Element Ratios and Aquatic Food Webs

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ABSTRACT: Organic matter is the result of concentrating a few non-metals that are relatively rare in the earth's crust. Most of these essential elements are in a rough proportionality within phylogenetic groupings. Life is thus working against a concentration gradient to extract or accumulate these elements, and this metabolic work is accomplished in interrelated and often subtle ways for many other elements. The physiological requirement to sustain these elemental ratios (commonly discussed in terms of the N:P ratios, but also C:N, C:P, and Si:N ratios) constrains organization at the cellular, organism, and community level. Humans, as geochemical engineers, significantly influence the spatial and temporal distribution of elements and, consequently, their ratios. Examples of these influences include the changing dissolved Si: nitrate and the dissolved nitrate:phosphate atomic ratios of water entering coastal waters in many areas of the world. Human society may find that some desirable or dependent ecosystem interactions are compromised, rather than enhanced, as we alter these elemental ratios. Human-modulated changes in nutrient ratios that cause an apparent increase in harmful algal blooms may compromise the diatom-zooplankton-fish food web. It will be useful to improve our understanding of aquatic ecosystems and for management purposes if the assiduous attention on one element (e.g., N or P) was expanded to include the realities of these mutual interdependencies.

Introduction

This brief paper is about the ubiquitous influence of element ratios in aquatic food webs, an influence that transcends the metrics of individual element loading rates or concentrations. It begins with a discussion of the evolutionary origins of element stoichiometry that establishes their unmitigated influence on organic composition. Some of the early ideas about elemental ratios are reviewed to document their usefulness, even when only partially developed. Recently developed examples of how ecosystems and their parts behave from a stoichiometric perspective are then introduced, including a separate discussion of silicon (Si). It ends with some observations of how human-mediated changes in elemental flows have implications for understanding ecosystems. The major perspective of this paper is how the reciprocity of elemental flows in ecosystems produces inescapable constraints on aquatic ecosystems. Most of these generalities are not new (sensu Morowitz 1968), but they are worth occasionally restating them within a modern context, which is what I attempt here. The discussion is limited to carbon (C), nitrogen (N), phosphorus (P), and Si, but could be fruitfully expanded with additional data and space.

Life’s Elemental Consequences

There was no oxygen in the Earth’s original atmosphere ca. four to five billion years ago. The atmosphere then was an anaerobic mixture of mostly NH₄, CO, CO₂, H₂, CH₄, N₂, and water vapor. Somehow, life on Earth began and evolved about a billion years later. Life forms creating and using gaseous divalent oxygen began their ascendency about 2.3 billion ybp, but the toxic effects of oxygen for anaerobes were avoided as anaerobic metabolism became isolated within cells, a kind of metabolic refuge or strategic retreat. Gradually the Earth’s thin surface layer became transformed, and not just in terms of its oxygen content, but also for many other elements.

The evolving organic matrix on the Earth’s surface turned out to be quite different from the Earth’s crust. About 99% of the Earth’s crust consists of 46.4% O, 28.2% Si, 8.2% Al, 5.6% Fe, 4.2% Ca, 2.4% Na, 2.3% Mg, and 2.1% K. All of these eight are metals, except oxygen. In contrast, the organic matter in plants is mostly comprised of nine macronutrients: 44.5% C, 42.5% O, 6.5% H, 2.5% N, 0.3% S, 0.2% P, and three alkali or alkaline earth metals (1.9% K, 1.0% Ca, and 0.2% Mg). Organic matter is thus the result of concentrating the relatively rare non-metals in the earth’s crust. Plant nutritionists have identified additional elements known as micronutrients which are required for plant growth, but found in reduced quantities (Cl, Si, Mn, Na, Fe, Zn, B, Cu, Cr, Mo, and Co). Through an analysis of their functional role in plants and on an inter-elemental correlation analyses of their occurrence, Markert (1994) suggested that, in addition to the 11 elements mentioned, many other elements will be found to be essential for some organisms once measurement issues are resolved. Si (to be discussed later), for example, is

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essential for diatoms, but is not significant in most higher plants, and, Ca, B, and Cl are not considered essential in some bacteria and fungi (Markert 1998). The concentrations of these essential nutrients in plant biomass are highly correlated \( r^2 > 0.8 \) with one another in the aggregate, as well as in different proportions within phylogenetic groupings (Markert 1994).

The concentration of elements and the evolution of elemental ratios in organic matter tells us quite a bit about the quantities and diversity of life forms. It tells us that life is working against a concentration gradient to extract or accumulate these elements, and that this metabolic work is not done element by element, but simultaneously in inter-related and, perhaps, subtle ways for many elements. The implication of this simple observation is that affecting the availability of one element will have consequences for individuals and populations. The result is that the evolution of life’s biogeochemistry has yielded a reciprocal arrangement of abiotic and biotic parts whose status and functional abilities are co-dependent.

The examples discussed below are meant to illustrate how this reciprocity is reflected in the proportionality of elements moving into, accumulating within, and moving out of the biochemical packages (which are not inert machinery, as sometimes described, because they are capable of inventive adaptation) ranging from cells to ecosystems. I use examples from the aquatic sciences, because of the aquatic emphasis of this journal. The general issues, I think, should be applicable to all ecosystems (and at many scales) and are important in the management of ecosystems.

**Early Quantification of Elemental Stoichiometry in Aquatic Food Webs**

Results from early quantifications of ecosystem stoichiometry have had such profound influences on our understanding of aquatic systems that further work on the subject seems eminently worthwhile. Redfield (1973) had some keen insights about these biotic-abiotic relationships which began with measurements of nitrate and phosphate in the ocean. When Redfield looked at some results of chemical analyses to determine the concentration of phosphate, nitrate, and carbonate C above 1,000-m depth in the western Atlantic Ocean, he observed that the concentration of C, N, and P not only changed with depth, but that these changes also varied proportionally. The ratio of the newly appearing C, nitrate, and phosphate was the same in the organisms originally in the surface waters before they sank to deeper waters, undergoing decomposition along the way (Fig. 1). These ratios became known as Redfield ratios. Redfield (1973, p. 14) said that his ideas about nutrient ratios:

> “sprung entirely from my teaching of physiology. Where one could determine, by measuring the nitrogen in the urine, the oxygen and carbon dioxide exchange in the lung . . . the idea was what the body gave out was a product of what it was burning. And it was burning things in a perfectly definite proportion.”

Redfield (1958 p. 14) noted the generality of these observations:

> “It is a recognized principle of ecology that the interaction of organisms and environment are reciprocal. The environment not only determines the conditions under which life exists, but the organisms influence the conditions prevailing in their environment” (Note that this paper has a ratio of 1:15:105::P:N:C. Richards [1958] added silicate to the list and slightly modified the ratios, which were determined to be 1:16:16:270::P:Si:N:O).”

Redfield (1938) distinguished between two different nutrient ratios based on the concentration of an element and the amount of that element released by the organism upon death. His idea was about the products of decomposition, which were determined by knowing the concentration of nutrients in the surface waters and in the water with the decomposing organisms. It was the change in the constituents that he monitored and drew his conclusions from, not the in situ concentration of the elements. The release of elements upon death is in nearly constant proportions, but may be dif-
ficult to observe amidst the confounding influence of other factors, including a relatively low rate of change compared to initial concentrations. The in situ concentration was the result of a continuing dance conducted under the influence of various biotic and abiotic conductors. It was the elemental ratios of the changes in concentration that were similar to the cellular constituents.

Redfield (1973) thought it the most important idea that he'd ever had, and it appears to be his most famous idea. It has been broadly applied to other locations and ecosystems because it was documented well, presented persuasively at the right time and place, and has robust practical and theoretical usefulness. Support for the idea of growth limiting nutrients sprang from these relationships. Because an organism was composed of elements with certain proportions relative to one another, the uptake of these same elements might be affected by the balance between protoplasmic demand and external availability. If a nutrient concentration was sufficiently high to overcome substrate limitations (and not too high to inhibit—a rare circumstance), then one element and not another might limit growth if its supply (or loading) was low enough, for example, under the influence of varying light, temperature, turbulence, or a third element. A system or organism might be influenced by these changes as it moved vertically or horizontally, or remained in place. Species extirpation and exploitation might accompany these adjustments which occur everywhere in the microscopic to the macroscopic worlds. Species live in relationship to the elemental supply of not one element, but of a matrix of elements. This perspective can be much more realistic than an approach that includes only the flow of energy among various ecosystem parts. It still undervalues the complexity of ecosystems if only because the behavior of organisms is not included (e.g., Verity and Smetacek 1996; Dayton and Sala 2001). It also provides some insights that single-element perspectives do not.

Element Stoichiometry in Cells and Ecosystems

Three simple observations about food webs contribute to understanding food web stoichiometry: nutrient deficiency is commonly observed for primary producers and consumers, all predators require food, and prey are a heterogeneous mixture of nutrients. Although the following examples come from freshwater systems rather than marine systems, because they are a ready source for many parts of freshwater lakes, the discussion is intended to be appropriate for all aquatic ecosystems. This is not an unreasonable conclusion for many reasons, including the observation that both freshwater and marine systems behave similarly to changing N and P concentrations and ratios (e.g., Guildford and Hecky 2000).

Cellular Level

Cellular organelles (e.g., nucleus, ribosomes, membranes, mitochondrion, etc.) are not stoichiometrically equal, which implies that their balance must be considered in view of all processes of the entire cell. The variation in their N and P content may range from 9% to 15%, and from 0.3% to 5%, respectively, creating N:P ratios ranging from >100:1 to 5:1 (Elser et al. 1996). The functions of organelles are therefore dependent on the supply and turnover of elements, and may not be able to perform their tasks as well if the rest of the cell does not have sufficient elemental resources and in the right combination. Rapid growth in prokaryotes, for example, requires ribosomal DNA (for cell division), which has a relatively higher P content and lower N:P ratio than eukaryotic ribosomes. Faster growing organisms contain more ribosomal RNA which is rich in P. Slower growth results in a lower percent P in the whole organism, and a higher N:P ratio. If P is in sufficient supply, then the C:N ratio may reflect the growth rate, e.g., in algae (Fig. 2). These elemental relationships might change during different growth stages.

Predators and Prey

Predators and prey have different nutritional requirements which affect element recycling rates,
element ratios, and organism growth efficiency. Because plants are relatively enriched in C compared to predators, the plant’s energy can be used by consumers to accumulate nutrients. If nutrients are deficient, the ingested plant’s energy may be dissipated by the consumer rather than within the larger food web; the consumer may even abandon one prey search pattern for another. The human equivalent might be a sandwich: the hungry among us will eventually search for at least a minimum level of quality and amount of food to be put between the two slices of bread, or we will search for alternative food. Plath and Boersma (2001) provide a freshwater example. They examined the nutritional quality of algae fed to Daphnia magna, a freshwater crustacean. They experimentally altered the P content of the algae and examined the response of Daphnia in terms of its growth parameters. The variations in the C:P ratio of the algae affected Daphnia growth rates which were greatest at an intermediate level (Fig. 3). A lower nutritional quality of food was compensated for by a higher feeding activity (not shown), however. Plath and Boersma interpreted these results to demonstrate that the energy in the C bonds was used to acquire the P in short supply. Plath and Boersma (2001, p. 1267) carried these observations further, noting that there will be consequences of this differential uptake efficiency for microbes: “As excess carbon most likely mainly dissipates as carbon dioxide, it will not be available to other trophic levels, and hence we could not expect a higher bacterial biomass in phosphorus-limited systems.”

**Consumer Competition**

The variations in element recycling rates affect a species’ elemental ratios and possibly the result of interspecific competition. Main et al. (1997) showed how differences in freshwater zooplankton N:P ratios are related to their specific growth rates. Compared to calanoid copepods, Daphnia have a higher grazing rate, grow faster (higher P content), and have a lower N:P ratio. While feeding on food with a low N:P, calanoid copepods will recycle ingested food (as a by-product) at an even lower N:P ratio than that in their food. In this way a calanoid copepod will preferentially retain the relatively scarcer N. Daphnia, which have a lower N:P ratio, recycle ingested food with a relatively higher N:P ratio than is in their food, and recycle P with less efficiency. Calanoid copepods recycle the N in their food resources efficiently if N is scarce, resulting in the conservation of limiting nutrients (Sterner 1990). These differences in energy and nutritional costs can determine the outcomes of interspecific competition.

**Food Webs**

Elser et al. (1988) provide an example of how the behavior of predators can change the N:P ratios of food webs in lakes. They manipulated the zooplankton food web in two freshwater lakes by controlling zooplankton predators (i.e., minnows), and indirectly affected phytoplankton growth limitation because of the altered N:P ratio in the recycled materials. They accomplished this result by adding or removing bass which fed on the minnows (minnows prefer Daphnia magna over the alternative food source, a calanoid copepod; Fig. 4). As described in the previous example, Daphnia grow faster than calanoid copepods, and have a relatively higher P content (higher rRNA requirement). The accumulation of P results in a lower N:P ratio for the zooplankton community. Compared to calanoid copepods, Daphnia is a relatively poor recycler of P, and its presence or absence determines if the N:P ratio available to phytoplankton is higher or lower, respectively. When bass are present, they graze on the minnows who prey on Daphnia. The result is that when bass are added, then...
minnow grazing of Daphnia declines, the Daphnia population increases and stores P, and phytoplankton growth limitation changes from N to P limitation. It was the presence or absence of Daphnia, controlled by predation, that changed the N:P ratio in the zooplankton community and thus affected the phytoplankton community composition.

Direct stoichiometric control by fish is also observed. The percent N and P in four different cyprinid fish species were examined by Sterner and George (2000) who were interested in the degree to which these ratios varied in relationship to the quality of their fishes food supply. Sterner and George concluded that the C:N:P ratios of the predators were more constrained than the food they ate, meaning that the predator had to actively control its diet. They provide the example of a fathead minnow (Pimphales promelas) which consumed food with a C:N ratio ranging between 7 and 10.5, but whose whole-body C:N ratio was a relatively constant 15. The homeostatic control had to arise from differences in either N uptake or retention, or from lower gross growth efficiency. The N:P ratio in minnows and their food was similar, but varies among major fish species (Fig. 5), in part because of size, but also because of the proportional amount of bone structure. Assuming that their results apply generally, they concluded that the homeostatic modulation of nutrient flux by fish has an energetic cost arising from variations in food quality, which influences algal species composition. Other feedbacks can extend to beyond the feeding site if fish recycle nutrients back to their environment in different elemental ratios or even locations from the initial uptake site. Migratory fish, for example, provide significant amounts of P and N to freshwater and marine habitats (Krokhin 1975; Durbin et al. 1979; Helfield and Naiman 2001; Finney et al. 2002).

Microbes

We may focus attention on the large or charismatic organisms, but it is worthwhile to consider that the regulation of elemental ratios within aquatic food webs is strongly influenced by microbes, if only because they may dominate ecosystem biomass, the numbers of organisms, and the total ecosystem C flow (Pomeroy 2001). To paraphrase Karl (1999; cited by Pomeroy 2001): “Fish swim in a sea of microbes”. Energetically, bacteria are directly dependent on the organics leaked from cells (e.g., dissolved organic matter leachates from phytoplankton) or lost when membranes are compromised (e.g., from the sloppy feeding of zooplankton or as a result of viral infection). Both fish and phytoplankton are also dependent on microbes because elemental recycling and re-absorption is dependent on, or passes through, microbes. A result of microbial death and growth is the return of nutrients to phytoplankton or the assimilation by microbial predators. Phytoplankton, microbes, and mesozooplankton (for example) seek their own elemental equilibrium with each doubling, and these doubling rates vary enormously. Compared to eukaryotes, the percent P of bacteria plasmalemma and ribosomes is three and two times higher, respectively (Elser et al. 1996) and the doubling rate of bacteria can be less than 1 h compared to 2 wk for zooplankton. The microbial community thereby indirectly affects food webs through a cascading series of influences that include regulation of element flows.

The Stoichiometry of Silicate

Understanding the role of Si in aquatic food webs is of special interest for several reasons, and notably so because of diatom-zooplankton-fish food webs.

Si is 28% of the Earth’s crust, but the content in most plant material is less than 0.1%, with a few important exceptions. Before the Paleozoic (ca. 570–225 × 10⁶ ybp) there was no biological precipitation of silica (Siever 1992). The silica cycle before then was dominated by non-biological reactions among minerals, organic matter, and dissolved silica. Then, as now, the amount of silica loading to aquatic systems was controlled by tectonic activity, weathering, and hydrothermal seep activities. Sponges, radiolarians, and silica-secreting plants first appeared in the Paleozoic, long before diatoms arrived in the Cenozoic (65 × 10⁶ ybp) and began to control the oceanic silica cycle.

Dissolved silicate is absorbed by diatoms to form the frustule, which is the external structure that can be quite beautiful and distinctive. Conley et al. (1989) assembled data on the silica content of di-
atoms and found that freshwater diatoms average one order of magnitude more silica per biovolume than marine diatoms (Fig. 6). Differences in the relative availability of silica in freshwater and marine systems might explain these disparities. Marine and freshwater diatom uptake of silica and growth depends on the silica content in the culture medium (Guilland et al. 1973; Paasche 1973; Tilman and Kilham 1976). Freshwater systems usually have a much higher concentration of silica than oceanic systems (typically < 2 μM silicate in the open ocean), so evolutionary pressures favor lightly silified marine diatoms. Conley et al. (1989) concluded that the half-saturation constants for the uptake of dissolved silica for marine species are an order of magnitude lower than those of many freshwater species. An additional consideration is that, unlike freshwater systems, re-entry into the upper mixed layer is difficult once marine diatoms sink out of the photic zone. The movement of the silica-bearing frustules and enclosed organic matter thus is a significant mechanism for element transfers within oceans.

Some evidence that the concentration of silicate is an important determinant of diatom abundance arises from field experiments by Egge and Aksnes (1992). These investigators studied the development of coastal phytoplankton communities in floating enclosures positioned near Bergen, Norway. They added various combinations of nutrients with and without silica to 11-m³, 4-m deep plastic bags and found that diatom dominance (usually Skeletonema costatum Grev. Cleve) occurred if the silicate concentration was above an approximate threshold of 2 μM, regardless of season (Fig. 7). Phaeocystis sp., a flagellate, appeared after a diatom bloom, but never when silicate concentrations were high. Diatom growth was 5% to 50% higher than flagellate growth when silica was not limiting. This growth rate is consistent with a literature review by Furnas (1990) who concluded that diatoms, under non-limiting conditions, have a much higher growth potential than non-diatoms, with a maximum in situ doubling rate of between 2 and 4 times daily, but that non-diatom growth rates are generally below 2.5 doublings per day. An important conclusion here is that diatom growth can be limited by the concentration of silicate, independent of the silicate : nitrate ratio.

The invention of diatoms had important consequences for the global cycling of other elements. Tréguer and Pondaven (2000) have argued that the increased supply of silica-containing dust to the oceans during the last glacial maximum (ca. 18,000 ybp) resulted in enough additional diatom production to explain how the atmospheric CO₂ concentration dropped to 40% below present. This was a result, they argue, of the increased C sequestration in oceanic sediments through the favoring of the diatom growth over that of non-diatoms, and the subsequent lower recycling rate of plankton production back to the atmosphere.

Officer and Ryther (1980) proposed that Si is often the controlling nutrient determining whether an estuarine or marine phytoplankton community is composed of either diatoms or non-diatoms. The diatom based food web was described as contributing to desirable fishable populations and the non-diatoms to a flagellate ecosystem that often (but not always) was poor food for most grazers.
and the motile species were able to concentrate to undesirable concentrations, some of which were toxic or noxious. Richards (1958) used approaches similar to those of Redfield (1934) to determine that Si and N are incorporated into diatoms at a 1:1 atomic ratio, which reflects the Si:N in their protoplasm. Officer and Ryther (1980) noted that dinoflagellates increase following silica depletion in many systems and noted the varying and important differences in the recycling rates of Si, P, and N, but made no specific mention of Si:N ratios. Smayda (1990) did take notice of their importance, however. He reviewed the empirical coincidence of higher N and P nutrient loading, declining Si:N and Si:P ratios, and increasing world-wide incidence of often recurring blooms of non-siliceous phytoplanktonic groups, including harmful algal blooms (HAB). He developed the strong inference that nutrient ratios and the appearance of nuisance phytoplankton blooms were causally related. The results of many recent field experiments, in which nutrient loading rates have been experimentally-manipulated, support Officer and Ryther’s (1980) and Smayda’s (1990) conclusions (Table 1): the addition or reduction of silicate supplies results in a rise or fall in diatom abundance; the Redfield ratio of Si:N::1:1 is a sensitive pivot point below which diatoms, their predators, and zooplankton fecal pellet production declines precipitously; and the flagellate food web is competitively enabled when the Si:N is < 1:1, and may contain noxious or toxic phytoplankton. Changing either the supply of Si or the ratio of Si:N can, it seems, have quite dramatic effects on these aesthetically and economically important aquatic food webs, which also include avians and mammals.

A World View of N:P and Si:N Ratios

These stoichiometric relationships within natural systems occur within the context of probable future changes in nutrient loadings. The significance of human changes to C, N, and P cycling (e.g., fertilizers, mining, industrial production, and air pollutants) can be illustrated by expressing their commercial production as a percentage of the standing stocks of these elements in vegetation. Markert (1998) provided both numbers, and these data were updated in the case of N production to include N fixation by agricultural legumes and rice, and for NOx emissions (Kaiser 2001). A comparison was not made for dissolved silicate (DSi) because data are only available for Si, which would

<table>
<thead>
<tr>
<th>Source</th>
<th>Area and Conditions</th>
<th>Nutrients</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smayda (1990)</td>
<td>review</td>
<td>Si:N &lt; 1:1</td>
<td>based on strong inference, suggested that the world-wide coincidental occurrence of HAB and changing Si:DIN ratios were related (but not to a specific ratio)</td>
</tr>
<tr>
<td>Egge and Aksnes (1992); Egge and Heimdal (1994); Egge and Jacobsen (1997)</td>
<td>Bergen, Norway 11 m³</td>
<td>+nitrate, +phosphate, +silicate</td>
<td>diatom growth prevented by low Si concentration, increases with +Si; increasing N:P reduces diatoms when Si sufficient, in favor of flagellates</td>
</tr>
<tr>
<td>Jacobsen et al. (1995)</td>
<td>Norwegian fjord 11 m³</td>
<td>+nitrate, +phosphate</td>
<td>diatom increase until silicate deficiency, when flagellates appeared; no increase in chl a biomass or primary production; change in species composition</td>
</tr>
<tr>
<td>Turner et al. (1998)</td>
<td>Mississippi River delta</td>
<td>Si:N &lt; 1:1</td>
<td>collapse of the diatom-zooplankton food web, less fecal pellet production, at Si:N::1:1 pivot point</td>
</tr>
<tr>
<td>Kuuppo et al. (1998)</td>
<td>Baltic 150 liters</td>
<td>+nitrate, +silicate, −mesozooplankton</td>
<td>diatom bloom developed with only small amounts cascading into the heterotrophic (microbial) food webs</td>
</tr>
<tr>
<td>Chauvaud et al. (2000)</td>
<td>Bay of Brest</td>
<td>Si:N &lt; 1:1</td>
<td>smaller spring bloom despite higher N loading; coincidental increase in suspension feeding (exotic gastropod, Crepidula fornicata) led to increased biodeposition; slow Si recycling sustains diatom population during summer with less overall seasonality; avoidance of undesirable blooms while the Si:DIN ratio decreased (and N increased)</td>
</tr>
<tr>
<td>Svensen et al. (2001)</td>
<td>Bergen, Norway 27 m³</td>
<td>+nitrate, +phosphate, +silicate</td>
<td>+Si triggered a diatom bloom; +NP (lower Si: N ratios) had higher sedimentation rates</td>
</tr>
<tr>
<td>Keller et al. (1990)</td>
<td>Narragansett, Rhode Island</td>
<td>+N, +Si</td>
<td>fish growth low in control, intermediate with +N; highest with +N+Si (+Si not done)</td>
</tr>
</tbody>
</table>
Fig. 8. The relationship between nitrate concentration (x axis) and the dissolved Si:nitrate ratio in the main channel of large rivers of the world, 42 major sub-basins of the Mississippi River, and 82 small U.S. watersheds. The data are described in Turner et al. (in press).

not be soluble, in most cases, unlike most forms of N and P. In order of increasing percentages they were: P < N < C (0.03%, 0.41%, and 0.73%, respectively). N loading has been increasing in many rivers of the world (Howarth et al. 1996; Vitousek et al. 1997; Cloern 2001), primarily as the mobile nitrate ion (Turner et al. in press). The global supply of new silicate is relatively stable because it is primarily determined by weathering and dissolution, and not by human activity. Tilman et al. (2001) estimated that N and P fertilizer use (gross weight) will continue to increase by 2.4 and 2.7 times, respectively, the application rate in 2000. This increase is not equal for N and P when expressed on a molar basis. On a molar basis, the world’s use of N fertilizer each year is 50 times that for P fertilizer. These numbers suggest that P is becoming relatively more limiting as the world’s ecosystems move towards higher concentrations of N and P. The DSi:nitrate ratio should decline and the dissolved nitrate:P ratio should increase as N loading to aquatic systems continues to rise. These changes are already observed in many of the world’s largest rivers (Fig. 8) and in coastal waters over the last 20 years (Rahm et al. 1996; Fisher et al. 1988; Justic et al. 1995a,b; del Almo et al. 1997; Allen et al. 1998; Correll et al. 2000; Humborg et al. 2000). As nitrate concentration increases, the ratio of dissolved N:P increases above the Redfield ratio of 16:1 and below the DSi:nitrate ratio of 1:1. With further similar changes, the disruption of the diatom-zooplankton-fish food web is likely to occur with greater frequency and over a larger area.

Conclusions

Descriptions of the biogeochemical evolution of life on Earth indicates that there must be a balance among the accumulation of many elements, and that there is not just one master element. Life evolved and is sustained by concentrating a few relatively rare elements in the Earth’s crust into an organic matrix with semi-stable elemental ratios. These ratios may vary over the short term and long term within and among species, communities, and ecosystems, but there are long-term bounds to these ratios in life forms that determine the composition of ecosystems and the material flows within and among ecosystems. The examples discussed revealed several perspectives of just how sensitive plants, microbes, animals, and ecosystems are to variations in various elemental ratios. There is a growing set of empirical evidence demonstrating how nutrient availability and recycling and accumulation are intermingled with the activities of many life forms, and that the life forms are diverse because of these relationships. In other words, the response to nutrient additions and depletions is a community response and involves more than a single nutrient. The response affects many elemental ratios and therefore many species. These relationships have a bearing on how we manage our natural resources.

Some early attempts to manage aquatic ecosystems were based on the then-prevalent agricultural model of production. Experiments in Scotland were undertaken during World War II and thereafter to determine how fish production in semi-enclosed coastal basins responded to fertilizer applications (Nixon et al. 1986). The experiments were a success, more fish were produced. These were simple demonstrations of how nutrients influenced food webs that is now documented elsewhere. The model in these experiments was an agricultural model of more fertilizer = more food. Agriculturists have not stopped doing their experiments, but they are now much more sophisticated—they recognize that today’s society is much more complicated than when they started doing their experiments with single nutrient additions. Farm management now must be concerned about nutrient runoff, economics, hybridization, invasive species, pests, species losses, biocide contamination, ground water pollution, etc. Farmers know that there is an upper limit to the positive responses one nutrient has on crop yield and quality, and that there is sometimes a negative response. Aquatic ecosystem management is at least as complicated as farm crop management, if only because most marine crops are self-seeding, the economic product is a mixture of prey species, and the major har-
vest (usually fish) moves through many mediums throughout their cycle of spawning, growth, and harvest.

Human alteration of some elemental fluxes and domination of others make this management that much more difficult. We must expect that there are consequences for how and what organisms adapt to these alterations, now evident in the subtle and sometimes not-so-subtle changes of organism assemblages. We may find that some desirable or dependent interactions are compromised, rather than enhanced, as the great geochemical engineers, humans, alter elemental cycling rates and locations. Some of these compromises are of immediate significance, e.g., eutrophication, the loss of charismatic species, development of noxious pests, and effects on market economies and human health. The result of these changes may even be the creation of alternative steady states with distinctively different food webs. Ecosystem models based on nutrient stoichiometry for freshwater lakes predict the existence of alternating high grazer and grazer-free states with eutrophication (Andersen 1997) and manipulations of fish biomass can influence the presence or absence of macroalgal abundance with consequential effects on habitat structure (Scheffer 1990). An assiduous management of one species or one element (e.g., N in coastal systems and P in freshwater) must give way to the realities of the interdependencies within the human realm and the ecosystem of which we are a part. We need not only more experimentation and observation, but also a coalescence of perspectives that brings together natural history, physics, energy flow analyses, and nutrient stoichiometry (and others) into an integrated and testable whole view of life (e.g., Verity and Smetsack 1996; Dayton and Sala 2001). Being predictable does not mean that changes are desirable, or that societal behavior will change. Knowing the patterns is part of intelligent participation in the process of artful management, and providing that knowledge is a proper role for scientists.

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