ECOLOGICAL STOICHIOMETRY IN AQUATIC ECOSYSTEMS

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Summary

This chapter focuses on the balance of the elements carbon, nitrogen and phosphorus in ecological interactions and processes of aquatic ecosystems. Primary producers stand at the base of the food web, transforming inorganic nutrients, using light energy, into organic biochemicals. These biochemicals are characterized by a specific elemental composition, differing in the relative content of carbon, nitrogen and phosphorus. As the biochemicals are related to specific cellular functions, shifts in primary producer C:N:P stoichiometry may alter its growth, and affect the phytoplankton community composition. Subsequently, such changes at the base of the food web may cascade throughout the entire aquatic ecosystem.

In aquatic ecosystems, the main primary producer is phytoplankton. The elemental C:N:P ratio of phytoplankton typically reflects the so-called Redfield ratio of 106:16:1, but can also greatly vary. This variation is caused by differences in availability of inorganic carbon, light energy, and nutrients, which will influence resource allocation to biochemicals, and affect phytoplankton growth. Typically, phytoplankton carbon:nutrient stoichiometry increases with 1) decreasing growth rates as result of enhanced nutrient limitation, 2) decreasing nutrient availability relative to other non-limiting nutrients, and 3) enhanced light and CO_2 availability, in particular under nutrient limited conditions. Changes in phytoplankton growth and elemental composition may have consequences for the entire food web, as it determines the quantity and quality of food available for herbivorous zooplankton. In contrast to the elemental ratios of phytoplankton, zooplankton elemental ratios are more constraint, which is referred to as elemental homeostasis. This constraint is due to a fixed

allocation of elements to structural biochemicals, and due to the lack of efficient storage mechanisms.

Taking the variable elemental stoichiometry of phytoplankton into account, there is often a mismatch in elemental composition between autotroph and heterotroph. Typically, phytoplankton is more carbon rich as compared to zooplankton, resulting in higher carbon:nutrient ratios. Zooplankton developed several mechanisms to account for this mismatch, including selective feeding, enhanced turnover rates, and selective respiration or discharge. The extent to which a zooplankton species is affected by a stoichiometric mismatch with the available food will further depend on its elemental composition, its growth rate, and its size. The stoichiometric mismatch between phytoplankton and zooplankton may subsequently cascade to higher trophic levels.

Eutrophication and climate change will alter the availability of nutrients, carbon and light in aquatic ecosystems. These anthropogenic-driven changes in resource availability will likely affect phytoplankton C:N:P stoichiometry. This will have implications for consumer growth and reproduction, and thus may alter the structure and functioning of entire aquatic food webs.

All in all, the field of ecological stoichiometry provides a very useful framework to couple inorganic elements with ecosystem structure and functioning.

1. Introduction

All organisms are built from the same basic set of elements. Apart from hydrogen (H) and oxygen (O), predominant elements in life are carbon (C) and nitrogen (N). These four elements constitute up to 99% of living biomass. Many other elements are also important in cellular processes, such as for example magnesium in photosynthesis, or iron in oxygen transport through the body. Of these ‘lesser’ elements, phosphorus (P) plays the most prominent role as it is essential for both the storage and transfer of genetic information, and the energy metabolism within cells.

Primary producers link the non-living world with the living world by converting inorganic carbon and nutrients into organic compounds, mostly with the help of light as energy source. Where macrophytes and macro-algae may dominate in more shallow systems, microalgae (phytoplankton) are the key primary producers in most pelagic aquatic systems. They are the main prey of herbivorous grazers such as ciliates, rotifers and crustaceans (zooplankton). These primary consumers are in turn consumed by secondary consumers, for instance by fish (Stibor and Sommer 2004). Growth and reproduction of consumers obviously greatly depends on the quantity of their food, typically determined by the availability of carbon (i.e. energy). However, also the quality of the food is of importance, especially when the quantity of the food is so high that energy requirements of maintenance processes are met. In the stoichiometric context of this chapter food quality will be mainly determined by the relative availability of carbon and nutrients.

The balance of carbon and nutrients in phytoplankton depends on the availability of light and resources in the environment, which in turn affects the production of organic compounds. Zooplankton consumes phytoplankton, and thereby obtains energy and nutrients that were accumulated by the algae. The ratios between the elements available in phytoplankton do not always match the requirements of the consumers. The field of *ecological stoichiometry* studies the balance between these elements among organisms and their interactions with the environment. As such, the field of ecological stoichiometry incorporates ‘first principles’ like mass balance, and can be applied to a variety of processes from the cellular to ecosystem level.

For this chapter, we focus on aquatic ecosystems only, even though ecological stoichiometry obviously applies to all interactions between producers and consumers. Furthermore, we will focus on the elements carbon, nitrogen and phosphorus. These elements, apart from oxygen and hydrogen (mainly present in water), typically show the highest relative abundance in living organisms compared to the non-living world. As such, these elements have the highest potential to be limiting biological production. For detailed information on the complete field of *ecological stoichiometry* we refer to the seminal book of Robert W. Sterner and James J. Elser (2002).

2. Linking Biological Functions to Elemental Stoichiometry

Primary producers typically take up inorganic carbon and nutrients from their environment by using light energy (photosynthesis), and transfer inorganic elements with the obtained energy into organic biochemicals (Fig. 1). Hence, these biochemicals are the first step in coupling elemental composition of the non-living world with the stoichiometry of life. As the various biochemicals consist of different elements in different ratios, they depend differently on the elements that are acquired. Moreover, also the machinery necessary to synthesize these substances has different elemental requirements. The synthesized biochemicals are then used to build cellular compounds, with specific cellular functions. Can these cellular functions be coupled with a specific C:N:P stoichiometry? To answer that question, the acquisition and assimilation of carbon, nitrogen and phosphorus from inorganic elements towards structural compounds will be discussed in this paragraph.

2.1. Conventions about Element Ratios

In literature associated with ecological stoichiometry the relative content of an element in an organism is expressed in different sorts of units (e.g. as percentage of dry weight, or as atomic ratios). Here we aim to structure these units in line with Sterner and Elser (2002). Where we discuss elemental content, amounts are expressed as mass of an element relative to the raw dry-mass (i.e. including inorganic and organic compounds) of the whole organism (e.g. %C by mass). Preferentially, however, units are converted to atomic ratios of elements (e.g. C:N), as chemical reactions are also described by atom-to-atom interactions, and when we think in building blocks of different organic compounds, ratios are the measure of choice. Elemental ratios are useful in describing the relative contribution of one element to another. Ratios however, do not give information about the absolute amount of respective elements. For instance, a high C:P ratio may indicate a relatively high amount of carbon, relative to the phosphorus content, but gives no information on the absolute amount of both carbon and phosphorus in the organism, which may be low or high.

2.2. Nutrient Acquisition

Phytoplankton obtains its carbon from dissolved CO_2 and bicarbonate (HCO_3^-) during photosynthesis. Therefore, the availability of both inorganic carbon and light plays an important role in carbon acquisition of phytoplankton. The inorganic carbon is converted into carbohydrates, which can be used for synthesis of polysaccharides, amino acids and nucleotides, or converted into fatty acids and lipids (Fig. 1). Nitrogen is taken up as nitrate (NO_3^-), nitrite (NO_2^-) or ammonium (NH_4^+). Several cyanobacteria species can fix nitrogen from N_2, and other species can take up nitrogen in the organic form, for instance as urea. Once taken up, inorganic nitrogen is incorporated into a carbon-backbone and assimilated to amino acids (Fig. 1). Phosphorus is usually taken up as ortho-phosphate, which includes phosphate (PO_4^{3-}), hydrogen phosphate (HPO_4^{2-}), and dihydrogen phosphate ($H_2PO_4^-$), but a few examples also exist of uptake of organic phosphorus compounds. Cellular inorganic phosphorus (P_i), together with amino acid derived nucleobases, is incorporated into a carbon-backbone forming nucleotides (Fig. 1).

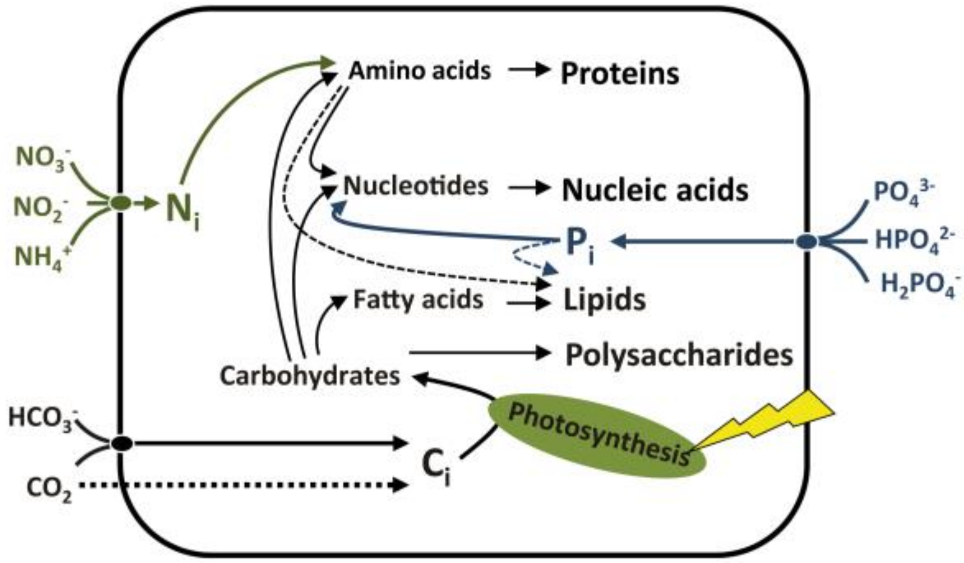

Figure 1. Schematic diagram of carbon, nitrogen and phosphorus uptake and assimilation in phytoplankton. C_i, N_i and P_i refer to cellular inorganic carbon, inorganic nitrogen, and inorganic phosphorus, respectively.

2.3. From Inorganic Nutrients to Organic Compounds

Inorganic elements taken up by primary producers are assimilated into biochemicals and cellular structural compounds. The key biochemicals are carbohydrates, lipids (consisting of fatty acids), proteins (consisting of amino acids), and nucleic acids (consisting of nucleotides). The different biochemicals comprise varying elemental ratios. Hence, changes in the relative composition of these biochemicals will affect the C:N:P stoichiometry of organisms. As the biochemicals fulfil different cellular functions, the C:N:P stoichiometry of the cell as a whole may be coupled to these functions.

2.3.1. Carbohydrates

Glucose is the most commonly known carbohydrate and it plays a central role in the energy metabolism of organisms. Carbohydrates also serve as important carbon and energy storage compounds, for instance as polysaccharides such as starch and glycogen. In addition, polysaccharides are also part of the structural biomass, for instance as cellulose in plants, as peptidoglycan in bacterial cell membranes, and as chitin in fungi and invertebrates.

Cellulose is a chain of glucose and consists of water and carbon, i.e. it does not contain nitrogen or phosphorus (Table 1). Peptidoglycan and chitin also contain nitrogen, resulting in a structural atomic C:N ratio of 2.6 and 5.9 respectively (Sterner and Elser 2002). Thus, increases in relative glucose content of cells will enhance the C:N ratio of the cell. Increases in peptidoglycan and chitin content will increase the cellular carbon content, but the nitrogen content as well, thereby enhancing the cellular N:P ratio.

2.3.2. Lipids

Lipids are biomolecules used amongst others for storage of energy and as structural compounds in cell membranes, but also as potential signaling compounds (e.g. sterols). Typical lipids used for energy storage are the tricylglycerols, which consist of three fatty acids linked to a glycerol molecule. These tricylglycerols have a high carbon content, and are well suited for carbon (energy) storage (Table 1). Fatty acids and glycerols do not contain nitrogen and phosphorus. Hence, tricylglycerols are carbon rich biochemicals, devoid of nitrogen and phosphorus. Another important group of lipids, prominently involved in cellular membranes, are phosphoglycerides. This group of lipids contains a phosphoester or phosphonate linkage between the fatty acids and a variable terminal functional group.

As the functional groups often contain some nitrogen, phosphoglycerides contain carbon, nitrogen and phosphorus. Nitrogen however is only present in minor amounts (Table 1). Hence the compounds contain a relatively high amount of phosphorus. Thus, increases in the relative cellular tricylglycerol content will enhance the cellular carbon:nutrient ratio, while an increase in the relative phosphoglyceride content will enhance the overall carbon content, but reduce the N:P ratio.

2.3.3 Proteins

Proteins are involved in many cellular processes and in particular in the form of enzymes. As a result, proteins play a key role in the cellular metabolism. In addition, proteins are important structural compounds, and are involved in cell signaling. Proteins are comprised of one or more polypeptides, which are typically built from chains of different combinations of 20 proteinogenic amino acids. These amino acids are nitrogen based biochemicals, with nitrogen contents varying between 8% in tyrosine to 32% in arginine (by mass; see also Table 1).

Assuming a protein is comprised from an equal proportion of the 20 amino acids, the average carbon content will be 47% (by mass), the nitrogen content will be 15% (by mass), and the overall atomic C:N ratio will be 3.6 (see also Table 1). This may deviate if proteins contain more N-rich or N-poor amino acids. Yet, the average nitrogen content of 15% (by mass) seems representative for proteins (Sterner and Elser 2002). Hence, increases in the relative protein content may greatly reduce the C:N ratio, but particularly may increase the N:P ratio.

2.3.4 Nucleic Acids

Nucleic acids contain the genetic information of all organisms. DNA and RNA are used to encode, transmit and express genetic information. DNA and RNA are constructed from nucleotides that consist of a phosphate group, a nucleobase and a pentose sugar. The nucleobases that can be incorporated are the purines adenine and guanine, and the pyrimidines cytosine, uracil and thymine. The purines and pyrimidines differ in their elemental composition, but as their contribution to nucleic acids is typically equal (Lehninger et al. 1993), an average has been assumed to estimate their carbon, nitrogen and phosphorus content.

Following this assumption, the nucleic acids comprise an average nitrogen content of 14-15% and an average phosphorus content of 8-9% (by mass; see also Table 1). The nitrogen content is relatively high and comparable to proteins. As the nucleic acids also contain a relative high amount of phosphorus, their N:P ratio is relatively low. Thus an increase in the relative cellular content of nucleic acids will likely cause minor changes in the cellular C:N ratios, but will decrease the cellular N:P ratio.

		%C	**%N**	**%P**	**C:N**	**N:P**
			(mass)		**(atomic)**	
Carbohydrates		37	0	0	-	-
Fatty acids	Butyric acid (C4:0)	55	0	0	-	-
	Lignoceric acid (C24:0)	78	0	0	-	-
Amino acids	Tyrosine	60	8	0	8.7	-
	Arginine	41	32	0	1.5	-
Nucleotides	DNA[a]	33	15	8.7	2.6	4.0
	RNA[a]	30	14	8.4	2.4	3.8
Lipids	Triacylglycerols[b]	75	0	0	-	-
	Phospholipids[c]	65	1.6	4.2	48	0.9
Proteins	Average[d]	47	15	0	3.6	-

Table 1. Relative contribution (by mass) of carbon, nitrogen and phosphorus, and the atomic C:N and C:P stoichiometry, of several key biochemicals.

2.3.5. Biominerals

Some organisms contain large amounts of biominerals such as calcium carbonates, silica and hypoxyapatite. Calcium carbonates ($CaCO_3$) can be found in exoskeletons of crustaceans, but are much more visible in for instance mollusk shells, foramineferal tests and coccolithophorid cell walls. The latter two groups play a key role in the biogeochemical cycling of calcium and carbon. Silica (or opal; amorphous hydrated silica SiO2 . nH_2O) is a major constituent of diatom frustules, giving diatoms a unique molar Si:C ratio of ~1 (Sommer 1986). Hence, diatoms play a key role in the biogeochemical silicon cycle. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is the key component of bones and bony materials (e.g. teeth and antlers) of vertebrates. Bones play an important role in determining the elemental stoichiometry of vertebrates. In particular due to the high phosphorus content, bone content may greatly affect organism C:P ratios (see also 4.3).

2.4. Turning Things Around

From the above it has become clear that the elemental composition of an organism is intricately linked to its biochemical composition. This, we can also turn around. Organisms with high C:N and C:P ratios will have a relative high amount of carbon-based biochemicals such as carbohydrates and lipids, whereas they will have relatively low amounts of nitrogen- and phosphorus-based biochemicals such as proteins and nucleic acids, respectively. Thus, the elemental composition of an organism may indicate its relative biochemical composition, which in turn can be associated to specific cellular functions.

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Bibliography

Allen M.M. (1984). Cyanobacterial cell inclusions. *Annual Review of Microbiology* 38, 1-25. [A comprehensive overview of intracellular inclusions in cyanobacteria]

Anderson D.M., Glibert P.M. and Burkholder J.M. (2002). Harmful algal blooms and eutrophication: nutrient sources, composition, and consequences. *Estuaries* 25, 704-726. [A comprehensive overview showing trends in eutrophication and the consequences for harmful algal blooms]

Becker C, and Boersma M (2010) Limiting levels of eicosapentaenoic acid: What do we really know? Limnology and Oceanography 55, 459-462. [A study discussing biochemical versus elemental limitations]

Behrenfeld M.J., O'Malley R.T., Siegel D.A., McClain C.R., Sarmiento J.L., Feldman G.C., Milligan A.J., Falkowski P.G., Letelier R.M. and Boss E.S. (2006). Climate-driven trends in contemporary ocean productivity. *Nature* 444, 752-755. [A study that links ocean primary productivity with climate variability]

Boersma M (2000) The nutritional quality of P-limited algae for *Daphnia*. Limnology and Oceanography 45, 1157-1161. [A study discussing the relative importance of mineral and biochemical limitations for zooplankton]

Boersma M. and Elser J.J. (2006). Too much of a good thing: on stoichiometrically balanced diets and maximal growth. *Ecology* 87, 1335-1340. [An overview of the impact of high phosphorus food on zooplankton growth]

Boersma M. and Kreutzer C. (2002). Life at the edge: is food quality really of minor importance at low quantities? *Ecology* 83, 2552-2561. [An overview of the effect of different quantities of phosphorus limited food on zooplankton growth, discussing the impact of food quality versus food quantity]

Boersma M., Aberle N., Hantzsche F.M., Schoo K.L., Wiltshire K.H. and Malzahn A.M. (2008). Nutritional limitation travels up the food chain. *International Review of Hydrobiology* 93, 479-488. [An overview of the impact of nutrient limited primary production on higher trophic levels]

Cassadevall M., Casinos A., Viladiu C. and Ontañon M. (1990). Scaling of skeletal mass and mineral contents in teleosts. *Zoologischer Anzeiger* 225, 144-150. [A study that shows the ratio between skeletal mass and body mass of fishes]

Cowles T.J., Olson R.J. and Chisholm S.W. (1988). Food selection by copepods: discrimination on the basis of food quality. *Marine Biology* 100, 41-49. [A study on the selection of food by a marine copepod based on diatom elemental composition and protein content]

DeMott W.R. (1986) The role of taste in food selection by freshwater zooplankton. *Oecologia* 69, 334-340. [A study on the selection of polystyrene spheres over untreated spheres by various zooplankton species]

Dickman E.M., Vanni M.J. and Horgan M.J. (2006). Interactive effects of light and nutrients on phytoplankton stoichiometry. *Oecologia* 149, 676-689. [A study on the impact of various light availabilities and high and low nutrient concentrations on the C:N:P stoichiometry of freshwater phytoplankton communities]

Droop M.R. (1973). Some thoughts on nutrient limitation in algae. *Journal of Phycology* 9, 264-272. [A study relating phytoplankton growth to cellular nutrient quota]

Elser J.J. and Hassett P. (1994). A stoichiometric analysis of the zooplankton-phytoplankton interaction in marine and freshwater ecosystems. *Nature* 370, 211-213. [An overview of phytoplankton and zooplankton N:P ratios in freshwater and marine ecosystems]

Elser J.J. and Urabe J. (1999). The stoichiometry of consumer-driven nutrient recycling: Theory, observations, and consequences. *Ecology* 80, 735-751. [An overview of the relation between elemental composition of zooplankton, nutrient recycling by zooplankton, and the elemental composition of phytoplankton]

Elser J.J., Dobberfuhl D.R., MacKay N.A. and Schampel J.H. (1996). Organism size, life history, and N:P stoichiometry. *BioScience* 46, 674-684. [An early report on ecological stoichiometry]

Elser J.J., Sterner R.W., Galford A.E., Chrzanowski T.H., Findlay D.L., Mills K.H., Paterson M.J., Stainton M.P. and Schindler D.W. (2000). Pelagic C:N:P stoichiometry in a eutrophied lake: Responses to a whole-lake food-web manipulation. *Ecosystems* 3, 293-307. [A study on the C:N:P stoichiometry of the food web in an eutrophic lake, discussing the role of N_2 fixation by cyanobacteria]

Elser J.J., Acharya K., Kyle M., Cotner J., Makino W., Markow T., Watts T., Hobbie S., Fagan W., Schade J., Hood J. and Sterner R.W. (2003). Growth rate-stoichiometry couplings in diverse biota. *Ecology Letters* 6, 936-943. [An overview of the relation between growth rate, RNA content and biomass phosphorus content in various heterotrophs]

Elser J.J., Andersen T., Baron J.S., Bergström A.K., Jansson M., Kyle M., Nydick K.R., Steger L. and Hessen D.O. (2009). Shifts in lake N:P stoichiometry and nutrient limitation driven by atmospheric nitrogen deposition. *Science* 326, 835-837. [An overview of the impact of atmospheric nitrogen deposition on the shift from nitrogen to phosphorus limited phytoplankton growth in freshwater lakes]

Falkowski P. (2000). Rationalizing elemental ratios in unicellular algae. *Journal of Phycology* 36, 3-6. [A discussion on the interpretation of the Redfield ratio]

Fee E.J., Hecky R.E., Kasian S.E.M. and Cruikshank D.R. (1996). Effects of lake size, water clarity, and climatic variability on mixing depths in Canadian Shield lakes. *Limnology and Oceanography* 41, 912-920. [A study on the role of size, water clarity and interannual climatic variability on stratification in lakes]

Frigstad H., Andersen T., Hessen D.O., Naustvoll L.J., Johnsen T.M. and Bellerby R.G.J. (2011). Seasonal variation in marine C:N:P stoichiometry: can the composition of seston explain stable Redfield ratios? *Biogeosciences* 8, 2917-2933. [A study on seasonal variability of dissolved and seston C:N:P ratios in coastal waters]

Goldman J.C., McCarthy J.J. and Peavey D.G. (1979). Growth rate influence on the chemical composition of phytoplankton in oceanic waters. *Nature* 279, 210-215. [A chemostat study about the relation between growth rate and phytoplankton C:N:P stoichiometry]

Guisande C, Riveiro I, and Maneiro I (2000) Comparisons among the amino acid composition of females, eggs and food to determine the relative importance of food quantity and food quality to copepod reproduction. Marine Ecology-Progress Series 202, 135-142. [A study showing the importance of essential amino acids in the food of zooplankton]

Hansen P.J. (2002). Effect of high pH on the growth and survival of marine phytoplankton: implications for species succession. *Aquatic Microbial Ecology* 28, 279-288. [A study describing the role of pH limitation on phytoplankton succession with special focus on dinoflagellates]

Hessen D.O. and Lyche A. (1991). Interspecific and intraspecific variations in zooplankton element composition. *Archiv für Hydrobiologie* 121:343-353. [A study investigating variation in C:N:P content in zooplankton]

Hessen D.O., Andersen T., Brettum P. and Faafeng B.A. (2003). Phytoplankton contribution to sestonic mass and elemental ratios in lakes: implications for zooplankton nutrition. *Limnology and Oceanography* 48, 1289-1296. [A study showing the elemental composition of lake seston, discussing whether this causes food quantity or quality limitation in zooplankton]

Hessen D.O. and Anderson T.R. (2008). Excess carbon in aquatic organisms and ecosystems: physiological, ecological, and evolutionary implications. *Limnology and Oceanography* 53, 1685-1696. [A study showing the fate of organic material dependent on the uptake in the food]

Lampert W. and Schrober U. (1980). The importance of “threshold” food concentrations. In *Evolution and Ecology of Zooplankton Communities* (Ed. Kerfoot W.C), University Press of New England, Hanover, NH, USA, pp 264-267. [A book chapter about the impact of food concentrations on zooplankton reproduction]

Lampert W. (1978). Release of dissolved organic carbon by grazing zooplankton. *Limnology and Oceanography* 23, 831-834. [An early study that shows sloppy feeding; the loss of DOC by zooplankton grazing]

Loladze I. and Elser J.J. (2011). The origins of the Redfield nitrogen-to-phosphorus ratio are in a homoeostatic protein-to-rRNA ratio. *Ecology Letters* 14, 244-250. [A study showing that the protein:rRNA ratio in microorganisms can determine the Redfield N:P ratio]

Loladze I., Kuang Y. and Elser J.J. (2000). Stoichiometry in producer-grazer systems: Linking energy flow with element cycling. *Bulletin of Mathematical Biology* 62, 1137-1162. [A model study showing the paradox of energy enrichment on predator-prey interactions]

Meunier C., Hantzsche F., Cunha-Dupont A., Haafke J., Oppermann B., Malzahn A. and Boersma M. (2012). Intraspecific selectivity, compensatory feeding and flexible homeostasis in the phagotrophic flagellate *Oxyrrhis marina*: three ways to handle food quality fluctuations. *Hydrobiologia* 680, 53-62. [A study showing three different strategies of the marine protist *Oxyrrhis marina* to deal with nutrient poor food]

Müller-Navarra D.C. (1995). Biochemical versus mineral limitation in *Daphnia*. Limnology and Oceanography 40, 1209-1214. [A study discussing the relative importance of mineral and biochemical limitations for zooplankton]

Müller-Navarra D.C. (2008). Food web paradigms: The biochemical view on trophic interactions. *International Review of Hydrobiology* 93, 489-505. [An overview of the role of biochemicals on food quality]

Müller-Navarra D.C, Brett M.T, Liston A.M. and Goldman C.R. (2000). A highly unsaturated fatty acid predicts carbon transfer between primary producers and consumers. Nature 403, 74-77 [A study highlighting the role of polyunsaturated fatty acids in the food of zooplankton]

Nixon S.W. (1995). Coastal marine eutrophication: a definition, social causes, and future concerns. *Ophelia* 41, 199-219. [An overview on the basics of eutrophication in coastal marine ecosystems]

Peñuelas J., Sardans J., Rivas-Ubach A. and Janssens I.A. (2012). The human-induced imbalance between C, N and P in Earth's life system. *Global Change Biology* 18, 3-6. [An overview of the impact of global carbon and nitrogen enrichment and phosphorus exhaustion on the C:N:P balance in ecosystems]

Pilati A. and Vanni M.J. (2007). Ontogeny, diet shifts, and nutrient stoichiometry in fish. *Oikos* 116, 1663-1674. [A study that describes ontogeny as main driver for fish N:P stoichiometry, whereas diet N:P mainly affects excreted N:P]

Plath K. and Boersma M. (2001). Mineral limitation of zooplankton: Stoichiometric constraints and optimal foraging. *Ecology* 82, 1260-1269. [A study showing the importance of phosphorus content of algae in determining food quality and feeding activity of zooplankton]

Redfield A.C. (1934). On the proportions of organic derivatives in sea water and their relation to the composition of plankton. In: *James Johnstone Memorial Volume* (Ed. Daniel R.J.), Liverpool University Press, Liverpool, UK. pp 176-192. [A classical paper showing for the first time the remarkable correspondence between plankton N:P ratios and the nitrate:phosphate ratio in the water]

Redfield A.C. (1958). The biological control of chemical factors in the environment. *American Scientist* 46, 205-221. [A canonical paper giving an overview of the impact of autotrophs on biogeochemical cycles]

Rhee G.Y. (1973). A continuous culture study of phosphate uptake, growth rate and polyphosphate in *Scenedesmus* sp. *Journal of Phycology* 9, 495-506. [A chemostat study on the relation between growth rate and phosphorus uptake, phosphorus availability, phosphorus quota, and alkaline phosphatases in a freshwater green alga]

Rhee G.Y. (1978). Effects of N:P atomic ratios and nitrate limitation on algal growth, cell composition, and nitrate uptake. *Limnology and Oceanography* 23, 10-25. [A chemostat study showing the impact of nitrate and phosphate limitation on cellular carbon, nitrogen and phosphorus quotas, and biochemical composition in a green alga]

Riebesell U. and Tortell PD. (2011). Effects of ocean acidification on pelagic organisms and ecosystems. In: *Ocean acidification* (Eds. Gattuso J.-P. and Hansson L.), Oxford University Press, Oxford, UK, pp. 99-121. [An overview of the impact of ocean acidification on a wide range of planktonic processes]

Rosenzweig M.L. (1971). Paradox of enrichment: Destabilization of exploitation ecosystems in ecological time. *Science* 171, 385-387. [A first description of the paradox of enrichment, showing that enrichment of a model ecosystem can cause a reduction in its food yield]

Smith V.H., Tilman G.D. and Nekola J.C. (1999). Eutrophication: impacts of excess nutrient inputs of freshwater, marine, and terrestrial ecosystems. *Environmental Pollution* 100, 179-196. [A review describing the impact and management of cultural eutrophication in freshwater, marine, and terrestrial ecosystems]

Smith V.H., Joye S.B. and Howarth R.W. (2006). Eutrophication of freshwater and marine ecosystems. *Limnology and Oceanography* 51, 351-355. [An overview of a special issue, describing the impact of eutrophication in aquatic ecosystems]

Solomon S., Qin D., Manning M., Marquis M., Averyt K., Tignor M.M.B., Miller Jr. H.L. and Chen Z. (2007). *Climate change 2007: the physical science basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, UK. [A thorough overview on human and natural drivers of climate change, observed climate change, climate processes, and estimates of projected future climate change]

Sommer U. (1986). Nitrate- and silicate-competition among Antarctic phytoplankton. *Marine Biology* 91, 345-351. [A study on the impact of nitrate and silicate availability on growth and competition of natural Antarctic phytoplankton species]

Sommer U. and Sommer F. (2006). Cladocerans versus copepods: the cause of contrasting top-down controls on freshwater and marine phytoplankton. *Oecologia* 147, 183-194. [A mesocosm study on the different impacts of cladocerans and copepods on phytoplankton, and the C:N:P stoichiometry of seston in freshwater and marine ecosystems]

Sterner R.W. (1997). Modelling interactions of food quality and quantity in homeostatic consumers. *Freshwater Biology* 38, 473-481. [A model study discussing carbon (food quantity) or C:P (food quality) limitation in producer-consumer interactions]

Sterner R.W. and Elser J.J. (2002). *Ecological Stoichiometry: The biology of elements from molecules to the biosphere.* Princeton University Press, Princeton, USA. [A detailed overview on the balance of elements, mainly carbon, nitrogen and phosphorus, in ecological interactions and processes]

Sterner R.W., Elser J.J., Fee E.J., Guildford S.J. and Chrzanowski T.H. (1997). The light:nutrient ratio in lakes: The balance of energy and materials affects ecosystem structure and process. *The American Naturalist* 150, 663-684. [A study showing and discussing the correlation between light:phosphorus availability with seston C:P ratio in freshwater lakes]

Stibor H. and Sommer U. (2004). Ocean food webs and trophic dynamics. In: *Marine Ecology* (Eds. Duarte C.M. and Lot A.), in *Encyclopedia of Life Support Systems (EOLSS)*, Developed under the Auspices of the UNESCO, Eolss Publishers, Oxford, UK. [An overview of trophic interactions in marine pelagic food webs]

Urabe J. and Watanabe Y. (1992). Possibility of N or P limitation for planktonic cladocerans: an experimental test. *Limnology and Oceanography* 37, 244-251. [A study on the threshold N:C and P:C ratios of two cladoceran species]

Urabe J. and Waki N. (2009). Mitigation of adverse effects of rising CO_2 on a planktonic herbivore by mixed algal diets. *Global Change Biology* 15, 523-531. [A study showing that reduced food quality of phytoplankton, indicated by enhanced C:P ratios, can be mitigated by higher species diversity]

Van de Waal D.B., Verschoor A.M., Verspagen J.M.H., Van Donk E. and Huisman J. (2010). Climate-driven changes in the ecological stoichiometry of aquatic ecosystems. *Frontiers in Ecology and the Environment* 8, 145-152. [A review on the implications of climate change on the C:N:P stoichiometry of aquatic ecosystems]

Van de Waal D.B., Verspagen J.M.H., Finke J.F., Vournazou V., Immers A.K., Kardinaal W.E.A., Tonk L., Becker S., Van Donk E., Visser P.M. and Huisman J. (2011). Reversal in competitive dominance of a toxic versus non-toxic cyanobacterium in response to rising CO_2. *The ISME Journal* 5, 1438-1450. [A chemostat study on the competition for inorganic carbon between toxic and non-toxic cyanobacteria strains]

Verschoor A.M., Vos M. and Van der Stap I. (2004). Inducible defences prevent strong population fluctuations in bi- and tritrophic food chains. *Ecology Letters* 7, 1143-1148. [A study on the impact of inducible defenses and phosphorus limitation on a freshwater bi- and tri-trophic food-chain]

von Elert E., Martin-Creuzburg D. and Le Coz J.R. (2003) Absence of sterols constrains carbon transfer between cyanobacteria and a freshwater herbivore (*Daphnia galeata*). Proceedings of the Royal Society of London Series B-Biological Sciences 270, 1209-1214. [A study showing that sterols may play a role in determining the quality of algal food for zooplankton]

Vrede T., Andersen T. and Hessen D.O. (1999). Phosphorus distribution in three crustacean zooplankton species. *Limnology and Oceanography* 44, 225-229. [A study on the allocation of phosphorus to different biochemicals in three freshwater crustacean zooplankton species]

White T.C.R. (1993). *The Inadequate Environment: Nitrogen and the abundance of animals*. Springer Verlag, Berlin, Germany. [A book on the importance of nitrogen availability in ecological processes]

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