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Stoichiometry and Homeostasis

There is no science that claims the ecologists' leftovers.—Slobodkin (1988)

What are some of the most powerful explanatory ideas in all of science? Here are a few of our favorites: natural selection, the periodic table of elements, conservation of matter and energy, positive and negative feedback, the central dogma of molecular biology, and the ecosystem. This book you have just opened involves all of these. It is a book about how chemical elements come together to form evolved, living species in ecosystems. It is a book that takes very seriously the constraints of matter and energy. These are among the most powerful forces in nature, and a good understanding of physical and chemical barriers is one of the most helpful paths in understanding the things that are actually achieved. It is a book about biology and chemistry and to a lesser extent about physics and geology. As Slobodkin's statement above points out, ecologists often make serious use of the work from a great many disciplines. This is a book about many things, but it is organized around a single conceptual framework: **ecological stoichiometry** (see p. 42 for definitions of words in bold). We will soon elaborate in some detail on the history and meaning of the term "**stoichiometry**". To the uninitiated, it refers to patterns of mass balance in chemical conversions of different types of matter, which often have definite compositions. Most scientists run into it in beginning chemistry class when they learn to balance chemical reactions.

What is it you notice when you observe an ecosystem such as a grassland, lake, or stream? All biologists perceive things in their own way and that way is much simpler than the reality in front of them. Some have a conception based on the names of the species that they see. Some focus their minds on what they know or infer about the recent or distant history of the site. Some focus on the animals, others on the plants, and still others on the soil and microbes. Some concentrate on the structure, some dwell on the function. Some see constancy while others see dynamic change. Some might wonder how it's possible that the information necessary to build all of the organisms present could possibly be stored and processed by tiny molecules. All of these views are "right" in their own way. As Lev-

ins and Lewontin (1980) put it, “The problem . . . is to understand the proper domain of each abstraction rather than becoming its prisoner.” The human mind is incapable of grasping at once the enormous complexity of the entirety of natural systems, and it seeks simpler abstractions as a path to knowing. The abstraction we will follow is this: organisms can be thought of as complex evolved chemical substances that interact with each other and the abiotic world in a way that resembles a complex, composite, chemical reaction. Ecological interactions invariably involve chemical rearrangements. Like any other “normal” chemical rearrangement at the surface of the Earth, when organisms interact, mass must be conserved and elements are neither created nor destroyed (we will ignore the other more exotic things that can happen, especially at high energy or in radioactive substances, which a nuclear physicist could explain). There is stoichiometry in ecology, just as there is in organic synthesis in a test tube.

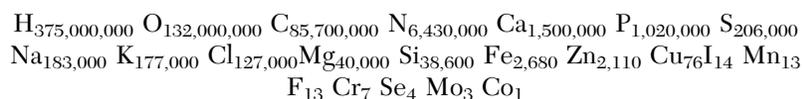
The stoichiometric approach considers whole organisms as if they were single abstract molecules. While this is, of course, not strictly true, note that if we wish to identify and understand those properties of living things that are truly biological, we must first identify those features that arise simply from the chemical nature of life. The science of chemistry has persisted despite, and indeed profited from, a deep understanding of the physics of the atom. Likewise, a rich and predictive science of biology will continue to develop as we better understand the chemical nature of life and how its consequences are expressed at all levels of biological organization. Some might find our approach to be a radically reductionist agenda, a charge to which we join Wilson (1998) in pleading “guilty.” Wilson’s “consilience” concept regards the fragmentation of knowledge and resulting isolation as artifacts of scholarship rather than reflections of how the world is really organized. We have been excited to see stoichiometric reasoning correctly predict very macroscopic phenomena using its very microscopic principles (for example, in the studies of herbivores in light gradients that we will cover in Chapter 7). This book starts with the basic physical chemistry of the elements and progresses in a linear fashion from atoms to ecosystems with an utter disregard for where chemistry ends and biology starts, or where evolution starts and ecology ends, and so forth. Deep philosophizing aside, all organisms must obey the principles of conservation of energy and mass, and it is time we put these principles to new ecological uses.

In this first chapter, we will explain the book’s scope and define a set of core concepts. As long as elements are neither created nor destroyed, any multiple-element system will follow many of the rules we discuss here. However, a driving mechanism behind many of the patterns is the difference in stoichiometric variability among different organisms, species, nutritional modes, trophic levels, etc. The chemical composition of different

ecological players is constrained to different degrees, and it is this difference in variation, in addition to differences in mean values, that has interesting effects. The chapter continues with some consideration of closely related concepts, including the idea of “yield” as used in ecology and agriculture, an extended discussion of the “Redfield ratio” in terms of organismal C:N:P ratios, and some pragmatic notes about how ratios and growth rates are expressed. Finally, to foreshadow the wide-ranging scope of the materials to follow, we describe a logical structure for stoichiometric analysis first articulated by Reiners (1986), from which we have drawn great inspiration.

SCOPE

To begin to define this book’s scope, let us start by considering what portion of chemistry and physics we cover. Our focus is almost entirely on the elements. All of life requires the macroelements C, H, O, N, P, etc., as well as a set of trace elements including Fe, Mg, and others (Fig. 1.1). These provide for a diverse set of functions including structure (such as C, H, and O in cellulose fibers), oxidation-reduction (such as Fe as a cofactor in enzymes), and others (see Chapter 2). The patterns of abundance of elements in living things are major components of ecological stoichiometry. Take humans as an example. The concentrations of at least 22 elements in humans have been determined; these range in total amount in a typical live individual from 35 kg (O) to 1 mg (Co) (Heymsfield et al. 1991; Williams and Fraústo da Silva 1996). From information on the quantities of individual elements, we can calculate the stoichiometric formula for a living human being to be



That is, there are about 375 million H atoms for every Co atom in your body (the formula is based on “wet weight”). This formula combines all compounds in a human being into a single abstract “molecule.” This formula sets the value of the scarcest substance (cobalt, mass in humans \approx 1 mg) equal to a stoichiometric coefficient of 1 and shows relative amounts, not absolute ones. Most stoichiometric analyses are in fact concerned with relative abundances. The large stoichiometric coefficients for H and O, the most numerous atoms in our bodies, arise partly from the fact that life is aqueous and partly from the fact that H and O are key components of many (or all, in the case of H) organic molecules. Our main purpose in introducing this formula for the “human molecule” is to stimulate you to

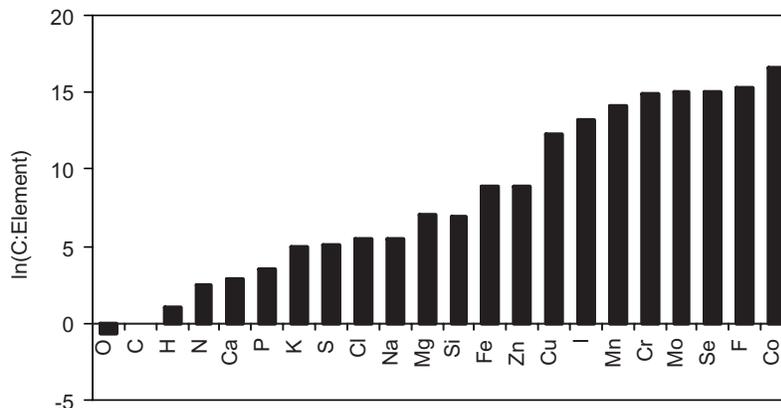


Fig. 1.2. Abundance of 22 elements in humans, expressed relative to carbon (mass:mass) and natural-log-transformed for clarity. High values indicate substances in low relative abundance. Data obtained from two sources, with averages taken when multiple values were available (Heymsfield et al. 1991; Williams and Fraústo da Silva 1996). For a historical presentation of similar information, see Fig. 2.1.

begin to think about how every human being represents the coming together of atoms in proportions that are, if not constant, at least bounded and obeying some rules. Humans must obtain these elements in sufficient but not (for some) oversufficient quantities from an environment that may or may not have similar proportions of these elements. Human physiology must take complex chemical resources containing multiple elements arranged in myriad different molecules, absorb some, metabolize some, rearrange many, and excrete or otherwise release a great deal. This book is concerned both with the way that organisms do this and with its consequences for ecological dynamics.

We will often express element content relative to carbon. A high C:element ratio means that element is in low quantity relative to C. Figure 1.2 shows the distribution of the matter of a human among component elements. The total mass of elements for this human is 64.0 kg, and we can account for 99% of the mass with the elements up to and including K. Although it is customary to speak of “macro” and “micro” elements to contrast those that are in high versus low abundance, there is no clear breakpoint between the two. It should not be assumed that elements in low abundance are unimportant; frequently, in fact, the opposite is the case. Ecological stoichiometry takes information like that illustrated in this figure, combines it with similar information on potentially interacting spe-

cies, including the resources that are consumed, and makes testable predictions about such things as, “How fast will the organism grow? What nutrients will become limiting in an ecosystem? What accounts for the foraging decisions consumers make? How does the environment constrain the evolution of particular life histories?”

Why do we focus so on the elements? To a certain extent we do this because we are limnologists trained to take an ecosystem perspective and focus on pools and fluxes of energy and matter in the environment. But there are grander reasons to focus on elements. They provide a framework for easily moving between levels of biological organization, as we can calculate the elemental composition and estimate the fluxes of chemical elements to and from a wide variety of biological entities, ranging from organelles and cells to watersheds and indeed the biosphere. In this book we will present data across this entire range and in doing so we hope at least to raise the possibility that stoichiometric analysis may help increase the degree of conceptual and intellectual consilience in modern biology.

A more pragmatic reason for focusing on the elements is that they (at least the nonradioactive ones) are immutable and thus we can put the law of mass conservation to use. For stoichiometry to work, the chemical substances of interest must not be created or destroyed; otherwise we could not rely on conservation rules. This reason implies that stoichiometric analysis might also be applied to certain biochemicals (for a recent application, see Anderson and Pond 2000). For example, some contaminants may follow stoichiometric principles, since organisms do not synthesize them, and they are also highly resistant to biological breakdown. If these substances also showed variability in their concentrations in key ecosystem components, principles of ecological stoichiometry developed for elements might be useful in understanding the distribution of contaminants in ecosystems. With active regulation of contaminant concentration by certain members of an ecosystem, the comparison between elements and contaminants would be very apt. Other biochemicals are essential in consumer diets. “Essential” can be taken to mean they cannot be synthesized at rates necessary to sustain growth and survival, and thus they must be obtained from the food. If catabolism also is negligible, again we might be able to use the same principles discussed here to understand those nutritive biochemicals. There likely are some good applications of ecological stoichiometry to biochemicals; however, in general the data to do so are not yet widely available. The majority of this book is about elements, reflecting the state of the art but perhaps not the ultimate applicability of the ideas.

A focus on elements raises the question of how safe it is to ignore the biochemical arrangement of elements in organisms. Although stoichiometry represents organisms as single abstract molecules, they are of course wondrous collections of countless individual biochemicals and even most

biologically active substances are composed of multiple elements. We recognize that an animal's N budget is primarily determined by the physiology and biochemistry of amino acids and proteins, not zillions of independent atoms of N. The biochemical nature of the precise arrangement of elements into compounds and molecules affects how organisms utilize those elements. A different and more detailed approach, based on proportions of different chemical bonds (C—C vs. C—N, etc.), has also been considered (Hunt et al. 1983). Our point in this work is not that organisms *are* bags of independent elements. Rather we wish to see how far this abstraction will take us; we are confident it will take us further than any approach using a single currency (e.g., total mass, energy, C only, P only, etc.). Deevey (1970) considered the “architecture” of assembling elements into compounds and put it this way: “A listing of elements and compounds does not reveal that architecture. There is a big difference between a finished house and a pile of building materials. Nevertheless, a list is a useful point of departure. If it is made with care, it can protect ecologists from the kind of mistakes that architects sometimes make, such as forgetting the plumbing.”

We sometimes hear the criticism that we wish to treat organisms as if they were “just” chemical reactions. Our response is, “What do you mean by ‘just’?” We are not only reasoning by analogy. Organisms *are* chemical entities and are produced, maintained, and propagated by chemical reactions, albeit in the form of highly complex coupled networks, which are the product of evolution. Statements about nature that are so well accepted as to be referred to as “laws” are exceedingly rare. The **law of conservation of matter** is as close as we get in science to a “fixed point” in nature and we should make good use of it as our understanding of the living world grows.

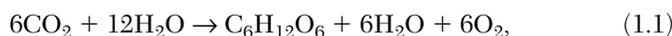
During the years that the two of us have participated in the development of this field, we have alternately heard that ecological stoichiometry is either too complicated to understand or too simple to be true. With respect to the former, we hope this volume makes things clearer. With respect to the latter, we acknowledge that ecological stoichiometry is unlikely to be a “final theory” (is anything?) and that it does not and cannot explain everything of interest in the ecological and evolutionary worlds. However, bear in mind that simple mechanisms can produce surprisingly complex outcomes, evolution by natural selection being the shining example. Hence, we take inspiration from the words of the physicist Percy Bridgman in 1927 (as quoted by Ferris 2001), who commented on the importance of “conviction” in scientific discovery: “Whatever may be one’s opinion as to the simplicity of either the laws or the material structures of Nature, there can be no question that the possessors of such conviction have a real advantage in the race for physical discovery. Doubtless there are many simple connections still to be discovered, and [s/he] who has a strong conviction of the existence of these simple connections is much

more likely to find them than [s/he] who is not at all sure that they are there.”

STOICHIOMETRY AND HOMEOSTASIS

Let us turn now to a more complete explanation of stoichiometry and several key related concepts. In its common chemical usage, the term “stoichiometry” refers to patterns of proportions of elements in reactants and products of chemical reactions. Stoichiometry can be defined as a branch of chemistry that deals with the application of the **law of definite proportions** and conservation of mass. Lotka (1925) wrote: “we may employ the term Stoichiometry to denote that branch of the science which concerns itself with the material transformations, with the relations between the masses of the components.” The word “stoichiometry” comes from the Greek root “stoicheion” for element. “Stoichiometry” thus means “measuring elements.” During the earliest days of chemistry, it was discovered that some substances reacted in constrained ways; that is, they combined only in set proportions. This was a key observation in the discovery of the elements, suggesting that something indivisible was combining so that proportions could always be reduced to integers.

Consider a familiar example. On each side of the chemical reaction for photosynthesis,



there are six atoms of C, 24 atoms of O, and 24 atoms of H. The reaction stoichiometry indicates that one diatomic molecule of oxygen (O_2) must be produced for every molecule of carbon dioxide that is used. The most important thing about stoichiometry is that it constrains allowable states. Stoichiometry says you can't combine things in arbitrary proportions; you can't, for example, change the proportion of water and dioxygen produced as a result of making glucose. In this reaction, six molecules of each must be produced for every molecule of glucose generated. Stoichiometry also controls the quantitative relations between reactants and products. If you simply added one CO_2 , for example, it would be in excess and would not react (and the yield of glucose from carbon dioxide would be diminished, as we explain below). Were it not for the constraints of stoichiometry, chemistry would be a highly chaotic subject. Chemical stoichiometry is essentially a very large set of constraints that greatly limit the combinations of chemical elements and how those combinations interact with each other. As we will see as we go further, ecological stoichiometry sets similar limits to interacting biological systems. These limits to composition combine with those imposed by the conservation of matter. Establishing these constraints

and examining how they impinge on ecological processes is what makes ecological stoichiometry potentially a very powerful heuristic and predictive tool.

In the context of ecological stoichiometry, conservation of energy presents somewhat of a semantic problem. The term “stoichiometry” normally refers only to the conservation of matter. The conservation of energy is typically considered separately (in thermodynamics). However, matter and energy are inextricably linked in biological systems as they are indeed in all systems. For example, it is possible to rewrite all mass fluxes in organisms in comparable energy terms (Kooijman 1995). In this book, we will often want to be able to combine energy fluxes and matter processing when considering solar energy and nutrient fluxes to plants. When this happens, we adopt a broad definition of stoichiometry, one that includes energy transformations and conservation as well as conservation of matter. Whether or not this is really stoichiometry is just a semantic nuisance.

The term “stoichiometry” has also been used to refer to the quantitative relationship between constituents in a chemical substance, i.e., the quantitative relationship between two or more substances making up a composite substance, such as in our formula for the chemical makeup of a human given above. In this sense of the word, this chemical formula represents “the stoichiometry of a human.” An interesting but archaic term is “stoichiology,” which refers to that part of the science of physiology that treats the elements composing animal tissues (*Webster’s New Universal Unabridged Dictionary*, 2nd ed., 1983). Actually, it could be said that much of this book is about “stoichiology,” not “stoichiometry,” but we will not attempt to reverse any etymological tides here; we’re perfectly happy with “stoichiometry.”

Although many compounds are formed with elements in strict and definite proportions, not all are. In some circles, the former compounds are called stoichiometric and the latter are called nonstoichiometric (Rao 1985; Williams and Fraústo da Silva 1996). Covalently bonded substances such as $C_6H_{12}O_6$ or compounds characterized by ionic bonds and crystalline lattices such as NaCl are stoichiometric. According to this terminology, in stoichiometric substances, the precise pattern of bonding between atoms means that elements must occur in fixed proportions in the material. However, not all substances are like this. Compounds lacking fixed proportions of elements include certain salts, minerals, and alloys. One notable example is semiconductors, some of which are allowing these words to be written (and edited and reedited!) on a personal computer. Another is below your feet. The silicates of Earth are composed of a principal Si-O unit that builds itself in countless ways with Na^+ , Mg^{2+} , Al^{3+} , and Ca^{2+} into a vast variety of strings, planes, and three-dimensional structures, making this major portion of the Earth’s crust nonstoichiometric. In substances

like semiconductors and siliceous minerals, proportions of chemical elements are not fixed. The proportions that are found are largely a function of the proportions of elements available when the substance is made, much as the shade of light blue paint one gets depends on the proportion of white and blue paints being mixed.

To our eyes, the hallmark of the nonliving world (e.g., rocks, air, substances dissolved in water) is stoichiometric variability. Indeed, the stoichiometric composition of certain portions of the abiotic world is fundamentally limitless. The most extreme stoichiometric composition of any material would be 100% of a single element. The characteristics of some of the pure elements are very familiar. Carbon can be found in pure form as graphite, diamond, or even the more exotic C_{60} buckminsterfullerene. As a colorless, odorless gas, pure nitrogen is the major single component of today's atmosphere. Pure phosphorus is a waxy solid, colorless, transparent, and spontaneously combustible. Pure iron and pure gold are both well known to all, the latter at least by reputation. Combinations of elements in inorganic matter do not entirely lack constraints; some combinations of elements spontaneously react, forming products that may have definite proportions. Some refuse to coexist for other reasons. But many common elements are able to combine in (approximately) limitless combinations. For example, common igneous rocks can contain from near zero to more than 50% MgO (Cox 1995). The chemical evolution of Earth has included massive changes in atmospheric chemistry, from a highly reduced state containing 10 atm CO_2 along with N_2 and CH_4 and virtually no O_2 to today's air with 10^{-3} atm CO_2 and N_2 and O_2 as major components; in other words, there has been a major shift in composition from carbon to oxygen (Schopf 1982). The chemistry of aqueous solutions is critical to understanding life, and there are some important purely inorganic controls on the chemistry of aqueous solutions. Ionic strength, which responds to the balance between precipitation and evaporation, has a major influence on the composition of surface waters (Gibbs 1970; Gorham et al. 1983; Kilham 1990). Phosphorus availability in high-oxygen waters is strongly dependent on concentrations of metals such as Fe and Mn (Mortimer 1941, 1942), oxidized precipitates of which bind with P and greatly lower its availability (we will discuss this relationship again near the end of the book). Metals variously speciate and react depending upon pH and oxidation-reduction potential, and so forth. These are some of the purely chemical constraints on the stoichiometry of the abiotic world. However, as we will see as we go, those constraints are so loose, at least in comparison to the stricter ones in living biological systems, that we view the inorganic world as having great stoichiometric variability. In the final chapter of this book we present some summary data comparing the stoichiometry of abiotic and biotic systems.

Let us look in more detail at some of the major components of the nonliving natural world, because there are some interesting and important stoichiometric patterns of elements there. In a progression from the solar system, to the whole Earth, to the Earth's crust, to seawater (Table 1.1), there are numerous gigantic shifts in chemical content of 10^3 , 10^6 , and even 10^9 parts per mass. The two lightest elements, H and He, are the most abundant elements in the solar system (the mass of which is almost entirely made up by the sun) with oxygen also making up about 1% of total mass. Stoichiometric shifts associated with the formation of the Earth resulted in much greater concentrations of Li and much lower concentrations of He and Ne. Other elements in greater concentration in the Earth than in the solar system as a whole include Be, Mg, Al, Si, S, Ca, Sn, V, and Fe. Stoichiometric shifts in the formation of the crust from the whole Earth are somewhat less extreme, although there is a very large drop-off in H and increases in the concentrations of Fe, B, Ne, Na, and K. Many very large and very important differences in the chemical content of seawater as compared to Earth's crust include massively lower concentrations of Be, Al, Sn, Ti, Cr, Mn, and especially Fe in the sea than in the crust. The inorganic chemistry of the elements, and many very intriguing patterns in abundance as related to fundamental aspects of chemistry, have been engagingly considered by Cox (1989, 1995) and by Williams and Fraústo da Silva (Williams 1981; Williams and Fraústo da Silva 1996). In particular, the latter duo's major opus of 1996, with its stated purpose "to show the relationship of every kind of material around us, living and non-living, to the properties of the chemical elements of the periodic table," is required reading for all those interested in ecological stoichiometry.

Now, what of the transition to living things? As Williams (1981) wrote, "Evolution through natural selection implies that there must be a drive within biology to readjust the given accidental abundances of the Earth's crust so as to optimize biological chemistry." Table 1.1 also shows some major stoichiometric jumps in going from modern seawater to the human body. Putting aside the thorny issue of how much the chemistry of today's ocean resembles the setting for the evolution of life many years ago, we can see that, at a coarse level, the recipe for this representative living thing differs dramatically from the bulk of Earth's surficial water today. The human body has much greater concentrations of N, P, and Fe (three elements very commonly regarded as limiting to living systems—no coincidence there), and a much lower concentration of, for example, Ar.

At a deeper level, we must consider whether organisms are like immensely complex covalently bonded molecules, with elements appearing in fixed proportions. If organisms were like covalent molecules, mass flux through them would be highly constrained in the same way that C, H, and O are constrained to combine only in one way in the formation of glucose.

TABLE 1.1

Approximate concentrations of the first 26 elements in the solar system, in the whole Earth, in the Earth's crust, in seawater, and in humans. Concentrations are divided into categories differing by multiple orders of magnitude. As parts by mass they are $A > 10^{-2}$ ($> 1\%$), $10^{-2} > B > 10^{-6}$ (between 1 ppm and 1%), $10^{-6} > C > 10^{-9}$ (between 1 ppm and 1 ppb), and $D < 10^{-9}$ ($< 1\text{ppb}$). Less-than and greater-than symbols are used in the table to indicate changes in categories for individual elements between columns (hence large fractionations). Several elements for humans are reported as "0" as these are not detectable. Graphical depictions of similar data for crust and for humans are given in Figures 1.2 and 2.1. Data from Cox (1995).

Atomic Number	Symbol	Atomic Mass	Solar System	Whole Earth	Earth's Crust	Seawater	Human Body				
1	H	1	A	>	B	>>	D	A			
2	He	4	A	>>	D		D	>	0		
3	Li	7	D	<<	B		B	<	C		
4	Be	9	D	<	C	<	B	>>	D		
5	B	11	C		C	<	B		B		
6	C	12	B		B		B		B		
7	N	14	B		B		B	<	C	<<	A
8	O	16	A		A		A		A		A
9	F	19	B		B		B		B		B
10	Ne	20	B	>>	D	<	C	>	D	>	0
11	Na	23	B		B	<	A		A	>	B
12	Mg	24	B	<	A		A	>	B		B
13	Al	27	B	<	A		A	>>	D	<	C
14	Si	28	B	<	A		A	>	B		B
15	P	31	B		B		B	>	C	<<	A
16	S	32	B	<	A	>	B		B		B
17	Cl	35	B		B		B	<	A	>	B
18	Ar	40	B	>	C		C		C	>>	0
19	K	39	B		B	<	A	>	B		B
20	Ca	40	B	<	A		A	>	B	<	A
21	Sc	45	C	<	B		B	>>	D	>	0
22	Ti	48	B		B		B	>>	D	<	C
23	V	51	C	<	B		B	>	C		C
24	Cr	52	B		B		B	>>	D	<	C
25	Mn	55	B		B		B	>>	D	<	C
26	Fe	56	B	<	A		A	>>	D	<<	B

Reiners (1986) suggested that organisms lacking major support structures (he called such creatures "protoplasmic life") were like that: "Protoplasmic life has a common stoichiometry of chemical elements in particular proportions." Or are organisms more like Earth's crust, with a variable chemistry formed from differing proportions of a limited set of constituents and with **nutrient content** largely determined by the proportions of elements that they are exposed to? Herbert (1961) wrote, "There are few characteristics of micro-organisms which are so directly and so markedly affected by the environment as their chemical composition. So much is this the

case that it is virtually meaningless to speak of the chemical composition of a microorganism without at the same time specifying the environmental conditions that produce it.” Similarly, in writing about insect nutrition, Mattson and Scriber (1987) wrote, “Food has profoundly influenced the evolution of animals because in so many respects an animal is what it eats.”

The contrast in these stated views is partly a matter of perspective, including whether one is considering physiological, ecological, or evolutionary time scales. Any difference looks small from a great distance or relative to even bigger differences. To resolve these differences in points of view, we will consider how consumer stoichiometry varies with resource stoichiometry, both in terms of theoretical expectations and in a series of empirical examples. First, we will describe the general features of plots of consumer versus resource stoichiometry; then, we will look at some mathematical models that capture key aspects of these patterns.

One situation is both easily analyzed and readily understood. If a consumer’s nutrient content passively reflected the content of the resources it consumed—in other words, if a consumer truly *was* what it ate—then all points in a plot of consumer stoichiometry versus resource stoichiometry would lie on a line with slope 1 and intercept zero (Fig. 1.3A, dotted line) (for all such plots, we use the same scale for consumer and resources). For this to occur, species must assimilate and retain the nutrients being plotted in identical proportions to their relative abundance in the food. (We will see later in the book that the relevant term describing this assimilation and retention is the gross growth efficiency.) This “you are what you eat” model provides one simple way that stoichiometries of consumer and resource may be related: they may be equal.

Let us consider **nonhomeostatic** elements within organisms more deeply. These at first seem to violate the idea that **homeostasis** is the essence of life. It is self-evident that no organism can be totally non-homeostatic and still be alive. There are limits to what combinations of chemical elements can function as a living cell (in its absurd limit, cells cannot take on the composition of pure C, N, P, or any other single element). We will develop those ideas from a molecular and cellular standpoint in the next chapter. However, it is clear already that the stoichiometry of any living system must be bounded. This is one aspect of a complete understanding of the determinants of consumer stoichiometry.

Returning to our plot, departures from the 1:1 line would be caused by differential nutrient processing of the two elements. If the stoichiometry of the consumer was some constant of proportionality multiplied by the stoichiometry of the resource, a family of lines with constant slope and zero intercept would be obtained (Fig. 1.3A, solid lines). We will call this the constant proportional model. Although the two hypothetical consumers represented by the solid lines in Figure 1.3A are not what they eat, they

still are passive consumers that do not adjust their stoichiometric balance in response to the stoichiometry of the resources they can consume. In one case, their stoichiometry is a constant multiple higher than the resource stoichiometry, and in the other case, their stoichiometry is a constant multiple lower than the resources. They may generally be more variable than the food they eat (Fig. 1.3A, upper solid line) or less variable than the food they eat (Fig. 1.3A, lower solid line), but they are not regulating their stoichiometry in response to their food. They could be following a simple rule such as, “always retain A percent of all resource 1 ingested and B percent of all resource 2 ingested.” Written out in this way, it is apparent that in these sorts of patterns, there is no feedback between the resource’s elemental composition and that of the consumer.

Negative feedback (opposite to the direction of perturbation) between an internal condition (such as consumer stoichiometry) and an external condition (resource stoichiometry) in biological systems is a **homeostatic** regulation. We have already noted the use of the terms “stoichiometric” and “nonstoichiometric” compounds to represent different degrees of constancy of element proportions in chemistry. However, in biology “homeostasis” is a more widely accepted term. “Homeostasis” is the resistance to change of the internal milieu of an organism compared to its external world. It has been said that homeostasis is the essence of life. Organisms regulate many of their properties, including water balance, pH, and others. In ecological stoichiometry, homeostasis is observable in the patterns of variation in nutrient elements in organisms relative to their external world, including the resources they eat. Kooijman (1995) defined homeostasis in a stoichiometric context as follows: “The term homeostasis is used to indicate the ability of most organisms to keep the chemical composition of their body constant, despite changes in the chemical composition of the environment, including their food.” An organism’s stoichiometry is the pattern that results from different degrees of homeostasis operating on chemical composition. Homeostasis generates different degrees of variation in chemical substances in living things. Because in ecological stoichiometry, homeostasis refers to changes in matter in living things, it is often used when discussing growth. However, as a general biological concept, homeostasis may occur with or without growth. We will see that differences in the strength of homeostasis have numerous ecological consequences. Homeostasis is a major reason for this book’s existence. Without it, ecological stoichiometry would be a dull subject.

Another easily understood case would be if a consumer’s nutrient content were independent of the chemical composition of its food. In our now familiar plot of consumer versus resource stoichiometry, any horizontal line segment above, below, or intersecting with the 1:1 line would represent this situation. We refer to these situations as “**strict homeostasis**”

(Fig. 1.3B, solid lines). A related term that will come up frequently later is **balanced growth**. These two terms describe a **stoichiometric equilibrium** where the proportions of substances in an organism do not change. Strict homeostasis means that consumer stoichiometry does not vary with resource stoichiometry. However, strict homeostasis does not necessarily mean that a group of individuals of such a species from nature, including diverse ages, life stages, sexes, etc., will exhibit zero variation in their chemical content. Individual organisms often show differences in stoichiometry during their life cycles. Young organisms may have different composition from older ones, reproductive organisms may be different from nonreproductive, males may be different from females, etc. For example, a plot of body C:P versus size for a species might show a trend, but if that allometric trend is “hard wired” (not a function of food ingested), such a plot could be consistent with a strict homeostasis of C:P in that species. Intraspecific variation in chemical content alone does not disprove the presence of strict homeostasis.

Also, please be warned that the word “balance” will be used in several other ways in this book. One usage is in the sense of balancing a budget: for example, in the water cycle or nutrient cycles, mass conservation means that input equals output in an equilibrium system, and this is a “balancing.” Another usage is in the general sense of where nutrient or energy and nutrient ratios lie relative to some reference point: for example, inorganic N:P ratios in the environment that happen to be similar to those found in the tissues of living things can be considered balanced. Finally, when we discuss interacting stoichiometric systems (such as consumers and their resources), we will consider two things having similar stoichiometry to be “balanced,” and two things having dissimilar stoichiometry to be “imbalanced.” In that context, **elemental imbalance** is a measure of the dissimilarity in relative supply of an element between an organism and its resources.

Figure 1.3 therefore presents two extremes: the complete absence of stoichiometric regulation by a consumer (panel A) and a regulation so thorough that the consumer’s state is independent of the resource state (panel B). These are limits. As we shall soon see, nature often dwells in the space between these end points. Therefore, we need to consider what to do with imperfect homeostatic regulation. What if there is a negative feedback between resource and consumer stoichiometry, but the outcome is not a truly fixed elemental composition? It is important to define homeostasis as precisely as possible because it is a core concept in ecological stoichiometry.

Differing levels of homeostatic regulation can be analyzed both graphically and with equations. First, graphically: Consider an arbitrary point x,y in a plot of consumer versus resource stoichiometry. Homeostatic regulation of nutrient content at x,y can be diagnosed as a slope lower than the

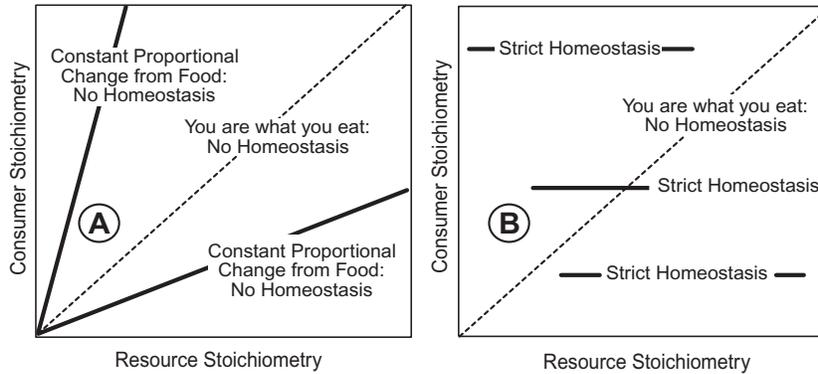


Fig. 1.3. Generalized stoichiometric patterns relating consumer stoichiometry to resource stoichiometry. Horizontal and vertical axes are any single stoichiometric measure, such as N content or C:P ratio. A. Points on the 1:1 line (slope 1, intercept 0) represent identical stoichiometry in consumer and resources. This dashed line represents a consumer with stoichiometry that always matches the stoichiometry of its resources. This is the “you are what you eat” model. The solid lines represent consumers that perform constant differential nutrient retention. These represent the “constant proportional model.” B. Strict homeostasis is defined as any horizontal line segment (slope 0, intercept > 0).

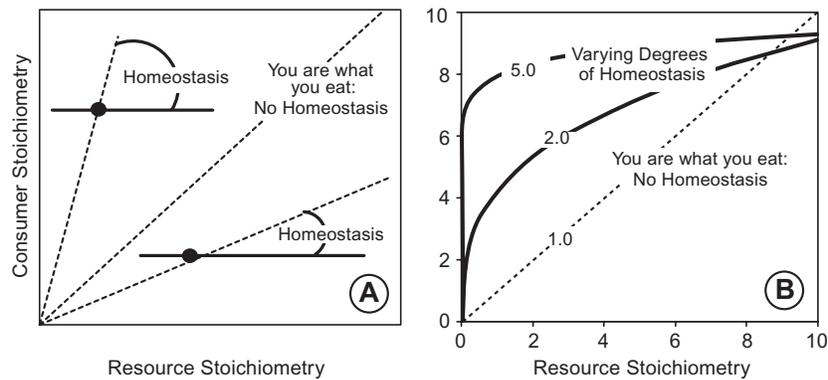


Fig. 1.4. Homeostatic regulation of elemental content. A. Graphically, homeostasis at a point x,y can be defined as a slope between 0 and y/x . B. Degrees of homeostatic regulation based on models with constant coefficient of regulation [H, Eq. (1.3)]. The three curves use values for the coefficients of c and H of 1 and 1, 2 and 3, and 5 and 6, and they are labeled by their value of H. The line marked “1.0” represents no homeostatic regulation. Increasing values of H mean increased regulatory strength.

slope from a constant proportional response shown in Figure 1.3A. In other words, homeostasis is a slope at x,y less than y/x , down to an expected lower limit of zero (Fig. 1.4A). Thus, the arcs in Figure 1.4 indicate expected ranges of homeostatic regulation of consumer stoichiometry. An important thing to understand from this plot is that the slope alone cannot diagnose homeostasis (except where the slope is truly zero). Notice that slopes may be fairly steep and still be consistent with homeostatic negative feedback. Similarly, even fairly shallow slopes may be consistent with an absence of homeostasis.

We now can formalize this concept of stoichiometric homeostasis. First, note that the model of constant proportionality (Fig. 1.3A) can be rewritten as $dy/dx = y/x$, where y = consumer stoichiometry and x = resource stoichiometry (measured on identical scales). By “stoichiometry” here we mean any sort of ratio of substances or masses (e.g., percent P, N:P, etc.). Thus, we use the general symbols y and x here to represent the vertical and horizontal variables. Now, regulation as conceptualized graphically in Figure 1.4A would be given by

$$\frac{dy}{dx} = \frac{1}{H} \frac{y}{x}, \quad (1.2)$$

where H (η) is a regulation coefficient greater than 1. For x large enough (note it is in the denominator of the last term), as the regulation coefficient approaches infinity, the slope of consumer versus resource stoichiometry approaches zero (i.e., regulation approaches strict homeostasis). Equation (1.2) can be rearranged to show that $1/H$ relates the proportional change in y (dy/y) to the proportional change in x (dx/x). Equation (1.2) can be integrated to give

$$y = cx^{\frac{1}{H}}, \quad (1.3)$$

where c is a constant. In Figure 1.4B, we have plotted several realizations of Equation (1.3). The three functions in this plot differ in their values of c and H . The latter parameter accounts for the “bendiness.” A surprising conclusion from this plot is that, at extremely low values on the resource stoichiometry axis, even a seemingly high sensitivity of consumer stoichiometry to resource stoichiometry may be consistent with homeostatic regulation (note the steep slopes at the left portion of the graph).

A perhaps more useful way to study homeostasis is to linearize Equation (1.3) using logarithms:

$$\log(y) = \log(c) + \frac{\log(x)}{H}. \quad (1.4)$$

Equation (1.4) indicates that we can easily diagnose homeostatic regulation of consumer stoichiometry by plotting the logarithms of consumer versus resource stoichiometry. On such a plot, slopes $(1/H)$ between 1 and 0 indicate a negative feedback between resources and consumers, and hence indicate homeostatic adjustment of nutrient content because they indicate a lower proportional change in consumer stoichiometry than in resource stoichiometry.

Now that we are equipped to think more precisely about these patterns, let us consider several examples showing how consumer and resource stoichiometry are related. Variation in stoichiometry in living things is in some ways similar to the classical ecological terminology of “regulators” and “conformers.” The former have internal conditions (e.g., temperature) little changed by external conditions, while in the latter, inside matches outside. Let us see how closely some real species come to matching these ideal expectations. We will now consider as tests of the degree of homeostasis a set of studies that took a single standardized set of individuals of common age, stage, etc., and fed them different diets experimentally. Studies using collections of miscellaneous individuals of differing ages, etc., might well be interesting for other purposes, but they do not necessarily test homeostasis.

A clear example of nonhomeostasis of a chemical parameter comes from the algae studied by Rhee (1978), who cultured *Scenedesmus* (a Chlorophyte to which we will often refer) at a range of nitrate concentrations, holding phosphate concentration constant, and thus producing a range of N:P resource ratios. He grew his cultures to equilibrium in chemostats (for more on the operation and theory of chemostats, see Chapter 3). Rhee’s *Scenedesmus* had a cellular N:P that almost perfectly matched the N:P in its environment (Fig. 1.5). Note that the “you are what you eat” model (Fig. 1.3) holds for this situation on both linear (Fig. 1.5A) and logarithmic (Fig. 1.5B) axes, as it should given Equations (1.3) and (1.4) and letting $H = 1$. Within the range studied, the alga shows no evidence for homeostasis of N:P. However, does this plot indicate that we might be able to grow *Scenedesmus* of any arbitrary N:P, just by expanding the range of the chemostat conditions? A moment’s reflection proves that the answer must be “no.” Although Rhee’s results do not demonstrate the bounds to cellular N:P, they surely must exist; living algae could never be made of pure N or P nor could they have been grown in the complete absence of P (or N). Our interpretation is that within the range of intermediate N:P he studied, algal homeostasis is essentially absent. We predict that homeostasis would be observed at more extreme values of N:P in the medium. Vascular plants also show similar patterns to these algae. Shaver and Mellilo (1984) reported a wide range of plant N:P ratios in several species of marsh plants as a function of N:P supplied to the plants. We will consider variability in

autotrophic C:N:P stoichiometry in much greater detail in Chapter 3 (an analogous plot to Rhee's algal study, but for vascular plants, is shown in Fig. 3.3B).

The next example shows a strict homeostasis. Goldman et al. (1987b) grew natural assemblages of marine bacteria on substrates of differing C and N sources (amino acids, glucose, and NH_4^+), spanning a range of C:N from 1.5 to 10. They determined a number of physiological features we will consider further in Chapter 5. Here, we consider the C:N of the bacterial biomass. Figure 1.6 shows the bacterial C:N as a function of substrate C:N. It is clear that bacterial C:N is homeostatically regulated here. The slope is not statistically different from zero on linear (Fig. 1.6A) or logarithmic (Fig. 1.6B) axes. Note that the range of substrate C:N examined was both higher and lower than the C:N in the bacteria themselves (unweighted mean of 5.6), so that it is reasonable to surmise that bacterial C:N would be homeostatic over nearly any other substrate C:N that could be examined. From these two examples, it is tempting to think of algae as conformers and bacteria as regulators. However, homeostatic regulation is a function of both the species and the resource. As we will see later (Fig. 5.8), bacterial N:P does vary with medium N:P, similar to the patterns we just described for algae. However, Figure 1.6 shows that C:N in this bacterium is homeostatic. Our purpose in giving the two examples in Figures 1.5 and 1.6 is to show two extreme examples, an absence of homeostasis and a strict homeostasis, not to directly compare identical resources in two different species.

Now, we will look at several more complex examples. Levi and Cowling (1969) raised the wood-consuming fungus *Polyporus versicolor* in a synthetic medium containing varying amounts of C and N provided as the sugar glucose and the amino acid asparagine. They sampled the fungus and determined its chemical composition through time, with incubation times ranging from as little as 5 d to as much as 56 d. Within a single medium type, fungal N:C generally increased with time from the first sampling to the last. In Figure 1.7, we have plotted all the data from all sampling dates (which accounts for some of the variation observed at particular N:C values). This interesting example shows that the linear and logarithmic plots can give very different impressions. On the linear axes (Fig. 1.7A), N:C in the fungus seems to show weak or no homeostasis at low N:C in the medium, but fungal N:C is not as variable with substrate N:C at higher values in the medium, where fungal N:C seems to approach a strict homeostasis. In contrast, the logarithmic axes (Fig. 1.7B) suggest a constant homeostatic adjustment over the entire range of the data (the data are reasonably fitted by a straight line). Given the inherent "bendiness" of homeostatic relationships on linear axes (see Fig. 1.4B), we suggest that logarithmic axes are superior for diagnosing the existence and

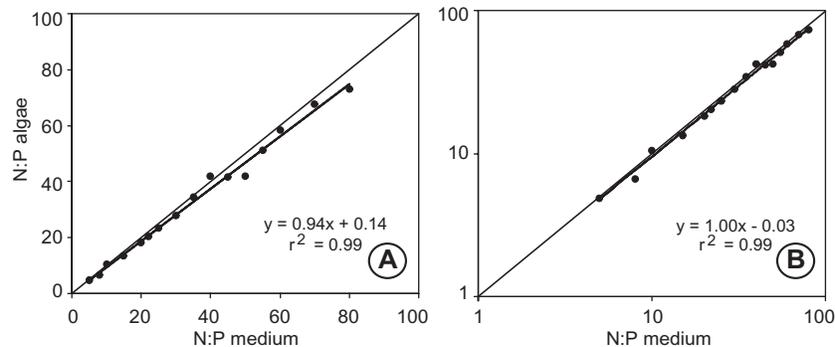


Fig. 1.5. Absence of homeostasis as seen in the N:P of *Scenedesmus* algae at growth rate equilibrium as a function of the N:P in the medium supplied. Cellular nutrient ratios are almost identical to the ratio in the surrounding environment (slope is near 1, intercept is near zero), which is apparent both in the plot with linear axes (A) and in the plot with logarithmic axes (B). Both the regression line and the 1:1 line are plotted. The regulatory coefficient H from Equation (1.3) is the inverse of the slope fitted to the log-log plot, which in this case is 1.00, indicating an absence of homeostasis. Based on Rhee (1978)

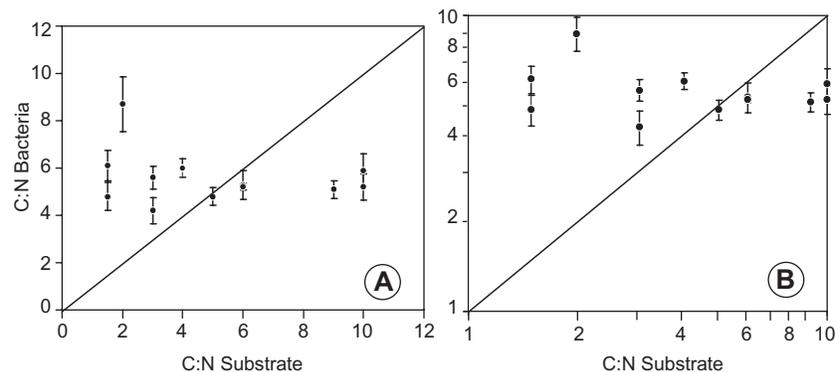


Fig. 1.6. A strict homeostasis. Bacterial C:N (mean \pm standard deviation) does not vary systematically over a wide range of substrate C:N. The trend is not statistically significant in either linear (A) or logarithmic (B) plots. The regulatory coefficient H can be taken to be essentially infinity, given the apparent zero slope. For a description of homeostasis of bacterial N:P ratios, see Fig. 5.8. Based on Goldman et al. (1987b).

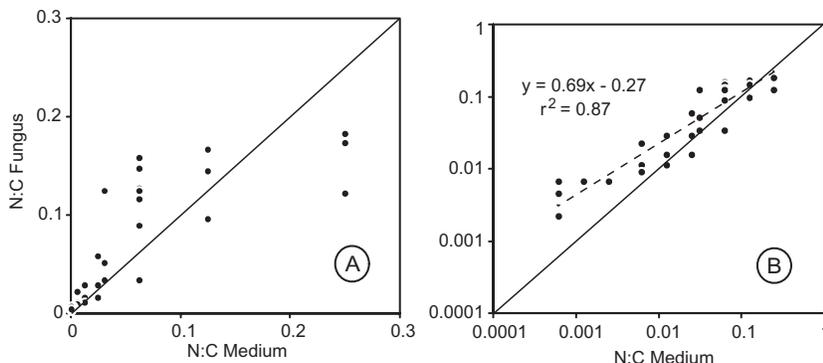


Fig. 1.7. Homeostatic regulation of fungal N content. On the linear axes (A), it appears that there are different degrees of regulation in different ranges of N:C in medium. When medium N:C < 0.05, fungal N:C varied strongly with the stoichiometry of the growth medium ($y = 1.65x + 0.004$, $r^2 = 0.56$). However, an upper bound seems to be approached, and when medium N:C > 0.05, fungal N:C seems to be less sensitive to medium N:C ($y = 0.52x + 0.05$, $r^2 = 0.46$). In contrast, on logarithmic axes (B), there is less of a convincing case for changes in homeostatic regulation in the different ranges. Nevertheless, the slope is clearly less than 1, indicating homeostasis, although not strict. The regulatory coefficient H is 1.4 (1/0.69), indicating a weak homeostatic regulation. Based on Levi and Cowling (1969) (assumes C is 0.45 of mass).

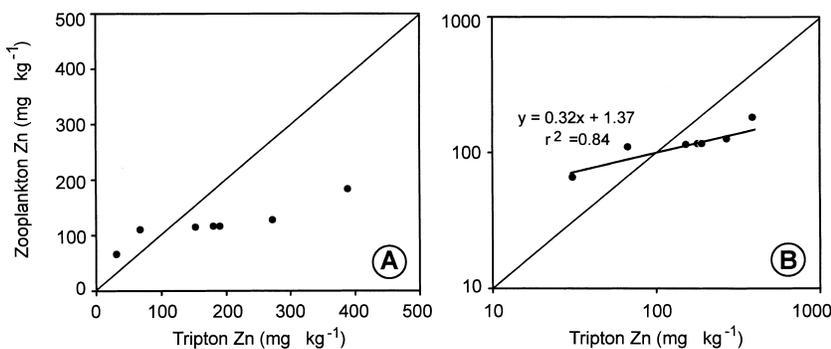


Fig. 1.8. Zinc content in zooplankton and tripton in lakes on linear (A) and logarithmic (B) axes. The regulatory coefficient H is 3.1, a relatively strong homeostasis. Based on Zauke et al. (1998).

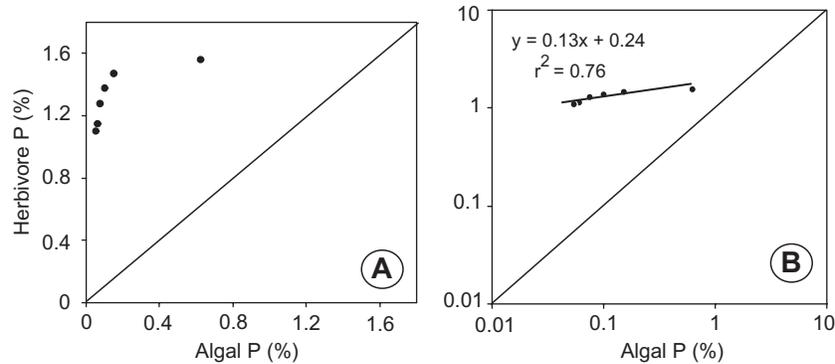


Fig. 1.9. Phosphorus content in *Daphnia* and algal food on linear (A) and logarithmic (B) axes. Although the linear plot makes it appear that there is a breakdown in homeostatic regulation at low food P content, a close to strict homeostasis is evident on the logarithmic axes. The regulatory coefficient H is 7.7, a strong but not strict homeostasis. Based on DeMott et al. (1998).

degree of homeostasis. A constant regulatory parameter H does different things on the linear axes in different portions of x,y space.

Two studies on zooplankton complete our examples. Zauke et al. (1998) measured the concentrations of zinc in freshwater zooplankton and tripton (settling particles) in several lakes in north central Poland. We will take the values in tripton to be a measure of the stoichiometry of the food available to the zooplankton. Zinc content was much less variable in the zooplankton than in tripton, and Zn content in zooplankton was strikingly consistent at intermediate Zn levels in tripton (Fig. 1.8). Both linear (Fig. 1.8A) and logarithmic (Fig. 1.8B) axes give a very similar impression. The zooplankton regulate at or very close to a strict homeostasis in the intermediate range of resource stoichiometry. At very low or very high Zn in the resources, homeostatic regulation breaks down. This example is unique in our set in suggesting a breakdown in consumer stoichiometric homeostasis at high levels of the element (Zn) in the resource. This may be the rule under conditions of toxicity. In a different study on zooplankton stoichiometry, DeMott et al. (1998) raised the cladoceran herbivore *Daphnia* (you will be treated to a great deal of information on this taxon in this book) in the laboratory on algal foods of different P content. Their results plotted on linear axes (Fig. 1.9A) seemingly demonstrate a great sensitivity of consumer P content to food P content at low food P content. But beware—and recall the bendiness of Figure 1.4B. When replotted on logarithmic axes, the strongly homeostatic nature of P in *Daphnia* is evident.

These examples illustrate some of the patterns of homeostatic element

regulation in different organisms. Further examples will be encountered later in the book (e.g., Figs. 5.8 and 5.9). In Chapters 4–6 we will continue to discuss patterns of nutrient content in Metazoa and the ecological consequences of their physiological regulation. The concepts of homeostasis and stoichiometry in organisms are at first sight complex but are reasonably well captured by some simple theory. The examples we saw serve to illustrate the basic set of generalized patterns of variation in nutrient content of an organism as a function of nutrients in its environment. The degree of homeostasis is a function of several major things: the consumer, its life stage, the chemical, and the range of the data perhaps are the most important of these. The main point of considering these examples is to realize that creatures are, generally, *not* what they eat. Life requires a complete set of sustaining functions: mechanical support, metabolism, gene replication, production, reproduction, etc. Biochemical means to each of these ends are limited (Chapter 2). Hence, the need for life-sustaining processes creates limitations in the possible chemical formulas for living things. If organisms were what they ate, this would be a short book. But they aren't, and it isn't. Instead, organisms are what they first eat but then do not ingest, defecate, excrete, lactate, exhale, or otherwise release back to the external world. In general, these are actively regulated processes, often under close control by the organism's physiology and thus subject to evolution by natural selection. Homeostatic regulation of stoichiometry can occur in multiple ways. It can involve food choice, habitat selection, assimilation, or excretion. Examples of each of these will be seen at different points in the book.

Homeostasis makes ecological stoichiometry interesting. If every living thing were what it ate, most of the phenomena discussed in this book either would not occur or would be considerably trivialized. Our message is that this active regulation of matter processing within organisms underlies myriads of ecological phenomena. So what general patterns in homeostasis might there be? How can we make some sense out of all the possible differences in stoichiometry in organisms? At this point, we can offer a few generalizations and propose some hypotheses. Hopefully, in the future as more data are collected, additional patterns will be revealed. We need much more information on the patterns of homeostatic regulation of different chemical resources in different organisms. These are fundamental data! A few patterns seem well enough defined to consider them as generally valid.

As we have just seen, some elements are more stoichiometric than others. Macroelements such as C and N are more stoichiometric than microelements (e.g., Goldman 1984). Carbon, for instance, is roughly 40–50% of the dry biomass of most living things (when we neglect massive noncarbonaceous support structures). Reasons for the relative constancy of C and

N content are discussed in Chapter 2. Trace elements have some particularly interesting patterns of concentration. Baines and Fisher (2001) showed that Se concentrations in algae (per unit volume) varied across algal species by almost four orders of magnitude when algae were exposed to common concentrations of Se in the water. They also found that cellular Se concentration varied only by two- or threefold when exposed to selenite concentrations that varied by 30-fold. The stoichiometry of trace elements provides enough variability that it has been used as a tool to trace the dispersal of mobile life stages of certain organisms (DiBacco and Levin 2000). Another major general contrast occurs across nutritional strategies. Recall that autotrophs are organisms that use an energy source such as light to fix organic carbon from inorganic carbon. In contrast heterotrophs are organisms that rely on already fixed carbon sources both for structure and for energy. As we will amplify in the coming pages, autotrophs (Chapter 3) generally are less homeostatic than heterotrophs, particularly in the case of multicellular metazoans (Chapter 4). We are still lacking a good concept of how poorly studied trophic strategies, such as bacterivory, detritivory, and the like, fit into this general pattern. As we will see (Chapters 5 and following), the consequences of these facts of life for ecological dynamics are considerable.

It is also important to emphasize that the degree of homeostasis depends on both the element under consideration and the organism involved. In other words, different degrees of variation are associated with both the identity of elements and the identity of organisms. There are a number of ways in which we could think about a nonstrict homeostasis. For example, in Chapter 3, we will look at models that assume strict homeostasis within certain physiological pools (e.g., structure vs. energy reserves) but allow the relative proportion of those pools to vary with time (other examples are given by Kooijman 1993, 1995).

This book will review and develop considerable theory related to how homeostasis and other stoichiometric constraints impinge on ecological systems. We propose the term “stoichiometrically explicit” to refer to such theory, because these models formally incorporate the limitations imposed by the mass balance of multiple elements during ecological interactions. We chose this term to be analogous to “spatially explicit” ecological models that recognize how space and rates of movement through space constrain ecological dynamics. Stoichiometrically explicit models have the advantage of preserving mass balance at all points in the model; alternatives, such as allometric expressions of nutrient release, lack that reality check. As Andersen (1997) described it, if zooplankton released nutrients at a fixed rate relative to their body size regardless of food consumption or actual growth (as they do in some food-web models in the literature), under various food conditions animals may be represented as synthesizing new nutrient atoms

in their bodies! This would be an unacceptable model property. Instead we need models that obey conservation laws. Such approaches should acknowledge that animal biomass is constructed of multiple elements in relatively fixed proportions (Chapter 4) and that animals can independently adjust the efficiencies with which they retain various elements (Chapter 5). Thus, the rates and ratios of elements released by the animal (Chapter 6) will be a function of the elemental composition of the food being ingested (Chapter 3), the elemental composition of the animal biomass being formed, and the efficiency of retention by the animal of nutrient elements when they are limiting.

In spite of the importance of homeostasis as an ecological and evolutionary force, few have considered the fundamental, ultimate reasons that some organisms are more variable in their chemical content than others. We offer a variety of hypotheses later in this book. Others who have considered the question include Williams and Fraústo da Silva (1996), who suggested that there was a broad evolutionary trajectory of increased homeostasis in the progression from early procaryotes to later procaryotes, then to unicellular eucaryotes, and finally to multicellular eucaryotes. They related this hypothesized trend to such features as the evolutionary development of ion pumps in membranes, increased cellular compartmentalization, and increased biochemical complexity. Basic thermodynamics suggests that for organisms to maintain a chemical content different from what they have available, energy must be expended. Assuming that energy expenditures impact individual fitness, homeostasis needs to be considered from the standpoint of adaptive reasoning. Taghon (1981) and Calow (1982) have written about the apparent evolutionary paradox of the evolution of constrained chemical content. An unanswered question is, “What are the advantages that outweigh the known costs of homeostasis?” Why does it evolve? Perhaps explicitly acknowledging the chemical nature of living things will help us better understand the forces driving and constraining the evolution of biological complexity. There are big unanswered questions about the nature and evolutionary history of the variation of chemical content in organisms. Our hope is that this book will suggest some possible answers and, by demonstrating how important these patterns actually are, stimulate others to delve into the subject in the future.

YIELD

One of the key stoichiometric concepts we will encounter in many places in this book is **yield**. Yield has a common biological or agricultural meaning: it is the amount of biomass, e.g., of a crop, obtained from a given unit of investment, such as resource or effort. Examples are bushels of corn per

kg N fertilizer applied. In the chemical literature, “stoichiometric yield” also has a precise definition. Stoichiometric yield is the amount of a product one obtains from a unit of reactant. For example, in photosynthesis, the maximum yield of glucose is one molecule for every six molecules of carbon dioxide. In a simple chemical reaction involving several reactants and several products, the reactant that is present in the smallest equivalent stoichiometric amount limits how much product will be produced; it is called the “limiting reagent.”

Stoichiometric yield can be helpful in understanding more complex systems as well. Consider the entire suite of biochemical reactions involved during the growth of a cell. Zeng et al. (1998) studied a number of aspects of stoichiometry and yield in mammalian cell cultures. They compared the rate of lactate production to the rate of glucose uptake using an empirical analysis of data obtained from several different studies. Plotting these two variables yielded an apparent straight line with a slope of 1.6–1.7 (Fig. 1.10A). This plot shows one way of interpreting a stoichiometric coefficient: it is the slope of a plot of reactants versus products, such as in Figure 1.10A, and it is also a yield. Initially, inspection of Figure 1.10A suggests that there is a constant yield of lactate from glucose. However, foreshadowing other situations we will see later, when the data were studied further, it was revealed that the stoichiometric yield was not constant. There were differences in lactate yield at low glucose levels, which can be seen by plotting the ratio lactate formation:glucose uptake (which now has dimensions of a molar ratio) against residual glucose concentration in the cultures (Fig. 1.10 B). Closer inspection of Figure 1.10A reveals a tight cluster of points above the trend line at very low glucose. These points are made more obvious by plotting the ratio, as in Figure 1.10 B. By examining several relationships such as this, the authors concluded that key stoichiometric yields in mammalian cells are not constant at low resource concentration, even though previous research had assumed a constant yield under all conditions.

The concept of yield is very much a part of ecological stoichiometry. Consider again the patterns of nitrogen content in a fungus as a function of the growth medium (Fig. 1.7). At low medium N, fungal N content was low. Inverting, we could say that the yield of fungal biomass per unit N was high in the low-N medium. In contrast, yield was low when the medium was N rich. Yield is a useful concept at the organismal level, such as when we talk about evolution working on growth production (Chapter 4). Or, for another example, the yield of animal biomass from a unit of nutrient input to a system may be important if animals are being harvested, or if they are important keystone predators in the system. It is also useful at the ecosystem level when we talk about nutrient use efficiency of whole ecosystems or constraints on C sequestration in the biosphere (Chapter 8). For exam-

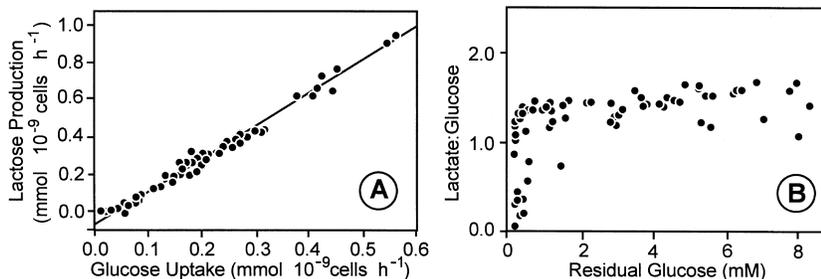


Fig. 1.10. Stoichiometric yield of an end product (lactose) from a reactant (glucose) in mammalian cell culture. A. Plotting the rate of formation of product vs. the rate of consumption of reactant generates a line with an apparent constant slope. B. Departures from constant stoichiometry are seen when one plots the ratio of lactate:glucose vs. the residual glucose concentration in the cell culture medium. At low glucose concentration, lactate yield per glucose drops. Based on Zeng et al. (1998).

ple, in pollution management and control, the yield of algal biomass obtained per unit of nitrogen or phosphorus incorporated into biomass can have great consequences; this yield may vary substantially across ecosystems and across different rates of N and P supply. Biological systems from single cells (Chapter 3) to multicellular organisms (Figs. 1.7 – 1.9) to communities (Chapter 7) to whole ecosystems (Chapter 8) often follow a commonsense pattern: the biomass yield per nutrient consumed is greater when nutrients are scarce. Fundamental patterns of homeostatic regulation of nutrient content thus have many implications for diverse ecological questions.

THE REDFIELD RATIO

Although we should be able to apply stoichiometric principles to all stable elements in the periodic table, the three elements C, N, and P are a special focus of this book. We will see some reasons why in an upcoming chapter. Perhaps the most famous reference point in ecological stoichiometry deals with C, N, and P in oceanic ecosystems. This is the **Redfield ratio**, named after Alfred C. Redfield (1890–1983), an oceanographer from Harvard and the Woods Hole Oceanographic Institute. Redfield discovered an unexpected congruence in C:N:P in numerous regions in the world's oceans and then used that congruence to infer something about the large-scale operation of the global biogeochemical system (Redfield 1934,

1942, 1958; Redfield et al. 1963). The Redfield ratio is such a cornerstone that we will cover it in some detail here in the beginning of the book.

Redfield found that the atomic ratios of carbon, nitrogen, and phosphorus in marine particulate matter (seston) were the same as the ratios of the differences of dissolved nutrients in those waters. In other words, when he plotted values of one of dissolved C, N, or P against one of the others, he obtained straight lines with slopes equal to the corresponding ratios in particulate matter (Fig. 1.11B). Redfield found the elements to be related by the ratio $C_{106}:N_{16}:P_1$ (Fig. 1.11A). The constancy of the C:N:P ratio of plankton was soon “embraced by many biological oceanographers and geochemists as canonical values, comparable to such physical constants as Avogadro’s number or the speed of light in a vacuum” (Falkowski 2000).

Redfield’s congruence in nutrient ratios between plankton and their aquatic medium indicated a balanced flow of C, N, and P in and out of the biota. The “Redfield ocean” is a biological circulatory system with constant C:N:P stoichiometry moving vast quantities of constant proportions of these three elements vertically over thousands of meters. A second congruence was that the line describing the N and P data had a zero intercept, indicating that these two elements would be depleted from ocean waters simultaneously (Fig. 1.11B). The same was not true for carbon: there was a surplus of carbonate when N and P were depleted.

Simultaneous depletion of N and P was surprising. There is no *a priori* reason to expect ocean water to contain N and P in proportions identical to biological demand. Why then should this measure of the chemistry of the ocean—such a vast proportion of the Earth’s surface and subjected to major influences from geology, meteorology, and others—have an N:P ratio that matches biological demand? Redfield’s (1958) answer was that the biota itself determined the relative concentrations of N and P in the deep sea. He suggested that it was P that ultimately determined the biological productivity of the world’s oceans, and that biological feedbacks adjusted the level of N so that its availability matched the availability of P (Falkowski et al. 1998). Similar arguments were later applied to soils (Walker and Adams 1958, 1959). Redfield’s findings were important in a very broad context: his work was instrumental in fostering a view that the ocean’s biota has a major influence on the chemistry of even this vast volume of water.

Today’s larger data sets and more precise methods have been used variously to support or modify Redfield’s proposed ratio of $C_{106}:N_{16}:P_1$ in the ocean (references cited in Hoppema and Goeyens 1999), although we hasten to add that even the proposed deviations are modest in comparison to the big differences often observed in C:N:P in freshwater systems (Chapter 3). The concept of a constant Redfield stoichiometry in the offshore ocean has generally held up to modern data (Copin-Montegut and Copin-

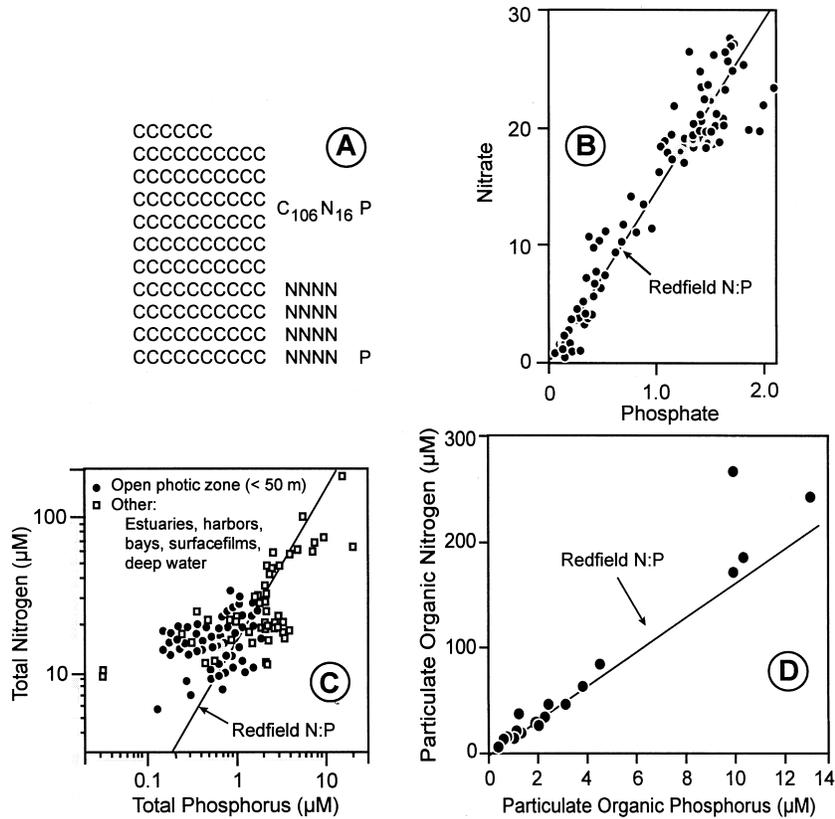
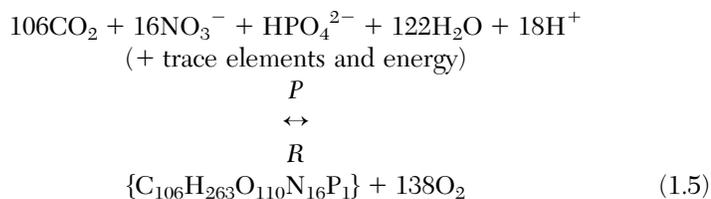


Fig. 1.11. A. The Redfield ratio with 106 atoms of C for 16 atoms of N for every one atom of P is a very famous ratio in ecological stoichiometry. This figure shows several examples of Redfield stoichiometry for N and P in different chemical fractions in marine waters. B. One of Redfield's original observations was that nitrate nitrogen and phosphate phosphorus (both dissolved) in waters of the western Atlantic have a proportionality of approximately 16:1. C. Total nitrogen and total phosphorus cluster roughly around Redfield proportions as well. Suggested systematic departures in open photic zone samples compared to others will be discussed further in Chapter 8. D. Marine particulate matter also generally shows Redfield N:P proportions. Panel B is based on Redfield et al. (1963), panel C is based on Downing (1997), and panel D is based on Copin-Montegut and Copin-Montegut (1983).

Montegut 1983; Karl et al. 1993; Hoppema and Goeyens 1999), although some interesting details have been layered on the classic picture of the Redfield ocean. For example, Downing (1997) proposed that there are systematic deviations in TN:TP ratios (TN and TP stand for total nitrogen and total phosphorus and they equal the sum of all nutrients, particulate and dissolved, in a water sample) between coastal and open ocean sites (Fig. 1.11C), suggesting that near-shore environments should become depleted first of N and off-shore sites should become depleted of P. Temporal trends on the scales of years to decades in deep-water N:P ratios (Pahlow and Riebesell 2000) and in riverine supplies to coastal zones (Justic et al. 1995) have been hypothesized and attributed to human influences on global biogeochemistry. Climatic couplings that have some influence on the composition of marine particulate matter have also been suggested (Karl et al. 1995); these will be discussed further in Chapter 8. Circumstances under which phytoplankton attain the Redfield ratio have been intensively studied (Chapter 3). And finally, although Redfield and colleagues considered both phytoplankton and zooplankton to have essentially the same C:N:P composition, systematic differences between these two ecosystem components and across the freshwater-marine contrast have been observed (Elser and Hassett 1994).

Although algae need not necessarily grow with C, N, and P in Redfield proportions, in the bulk of the ocean this seems to happen, and the Redfield ratio of $C_{106}:N_{16}:P_1$ has also been expanded to include comparable quantities of O and H. From this, a general equation for phytoplankton growth has been developed and related to biochemical fractions (carbohydrates, lipids, etc.) (Vollenweider 1985). Stumm and Morgan (1981) wrote this equation as,



where the curly brackets indicate algal biomass, and where movement to the right indicates photosynthesis (*P*) and movement to the left indicates respiration (*R*). Rearranging, algal biomass can also be expressed as



This expanded view with more elements allows for a deeper understanding of how cycles of C, N, and P relate to redox processes, a critical biogeochemical topic discussed briefly in Chapter 8. In Chapter 3, we will once

again return to questions of balanced growth, C:N:P, and their links to biochemistry associated with photosynthetic production.

CONVENTIONS AND CONCERNS ABOUT ELEMENT RATIOS

We will make extensive use of element ratios. Many of the raw data in this book in fact are composed of different sorts of ratios (e.g., P as a percentage of dry mass, C:N, etc.). Why? For one thing, stoichiometry is about proportions, plain and simple. We couldn't escape looking at ratios even if we wanted to. For another, ratios have been important in one of the most successful theories predicting ecological outcomes from mechanistic details. Resource ratios have a long history in ecology (Rodhe 1948). Resource competition theory (Tilman 1982; Tilman et al. 1982; Grover 1997) has made extensive use of ratios of different kinds—fluxes, concentrations—to predict patterns of species dominance, coexistence, and diversity in communities (e.g., Smith and Bennett 1999; Interlandi and Kilham 2001). So, although the technicalities of using ratios can be tricky, there are good ecological reasons to use them. In basing so much of what we do on ratios though, some questions will naturally arise (Lampert 1999). Ratios are proportions. A molar C:P of 200 means that there are 200 atoms of C for every atom of P, but it does not say anything about absolute amounts of either C or P. One must realize what ratios do, and not expect them to do inappropriate things. The C:P of food, for example, is basically irrelevant to animal growth if there is next to nothing to eat.

To equip the reader to think about ratios throughout the book, we will touch on some technical issues here. This section is an “aside” and skipping it will do no particular harm to the casual reader looking mainly for concepts. A ratio is a complete description of relative proportions between two substances, but there are some hidden traps. Ratios are sometimes presented on a mass:mass basis (“mass ratios”) and sometimes they are presented on a mole:mole basis. The latter are referred to as “atomic” or “molar” ratios. Either ratio is a complete description, but they are not numerically identical. Which is preferable? Mass units are appealing because we are accustomed to thinking about organism body mass or estimating total biomass of particular species or components in ecosystems. “Percent phosphorus,” for instance, is derived from a ratio of the mass of phosphorus to the total mass. However, chemical reactions proceed by atom-to-atom interactions. We prefer molar ratios. Our main reason is that they minimize confusion when thinking about ions or compounds. One mole of NO_3^- is an unambiguous statement of quantity, but in discussion of the nitrogen cycle, that same mole of NO_3^- would represent 14 g of N or 42 g of nitrate. In this book, any ratios not specifically labeled should be

taken to be molar ratios. Another source of confusion is that different studies may present the proportion of the “minor” element (e.g., N or P) relative to C (P:C or N:C) while others present the proportion of carbon relative to the minor element (C:N, C:P). Following the precedent of Redfield, we tend often to present data in the order of C:N:P (including C:N, N:P, and C:P). However, in keeping with the original studies sometimes we invert these. We apologize in advance for any mental knots this creates.

We also need to clarify the idea of “nutrient content” of biota. It is commonplace in the literature to express the elemental composition of an organism in terms of its “nutrient content.” There are two ways in which this is generally done. In the first way, the whole-cell or whole-organism amount of an element is reported. For example, in phytoplankton ecology this often involves the expression of nutrient content as a “cell quota” in terms of mass or number of atoms per cell (generalizing, we will refer to the quantity of any particular substance within any individual as a **quota** and use the symbol Q ; see the Appendix). We will define and work with the concept of the cell quota more formally in Chapter 3. While useful from the perspective of population dynamics, this approach has limited utility when diverse organisms need to be compared or when phenomena at higher levels such as the community or ecosystem are considered. In general, we will convert cell-quota data to elemental ratios using information about cell size and size-to-carbon conversions. Second, nutrient content is very frequently presented as a percentage or other proportion of dry weight. We will use the symbol Γ_x to represent the proportion of the total mass made up by a single substance. Such data are readily comparable across biota but are not directly stoichiometric. Indeed, in some cases they can mask significant stoichiometric variation, as in the case of organisms such as diatoms whose biomass comprises significant amounts of elements other than C. In general, we will convert data presented on a per dry weight basis to C:nutrient ratios using pertinent C:dry weight conversion factors. As mentioned above and discussed more fully later in the book, the range of variation in C content (e.g., % C by weight) is relatively narrow and thus such conversions are generally reliable within a circumscribed group of organisms.

Ratios present other mathematical issues. We often want to compare the variability of ratios, either directly when we talk about how different ecosystem components vary in their stoichiometry, or implicitly in statistical tests such as ANOVA (analysis of variance). To understand these things, one must know about propagation of errors. Error propagation (Bevington 1969) is a means of calculating the uncertainty of a composite calculation from the uncertainty of the component parts. Consider the composite value z calculated as a ratio of u and w ,

$$z = \pm \frac{au}{w}, \quad (1.6)$$

where a is a constant and u and w are variables measured with error. Error propagation follows the following formula:

$$\frac{\sigma_z^2}{z^2} = \frac{\sigma_u^2}{u^2} + \frac{\sigma_w^2}{w^2} - 2 \frac{\sigma_{uw}^2}{uw}, \quad (1.7)$$

where the σ indicate standard deviations and the last term refers to covariance between the two variables u and w . If one can assume that measurements of u and w are independent, the third term drops out. As an example, consider the following independent measurements and their associated standard deviations (errors):

$$\begin{aligned} C &= 100 \pm 1, \\ P &= 1 \pm 0.1. \end{aligned}$$

The C:P equals 100, but what is the variability associated with this ratio? To find the variability of the composite, perform the calculation

$$\sigma_{C:P} = 100 \sqrt{\left(\frac{1}{100}\right)^2 + \left(\frac{0.1}{1}\right)^2}. \quad (1.8)$$

If you do the math, you'll find this works out to 10.05. The relative errors of the individual measurements were 1% (for C) and 10% (for P). The fractional error of the composite (10.05/100) converted to a percentage (10.05%) is slightly larger than the larger of the two individual errors but smaller than their sum. This example points out one disadvantage to ratios; the relative error will never be less than the error associated with the variable with the greatest error. In this example, if you were trying to learn something specifically about C, working with C:P would be a bad approach. Another property of the variance of ratios is that the relative error of a given ratio will be the same as the relative error of the inverse of the ratio. In other words, the coefficient of variation (standard deviation divided by the mean) of P:C will equal the coefficient of variation of the C:P ratio. If one is about 10%, so will its inverse be.

One unfortunate aspect to working with ratios is that they raise a whole set of important statistical problems. The literature is full of warnings and prescriptions (Atchley et al. 1976; Atchley and Anderson 1978; Pendleton et al. 1983; Tonkyn and Cole 1986; Buonaccorsi and Leibhold 1988; Prairie and Bird 1989; Jackson et al. 1990; Raubenheimer and Simpson 1994; Berges 1997; Knops et al. 1997). Certainly, it is easy to make bad blunders. We urge caution and care. However, some of the arguments against using ratios in statistical tests seem to us to sacrifice scientific insight on the altar of statisti-

cal purity. For example, we have often read that if only one of the two variables in a ratio is strongly associated with some predictor variable, then it is incorrect to conclude anything about the ratio. Say z is related to u , but not to w . Some argue that examining $u:w$ versus z is wrong. We disagree with this point of view. We view such a situation as evidence for a changing balance between u and w . If one variable changes, but the other does not, the balance between the two changes. Although it may also be correct, and it is probably statistically more transparent, to toss out the ratio and work only with the variable that changes, this is unacceptable if you are in fact interested in what the ratio does.

For example, imagine that we grew algae in chemostats at varying light intensity and measured algal C and P concentration in response to light. Imagine next that algal P was constant with increasing light intensity but algal C increased (i.e., algal C:P went up). Now imagine that we wonder how zooplankton growth would relate to light intensity if these algae were fed to zooplankton. Should our focus remain only on the algal variable that responded to light (algal C)? But what if the animals were sensitive to the P content of their food? We will see just such an experiment in Chapter 7 where we need to know about changing C and P balance in light gradients. This example calls attention to one reason why working with ratios is important: they capture the important aspect of dilution of potentially key nutrients in food biomass and thus become a means for directly incorporating food quality into food-web theory. Thus, we believe that a strong focus on elemental ratios has major heuristic, conceptual, and theoretical benefits. By saying all this, however, we are not trying to give license to incorrect analysis or artificial inflation of r^2 values, both of which are easy to do! This book does not attempt to prescribe statistical solutions to these problems. The interested reader can refer to the papers cited above and should become familiar with this literature.

SOME CONVENTIONS ABOUT GROWTH RATE

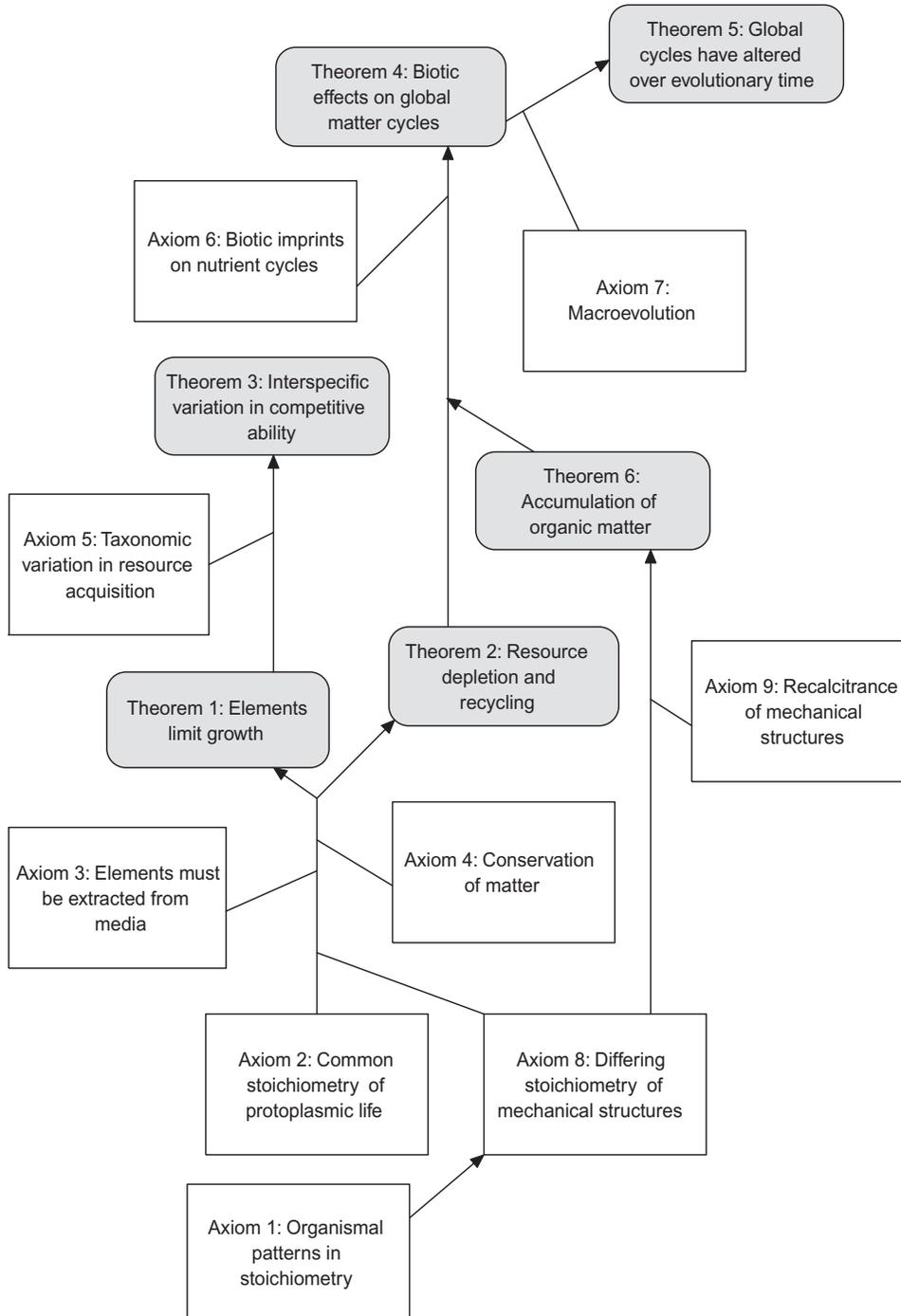
A major theme of this book is that organism growth rate and elemental composition are closely linked (Chapters 3 and 4). We are also very much interested in the phenomenon of nutrient limitation of growth rate, both in autotrophs and in consumers. Unfortunately, there are many contradictory ways that organism growth rate and nutrient limitation are expressed in the literature. In particular, expressions differ systematically between terrestrial and aquatic literature. To cover both subjects in one place, we need to set some conventions. Let us define two terms. The first is **specific growth rate** (μ ; units of time^{-1}), which refers to the exponential rate of change of biomass of the organism, normalized to its biomass. In continuous time,

$\mu = dM/Mdt$ where M is the biomass. In practice, one measures the specific growth rate by measuring the biomass at two times and applying the formula for discrete time. In discrete time, μ is given by $\ln(M_t/M_0)/t$ where M_t is the biomass at time t and M_0 is the biomass at the start of the interval. Throughout the book when we use the term “growth rate” we mean “specific growth rate.” This terminology is conventional in the aquatic literature. However, in the terrestrial plant literature this parameter is commonly referred to with the term “relative growth rate” (e.g., Grime and Hunt 1975). Here, we use the definition of the term **relative growth rate** (RGR) as the proportion of an organism’s **maximum growth potential** (μ_m) that is actually achieved in any particular situation. In this book, RGR (μ/μ_m) is a measure of the severity of some limitation of growth rate and varies from 0 (severe growth limitation) to 1. We beg the pardon of our colleagues most familiar with the terrestrial plant literature and hope the change in lingo will not be too stressful.

A LOGICAL FRAMEWORK

Some of ecology’s major operative concepts have been criticized as being “tautologies,” “semantical,” or with other dismissive terms. Perhaps this is because we ecologists do not pause often enough to try to organize our thoughts into a formal logical structure. Perhaps doing so too frequently would be a waste of time and ink. However, logical systems can clarify our thinking and tell us how it is we know what we think we know. Let us define some epistemological terms in simple language. An axiom is a statement taken to be true—in other words, a proposition taken to be self-evident and not needing proof (e.g., the whole is greater than a part). A theorem is a statement that is not self-evident but that can be proved using axioms and rules of logic. Reasoning from a premise to a specific conclusion is called “deduction,” as is reasoning from the general to an unknown specific case. “Induction,” on the other hand, is a form of reasoning where a general statement is constructed from a number of specific facts or individual cases.

Reiners (1986) presented a logical structure for ecological stoichiometry. He did not use the term “ecological stoichiometry.” He said he was offering a “complementary” view of ecosystems (based on matter) to go along with a classical view built on energetics. Reiners’ complementary model contained many of the core concepts we will discuss, so considering his logical reasoning does double duty for us here in the beginning of the book. He assembled a series of statements ranging from the cellular level to the global level into a logical flow chart using axioms to derive theorems (Fig. 1.12). This flow chart shows the way that lower-level stoichiometric processes (occurring at the cellular, population, and community levels) create higher-level specific pro-



cesses and patterns (at the ecosystem and global levels). We begin with the first four axioms (Reiners' exact wording is used in the text below—we have paraphrased these axioms and theorems in the accompanying figure).

Axiom 1: *Groups of organisms have regular chemical stoichiometries.*

Axiom 2: *Protoplasmic life has a common chemical stoichiometry.*

Axiom 3: *Organisms have evolved mechanisms for extracting elements from media to synthesize biomass.*

Axiom 4: *Law of conservation of matter.*

These four statements relate to material we will cover primarily in Chapters 2–4. We can take these statements about “protoplasmic life” to refer to mass flow in microbial production. At the time he wrote his paper, Reiners lacked the information we now have on stoichiometric patterns in many organisms. He mainly had the observations of Redfield (discussed above) and a compilation of element data by Bowen (1979) with only a few data for living creatures (Bowen's compilation remains the single most comprehensive). Thus it is understandable that Axioms 1–4 describe the stoichiometrically balanced ocean with a single biotic C:N:P. Reiners had an overly simplistic outlook on the stoichiometry of organisms lacking major structural components, those that he called “protoplasmic life.” As we have just seen (e.g., Fig. 1.5) and will continue to see throughout the book, microbes do not in fact have a “common chemical stoichiometry.” Neither are they strictly homeostatic. Instead, they have differing adaptations for nutrient storage and have different C:nutrient balances depending upon such factors as the relative availability of light and nutrients (Chapter 3). We also understand much better today how differential biochemical investments in storage, proteins, and RNA result in differential cellular stoichiometry (Chapters 3 and 4). Finally, we are beginning to understand differences in the stoichiometry of autotrophs and heterotrophs, even at the microbial level. As we will reinforce in chapters to come, the biosphere in general is not like the Redfield ocean.

It may be disconcerting to begin with statements labeled as axioms, meaning that they should be self-evident without proof, but then immediately suggest additions and modifications. Are these statements axioms after all? What if we take them to be approximations? Table 1.1 and numerous other examples in this book make the point that the stoichiometry of the inorganic world can certainly be extremely variable in comparison to “protoplasmic

Fig. 1.12. A logical structure for stoichiometric theory. Clear boxes are axioms and shaded boxes with rounded corners are theorems. A small number of logical steps takes us from axioms about biochemistry to theorems about planetary biogeochemical cycling. Based on Reiners (1986).

life.” From this very broad perspective, the members of the world’s biota are in fact regular in composition. Hence, we may be able to predict something about mass flow and resource limitation from knowledge of inorganic nutrient supply alone, independent of these biological details. Few if any interesting statements in ecology can be taken to be axiomatic in every possible context.

Reiners’ logical scheme recognizes differential organism stoichiometry primarily due to differing mechanical structures.

Axiom 8: *Mechanical structures of variable stoichiometries different from those of protoplasmic life have evolved over geological time.*

With this, Reiners recognized that the elemental composition of a tree differs from that of a mammal and those differ from that of an insect. From Axioms 1–4 and 8 one can deduce two theorems that relate organism growth to the mass balance of nutrient uptake.

Theorem 1: *Organic synthesis and metabolic rate are limited by the supply rate of essential elements.*

Theorem 2: *Net change in biomass will alter the amount of essential elements in surrounding media.*

Theorem 2 can be deduced logically from the preceding axioms. Theorem 1, on the other hand, has an unstated premise that matter matters. In other words, its premise is that organisms will be sufficiently numerous and active to deplete element resources to limiting levels. An ecological population held in low abundance by a predator or by stressful conditions could be considered a counterexample to Theorem 1. In addition, Reiners’ “complementary” view is not about energetics. Theorem 1 might be refuted if energy, not elements, limits organic synthesis and metabolic rates. With these caveats and limitations, Theorem 1 follows by logic. These theorems summarize the stoichiometric constraints on organism function that are an inevitable result of cellular allocation, the finite resources of the environment, and mass balance. We will cover these topics in detail later in the book, and for now we shall press on to add another of Reiners’ axioms.

Axiom 5: *There are differences among species in the means and rates at which they can sequester limiting elements.*

This axiom refers to the existence of many different adaptations for resource acquisition, including differential nutrient uptake, differential foraging efficiency, etc. We will discuss those adaptations further in Chapters 3, 4, and 7. From all this, you get another theorem.

Theorem 3: *There are differences among species in ability to live in particular environments or to compete for chemical resources.*

This theorem is the core of resource competition theory (Tilman 1982; Grover 1997). It relates to patterns we will discuss in Chapter 5.

We now progress to the ecosystem level by adding two more axioms.

Axiom 6: *Biological effects on the availability and chemical form of elements are unique in kind and magnitude.*

Axiom 7: *The world biota has changed quantitatively and qualitatively through geological time.*

Whether the statement that biological effects on elements are unique in kind and magnitude is an axiom or should be thought of as a theorem derived from the preceding axioms seems debatable. Nevertheless, the logic flow chart shows us how consideration of mass balance in organism growth (Axioms 1–6) ties together the concepts of resource limitation (Theorems 1 and 2 and Chapters 3 and 5) and nutrient cycling (Axiom 6 and Chapter 6).

From all the preceding, we can obtain two theorems about global biogeochemical cycles.

Theorem 4: *The world biota drives and regulates the global biogeochemical cycles.*

Theorem 5: *Global biogeochemical cycles have been altered by life over time.*

A stunning aspect of this logical scheme chart is how few steps it takes to get from statements about cellular allocation (Axiom 1) to statements about the largest spatial and longest temporal scales relevant to Earth's biota (Theorem 5). This amazing sweep is part of ecological stoichiometry's allure. We will come back to global processes in Chapter 8. Another ecosystem-level statement is this next axiom.

Axiom 9: *Mechanical structures are resistant to decay.*

Rates of mineralization are very dependent on element balance, as well as on other chemical aspects. We cover this material in Chapters 6 and 7.

Theorem 6: *Accumulation of resistant mechanical structures alters soils and sediments.*

This theorem refers to the buildup of organic matter over long time scales. The subject of carbon storage will be described in Chapter 8.

Reiners' flow chart illuminates an intellectual pathway from atoms to ecosystems, with ecology and evolution both occupying prominent places. We are unaware of any similar logical structures that have been spelled out in ecology. Where does this consideration of logic take us? For one thing, it lays bare the connections among different components of an overall theory of how biological systems are controlled by and, in turn, control mass flow. It

is interesting that an epistemological structure for stoichiometry does not consist of a series of hypotheses; rather, it uses the language of mathematics: axiom and theorem. Mass balance, after all, is nothing less than the law of mass conservation and hardly needs to be tested. Because ecological stoichiometry in its broadest sense is a version of thermodynamics, it is not a hypothesis or series of hypotheses. Rather, we view ecological stoichiometry as a lens, a means of organizing thoughts, a hypothesis-generation machine, and a window to interesting connections in the biotic and abiotic worlds. It is a tool to use in appropriate places. Let's get to it.

THE STRUCTURE OF THIS BOOK

The organization of this book follows more or less the movement of materials through ecological systems and the scale considered increases as the book progresses. We start in Chapter 2 with an overview of the biological chemistry of the major elements, and how they are coupled in the structures of the major molecules used by organisms. Next, in Chapter 3 we consider the incorporation of C, N, and P into photoautotrophic organisms (both algae and higher plants) and how various environmental and interspecific factors generate variation in C:N:P stoichiometry at the base of food webs. In Chapter 4 we examine the stoichiometry of metazoans and how and why the C:N:P composition of higher animals differs among and within species of animals. The emphasis is primarily on invertebrates but we also consider vertebrates, with their special requirements for minerals in the formation of bone. Interspecific interactions enter the picture in Chapter 5, where we analyze autotroph-grazer interactions from a stoichiometric perspective. Here we begin to see the profound consequences for secondary production when variable and nutrient-deficient autotroph biomass is consumed by homeostatic herbivores. In Chapter 6 we will consider an end product of this interaction: nutrient recycling by consumers. We will see that the relative imbalance in elemental composition between consumed food and the requirements of the consumer has direct effects on the rates and ratios of nutrients that they recycle. These consequences in turn can affect nutrient availability in the system and a complex set of reciprocal interactions is established. In Chapter 7 we further consider the consequences and feedbacks established by stoichiometric balance, discussing food-web structure, trophic dynamics, interaction strength, and a variety of other characteristics of communities. Ecosystems are the subject of Chapter 8, where we examine the broadest-scale patterns in ecological stoichiometry. We also see how the small-scale coupling of elements in biological molecules has effects on a grand scale, impinging even on global biogeochemical cycles. This stoi-

chometric coupling has ramifications for global climate and the potential outcome of humankind's unplanned experiments with our global habitat, in which the cycles of C, N, and P are disrupted simultaneously but to differing degrees and in different places.

A collection of symbols and their definitions appears in the Appendix. Each chapter includes a "Summary and Synthesis" section that repeats major points and integrates across concepts within the chapters. In addition, Chapters 3–8 include a list of key unanswered questions. We hope that by calling attention to those things that we feel are unanswered or require more information or deeper study we will accelerate future research. Hence, we have called these "Catalysts for Ecological Stoichiometry." The book closes (Chapter 9) with a comprehensive integration of major themes presented in various chapters and with a discussion of the general utility and potential future for stoichiometric theory in ecology and biology.

SUMMARY AND SYNTHESIS

This chapter laid the foundation for what is to come. It explored the nutrient contents of organisms as compared to the rest of the material world. Stoichiometry represents organisms as single abstract molecules where constituent elements exhibit mass conservation.

The rules determining the constraints on organismal chemical content are complex and vary with the organism, its feeding mode, and the chemicals involved. We derived a new, precise definition of stoichiometric homeostasis and showed how it can be used to diagnose regulation of nutrient content in biota. In our empirical examples, absence of homeostasis was seen in the N:P of autotrophs. A strict homeostasis was seen in the C:N of heterotrophic bacteria. Other taxa and chemical elements exhibited intermediate degrees of homeostasis.

We defined the key terms to be used throughout the book. Stoichiometry relies on mass conservation laws. Substances that are subject to stoichiometric balancing are conservative, like elements. They are neither created nor destroyed (obviously, we are dealing only with normal chemical reactions here).

A key reference point is the Redfield ratio (C:N:P = 106:16:1). The offshore ocean is a stoichiometrically balanced system with those three elements moving between the biotic and abiotic world in balanced proportions.

Ecological stoichiometry can be placed in an epistemological structure that uses the language of mathematics (axiom and theorem). It is about constraints of matter and energy at scales ranging from the atom to the biosphere.

KEY DEFINITIONS

These are “our” definitions and we have taken care to use them consistently throughout the book. The reader should be advised when reading the primary literature that not all studies use the same definitions. For example, in some papers, the term “Redfield ratio” is used to refer to any C:N:P ratio.

Balanced growth—Equal specific rates of change of elements during growth (dX/Xdt where X is any chemical substance). Under balanced growth, nutrient content does not change. Note also that chemical composition can be regulated actively (homeostatically) at a fixed level even in an organism that is not growing; thus, “strict homeostasis” is not interchangeable with “balanced growth.”

Ecological stoichiometry—The balance of multiple chemical substances in ecological interactions and processes, or the study of this balance. Also sometimes refers to the balance of energy and materials.

Elemental imbalance—Dissimilarity in nutrient content between two things, such as consumer and food resources or between an autotroph and the inorganic medium. If consumer and resource have identical stoichiometry, they are perfectly balanced. The greater they differ, the more their imbalance.

Homeostasis—Physiological regulation of an organism’s internal environment reducing changes within the organism. In stoichiometry, homeostasis results in a narrowing of variation in chemical content in an organism compared to the resources it consumes.

Homeostatic—Regulated by a negative feedback so that the state of the organism (e.g., its nutrient content) is less variable than predicted based on external variation.

Law of conservation of matter—In an ordinary chemical reaction, matter and component elements are neither created nor destroyed.

Law of definite proportions—Generally attributed to Proust, who in 1797 wrote that iron and oxygen combined in a fixed ratio of FeO_2 . This law states that the relative amount of each element in a particular compound is always the same, regardless of preparation or source.

Maximum growth potential (μ_m)—The specific growth rate (dM/Mdt where M is biomass) achieved under conditions of resource surplus such that an organism is growing at its full, genetically determined, capacity for those physical conditions.

Nonhomeostatic—Lacking homeostatic regulation. In ecological stoichiometry, nutrients in nonhomeostatic organisms track their availability in the external surroundings.

Nutrient content (or composition)—The amount of nutrients in an organism. Nutrient content is generally expressed in units such as g P per dry weight, (or as a percent). We represent nutrient content using the symbol Γ_x where x is an element. Since biomass C content is relatively constant as a function of dry weight for most living things, nutrient content is generally proportional to the nutrient:C ratio.

Quota (Q)—The amount of any chemical substance in a single individual organism.

Redfield ratio—Proportions of elements equal to 106 atoms of C per 16 atoms of N per 1 atom of P.

Relative growth rate (RGR)—The proportion of an organism's maximum growth potential that is actually achieved, μ/μ_m .

Specific growth rate (μ)—The exponential rate of change of biomass of the organism normalized to its biomass ($\mu = dM/Mdt$ where M is biomass). In discrete time, μ is given by $[\ln(M_t/M_0)]/t$ where M_t is biomass at time t .

Stoichiometric equilibrium—see “balanced growth.”

Stoichiometry—1. A branch of chemistry that deals with the application of the laws of definite proportions and the conservation of mass and energy. 2. The quantitative relationship between constituents in a chemical substance.

Strict homeostasis—In living and nonliving things, having elements occurring in fixed, definite proportions.

Yield—The amount of something produced relative to an investment. Yield is often given relative to a resource or a reactant, e.g., biomass produced from a given quantity of nutrients. Yield of biomass per nutrient invested is the inverse of nutrient content.