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The Invisible Hand of the Periodic Table: How Micronutrients Shape Ecology

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Abstract

Beyond the better-studied carbohydrates and the macronutrients nitrogen and phosphorus, a remaining 20 or so elements are essential for life and have distinct geographical distributions, making them of keen interest to ecologists. Here, I provide a framework for understanding how shortfalls in micronutrients like iodine, copper, and zinc can regulate individual fitness, abundance, and ecosystem function. With a special focus on sodium, I show how simple experiments manipulating biogeochemistry can reveal why many of the variables that ecologists study vary so dramatically from place to place. I conclude with a discussion of how the Anthropocene's changing temperature, precipitation, and atmospheric CO_2 levels are contributing to nutrient dilution (decreases in the nutrient quality at the base of food webs).

PROLOGUE: THE STORY OF IODINE

In 1917, many US Army recruits could not fit into their uniforms. They had goiters—swollen necks generated by hypertrophied thyroids—that prevented them from buttoning their collars (Feyrer et al. 2017). Most of these recruits were from northern states. The Army was in a good place to analyze and fix the problem. First, the 151 district draft boards compiled mountains of data on the health of this cross section of the human population (Love & Davenport 1919). Second, they knew the cause of goiter: a dietary deficiency of iodine (I) that causes the thyroid to swell. Third, they had a treatment: Hippocrates prescribed seaweed and sponges to his goitrous patients. In 1811, Courtois discovered the active ingredient, I, in a puff of purple smoke from burned seaweed (McDowell 2003a). The sun's rays, in an analogous process, oxidize 400,000 tons of ocean iodate (IO_3^-) that falls to earth again in rain. By the end of the century, Swiss doctors treated goiters with I.

The US began a policy of adding I to table salt (NaCl). Recruiting years later for World War II, the Army generated a before-and-after data set documenting the effects of the I supplements. They discovered another effect of I shortfall. Districts that had reported the most goiters showed the largest increases—one standard deviation (SD)—on Army IQ tests 20 years later (Feyrer et al. 2017). It turns out I shortfall in utero was a key source of infant malnutrition (Black et al. 2008, de Benoist et al. 2008, Feyrer et al. 2017).

The story of I is just one example of the potential for micronutrient shortfall to have profound consequences in ecological systems. Most of life's 25 or so essential chemical elements occur in trace quantities but can have substantial—if still largely unexplored—effects on the fitness of individuals and populations. Thus far, such effects have been quantified mostly for humans and domesticated animals and plants. Some of the greatest examples of shortfall are expressed in mothers that must safeguard their own quotas of I, zinc (Zn), and sodium (Na), while building new individuals who also require their own quotas; even temporary shortfall in developing humans can leave lasting abnormalities in nervous and muscle tissues (Al-Dahhan et al. 2002). In addition, the magnitude of micronutrient limitation has a geography linked to supplies in soils and aerosols. And yet, despite the clearly documented effects of micronutrients on the health and productivity of humans and their agronomic model systems (Cohen 2004, Smith 1987, Wertz 1987), ecologists have only begun to study the effects of micronutrients in wild populations, communities, and ecosystems.

Here, I explore the role of micronutrients in ecology and document the many ways that micronutrient availability constrains individuals, populations, and communities, as well as ecosystem function, in the Anthropocene.

WHAT IS A MICRONUTRIENT?

The term micronutrient contrasts the amount of a substance (small) and its utility to health (essential). Definitions vary widely, and so we must make some choices in settling on one. Our first choice is to eliminate macromolecules like lipids, proteins, carbohydrates (CHOs), and vitamins. We focus instead on atomic elements. This focus on biogeochemistry jibes with G.E. Hutchinson's (1948) insight that the recipe for life is elemental, with humans continuing to rearrange that recipe's geography.

Our next step is to winnow this list down to the micro. Some agronomists, like McDowell (2003b), identify a threshold concentration in biomass: Elements with biomass concentrations >100 ppm (ppm = mg/kg) are major elements; the rest are trace. However, the elemental composition of prokaryotes and eukaryotes, and plants and animals, varies enough that this simple threshold is unsatisfactory for ecologists. For guidance, we turn instead to two masterworks of ionomics (the measurement of suites of elements in organisms). *The Biological Chemistry of the*

Elements (Frausto da Silva & Williams 2001) points out that just four elements—carbon (C), hydrogen (H), oxygen (O), and nitrogen (N)—make up 99% of the mass of most biological systems; *Ecological Stoichiometry* (Sterner & Elser 2002) elevates phosphorus (P) as ubiquitously important given its multitude of roles from constructing lipid membranes to fueling cells. Together these five macronutrients form the elemental skeleton of life's machinery. The remaining essential elements [in rough order of biomass concentration, potassium (K), calcium (Ca), magnesium (Mg), sulfur (S), sodium (Na), silicon (Si), iron (Fe), manganese (Mn), boron (B), zinc (Zn), chromium (Cr), copper (Cu), lithium (Li), nickel (Ni), molybdenum (Mo), cobalt (Co), and iodine (I)], which are collectively referred to as an organism's ionome (Salt et al. 2008), are far less studied by ecologists. Here, I refer to these 17 elements that collectively make up approximately 1% of life's biomass as micronutrients.

   Next, let us dwell for a moment on what a nutrient does. To plant agronomists like Sharma (2006) an element is an essential plant nutrient if it meets three criteria: (*a*) the plant is unable to complete its life cycle in the nutrient's absence, (*b*) no other nutrient can take its place, and (*c*) it has a metabolic function. This is a substantial beginning, as it links the element to the organism's survival, growth, and reproduction, leading to a basic criterion: experimental shortfalls should decrease fitness. Given the rarity of trace metals like Co or I (at <1 ppm in living tissue) such tests, typically performed on individual plants and animals, require carefully controlled conditions. An ecologist would likely see such lab experiments as quantifying a species' fundamental niche (Begon et al. 1996). A grumpy ecologist might also suggest that a calf fed Co supplements in the lab may respond differently to a calf in a snowfield on a cold Montana night.

   Ecologists are just as likely to be interested in an organism's realized niche, i.e., how an element's biogeochemical availability in situ—where the organism is surrounded by competitors, predators, and mutualists in an environment whose temperature and precipitation fluctuates—affects fitness and function (Begon et al. 1996). The realized niche includes elements that act not through a focal population's metabolic pathways but indirectly through interactions with other populations. Agronomic and ecological approaches to characterizing micronutrient concentrations in organisms can generate different results. Marine diatoms grown in (mono)culture tend to harvest and maintain lower quotas of metals like Fe, Zn, Mn, and Cu than those harvested from the open ocean (Baines et al. 2011, Twining & Baines 2013). Plants have little metabolic need for Na but may still manipulate their Na content to attract pollinators and dispersers or dissuade herbivores (Kaspari 2020, Rosenthal & Janzen 1979).

FUNCTIONAL GROUPS OF ELEMENTS

Most cellular machines are CHO skeletons buttressed by N and P. Let us consider the functional ecology of two other classes of micronutrients that I call structural micronutrients and fluxing micronutrients.

   Structural micronutrients contribute to the shape and function of biomolecules. Sulfur-rich amino acids facilitate protein folding; Zn fingers reinforce those folds (Frausto da Silva & Williams 2001). Others, like Mn, Fe, Co, Ni, Cu, Zn, Mo, Si, and Se, serve as catalytic centers of enzymes, attracting small molecules like H_2O, CO_2, and O_2. Metallomic enzymes may make up one-third of the approximately 4,000 known enzymes (Bairoch 2000, Waldron & Robinson 2009).

   Fluxing micronutrients (Na^+, K^+, Ca^{++}, and Mg^{++} and Cl^-) serve osmoregulatory, nervous, and motor systems by fluxing across membranes. This movement—and the resulting changes in the charge across those membranes—allows the transport of necessary substrates into cells and waste out of cells. Fluxing micronutrients also counterbalance the osmotic pressures that would otherwise lyse cells. The Na–K pumps of animals run at enormous cost to the individual,

Macronutrient: C, H, O, N, and P together make up approximately 99% of living biomass

K: potassium

Na: sodium

Zn: zinc

Mn: manganese

Cu: copper

N: nitrogen

P: phosphorus

Ni: nickel

Si: silicon

Ca: calcium

Mg: magnesium

accounting for 25–75% of a cell's entire ATP budget (Frausto da Silva & Williams 2001). As we shall see in the section titled The Role of Micronutrients in Herbivory, this has consequences for the ecological niches of animals, particularly herbivores and detritivores.

ABIOTIC SOURCES OF IONOMIC VARIATION

Where does life find its micronutrients? The elements of Earth's crust ride their way to the surface on tectonic plates only to eventually settle to the bottom of oceans via gravity and water flow. In the interim, those nutrients bioaccumulate from soils to plants and through herbivores and predators.

A soil's nutrient supply reflects the mineralogy and physical and chemical weathering of its underlying bedrock. The importance of this bedrock as a nutrient source can be seen in licks, outcrops rich in Na, Mg, and Ca that are dependably visited by animals to sate their mineral requirements (Jones & Hanson 1985). Over time, these soluble metal ions leach away (only N reliably increases with the age of the ecosystem by way of N-fixing plants). A soil's developmental age is thus a good first predictor of an ecosystem's nutrient availability, with higher micronutrient supply in younger, less weathered soils (e.g., see Wardle et al. 2004). The rate of nutrient loss is slowed in soils with finer texture (i.e., clays versus sands) and higher organic content.

Local topography, via gravity and leaching, can further rearrange soil nutrients. Moderate uplift—creating dry hilltops and wetter valleys—allows for the accumulation of micronutrients in valley soils and springs. A key reason why micronutrients like Na, Se, I, and Co are deficient in relatively flat Australia, compared to geologically similar southern Africa, may be the latter's uplift, which brings nutrient-rich bedrock to the surface and allows the downhill spread of nutrients through South African grasslands (Milewski & Diamond 2000).

Many micronutrients like Na, K, I, and Se are common in seawater, volatilized by wind and sun, and deposited elsewhere in precipitation (Milewski & Diamond 2000, NADP 2021). Thus, such elements are more readily available near ocean shores. As a result, with 90% of Earth's terrestrial environments >100 km from an ocean, nutrient shortfalls are more likely to occur inland (Kaspari et al. 2008b).

BIOTIC SOURCES OF IONOMIC VARIATION

Plants selectively take up nutrients from the soil, generating a patchwork of nutrient sources for the rest of the food web. In a survey of 54 North American grasslands, plant uptake from soils was contrasted for three classes of elements: (*a*) those essential for plants and animals, (*b*) those additionally required by animals, and (*c*) those with no known metabolic function (**Figure 1**) (Kaspari et al. 2021). In both herbaceous forbs and grasses, plant tissues mirrored soil availability in plant-essential nutrients. However, forbs discriminated against uptake of elements known to be essential nutrients for animals, while grasses were more likely to take up even nonessential elements like cadmium and strontium. Thus, the ionomes of prairie plants (and the food quality for herbivores) was more likely to track soil availability in grasses than forbs. This supports the hypothesis that the higher nutrient-use efficiency in grasses, which allows them to grow in low-nutrient patches (Vitousek 1982), is facilitated by decreased discrimination in nutrient uptake (Foy et al. 1978, Kaspari et al. 2021).

An element's bioaccumulation—its increase in tissue concentration from food source to consumer—suggests active selection by the consumer's metabolism (**Figure 2**). For example, herbivorous *Daphnia* had mostly higher concentrations of micronutrients than their algal food (**Figure 2*a***) (Jeyasingh et al. 2020). In a tropical brown food web (**Figure 2*b*** and ***c***), microbes bioaccumulated Fe and Cu from the leaf litter falling to the forest floor, likely reflecting microbial metabolic needs (Twining & Baines 2013). This litter–microbe matrix supported a rich diversity
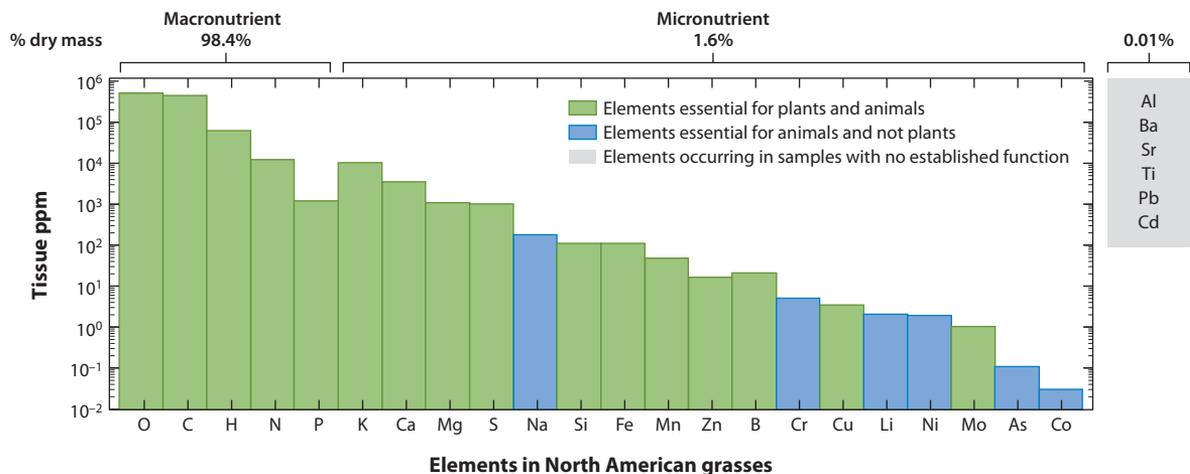
Figure 1

Breakdown of the average ionome of the grasses clipped from 54 grasslands, ranked in order of their abundance (ppm = mg/kg, note the $\log_{10}$ scale). Elements shaded green are essential for plants and animals, while those shaded blue are essential for animals and not plants. For the purposes of this review, P is grouped with the carbohydrates and N as macronutrients (98.4% of dry mass); the remaining 17 elements (1.6% of dry mass) are treated as micronutrients in this text. Those elements listed in gray occur in samples but have no readily agreed upon function. Abbreviations: Al, aluminum; As, arsenic; B, boron; Ba, barium; C, carbon; Ca, calcium; Cd, cadmium; Co, cobalt; Cr, chromium; Cu, copper; Fe, iron; H, hydrogen; K, potassium; Li, lithium; Mg, magnesium; Mn, manganese; Mo, molybdenum; N, nitrogen; Na, sodium; Ni, nickel; O, oxygen; P, phosphorus; Pb, lead; S, sulfur; Si, silicon; Sr, strontium; Ti, titanium; Zn, zinc. Data from Kaspari et al. (2021).

of invertebrates, including ants (**Figure 2c**), which accumulated some elements (N, P, K, and Zn) but not others (Ca, Fe, Cu, Mg, and Mn). Arthropod predators bioaccumulated Na, Zn, and Cu from herbivore prey (**Figure 2d**). Some elements dependably bioaccumulate: in **Figure 2**, Na is depicted in red to reflect its role as a super micronutrient—an element that is consistently bioaccumulated trophically (Kaspari 2020). In addition, consumers bioaccumulate some micronutrients as they age: Mature queens of a *Polistes* wasp had higher concentrations of seven of the eight elements quantified (**Figure 2e**). If accumulated elements enhance function, we predict that bioaccumulation will increase performance in higher trophic levels and (in the case of our *Polistes* wasps) older individuals. Let us return to that later.

Another source of ionomic variation arises from allometry, systematic changes with body size. As an organism grows, the network supporting and servicing each cell must expand with it. A plant's CHO-rich structural tissue thus scales as $Mass^{1.25}$ (Elser et al. 2010, Enquist & Niklas 2002). As a result, whole-body P tends to decline from bacteria to fruit flies as $Mass^{-1/4}$ (Gillooly et al. 2005). A similar decline was found across 71 aquatic invertebrates varying 1,000-fold in size (González et al. 2018) and across a 10,000-fold size gradient in desert insects (Woods et al. 2004). An individual must similarly expand its support network as it develops from egg to adult. I know of only one study of developmental changes in the ionome. Of the seven elements measured, six were denser by twofold (Zn) to fivefold (Fe) in tissues of first instar grasshoppers, while P content, in contrast, was fivefold higher in adults (Paul et al. 2016). The temporal change in an individual's ionome as it moves through its life history is ripe for exploration.

Another, underappreciated but concentrated, source of micronutrients can be found in the humble form of excreta. Consider fluxing micronutrients like Na, K, and Mg, which are lost in urine. Nutrient-stressed herbivores often eat where they excrete, creating dependable grazing
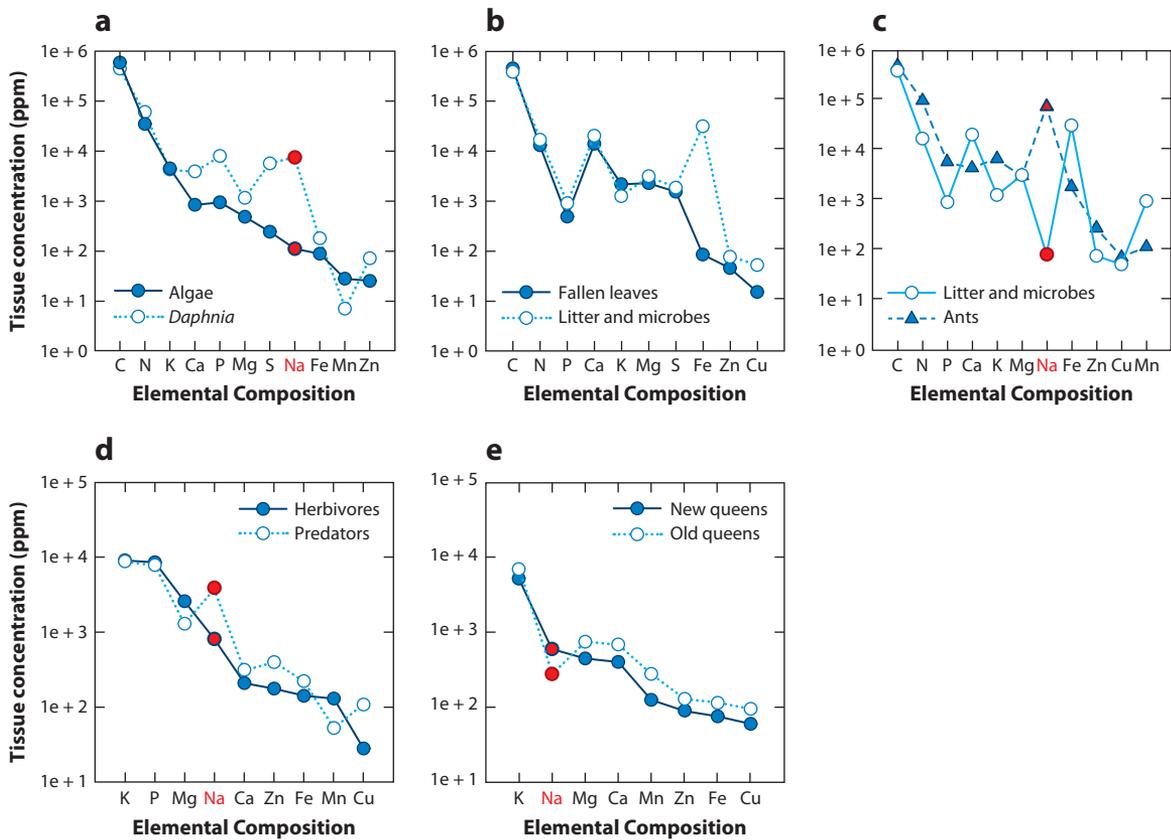
Figure 2

Examples of elemental bioaccumulation (note the log$_{10}$ axis for tissue concentration) with elements ranked by concentration in the source. (*a*) *Scenedesmus obliquus* algae fed on a low-P diet and then fed to *Daphnia pulicaria* (Jeyasingh et al. 2020). (*b*) Chemistry from leaf-fall traps in the Panama forest of Barro Colorado Island (control plots, data from Kaspari et al. 2008a) versus the microbe and leaf matrix from 10 sites on Barro Colorado Island (data from Kaspari & Yanoviak 2009). (*c*) The same microbe–leaf matrix versus the mean ionome of 20 resident ant species (M. Kaspari, unpublished data). (*d*) 16 herbivorous and 9 predacious invertebrates collected from the Yasuni (Ecuador) and Barro Colorado Island (Panama) forests (M. Kaspari, unpublished data). (*e*) Founding versus mature queens of the wasp *Polistes metrics* (data from Judd et al. 2010). Na is depicted in red to reflect its role as a super micronutrient—an element that is consistently bioaccumulated trophically. Abbreviations: C, carbon; Ca, calcium; Cu, copper; Fe, iron; K, potassium; Mg, magnesium; Mn, manganese; N, nitrogen; Na, sodium; P, phosphorus; S, sulfur; Zn, zinc.

lawns that recycle those nutrients (reviewed in Kaspari 2020, Knapp et al. 1999, McNaughton et al. 1997, Woodroffe et al. 1990). Far less studied, feces are rich in metals, reflecting the ionome of the animal and its bacterial gut flora (Munroe 2020). In a survey of 54 North American grass-lands, prairies grazed by cattle maintained higher levels of seven micronutrients in their plant tissues (Kaspari et al. 2021). Like bioaccumulation, differential patterns of excretion can also hint at limiting nutrients; for example, grasshoppers fed on a grass diet retained micronutrients like Cu and Mo but overexcreted plant-essential elements like B, Mg, and P (Peterson et al. 2021).

HYPOTHESES FOR MICRONUTRIENT LIMITATION

Armed with knowledge of an organism's ionomic recipe and a map detailing availability, we can assemble a theoretical framework that enables predictions of when and where micronutrients

should limit an individual's ability to survive, grow, and reproduce. Those same hypotheses can be scaled up to account for biogeochemical constraints on population growth and ecosystem function (Kaspari 2020, Sterner & Elser 2002).

Hypothesis 1: The More an Element Can be Lost from the Body, the More Likely It Is to Be Limiting

Compared to structural micronutrients bound up in carbon frameworks and sequestered within cells, fluxing micronutrients that spend time outside of cells and in interstitial fluid are prone to loss via excretion (McDowell 2003b). As we shall see in the section titled Micronutrients in the Anthropocene, anything that enhances metabolic rates enhances loss by excretion and thus potential demand for those excreted elements (Kaspari 2020, Prather et al. 2018b).

Likewise, the unique elemental mix of microbes in an animal's gastrointestinal tract (Dupont et al. 2006, Twining & Baines 2013) influences the structural micronutrients that are lost via the never-ending passage of material through the tube within a tube. One good example is Co, which is among the rarest micronutrients but one frequently deficient in diets of ruminants (McDowell 2003b). Co is ingested by herbivores not as an ion but as cobalamin (Vitamin B12) synthesized by bacteria on plant surfaces (Milewski & Diamond 2000). Once ingested, cobalamin incorporates into the herbivore's cells and microbiota, where it promotes the digestion of plant fiber. Herbivores must constantly replace Co lost in feces, especially when heavy rainfall washes bacteria off plants, lowering its bioavailability and leading to Co deficiency disease (McDowell 2003b).

A recurring theme is that a micronutrient's effect on performance, abundance, and ecosystem function depends on its availability, its optimal density (and those of its cofactors), and the rate of loss via excretion.

Hypothesis 2: An Element's Contribution to Survival, Growth, and Reproduction Follows a Law of Diminishing Returns

To model nutrient limitation, ecologists often use the Droop equation (Droop 1974):

$$g = g_m \left(1 - q/Q\right), \qquad\qquad 1.$$

where g is the biomass growth rate (day^{-1}) of a single cell, g_m is the maximum growth rate when the element is superabundant, q is the minimum amount necessary to keep the cell alive (moles per cell at zero growth), and Q is the actual cell availability (moles per cell). If we assume Q reflects ecosystem availability, then as Q increases from the minimum (bare survival), cell growth decelerates and plateaus.

Expanded to an organism's ionome, one can imagine the same basic equation, sharing a g_m but with each element's unique q and Q varying 10,000-fold from K to Co. Since shortfall of any element can lead to death ($g < 0$), an individual's growth rate is likely proportional to the geometric mean of its g for each of the 17 elements of its ionome:

$$g \propto \sqrt[17]{g_K g_{Ca} g_{Mg} \cdots g_I}, \qquad\qquad 2.$$

where $g_K, g_{Ca}, g_{Mg}, \ldots, g_I$ are the growth rates based on levels of K, Ca, Mg, through I.

Hypothesis 3: Distinct Limitation Scenarios Leave Unique Signatures in Experiments

Imagine you are interested in quantifying the elements that limit growth of a plant species (**Figure 3**). You have data from a cocktail experiment that added a variety of elements

a Cocktail

b Bioaccumulation

c Factorial
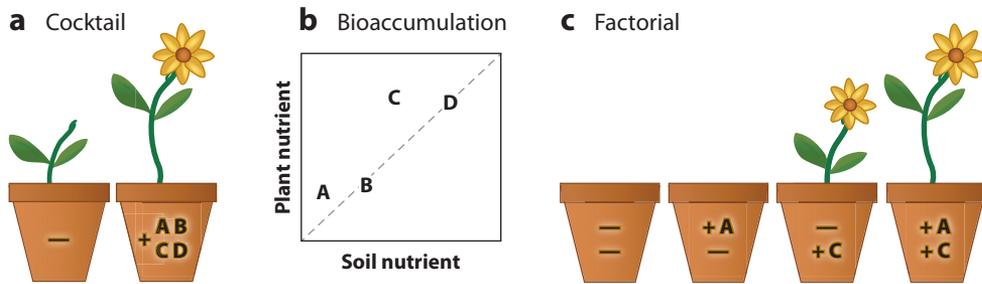
Figure 3

A protocol testing for nutrient limitation of a plant species. (*a*) A micronutrient cocktail indicates that at least one of four elements (A, B, C, D) promotes plant growth and reproduction. (*b*) A study of bioaccumulation from the soil to the plant identifies two likely candidate elements: A and C. (*c*) Factorial tests then entertain four hypotheses: single limitation, independent colimitation, simultaneous colimitation, or (as shown here) serial colimitation, where A is ineffectual by itself but catalyzes the effect of C on plant biomass.

simultaneously. The elements in the cocktail promoted plant growth. But which one was limiting? One clue can be found in bioaccumulation, i.e., the active uptake and concentration of nutrients from the soil to the plant. The logic here is right out of Liebig (1855)—if an organism invests energy and resources to harvest elements against their concentration gradient of availability, this strongly suggests some utility in doing so (see the sidebar titled The Curious Case of Luxury Consumption). Such comparisons, of course, require using the same tools (e.g., a CN elemental analyzer or inductively coupled plasma atomic emission spectroscopy) to measure element concentrations in both the source and the entity doing the harvesting.

So, you compare the concentrations of elements in the plant tissues with those in the soil, noting that C and, to a lesser extent, A bioaccumulate in plant tissue (**Figure 3**). Next, you set up a factorial fertilization experiment to test for four different kinds of limitation (Fay et al. 2015, Harpole et al. 2011, Kaspari & Powers 2016, Sperfeld et al. 2015).

In classical single (or Liebig) limitation, the experiment yields the following pattern of plant biomass: control = A < C = A and C combined. You conclude that only shortfall of C constrains the fitness and biomass of plants.

THE CURIOUS CASE OF LUXURY CONSUMPTION

Luxury consumption—defined as the "increase in organismal nutrients over and above what is immediately required for growth" (Sterner & Elser 2002, p. 82)—may seem to be an exception to Hypothesis 3. Implicit in the definition (borrowed from consumer economics) is that an organism invests energy and resources in acquiring what it does not need. Why would an organism do this, and does it comprise an exception to Hypothesis 3?

Probably not. First, Hypothesis 3 requires that the element's concentration in the consumer is greater than that in the source, i.e., that it is actively harvested, not simply absorbed via diffusion. Second, luxury consumption refers to an immediate need. As an example, Sterner & Elser (2002) point out that plants harvest P from the soil and store it inertly in their seed's endosperm. But this is temporary. That luxury P, over the life cycle of the plant, becomes metabolized P purposed to jump-start growth in offspring. The apparently hidden benefit of luxury consumption is thus likely to be revealed at appropriate time scales. Indeed, it is difficult to imagine scenarios where elements are actively concentrated but provide no clear contribution to fitness or performance. Such interesting scenarios, however, clearly contradict Hypothesis 3.

In independent colimitation, the experiment yields the following pattern of plant biomass: control < either A or C < A and C combined. You conclude that both elements independently limit plant fitness and biomass, likely because A and C contribute to fitness in different ways.

In the other two scenarios, A and C interact synergistically but for different reasons.

In serial colimitation, the experiment reveals that plant biomass in control = A < C < A and C combined. You conclude that A limits plant biomass only when increases in C, and the metabolic infrastructure it builds, increases demand for A (Jeyasingh et al. 2020).

In simultaneous colimitation, the experiment reveals the following pattern of plant biomass: control = either A or C < A and C combined. You conclude that the plant's demands for both A and C are coupled, perhaps because, as for nitrogenase, two micronutrients (Fe and Mo) are required to build the enzyme.

Hypothesis 4: Organisms, Communities, and Ecosystems Are Consortia

Ecology is full of interacting subsystems, often built from different ionomic recipes. In metabolic pathways, what happens in one part of the network changes the demand for elements downstream (Frausto da Silva & Williams 2001). A cow and its microbial gut symbionts are each built from a different mix of structural micronutrients (Dupont et al. 2006, Twining & Baines 2013). In a square meter of forest floor, the local community of microbial and invertebrate detritivores (again with their own ionomes) combine to decompose every manner of substrate (Kaspari & Yanoviak 2009, Swift et al. 1979). From individuals to symbioses to ecosystems, performance and function depend on the coaction of components with different micronutrient requirements. This leads to the working hypothesis that the larger and more complex the biological system (e.g., eukaryotes versus prokaryotes, symbioses versus individuals, decomposition of whole leaves versus decomposition of cellulose), the greater the variety of micronutrients that limit the fitness, abundance, or performance of different components of the system (Appling & Heffernan 2014).

Hypothesis 5: There Exists an Ionome that Maximizes the Fitness, Abundance, or Performance of Any Ecological System

Based on Hypotheses 1–4, it is axiomatic that any ecological phenomenon—from an organism's fitness to the decomposition rate in a square meter of forest floor—has a local maximum determined (in part) by that patch's nutrient supply. There must also exist a global maximum of the same phenomena where all nutrients are superabundant. This global maximum is set by the vagaries of evolution played out against the rules of physics and chemistry. The local maximum reflects the challenge to the field ecologist exploring natural variation across space and time; the global maximum is the grail for the agronomist seeking to maximize crop production or milk yield.

TESTING FOR MICRONUTRIENT LIMITATION

The number of elements—and their 1,000,000-fold concentration range in living tissue—poses challenges for tests of nutrient limitation (Kaspari & Powers 2016). Just consider a field experiment that tests responses to two dosages each of 25 elements in all possible two-way combinations: one replication would require 625 plots. A full factorial design—from single elements to a cocktail of 25—would entail 1.6×10^{25} samples, just tenfold less than the number of stars in the universe. Clearly, even with undergraduates helping, this is an untenable proposition.

Figure 3 suggests one path forward: winnowing the list of candidate elements via a combination of nutrient cocktails and patterns of bioaccumulation, followed by a limited set of factorial experiments (Kaspari & Powers 2016). A second approach is holistic: applying nutrients in naturally occurring cocktails like urine (Clay et al. 2014a, Steinauer & Collins 1995), rainfall

(Kaspari et al. 2014), or feces (Lucas et al. 2019). What the latter approach lacks in identifying the specific limiting nutrients, it makes up for by presenting nutrients in realistic packages.

A final caution: micronutrients often contaminate macronutrient fertilizers. Such was the case in a study of Mo and P limitation of nitrogen fixation in which rock-based phosphate had trace amounts of Mo (Barron et al. 2008). Likewise, bush sickness in livestock appeared to be cured with Fe supplements, only to discover later that Co—a contaminant and among the rarest of micronutrients—was the active ingredient curing this illness (Smith 1987).

MICRONUTRIENTS AND LIFE HISTORY

Ecological performance at the individual level is, at minimum, a matter of staying in the game (surviving) and building a new copy competent enough to do the same (reproducing). There is ample evidence that ionomic shortfalls constrain both individual survival and reproduction.

Studies of humans and their domesticated animals reveal how micronutrient shortfall targets the ability of a female to maintain her own ionome while building offspring, each with their own ionomic demands. Pregnant cattle require 20–40% increases in fluxing micronutrients like Na (Natl. Res. Counc. 2005). And even temporary shortfall can leave a lasting developmental abnormality, especially in nervous and muscle tissues (Al-Dahhan et al. 2002). Shortfalls of Zn, Fe, and I contribute annually to 400,000 deaths and disability cases in human mothers and children (Black et al. 2008).

Caterpillars are models for exploring the developmental effects of Na shortfall. The host plant of monarch butterflies, *Asclepias*, has one of the highest foliar Na levels in its prairie habitat (Snell-Rood et al. 2014). Caterpillars feeding on *Asclepias* exposed to road salt maintained sixfold more tissue Na; males grew larger thoraces, and females grew larger eyes [associated with brain size (Snell-Rood et al. 2014)]. Moreover, butterfly species that feed on salty plants have larger mass-corrected brains (Swanson et al. 2016). Na effects on muscle and neural development cross taxonomic orders: grasshoppers fed a diet of either low, intermediate, or high sodium developed larger eyes on the high sodium diet and, intriguingly, the ability to jump longer distances in response to simulated predation attempts (Peterson et al. 2021). Spermatophores—Na-rich nuptial gifts that increase female reproductive success (Pivnick & McNeil 1987)—are further evidence for micronutrient limits on development.

Micronutrient bioaccumulation may underlie two patterns from life history: high mortality in the young and the increase in clutch size with female age (Begon et al. 1996). Micronutrients can bioaccumulate with age (see **Figure 2e**); Zn does so in roe deer (Hermoso de Mendoza García et al. 2011), as do Se and arsenic in cod (Burger et al. 2007) and Fe in moose (Medvedev 1999). If inadequate quantities of structural micronutrients impede metabolism, this may help explain why moose show their maximum litter size (and the lowest hunting mortality) at intermediate age (Ericsson et al. 2001). Likewise, the corrosive effects of metabolic byproducts like superoxides (O_2^-) are thought to promote senescence (Ricklefs 2010). Metal-rich superoxide dismutases (Frausto da Silva & Williams 2001) are enzymes that use Cu, Zn, Fe, Mn, and Ni atoms to scrub superoxides from cells before they can damage DNA. All this suggests that life history biologists may profit by adding micronutrient supplements and fertilization experiments to their toolkit.

I end this section by highlighting Milewski & Diamond (2000), who offer a cogent argument for the impact of micronutrient shortfall in wild populations, focusing on I (critical for both thermogenesis and brain development), Co (gut fermentation), and Se (metabolic damage repair). Shortfalls of I, Co, and Se are common in Australia's old, highly weathered soils and exacerbated by low concentrations in plants and the elements' ready loss through excretion. They suggest the small size and low metabolic rates of Australia's megaherbivores may be adaptations to these shortfalls.

ABUNDANCE AND PRODUCTIVITY

Next, I summarize the promising evidence for the importance of micronutrients in creating gradients of abundance and productivity across food webs.

Primary Producers

Shortfalls of the macronutrients N and P frequently constrain primary production in aquatic ecosystems (Elser et al. 2007). A comparative study of 292 streams and rivers, for example, yielded a near-linear increase of Chlorophyll A (an index of algal productivity) over a 100-fold range of total P (Wurtsbaugh et al. 2019). However, evidence is accumulating that Fe can limit primary productivity in some marine systems. For example, the apparent surpluses of N and P in ocean surface waters has highlighted likely colimitation by Fe and light in culture experiments (Sunda & Huntsman 1997). Likewise, in situ Fe enrichments at the 50-km^2 scale promoted blooms of bacteria and diatoms in the southern Pacific (Boyd et al. 2000). Such limitation by Fe likely arose after the Great Oxygenation Event 2,300 Mya, when Fe^{3+} began to oxidize and sink to the ocean floor (Hassler et al. 2011).

Syntheses from terrestrial ecosystems like grasslands and tropical forests also report that N and P regularly colimit plant production. Terrestrial ecologists frequently combine factorial N, P, and K experiments with a cocktail of plant essential micronutrients. A synthesis of tropical forest studies found only K plus N colimited plant growth, and then only for saplings (Wright et al. 2018). In grasslands, fertilization experiments consistently revealed how micronutrient cocktails, when added with NPK, modestly enhanced productivity (Fay et al. 2015, Harpole et al. 2011, Prather et al. 2020). Further evidence for serial colimitation arrives from a comparative study of 54 grasslands, where grasses increased their concentrations of six micronutrients when they acquired more N and P (Kaspari et al. 2021). These studies suggest that increasing macronutrient availability drives the demand for micronutrients (Jeyasingh et al. 2020).

Micronutrients can also increase macronutrient supply. N-fixing bacteria use both Mo and Fe to build the nitrogenase that fixes atmospheric N_2. In this globally important symbiosis, fertilization of a Panama forest floor community with the micronutrient Mo generated 2–3 fold increases in the biological production of a macronutrient, organic N (Barron et al. 2008).

Mycorrhizae—fungal-root symbioses present in approximately 90% of plant species—serve to deliver nutrients to plants, greatly expanding their biogeochemical footprint (Teotia et al. 2017). Mycorrhizal fungal symbionts also prevent overaccumulation of metals in their plant host by regulating uptake and via active detoxification (Ruytinx et al. 2020). In one experiment, *Zea mays* had higher levels of Zn, Cu, and Fe when grown in control soils inoculated with mycorrhizal fungi compared to plants treated with both mycorrhizal fungi and micronutrients (Liu et al. 2000). This suggests two possibilities: (*a*) that mycorrhizal fungi transport micronutrients only when those nutrients are rare in the soil and/or (*b*) that mycorrhizal fungi are inhibited by higher levels of micronutrients, perhaps by free-living microbial competitors. I describe how micronutrients shape microbial decomposer communities in the next section.

Micronutrient Limitation of Plant Consumers: Herbivores and Detritivores

Bottom-up studies (i.e., those examining resource control) of plant consumers have also focused on macronutrients. As per the Droop equation, fish biomass was a positive decelerating function of available N across 48 subtropical lakes (Wurtsbaugh et al. 2019). Across 365 northern lakes, the proportion of *Daphnia* in plankton was a unimodal function of lake P (Jeppesen et al. 2003).

Herbivores also track gradients of micronutrients. Across 17 grasslands, grasshopper abundance tracked foliar concentrations of N, P, Mg, Na, and K (Joern et al. 2012). Prairies grazed by

ungulates maintained higher levels of seven micronutrients in their plant tissues (Kaspari et al. 2021) and such grazing lawns supported 0.4- to 1.9-SD higher densities of grasshoppers (Ozment et al. 2021). A distributed experiment in 54 grasslands revealed Na limitation of insect herbivores (e.g., grasshoppers and leafhoppers) that grew in severity as Na levels in the plants dropped (Welti et al. 2019). Likewise, fertilization of an element already at high levels of ecosystem availability can be deleterious: On a coastal prairie with high Na and K aerosol inputs, Na plus K fertilization suppressed numbers of an invasive omnivorous ant by 45% (Reihart et al. 2021). However, when added with the macronutrients N and P, Na in this same system boosted herbivore abundance by 60% in a clear example of serial colimitation (Prather et al. 2018a).

Detritivores typically eat lower quality plant tissue and show similar responses to natural and experimental gradients of micronutrients. In a Panama rainforest, an NPK factorial fertilization experiment on 32 plots that measured 40 m × 40 m included a micronutrient cocktail added to four additional plots (Kaspari et al. 2017). After 13 years, N additions had suppressed the abundance of invertebrates and the diversity of fungi, prokaryotes, and invertebrates. By contrast, micronutrient plots supported the largest (>1 SD) increases in the two eukaryotic groups, fungi and invertebrates. These micronutrient cocktails focus on plant-essential nutrients and leave out animal-essential nutrients like Na. But as with herbivores, Na shortfall frequently limits the abundance of detritivores. In a Peru brown food web, Na pulses generated 7-SD increases in detritivore abundance (Clay et al. 2014b). The biggest increase was in termites, whose numbers were enhanced sevenfold on plots with added Na in a Peruvian forest after only 2 days (Kaspari et al. 2009) and 17-fold in an Ecuador forest over the course of a year (Kaspari et al. 2014, see also Dudley et al. 2012). The sensitivity of a second major decomposer—the fungi—to Na shortfall is far less explored, despite their bioaccumulation of Na (Kaspari 2020, Scharnagl et al. 2017).

If micronutrients boost the abundance of detritivores, we should expect corresponding increases in decomposition rates. In a review of north temperate litter decomposition studies, increases in N, Ca, and Mn content were all correlated with higher decomposition rates (Berg et al. 1996). Incubations of Costa Rican leaf litter revealed higher mass loss and CO_2 efflux with added P and Zn (Powers & Salute 2011). In the large-scale Panama field experiment referenced above, at least three elements—P, K, and at least one more micronutrient—enhanced decomposition of cellulose, wood, and/or leaf litter (Kaspari et al. 2008a). Na again plays the role of supermicronutrient in decomposition. In a Peruvian Amazon forest, a pulse experiment simulating a urine deposit enhanced litter mass loss by 41% (Kaspari et al. 2009); a year-long press experiment simulating coastal rainfall enhanced wood decomposition 29–78% (Kaspari et al. 2014). As in the case of herbivores (Welti et al. 2019), background levels of Na matter: Wood decomposed twice as fast in plots treated with NaCl in the Amazon, with 20-fold increases in termite densities, but in a salt-rich Panama rainforest, NaCl treatments depressed decomposition (Clay et al. 2014a). Indeed, Na shortfalls among decomposers contribute to the deeper litter of inland tropical forests compared to that of micronutrient-rich coastal forests (Clay et al. 2014a, Kaspari et al. 2014). Such sodium shortfalls in Earth's vast interior forests—from Siberia to the Congo to the Amazon—likely help keep detrital carbon out of the atmosphere (Kaspari et al. 2009).

A recent review of fertilization effects on grassland food webs (Prather et al. 2020) suggests an important mode of action for micronutrients: enhancing the beneficial effects of macronutrients (i.e., serial colimitation) (**Figure 4**). Across 62 grasslands, adding NPK enhanced both plant and invertebrate abundance by approximately 0.5 SD, while micronutrient additions alone had little (or a weakly negative) effect. However, when micronutrients were added with macronutrients, invertebrate effect sizes tripled. This catalysis of macronutrients by micronutrient cocktails is even more remarkable because the cocktails commonly used in plant fertilization studies typically do not include the seven or eight animal essential micronutrients not required by plants.
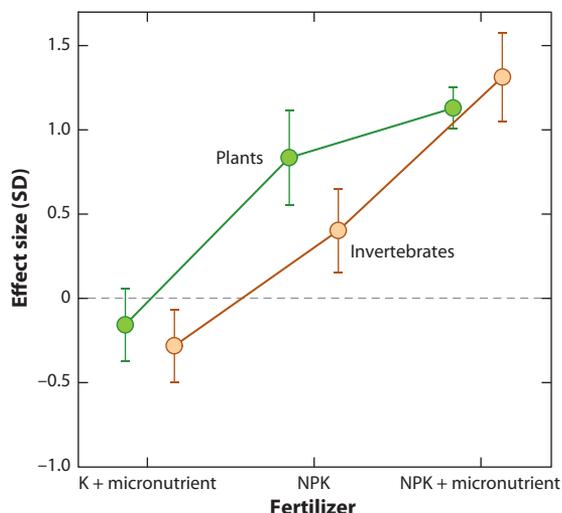
Figure 4

Summary of factorial applications of micronutrients and macronutrients on the abundance of grassland plants and invertebrates. Micronutrients alone have little, or slightly negative, effects on plant and animal abundance but catalyze the impact of NPK fertilization for invertebrates. Effect sizes are Cohen's *d*. Figure adapted from Prather et al. (2020). Abbreviations: K, potassium; N, nitrogen; P, phosphorus.

Such results counter the generation-old dogma that terrestrial herbivores are primarily nitrogen limited (White 1978). It also expands our interest beyond the plant CHO production so often used in models of trophic regulation (Power 1992). Micronutrients are key players regulating the abundance of plant consumers.

Why are micronutrient cocktails apparently less beneficial to plants than to plant consumers? A composite data set (**Table 1**) suggests that herbivores and predators each bioaccumulate five

Table 1   Mean tissue concentration of forbs from 52 North American prairies and 16 herbivorous and 9 predacious invertebrates collected from the Yasuni (Ecuador) and Barro Colorado Island (Panama) forests

Element	Mean tissue concentration (ppm)		
	Forbs[a]	Herbivores[b]	Predators[b]
K	14,500	9,121	8,869
Ca	13,301	209[c]	312[d]
Mg	2,336	2,581	1,295[c]
P	1,478	8,533[d]	7,849
Fe	111	141	221[d]
Na	95	811[d]	3,906[d]
Mn	50	130[d]	52[c]
Zn	28	177[d]	397[d]
Cu	8	28[d]	108[d]

[a]Data from Kaspari et al. (2021).
[b]M. Kaspari, unpublished data, see also **Figure 2**.
[c]Consumer concentration represents ≥50% decrease over the lower trophic level.
[d]Consumer concentration represents ≥50% increase over the lower trophic level.

essential elements. Three of these—Cu, Zn, and potentially Fe—are found in the micronutrient cocktails. The higher densities of these plant-essential elements in animal tissues, in addition to a suite of eight elements not required by plants, suggests a more complex metabolome in consumers. Plant consumers often host a microbiome of archaea, bacteria, fungi, and protists to capture, conserve, and synthesize nutrients from low-quality plant tissue (Chaucheyras-Durand & Ossa 2014, Filipiak & Weiner 2014, Maurice & Erdei 2018). As prokaryotes diverge from eukaryotes in their structural micronutrients, plant consumers like ruminants and termites that form symbioses with microbes are more ionomically complex.

The Role of Micronutrients in Herbivory: Do Plants Manipulate Their Ionome?

So far, we have seen that (*a*) plant ionomes include elements essential to their own metabolism, as well as those metabolically essential only to their consumers (**Figure 1**); (*b*) plant ionomes vary 100-fold within and across communities (Borer et al. 2019, Han et al. 2011, Welti et al. 2019); and (*c*) plant consumers often achieve micronutrient levels twofold or more higher than those found in their food (**Table 1**). What is the functional significance of this variation in a plant's micronutrient content?

First, accumulating animal-essential micronutrients can come with a cost of increased herbivory. Across four Great Plains grasslands, grasses fertilized with NaCl suffered 50% higher herbivory, mainly by fungal pathogens and leaf miners (Welti & Kaspari 2021). In another distributed experiment across 26 grasslands, high-Na plant species were eaten more on plots fertilized with NPK (Borer et al. 2019), suggesting the catalytic effect of Na on macronutrients predicted by Prather and colleagues (2020). For this reason, some plant species likely have lower micronutrient concentrations because of selection to reduce their attractiveness to herbivores (Arms et al. 1974, Freeland et al. 1985, Kaspari 2020, Orians & Milewski 2007). If so, some of the low end of the 10,000-fold variation in micronutrient concentration among plant species (Borer et al. 2019, Han et al. 2011)—especially for animal-essential nutrients—may be generated via selection acting on the plants themselves. Plants have also evolved a different tactic to the same end: generating compounds that prevent the uptake of key elements needed by consumers. For example, thiocyanates in the Brassicaceae and cyanogenic glycosides in some grasses and Euphorbiaceae interfere with uptake of I (Milewski & Diamond 2000).

But what then would account for the existence of plant species that concentrate micronutrients at higher levels than their neighbors, especially those nutrients attractive to herbivores? One possibility is that those micronutrients are incorporated into, or allow the construction of, defenses against herbivory. Open-ocean Fe supplements, for example, can lead to surging diatom populations full of neurotoxins (Trick et al. 2010). Increased plant defenses were also suggested as the reason for decreased herbivory despite increases in the abundance of herbivorous insects on the high end of an NPK plus micronutrient fertilization gradient (R.M. Prather & M. Kaspari, unpublished data). One possible mechanism is that plants use micronutrients to fortify nectar, pollen, and food bodies toward attracting insect bodyguards like wasps and ants (Filipiak & Weiner 2017, Heil et al. 2004, Rico-Gray & Oliveira 2007, Wäckers 2004).

If a plant's ionome shapes its interactions with herbivores, then plants may manipulate that ionome in the same way they do secondary compounds like alkaloids and phenolics (Rosenthal & Janzen 1979): to manipulate their herbivores and mutualists (Kaspari 2020). If so, fertilization experiments, long used to quantify the nutrient limitation of plant production (e.g., Fay et al. 2015), are also excellent vehicles to explore plant–consumer interactions (Borer et al. 2019, R.M. Prather & M. Kaspari, unpublished data).

MICRONUTRIENTS IN THE ANTHROPOCENE

Humans are adding micronutrients to Earth's ecosystems in a variety of ways, from the trace elements in fossil fuels (Milewski & Diamond 2000) to the fertilizers of agriculture (Jones & Hanson 1985) to applications of road salt (Kaspari et al. 2010). Less conspicuous, and potentially more profound, may be the global impacts of increasing temperature, changing precipitation, and the accumulation of CO_2 on micronutrient demand and supply.

Changing Temperature and Rainfall

As ectotherms warm, their metabolic rate gradually accelerates then rapidly crashes (Kingsolver & Huey 2008). Higher metabolic rates, in turn, enhance the excretion (and hence demand) for fluxing micronutrients like Na and K (Prather et al. 2018b). While humans can turn to sports drinks to meet their increased need for salts, ectotherm herbivores and detritivores facing shortfall must either find and harvest more ions from their environment or suppress metabolism through decreased activity (Kaspari 2020). Given the ubiquity of Na shortfall in continental ecosystems, and the acceleration of Na loss as temperatures rise, a warmer Earth is likely to exacerbate limitation of populations and processes by Na and other fluxing micronutrients.

Tropical storms can transport oceanic ions like Na and K hundreds of kilometers inland (Emanuel 2005), and shortfall of these two fluxing micronutrients can slow decomposition (Kaspari et al. 2008a). If, as predicted, the warming Earth generates tropical storms with greater frequency and/or intensity (Gherardi & Sala 2019), more Na and K may be deposited further inland. In these areas, with the biochemical constraint on decomposers eased, the residence time of detritus in the soil may decrease, as more is converted to CO_2.

Increased precipitation can also reduce micronutrient limitation via mass flow, bringing ions within reach of root transporters (Cataldo & Wildung 1978). In arid regions with sparse, dispersed plants, this may serve to increase both plant biomass and nutrient density for plant consumers, as ions distant from roots become more accessible. In more mesic and productive regions, those same nutrients may be closer to equilibrium between plants and soil, with increased precipitation leading to soil impoverishment through increased leaching.

The Greening of the Earth by Increased CO_2 and the Threat of Nutrient Dilution

One emerging challenge to Earth's populations occurs when increases in atmospheric CO_2—accompanied by increases in temperature and/or rainfall—promote carbon fixation at the expense of a plant's macro- and micronutrient supplies (Welti et al. 2020). Such nutrient dilution has been recorded from CO_2 addition experiments, where 130 plant species/cultivars showed an average 8% decrease in mineral concentrations in plant tissue (Loladze 2014). Examples of nutrient dilution are also emerging from time series. From 1845 through the 1960s at Rothamsted, UK, wheat cultivars had stable concentrations of Fe, Cu, Zn, and Mg followed by steady declines up to the present (Fan et al. 2008). A similar summary of 30-year trends for foliar nutrients in European forests revealed declines in N (5%), P (11%), K (8%), S (6%), and Mg (7%) (Penuelas et al. 2020).

Beyond increases in CO_2, any factor promoting net primary production (NPP) can have similar dilution effects by enhancing carbon fixation without changes in underlying biogeochemistry. Grasslands showed the highest year-to-year NPP variance of any terrestrial ecosystem, and a survey of 54 grasslands implicated increases in NPP with decreases in 14 micronutrient concentrations in plant tissues (Kaspari et al. 2021). Given the relationship between metabolic rate and temperature (Anderson-Teixeira et al. 2008), recent warming, by promoting more carbon fixation, may also have the global effect of furthering nutrient dilution.

Meta-analyses like Prather et al. (2020) and in-depth diet studies of insect pollinators (Filipiak 2019) suggest that declines in plant macro- and micronutrients hurt plant consumers. Indeed, reports of nutrient dilution coincide with those of 20-year insect declines targeting grazing herbivores and omnivores (Seibold et al. 2019, Wepprich et al. 2019). The most compelling picture of this phenomenon, from a Great Plains grassland, reveals how grass biomass production has nearly doubled over the last 30 years, while N concentration declined by 42%, P by 58%, K by 54%, and Na by 90% (Welti et al. 2020). Over the same time period, abundance of the main insect herbivore, grasshoppers, declined by approximately 2% per year (Welti et al. 2020).

The mechanisms of nutrient dilution remain unclear but are relevant to its impact and remediation. If a plant's ionome is already at equilibrium with its soil supplies, and if CHO-rich structural tissue scales to whole-plant mass changes as $Mass^{1.25}$ (Elser et al. 2010, Enquist & Niklas 2002), then higher carbon fixation may allow plants to invest in CHO-rich stems, lifting nutrient-rich leaves skyward and intercepting more light (Harpole & Tilman 2007, Orians & Milewski 2007). Nutrient dilution in this scenario then targets large consumers (e.g., ungulates) that eat whole plants, not just the leaves. However, most of the evidence thus far, including that summarized above, suggests that nutrient dilution is distributed across plant tissues. If so, all of the effects of micronutrient shortfall cataloged here may become even more commonplace as the Anthropocene continues.

SUMMARY AND PRIORITIES FOR FUTURE RESEARCH

Of the approximately 25 elements essential for life on Earth, we know little about the ecological roles of most. There is enormous potential to learn from fertilization experiments that track how micronutrients bioaccumulate from soil or water to plants and plant consumers, affecting individual fitness, population abundance, and ecosystem processes like photosynthesis and decomposition.

An essential nutrient's rarity in an organism or ecosystem's ionome does not reduce its likelihood as a candidate for micronutrient limitation. I, Mo, and Co are examples of extremely rare micronutrients for which shortfalls have been demonstrated to constrain fitness, abundance, and ecosystem function. Bioaccumulation, however, informs the ecologist which nutrients the organism has invested in harvesting.

Population biology, particularly life-history studies, is one of the most promising subjects for micronutrient ecology. The challenge of creating offspring—each with its own complement of micronutrients—as well as the deleterious developmental effects of shortfall, suggest that variation in clutch size and body size of offspring may be linked to ecosystem biogeochemistry.

The bioaccumulation of structural micronutrients as organisms age may go some way toward explaining how and why reproductive output increases with age. Supplements, fertilization experiments, and studies of bioaccumulation over an organism's life span offer straightforward ways to test this hypothesis.

Given the accruing evidence for colimitation, factorial experiments combining micro- and macronutrients should be the norm. This is especially true for studies of consumers, where micronutrients likely have strong catalytic effects.

Fungi are major ecosystem players as decomposers, pathogens, and symbionts; fungi accumulate a variety of micronutrients in their fruiting bodies, yet they are woefully understudied for their nutritional ecology compared to plants and animals (e.g., Scharnagl et al. 2017). While a fungi's existence as diffuse webs of hyphae poses a challenge for the investigator, an early focus on fruiting bodies may be one entry point to the ionomics of this fascinating group.

Just as studies in the last century revealed how plants use secondary compounds like phenolics and alkaloids to manipulate their herbivores, studies of interspecific variation in plant ionomes are likely to reveal similar manipulations by plants of their herbivores and mutualists.

Nutrient dilution driven by increasing CO_2 may be producing green deserts of plants with low nutritional quality. Understanding the ubiquity of this phenomenon in Earth's agronomic and natural ecosystems, and its culpability for declines in animal populations, is a major priority in micronutrient ecology.

DISCLOSURE STATEMENT

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