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Scale-dependent carbon : nitrogen : phosphorus seston stoichiometry in marine and freshwaters

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Abstract

The classical Redfield ratio of $\text{carbon}_{106}:\text{nitrogen}_{16}:\text{phosphorus}_1$ is a cornerstone of biogeochemistry. With the use of >2,000 observations of the chemistry of particulate matter from small and large lakes, as well as near- and off-shore marine environments, we found that the best model to describe seston stoichiometry depended on the scale of analysis. We also found that there were better estimates for seston chemistry than the classical ratio for all habitats, whether freshwater or marine. Across the entire data set, a constant proportionality of $C_{166}:N_{20}:P_1$ (±error) described the data, which implies higher C sequestration per unit of N and P in surface waters than given in the classical ratio. At a regional scale, however, C : P and C : N often declined with increasing seston abundance, rejecting a constant ratio model. Within both freshwater and marine habitats, higher seston abundance is often associated with lower C : P and C : N ratios (higher nutrient content). The difference in appropriateness of the constant ratio model with respect to the entire data compared with subsets of the data indicates a scale dependence in stoichiometric relationships in seston C : N : P ratios. Given these consistent shifts in seston chemistry with particle abundance, the narrower variation in seston chemistry associated with marine seston chemistry could occur because of a reduced range of particulate nutrient concentration. For all but the largest scales, the classical Redfield model of biogeochemical cycling should be replaced with a more general power function model.

The C : N : P ratio of particulate matter (seston) in lakes and oceans is widely held to relate in fundamental ways to biogeochemical cycling. A. C. Redfield observed that the C : N : P ratios of particles in the surface offshore ocean were similar to the ratios of linked variability of the dissolved species of these same elements in deep water (Redfield et al. 1963). This congruence between actual surface particulate ratios and linked changes in deep-water ratios led him to propose that marine chemistry reflects a strong biotic influence (*see also* Falkowski 2000; Sterner and Elser 2002; Sarmiento and Gruber 2006). In contrast, freshwater systems exhibit greater variability of seston C : N : P ratios (Hecky et al. 1993; Elser et al. 2000), variation that has been shown to affect patterns of nutrient cycling, secondary production, and community structure (Sterner and Elser 2002; Hessen 2005; Hessen and Elser 2005). Couplings of C, N, and P bear strongly on issues such as the biological pump (Sigman and Boyle 2000; Omta et al. 2006), consumer-driven recycling processes (Urabe 1993), secondary production (Demott 2003), and the efficiency of carbon sequestration (Hessen et al. 2004; Christian 2005).

Acknowledgments

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Many questions remain about broad-scale patterns of variability in seston ratios both in marine and fresh waters. It seems not to be widely recognized that Redfield's original papers contain very little data on particulate nutrients, and those that are reported are scantily documented and include organisms such as zooplankton, not just bulk particles. Even today, marine studies reporting particulate C and N and their ratio are very common, but few studies report particulate P data. Thus, although there have been extensive analyses of deep-water nutrient ratios (e.g., Fanning 1992), to date there still have been surprisingly few examinations of particulate C : N : P ratios in the global ocean. Constant C : N : P ratios in the ocean are often invoked even though there is disagreement regarding the applicability of a global constant Redfield ratio of $C_{106} : N_{16} : P_1$ (all ratios are presented in molar units). Departures from the classical Redfield proportions in dissolved (Takahashi et al. 1985; Sambrotto and Savidge 1993; Sarmiento et al. 2004) and particulate (Schneider et al. 2003) as well as total nutrients (Guildford and Hecky 2000) have been reported for the oceans. Work by Li et al. (2000) supported a revised remineralization ratio of $C_{135} : N_{13} : P_1$. Nevertheless, $C_{106} : N_{16} : P_1$ remains the paradigm (Lenton and Watson 2000; Arrigo 2005; Sarmiento and Gruber 2006). It has been suggested that conflicting conclusions regarding the variability in C : N : P ratios could be due to "the spatiotemporal scale of the observations on which they are based" (Sarmiento and Gruber 2006). However, this hypothesis of scale dependence has not been directly tested with data spanning multiple scales of observation. Scale dependence is observable in how pattern and variability change with the scale of observation (Levin 1992).

In contrast to seawater, the reigning paradigm for C : N : P ratios in lakes focuses on variation, not constancy. Lakes are generally noted to have seston with overall higher mean C : P and C : N ratios than the offshore ocean, as well as higher spatial and temporal variability (Hecky et al. 1993; Elser and Hassett 1994). These contrasts between marine and freshwater seston ratios have been related to patterns of nutrient limitation in the two habitats (Howarth et al. 1988; Elser and Hassett 1994), as well as to the highly contrasting hydraulic residence times of these systems (Hecky et al. 1993; Lenton and Watson 2000). Models to explain this variability within freshwater systems mechanistically have been advanced (Sterner et al. 1997) and repeatedly tested (e.g., Diehl et al. 2002; Dickman et al. 2006; Hall et al. 2007).

The most comprehensive analysis of marine seston C : N : P ratios to date can be found in Copin-Montegut and Copin-Montegut (1983). Only two studies have undertaken systematic comparisons of marine and freshwater C : N : P relationships. Hecky et al. (1993) found higher and more variable C : P and C : N in lakes than the Copin-Montegut and Copin-Montegut data cited above. Hecky et al. also found higher and more variable C : P and C : N in small lakes compared with large lakes. Elser and Hassett (1994) also found these same differences for marine and freshwater seston and presented evidence for systematic differences in seston versus zooplankton chemistry in marine compared with fresh waters. Marine data in the Elser and Hassett study were largely from nearshore and estuarine samplings.

In this study, we examine couplings among carbon, nitrogen, and phosphorus in seston in near- and offshore marine studies, as well as small and large lakes, and examine the data for its consistency with the classical Redfield ratio.

Materials and methods

Data collection—A total of 2,855 observations of seston carbon, nitrogen, and phosphorus were assembled from every published and unpublished source known to the authors that included measurements of seston P (Table 1). One data set (Bermuda) lacked observations for seston N. The locations studied include four of the world's largest lakes, several coastal or brackish water systems, and six oceans. They include some of the least and some of the most productive pelagic ecosystems on Earth, and they span a broad salinity range. For assessing broad-scale habitat differences, data were considered to be from oceans (offshore marine), coastal zones (nearshore marine), or large or small lakes. The entire data set of seston chemistry measurements is found in Web appendix 1 at www.aslo.org/lo/toc/vol_53/issue_3/1169a1.html.

Seston elements were measured by standard methods in all studies. Any corrections for calcium carbonate or other inorganic material on seston C, N, or P were study specific and we lack systematic information on how large those corrections would have been or how effective they were. Under stratified conditions, only data from the surface layer were used (*see* Table 1). For 281 small lakes (<500 km^2), data from four multilake surveys on three continents were used; in these, individual observations were either single samplings or means of multiple observations of summertime conditions in individual lakes. For large lakes (>500 km^2), coastal zones, and oceans, relationships in single waterbodies over space and time were examined.

Mathematical definition of constant ratios—"Constancy" of a nutrient ratio might be taken to imply zero variation in $Y : X$, but this is not a relevant model because measurements of element concentration will always be subject to sampling variation and analytical error and ratios will reflect this variability. Hence, some variation in the ratio in space and time always is expected.

Ratios can be said to be not constant in two mathematically distinct ways. One is

$$Y/X = a \times e$$
$$\text{or } \log Y = \log a + \log X + e \tag{1}$$

where X and Y are the concentrations of two elements, a is a proportionality constant (a stoichiometric coefficient), and e is an unspecified error term with mean and variance. One meaning of "constant ratio" would be if the model of Eq. 1 (Model 1) fits the data and the error term e is small relative to a. Model 1 would be consistent with nutrient ratios that have nonzero variance but have the same

Table 1. Data information and sources.

Database	Notes	Attribution
Hokkaido	Lakes (18) in Hokkaido Island, Japan, sampled once in summer 2004. Depths 0–20 m.	Urabe et al. 2006
N America	Lakes and ponds (130) in upper Midwest of the U.S. sampled once either in 2000 or 2001. Two depths (from above the thermocline when stratified) averaged.	Sterner et al. (unpubl. data)
Norway lakes	Stratified lakes (116) widely distributed throughout Norway sampled in Jun–Aug from one to nine times (usually three) during 1988–1999. Depths 0–10 m for each site taken at twice the Secchi depth.	Hessen 2006
Toolik lakes	Arctic lakes (17) sampled once during 1997. Depths 0–10 m.	Dobberfuhl and Elser 2000
Baikal	Stations (6) sampled six times during Jun–Oct 1999. Depths 0–25 m.	Genkai-Kato et al. 2002
Biwa	Offshore station (1) sampled several times during each of 1992, 1996, and 1997. Depths 0–15 m.	Urabe et al. 1999
Hövsgöl	Sites (5) sampled in both Jul 1997 and 1998. Depths 0–30 m.	Urabe et al. 2006
Superior	Stations (5) in the western arm sampled one to eight times during each of 1996–2001. Depths 0–20 m.	Sterner (unpubl. data)
Norway coastal	Stations (5) sampled 72–615 times year-round during 1990–1999. Depths 0–10 m. Salinity > 30.	Magnusson (unpubl. data)
Oslofjord	Stations (3) sampled Mar–Oct 1986. Depths 2–8 m. Salinity 15–30.	Paasche and Erga 1988
Riga	Stations (5) of the Riga Bay in the Baltic Sea sampled during summertime 1993–1994. Upper layer defined by temperature and/or salinity.	Reigstad and Wassmann 1999
Yenisey	Kara Sea, transect from mouth of Yenisey River into the Arctic Sea. Depths 0–8 m.	Hessen (unpubl. data)
Atlantic	Multiple cruise transects in SE Atlantic sampled 1971–1980. Depths 0–30 m. (From this large study and another [Copin-Montegut and Copin-Montegut 1978], only samplings with data for all of C, N, and P were included.)	Copin-Montegut and Copin-Montegut 1983
Bermuda	Single station sampled twice (1992, 1993). Depths 0–40 m.	Cotner et al. 1997
Indian	Southern Indian Ocean. Depths all 5 m.	Copin-Montegut and Copin-Montegut 1978
Mediterranean	Borha II buoy during two cruises in 1975. Depths 0–30 m.	Copin-Montegut and Copin-Montegut 1983
Hawaii	HOT site during cruises 1988–1996 with cruise means for depths 0–100 m.	Karl (unpubl. data)
Sea of Japan	Stations (19) sampled during summer 1992. "Surface" samples.	Chen et al. 1996

expected value across the whole range of both variables. As is apparent from the logarithmic version of Eq. 1, this model can be tested statistically by examining the null hypothesis of slope = 1 in log-log space.

A different departure from constant ratios would be a systematic lack of fit of Model 1, which would indicate a more complicated underlying linkage between elements. For example, an alternative to Eq. 1 is a power function model,

$$\log Y = b + c \log X + e \qquad (2)$$

where X, Y, and e are as above and b and c are constants. In log-log space, Eq. 2 also produces a straight line, but the slope c is not constrained to equal 1. Where $c < 1$, Model 2 means that $Y : X$ is lower for higher values of Y and X. Model 2 represents one possible linkage between elements in which expected ratios vary predictably across the range of variables.

In general, "scale" in ecology refers to both spatial and temporal dimensions. Our analysis is based primarily on a spatially determined hierarchy. However, because spatial and temporal scales are often associated, our analysis probably also relates to temporal scales of observation too. Our analytical approach to detecting scale dependence in stoichiometric variables is to examine the data hierarchically. The largest scale of analysis is the entire data set. We examined the properties of the set of means of individual data sets, and we also considered the entire set of individual observations. A smaller observational scale then consists of partitioning the data into the four major habitats (small lakes, large lakes, coastal oceans, and offshore oceans). Finally, the smallest scale of analysis here is the data within individual data sets.

Statistics—In symmetric relationships such as those being studied here, there is no clear dependent and independent variable and there is no reason to assume deviations from a line fit to the data arise in just one of the two variables (McArdle 1988). When interest is in the value of the slope of a line fit to data or a test of whether the slope equals a specific value, ordinary least squares (OLS) regression slopes are biased (too shallow), except in specific, restrictive circumstances. Major axis (MA) or standardized major axis (SMA) estimations are procedures recommended for testing the null hypothesis that a slope equals some specific value in most bivariate line fitting in which residuals in both the x and y directions are relevant to the interpretation (Warton et al. 2006). In the specific

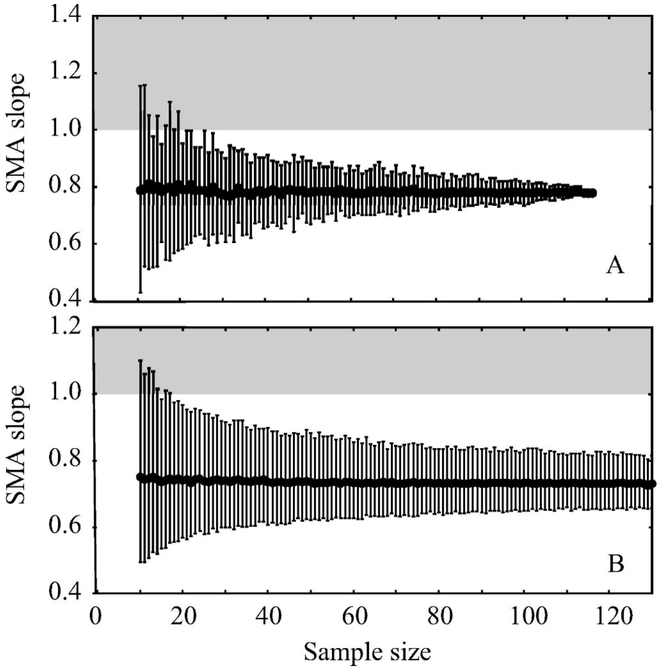

Fig. 1. Two example bootstrap analyses of SMA slopes fit to lake seston data. (A) Norway lakes: 100 draws of varying size (plotted on the *x*-axis) with no replacement. (B) North American lakes: 1,000 draws of varying size performed with replacement. Confidence limits that do not overlap 1 (shaded area) indicate good power to reject the null hypothesis. Other bootstrap results were very similar to these two.

case of a slope equal to 1, MA and SMA are equivalent tests. The software SMATR Ver. 2.0 (http://www.bio.mq.edu.au/ecology/SMATR/) was used to calculate SMA slopes and intercepts along with *p* values and confidence intervals.

Even in MA and SMA fitting, it is important to distinguish between "equation error" and "measurement error" (Warton et al. 2006). The former relates to deviations of true values from a straight line and the latter (which can be estimated from repeated sampling) refers to sampling variance plus analytical error. Measurement error (ME) can bias slopes in any line-fitting technique. McArdle (1988) suggested that one approach to dealing with ME is to regress both *y* on *x* and *x* on *y*; ME is always associated with the predicted variable. Thus, one of these assumes all the ME is in one variable and the other assumes it is in the other variable. The true slope must lie between the two estimates.

To examine the effect of sample size on significance testing in these data, SMA slopes were calculated by bootstrapping with and without replacement both the North American and Norway lakes data sets, drawing either 100 or 1,000 samples of different sizes. For all these comparisons, the SMA slopes were unbiased even with sample sizes as low as 10 lakes (Fig. 1). Also, the 95% confidence interval (CI) for the bootstrapping differed from one for sample sizes of approximately ≥20, indicating good power to detect slopes of <1 in these data.

Results

We first examined the stoichiometric ratios for the four different major habitat types compared with the classical Redfield ratio ($C_{106}:N_{16}:P_1$). We expected to see good correspondence to the Redfield ratio in the offshore ocean but poor correspondence in other habitats, especially freshwater. Mean C : P, C : N, and N : P in all the four major habitat types exceeded Redfield proportions (*t*-tests all $p < 0.001$), indicating that seston in all aquatic habitats on average was generally poorer in P and N relative to C and poorer in P relative to N than given in Redfield proportions (Table 2). As expected, freshwater seston ratios were higher than marine. The asymmetry of the underlying data is an important consideration, however. When medians are examined instead of means, correspondence of marine habitats to Redfield proportions is better (Fig. 2). Median C : N for offshore marine habitats in fact was exactly the same as the classical Redfield proportion of 6.6; C : P and N : P were only slightly elevated. Again, even in terms of medians, freshwater ratios were higher than marine.

For further description of the right tail of the seston C : P distribution, we also calculated the percentage of C : P ratios >300, a benchmark element ratio threshold above which some aquatic herbivores exhibit P-limited growth (Urabe and Watanabe 1992). The distinction in the fraction of freshwater versus marine systems was fairly clear with $C:P > 300$. All lake data sets contained observations >300. Lake Biwa had seston $C:P > 300$ in more than half of the observations; the next highest was the Toolik lakes data set with 35% of observations >300. Coastal systems in general had the lowest proportion of $C:P > 300$; all were <5%. Other systems, including oceans, were intermediate.

We next evaluated the constant ratio model at large spatiotemporal scale. Equation 1 provided a good fit to the set of site means (Fig. 3). At this scale of analysis, slopes of C versus P, C versus N, and N versus P (log-transformed) all are close to, and not significantly different from, 1. Slopes of 1 indicate no change in the expected value of seston ratio with increasing seston abundance. The best fit lines, however, were not consistent with the classical proportions. Again, C : P, C : N, and N : P were greater than classical Redfield proportions. The "mean" global seston ratio calculated from the anti-log of the intercepts of the regression equations in Fig. 3 is $C_{166}:N_{20}:P_1$.

We then considered seston ratios at successively smaller scales, and we found that Eq. 1 was often rejected. The differing models needed to describe seston nutrient linkages at different scales of observation indicate scale dependence in stoichiometric relationships. For both small lakes and oceans, slopes of log-transformed C : P, C : N, and N : P all were significantly <1 (Fig. 4). Large lakes and coastal oceans had a mixture of slopes, some >1, some indistinguishable from 1, and some <1. Slopes different from 1 on these plots mean one cannot extrapolate from one data set to another. For instance, at $P = 0.1\ \mu\text{mol L}^{-1}$, regression lines predict approximately two times more C in small lakes than oceans (19 vs. 8.8 μmol L^{-1} and C : P of 190 vs. 88).

Table 2. Stoichiometric ratios (mean, SD) and percent of observations with C : P higher than 300. For all three ratios in all four habitat types, means were significantly higher than the corresponding classical Redfield Ratio (one sample *t*-tests on untransformed data, $p < 0.001$). For medians and other descriptors of the data, *see* Fig. 2.

		C : P			N : P			C : N			
		Mean	*n*	SD	Mean	*n*	SD	Mean	*n*	SD	C : P (percent >300)
Classical	Redfield ratio	106			16			6.6			
Small lakes	Hokkaido	195	18	112	23	18	9	8.6	18	3.9	11%
	North America	212	130	134	22	130	12	10.0	130	2.9	17%
	Norway	239	116	188	23	116	16	10.4	116	2.8	21%
	Toolik	248	17	113	37	17	23	7.8	17	2.3	35%
	Combined	224	281	156	23	281	15	10.0	281	3.0	
Large lakes	Baikal	129	61	144	17	61	21	7.8	61	0.9	5%
	Biwa	329	76	134	39	76	18	8.8	76	1.6	57%
	Hövsgöl	266	25	68	28	25	7	9.8	25	2.2	16%
	Superior	176	133	98	19	82	8	10.5	82	4.9	12%
	Combined	225	4	89	26	4	10	9.2	4	1.2	
Coastal	Norway coastal	137	1546	82	19	1546	13	7.6	1549	5.0	2%
	Oslofjord	154	230	49	17	230	5	9.2	230	2.5	1%
	Riga	171	57	40	18	57	5	9.9	57	2.9	4%
	Yenisei	108	37	30	15	37	8	7.8	37	2.8	0%
	Combined	142	4	27	17	4	2	8.6	4	1.1	
Oceans	Atlantic	112	19	24	17	19	3	6.7	19	0.7	0%
	Bermuda	235	93	84		0			0		14%
	Indian	101	159	37	15	159	5	6.5	159	1.2	0%
	Mediterranean	202	50	65	26	50	10	8.3	50	3.3	10%
	Hawaii	128	62	29	19	62	6	7.2	62	3.1	0%
	Sea of Japan	153	30	99	16	30	10	9.3	30	2.4	10%
	Combined	155	6	53	19	6	4	7.6	6	1.2	

At the level of the individual data sets, the smallest scale considered here, the constant ratio model (Eq. 1) often failed to describe the data, indicating consistent shifts in stoichiometric ratios with changes in seston abundance. We examined both SMA slopes (±95% CI; Fig. 5) and the range of slopes given by OLS on *y* versus *x* compared with *x* versus *y* (Table 3). The two kinds of tests yielded similar, though not identical, results, and both tests rejected the null hypothesis of slope = 1 in numerous cases. Lack of fit of Model 1 to the data at this scale indicates not just the presence of variation, but systematic shifts in ratios with changed particle abundance. Systematically varying seston ratios were observed in all four major habitats but seemed to be most prevalent in small lakes and offshore oceans. For a small number of fits, standard correlation coefficients were low (<0.1), but SMA slopes were relatively high and did not overlap 0 (e.g., N vs. P for the Hawaii data). This apparent contradiction arose from modest sample sizes with influential datapoints. Little weight was placed on these ambiguous cases in forming our general conclusions from the data.

For C : P and C : N, the collection of slopes of individual data sets clearly favored values <1 (Fig. 5), which means that these two ratios often decline with increasing levels of seston abundance (lower C : P and C : N with increased seston nutrient concentration). The sets of slopes reported in Fig. 5 were tested against the null hypothesis of slope by *t*-tests for single samples; these were significant for C : P ($p < 0.001$, $t = -4.09$, df = 21) and C : N ($p = 0.01$, $t = -2.84$, df = 20), but not for N : P ($p = 0.9$, $t = 0.07$, df = 20). Surprisingly, and contradicting expectations on the basis of classical ideas, some of the shallowest slopes (greatest departure from the classical constant ratio model) were seen in oceans, indicating a nonconstant coupling of carbon to phosphorus and nitrogen in those environments, rather than the strict proportionality often assumed. Thus, at a local or regional scale of analysis, the constant ratio model often fails, even though the constant ratio model is excellent for the entire data set (Fig. 3, rightmost points in all panels).

Discussion

Overview—We found that mean seston macroelement ratios in both freshwater and marine habitats tend to depart from the classical proportion of $C_{106}:N_{16}:P_{1}$. Departures arose two different ways. First, the classical Redfield ratio might not represent the single best point estimates of seston element ratios. Depending on the choice of statistical descriptor, even in the offshore ocean, higher C : P and N : P values than represented in the classical ratio were observed. More fundamentally, however, within major habitat types or within single ocean basins, single nearshore marine sites, single large lakes, or regionally based sets of small lakes, elements are often not coupled through any single ratio of proportionality. Instead, these ratios often shift systematically with changed seston nutrient concentrations. In most cases, higher seston nutrients were associated with lower seston C : P and

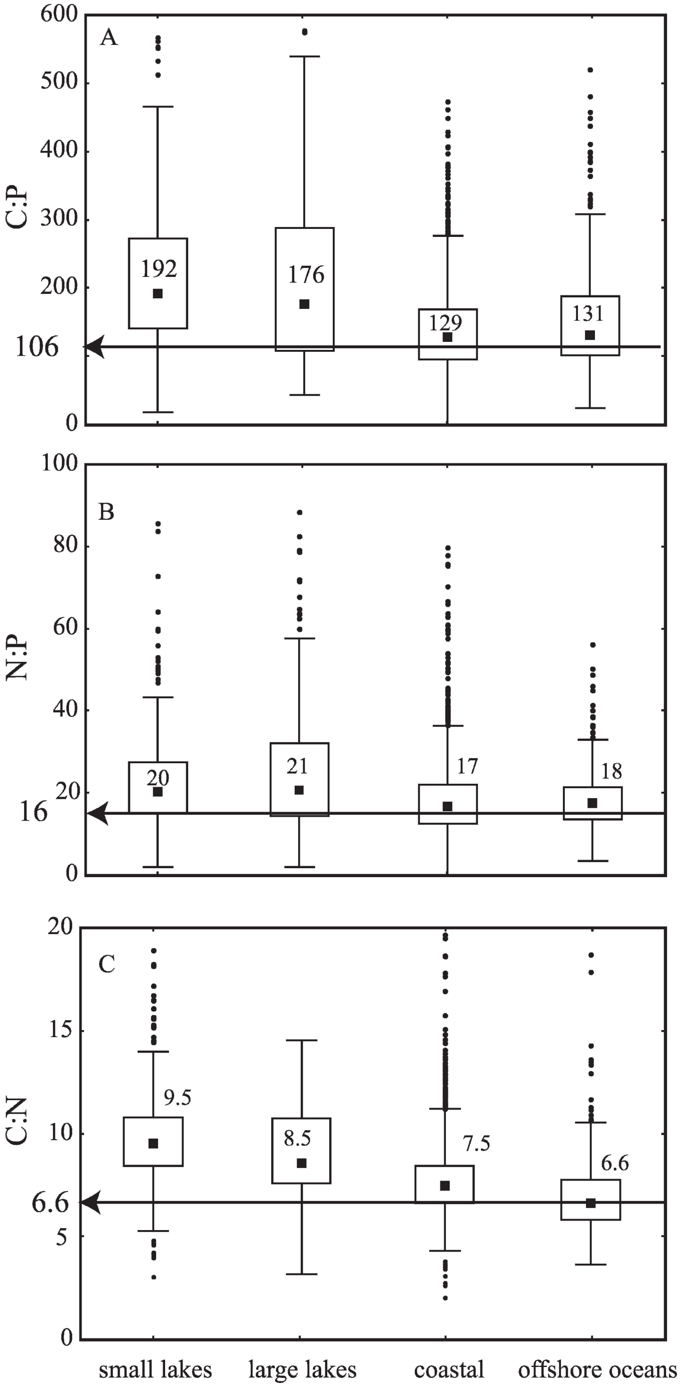

Fig. 2. Stoichiometric ratios by major habitat type. This figure presents the medians (filled squares and value) along with 10% and 90% quantiles. The Redfield ratio values are plotted on the left of each panel (indicated with an arrow). For means and statistical tests, *see* Table 2. (A) C : P, (B) N : P, and (C) C : N.

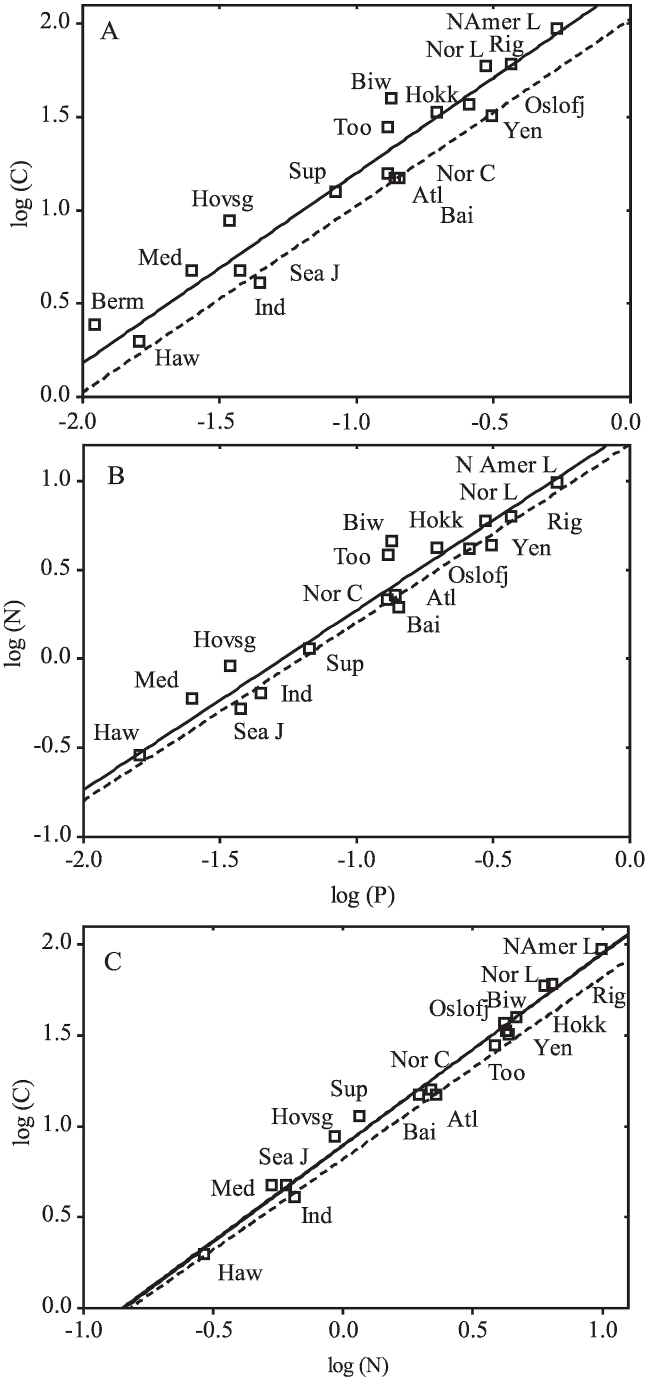

Fig. 3. Site means for seston C, N, and P. Solid lines indicate the SMA fits. (A) C versus P: the regression line is $y = 2.221 + 1.02x$ ($r^2 = 0.916$). (B) N versus P: $y = 1.284 + 1.01x$ ($r^2 = 0.931$). (C) C versus N: $y = 0.894 + 1.06x$ ($r^2 = 0.984$). The slopes are not significantly different from 1 (A: $p = 0.76$, $F_{1,16} = 0.096$; B: $p = 193$, $F_{1,15} = 0.008$; C: $p = 0.0907$, $F_{1,15} = 3.268$). The dashed lines indicate the classical Redfield proportions.

C : N. Biogeochemical studies at these regional scales could be improved by incorporation of a power function model (Eq. 2) rather than an assumption of constant (±error) proportionality.

Marine seston C : N : P—A great deal of effort has gone into resolving the stoichiometric relationships of nutrient recycling, export production, and other factors that all hinge on seston C : N : P ratios. In spite of a paradigm of constant ratios, questions have been raised repeatedly about the strictness with which Redfield C : N : P ratios appropriately characterize marine organisms (Sigman and

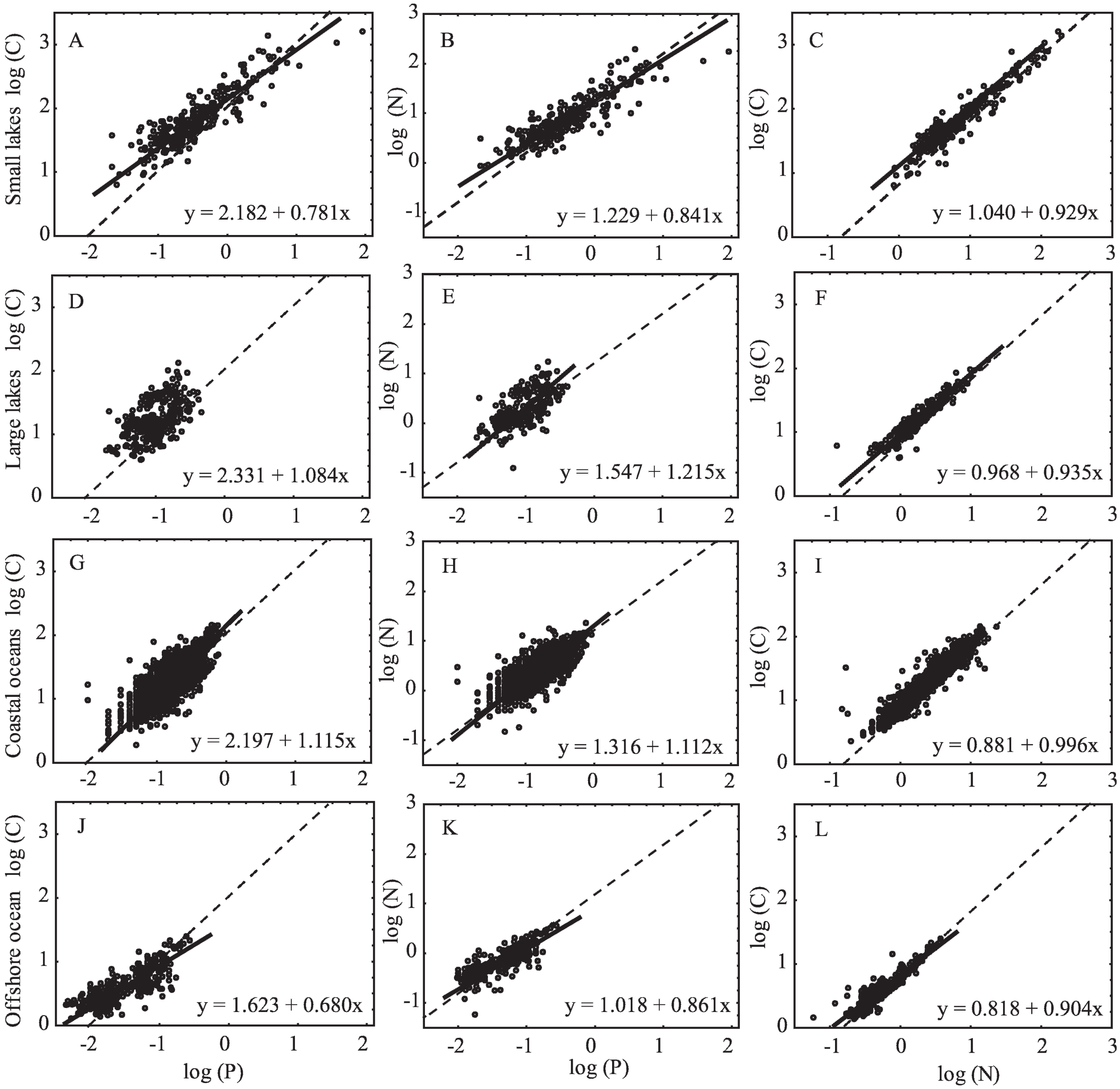

Fig. 4. (A, B, C) Seston chemistry within all small lakes, (D, E, F) large lakes, (G, H, I) coastal oceans, and (J, K, L) offshore oceans. The Redfield ratio for element pairs is indicated on each panel by dotted lines. SMA slopes were significantly different from 1 except for C versus P for large lakes (panel D) and C versus N for coastal oceans (panel I); SMA slopes significantly different from 1 ($p < 0.05$) are plotted as solid lines, and equations are given in the panels.

Boyle 2000; Arrigo 2005). Shifts in marine C : P ratios in organic settling debris of only 30% (i.e., from the Redfield ratio of 106 to 138) result in globally significant shifts of C storage in ocean deep waters (Broecker 1982; Heinze et al. 1991). Allowing for variable seston C : N : P ratios improves modeling of mixed-layer dynamics in the subtropical surface ocean (Christian 2005), suggesting variable ratios must be considered to capture certain aspects of system dynamics. All of the above questions are potentially crucial in understanding atmospheric CO_2 uptake into aquatic ecosystems, sinking flux of fixed C, and, potentially, the long-term storage of C in marine and fresh waters (Heinze et al. 1991; Riebesell et al. 2007). Progress in this area is hindered because few systematic examinations of seston C : N : P have been made in the world's oceans. Better documenting the constraints and patterns of variability in seston C : N : P ratios will help improve our understanding of marine and freshwater environments exposed to large perturbations to carbon and nutrient cycling.

As expected, seston ratios were generally closer to the Redfield Ratio in the open ocean than in small or large lakes. Even in oceans, however, mean and median seston C : N : P differed from Redfield proportions. Although particulate P is not often measured in the ocean, particulate C and N are, and a study that looked at more than 10,000 observations of particulate C and N in the ocean also reported a higher C : N than the Redfield ratio (Schneider et al. 2003). In spite of continued reliance on the Redfield

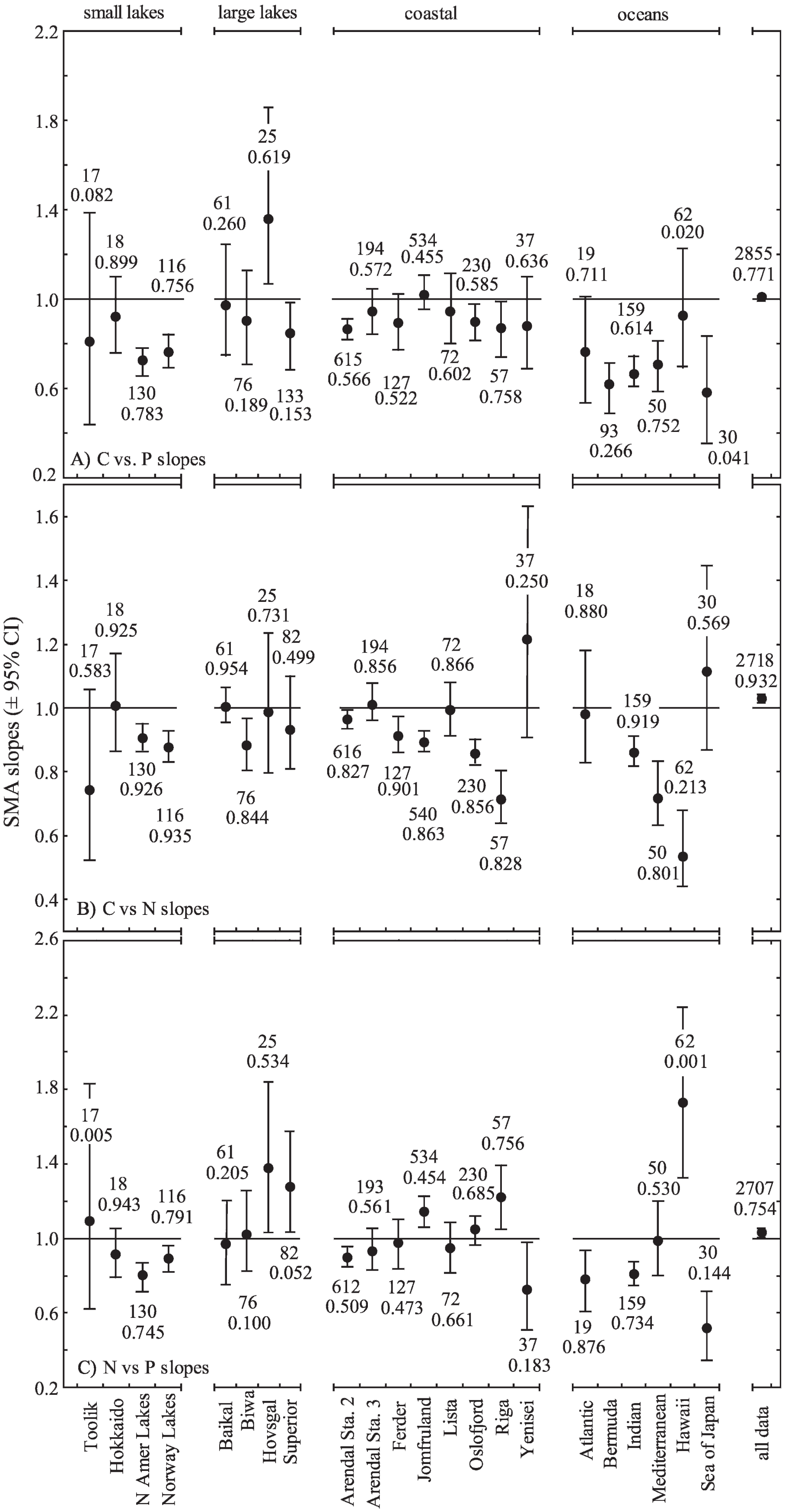
small lakes
large lakes
coastal
occeans
SMA slopes (± 95% CI)
A) C vs. P slopes
2.2
1.8
1.4
1.0
0.6
0.2
17 0.082
18 0.899
130 0.783
116 0.756
61 0.260
25 0.619
76 0.189
133 0.153
615 0.566
194 0.572
127 0.522
534 0.455
72 0.602
230 0.585
57 0.758
37 0.636
19 0.711
93 0.266
159 0.614
50 0.752
62 0.020
30 0.041
2855 0.771
B) C vs N slopes
1.6
1.4
1.2
1.0
0.8
0.6
0.4
17 0.583
18 0.925
130 0.926
116 0.935
61 0.954
76 0.844
25 0.731
82 0.499
616 0.827
194 0.856
127 0.901
540 0.863
72 0.866
230 0.856
57 0.828
37 0.250
18 0.880
159 0.919
50 0.801
62 0.213
30 0.569
2718 0.932
C) N vs P slopes
2.6
2.2
1.8
1.4
1.0
0.6
0.2
17 0.005
18 0.943
130 0.745
116 0.791
61 0.205
76 0.100
25 0.534
82 0.052
612 0.509
193 0.561
127 0.473
534 0.454
72 0.661
230 0.685
57 0.756
37 0.183
19 0.876
159 0.734
50 0.530
62 0.001
30 0.144
2707 0.754
Toolik
Hokkaido
N Amer Lakes
Norway Lakes
Baikal
Biwa
Hovsgal
Superior
Arendal Sta. 2
Arendal Sta. 3
Ferder
Jomfruland
Lista
Oslofjord
Riga
Yenisei
Atlantic
Bermuda
Indian
Mediterranean
Hawaii
Sea of Japan
all data

Table 3. Data sets with range of slopes (tested as *x* vs. *y* and 1/[*y* vs. *x*]) not overlapping 1. Most slopes were <1 except for those marked with an asterisk (*). These are similar, but not identical to the databases with SMA slopes not overlapping 1 (Fig. 5).

C : P	
Small lakes	Hokkaido
	North America
	Norway
Oceans	Atlantic
	Indian
	Mediterranean
	Hawaii
C : N	
Small lakes	Toolik lakes
	North America
	Norway
Large lakes	Biwa
Coastal	Ferder
	Jomfruland
	Oslofjord
	Riga
Oceans	Mediterranean
	Hawaii
N : P	
Small lakes	Hokkaido
	North America
Large lakes	Hovsgal*
Coastal	Riga*
	Yenisei
Oceans	Atlantic
	Indian

ratio to represent linkage of carbon and nutrients in oceanic studies, suspended particulate matter is generally more carbon rich, or less concentrated in both N and P, than represented in the classical 106 : 16 : 1 proportionality. The results presented here showed that studies assuming classical Redfield proportions for seston chemistry is subject to some error and the seriousness of the error depends on the given waterbodies or the scale of analysis.

Seston chemistry in other habitats—Freshwater seston tends to have higher C : P, N : P, and C : N ratios than marine seston. Our numbers compare well with the previous largest compilation of seston C : N : P ratios (Elser et al. 2000, as summarized in Sterner and Elser 2002). Our means for lakes and oceans are within 12% of the previously reported means except for N : P for small lakes, for which the numbers reported here are 30% lower than in the Elser et al. (2000) compilation. Our new compilation helps resolve patterns in nearshore compared with offshore oceans, which hasn't been explicitly addressed before, and in large compared with small lakes, which was also considered by Hecky et al. (1993). Although differences among all habitats were statistically significant, to a first approximation, mean and median seston ratios were most contrasting across freshwater compared with marine habitats. Large lakes were more like small lakes than oceans, and nearshore marine habitats were more like offshore marine sites than inland, freshwater sites (Figs. 2, 4). Hecky et al. (1993) attributed the high lake C : P and C : N ratios to in-lake processes rather than atmospheric or streamborne particles, but the importance of detrital carbon in influencing these seston ratios is still not well worked out and could contribute to the freshwater–marine comparison.

Scale dependence—Like numerous other ecological variables (Levin 1992), functional linkages among elements can depend on the scale of analysis. We found that at the broadest scale we could examine with our data, a constant ratio model for seston C : N : P ratios is appropriate, although the absolute values of the ratios differ from classical values. This is observable in the closeness of slopes to a value of 1 in the data averaged by site (Fig. 3) and in the fit of individual observations across the entirety of the data set (Fig. 5, "All data").

In contrast, at smaller scales, the constant ratio model often failed. Only three individual data sets (Baikal, Arendal Sta. 3, and Lista) out of 22 were consistent with the constant stoichiometry model (Eq. 1) with the use of all statistical evaluations performed on all ratios. Both freshwater and marine habitats often exhibited lower C : P and C : N with increasing seston abundance, even if those site means fell along a constant ratio line (Fig. 6).

Although previous studies have emphasized the contrasts in the stoichiometry of marine and fresh waters, our new analysis also reveals an underlying functional similarity. Analysis of site means (Fig. 3) emphasizes the overall similarity of C : N : P in seston, regardless of the habitat. More importantly though, the strong propensity for all of these systems to show reduced C : P and C : N at higher levels of particle density potentially indicates a common set of mechanistic forces at work. A simplistic view that seston ratios are constant in oceans but variable in lakes clearly does not capture the full picture. Because of the power model relationships, for instance, we would expect more variability in seston ratios where the range of seston abundances in greatest, regardless of habitat type. Note in Fig. 3 that oceans generally have a lower range of particle abundance than small lakes—this reduced range of particle abundance contributes to the already-described difference in variability in seston ratios in marine compared with fresh waters. In some of these sites, the functional coupling

←

Fig. 5. SMA slopes with 95% CIs for individual sites as well as the entire data set. Samples size and correlation coefficient (r^2) also are given. The cases with slopes different from 1 in an OLS test using *y* versus *x* and *x* versus *y* are similar but not identical to those with confidence limits not overlapping 1 (Table 3). (A) C versus P, (B) C versus N, and (C) N versus P slopes.

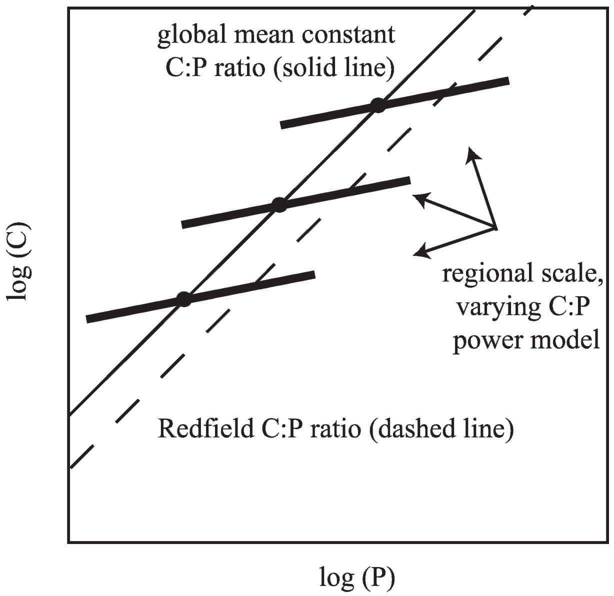

Fig. 6. Conceptual diagram indicating the scale-dependent linkages of carbon and phosphorus (C vs. N would be similar). Means across sites fall along a constrained, constant ratio line of slope = 1, slightly higher than the classical ratio. In contrast, linkages within sites are more complex and exhibit systematic shifts in ratios.

(slope) differs greatly from constant ratio expectations, but the limited range of variables means that not much of this potential variability is realized.

The scale-dependent relationships we observed resemble patterns observed in terrestrial environments (McGroddy et al. 2004). At the biome level, foliar and litter C : N : P relationships fit a constant ratio model, whereas within individual biomes and ecosystems, more complex linkages were observed. To a first order, and given the looseness of connection of seston abundance versus primary production, within habitats, more productive ecosystems in both terrestrial and aquatic realms seem often to exhibit higher nutrient content at the base of the food chain than is seen at lower production, but this is true only within habitats, not necessarily across them. The seeming ubiquity of these statistical patterns suggests an underlying functional similarity in ecosystem linkage of macroelements in biomass.

Modeling—We conclude that the best statistical model to describe macroelement proportions in particulate matter in both freshwater and marine systems depends on the scale of interest. At large spatiotemporal scales, a constant ratio model—richer in C and poorer in N and P than the classic Redfield ratio—is appropriate. At this scale, the intrinsic similarity of these ecosystems and a common biological stoichiometry shines through.

At regional or smaller scales, a model more appropriate than constant element proportions is one based on power functions

$$\text{seston C : N : P} = \alpha C^{\beta} : \gamma N^{\delta} : P \qquad (3)$$

in which the two exponents are generally <1. The power function model above describes the data faithfully and indicates that C : P and C : N generally decline with increasing particle abundance and therefore to a first approximation with ecosystem trophic status. At the present state of development of this statistical model, we cannot advocate any one set of parameters for Eq. 3 to fit all circumstances. Figure 5 gives representative values for the exponents in this model.

Mechanisms and implications—This study was aimed primarily at revealing the most appropriate phenomenological statistical model to represent C : N : P linkages in particles suspended in water columns. The underlying mechanistic processes resulting in those patterns are still somewhat mysterious.

Systematic increases in nutrient content (i.e., lower C : P and C : N) with increasing productivity or biomass have been discussed before in the context of changing nutrient use efficiency in ecosystems, particularly in terrestrial systems (Vitousek 1982), but also more recently in aquatic systems (Sterner and Elser 2002). Shifting nutrient use efficiency is an alternative to the constant stoichiometry model of Redfield. Reduced nutrient use efficiency at higher productivity could arise because of the introduction of other limiting factors (light or other nutrients) when any given nutrient becomes high in concentration. In water columns, higher seston abundance will reduce light levels because of self-shading. Lower light in turn will generally depress C : P and C : N (Sterner and Elser 2002). Shifting nutrient use efficiency provides an explanatory framework to understand the data at the regional scale; but how then is Redfield balancing of C : N : P occurring at the largest scales?

To explain the scale dependence in stoichiometric relationships, we advance here the "biogeochemical mosaic" hypothesis. This hypothesis explicitly recognizes that different critical biogeochemical processes such as N fixation and denitrification occur under contrasting conditions and often are spatially separated. For instance, N fixation might be localized mainly to the Atlantic Ocean, but denitrification occurs in low-oxygen regions such as the Indian Ocean (Gruber and Sarmiento 1997). Separation of these processes occurs in lakes as well and other aquatic habitats. The stoichiometric balancing of elements first hypothesized by Redfield thus should be associated with larger scales of observation, as we found they are. At small scales of observation, only a subset of the entire biogeochemical mosaic is present and other forces, such as shifting nutrient use efficiency, take precedence.

This study provides an updated view on the functional linkages among macroelements in freshwater and marine water columns. Our findings do not of course reject the seminal conclusions of Redfield about the oceans, but they do add some subtlety and nuance. Even small departures of nutrient ratios from the classical proportions can have large consequences at the scale of global modeling because of the vast mass of material involved. Furthermore, the use of the power function rather than a constant ratio should likely result in improved analysis at the level of any given ecosystem.

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