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Concentration and biochemical gradients of seston in Lake Ontario

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ABSTRACT

Spatial variability in resource quantity and quality may have important implications for the distribution and productivity of primary consumers. In Lake Ontario, ecosystem characteristics suggest the potential for significant spatial heterogeneity in seston quantity and quality, particularly due to the potential for nearshore-offshore gradients in allochthonous nutrient supply, and the formation of a deep chlorophyll layer (DCL) in July. We assessed total and zooplankton food particle size-fractionated chlorophyll *a* concentrations, as well as carbon-to-phosphorus stoichiometry and essential fatty acid composition of seston across a distance-from-shore and depth transect. We observed time, sampling depth, and distance from shore to be the best predictors of chlorophyll *a* concentration. Resource quality was much more homogenous in space, but there were strong patterns through time, as both stoichiometric and fatty acid qualities in general were greatest in May, and lowest in July/August. We did observe a peak in essential fatty acid concentration near the DCL in during time of formation, possibly due to differences in phytoplankton community composition between the DCL and epilimnion. These results suggest the potential for a spatially and temporally dynamic resource base for consumers in Lake Ontario, which may be important in developing a broader understanding of variable consumer productivity.

Introduction

Heterogeneity in resource availability and resource quality may have important implications for lake primary consumers (Hunter and Price, 1992). While resource quantity can be an important determinant of consumer biomass, there is also evidence that resource quality may exert a stronger influence on consumer biomass than resource availability (Hessen, 1992; Marcarelli et al., 2011). In particular, the elemental stoichiometry (specifically carbon-to-phosphorus ratio; Sterner and Elser, 2002) and composition or concentration of essential fatty acids (Müller-Navarra, 1995; Brett and Müller-Navarra, 1997) have been demonstrated to act as nutritional constraints, and key regulators of consumer biomass across lakes. Therefore, a heterogeneous landscape of resource quantity or quality may have important implications for consumer growth, possibly creating "hot spots" of high quality nutritional composition (DeMott et al., 2004).

Physical and biological factors may drive heterogeneity in seston (zooplankton food resources) quantity and quality in Lake Ontario. Hydrodynamics allow for differentiation of nearshore and offshore habitats in nutrient concentrations as wind-driven coastal boundary layers separate nearshore water from the open lake (Rao and Schwab, 2007). Nearshore areas may also be differentiated in terms of nutrients due to direct loading and plumes from tributaries (Howell et al., 2012; Makarewicz et al., 2012), and in particular the Niagara River, which has strong influence on lake nutrient conditions (Stevens and Nielson, 1987). These dynamics may create gradients of nutrient concentrations and trophic status as distance from shore is increased and connection to nearshore waters is reduced (Wetzel, 2001), thereby altering seston quantity and quality. Alternatively, dreissenid mussels may remove particulate phosphorus from the water column (Idrisi et al., 2001), potentially having consequences for seston carbon-to-phosphorus stoichiometry. Densities of dreissenids as of 2008 were approximately 700–7000 individuals per m^2, peaking in density at locations 30–90 m in depth, and lowest in locations >90 m (Birkett et al., 2015). Despite lower densities in shallower water compared to deeper sites, it's possible that mussels may have a larger effect on seston quality due to the reduction in water column depth, and a possibility to impact a greater proportion of the water column. Therefore, high densities of dreissenid mussels in Lake Ontario may filter out a significant amount of particles and nutrients nearshore, creating the potential for reduced seston quantity and quality (Hecky et al., 2004; Naddafi et al., 2008; Holeck et al.,

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2015) in nearshore areas compared to deep, offshore areas (Hall et al., 2003).

In addition to the potential for "horizontal", or distance-from-shore gradients in seston quantity and quality in Lake Ontario, there exists a possibility for vertical gradients due to the formation of a deep chlorophyll layer (DCL). Multiple mechanisms that contribute to the formation of a DCL may influence seston quality in that layer including physiological shade adaptation by metalimnetic phytoplankton that to lead to lower carbon-to-chlorophyll ratios (Barbiero and Tuchman, 2004). Alternatively Twiss et al. (2012) identified higher phytoplankton growth rates within the DCL compared to the epilimnion, and therefore the potential for greater phytoplankton availability for consumers within the DCL. The same mechanisms that produce reduced carbon-to-chlorophyll in phytoplankton under reduced light conditions may also improve seston quality. Low light reduces phytoplankton carbon-to-phosphorus (C:P) ratios (Sterner et al., 1997), and increases the concentration of essential fatty acids (EFAs; Thompson et al., 2004). Twiss et al. (2012) also identified a high proportion of DCL phytoplankton in Lake Ontario as Heterokontophyta and Pyrrophyta, which may contain a higher concentration of EFAs compared to other taxa (Arts et al., 2001).

Our study quantifies spatial and temporal variation in Lake Ontario seston quantity and quality. We predict an increase in seston quantity (chlorophyll concentration) and quality (seston carbon-to-phosphorus ratios and EFA concentration) below the thermocline during the formation of a deep chlorophyll layer. We also predict a general pattern of increasing seston quantity and quality with increased distance from shore due to reductions in interaction with dreissenid mussels. Our results quantify variability in seston quantity and quality and can potentially identify habitats that serve as food web "hot spots" with greater potential for zooplankton growth in Lake Ontario.

Methods

Sample collection

Seston concentration (chlorophyll *a*, size-fractionated chlorophyll *a*) and quality (carbon-to-phosphorus ratio, total fatty acids) were measured throughout the water column, from April through October 2013, at sampling sites along a transect extending offshore (distance from shore = 0.5, 3, 5, 8, and 14 km) into Lake Ontario at depth of 5, 20, 50, 100, and 200 m (Fig. 1). Samples for seston quality were collected less frequently than for chlorophyll concentration (five times for C:P from May through September; eight times for fatty acid composition from July through October). Temperature and fluorometer-based chlorophyll *a* profiles from a water profile logger were used to delineate sampling based on thermocline and DCL depths. Water was collected at 2–8 specific depths, depending on station depth, using a pump or Van Dorn sampler. Specific sampling depth varied with thermocline depth but generally included multiple epilimnetic samples (1 m and 3–10 m water depth), multiple metalimnetic samples (12–25 m) and multiple hypolimnetic samples (30–60 m).

Chlorophyll a analysis

Water samples (0.1–0.5 L) for chlorophyll *a* concentration were vacuum filtered through different filter types: Whatman ® 47 mm glass fiber filters (GF/F, pore size 0.7 μm; 934-AH, pore size 1.4 μm) and Sterlitech ® polycarbonate membrane filters (pore sizes 0.2 μm, 2.0 μm and 20 μm). Vacuum pressure did not exceed 10 mmHg and was shut off immediately when filtration was complete. Filters were folded, wrapped in aluminum foil and stored frozen. Within 3 weeks of collection, chlorophyll was extracted by adding a filter and 10 mL of buffered acetone (100 mL saturated $MgCO_3$ solution per 900 mL acetone) to a clean glass vial, ensuring that filters were submerged in the acetone. Vials were sonicated in an ice bath (20 min) then wrapped in foil and stored in a freezer for 16 to 24 h. Following the extraction period, vials were brought to room temperature. Vials were decanted into a disposable glass culture tube and placed into a Turner Designs Trilogy® Laboratory Fluorometer to measure chlorophyll *a* fluorescence in RFU (Raw Fluorescence Units). A solid red blank was run in the fluorometer twice each time samples were run to maintain a record of instrument accuracy. An equation to calculate chlorophyll *a* concentrations (μg L^{-1}) was derived from a measured value of a buffered acetone blank (0.53 RFU) and a measured value for a certified standard (21.3 μg L^{-1} standard measured at 313.05 RFU), where V is the volume of water (mL) filtered during sample processing and F is the measured fluorescence (RFU). $[\text{chlorophyll } a] = (F - 0.53) / 14.672 * 10/V$.

Seston C:P stoichiometry

Samples for C:N:P ratio analysis were filtered onto 0.2 μm filters, scraped and transferred to a glass slide and dried at 60 °C. Dried seston was later scraped and tinned for analysis. For the determination of seston phosphorus content, dried and pre-weighed seston samples were combusted at 450 °C for approximately 2 h before analysis to remove excess organic carbon. Samples were then combined with 30 mL reverse osmosis water, and analyzed colorimetrically following persulfate digestion (Menzel and Corwin, 1965). For seston carbon and nitrogen content, dried seston samples were analyzed with a Carlo Erba elemental analyzer (Carlo Erba, Val-de-Reuil, France).

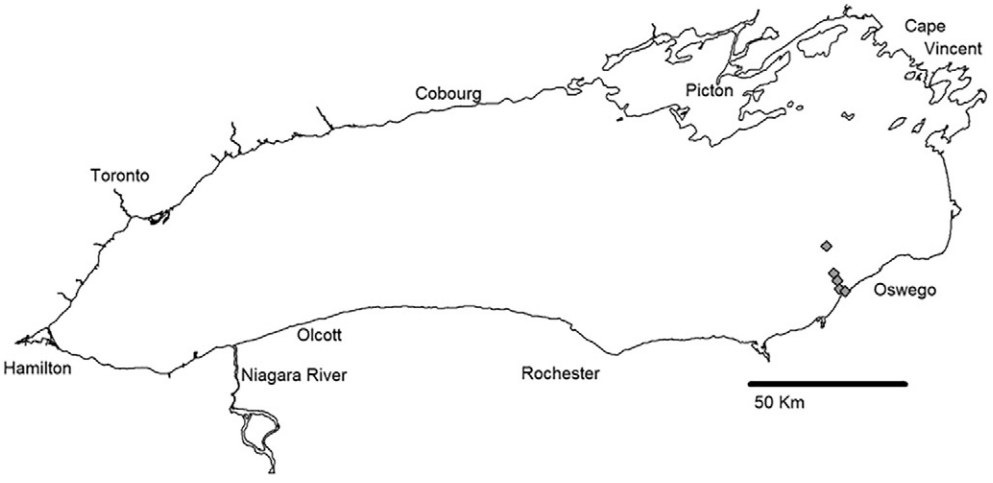

Fig. 1. Sampling locations along a transect extending from nearshore to offshore in Lake Ontario, just west of Oswego NY, 2013. The five sampling stations were located at depths of 5, 20, 50, 100, and 200 m.

Seston fatty acid composition

For the analysis of seston fatty acids, lake water was filtered immediately through 0.7 μm GF/F filters in the field at the maximum volume that would pass through the filter, then stored at −80 °C until extraction. Seston fatty acids were extracted and analyzed using methods outlined in Heissenberger et al. (2010). Freeze-dried samples (2–60 mg) were stored overnight in chloroform (2 mL) at −80 °C. Lipids were extracted using a 2:1 chloroform:methanol solution (1 mL) after homogenization with glass beads and the addition of NaCL (0.8 μL). After centrifugation, the organic lipid-containing layer was extracted with subsequent washes with chloroform, and evaporated with N_2 down to 0.5 mL. An aliquot (100 μL) of extracted lipids was dried and weighed (±1 μg) to obtain total lipid weight per sample. Remaining sample was evaporated to dryness using N_2, and then esterified with toluene (1 mL) and H_2SO_4 (2 mL, 1% *v*/v), and stored at 50 °C for 15 h. After incubation, $KHCO_3$ (2 mL, 2% *v*/v) and 1:1 Hexane:methyl tert-butyl ether (5 mL) were added and samples centrifuged. After centrifugation, the top layer was removed and evaporated using N_2, and then re-dissolved in hexane for analysis.

Fatty acid methyl esters (FAME) were analyzed with a gas chromatograph (Thermo Scientific, Waltham, MA USA; detector: FID, carrier gas: Helium, oven: 140 °C for 5 min. to 240 °C at 4 °C/min., holding at 240 °C for 15 min, injector: 1 μL, 260 °C), and identified with a 37 FAME standard mix (Supelco, St. Louis, MO USA). Specific FAME concentrations were determined using a standard curve dilution of the FAME standard mix. Quantification of peak areas from the GC output was performed by Xcalibur software (Thermo Scientific, Waltham, MA USA). We did not have information on the volume of water filtered through each filter for analysis, and therefore report fatty acid quantification as percent of total identified fatty acids (those included in the 37 FAME standard), similar to Ravet et al. (2010) and Smith et al. (2007). Higher quality seston is characterized by higher percentages of essential fatty acids. Essential fatty acids were classified as 18:2ω6 (Linoleic acid; LIN), 18:3ω3 (α-Linolenic acid; ALA), 20:4ω6 (Arachidonic acid; ARA), 20:5ω3 (Eicosapentaenoic acid; EPA), and 22:6ω3 (Docosahexaenoic acid; DHA) (Kainz et al., 2004).

Data analysis

We illustrated chlorophyll *a* and seston quality across vertical and distance-from-shore gradients through the course of the season to understand spatial and temporal patterns. We compared suites of predictors in generalized additive models (GAM) to determine best predictors of chlorophyll *a* concentration, seston C:P ratios, and seston percent essential fatty acids (%EFAs of all identified fatty acids). The predictors used in models included linear forms of day of year, sample depth, distance from shore, and water temperature (at sample depth). As some relationships between seston quantity and quality variables and predictors appeared to be nonlinear, we also used non-linear GAMs with smoothed (spline) predictor variables. This smoothing procedure fits nonparametric nonlinear functions to the variables using the data as opposed to pre-defined parameters. Models were compared using the full suite of both linear and smoothed (and combinations of linear and smoothed) predictors to find the best model. Best models were chosen by comparison of Akaike information criterion (AIC). Models within 2 AIC of the best model were considered to have similar model performance, and in such cases, best models were selected as those with the most explanatory power (highest R^2). We visualize the effect of predictor variables by plotting the linear or smoothed functional effect of the individual predictors on the response variable using partial residual plots. All analyses were made in the R statistical environment (R Core Team). All GAM models fit using the *gam()* function in the *mgcv* package, and smoothing performed using the *s()* function within the *gam* model.

We also assessed whether changes in seston C:P were due primarily to variations in seston carbon or seston phosphorus, as the two may vary independent of one another. We used a measure of effect size (Cohen's f^2) for each of seston carbon and seston phosphorus in a multiple regression model predicting seston C:P ratio (i.e. C:P ~ seston C + seston P). We calculated Cohen's f^2 for seston carbon as follows:

$$f^2 = \frac{R^2_{CP} - R^2_P}{1 - R^2_{CP}}$$

where R^2_{CP} is the coefficient of determination for the full model predicting seston C:P including both carbon and phosphorus, and R^2_P is a regression model predicting seston C:P with including only phosphorus. Effect size for seston phosphorus was calculated similarly, replacing R^2_P with the coefficient of determination for a regression model predicting seston C:P including only carbon (R^2_C).

Using total chlorophyll *a* concentration could be misleading when making inference about primary consumers because most macro zooplankton and *Dreissena* sp. do not effectively filter or use picoplankton (0.2–2.0 μm) (Sprung and Rose, 1988). Therefore, we compare patterns in spatial and temporal gradients of total chlorophyll *a* results to those using consumer-appropriate sized sestonic chlorophyll concentration (2.0–20.0 μm; hereafter referred to as "size-fractionated chlorophyll").

Results

Chlorophyll concentration

The best predictive model for size-fractionated chlorophyll (zooplankton food particle size) included smoothed seasonal and sample depth, and linear distance from shore (Table 1), with an additional temperature parameter not significantly changing model performance (ΔAIC = 1.6). These models predict a peak in size fractionated chlorophyll concentration in July at 10–20 m in depth, increasing in concentration with distance from shore (Figs. 2, 3). The average chlorophyll concentration peaked in the DCL in July, and then decreased to near epilimnetic concentrations in August. This increase in chlorophyll in July corresponded to a strong DCL that set up in the offshore sites at around 10–20 m and then decreased in August. Lowest chlorophyll concentrations were recorded mainly in the early part of the season throughout the water column (Fig. 3), and maximum chlorophyll concentrations were observed in the DCL. Patterns in total chlorophyll *a* concentration and best predictor models (Table 1) were similar to those for size-fractionated chlorophyll. Therefore, we only present data for size-fractionated chlorophyll, but supply total chlorophyll data in supplementary (Electronic Supplementary Material (ESM) Table S1).

Table 1
Candidate model set and results for predicting size fractionated (2–20 μm) and total chlorophyll *a* concentration using seasonal and spatial predictors in Lake Ontario, 2013. Predictors included smoothed and linear sample depth (sample z), day of year (DOY), distance from shore (dist.), and water temperature (temp). Table only includes candidate models within 2 AIC of the best model.

Model	N	Residual df	Adj. R^2	ΔAIC
Size-fractionated chlorophyll *a*				
Chl ~ s(sample z) + s(DOY) + dist.	198	185.3	0.49	0.0
Chl ~ s(sample z) + s(DOY) + dist. + temp	198	184.4	0.48	1.6
Total chlorophyll *a*				
Chl ~ s(sample z) + s(DOY) + dist.	185	173.1	0.45	0.0
Chl ~ s(sample z) + s(DOY)	185	174.2	0.44	1.6
Chl ~ s(sample z) + s(DOY) + dist. + temp	185	172.1	0.45	1.9

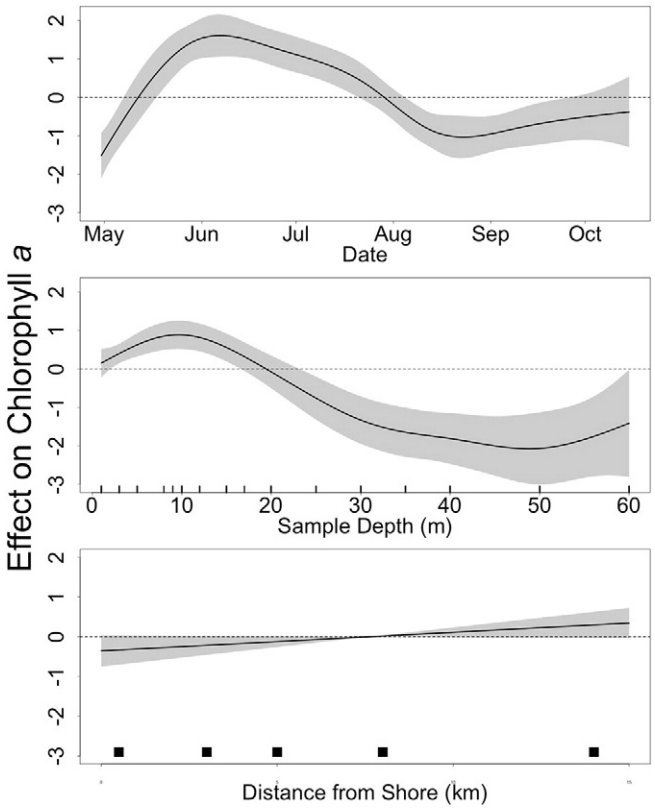

Fig. 2. Nonlinear and linear coefficients across time and space from a general additive model predicting size-fractionated chlorophyll a (size fraction 2.0–20 μm) based a seasonal day of year, sample depth (meters) predictor and distance from shore (km). The black line represents the coefficients effect on the mean chlorophyll layer and the gray band represents the estimated two standard errors for that coefficient. Black squares on bottom panel represent approximated locations of sampling stations.

Seston quality

Across all seston quality samples, a nonlinear pattern was evident, with seston quality (both stoichiometric- and EFA-qualities) declining from May to late August, with an increase in quality in the fall (Fig. 4; Table 2). The best predictor of seston C:P ratios was a smoothed seasonal predictor (Table 3), while the best predictors of seston EFA content was a smoothed seasonal predictor and a smoothed term for sample depth with the highest concentration of EFAs at approximately 10 m ($N = 41$, residual d.f = 34.8, adj. $R^2 = 0.26$; Fig. 4). All other candidate models predicting EFA concentration were >2 AIC from the best model.

There was a large range of seston C:P ratios and % EFAs throughout the season and across station-depths. Seston C:P ranged from 116 to 764, with the lowest C:P ratio below the thermocline at the deepest station in early August (despite overall increases in C:P throughout the water column; Fig. 5), and a median C:P of 300. Variability in seston C:P ratios was due primarily to variability in seston phosphorus concentration ($f^2 = 2.73$), as opposed to seston carbon ($f^2 = 0.74$). Similarly, temporal changes in seston C:P were due to declines in particulate phosphorus concentrations rather than changes in particulate carbon concentrations from May to late August (Fig. 6).

Essential fatty acids as a percentage of total identified fatty acids ranged from 0 to 24% with a median of 16%. The greatest concentration of EFAs from all samples occurred near the DCL in July (at 15 m; Fig. 7), with the greatest contributor being ALA (12% of identified FAs). Primary contributors to seston EFA concentration were LIN (C18:2ω6; 0 to 9%), ALA (C18:3ω3, 0 to 12%), and EPA (C20:5ω3, 0 to 6%) (Table 4). ARA (C20:4ω6)) and DHA (C22:6ω3) concentrations were at or below detection in Lake Ontario seston in these samples. Saturated fatty acids (SAFAs) were the most abundant class of fatty acids identified, ranging from 48 to 84%, specifically, C14:0, C16:0, and C7:0 SAFAs were in greatest supply. Monounsaturated fatty acids (MUFAs) were the next most abundant group ranging from 8 to 34%. Polyunsaturated fatty acids ranged from 6 to 21%, and 18C PUFAs ranged from 0 to 13% with the greatest contributions from LIN. Fatty acids used as bacterial

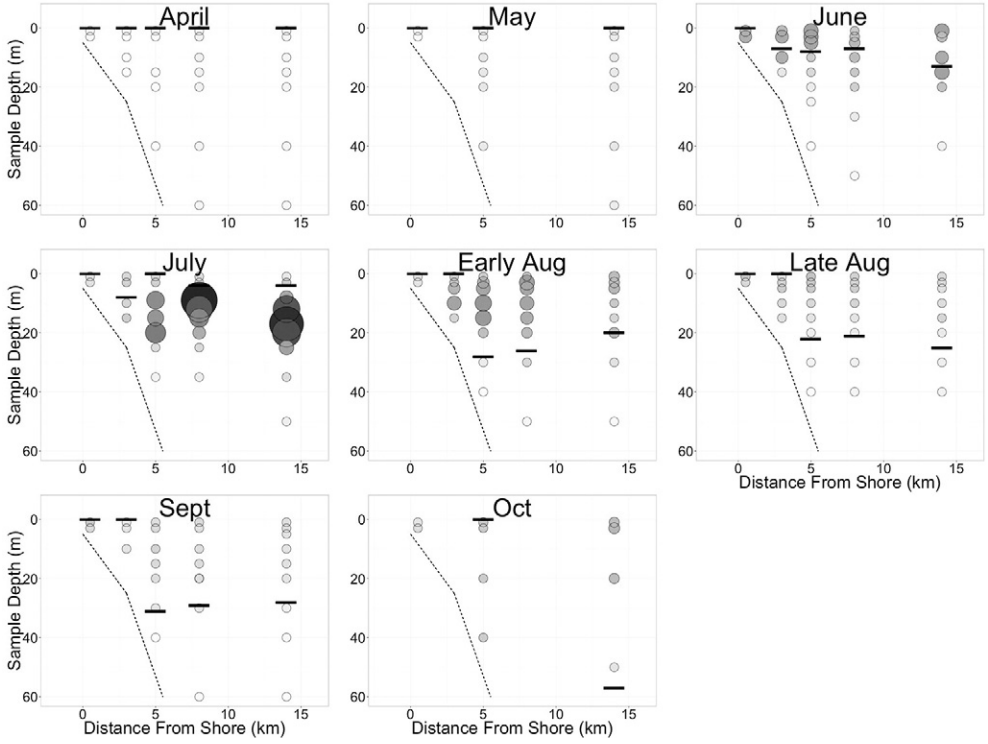

Fig. 3. Seasonal and spatial gradients of size fractionated chlorophyll a concentration (size fraction 2.0–20 μm) along a transect west of Oswego NY, in Lake Ontario, 2013. The color scale and point size are based on the fraction of the maximum value observed (~8.5 μg per liter of water), where darker and larger points represent greater chlorophyll concentrations. Each panel represents a sampling occasion through the season. The dashed line represents the lake bottom and the thick, short horizontal lines represent the thermocline.

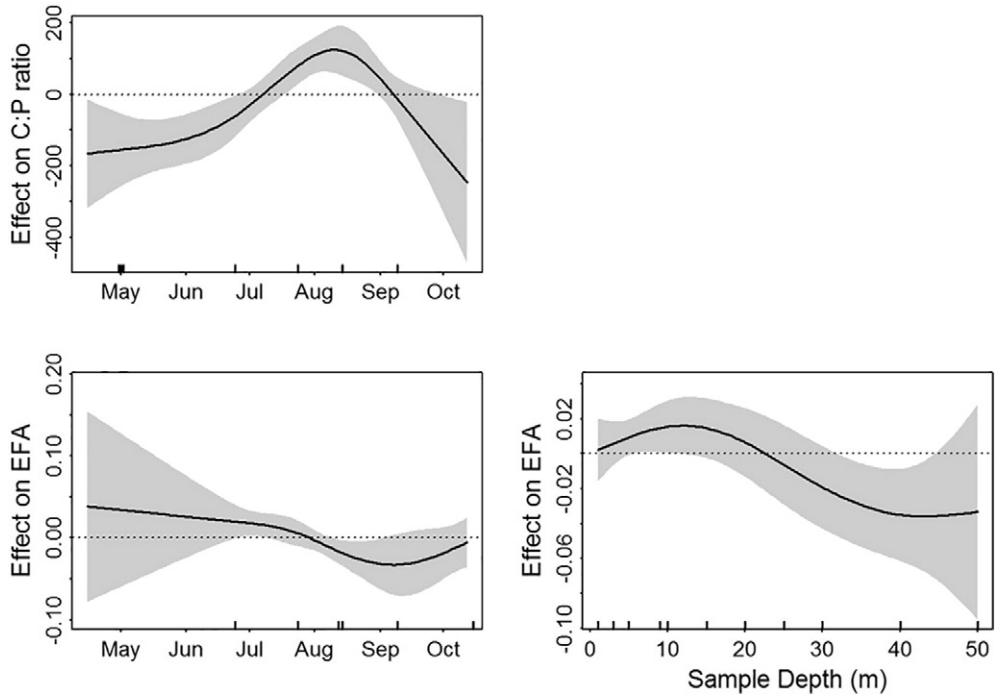

Fig. 4. Nonlinear coefficients across time and space from a general additive model predicting the seston carbon to phosphorus ratio (top panel, single predictor, day of year) and the seston proportion of essential fatty acids (EFA) in the total fatty acid concentration (lower panel, 2 predictors, day of year and sample depth. The black line represents the coefficients effect on the mean chlorophyll layer and the gray band represents the estimated two standard errors for that coefficient. All samples are from an onshore-offshore transect extending into Lake Ontario near Oswego NY, sampling depths from 5 m to 200 m.

biomarkers (C15:0 and C17:0) made small contributions to seston fatty acid composition, ranging from 0 to 4% of identified fatty acids. Complete seston biochemical composition (nutrient stoichiometry and fatty acid composition data) are supplied in ESM Tables S2, S3, and S4.

Discussion

Light and nutrient dynamics, hydrology, and food web gradients suggest the potential for variability in seston availability and biochemical composition from nearshore to offshore, and through the water column in Lake Ontario. We observed the formation of a strong deep chlorophyll layer that provided vertical heterogeneity throughout the water column in seston quantity, and an increase in essential fatty acid availability in the deep sites in July. However, we observed few patterns in seston stoichiometry in either horizontal or vertical gradients in 2013. In addition to spatial gradients in chlorophyll *a* concentration and EFAs, we identify strong temporal patterns in quantity and quality, with a general increase in chlorophyll concentration and a decline in seston quality (increasing C:P ratios and declining EFAs) from May to late August.

Spatial patterns in seston availability and biochemical composition

Epilimnetic chlorophyll *a* was low throughout the season, but there was formation of a strong DCL in June lasting until August that created both horizontal and vertical heterogeneity in chlorophyll *a* concentrations. This increase in chlorophyll *a* at sample depth represents an area of maximum biomass in the water column, as Scofield et al., 2017 demonstrated strong correlations between chlorophyll *a* concentrations and phytoplankton carbon concentrations during DCL formation. Therefore, the formation of the DCL in Lake Ontario can be an area of high resource availability for consumers. The DCL was observed below the thermocline at approximately 1% PAR depth as expected given phytoplankton light limitation threshold (Moll and Stoermer, 1982), and similar to past observations (Watkins et al., 2015) and elsewhere in the lake in 2013 (Scofield et al., 2017). Additionally, the DCL during the summer

Table 2
Summary of seston quality, including major fatty acid groups and carbon-to-phosphorus ratio (C:P). Fatty acids given as average percent of all identified fatty acids, and C:P given as a molar ratio. SAFA, MUFA, and PUFA represent saturated fatty acids, unsaturated fatty acids, and polyunsaturated fatty acids, respectively. ω3 and ω6 represent the sum of ω3 and ω6 fatty acids.

	SAFA	MUFA	PUFA	EFA	18:2n6 LIN	18:3n3 ALA	20:4n6 ARA	20:5n3 EPA	22:6n3 DHA	ω3	ω6	C:P
July												
Epi	60.66	19.81	19.46	18.15	7.02	6.88	ND	4.24	ND	11.12	8.33	255
Meta	62.31	20.63	17.04	16.60	5.30	7.02	ND	4.28	ND	11.30	5.74	310
Hypo	63.13	22.63	14.22	12.41	7.33	3.00	ND	2.08	ND	5.09	9.14	281
Early August												
Epi	62.02	22.84	15.12	15.12	6.06	6.76	ND	2.29	ND	9.06	6.06	493
Meta	59.87	21.89	18.23	16.41	5.89	6.05	ND	4.46	ND	10.52	7.70	188
Hypo	57.47	23.32	19.20	16.85	6.06	6.67	ND	4.11	ND	10.78	8.41	653
Late August												
Epi	58.03	27.31	14.64	14.64	6.07	6.09	ND	2.48	ND	8.57	6.07	504
Meta	71.16	20.07	8.75	8.75	8.75	ND	ND	ND	ND	ND	8.75	596
Hypo	57.24	32.74	10.01	6.62	2.69	2.13	ND	1.79	ND	3.93	6.08	353

Table 3
Candidate model set and results for predicting seston carbon to phosphorus ratio using seasonal and spatial predictors in Lake Ontario, 2013. Predictors included smoothed and linear sample depth (sample z), day of year (DOY), distance from shore (dist.), and water temperature (temp). Table only includes candidate models within 2 AIC of the best model.

Model	N	Residual df	Adj. R^2	ΔAIC
C:P ~ s(DOY)	56	52.3	0.16	0.0
C:P ~ DOY	56	54.0	0.13	1.7
C:P ~ s(DOY) + dist.	56	51.4	0.14	2.0
C:P ~ s(DOY) + s(sample z)	56	51.3	0.14	2.0

of 2013 was similar in both depth and magnitude as past observations of DCL in Lake Ontario (2003 and 2008; Watkins et al., 2015). In addition to increases in chlorophyll in the DCL in July, we observed an increase in epilimnetic chlorophyll in August as the thermocline deepened. This increase in surface layer chlorophyll could be due to mixing of DCL phytoplankton or nutrients into the epilimnion (Brooks and Torke, 1977; Watkins et al., 2015; Scofield et al., 2017).

Vertical heterogeneity in seston quality due to DCL formation was inconsistent between seston C:P ratios and EFA concentration. We did not see any characteristic patterns in the DCL suggesting altered C:P stoichiometry; however, a model that included smoothed sample depth (in addition to DOY) was the best predictor of seston %EFAs, with greatest EFA concentration around 15 m in July. This suggests the possibility for systematic vertical heterogeneity in EFA concentrations due to the formation of the DCL. Scofield et al., (2017) identified significant taxonomic differences characteristic of the DCL compared to the epilimnion, attributed to a greater abundance of diatoms in the DCL compared to dinoflagellates in the epilimnion. These results are similar to Twiss et al. (2012), who previously identified high proportions of characteristically EFA-rich phytoplankton in the DCL, but in contrast the epilimnion had greater contributions of low-EFA cyanobacteria. While Barbeiro and Tuchman (2001) suggested that shade adaptation

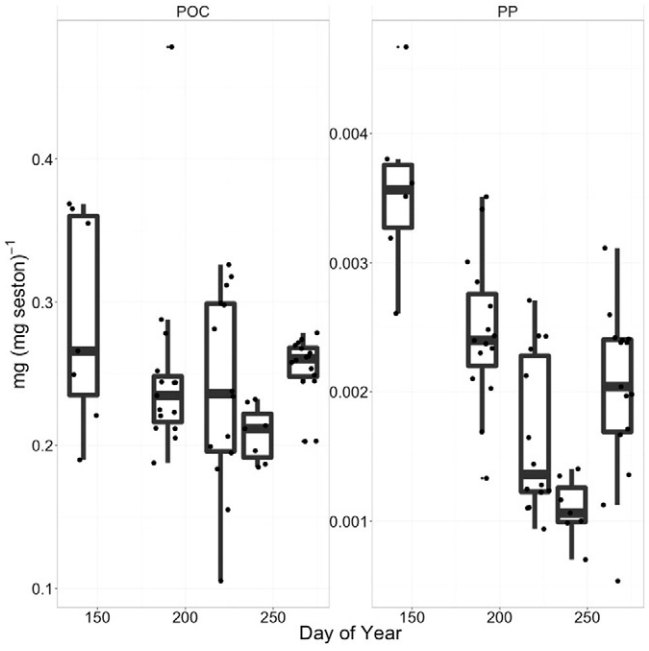

Fig. 6. Boxplots of seston carbon (POC) and phosphorus concentrations (PP; mg mg seston^{-1}) by sample date (all depths). Boxes represent the 5, 25, 50, 75, and 95% quantiles of the data, and points represent the actual data. Small points represent data outside of 95% quantile.

was an important contributor to the DCL in Lake Ontario, Scofield et al., (2017) observed little evidence for shade adaptation. Therefore, the differences in EFA profiles, and the relatively higher contribution of EFAs to total fatty acids in the DCL compared to the rest of the water column is likely a function of phytoplankton taxonomic composition as opposed to physiological adaptation.

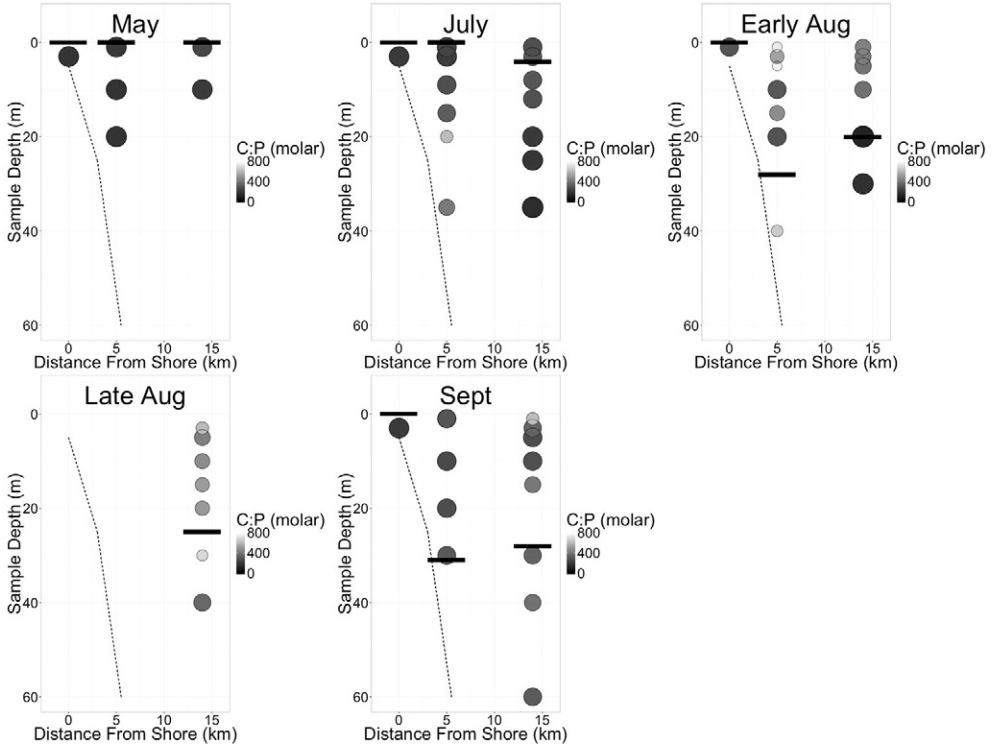

Fig. 5. Vertical and spatial gradients of the carbon to phosphorus ratio (C:P) for filtered seston (pore size = 0.7 μm) in Lake Ontario, 2013. The point shading and point size represents the scaled proportion where the larger points and darker color represent the lower C:P ratios, or higher quality seston.

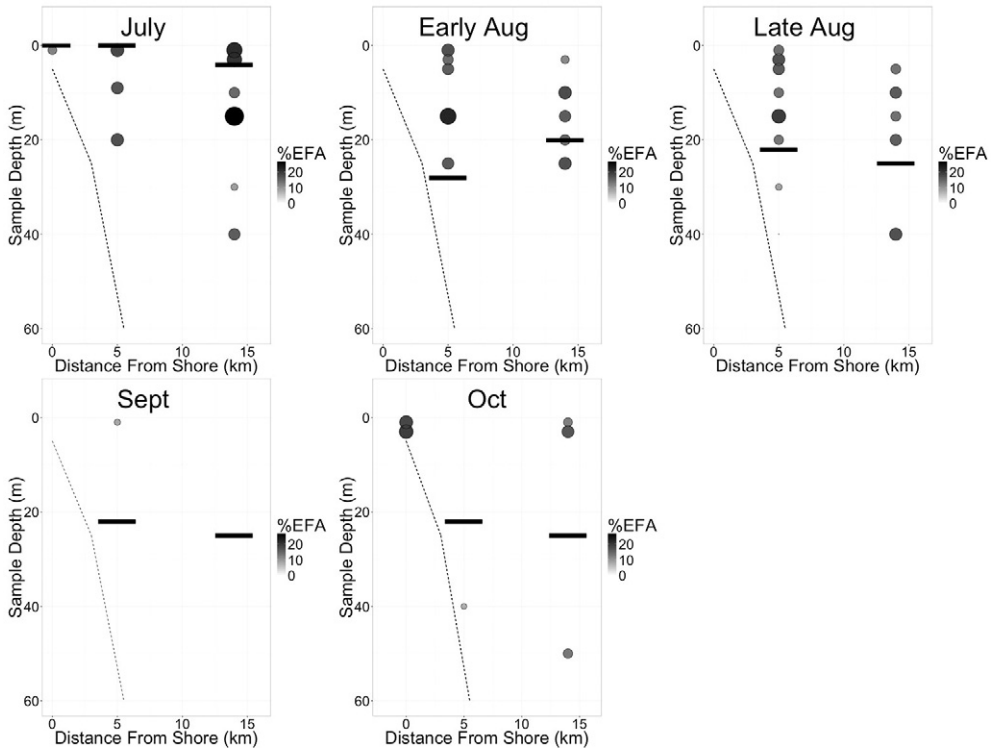

Fig. 7. Vertical and spatial gradients of the essential fatty acid concentration (EFAs) as percentage of all identified fatty acids for filtered seston (pore size = 0.7 μm) in Lake Ontario, 2013. The point shading and size represents the scaled proportion where the darker and larger points represent greater EFA values, or higher quality seston.

The influence of light on phytoplankton was expected to alter biochemical composition of seston near the surface, including increased C:P ratios and a reduction in EFAs. We expected light gradients through the water column would create additional vertical heterogeneity in seston biochemistry beyond DCL formation. Although we did observe qualitatively greater epilimnetic seston C:P ratios, in general C:P ratios tended to be variable throughout the water column, and sample depth was not included in the best model predicting seston C:P. However, we did observe a pattern of declining seston carbon concentration with depth, as would be predicted with declines in light availability and similar to observations made in Lake Superior (Sterner, 2011).

Counter to predictions, we saw relatively high EFA concentrations in seston near the surface, similar to concentrations found within the DCL. Past research has shown strong support for increases in C:P ratios in phytoplankton under high light conditions due to increased carbon fixation and reduced light use efficiency (Sterner et al., 1997; Hessen, 2006) and/or suppression of phosphorus uptake (Sereda et al., 2011). High light has also been demonstrated to result in reduced EFA concentrations, as prolonged exposure may alter polyunsaturated fatty acid biosynthesis (Wang and Chai, 1994; Guschina and Harwood, 2009), or damage biochemical constituents through oxidation (Wang and Chai, 1994). This pattern would be especially pronounced in Lake Ontario, as light attenuation is low, yet we did not observe any evidence of EFA reduction due to light. Our results suggest the effect of light on seston biochemical composition may be variable, with less influence on creating vertical gradients of seston composition than expected.

Variability in nutrient concentrations throughout the water column may also cause heterogeneous seston quality, as nutrient concentration plays a role in phytoplankton nutritional composition (Müller-Navarra et al., 2004; Villar-Argaiz et al., 2009). However, nutriclines are not typically observed in Lake Ontario. Both Scofield et al., (2017) and Watkins et al. (2015) observed generally homogenous dissolved and total phosphorus concentrations throughout the water column, but noted that increased phosphorus concentrations were sometimes observed in the hypolimnion. This may be reason for a lack of systematic variation in seston biochemical composition with depth.

Distance from shore was not a strong predictor of either seston C:P or EFAs, suggesting little horizontal heterogeneity in seston quality

Table 4
Means and standard deviations of all identified fatty acids in all samples from Lake Ontario from July to October 2013.

Fatty acid	Mean	SD
C7:0	7.39	5.59
C8:0	0.16	1.06
C10:0	4.39	5.02
C11:0	0.11	0.70
C12:0	3.59	3.64
C13:0	0.81	1.66
C14:0	11.89	3.26
C14:1n5c	2.34	2.82
C15:0	0.71	1.44
C15:1n5c	0.09	0.59
C16:0	19.68	5.61
C16:1n7c	7.44	1.98
C17:0	0.14	0.66
C18:0	8.75	6.48
C18:1n9	4.07	4.18
C18:1n9c	7.81	3.22
C18:2n6c	5.93	1.83
C18:3n3	5.54	2.82
C18:3n6	0.09	0.42
C20:0	0.87	1.90
C20:1n9	1.33	1.70
C20:3n6	0.25	0.91
C20:4n6	0.06	0.41
C20:5n3	2.71	1.90
C21:0	0.16	1.03
C22:0	0.68	1.56
C22:1n9	0.42	0.99
C22:2n6	0.18	0.67
C23:0	2.13	2.13
C24:0	0.24	0.94
C24:1n9	0.05	0.33

along this transect. Recent data from Lake Erie suggest the potential for significant differences in seston fatty acid composition from nearshore to off shore due to higher abundances of cyanobacteria, especially near the mouth of the Maumee River (Larson et al., 2016). However, in contrast, Smith et al. (2007) observed no significant differences in nearshore-off shore essential fatty acids or C:P in in Lake Erie. The lack of differences in composition in the nearshore site of Lake Ontario compared to the off shore site may suggest that indiscriminate feeding by dressenid mussels does not significantly reduce seston quality for consumers (Smith et al., 2007); however, as little is known about the historical biochemical composition differences among nearshore and offshore sites, it is possible that nearshore seston used to be of greater quality compared to offshore in the past as a result of lower C:P ratios from tributary phosphorus loads and the formation of coastal boundary layers. Dreissenid mussel proliferation therefore may have resulted in more spatially homogenous seston composition. Additionally, it's possible that there was no nearshore-off shore differences in phytoplankton composition along this transect, contributing to relatively homoegenous seston fatty acid composition and C:P ratios.

Temporal patterns in seston availability and biochemical composition

Although the spatial gradients in seston quality were variable and less common than hypothesized, there was a strong temporal pattern of greater C:P and reduced EFA concentration from July to September. This change in phytoplankton biochemical composition coincides with a general decrease in nutrients in Lake Ontario during that time, as average water column total phosphorus decreased from approximately 9 to approximately 5 $\mu g\ L^{-1}$ (Scofield et al., 2017 Figure 3). Even small reductions when P concentration is low can have significant impacts on seston stoichiometry (Hessen et al., 2002; Hall et al., 2005), and we observed coinciding declines in seston particulate phosphorus from May through August (Fig. 6). The pattern of decreasing dissolved phosphorus throughout the season may not however be consistent from year-to-year, as there was an increase in total phosphorus concentrations from spring to fall in 2003, and relatively steady TP concentrations throughout the season in 2008 (Holeck et al., 2015). Therefore, the temporal pattern in seston biochemical composition may be dynamic, depending heavily on temporal nutrient concentration dynamics.

The overall predictive ability of the best models predicting seston C:P and EFA concentration are relatively weak (R^2 of 0.16 and 0.26, respectively); however, given the significant natural variation in biochemical composition of lake seston, we believe they still hold explanatory value. Both seston C:P ratios and fatty acid composition are regulated by a variety of different mechanisms, including light and nutrient availability (Sterner et al., 1997; Guschina and Harwood, 2009) and phytoplankton community composition (Sushchik et al., 2004). These mechanisms may vary significantly at fine-scale local spatial extents, either due to internal nutrient cycling (Sarnelle, 1992; Vanni and Layne, 1997) or grazing by zooplankton (Oliver et al., 2015). As such, highly predictable systematic variation through space or time within a specific lake may not be possible; yet we believe these patterns are robust, and have similar explanatory power as other studies assessing spatial or temporal patterns in seston quality (e.g. Chiandet and Xenopoulos, 2011).

Potential for In-lake variability in seston quality

Our study of seston concentrations and quality provides new insight into the relative magnitude of variability due to vertical, spatial, and temporal gradients, but interpretations from our single transect may not accurately represent all Lake Ontario regions. For instance, Lake Ontario rivers and tributaries and their associated plumes have been shown to have significant impacts on mineral nutrient concentrations into the lake (Howell et al., 2012; Makarewicz et al., 2012) that would likely influence seston dynamics. The prevailing longshore current at our study sites is from west to east (McKenna and Chalupnicki, 2011) which likely reduced the potential effect of the Oswego River plume (>10 km to the east) on our results. In addition, seston dynamics may differ in lake regions with thermal profiles that differ from those we observed. Our sampling site was in a lake region with a relatively long fetch length, deep thermocline, and warm surface water temperatures (Minns and Wichert, 2005). In contrast, north and western regions of Lake Ontario are generally cooler (Minns and Wichert, 2005) and frequently experience upwelling events that have been shown to create nutrient and chlorophyll *a* gradients (Howell et al., 2012).

Conclusions

We observed spatial and temporal heterogeneity in seston quantity and quality in Lake Ontario in 2013. While our results (and Scofield et al., 2017) suggest the DCL may be a "hot spot" in terms of seston quantity for primary consumers, seston quality changes were inconsistent, with unexpectedly variable seston C:P ratios throughout the water column. In contrast, we did observe strong temporal patterns in seston quality, with general declines in seston stoichiometric and fatty acid quality from May to late August. Taken together, these results suggest a better understanding of these temporal and spatial fluctuations may be important in understanding the spatial and temporal patterns of Lake Ontario primary consumers.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jglr.2017.03.007.

References

Arts, M.T., Ackman, R.G., Holub, B.J., 2001. "Essential fatty acids" in aquatic ecosystems: a crucial link between diet and human health and evolution. 58, 122–137.
Barbiero, R.P., Tuchman, M.L., 2004. The deep chlorophyll maximum in lake superior. J. Great Lakes Res. 30, 256–268.
Birkett, K., Lozano, S.J., Rudstam, L.G., 2015. Long-term trends in Lake Ontario's benthid macroinvertebrate community from 1994-2008. Aquat. Ecosyst. Health Manag. 18, 76–88.
Brett, M., Müller-Navarra, D., 1997. The role of highly unsaturated fatty acids in aquatic foodweb processes. Freshw. Biol. 38, 483–499.
Brooks, A.S., Torke, B.G., 1977. Vertical and seasonal distribution of chlorophyll *a* in Lake Michigan. J. Fish. Res. Board Can. 34, 2280–2287.
Chiandet, A.S., Xenopoulos, M.A., 2011. Landscape controls on seston stoichiometry in urban stormwater management ponds. Freshw. Biol. 56, 519–529.
DeMott, W.R., Edington, J.R., Tessier, A.J., 2004. Testing zooplankton food limitation across gradients of depth and productivity in small stratified lakes.
Guschina, I.A., Harwood, J.L., 2009. Algal lipids and effect of the environment on their biochemistry. In: Kainz, M., Brett, M.T., Arts, M.T. (Eds.), Lipids in Aquatic Ecosystems. Springer, New York, pp. 1–24.
Hall, S.R., Pauliukonis, N.K., Mills, E.L., Rudstam, L.G., Schneider, C.P., Lary, S.J., Arrenius, F., 2003. A comparison of total phosphorus, chlorophyll *a*, and zooplankton in embayment, nearshore, and offshore habitats of Lake Ontario. J. Great Lakes Res. 29, 54–69.
Hall, S.R., Smith, V.H., Lytle, D.a., Leibold, M.a., 2005. Constraints on primary producer N:P stoichiometry along N:P supply ratio gradients. Ecology 86, 1894–1904.

Hecky, R.E., Smith, R.E., Barton, D.R., Guildford, S.J., Taylor, W.D., Charlton, M.N., Howell, T., 2004. The nearshore phosphorus shunt: a consequence of ecosystem engineering by dreissenids in the Laurentian Great Lakes. Can. J. Fish. Aquat. Sci. 61, 1285–1293.
Heissenberger, M., Watzke, J., Kainz, M.J., 2010. Effect of nutrition on fatty acid profiles of riverine, lacustrine, and aquaculture-raised salmonids of pre-alpine habitats. Hydrobiologia 650, 243–254.
Hessen, D.O., 1992. Nutrient element limitation of zooplankton production. Am. Nat. 140, 799–814.
Hessen, D.O., 2006. Determinants of seston C : P-ratio in lakes. Freshw. Biol. 51, 1560–1569.
Hessen, D.O., Faerovig, P.J., Anderson, T., 2002. Light, nutrients, and P:C ratios in algae: grazer performance related to food quality and quantity. Ecology 83, 1886–1898.
Holeck, K.T., Rudstam, L.G., Watkins, J.M., Luckey, F.J., Lantry, J.R., Lantry, B.F., Trometer, E.S., Koops, M.A., Johnson, T.B., 2015. Lake Ontario water quality during the 2003 and 2008 intensive field years and comparison with long term trends. Aquat. Ecosyst. Health Manag. 18, 7–17.
Howell, E.T., Chomicki, K.M., Kaltenecker, G., 2012. Tributary discharge, lake circulation and lake biology as drivers of water quality in the Canadian nearshore of Lake Ontario. J. Great Lakes Res. 38, 47–61.
Hunter, M.D., Price, P.W., 1992. Playing chutes and ladders: heterogeneity and the relative roles of bottom-up and top-down forces in natural communities. Ecology 73, 724–732.
Idrisi, N., Mills, E.L., Rudstam, L.G., Stewart, D.J., 2001. Impact of zebra mussles (*Dreissena polymorpha*) on the pelagic lower trophic levels of Oneida Lake, New York. Can. J. Fish. Aquat. Sci. 58, 1430–1441.
Kainz, M., Arts, M.T., Muzumder, A., 2004. Essential fatty acids in the planktonic food web and their ecological role for higher trophic levels. Limnol. Oceanogr. 49, 1784–1793.
Larson, J.L., Richardson, W.B., Evans, M.A., Schaeffer, J., Wynne, T., Bartsch, M., Bartsch, L., Nelson, J.C., Vallazza, J., 2016. Measuring spatial variation in secondary production and food quality using a common consumer approach in Lake Erie. Ecol. Appl. 26, 873–885.
Makarewicz, J.C., Booty, W.G., Bowen, G.S., 2012. Tributary phosphorus loading to Lake Ontario. J. Great Lakes Res. 38, 14–20.
Marcarelli, A.M., Baxter, C.V., Mineau, M.M., Hall, R.O., 2011. Quantity and quality: unifying food web and ecosystem persepctives on the role of resource subsidies in freshwaters. 92, 1215–1225.
McKenna, J.E., Chalupnicki, M.A., 2011. A heuristic simulation model of Lake Ontario circulation and mass balance transport. J. Freshw. Ecol. 26, 123–132.
Menzel, D., Corwin, N., 1965. The measurement of total phosphorus in seawater based on the liberation of organically bound fractions by persulfate oxidation. Limnol. Oceanogr. 10, 280–282.
Minns, C.K., Wichert, G.A., 2005. A framework for determining fish habitat domains in Lake Ontario and its drainage. J. Great Lakes Res. 31, 6–27.
Moll, R.A., Stoermer, E.F., 1982. A hypothesis relating trophic status and subsurface chlorophyll maxima of lakes. Arch. Hydrobiol. 94, 425–440.
Müller-Navarra, D.C., 1995. Biochemical versus mineral limitation in Daphnia. Limnol. Oceanogr. 40, 1209–1214.
Müller-Navarra, D.C., Brett, M.T., Park, S., Chandra, S., Ballantyne, A.P., Zorita, E., Goldman, C.R., 2004. Unsaturated fatty acid content in seston and tropho-dynamic coupling in lakes. Nature 427, 69–72.
Naddafi, R., Pettersson, K., Eklo, P., Eklov, P., 2008. Effects of the zebra mussel , an exotic freshwater species , on seston stoichiometry. Limnol. Oceanogr. 53, 1973–1987.
Oliver, S.K., Branstrator, D.K., Hrabik, T.R., Guildford, S.J., Hecky, R.E., 2015. Nutrient excretion by crustacean zooplankton in the deep chlorophyll layer of Lake Superior. Can. J. Fish. Aquat. Sci. 72, 390–399.
Rao, Y.R., Schwab, D.J., 2007. Trasport and mixing between the coastal and offshore waters in the great lakes: a review. J. Great Lakes Res. 33, 202–218.
Ravet, J.L., Brett, M.T., Arhonditsis, G.B., 2010. The effects of seston lipids on zooplankton fatty acid composition in Lake Washington, Washington, USA. Ecology 91, 180–190.
Sarnelle, O., 1992. Contrasting effects of *Daphnia* on ratios of nitrogen to phosphorus in a eutrophic, hard-water lake. Limnol. Oceanogr. 37, 1527–1542.
Scofield, A.E., Watkins, J.M., Weidel, B.C., Luckey, F.J., Rudstam, L.G., 2017. The deep chlorophyll layer in Lake Ontario: extent, mechanisms of formation, and abiotic predictors. J. Great Lakes Res. 43, 782–794.
Sereda, J.M., Vandergucht, D.M., Hudson, J.J., 2011. Disruption of planktonic phosphorus cycling by ultraviolet radiation. Hydrobiologia 665, 205–217.
Smith, R.E.H., Parrish, C.C., Depew, D.C., Ghadouani, A., 2007. Spatial patterns of seston concentration and biochemical composition between nearshore and offshore waters of a Great Lake. Freshw. Biol. 52, 2196–2210.
Sprung, M., Rose, U., 1988. Influence of food size and food quantity on the feeding of the mussel *Dreissena polymorpha*. Oecologia 77, 526–532.
Sterner, R.W., 2011. C:N:P stoichiometry in Lake Superior: freshwater sea as end member. Inland Waters 1, 29–46.
Sterner, R.W., Elser, J.J., 2002. Ecological Stoichiometry: The Biology of Elements from Molecules to the Biosphere. Princeton University Press, Princeton, New Jersey.
Sterner, R.W., Elser, J.J., Fee, E.J., Guildford, S.J., Chrzanowski, T.H., 1997. The light: nutrient ratio in lakes: the balance of energy and materials affects ecosystem structure and process. Am. Nat. 150, 663–684.
Stevens, R.J.J., Neilson, M.A., 1987. Response of Lake Ontario to reductions in phosphorus load, 1967-82. Can. J. Fish. Aquat. Sci. 40, 2059–2068.
Sushchik, N.N., Gladyshev, M.I., Makhutova, O.N., Kalachova, G.S., Kravchuk, E.S., Ivanova, E.A., 2004. Associating particulate essential fatty acids of the w3 family with phytoplankton species composition in a Siberian reservoir. Freshw. Biol. 49, 1206–1219.
Thompson, P.A., Harrison, P.J., Whyte, J.N.C., 2004. Influence of irradiance on the fatty acid composition of phytoplankton. J. Phycol. 26, 278–288.
Twiss, M.R., Ulrich, C., Zapesta, A., Pick, F.R., 2012. On phytoplankton growth and loss rates to microzooplankton in the epilimnion and metalimnion of Lake Ontario in mid-summer. J. Great Lakes Res. 38, 146–153.
Vanni, M.J., Layne, C.D., 1997. Nutrient recycling and herbivory as mechanisms in the "top-down" effect of fish on algae in lakes. Ecology 78, 21–40.
Villar-Argaiz, M., Medina-SÁnchez, J.M., Bullejos, F.J., Delgado-Molina, J.a., PÉrez, O.R., Navarro, J.C., Carrillo, P., 2009. UV radiation and phosphorus interact to influence the biochemical composition of phytoplankton. Freshw. Biol. 54, 1233–1245.
Wang, K.S., Chai, T., 1994. Reduction in omega-3 fatty acids by UV-B irradiation in microalgae. J. Appl. Phycol. 6, 415–422.
Watkins, J.M., Weidel, B.C., Rudstam, L.G., Holeck, K.T., 2015. Spatial extent and dissipation of the deep chlorophyll layer in Lake Ontario during the Lake Ontario lower foodweb assessment, 2003 and 2008. Aquat. Ecosyst. Health Manag. 18, 18–27.
Wetzel, R.G., 2001. Limnology: Lake and River Ecosystems. third ed. Academic Press, San Diego, California.