OIKOS 109: 52–62, 2005

Applications of ecological stoichiometry for sustainable acquisition of ecosystem services

Robert Ptacnik, G. Darrel Jenerette, Antonie M. Verschoor, Andrea F. Huberty, Angelo G. Solimini and Justin D. Brookes

Ptacnik, R., Jenerette, G. D., Verschoor, A. M., Huberty, A. F., Solimini, A. G., and Brookes, J. D. 2005. Applications of ecological stoichiometry for sustainable acquisition of ecosystem services. – Oikos 109: 52–62.

Human activities have differentially altered biogeochemical cycling at local, regional and global scales. We propose that a stoichiometric approach, examining the fluxes of multiple elements and the ratio between them, may be a useful tool for better understanding human effects on ecosystem processes and services. The different scale of impacts of the elements carbon, nitrogen and phosphorus and the different nature of their biogeochemical cycles, imply a large variation of their stoichiometric ratios in space and time and thus divergent impacts on biota.

In this paper, we examine the effects of anthropogenic perturbations on nutrient ratios in ecosystems in two examples and one case study. Altered stoichiometry in agricultural systems (example 1) can affect not only crop yield and quality but also the interactions between plants and their pollinators, pests and pathogens. Human activities have also altered stoichiometry in coastal ecosystems (example 2). Increased N loading has especially lead to increased N:P and reduced Si:N ratios, with detrimental effects on ecosystem services derived from coastal pelagic food webs, such as fish yield and water quality. The terrestrial–aquatic linkage in stoichiometric alterations is illustrated with a case study, the Mississippi River watershed, where anthropogenic activities have caused stoichiometric changes that have propagated through the watershed into the northern Gulf of Mexico.

Coupled with altered stoichiometric nutrient inputs are the inherent differences in variation and sensitivity of different ecosystems to anthropogenic disturbance. Furthermore, the connections among the components of a watershed may result in downstream cascades of disrupted functioning. Applying a multiple element perspective to understanding and addressing societal needs is a new direction for both ecological stoichiometry and sustainability.

R. Ptacnik, Leibniz Institute for Marine Sciences, Düsternbrooker Weg 20, DE-24105 Kiel, Germany (rptacnik@ifm-geomar.de). – G. D. Jenerette, Arizona State Univ., School of Life Sciences, Tempe, AZ, USA. – A. M. Verschoor, Netherlands Institute of Ecology, Centre for Limnology, Rijksstraatweg 6, NL-3631 AC Nieuwersluis, the Netherlands. – A. F. Huberty, Dept of Entomology, Univ. of Maryland, College Park, MD, USA. – A. G. Solimini, Institute for Environment and Sustainability, European Commission Joint Research Centre, Ispra, Italy. – J. D. Brookes, Cooperative Research Centre for Water Quality and Treatment, PMB 3 Salisbury, South Australia, 5108.

The science of sustainability has gained increased use as an effective way to assess factors affecting the long-term provision of ecosystem services for humans (Holling 1993, Wackernagel and Yount 1998, Kates et al. 2001, Swart et al. 2002, Clark and Dickson 2003). Ecosystem services are the set of ecological processes required for sustained social functioning and human activities (Costanza et al. 1997, Daily et al. 1997). These services

Accepted 24 October 2004

ISSN 0030-1299

include both direct services that produce specific materials consumed by humans (such as food, water, and renewable raw materials) as well as indirect services (such as material and energy transformations that remove wastes, fixation or mineralization of nutrients and the regulation of biodiversity). There is compelling evidence that current consumption patterns of natural resources are depleting the capacity for future production of ecosystem services (Lal 2000, Tilman et al. 2002, Wackernagel et al. 2002).

The diminishing rate of production for many ecosystem services can be linked to anthropogenic alterations of ecosystems. The impacts of humans on ecosystems have been divided into four classes: changes in climate, changes to landscape structure, changes in species composition, and changes in absolute material inputs (Vitousek 1994). With respect to latter, it has been noted that human activities can also differentially alter elemental fluxes (Falkowski et al. 2000).

Alterations in fluxes of a given element affect the relative availability of this element within a given ecosystem. For example, an increased input of nitrogen to a grassland ecosystem will likely increase its overall productivity, with several implications for the ecosystem (e.g. standing crop, species composition). However, an altered nitrogen input will also change the relative availability of this element in the system, as the nitrogen:phosphorus ratio in the soil. As a consequence thereof, the carbon:nitrogen and nitrogen:phosphorus ratios in the plant biomass can increase, as the plants develop P limitation of growth (Sterner and Elser 2002). In turn, an altered stoichiometry of plant biomass can affect plant–herbivore interactions (Sterner and Elser 2002). Thus, the effects of the altered input of N are felt not only in the quantity of production but also in its quality. A stoichiometric perspective, examining multiple elements and the ratios among them, offers an approach for understanding human impact on ecosystems but has not been considered to date in the context of ecosystem services. We propose that a stoichiometric perspective, i.e. a focus on multiple elements and their ratios, gives further insights in how altered biogeochemical cycling affects ecosystems than a single element approach alone. Therefore, stoichiometric analysis may become an important tool for the management of human impact on ecosystems.

In this paper we first identify how humans are affecting ecosystems through altered stoichiometry of material inputs. Then we briefly review how these alterations influence ecological processes and how these altered processes impact the production of ecosystem services. We exemplify the anthropogenic impact on ecosystem services as a result of changing stoichiometry by looking at two highly impacted ecosystem types, agricultural and coastal ecosystems. In a case study, we highlight the terrestrial–aquatic linkage between different ecosystems for the Mississippi River watershed and the northern Gulf of Mexico. We conclude by reviewing how ecological stoichiometry expands our view of societal–ecosystem interactions and sustainability of these interactions.

Anthropogenic impacts on ecosystems: variability in multi-elemental flux

From the onset of industrialization, increasing utilization of fossil fuels and changes in land use (e.g. deforestation) have caused an increase in global atmospheric CO_2 levels from the pre-industrial level of 280 ppm to the current level of 370 ppm (Houghton et al. 2001). Similarly, the total amount of reactive nitrogen (N_r) has greatly increased since industrialization (Vitousek 1994, Galloway et al. 2002) reaching a human N_r production of 140 Mton yr^{-1}, which is added to the natural production of 300 Mton yr^{-1} (Mackenzie et al. 2002). In contrast to the global effects of CO_2, N_r deposition is more regional (i.e. national-continental) and deposited in the order of hundreds of kilometres near the N_r source. Phosphorus cycling has also been affected by human action, increasing from the pre-industrilisation rate of 9 Mton yr^{-1} of mobilized phosphorus to the current rate of 55 Mton yr^{-1} (Mackenzie et al. 2002). In contrast to carbon (C) and nitrogen (N), phosphorus (P) has a very limited atmospheric component and predominantly enters ecological cycles after release from lithic material through weathering and is transported through hydrologic networks at local scales. The different scale of impacts of the elements C, N and P, and the different nature of their biogeochemical cycles imply a large variation of their stoichiometric ratios in space and time.

To provide an example of stoichiometric variation in anthropogenic impacts on ecosystems, we linked the anthropogenic changes in atmospheric CO_2 concentrations with changes in N deposition in the conterminous United States (US) from 2001 (Fig. 1). The eastern and central US exhibit high rates of N deposition because of extensive industry and agriculture, resulting in reduced C:N loading ratios compared to pre-industrial levels (Fig. 1). Conversely, low N deposition in areas of the western US results in C:N ratios equal to or higher than pre-industrial levels. This spatial variation of C:N patterns illustrates the scale differences of human impacts on biogeochemical cycling. Although this analysis assumes spatially homogeneous atmospheric CO_2 concentrations and does not include temporal variation in either N deposition or CO_2 concentrations, our first approximation using readily available data provides potentially useful insight into patterns of change within the US. These patterns demonstrate that although human activity has markedly increased the

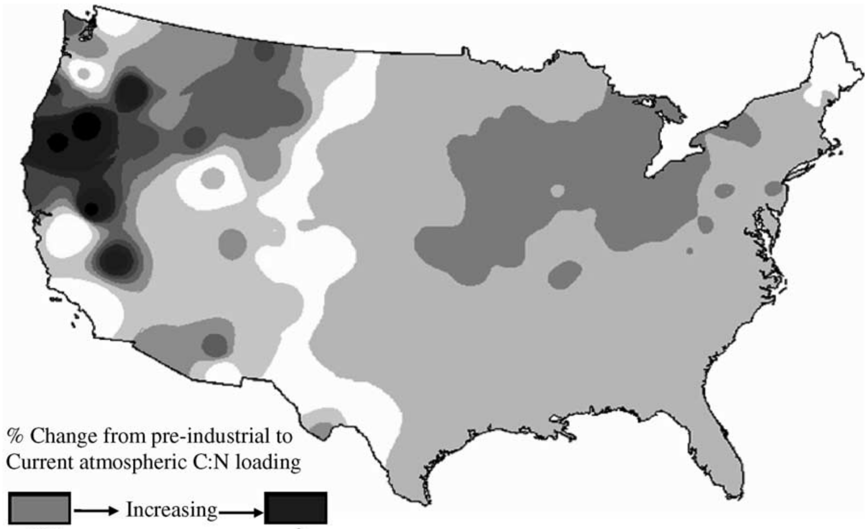

Fig. 1. Percent change in mass C:N inputs throughout the conterminous United States from pre-industrial to current patterns. Atmospheric CO_2 concentrations were considered to be homogeneous using the annual pattern observed from the Mauna Luao observation station (Keeling and Whorf 2004). This was overlaid this with the pattern of annual total wet N deposition observed in the National Atmospheric Deposition monitoring network. As a simplified estimate of pre-industrial CO_2 concentrations, ice-core derived CO_2 patterns were averaged for the period between 1010–1800 (U.S. National Atmospheric Deposition Program http://nadp.sws.uiuc.edu). Pre-industrial nitrogen deposition was characterized as the minimum observed N deposition from the 2001 data. By subtracting the current observed from the historically estimated C:N loading, an estimate of the spatial variation in altered C:N atmospheric inputs to ecosystems was developed.

supply of both C and N, the nature of the change in the ratio of these inputs (increase and decrease) depends on locality. These patterns also highlight the scale differences between the biogeochemical cycles of multiple elements.

Effects of stoichiometric alterations on ecological processes and ecosystem services

A variety of studies have investigated the impact of increased single element flux from anthropogenic activities (e.g. effects of elevated CO_2 or N driven eutrophication; Amundson 2001, Galloway et al. 2002). We suggest that by examining multiple elements, and the ratio between them, we can obtain additional insight on the effect of anthropogenic activities on ecological processes. In the following, we present two examples of ecosystems under strong anthropogenic impact, agriculture systems and coastal ecosystems. In a case study, we then illustrate the importance of the terrestrial–aquatic linkages for the Mississippi River watershed and the northern Gulf of Mexico.

The first example examines the relationship between altered stoichiometry and a single ecosystem service, agriculture. In addition to its fundamental importance for human survival, agriculture has profound indirect effects both on terrestrial and downstream aquatic ecosystems. In the second example, coastal ecosystems represent an example of a single ecosystem type that is represented worldwide. Here we focus on the role of altered nutrient stoichiometry on coastal pelagic food webs and the implications for ecosystem services. In the Mississippi River watershed (MRW) case study, we illustrate a coherent system of different sub-drainages experiencing strong anthropogenic impact. As the MRW is probably one of the best studied large watersheds of the world, we can investigate the cumulative effect of different anthropogenic impacts on stoichiometric alterations and their effects on ecosystem services. In addition, several approaches for amelioration of stoichiometric changes for the MRW have been elaborated and provide inspiration for management of similar disturbed systems. Furthermore, the MRW case study integrates the previous examples because the MRW has high densities of agricultural lands and flows into the

Gulf of Mexico coastal ecosystem. With these two examples and the case study, we aim to show how human activities have changed elemental concentrations and their ratios in these sensitive ecosystems, and to describe the major effects of these activities on important ecosystem services, such as food production and coastal water quality.

Agriculture systems

Agriculture systems are intensively managed to increase food production for human needs and more recently are managed to reduce unintended exports to downstream systems. Stoichiometric changes to agricultural systems will obviously affect food yield production, but the consequences of maximizing this ecosystem service are that other services, such as food quality (nutritive value) and material exports, may deteriorate.

Effects of stoichiometric perturbations on crop yield and quality

The effects of anthropogenic increases of C and N inputs on crop yield have been extensively examined as independent factors. Elevated CO_2 (Jablonski et al. 2002) or increasing N fertilisation (Howard et al. 2002) typically results in increased crop yield, but the coupling of elements (C:N) to determine realistic effects on food production has not been thoroughly investigated (Loladze 2002). While crop yield does increase under elevated CO_2, crops produced under these conditions exhibit increased C:nutrient ratios (e.g. N, P, Se, Fe, Zn) and thus might lead to micronutrient deficiencies in populations already malnourished (Loladze 2002). With respect to N fertilization, changes in management practices may alleviate N deficiency in crops by increasing fertilizer use. In addition, atmospheric N-deposition may compensate for the higher N demand caused by elevated CO_2-levels However, although the reduction of crop C:N ratio due to deposition or application of fertilisers likely makes the crops more nutritious from the perspective of protein and N content (Townsend et al. 2003), application of commercial fertilizers and especially N deposition will not necessarily boost levels of other vital nutrients in crop biomass. Thus increased inputs of C and N deposition in agricultural systems initially may seem advantageous in terms of yield and quality, but failure to recognize the effects on the multiple C: nutrient ratios of yield may ultimately diminish this ecosystem service by decreasing the nutritional value of crops (Loladze 2002).

Effects of stoichiometric perturbations on crop pest populations

Nitrogen is generally a limiting nutrient for insects (McNeill and Southwood 1978, Mattson 1980, White 1993). Thus anthropogenic induced elevation of plant C:N ratio in an already poor nutritional environment for herbivores will negatively affect pest performance (Coviella et al. 2002, Reddy et al. 2004). However, leaf chewing insects typically increase feeding to overcome nutrient deficits such as those induced by high plant C:N ratio due to elevated CO_2 (Bezemer and Jones 1998). When extended to crop management, the ability of leaf chewing insects to increase crop damage with no detrimental impact on insect fitness (Bezemer and Jones 1998) implies that pest management schemes will need to be modified in an enriched C:N environment. This may include re-examining the economic thresholds used to determine the implementation of pesticide applications.

When C:N ratio of a crop is decreased through fertilizer use, pest populations frequently increase (Cisneros and Godfrey 2001). What is less understood is if N deposition in agricultural fields will affect pest populations. Of the few field studies that have looked directly at the effects of N deposition on insect herbivore populations (Throop and Lerdau 2004), most have found a positive relationship between N deposition and herbivore performance. For example, the reduction in host plant C:N ratio due to N deposition has been linked to increased outbreaks of the heather beetle *Lochmaea suturalis* Thomson (Coleoptera: Chrysomelidae) (Bobbink et al. 1998). Unfortunately, studies investigating the effects of N deposition-induced changes on herbivore population dynamics in agricultural crops are severely lacking.

Biological control of pest populations in crops is an important component of sustainable agriculture, and changes in stoichiometry of crop plants due to changing elemental ratios may alter the performance of predators and parasitoids. The negative performance responses of pests when faced with increases in plant C:nutrient content may promote even greater control of pest populations by increasing predator efficacy. For example, growth rate for *Manduca sexta* (L.) (Lepidoptera: Sphingidae) is slower for individuals reared in low P conditions (Perkins et al. 2004). These longer development times for pest populations may allow for greater control of pests by predators (slow growth–high mortality hypothesis; Benrey and Denno 1997). However, reducing the C:nutrient content of plants through increased fertilisation (Cisneros and Godfrey 2001) or N deposition (Bobbink et al. 1998) may result in herbivore population outbreaks and a lack of sufficient pest control by natural enemies.

Effects of stoichiometric perturbations on pollinators and pathogens

Pollinator–plant relationships may be affected through multiple pathways and with a variety of implied consequences for agricultural food yield. CO_2-induced increases in plant C:N ratio may result in decreased flower attractiveness and thus modify pollinator foraging behavior, shift pollinator–plant species specificity, or reduce seed set (Rusterholz and Erhardt 1998, Lake and Hughes 1999, Poulton et al. 2001). These changes may have diverging yet substantial effects on agricultural production. Susceptibility of crops to disease due to changes in elemental ratios in the host plant has been recognized (Hoffland et al. 1999), but these effects are poorly understood due to the variation in stoichiometric relationship between pathogen and host (Hoffland et al. 2000, Solomon et al. 2003). Indirect effects of changing stoichiometry on disease susceptibility may influence crop yield. For example, increased C:N of litter slows decomposition (Thompson et al. 1993) resulting in long term retention of field residue, which may allow for greater amounts of pathogen inoculum to be present at the next planting (Coakley et al. 1999). These issues point to potentially substantial changes in crop production and sustainability in agriculture under altered stoichiometric regimes.

Nutrient export from agriculture

Agricultural practice generally aims to maximize yield and the stoichiometric perspective is that elemental supply to crops should be optimally balanced. If the balance is not optimal in terms of stoichiometric demands of the crop, the result will be that non-limiting nutrients are exported from the agricultural field to other ecosystems (Carpenter et al. 1998, Donner et al. 2004). For example, excess fertilization of crops, particularly in areas of high N deposition, will decrease C:N of the crop land, but may also increase the N content of leaching, and affect the Si:N and N:P ratios in the runoff. For the lower Mississippi River watershed McIsaac et al. (2001) calculated that a reduction in fertilizer application by 12% would reduce riverine nitrogen by 33% (case study below).

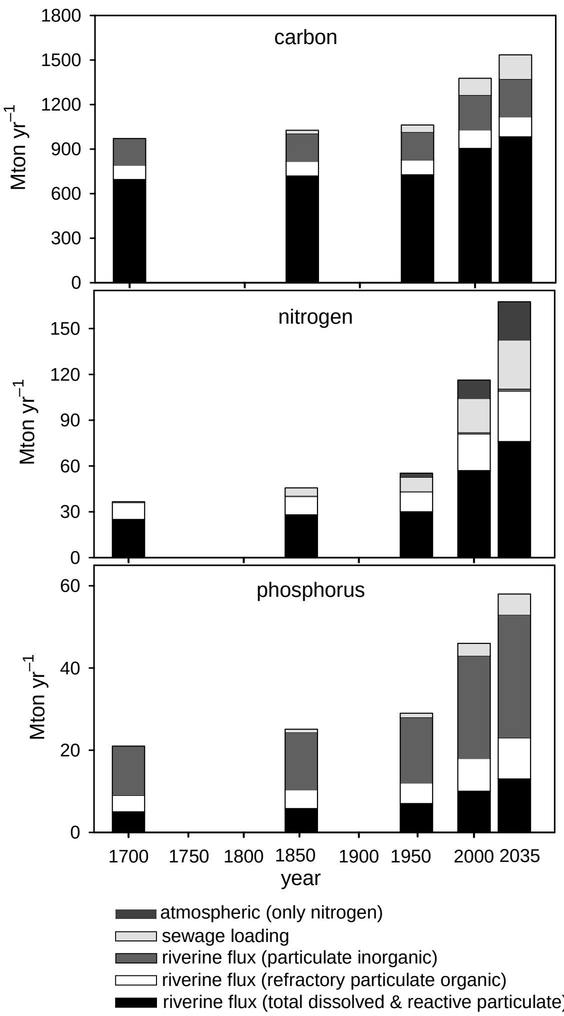

Fig. 2. Historical development and projections of global fluxes of carbon, nitrogen and phosphorus from atmospheric deposition, sewage loading and riverine flux into coastal ecosystems. After Mackenzie et al. (2002).

Coastal ecosystems

Human activities, such as changing land use, manipulation of river hydrology, and fertilizer use have dramatically changed the riverine inflow of nutrients into coastal ecosystems worldwide. Increased total nutrient loads have long been acknowledged as leading to eutrophication (Cloern 2001). Furthermore, direct sewage inflow has become increasingly problematic as a source of nutrients to coastal systems, and atmospheric deposition has become increasingly important in the case of nitrogen (Mackenzie et al. 2002). It is readily acknowledged that inputs of these elements (C, N, P) to the coastal ecosystem have increased over time (Fig. 2), but there has been less recognition of the possible roles of the stoichiometric ratios of these nutrients in altering ecosystem processes. Likewise, there is clear evidence for recent increase of noxious and harmful algal blooms in coastal waters (Paerl 1997), but the total load of nutrients seems to be a rather weak predictor for such events (Anderson et al. 2002, Sellner et al. 2003).

The stoichiometric perspective reveals that there have been accelerated changes in elemental ratios since the 1950's (Fig. 3). The increasing contribution of sewage (C:N = 6; Mackenzie et al. 2002) and atmospheric deposition (N only) have caused the total C:N ratio of coastal influx to decline towards Redfield values (C:N = 6.6; Redfield et al. 1963; Fig. 3). The C:P ratio of the total influx to the global coastal ecosystems reflects the dominant contribution of riverine P input, whereas sewage input appears to be less important. The C:P ratio dropped below Redfield ratio (106:1) at the beginning of

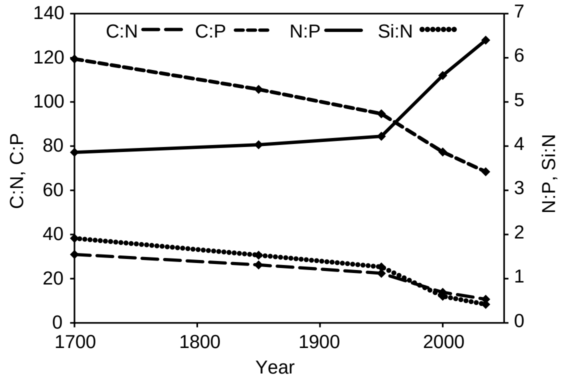

Fig. 3. Historical and projected changes of elemental ratios (molar) of the nutrient flux into global coastal ecosystems, based upon sum totals of all inputs for each element presented in Fig. 2 (after MacKenzie et al. 2002) and the global Si inflow estimate by Conley (2002).

industrialisation, indicating that in general coastal ecosystems now receive a net surplus of phosphorus. Nevertheless, N:P ratios are currently increasing, reflecting a greater increase in N influx compared to the increase in P influx (Fig. 3, 4). Finally, there are fewer records for silica (Si) in riverine systems, so long-term trends are difficult to assess at a global scale. Assuming Si influx is constant, Si:N ratios would decrease due to increasing N (Fig. 3). This decline in Si:N ratios is probably much higher than depicted here as a result of increasing Si retention in watersheds due to the ongoing construction of dams for flow regulation (Humborg et al. 2000; below).

Si:N in the coastal pelagic

The globally decreasing Si:N ratios have led to a reduction in diatom abundance (Humborg et al. 2000, Sommer et al. 2002). Diatoms are a primary food source for copepods (Irigoien et al. 2002), which in turn serve as food for marine pelagic fish species (Kristiansen and Hoell 2002, Van Nieuwerburgh et al. 2004). Indeed, the share of copepods in the pelagic food web is directly dependent on the Si:N ratio (Turner et al. 1998). Thus, pelagic fish resources are likely to deteriorate with decreasing Si:N. Since fish are a major source of protein, as well as of diatom-derived essential fatty acids for humans (Holmlund and Hammer 1999, Sommer et al. 2002), these stoichiometric shifts have major implications for the human benefits of sustained fisheries production. Making matters worse, the resulting shift from diatoms to flagellates in the phytoplankton community also results in a higher share of primary production not being channelled up the food web (Sommer et al. 2002, Cebrian 2002, 2004), fuelling the microbial food web and undesired consumers such as tunicates and appendicularians that are not consumable or have low nutritional value for fish.

Nutrient ratios and harmful algal blooms

The occurrence of harmful algal blooms (HABs) has significantly increased since the onset of industrialization (Paerl 1997, Anderson et al. 2002). HABs include both nuisance blooms that may reduce water quality and cause temporal hypoxia due to post-bloom decomposition of their biomass, as well as true toxic blooms by potential toxic species. Especially the latter compromise human needs in coastal areas by their toxic effects on human beings, either through direct toxicity or through accumulation in marine food resources (e.g. shellfish poisoning; Klopper et al. 2003). Several recent studies of a variety of such taxa show that their toxicity is positively related to deviations from Redfield ratio in

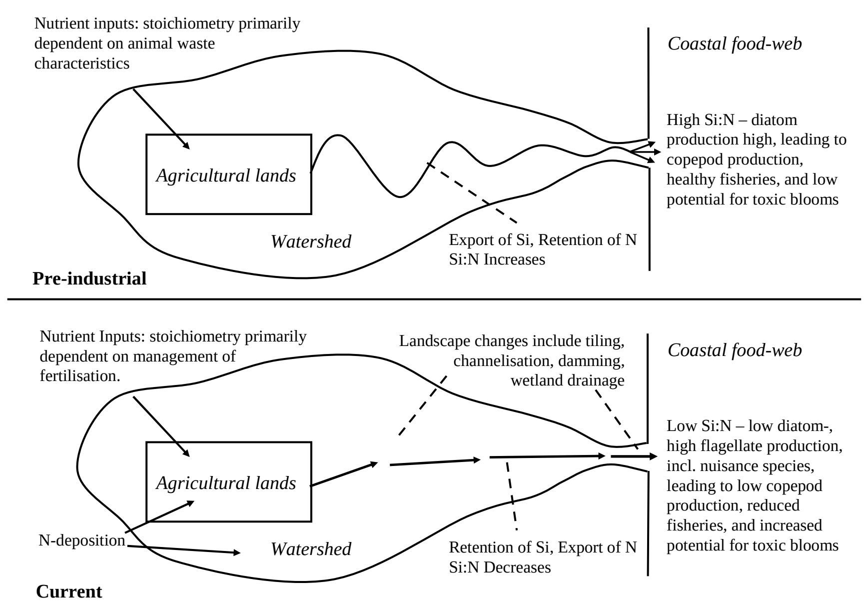

Fig. 4. Pre-industrial (upper panel) and current (lower panel) anthropogenic impact on nutrient cycles and thus stoichiometry in a watershed and its effect on the coastal ecosystem.

nutrient supply. In particular, P limitation favours toxicity in several flagellates (Johansson and Granéli 1999, Flynn 2002, Granéli and Johansson 2003, Frangopulos et al. 2004), and the diatom genus *Pseudo-nitzschia* (Pan et al. 1996).

The balance between C and inorganic mineral nutrients (N, P, Si) is another aspect contributing to the occurrence of undesirable algal species. Dinoflagellates and prymnesiophytes, which cause the majority of nuisance algal blooms, are relatively poor competitors for dissolved inorganic mineral nutrients, but compensate for this disadvantage by mixotrophic abilities. Due to their mixotrophy, these species are able to compete for organically bound nutrients, for example by ingesting bacteria and by utilizing a variety of organic N compounds (Smayda 1997, Anderson et al. 2002). High levels of organic nutrients and DOC therefore favour blooms of these species (Smayda 1997, Rabalais 2002). Again, the low nutritional value of these species reduces the efficiency of the pelagic food web, which affects higher-level consumers and increases respiration rates. Thus, the observed changes in C:N and N:P in the nutrient loading of the coastal zone (Fig. 3) are well in accordance with the increased occurrence of HABs.

The Mississippi River watershed: a case study of a human dominated ecosystem

The Mississippi River watershed (MRW) is heavily disturbed by human activities on various scales, such as various structural changes (drainage, changes from forests and wetlands to agricultural land, river channelisation; Fig. 4) and high external nutrient input (fertilisation and atmospheric deposition). The nutrient load that is transported by the Mississippi river to the Gulf of Mexico has increased drastically during the last 200 years (Turner and Rabalais 2003). Changes from 1960 to 1998 are particularly well documented (McIsaac et al. 2001, Mitsch et al. 2001).

The MRW provides essential ecosystem services to the regional population. However, changes in the MRW affect not only services within the area, but also in the northern Gulf of Mexico, a coastal system that is tightly related to the water brought by the MRW and the Atchafalaya river system. Emerging environmental problems both in the watershed and in the coastal zone have promoted intensive research in this area, allowing us to investigate the underlying mechanisms by using the stoichiometric perspective.

Si:N in the northern Gulf of Mexico

A major focus in recent research is the effect of anthropogenic impact on the Si:N ratio that crucially affects ecosystem services in Gulf of Mexico coastal zone (Mitsch et al. 2001, Turner and Rabalais 2003, 2004). From 1960 to 1998, the net anthropogenic N input (NANI; input to watershed minus N exported by food and feed) to the MRW has increased by 80% (Mitsch et al. 2001). Of this increase, approximately 52, 35, 11 and 2% originate from agricultural fertilisation, legume N fixation, atmospheric NO_3^- deposition and from municipal and industrial point-sources, respectively (Mitsch et al. 2001). The fraction of NANI that reaches the Mississippi River and finally the Gulf of Mexico, however, is a function of both the N input into the corresponding system (e.g. agricultural land) and of structural changes in the watershed. Among the common crops in the MRW, soybean (an N-fixer) and maize (high application of fertilisers) have been identified as causing the highest relative areal nutrient losses in runoff (Donner et al. 2004). Indeed, Donner (2003) found that the Si:N ratio of the runoff in a given sub-basin is tightly correlated with the relative cover of maize and soybean, leading to the conclusion that the increasing cover of these crops is one of the major factors that has lead to the observed decrease in the Si:N ratio of the Mississippi River (Donner 2003). In addition to the increased amount of NANI, structural changes in the watershed have reduced N retention and denitrification. Overall, the combined effect of increased NANI together with structural changes have resulted in a 2.5-fold increase of reactive nitrogen (N_r) in the Mississippi River from 1960 to 1998 (McIsaac et al. 2001). On the other hand, Si tends to be retained increasingly in the watershed. Construction of dams along the rivers in the MRW has facilitated diatom blooms within the basin. Consquently, uptake of silicate by diatoms has resulted in a decrease of dissolved silicate by 50% in the lower Mississippi during the last century (Bollinger et al. 2000 in Donner 2003). The combined effect of increasing N-load with decreasing Si-load has lowered the Si:N ratio from 4.6 to below 1 in the lower Mississippi during the last century (Turner and Rabalais 2004).

Effects on the coastal food web

The changes in the Si:N ratio have negative effects on food web efficiency and fish production, and promote the occurrence of harmful algal blooms (outlined in the previous section). For the coastal zone near the Mississippi Delta, Turner et al. (1998) have shown that the share of copepods in mesozooplankton decreases drastically (from 0.75 to <0.4) when the Si:N ratio falls clearly below 1. In addition, Parsons et al. (2002) found a significant correlation between the increasing occurrence of toxic diatoms of the genus *Pseudonitzschia* and decreasing Si:N ratios. As the coastal food web of the northern Gulf of Mexico provides 25% of the total US fisheries landing (Turner and Rabalais 2004), detrimental impacts on this system have far-reaching consequences for societal benefits from fisheries production.

Possible remedial measures

The altered Si:N ratio in the northern coastal zone of the Gulf of Mexico can be addressed both by reducing the N input, and by increasing the Si load by the Mississippi River. Control of agricultural N drainage via best agricultural practice, point- and non-point source control, restoration of wetlands and riparian zones, flood control and restoration of original delta functioning have been suggested as potential remedial measures in a recent review by Mitsch et al. (2001). Finally, Lane and colleges have shown experimentally that river diversions in the Mississippi delta may increase the Si:N ratio, and decrease the N:P ratio in the diverted water (Lane et al. 2004; see Mitsch et al. 2001 for a review on all possible measures).

The Si-input to the Gulf of Mexico could be enhanced by reducing dams in the MRW, an action that is becoming increasingly considered for a variety of ecosystem management reasons (Bednarek 2001, Doyle et al. 2003). In addition, direct Si fertilisation into the coastal zone is a conceivable management option to restore the Si:N ratio and increase diatom abundance. However, restoring a higher Si:N ratio at current high levels of N input may well increase the share of diatoms in the community but would also result in increased export of organic matter from surface to bottom waters by sedimentation of enhanced diatom production. This would increase hypoxia in deeper strata with detrimental effects on the benthic food web (Turner et al. 1998, Lane et al. 2004). Thus, Si enrichment without reducing N input is not an advisable option for restoring the food web in the northern Gulf of Mexico.

Synthesis: how ecological stoichiometry may help in improving the sustainability of ecosystem services

Several considerations can be made when integrating the information from our examples presented in the previous section. First, the stoichiometric implications of the physical linkages between terrestrial and aquatic systems appear of great importance for the sustainability of ecosystem services. Avoiding stoichiometric imbalances between the supply and demand for nutrients is necessary to maintain the delivery of services not only within a single ecosystem but also between functionally linked ecosystems. Stoichiometric principles provide management tools that complement other approaches for ensuring sustainable acquisition of ecosystem services, as outlined in the case study of the Mississippi River watershed.

Second, coupled with altered stoichiometric inputs is inherent variation in the response of different ecosystems to anthropogenic disturbance. Within a single watershed, different components vary in sensitivity to stoichiometric alterations. Because the supply with phosphorus from chemical weathering generally decreases downstream along a watershed, soils tend to be N limited unpstream, but may exhibit P limitation further downstream (Walker and Syers 1976, Vitousek and Farrington 1997). Thus, N deposition is likely to increase P limitation especially downstream, with yet largely unknown consequences for the concerning ecosystems. Moreover, connectivity between components of a watershed may result in downstream cascades of disrupted functioning (Shade et al. 2005). Increased P limitation in terrestrial ecosystems may enhance P retention in these ecosystems, that will in turn increase P limitation in adjacent aquatic ecosystems. These downstream influences are particularly relevant for the transition from riverine to coastal zones that have distinct sensitivity to altered stoichiometric inputs.

Third, a growing body of theory and empirical evidence suggests that ecosystem responses to perturbsations, including human-induced ones, are highly nonlinear (Carpenter et al. 1999, Carpenter and Gunderson 2001, Gunderson and Holling 2002, Redman and Kinzig 2003). These systems may flip between alternative stable states, thereby rapidly altering the provisioning of ecosystem services. Once a threshold state is crossed and the system switches to a different state, returning the system to the previous condition can require relatively large changes in key drivers at potentially large costs (Scheffer et al. 2001). Because stoichiometric constraints can give rise to multiple attractors in community dynamics (reviewed by Moe et al. 2005), changes in stoichiometry may be a subtle pathway to catastrophic shifts in the production of ecosystem services (Sterner and Elser 2002). Another important aspect in this context is the facilitation of species invasion by altered nutrient regimes in ecosystems (Weltzin et al. 2004), as species invasion may cause dramatic shifts in ecosystem functioning (Crooks 2002).

Conclusions

We propose that stoichiometric alterations of inputs to ecosystems are important drivers of ecosystem dynamics and require consideration along with other human impacts such as perturbations of climate, landscape structure, species composition, and single element inputs. Because of scale differences in the biogeochemical cycles of individual elements, rich patterns in the stoichiometric balance of inputs exist, as shown in our analysis of atmospheric C:N deposition in the U.S. We have shown that elemental balances can change in either direction depending on local conditions. The differential response of ecological processes to these changes reduces the predictability of ecosystem service provision.

Maintaining the provision of ecosystem services is required for sustainable human-ecological systems at all scales. Differential supply of multiple elements may have important consequences for the production of many services. With an ecological stoichiometric perspective, changes to ecosystem service production rates may be better understood for two reasons. First, ecological stoichiometry is itself a source of non-linearity that could be a causal mechanism for inducing catastrophic shifts in the production rates of ecosystem services. Second and more encouraging, because an ecological stoichiometric approach simultaneously examines multiple currencies, surprises are less likely than when employing a single currency approach.

Applying a multiple element perspective to understanding and addressing societal needs is a new direction for both ecological stoichiometry and sustainability. For example, managing the nutrient ratio may be a necessary component for maintaining ecosystem integrity. Many important research questions exist at the interface of these growing disciplines. Understanding how anthropogenic stoichiometric change interacts with other components of global change is one necessary direction. For example, what are the stoichiometric drivers of global climate change and how can these changes be mitigated through applications of stoichiometric thinking? How do stoichiometric changes influence alterations to species composition in communities? Of particular relevance for agricultural systems, how does stoichiometric variation interact with genetically modified crops? Here we proposed only a few of the many potentially exciting questions that are significant for a basic understanding of current biospheric patterns and processes and can be directly applied to identifying pathways towards sustainable development.

Acknowledgements – We thank Dag Hessen, Jim Elser, and the Centre for Advanced Study, Oslo, for organising the Woodstoich workshop in Finse. We are grateful to Jim Elser and Dag Hessen for helpful comments on the manuscript.

References

Amundson, R. 2001. The carbon budget in soils. – Annu. Rev. Earth Planetary Sci. 29: 535–562.

Anderson, D., Glibert, P. and Burkholder, J. 2002. Harmful algal blooms and eutrophication: nutrient sources, composition, and consequences. – Estuaries 25: 704–726.

Bednarek, A. T. 2001. Undamming rivers: a review of the ecological impacts of dam removal. – Environ. Manage. 27: 803–814.

Benrey, B. and Denno, R. F. 1997. The slow-growth-high-mortality hypothesis: a test using the cabbage butterfly. – Ecology 78: 987–999.

Bezemer, T. M. and Jones, T. H. 1998. Plant-insect herbivore interactions in elevated atmospheric CO2: quantitative analyses and guild effects. – Oikos 82: 212–222.

Bobbink, R., Hornung, M. and Roelofs, J. G. M. 1998. The effects of air-borne nitrogen polluntants on species diversity in natural and semi-natural European vegetation. – J. Ecol. 86: 717–738.

Carpenter, S. R. and Gunderson, L. H. 2001. Coping with collapse: ecological and social dynamics in ecosystem management. – Bioscience 51: 451–457.

Carpenter, S. R., Caraco, N. F., Correll, D. L. et al. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. – Ecol. Appl. 8: 559–568.

Carpenter, S. R., Ludwig, D. and Brock, W. A. 1999. Management of eutrophication for lakes subject to potentially irreversible change. – Ecol. Appl. 9: 751–771.

Cebrian, J. 2002. Variability and control of carbon consumption, export, and accumulation in marine communities. – Limnol. Oceanogr. 47: 11–22.

Cebrian, J. 2004. Role of first-order consumers in ecosystem carbon flow. – Ecol Lett. 7: 232–240.

Cisneros, J. J. and Godfrey, L. D. 2001. Midseason pest status of the cotton aphid (Homoptera: Aphididae) in California cotton: is nitrogen a key factor? – Environ. Entomol. 30: 501–510.

Clark, W. C. and Dickson, N. M. 2003. Sustainability science: the emerging research program. – Proc. Natl Acad. Sci. USA 100: 8059–8061.

Cloern, J. E. 2001. Our evolving conceptual model of the coastal eutrophication problem. – Mar. Ecol. Prog. Ser. 210: 223–253.

Coakley, S. M., Scherm, H. and Chakroborty, S. 1999. Climate change and plant disease management. – Annu. Rev. Phytopathol. 37: 399–426.

Conley, D. 2002. Terrestrial ecosystems and the global biogeochemical silica cycle. – Global Biogeochem. Cy. 16: Art. No. 1121.

Costanza, R., dArge, R., deGroot, R. et al. 1997. The value of the world's ecosystem services and natural capital. – Nature 387: 253–260.

Coviella, C. E., Stipanovic, R. D. and Trumble, J. T. 2002. Plant allocation to defensive compounds: interactions between elevated CO_2 and nitrogen in transgenic cotton plants. – J. Exp. Biol. 53: 323–331.

Crooks, J. 2002. Characterizing ecosystem-level consequences of biological invasions: the role of ecosystem engineers. – Oikos 97: 153–166.

Daily, G. C., Alexander, S., Ehrlich, P. R. et al. 1997. Ecosystem services: benefits supplied to human societies by natural ecosystems. – Issues Ecol. 2: 1–16.

Donner, S. 2003. The impact of cropland cover on river nutrient levels in the Mississippi River Basin. – Global Ecol. Biogeogr. 12: 341–355.

Donner, S., Kucharik, C. and Foley, J. 2004. Impact of changing landuse practices on nitrate export by the Mississippi River. – Global Biogeochem. Cy. 18: Art. No. GB1028.

Doyle, M. W., Harbor, J. M. and Stanley, E. H. 2003. Toward policies and decision-making for dam removal. – Environ. Manage. 31: 453–465.

Falkowski, P., Scholes, R. J., Boyle, E. et al. 2000. The global carbon cycle: a test of our knowledge of earth as a system. – Science 290: 291–296.

Flynn, K. 2002. Toxin production in migrating dinoflagellates: a modelling study of PSP producing *Alexandrium*. – Harmful Algae 1: 147–155.

Frangopulos, M., Guisande, C., deBlas, E. et al. 2004. Toxin production and competitive abilities under phosphorus limitation of *Alexandrium* species. – Harmful Algae 2: 131–139.

Galloway, J. N., Cowling, E. B., Seitzinger, S. P. et al. 2002. Reactive nitrogen: too much of a good thing? – Ambio 31: 60–63.

Granéli, E. and Johansson, N. 2003. Increase in the production of allelopathic substances by *Prymnesium parvum* cells grown under N- or P-deficient conditions. – Harmful Algae 2: 135–145.
Gunderson, L. H. and Holling, C. S. (eds). 2002. Panarchy: understanding transformations in human and natural systems. – Island Press.
Hoffland, E., van Beusichem, M. L. and Jeger, M. J. 1999. Nitrogen availability and susceptibility of tomato leaves to *Botrytis cinerea*. – Plant Soil 210: 263–272.
Hoffland, E., Jeger, M. J. and van Beusichem, M. L. 2000. Effect of nitrogen supply rate on disease resistance in tomato depends on the pathogen. – Plant Soil 218: 239–247.
Holling, C. S. 1993. Investing in research for sustainability. – Ecol. Appl 3: 552–555.
Holmlund, C. M. and Hammer, M. 1999. Ecosystem services generated by fish populations. – Ecol. Econ. 29: 253–268.
Houghton, J. T., Ding, Y., Griggs, D. J. et al. 2001. Climate change 2001: the scientific basis. – Cambridge Univ. Press.
Howard, D. D., Newman, M. A., Essington, M. E. et al. 2002. Nitrogen fertilization of conservation-tilled wheat. I. Sources and application rates. – J. Plant Nutr. 25: 1315–1328.
Humborg, C., Conley, D. J., Rahm, L. et al. 2000. Silica retention in river basins: far reaching effects on biogeochemistry and aquatic food webs. – Ambio 29: 45–50.
Irigoien, X., Harris, R., Verheye, H. et al. 2002. Copepod hatching success in marine ecosystems with high diatom concentrations. – Nature 419: 387–389.
Jablonski, L. M., Wang, X. and Curtis, P. S. 2002. Plant reproduction under elevated CO2 conditions: a meta-analysis of reports on 79 crop and wild species. – New Phytol. 156: 9–26.
Johansson, N. and Granéli, E. 1999. Cell density, chemical composition and toxicity of *Chrysochromulina polylepis* (haptophyta) in relation to different N:P supply ratio. – Mar. Biol. 135: 209–217.
Kates, R. W., Clark, W. C., Corell, R. et al. 2001. Environment and development-sustainability science. – Science 292: 641–642.
Keeling, C. D. and Whorf, T. P. 2004. Atmospheric CO_2 records from sites in the SIO air sampling network. – In: Trends: a compendium of data on global change. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Dept of Energy, Oak Ridge, TN.
Klopper, S., Scharek, R. and Gerdts, G. 2003. Diarrhetic shellfish toxicity in relation to the abundance of *Dinophysis* spp. in the German Bight near Helgoland. – Mar. Ecol. Progr. Ser. 259: 93–102.
Kristiansen, S. and Hoell, E. E. 2002. The importance of silicon for marine production. – Hydrobiologia 484: 21–31.
Lake, J. C. and Hughes, L. 1999. Nectar production and floral characteristics of *Tropaeolum majus* L. grown in ambient and elevated carbon dioxide. – Ann. Bot. Lond. 84: 535–541.
Lal, R. 2000. Soil management in the developing countries. – Soil Sci. 165: 57–72.
Lane, R., Day, J., Justic, D. et al. 2004. Changes in stoichiometric Si, N and P ratios of Mississippi River water diverted through coastal wetlands to the Gulf of Mexico. – Estuar. Coast. Shelf S. 60: 1–10.
Loladze, I. 2002. Rising atmospheric CO2 and human nutrition: toward globally imbalanced plant stoichiometry. – Trends Ecol. Evol. 17: 457–461.
Mackenzie, F. T., Vera, L. M. and Lerman, A. 2002. Century-scale nitrogen and phosphorus controls of the carbon cycle. – Chem. Geol. 190: 13–32.
Mattson, W. J. 1980. Herbivory in relation to plant nitrogen content. – Annu. Rev. Ecol. Syst. 11: 119–161.
McIsaac, G., David, M., Gertner, G. et al. 2001. Nitrate flux in the Mississippi River. – Nature 414: 166–167.
McNeill, S. and Southwood, T. R. E. 1978. The role of nitrogen in the development of insect/plant relationships. – In: Harborne, J. B. (ed.), Biochemical aspects of plant and animal coevolution. Academic Press, pp. 77–98.
Mitsch, W., Jr., J. D., Gilliam, J., Groffman, P. et al. 2001. Reducing nitrogen loading to the Gulf of Mexico from the Mississippi River Basin: strategies to counter a persistent ecological problem. – Bioscience 51: 373–388.
Moe, S. J., Stelzer, R. S., Forman, M.R. et al. 2004. Recent advances in ecological stoichiometry: insights for population and community ecology. – Oikos 109: 29–39.
Paerl, H. W. 1997. Coastal eutrophication and harmful algal blooms: importance of atmospheric deposition and groundwater as "new" nitrogen and other nutrient sources. – Limnol. Oceanogr. 45: 1154–1165.
Pan, Y., Rao, D. and Mann, K. 1996. Changes in domoic acid production and cellular chemical composition of the toxigenic diatom *Pseudonitzschia multiseries* under phosphate limitation. – J. Phycol. 32: 371–381.
Parsons, M. L., Dortch, Q. and Turner., R. E. 2002. Sedimentological evidence of an increase in *Pseudo-nitzschi*a (Bacillariophyceae) abundance in response to coastal eutrophication. – Limnol. Oceanogr. 47: 551–558.
Perkins, M. C., Woods, H. A., Harrison, J. F. et al. 2004. Dietary phosphorus affects the growth of larval *Manduca sexta*. – Arch. Insect Biochem. 55: 153–168.
Poulton, J. L., Koide, R. T. and Stephenson, A. G. 2001. Effects of mycorrhizal infection and soil phosphorus availability on in vitro and in vivo pollen performance in *Lycopersicon esculentum* (Solanaceae). – Am. J. Bot. 88: 1786–1793.
Rabalais, N. N. 2002. Nitrogen in aquatic ecosystems. – Ambio 31: 102–112.
Reddy, G. V. P., Tossavainen, P., Nerg, A.-M. et al. 2004. Elevated atmospheric CO2 affects the chemical quality of *Brassica* plants and the growth rate of the specialist, *Plutella xylostella*, but not the generalist, *Spodoptera littoralis*. – J. Agr. Food Chem. 52: 4185–4191.
Redfield, A. C., Ketchum, B. H. and Richards, F. A. 1963. The influence of organisms on the composition of seawater. – In: Hill, M. N. (ed.), The sea. Interscience, pp. 26–77.
Redman, C. L. and Kinzig, A. P. 2003. Resilience of past landscapes: resilience theory, society, and the Longue Duree. – Conserv. Ecol. 7: 000–000.
Rusterholz, H. P. and Erhardt, A. 1998. Effects of elevated CO_2 on flowering phenology and nectar production of nectar plants important for butterflies of calcareous grasslands. – Oecologia 113: 341–349.
Schade, J, Espeleta, J., Klausmeier, C. A. et al. 2004. Stoichiometry from ecosystems to landscapes – Oikos 109: 40–51.
Scheffer, M., Carpenter, S., Foley, J. A. et al. 2001. Catastrophic shifts in ecosystems. – Nature 413: 591–596.
Sellner, K. G., Doucette, G. J. and Kirkpatrick, G. J. 2003. Harmful algal blooms: causes, impacts and detection. – J. Ind. Microbiol. Biotechnol. 30: 383–406.
Smayda, T. J. 1997. Harmful algal blooms: their ecophysiology and general relevance to phytoplankton in the sea. – Limnol. Oceanogr. 42: 1137–1153.
Solomon, P. S., Tan, K. C. and Oliver, R. P. 2003. The nutrient supply of pathogenic fungi; a fertile field for study. – Mol. Plant Pathol. 4: 203–210.
Sommer, U., Stibor, H., Katechakis, A. et al. 2002. Pelagic food web configurations at different levels of nutrient richness and their implications for the ratio fish production: primary production. – Hydrobiologia 484: 11–20.
Sterner, R. W. and Elser, J. J. 2002. Ecological stoichiometry: The biology of elements from molecules to the biosphere. – Princeton Univ. Press.
Swart, R., Raskin, P. and Robinson, J. 2002. Critical challenges for sustainability science. – Science 297: 1994–1994.
Thompson, G. B., Brown, J. K. M. and Woodward, F. I. 1993. The effects of host carbon-dioxide, nitrogen and water-supply on the infection of wheat by powdery mildew and aphids. – Plant Cell Environ. 16: 687–694.

Throop, H. L. and Lerdau, M. T. 2004. Effects of nitrogen deposition on insect herbivory: implications for community and ecosystem processes. – Ecosystems 7: 109–133.
Tilman, D., Cassman, K. G., Matson, P. A. et al. 2002. Agricultural sustainability and intensive production practices. – Nature 418: 671–677.
Townsend, A. R., Howarth, R. W., Bazzaz, F. A. et al. 2003. Human health effects of a changing global nitrogen cycle. – Front. Ecol. Environ. 1: 240–246.
Turner, R. and Rabalais, N. 2003. Linking landscape and water quality in the Mississippi River Basin for 200 years. – Bioscience 53: 563–572.
Turner, R. E. and Rabalais, N. N. 2004. Suspended sediment, C, N, P, and Si yields from the Mississippi River Basin. – Hydrobiologia 511: 79–89.
Turner, R., Qureshi, N., Rabalais, N. N. et al. 1998. Fluctuating silicate: nitrate ratios and coastal plankton food webs. – Proc. Natl Acad. Sci. USA 22: 13048–13051.
Van Nieuwerburgh, L., Wanstrand, I. and Snoeijs, P. 2004. Growth and C: N: P ratios in copepods grazing on N- or Si-limited phytoplankton blooms. – Hydrobiologia 514: 57–72.
Vitousek, P. M. 1994. Beyond global warming: ecology and global change. – Ecology 75: 1861–1876.
Vitousek, P. M. and Farrington, H. 1997. Nutrient limitation and soil development: experimental test of a biogeochemical theory. – Biogeochemistry 37: 63–75.
Wackernagel, M. and Yount, J. D. 1998. The ecological footprint: an indicator of progress toward regional sustainability. – Environ. Monit. Assess. 51: 511–529.
Wackernagel, M., Schulz, N. B., Deumling, D. et al. 2002. Tracking the ecological overshoot of the human economy. – Proc. Natl Acad. Sci. USA 99: 9266–9271.
Walker, T. W. and Syers, J. K. 1976. The fate of phosphorus during pedogenesis. – Geoderma 15: 1–19.
Weltzin, J., Belote, R. and Sanders, N. 2004. Biological invaders in a greenhouse world: will elevated CO_2 fuel plant invasions? – Front. Ecol. Environ. 1: 146–153.
White, T. C. R. 1993. The inadequate environment: nitrogen and the abundance of animals. – Springer-Verlag.