorophyll *a* measurements alone.

Methods

Study Area

Simpson Bay is a shallow fjord in eastern PWS that consists of three distinct basins (Fig. 1) based on geomorphology and freshwater inflows (Noll et al. 2009). North Bay is 4 km long by 0.70-1.3 km wide with a maximum depth of 85 m. The hydrography of North Bay is substantially influenced by freshwater inflows (watershed: basin surface area ratio of 20:1). West Bay is the largest (4 km long by 2 km wide) as well as the shallowest (25-55 m) of the three sub-bay systems. West Bay exchanges directly with PWS and has the smallest input of freshwater (from shoreline creeks) with a watershed/basin surface area ratio of 1:1. East Bay also exchanges directly with PWS; it is 4 km long and 2 km wide at the head, narrowing to 1 km wide at the mouth and has a watershed/basin surface area ratio of 7:1. Differences in watershed/basin surface area ratios directly impact freshwater input, sediment load, and organic matter input. This system was highly stratified during the study period with a chlorophyll fluorescence maximum at ~10 m (Quigg et al. 2013).

Sampling in 2008 & 2009

Sampling was designed to elucidate variability in phytoplankton community composition during June, July and August between the three sub-bays of Simpson's Bay. Water samples were collected at the surface and 10 m at nine stations (3 in each sub-bay for a total of 6 samples from each sub-bay for each month; Fig. 1). Samples were processed for chlorophyll (chl) *a*, pigment

analysis, dissolved nutrients, particulate organic carbon (POC), particulate organic nitrogen (PON), particulate carbon (PC), and particulate nitrogen (PN). Samples were collected for microscopic identification of the dominant phytoplankton using a (64 µm mesh plankton net towed through the water for 5 min while at each station).

Export

Sediment traps (1 m tall, 8 cm center diameter with a honeycomb baffle at the top to reduce loss from resuspension) were suspended 20 m and 40 m below the surface. Traps were deployed once each month (one set in each bay) for 48 hrs (Fig. 1). After recovery, material in the traps was allowed to settle for 4-6 hrs before the top water was poured off (via a hole in the trap) leaving the concentrated sample (1.5 L) in the bottom. Samples were filtered for chl *a*, pigments, and POC, PON, PC and PN. Hereafter we refer to the average amount of material collected in sediment traps divided by area of trap opening and the number of days deployed as export.

Sampling in 2010

The 2010 summer sampling sought to begin elucidating pathways of carbon through the lower portions of the food web in Simpson Bay. Water samples were collected before, during and after the annual summer *Noctiluca* sp. bloom and analyzed for pigment composition, chl *a*, stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) and dissolved nutrients. Size fractionated plankton samples were collected using a 64 µm plankton net and then fractioned using a 118 µm sieve. Material remaining on the sieve were transferred/filtered onto 25 mm precombusted (500ºC, 5 hrs) Whatman GF/F (> 118µm sample). Material which passed through the sieve was transferred onto a separate 25 mm precombusted Whatman GF/F (< 118µm sample).

Muscle tissue from butter clams (*Saxidomus giganteus*), Pacific blue mussels (*Mytilus trossolus*), juvenile herring (*Clupea pallasii*), and herring roe were collected for stable isotope ($\delta^{13}C$ and $\delta^{15}N$) analyses, rinsed with filtered sea water (< 0.7 µm) and then frozen. Clams were collected from mean tide line < 25 cm deep while mussels were collected from rockweed (*Fucus gardneri*) in the intertidal zone. Herring muscle tissue was collected from beached fish, which were then filleted, rinsed with filtered sea water and frozen. Herring roe attached to eel grass in the subtidal zone was removed and placed on 118 µm sieve and rinsed with filtered sea water.

All samples were stored frozen in the field until transported to the lab where they were stored at -80ºC until analysis.

Particulate Carbon and Nitrogen Analyses

Samples for particulate organic C and N were collected on filters (13mm Gelman filters, precombusted at 600 ºC for 4 hrs) using gentle vacuum filtration then frozen prior to analysis on a Perkin-Elmer 2400 CHNS analyzer. Filters were dried for 24 hrs at 60 ºC, then acidified by placing samples in a desiccator with 8N HCl for 24 hrs, and subsequently dried for another 24 hrs. Dried, acidified samples were weighed (accuracy to 0.01 mg), packed in tin capsules, and run. Calibration curves were prepared prior to starting a batch of samples, and an acetanilide standard (C 71.09%, N 10.36%) was run after every 10 samples to monitor machine drift ($StdDev_C$ <1.5%, $StdDev_N$ <0.25).

Pigment Analysis using High Performance Liquid Chromatography (HPLC)

HPLC was performed using protocol outlined by Pinckney et al. 1998, except that pigments were extracted using 90% Acetone (500µl) at -20 °C for 18-20 h. Prior to solvent extraction, filters were lyophilized (-50 °C, 0.57 mbar, 12h; Labconco FreeZone 2.5). Synthetic carotenoid β-apo-8'-carotenal was added (Sigma, cat. No. 10810; 50 µl) as an internal standard. After extraction the sample was filtered through a 0.45 µl PTFE filter (Gelman Acrodisc) to remove particulates. Prior to analysis, an ion-pairing solution (1.00 M ammonium acetate) was added to the sample vial in a ratio of 4 parts extract to 1 part ammonium acetate. Two different reverse-phase HPLC C_{18} columns were connected in series. A single monomeric guard column (Rainin Microsorb, 0.46 x 1.5 cm, 3 µm packing) was followed by a momomeric reverse-phase C_{18} column (Varian Microsorb-MV 100 – 3, 0.46x10 cm, 3 µm packing) and a polymeric reverse-phase C_{18} column (Vydac 201TP54, 0.46 x 25cm, 5 µm packing).

Photopigment peaks were quantified at 440 nm (Jeffrey et al. 1997) and identified based on retention time and spectral matches with pigment spectra obtained from liquid standards (DHI, Hørsholm, Denmark). Peak areas were quantified using Shimadzu Client/Server 7.2.1 SP1 software. A total of 17 pigments were identified in each sample: chl c_3, chl c_1 and c_2, peridinin, fucoxanthin, 19'-hexanoloxyfucoxanthin, neoxanthin, violaxanthin, diadinoxanthin, alloxanthin, diatoxanthin, lutein, zeaxanthin, chl *b*, β,β-carotene, prasinoxanthin, and chl *a*. Because chl c_1

and c_2, cannot be separated with our HPLC method, the two pigments were counted together as one pigment in our analysis.

Dissolved Nutrients

Filtrate from pigment analysis samples was used to rinse the filter tower twice prior to collection of samples for nutrient analysis. Filtrate was collected in acid-washed 60 ml Nalgene bottles and frozen. Dissolved inorganic nutrients (SiO_3, NH_4^+, NO_3^-, NO_2^-, and PO_4^{3-}) were analyzed by the Geochemical and Environmental Research Group at Texas A&M University, College Station. Dissolved inorganic nitrogen (DIN) concentrations were calculated as the sum of NH_4^+, NO_3^-, and NO_2^-.

Stable Isotopes

All faunal and size fractioned POM samples were dried at 60 ºC, coarsely ground and split. Half of each sample was ground to a fine powder using a mortar and pestle for $\delta^{15}N$ analysis. The other half of the sample was processed using a Dionex accelerated solvent extractor (ASE) to remove lipids (Barrow et al. 2008) then acidified in 8N HCl fumes for >7 days to remove calcium carbonate (Armitage and Fourqurean 2009). Acidified samples were dried again at 60 ºC, then weighed and packaged into tin boats with the optimal N load of 50 µg. Samples were analyzed at the University of California (Davis) Stable Isotope Facility.

Statistics

Community compositional changes were evaluated using pigment data obtained from HPLC analyses. Pigment data were divided by chl *a* from the same station (standardization to maximum) and then divided by the sum of all accessory pigments from the same station (standardize to total); the resultant values are equal to the fraction of each accessory pigment in relation to chl *a* (Dorado et al. 2012). Using PRIMER 6 and PERMANOVA + software (Clarke and Gorley 2006) a resemblance matrix of normalized pigment concentrations was calculated using the Euclidian distances index. Visualization of the differences between samples was achieved using principal coordinates analysis (PCO; Anderson et al. 2008). Determination of the primary accessory pigments responsible for the observed variation was achieved using vector overlays of pigment variables. Only vectors who's length is greater than 0.6 (Spearman

correlation) were included; the length and direction of the vectors is representative of strength and sign of the relationship between that pigment and the PCO axes. Mean values of the 5 pigments (alloxanthin, zeaxanthin, chl *b*, fucoxanthin, and chl c_1 and c_2) showing significant correlation for each bay for each month were calculated; differences of the values from the "global" mean (average of all pigment values for all samples) were also calculated in order to explore the quantitative and qualitative differences on a spatial and temporal basis. PERMANOVA (Type III, permutation of residuals under a reduced model, 999 permutations) analyses were run using (Bray –Curtis resemblance calculation) to determine statistical spatial and temporal differences in the overall community composition by bay and across months. Subsequent pairwise PERMANOVA tests (Type III, permutation of residuals under a reduced model, 999 number of permutations) using a priori groups of "Bays" and "Months" were performed to understand the temporal and spatial variations which were similar/different.

In situ environmental data were transformed by log (x+1). These data were analyzed using Euclidian Distances. A sub set of the data where all pigment and environmental factors were measured for all bays and all months (June, July, and August 2008) were selected in order to evaluate the drivers in the community composition. Non-metric Multi-Dimensional scaling (NMDS; stress = 0.06; Clarke 1993) was used to visualize the separation in the phytoplankton community (using normalized pigment concentrations – Euclidean distance resemblance matrix); the resultant pattern for the subset of the data is similar to that observed for the overall data set. Normalized environmental parameters were overlain as vectors (Spearman correlation ≥ 0.5).

SPSS (version 16.0) was used to perform standard statistical analyses. Export and stable isotopes data were analyzed for normality using the Kolmogorov-Smirnov statistic; none were normally distributed (alpha < 0.05). Kruskal-Wallis H tests were performed throughout. If data were significantly different then Mann-Whitney U tests were performed on variables (consecutive months for export, size classes or station for stable isotopes) to determine statistical similarities (using a Bonferroni correction, alpha=0.017) to minimize Type 1 error.

Results

Phytoplankton Variability

The primary determinant of community variability within this data set was "month" (Pseudo-F = 20.118, p=0.001; Fig. 2) and separates along the primary axis of the PCO (53.9% of the

variability). “Bay” was also significant (Pseudo-F = 5.0422, p = 0.001) as was the interaction between the two parameters (Pseudo-F = 2.1826, p=0.004) (Fig. 2). The five most significant (PCO, spearman correlation ≥0.6) pigments in driving these separations are alloxanthin, zeaxanthin, chl *b*, fucoxanthin, and chl c_1 and c_2. These pigments have been used as biomarkers or proxies for phytoplankton taxonomic groups (Table 1). Alloxanthin is used for cryptophytes, zeaxanthin for cyanobacteria, chl *b* for chlorophytes and prasinophytes, and fucoxanthin for diatoms (see Jeffrey et al. 1997; Aiken et al. 2009, Dorado et al. 2012). The only pigments that have not been previously used in this capacity are the chl c_1 and c_2 pigments, because chl *c* is present in all chromophytic algae (Falkowski and Raven 2007). In this study, this pigment set will be used as indicative of dinoflagellate biomass. The rationale is that the only group that does not have both chl c_1 and c_2 as well as fucoxanthin are the dinoflagellates and cryptophytes. The cryptophytes in this case are already indicated by alloxanthin which does not vary on the same axis as chl c_1 and c_2 (see Fig. 2). Further, fucoxanthin does not co-vary with chl c_1 and c_2, the only way for this to occur is if the primary contributor of that pigment does not also have fucoxanthin, leaving only the dinoflagellates (Table 1). It is important to note that the use of chl c_1 and c_2, as an indicator of dinoflagellate biomass, may not work in all cases and may not represent the entire dinoflagellate community (Zapata et al. 2012), in fact, the fucoxanthin that we state is an indicator of diatom biomass may be from the dinoflagellate community. Using the above 5 indicator pigments, further probing into the differences in community is possible. Individual pigments did not differ significantly between bays. However, significant differences were observed in the overall community composition between months (Table 2).

Closer inspection of these indicator pigments, separated by month and bay, shows variation of component groups of phytoplankton through the summer (Fig. 3), offering insight into the community changes occurring in Simpsons Bay. Elevated concentrations of fucoxanthin and chl c_1 and c_2 relative to other pigments suggested there was a phytoplankton bloom in East and West Bay portions of Simpsons Bay each year. In June, fucoxanthin (biomarker for diatom biomass) was 2x higher than in either July or August except for North bay which had concentrations similar to the values for July and August (Fig. 3). Similarly chl c_1 and c_2 (biomarker for dinoflagellates) were 2x higher in June than in any other month in all bays (only marginally higher in North Bay) (Fig. 3). The other pigment groups which are biomarkers of the smaller size classes of phytoplankton (cryptophytes, cyanobacteria, chlorophytes and

prasinophytes) had concentrations which were at or below average (Fig 3 right column). Microscopic evaluation of the plankton (Supp. Fig. 1) in the region in June showed the heterotrophic dinoflagellate *Noctiluca* sp. dominating samples. In July, all of the trends reversed—dinoflagellates accounted for the minority of the population while cryptophytes, chlorophytes and prasinophytes contributed more to the community composition. August represents the lowest concentration of phytoplankton (lowest pigment concentrations). Diatoms and dinoflagellates were again below average in their contribution to the community composition. Cyanobacteria, Cryptophytes, chlorophytes and prasinophytes were all very close to the global mean (the mean of all measurements of that particular pigment made during this study), indicating an equilibration of the community composition. The data presented reveals a clear bloom of *Noctiluca* sp. each June, followed by a "bust" in July and then return to a mixed assemblage in the phytoplankton community in August.

Nutrient concentrations of ≤ 1 μmol l^{-1} DIN and ≤ 0.2 μmol l^{-1} P_i are indicative of oligotrophic waters while nutrient ratios of DIN:P_i < 10 and DIN: P_i > 30 can be used to indicate N versus P_i limitation, respectively (Dortch and Whitledge 1992; Sylvan et al. 2006; Quigg et al. 2011). For the period of this study, DIN was generally < 5 μmol l^{-1} (DIN mean 2.23 = μmol l^{-1}; range 0.12-8.97 μmol l^{-1}) in surface waters, with occasional values up to 9 μmol l^{-1}. P_i was more variable but remained < 1.1 μmol l^{-1} at nearly all the stations (mean = 0.39 μmol l^{-1}; range 0 to 1.1 μmol l^{-1}. The combination of low DIN and relatively high P_i resulted in the low DIN:P_i ratios (mean = 7.63 μmol l^{-1}; range 0.36 to 49.95 μmol l^{-1}), suggesting N limitation of the phytoplankton community in this system each year, particularly in June.

Of the environmental parameters measured all months from all depths, the only significant (NMDS, Spearman correlation ≥ 0.5) correlates were POC, PON, PN, urea, NO_2, PO_4, and SiO_3 (Fig. 4). There was a reduction in dissolved SiO_3 in June, likely due to the increased abundance of diatoms (2x greater than in either July or August) utilizing this nutrient. POC and PON were positively correlated with June (green groups Fig 4); this increase is indicative of the increase in plankton biomass concurrent with a change in community composition consisting of more dinoflagellates. As the study area is primarily nitrogen limited, the positive correlation between urea and June is suggestive of an organic source of nitrogen driving the increase in phytoplankton biomass.

Water column (0-10m)

The highest POC and PON concentrations where measured in June each year, corresponding to the *Noctiluca* sp. bloom (Fig. 4, 5a). The increase in POC did not directly correlate with autotrophic biomass (chl *a*, Fig. 5b). Chl *a*:POC ratios increased through each summer due to the decrease in POC concentrations (Fig. 5b). The low chl *a*:POC ratios each June were consistent with a heterotrophic bloom. Therefore, the effect of the bloom on the phytoplankton community is clearer when parameters are compared directly with POC (Fig. 5). The increase in water column POC and PON was not equal as demonstrated by the slope < 1 in Fig. 5a; there was a greater increase in POC than PON. POC:PON demonstrate the qualitative changes in the particulate matter through the summer. June and July were not significantly different. POC:PON in August was significantly different from June but not July, demonstrating a slow decline in the C content of the particulate material. The Shannon Diversity Index decreased with increasing POC (Fig. 5c). Samples collected with the highest POC concentrations also represented those with the lowest diversity. As the summer progressed POC decreased and diversity increased.

Export from surface waters (0-10m) to sediment traps (20-40m)

Sediment traps were deployed in June to August in 2008were the most descriptive of the monthly variability of C and N export. Exported POC_{Trap} in June was significantly greater ($p<0.001$), nearly 2-4 times, than in either July or August (Table 3). Exported PON_{Trap} was also greater in June than July or August, though not significantly (Table 3). These trends paralleled those observed in the water column described above. Qualitatively POC_{WC}:PON_{WC} (ratio of POC:PON measured in the water column at 0 and 10m) measured immediately prior to deploying sediment traps was 13.97 compared to 13.88 POC_{Trap}:PON_{Trap} (median ratio measured in traps at 20 m and 40 m) in June (Table 3). In July the ratio did not change significantly in the water column or in the export. However, in August the POC_{WC}:PON_{WC} decreased to 8.99. POC_{Trap}:PON_{Trap} also decreased but not at the same magnitude. Though none of these changes are significant the rank (Mann-Whitney U test) is informative of the qualitative changes that occur between the water column and trap through the summer. In June the POC_{WC}:PON_{WC} > POC_{Trap}:PON_{Trap} (Rank 13.08 to 10.75 respectively). This relationship continued through July (20.38 to 19.05) but switched in August (6.78 to 8.80) suggesting there was elevated N recycling in the water column or excess C exported.

Food Web

Natural abundance stable isotope values for POM collected in July 2010 were not significantly different spatially (δ^{13} p = 0.496, n = 10; δ^{15}N p = 0.169, n = 10) or by size fraction (δ^{13} p = 0.602, n = 10; δ^{15}N p = 0.602, n = 10) (median = MD δ^{13}C = -19.58 ‰; MD δ^{15}N = 7.83 ‰) (Fig. 6; Table 4). The isotopic signature of herring (δ^{13}C -17.53 ‰, δ^{15}N 13.55 ‰) was approximately two trophic levels above that of the POM (difference is 2.06 ‰ δ^{13}C and 5.79 ‰ δ^{15}N) (Fig. 6). Values for *Noctiluca* sp. were δ^{13}C -17.70 ‰ and δ^{15}N 5.74 ‰, demonstrating a shift of inputs to the food web (higher δ^{13}C and lower δ^{15}N than the POM collected prior to the spawn/bloom; Fig. 6). Mussels and clams collected after the *Noctiluca* sp. bloom have C values (δ^{13}C -17.73 ‰) similar to those of *Noctiluca* sp., and enriched N values (δ^{15}N 8.29 ‰) common to the trophic difference.

Discussion

Heterotrophic dinoflagellates are an integral part of marine food webs (Hansen 1991, Sherr and Sherr 2002, Jeong et al. 2010). Often they are found in bloom concentrations following blooms of other phototrophic phytoplankton (Sherr and Sherr 2007), however, they have been shown to feed on a variety of prey and prey sizes (Hansen 1991, Sherr and Sherr 2002, Jeong et al. 2010). A bloom of the athecate, heterotrophic dinoflagellate *Noctiluca* sp. occurred in June of 2008-2010 in the East and West Bay portions of Simpson Bay, PWS, in response to an organic nitrogen increase. A dominance of dinoflagellates is recorded in June of each year, microscopic evaluation of plankton samples show *Noctiluca* sp. vastly out numbering other identifiable phytoplankton (Supp Fig. 1). This dominance of dinoflagellates is also represented in the pigment data (Fig. 2). Further the highest measured POC and PON concentrations were measured in June (Fig. 4) corresponding to the time of the largest concentrations of accessory pigments (Fig. 3) suggesting a large bloom. However, there is no corresponding increase in chl *a* (Fig. 5b). The lack of a peak in chl *a* during the June bloom (Fig. 5b) is consistent with heterotrophic dinoflagellate bloom rather than an autotrophic algal bloom like those typically observed early in April in this region (Eslinger et al. 2001). The disconnect between the chl *a* and POC in our study points to a dominance of a phytoplankton with either low chl *a* concentrations, or a species which is facultatively heterotrophic, such as the dinoflagellate

353 *Noctiluca* sp., which can use other dissolved/particulate organics for nutrition. By utilizing
354 multiple approaches to elucidate the dynamics of the phytoplankton community we were able to
355 clearly discern a consistent June phytoplankton bloom that has historically been unidentified.
356 The mechanism controlling this bloom differs from the spring bloom described by Eslinger et al.
357 (2001). Where the duration, intensity and transfer of the spring bloom rely on the frequency of
358 storms, this summer bloom is driven by an allochtnonous source of nutrients. It may be possible
359 that the Dinoflagellate bloom is a successional change from the spring bloom (dinoflagellates
360 follow diatoms, Tiselius and Kuylenstierna 1996) however the three years that were studied had
361 spring and summer wind speeds at or below the three year's previous (Supp. Fig. 2). Thus the
362 spring bloom in the years of this study would have been shorter in duration than the previous 3
363 years and likely not windier than "normal" and the succession would have occurred May or early
364 July at the latest.
365 The June bloom of *Noctiluca* sp. dissipates by July and is replaced by smaller
366 phytoplankton (cyanobacteria, cryptophytes, chlorophytes and prasinophytes) better able to cope
367 with lower concentrations of nutrients. The biomass of cyanobacteria, cryptophytes,
368 chlorophytes and prasinophytes remains above the average for this region during the summer
369 months but is less than the biomass observed in June. Pigment concentrations are lowest in
370 August, but hover around the mean. This may be indicative of a normalization of the
371 phytoplankton community biomass and composition. The pattern in biomass in Simpsons Bay is
372 indicative of a bloom followed by a shift in community composition and returning to equilibrium
373 in August. This pattern is also indicative of a pulse of nutrients to the system (boom, bust, then
374 return to equilibrium). Pulse responses are greatest for the trophic level directly supplied the
375 nutrient and may be missed in upper trophic levels (Chaloner 2007; Anderson et al. 2008; Yang
376 et al. 2008; Weber and Brown 2013), demonstrating the importance of understanding the
377 phytoplankton community dynamics in this region. Further, the group that responded, the
378 dinoflagellates, is one of the highest in nutritional quality to their consumers (Clocern and
379 Dufford 2005). This shift to larger plankton likely triggers a response in larger consumers,
380 reducing trophic transfers (and therefore losses of energy) to fishes and other consumers.
381 The impacts of this annual bloom in June are reflected in the export of particulate organic
382 matter from the surface, particularly in June 2008. Two-to-three times more POC was measured
383 in the sediment traps (20 m and 40 m) in June than either July or August (Table 3). Most of the

carbon exported in June was organic and likely from the bloom observed during this period. Qualitatively, the POC:PON ratios measured in the water column and in the sediment traps decreased through the summer. POC:PON ratios measured in water column (WC) relative to those measured in the traps (Trap) for June were nearly equal, indicating rapid export. Measured export was lowest in July; also, both WC and Trap ratios decreased indicating relatively less C export or increased N export. Notably, in August the ratio of POC:PON in the water column versus trap switched with a higher ratio measured in the trap, indicating a relative decrease in the amount of N reaching the traps and a relative increase in the water column, pointing to a recycling of N in the system. Thus, the nutrients in the system during the *Noctiluca* sp. bloom may still be an important source of nutrients for the food web of Simpson Bay for as long as two months.

In addition, stable isotopes of particulate organic matter, and faunal samples collected in this system showed that the bloom was accompanied by shifts in the sources of carbon and the composition of the phytoplankton community (Fig. 6). This shift from -19.59 ‰ (POM) to -17.70 ‰ (*Noctiluca* sp.) is indicative of a shift to more marine source of carbon (Fry 2006). Correspondingly, the shift in $\delta^{15}N$ from 7.76 ‰ to 5.74 ‰ suggests there was also a change to a marine source of nitrogen. Similar decreases in $\delta^{15}N$ values have been documented between neritic and oceanic POM (Dorado et al. 2012). The shift to a lower trophic level (depleted $\delta^{15}N$ values in *Noctiluca* sp.) is particularly interesting as *Noctiluca* sp. are known facultative heterotrophs and they appear at a lower trophic status than the POM. This may be indicative of the *Noctiluca* sp. feeding on heterotrophic bacterial biomass.

Ecosystems that receive natural resource subsidies often exhibit elevated biomass (Polis 1997); these resource pulses have legacy effects which can persist from months to years after the initial pulse (Yang et al. 2008). Thus, resource pulses may be an important contributing factor to sustained abundance and diversity of this ecosystem. Traditionally, allochthonous nutrient subsidies were thought to travel unidirectionally from upstream rivers to marine environments (Leroux and Loreau 2008) via runoff and/or fluvial systems. However, many studies have shown allochthonous subsides in the reverse direction - from open ocean to coastal systems (Helfield and Naiman 2001; Varpe et al. 2005; Leroux and Loreau 2008; Petticrew et al. 2011). The effect of these pulses relates to the amount of nutrient input relative to the area, and the permeability of the ecosystem subsidized (Polis et al. 1997). For example, many salmon in small streams have a

large effect that spreads into the riparian forests that surround these streams (Helfield and Naiman 2001; Chaloner et al. 2002; Hicks et al. 2005; Chaloner et al. 2007). Additionally, ecosystems with large areas, with less defined boundaries, have also been shown to benefit from seemingly small pulsed subsidies (eg. coral reef spawn Wild et al. 2008; Eyre et al. 2008; Guld et al. 2008).

Many resource subsidies have been identified in the PWS system. In particular, spawning salmon contribute to stream, river, and surrounding forest ecosystem productivity (Bilby et al. 1996; Wipfli et al. 1998; Hicks et al. 2005; Reisinger et al. 2013) as well as the Pacific herring. In addition, many vertebrate species, including the resident sea otter population in Simpson Bay (Lee et al. 2009) have been documented utilizing this ephemeral resource. More than 30 bird species have also been documented as predators of spawning herring and herring eggs (Roper et al. 1999; Willson and Womble 2006). Consumers which are capable of rapid growth and are the direct beneficiaries of the pulse-supplied nutrients will show the most rapid and the greatest numerical response, whereas those with slower growth rates and more trophic steps away from the level of the pulse will show smaller changes with increased time lag (Chaloner 2007; Anderson et al. 2008; Yang et al. 2008; Weber and Brown 2013), making identification and quantification of pulse impacts difficult. While many studies have been conducted on the ecosystem of this region, a paucity of literature is available on phytoplankton community and dynamics, which may be the immediate beneficiaries of many of these subsidies, and show the largest and most rapid responses (Yang et al. 2010).

We have described a bloom of dinoflagellates occurring regularly in June which is likely resultant from a pulse of marine derived nutrients (coinciding with other observations of fauna consuming of herring roe). Previous studies have shown these pulses to be important to higher trophic organisms in other ecosystems (Roper et al. 1999; Willson and Womble 2006). Schools of adult Pacific herring migrate into PWS in mid-spring (Norcross et al. 2001) and spawn in large aggregations along the coast. A spawning event generally lasts 5-21 days, and the eggs hatch 22-24 days later (Norcross et al. 2001). In 2007, an aggregation of sea otters in Simpson Bay was observed consuming herring roe on kelp between 11 June – 3 July (Lee et al. 2009), confirming an additional, apparently small, summer spawning event in the study area (as eggs hatch within 1.5-3 weeks (Wilson and Womble 2006). While the summer spawn of herring is smaller than the spring event, it may still contribute substantial amounts of nutrients to the bays

where it occurs (including Simpson Bay), as was observed in the current study. The pulse of nutrients alleviates the nitrogen limitation of primary productivity typically observed in fjords in PWS in the summer (Eslinger et al. 2001; Quigg et al. 2013). This study demonstrates that resource pulses can stimulate the system at trophic levels above and below the level of input. Further research is required to explicitly define the source and quantify the energy and nutrient input to Simpson Bay and PWS. These previously overlooked blooms (likely the result marine derived nutrient pulses) may be an important contributing factor to the sustained abundance of this ecosystem.

Acknowledgements

The authors would like to thank Kathryn Wheatly, Ryan Wolt, Ian Davis, Michelle Cortez, Olivia Lee, and Sylvia Osterrider for their extensive help in the field. Funding for this project was provided by various grants from the National Oceanic and Atmospheric Administration. Generous travel grants from Erma and Luke Mooney, Marine Biology Department at Texas A&M University at Galveston, and the Oceanography Department at Texas A&M University provided funds for travel to and from the field site. Allison McInnes was supported during the final writing stages by a Texas A&M University Dissertation Fellowship. The authors would also like to thank two anonymous reviewers for their thorough critique, improving the final version of this manuscript.

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Table 1 Phytoplankton groups depicted by size and accessory pigments compiled from Jeffrey et al. 1997. Bold pigments are marker pigments for different groups, underlined pigments have been used as marker pigments for that group in the past (Aiken et al. 2009, Dorado et al. 2012).

Group	Size	Pigments	Size Class
Bacillariophyta	2-200 µm up to 4 mm	chlorophyll *a*, c_2, β,β-carotene, <u>fucoxanthin</u>, diatoxanthin, diadinoxanthin, chlorophyll c_1 or c_3	Nano-Micro
Dinophyta	2-200 µm up to 2 mm	chlorophyll *a*, c_2, β,β-carotene, **peridinin**, **dinoxanthin**, diadinoxanthin, peridinin	Nano-Micro
Prymnesiophyceae	5-20 µm	chlorophyll *a*, c_1 or c_2, phytylated chlorophyll c-like pigment, β,β-carotene, 19'-butanoyloxyfucoxanthin and/or 19'-hexanoyloxyfucoxanthin, and diadinoxanthin and diatoxanthin	Nano
Chrysophyceae	2-3 µm coccoid, 10-100 µm silicoflagellates	chlorophyll *a*, c_1, c_2, fucoxanthin, 19'-butanoyloxyfucoxanthin and diadinoxanthin, violaxanthin	Nano-Micro
Cryptophyta	6-20 µm	Chlorophyll *a* and *b*, β,ε-carotene, **alloxanthin**, monadoxanthin	Nano
Raphidophyceae	30-100 µm	chlorophyll *a*, c_1, c_2, fucoxanthin, β,β-carotene, violaxanthin	Micro
Chlorophyceae *Prasinophyceae*	1-40 µm	Chlorophyll *a* and *b*, β,ε- and/or β,β-carotene, **lutein**, violaxanthin, zeaxanthin, neoxanthin (prasinophytes = **prasinoxanthin**)	Pico-Micro
Euglenophyta	15-50 µm	Chlorophyll *a* and *b*, β,β-carotene, diadinoxanthin, zeaxanthin, neoxanthin	Nano-Meso
Cyanophyta	1 µm to 2 mm colonies	chlorophyll *a*, β,β-carotene, <u>zeaxanthin</u>, **allophycocyanin-B, C-phycoerythrin, R-phycoerythrin, phycoerythrocyanin**	Pico
Prochlorophyta	0.5 µm, <1 mm (filaments), 10-25 µm (endosymbionts)	**divinyl chlorophyll *a*, divinyl chlorophyll *b***, MgDVP, β,ε-carotene, zeaxanthin (unicells)	Pico

Table 2 Results of PERMANOVA showing temporal and spatial differences in normalized pigment concentrations (Wisconsin double standardization) measured in Simpson's Bay 2008-2010. P-F is the pseudo-F statistic, p is the p-value, perm is the number of unique values of the test statistic calculated for each combination. Bold values indicate significant differences between factors.

	P-F	p	perm	P-F	p	perm	P-F	p	perm
	North			West			East		
Jun vs Jul	1.9718	**0.008**	999	5.7099	**0.001**	999	6.5049	**0.001**	999
Jul vs Aug	0.806	0.614	997	1.3511	0.101	998	2.941	**0.001**	998
Jun vs Aug	1.3505	0.124	999	4.139	**0.001**	998	2.7732	**0.001**	999
	June			July			Aug		
N vs W	2.645	**0.001**	998	1.1065	0.305	998	1.0919	0.359	998
N vs E	3.091	**0.001**	999	1.2817	0.182	998	1.4126	0.099	998
W vs E	2.176	**0.016**	998	0.3695	0.946	999	1.4758	0.084	999

Table 3 Median (MD) water column and export values for POC and PON measured throughout the three summers with standard deviation in parenthesis. Numbers in parenthesis are number of samples contributing to median value and were used for Mann-Whitney U tests. Bold values are significant with a Bonferroni correction of alpha 0.017. Sediment trap values are from 2008 only. Water column POC and PON values are median values from 0 and 10 m for both the East and West arms of Simpson Bay. Export values are median values from traps at 20 m and 40 m.

	June			**July**			**August**		
2008	MD	p	U	MD	p	U	MD	p	U
water column (µmol l^{-1})									
POC	57.89 (16.24)	**0.000**	0.0	15.11 (4.35)	**0.001**	11.0	28.14 (8.55)	**0.003**	4.0
PON	3.33 (1.70)	**0.000**	18.0	0.80 (0.91)	**0.000**	8.0	3.15 (1.46)	0.512	29.0
POC:PON	13.97 (6.69)	0.670	103.5	13.99 (7.78)	0.025	22.0	8.99 (1.76)	**0.001**	0.0
export (mg m^{-2} d^{-1})									
POC	5.18 (2.41)	**0.011**	9.0	2.47 (1.18)	0.025	12.0	1.46 (0.74)	**0.004**	0.0
PON	0.50 (0.19)	0.039	14.0	0.18 (0.13)	0.241	23.5	0.14 (0.10)	**0.016**	3.0
POC:PON	13.88 (4.24)	0.841	31.0	13.41 (7.67)	0.391	20.0	11.66 (2.36)	0.170	7.5

Table 4 Natural abundance C and N stable isotope values for key organisms in the Simpson Bay system measured during this study and compared with previously measured values. Values are averages where more than one sample was collected and the values in parentheses are the range. * indicates values reported for *Neocalanus* spp. (primary consumer) similar trophic relationship to the *Noctiluca* sp. reported in this study. Genera of filter feeders examined by Powers et al. (2005) were *Mytilus trossulus* and *Mya arenaria*. † indicates estimated value for Pacific herring consuming only prey from PWS and bays – measured values show usage of Gulf of Alaska food sources as well and range from -20.5 to -18.5.

POM		Noctiluca		Herring/Roe		Muscles/Clams		Reference
C	N	C	N	C	N	C	N	
-19.59 (0.90)	7.76 (2.05)	-17.70	5.74	17.64 (0.21)	13.61 (0.12)	-17.73 (0.01)	8.29 (0.56)	This study
-19 to -24	4 to 8							Fry 2006
		-17.2 to -17.5 GOA* -18.5 to -19.8 PWS*	8.4 to 9.5 GOA* 9.5 to 8.8 PWS*					Kline Jr. 2009
		-20.8*	8.4*	-22.6 (±0.67)	12.7 (±0.24)			Kline Jr. 1999
				-19 to -17†				Kline Jr. and Campbell, 2010
				-17.5	13.5			Hobson et al. 1994
						-16.85, -16.94	9.43, 9.59	Powers et al. 2005

List of Figures

Fig. 1. Map of study area with station locations. Insert of location within Prince William Sound and the state of Alaska. Locations of all sampling stations throughout the three summers are shown by numbers 1-9. Sub-bay divisions determined by watershed to basin surface area ratio are also marked on the map.

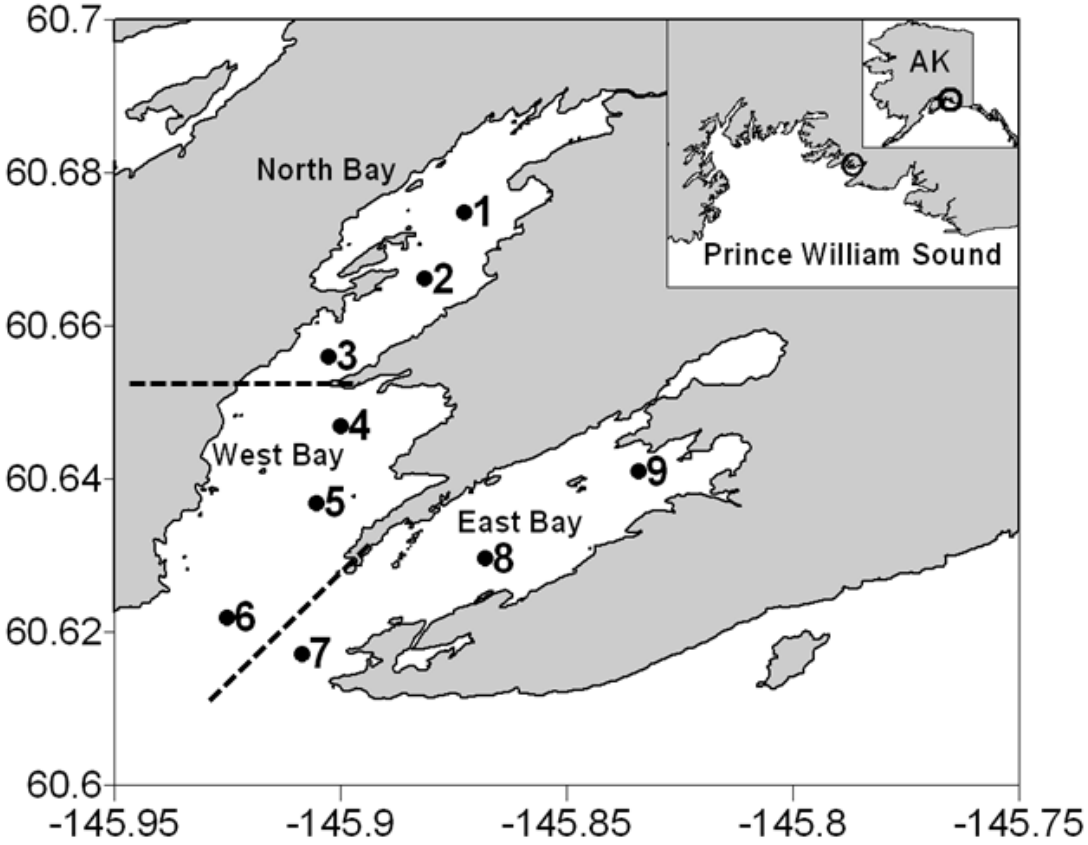
Fig. 2. Ordination of principal coordinates analysis (PCO) of standardized (wisconsin double standardization) pigment data, demonstrating 81% of the variability in the pigment data. Bray Curtis similarity, with overlay of significant pigment concentrations (Spearman correlation =>0.65). Shades of yellow and green represent June samples, orange and red hues represent July, blue symbols represent August. Shapes represent the different bays North Bay (triangles), West Bay (squares), East Bay (circles).

Figure 3: Mean diagnostic pigment (alloxanthin, zeaxanthin, chl *b*, fucoxanthin, and chl c_1 and c_2) concentrations (left column) for June (green), July (red), August (blue) separated by bays (different hues: lightest = North Bay, middle = West Bay, darkest = East Bay); whiskers represent the 95% confidence interval. Mean difference from the summer mean of each of the diagnostic pigments (right column).

Fig. 4. Non-metric multi-dimensional scaling ordination of standardized pigment values using Euclidian distance based resemblance matrix. Symbols are the same as Figure 2. Vector overlay of significant (Spearman Correlation ≥0.5) environmental variables.

Fig. 5. Community indicators measured in surface (0 and 10m) waters during the summers of 2008-2010. The POC:PON ratio (a) decreased through the summer The POC:chl *a* ratio (b) also decreased through the summer, indicating a switch from a more heterotrophic community to a more autotrophic community. The Shannon diversity index versus POC (c) reveals lowest diversity indices correspond to the highest POC concentrations, capturing the bloom of *Noctiluca* sp. observed during the summer in PWS. Open symbols represent surface samples (0 m), closed symbols represent samples collected at 10 m; diamonds = June, triangles = July, circles = August.

Fig. 6. Property property plot of natural abundance stable isotopes collected during this study combined with values from Kline Jr. (1999) for Amphipods, Decapods, Euphausiids, *E. elongata*, and *Neocalanus* spp..


60.7
60.68
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-145.95
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-145.8
-145.75
North Bay
West Bay
East Bay
Prince William Sound
AK
1
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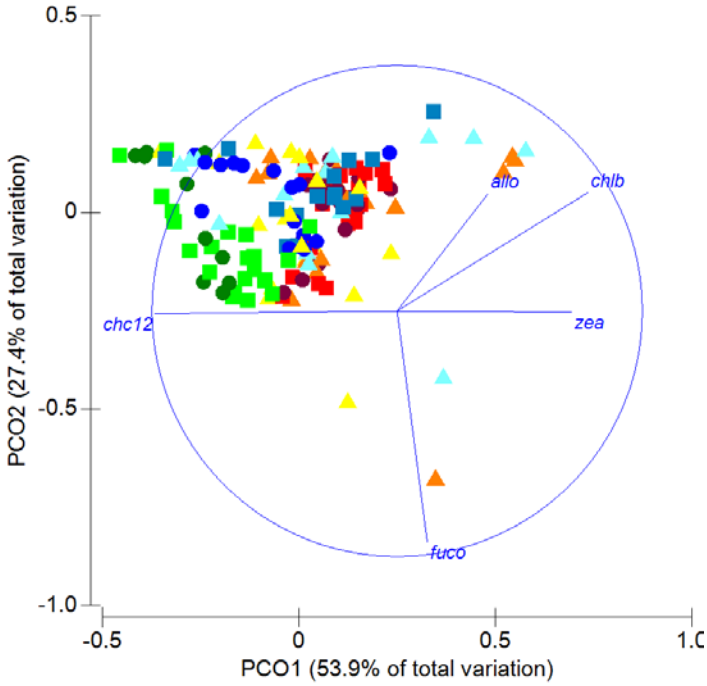
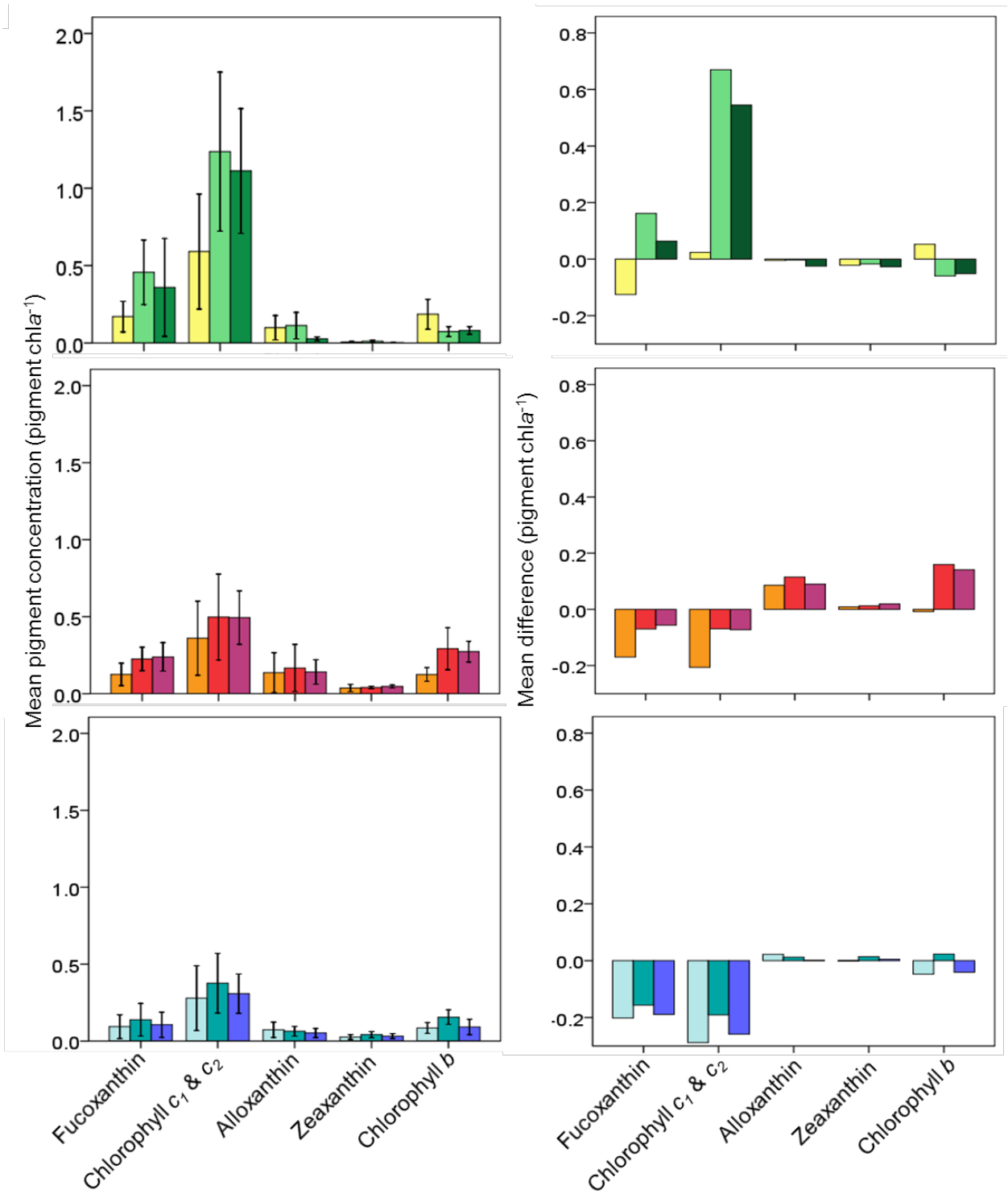
681

682

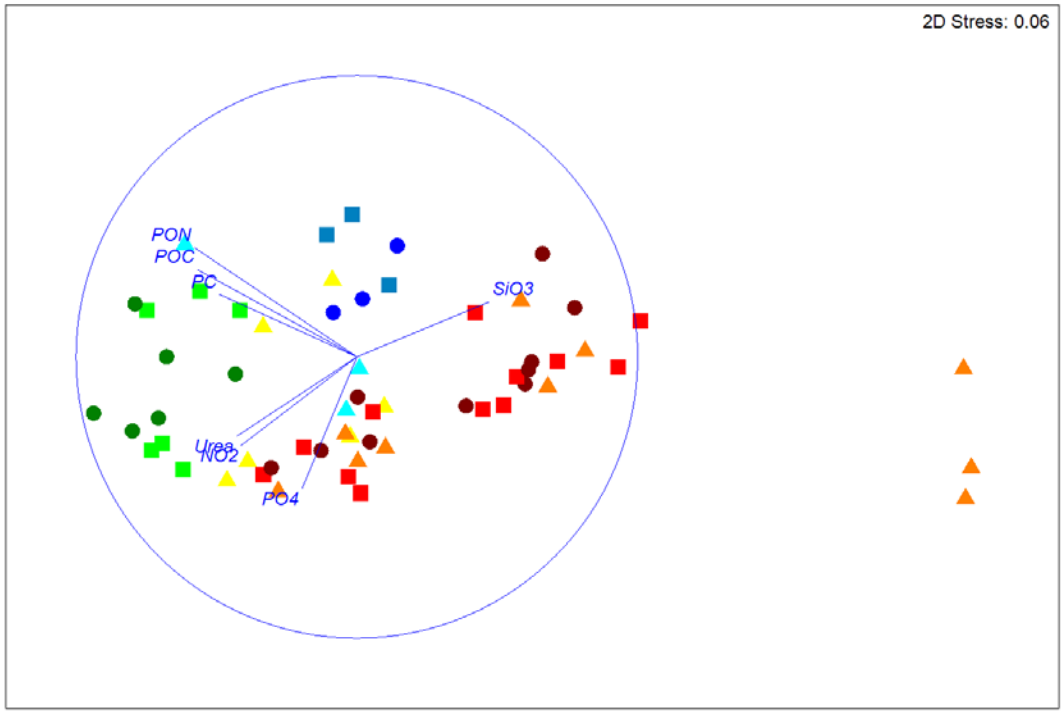

0.5
0
-0.5
-1.0
PCO2 (27.4% of total variation)
-0.5
0
0.5
1.0
PCO1 (53.9% of total variation)
allo
chlb
chc12
zea
fuco

683


Mean pigment concentration (pigment chla-1)
Mean difference (pigment chla-1)
2.0
1.5
1.0
0.5
0.0
0.8
0.6
0.4
0.2
0.0
-0.2
Fucoxanthin
Chlorophyll c1 & c2
Alloxanthin
Zeaxanthin
Chlorophyll b

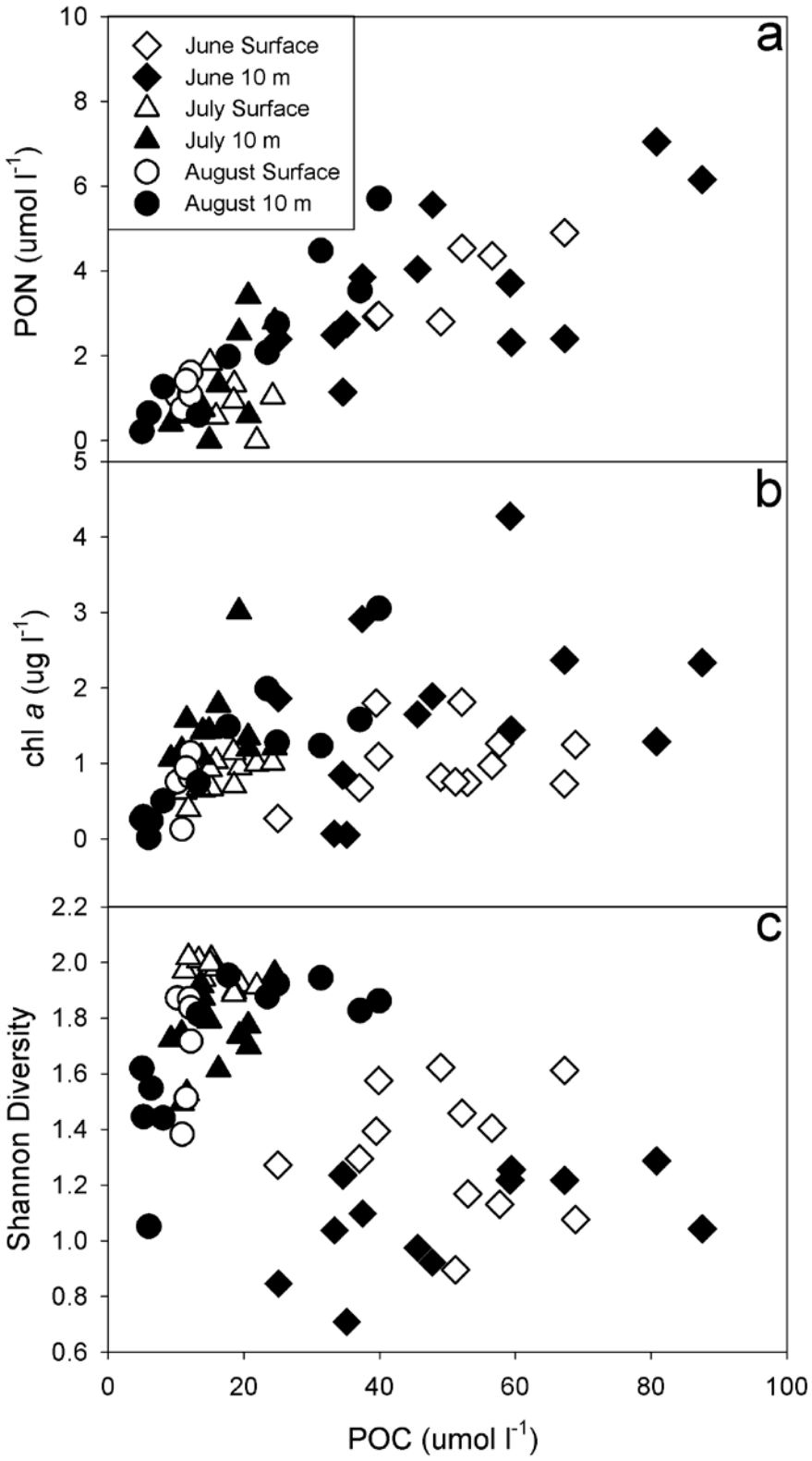
684

685



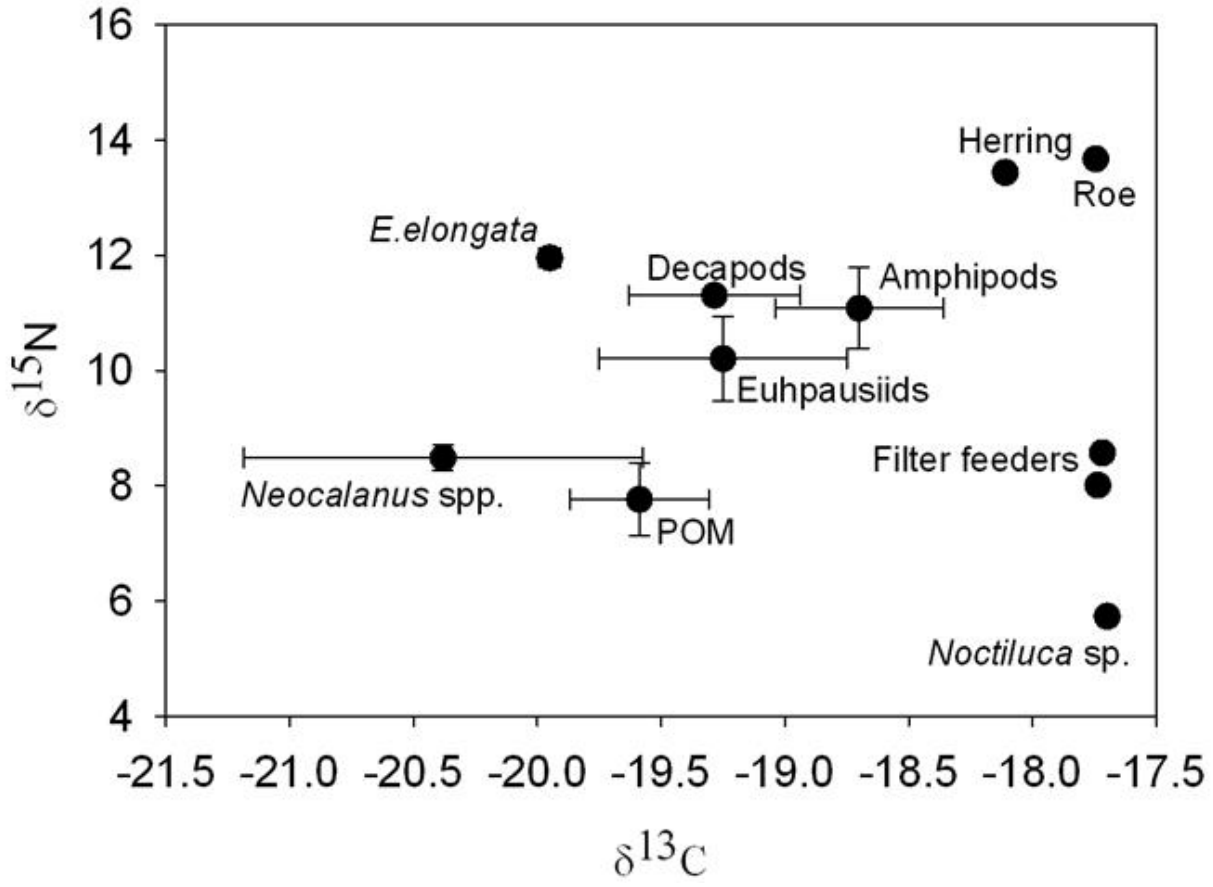
686

687


June Surface
June 10 m
July Surface
July 10 m
August Surface
August 10 m
a
b
c
PON (umol l-1)
chl a (ug l-1)
Shannon Diversity
POC (umol l-1)
0
2
4
6
8
10
0
1
2
3
4
5
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
0
20
40
60
80
100

688

689


16
14
12
10
8
6
4
$\delta^{15}N$
Herring
Roe
E.elongata
Decapods
Amphipods
Euhpausiids
Filter feeders
Neocalanus spp.
POM
Noctiluca sp.
-21.5 -21.0 -20.5 -20.0 -19.5 -19.0 -18.5 -18.0 -17.5
$\delta^{13}C$

690

691