

In the previous chapters, we have presented organic carbon in isolation from the other elements and focused on the biological processes involved in the transformation from inorganic to organic carbon and vice versa. This approach neglects the fact that the element carbon is part of molecules. The thermodynamic stability and reactivity of, and interactions among, these molecules eventually determine the function of organic carbon compounds and govern the rates of organic matter production, transformation and consumption. Organic molecules contain not only C, H and O, but also N, P, S and multiple other elements, and often in certain ratios, e.g. one P atom in each DNA or RNA nucleotide. Organic molecules have functional groups and stereochemistry that determine their interactions with the environment.

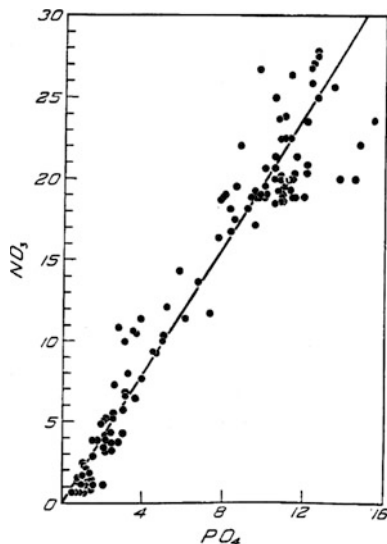
Following a concise discussion of Redfield organic matter and non-Redfield organic matter, we focus on organic matter as food for organisms, the compositional consequences of preferential consumption and the consequences for the composition of organic matter preserved and buried in marine sediments.

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## 6.1 Redfield Organic Matter

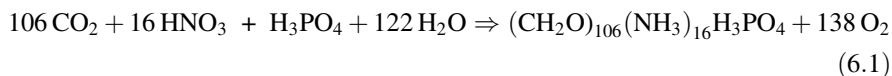
Chemical analysis of marine particulate organic matter, organisms and seawater by early oceanographers inspired Redfield (1934) to propose that marine plankton have relatively constrained atomic ratios of  $\sim 140$  C to  $\sim 20$  N and  $\sim 1$  P (Fig. 6.1). This empirical Redfield ratio was originally based on the similarity of these ratios in seawater and in marine plankton, and these ratios have since been shown to apply to assimilation ratios during phytoplankton growth and regeneration ratios during marine organic matter degradation. Redfield further noted the implications for oxygen consumption and later on (Redfield 1958) posed the intriguing question whether the biological processes control the proportions of these elements in the water.

**Fig. 6.1** Redfield's original correlation between phosphate and nitrate in seawater (Redfield 1934). The line has a slope of 20 rather than the modern value of 16 for ideal Redfield

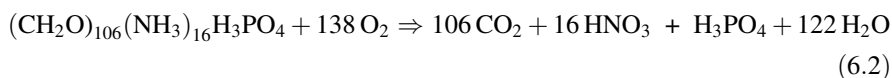


The Redfield ratio as formalized by Redfield et al. (1963), at 106C:16 N:1P, has been validated by thousands of observations, and the overall ratios appear to be robust. Redfield ratios have shown useful in a wide range of topics, from nutrient limitation to biogeochemical modelling in the present and past ocean. They are used in reconstruction of anthropogenic carbon inventories and are in the equations underlying Earth System modelling (Sarmiento and Gruber 2006). The original Redfield ratio has been extended to include other elements and heterotrophic organisms (ecological stoichiometry) and has been related to cellular level and global scale processes (Falkowski 2000; Sterner and Elser 2002; Box 6.1). At the cellular level, nitrogen is primarily used for the construction of proteins and phosphorus for the synthesis of ribosomal ribonucleic acids (rRNA). Loladze and Elser (2011) have shown that protein and ribosome synthesis results in a protein:rRNA ratio of  $\sim 3$ , which corresponds to an atomic N:P ratio of 16, as observed in the ocean for plankton. Moreover, they have shown that N and P limitation during cell growth results in N:P ratios below or above the Redfield ratio, respectively.

Redfield et al. (1963) presented the (canonical) overall reaction for marine organic matter production:



and consumption:



These RKR equations indicate that 138 units of oxygen are required for oxidation of one mole of Redfield organic matter: 106 oxygen molecules to convert  $\text{CH}_2\text{O}$  to  $\text{CO}_2$  and 32 oxygen molecules to convert the  $\text{NH}_3$  all the way to  $\text{HNO}_3$ . The  $\text{O}_2:\text{C}$  coefficient for aerobic respiration (including nitrification) is thus 1.3. Primary production based on nitrate (new production) or ammonium (recycled productions) has consequences for the quantity of oxygen released.

The problem with the traditional Redfield ratios as formulated in Eqs. 6.1 and 6.2 is that it simplifies marine organic matter into an elementary carbohydrate ( $\text{CH}_2\text{O}$ ), whereas newly produced marine organic matter is better represented as a mixture of proteins ( $\sim 65\%$ ), lipids ( $\sim 19\%$ ), and carbohydrates ( $\sim 16\%$ ) and other compounds (pigments and nucleic acids; Hedges et al. 2002; Bianchi and Canuel 2011). While simple carbohydrates are the first molecules formed during carbon fixation, the biosynthesis of proteins, lipids and polysaccharides results in the loss of hydrogen and oxygen. Hydrogen and oxygen loss results from dehydration, wherein  $\text{CH}_2\text{O}$  is transformed into  $\text{CH}_2$  chains in proteins and lipids. Moreover, there is also hydrogen loss during the transformation of the  $\text{NH}_3$ -group in ideal Redfield organic matter to the  $\text{NH}$ -amide group in proteins. Estimates of marine organic matter based on mixing of proteins, lipid, carbohydrates and nucleic acids and using modern analytical tools (Anderson 1995; Hedges et al. 2002), arrive at average compositions of  $\text{C}_{106}\text{H}_{175}\text{O}_{42}\text{N}_{16}\text{P}$  (Anderson 1995) and  $\text{C}_{106}\text{H}_{177}\text{O}_{37}\text{N}_{16}\text{PS}_{0.4}$  (Hedges et al. 2002) rather than  $\text{C}_{106}\text{H}_{260}\text{O}_{106}\text{N}_{16}\text{P}$  of the ideal Redfield ratio. This lower oxygen content has consequences for the  $\text{O}_2:\text{C}$  respiration coefficient. Equation 6.2 can be generalized to:



where  $\gamma = \alpha + 0.25\beta - 0.5\chi + 1.25\delta + 1.25\varepsilon$  and  $\lambda = -0.5\delta - 1.5\varepsilon + 0.5\beta$ . Substitution of these revised marine organic matter compositions in Eq. 6.3 results in  $\text{O}_2:\text{P}$  ratios of 150 to 154 and an  $\text{O}_2:\text{C}$  respiration coefficient ( $\gamma/\alpha$ ) of  $\sim 1.43$ . The latter result is consistent with the  $\text{O}_2:\text{C}$  ratio of  $\sim 1.46$  obtained from inverse analysis of water-column nutrient and oxygen changes along isopycnals (Anderson and Sarmiento 1994).

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## 6.2 Non-redfield Organic Matter

The composition of marine particles is rather uniform because phytoplankton and bacteria (and their remains) dominate plankton, and these organisms are primarily made up of proteins ( $>50\%$ ) supplemented by lipids, carbohydrates, nucleic acids and pigments. Individual species may deviate from ideal or revised Redfield ratios, but over larger spatial and temporal scales these differences average out. The composition of seagrasses and, in particular, emergent saltmarsh vegetation and mangrove trees deviates from unicellular primary producers: higher C:N and C:P ratios, less proteins and nucleic acids and more structural carbohydrates and lignins.

Moreover, there is much more variability in the composition of benthic primary producers, particularly in macrophytes. The higher variability is due to tissue differentiation: compounds involved in photosynthesis and carbon fixation are primarily in the leaves and not in the roots. Carbohydrates for storage (e.g. starch) can be transferred from leaves to rhizomes for long-term storage. These marine macrophytes re-allocate compounds and essential nutrients over the growing season: e.g. the resorption of nitrogen from senescent leaves and transfer to active growing leaves. Structural carbohydrates and lignins are needed for strength to deal with currents, waves and wind. Lignins are cross-linked phenolic polymers that occupy the space between structural carbohydrates, such as cellulose in the cell wall of macrophytes and trees. Polysaccharides are permeable to water, while the more hydrophobic lignins are not. Crosslinking between lignins and celluloses thus not only strengthens the cell wall but also provides capability to transfer water efficiently from roots to the leaves, where evapotranspiration occurs. The lignin-carbohydrate provided strength and stiffness are needed for saltmarsh plants and trees to stand and for submerged vegetation to resist currents and waves. These polymers are relatively rich in carbon and poor in nitrogen and phosphorus; this is the reason why seagrass, salt-marsh plants and in particular mangroves have high C:N and C:P ratios. These polymeric substances are difficult to degrade, with the consequences that the palatability of seagrasses, marsh vegetation and mangroves is relatively low (see Fig. 3.10).

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### 6.3 Organic Matter is Food

Organic matter, detritus as well as living biomass, is consumed because it is the primary source of energy and nutrition for heterotrophic consumers, i.e. it is food for animals and a substrate for heterotrophic microbes. Osmotrophic organisms either use dissolved organic matter directly or after extracellular (cell-attached or free) hydrolysis of polymeric substances into smaller units that can pass the cell membrane of these microbes. Animals ingest particulate organic matter, part of which is digested, and part is egested. The energy balance for animals is (Welch 1968):

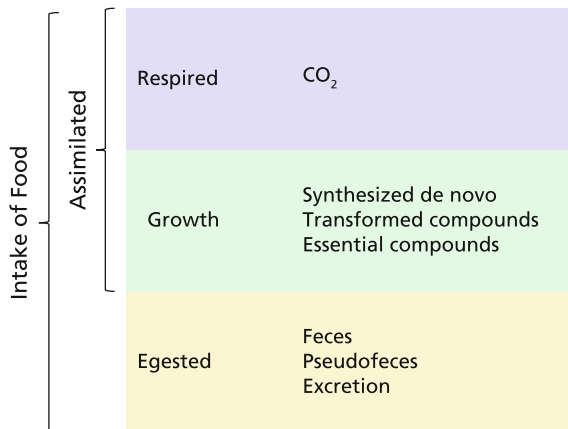
$$I = G + R + E \quad (6.4)$$

where *I* is the ingestion of food, *G* is growth and reproduction of the animal, *R* is respiration and *E* is egestion and excretion (e.g. feces). Food ingested by animals is digested physically (e.g. chewing, grinding), chemically (by enzymes) and biologically (by microbes in the digestion organs) to make it amenable to enter tissues, where it can be used for growth and respiration (energy). This simple equation can be used to define assimilation ( $A = G + R$ ), assimilation efficiency ( $A/I$ ), gross growth efficiency ( $G/I$ ) and net growth efficiency ( $G/A$ ).

Moreover, during periods of sufficient food, consumers can internally store part of the food assimilated for reserves in the form of carbohydrates and lipids.

Assimilation efficiencies vary widely depending on the food quality and the consumer: carnivores generally have higher assimilation efficiencies than herbivores and detritivores. However, this is partly compensated by higher net growth efficiencies for the herbivores, with the result that gross growth efficiencies vary over a rather narrow range (15–35%, Welch 1968). Assimilation efficiencies vary between elements, between biochemical classes of compounds (carbohydrates, amino acids, lipids) and among molecules within a class of compounds. For instance, carbohydrates and amino acids enriched in intracellular materials have higher assimilation efficiencies than those in cell-wall materials because cell-walls are less digested (Cowie and Hedges 1996). The composition of the diet and the material assimilated often differs from the composition of the consumers; consequently, some compounds (e.g. carbohydrates) are more used for respiration, while other compounds (e.g. amino acids) may be preferentially directed towards growth and synthesis of new tissues.

Detailed feeding studies of lipids, carbohydrates and amino acids at the compound levels with marine animals have revealed that some compounds are preferentially consumed and used for respiration, while others are used to synthesize compounds *de novo* or by transformation of assimilated compounds. These patterns have been shown not only to be taxon specific, but also to have a microbial processing signature (Woulds et al. 2014). The latter is consistent with the microbiome concept, i.e. microbes within animals' digestion system are key to the functioning of the animal. Moreover, there are a number of compounds that are



**Fig. 6.2** Animal processing of organic matter. Food taken in is either digested or not and then egested. Digested organic matter is used for respiration or for growth that occurs primarily via synthesis of new compounds, but also via transformation or retention of compounds taken in. Moreover, some compounds can be produced *de novo* or transformed by microbes in the digestive system

considered essential because consumers cannot synthesize them and have to assimilate them from their diet or from the microbes in their digestive system. These include some poly-unsaturated fatty acids and amino acids, such as threonine, valine, leucine, isoleucine, phenylalanine and lysine. The combined effect of compound specific processing during digestion, the use of compounds for growth, storage or respiration, and the need to acquire essential compounds and elements results in changes in the organic matter remaining, excreted and produced by these consumers (Fig. 6.2).

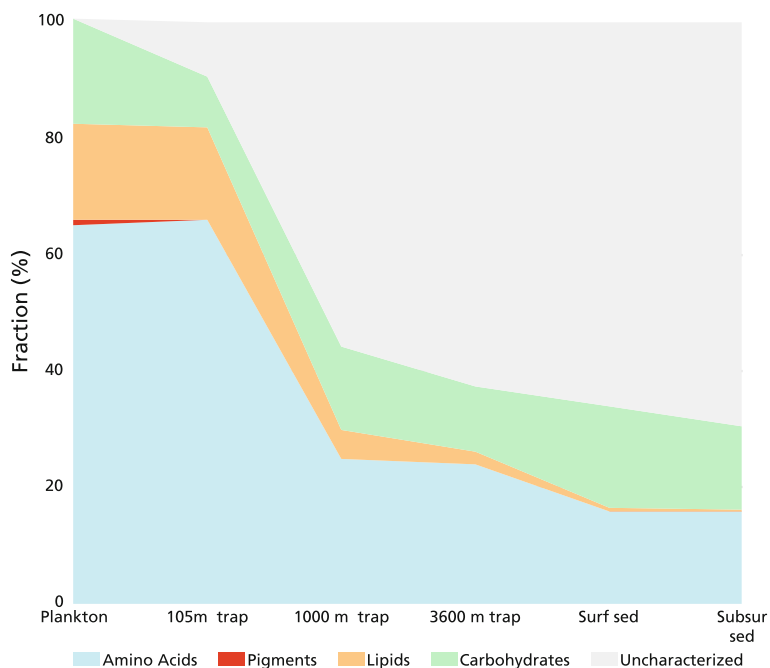
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## 6.4 Compositional Changes During Organic Matter Degradation

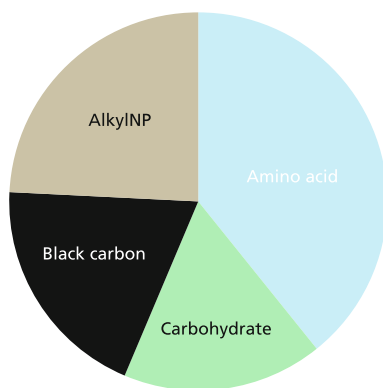
The above differences in assimilation efficiencies among various compounds and biochemical classes, and the preferential consumption of more labile components (Box 3.1; Fig. 3.9) have consequences for the composition of the organic matter remaining. Hedges, Wakeham, Lee and colleagues systematically studied the changes in the biochemical composition of organic matter during degradation from fresh phytoplankton, via sediment traps to surface and subsurface sediments (Wakeham et al. 1997). Amino acids (proteins), lipids and carbohydrates dominate the composition of phytoplankton and of detrital organic matter in shallow traps (Fig. 6.3). The composition changes rapidly upon degradation and organic matter in sediment traps below the surface mixed layer: amino acids decline from >60% to ~25% and lipids from ~10 to ~2%, while the relative carbohydrate contribution remains similar because some carbohydrates are structural components. Moreover, the proportion of organic matter that cannot be characterized molecularly increases with progressive degradation from a few % in fresh phytodetritus to >50% in sediment trap organic matter and >70% in deep-sea sediment organic matter (Fig. 6.3).

The majority of organic matter in deep-sea sediment traps and sediments cannot be characterized using solution or gas-based chromatographic methods because of low organic solvent extraction and hydrolysis yields. Solid-phase NMR techniques have been applied as an alternative, and these studies not only confirmed the proportions of amino acid and carbohydrate based on solution-based techniques but also revealed that non-hydrolysable carbon-rich material (i.e. black carbon) and non-protein alkyl group made up most of the molecularly uncharacterizable organic matter (Fig. 6.4). Accordingly, the organic matter buried in sediment not only represents a small fraction of that produced (few %, Chap. 4), but it also differs significantly and systematically from phytodetritus (Fig. 6.3). This complicates the use of bulk organic matter properties as a proxy for the origin of the organic matter and for reconstruction of paleoenvironments (Middelburg 2018).

The susceptibility towards degradation varies systematically among biochemical classes: pigments > lipids = carbohydrate > amino acids > lignin > black carbon. Pigments, DNA, RNA and other cellular constituents are the most easily degradable



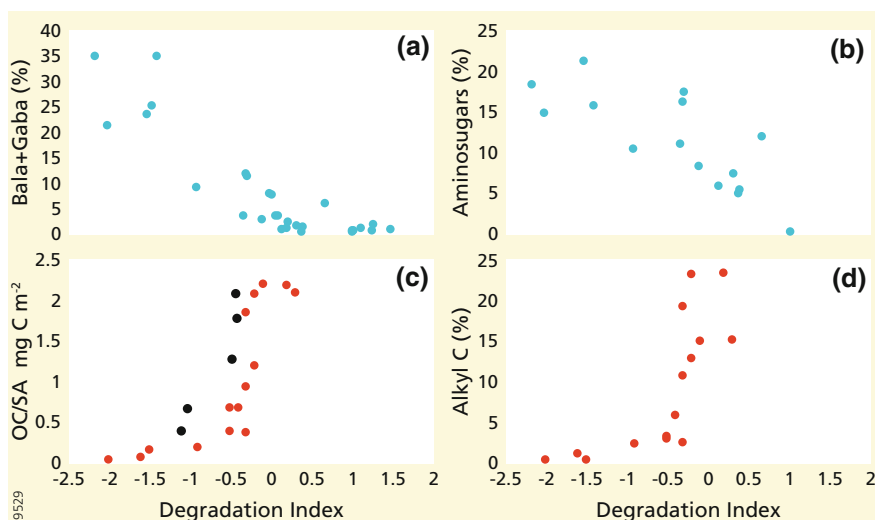
**Fig. 6.3** Changes in the biochemical composition of organic matter during degradation from plankton, via sediment traps at different depths to surface and subsurface sediments in the Pacific Ocean (Wakeham et al. 1997). Uncharacterized fraction was calculated by difference: the uncharacterized fraction increases with progressive degradation



**Fig. 6.4** Biochemical composition of marine sediments based on solid-phase NMR data (Gelinas et al. 2001). Four major compounds group were identified: amino acids, carbohydrates, black carbon and non-protein alkyl (AlkyINP)

compounds, followed by lipids, carbohydrate and amino acids (Fig. 6.3). While lignins are degraded in aerobic soils by fungi, these compounds are rather stable in the marine environments with the consequence that they have high preservation potential. Besides these differences among biochemical classes, there are also large differences among compounds within biochemical classes because of the inherent structural differences, as well as the macromolecular context. Structural carbohydrates are more stable than those involved in storage. Amino acids incorporated in large proteins are less available for consumers than those dissolved as free amino acids. Lipid reactivity towards degradation varies widely, as it depends on multiple factors, including the structure, stereochemistry, head-group, degree of saturation, and ether or ester linkages. While the relative reactivity of various compound classes and compounds within a biochemical class is systematic, absolute rates of degradation are largely context depending, i.e. identical compounds may have order of magnitude differences in kinetic parameters depending on the environment.

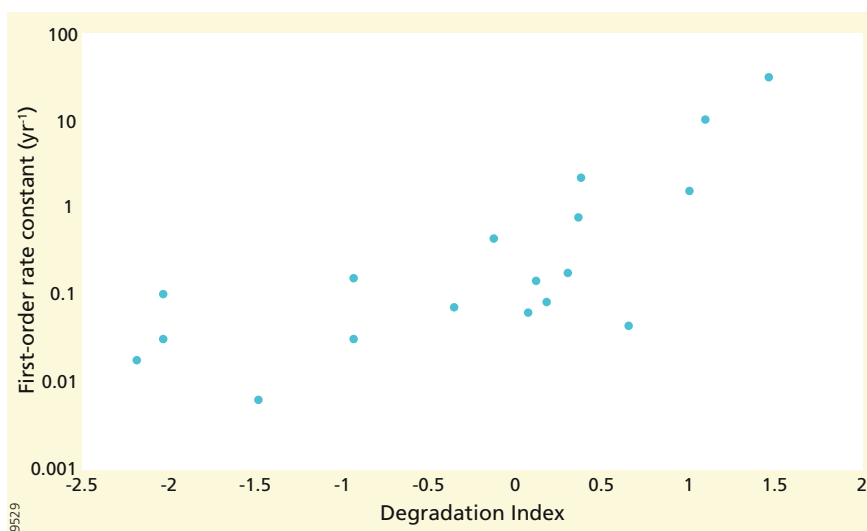
These systematic changes in organic matter composition due to degradation can be used to quantify the progress of degradation, or in other words, the degradation history. Often used degradation state parameters are intact to total pigment ratios,



**Fig. 6.5** Systematic changes in organic matter composition as degradation progresses. The degradation index of Dauwe and Middelburg (1998) is based on subtle changes in the amino acid composition. Fresh phytoplankton material has positive values, while extensively degraded sedimentary organic matter in deep-sea sediments has values  $< -1.5$ . Degradation causes relative accumulation of **a** non-protein amino acids Bala and Gaba and **b** aminosugars and a decrease in **c** the organic carbon content per sediment surface area (OC/SA) and **d** the fraction present as non-protein alkyl-C. Data are from Dauwe et al. (1999, blue), Gelinis et al. (2001, red) and Vandewiele et al. (2009, black)



pigment to carbon ratios, the contribution of amino acid carbon or nitrogen to the total carbon or nitrogen pool, the fraction of organic matter present as alkyl-C and the relative contribution of carbohydrates and amino acids to the total carbon pool. The most generic degradation state proxy is the amino acid based degradation index of Dauwe and Middelburg (1998). This degradation index is based on subtle changes in the amino acid composition of particulate organic matter. The resulting degradation index varies from +1.5 for fresh phytoplankton material to -2.5 for intensively degraded deep-sea sediment organic matter. The rationale is that the amino acid composition of phytoplankton is rather uniform and that changes measured in particulate organic matter can be attributed to mineralization processes. The degradation index correlates with multiple other organic matter degradation proxies, such as accumulation of microbial detritus (aminosugars, bacterial degradation products, D-amino acids derived from bacterial cell walls) and the decrease in organic carbon per unit surface area and contribution of alkyl-C (Fig. 6.5). The degradation index provides a continuous parameter to infer the organic matter degradation history, and one would expect a relation with the first-order rate constant for organic matter degradation shown in Fig. 3.9. Progressive degradation of organic matter should, according to the reactive continuum concept, lead to lower reactivity rate constant and to a lower degradation index. Figure 6.6 shows that the logarithm of the first-order rate constant and the degradation index of bulk organic matter are indeed correlated and that first-order rate constant can, in principle, be



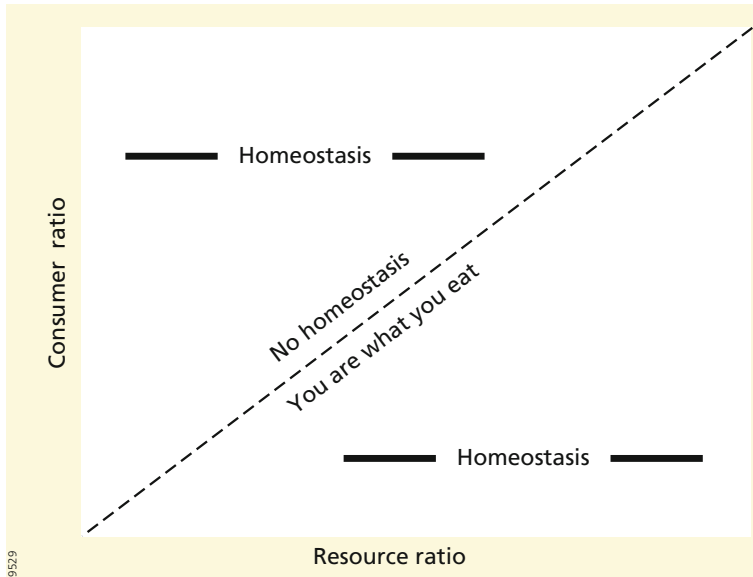
**Fig. 6.6** Relation between the degradation index and the first-order reaction constant (data from Dauwe et al. 1999). Phytoplankton has a degradation index of 1 to 1.5 and a first-order rate constant of  $>10 \text{ yr}^{-1}$ . Progressive degradation of organic matter lowers the degradation index and the reactivity constant

linked to organic matter composition. This does not imply that organic matter changes are the sole cause, but it does provide avenues to link kinetic biogeochemistry and organic geochemistry.

### **Box 6.1: Ecological stoichiometry**

The traditional approach towards food-web and ecosystem functioning focuses on carbon, i.e. energy, flows and ignores the role of other elements and the biochemical makeup of organic matter. In other words, the traditional approach focuses only on quantity and largely ignores the quality of the organic matter. This is unfortunate, as all organisms need at least 20 elements or more and many organisms also have to acquire some essential compounds from the environment or their diet. Ecological stoichiometry explicitly deals with the flow of nutrients (primarily N, P, but also others) from the environments via primary producers to herbivores, detritivores and carnivores.

Inspired by the pioneering work of Redfield in the early 20th century, ecologists (Sterner and Elser 2002) have developed the theory of ecological stoichiometry in which homeostasis is a central concept. Homeostasis is the property of organisms to maintain a constant composition, despite living in a variable environment or feeding on a variable diet (Fig. 6.7). Some organisms lack homeostasis, and their cellular nutrient levels reflect that in the environment (you are what you eat), while strict homeostatic consumers maintain their composition. Heterotrophs are, in general, more homeostatic than autotrophs, but intermediate behavior has been reported. Phytoplankton has been shown to have high flexibility in term nutrients, but suboptimal nutrient contents come at the expense of performance (e.g. growth rate). Consumers living on resources that deviate from their tissue composition have multiple ways of elemental adjustment: food selection, feeding behavior, regulation of assimilation and metabolism (e.g. diverting towards respiration or excretion). Most herbivores are richer in N and P than primary producers; this stoichiometric mismatch is smaller in aquatic systems than in macrophyte systems in which carbon-rich lignin and structural cellulose are more abundant. Mismatches between the composition of a consumer and its resources has consequences for trophic transfer efficiencies and growth rates. The growth rate hypothesis involves a direct link between the growth rate, phosphorus content and ribosomes: i.e. high P content imply high RNA and thus high potential for growth. Ecological stoichiometry links the elements via compounds to the functioning of organisms and organism-scale processes to the global biogeochemical cycles.



**Fig. 6.7** Generalised stoichiometric pattern relating consumer (N:P, C:N, etc.) ratio to resource ratios. Organisms lacking homeostasis reflect the ratio of their resource (dashed 1:1 line), while strictly homeostatic organisms maintain their composition irrespective of the environment or their diet (horizontal line)

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