

Global Biogeochemical Cycles[®]



RESEARCH ARTICLE

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Bioavailability of Macro and Micronutrients Across Global Topsoils: Main Drivers and Global Change Impacts

Key Points:

- Globally, the most bioavailable elements (Ca, Mg, and K) are amongst the most abundant in the crust, but N is more abundant than predicted
- Bioavailability was controlled by soil pH, organic matter content, texture, plant cover, and climate, and altered by global change
- Elements were highly spatially correlated (coupled), and coupling was predictable by the atomic properties of elements, particularly mass

Supporting Information:

Supporting Information may be found in the online version of this article.




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Abstract Understanding the chemical composition of our planet's crust was one of the biggest questions of the 20th century. More than 100 years later, we are still far from understanding the global patterns in the bioavailability and spatial coupling of elements in topsoils worldwide, despite their importance for the productivity and functioning of terrestrial ecosystems. Here, we measured the bioavailability and coupling of thirteen macro- and micronutrients and phytotoxic elements in topsoils (3–8 cm) from a range of terrestrial ecosystems across all continents (~10,000 observations) and in response to global change manipulations (~5,000 observations). For this, we incubated between 1 and 4 pairs of anionic and cationic exchange membranes per site for a mean period of 53 days. The most bioavailable elements (Ca, Mg, and K) were also amongst the most abundant in the crust. Patterns of bioavailability were biome-dependent and controlled by soil properties such as pH, organic matter content and texture, plant cover, and climate. However, global change simulations resulted in important alterations in the bioavailability of elements. Elements were highly coupled, and coupling was predictable by the atomic properties of elements, particularly mass, mass to charge ratio, and second ionization energy. Deviations from the predictable coupling-atomic mass relationship were attributed to global change and agriculture. Our work illustrates the tight links between the bioavailability and coupling of topsoil elements and environmental context, human activities, and atomic properties of elements, thus deeply enhancing our integrated understanding of the biogeochemical connections that underlie the productivity and functioning of terrestrial ecosystems in a changing world.

1. Introduction

Soil nutrient bioavailability drives the productivity and functioning of terrestrial ecosystems worldwide (Barber, 1995; Van Sundert et al., 2020), supporting ecosystem services from food production to global biogeochemical cycling (Fernández-Martínez et al., 2014; Schlesinger & Bernhardt, 2020; Van Sundert et al., 2020). The bioavailability of soil macronutrients such as nitrogen (N) and phosphorus (P), which are two of the most important limiting nutrients for plant growth (Du et al., 2020), is known to be simultaneously controlled by (a) climate (Schlesinger & Bernhardt, 2020); (b) soil properties, including texture, pH, redox potential, and organic matter content (Husson, 2013; Schlesinger & Bernhardt, 2020); (c) ecosystem type (Schlesinger & Bernhardt, 2020), including the composition and activity of animal, plant, and soil microbial communities (Chapin, 1980; Sardans & Peñuelas, 2012); and (d) anthropogenic activity, including emissions and deposition of elements like N (Du et al., 2016; Sardans & Peñuelas, 2012; Schlesinger & Bernhardt, 2020). However, much less is known about the global patterns in the bioavailability and drivers of the other ~25 elements that, like calcium (Ca), potassium (K), magnesium (Mg), sulfur (S), boron (B), iron (Fe), manganese (Mn), zinc (Zn), or copper (Cu), are also essential macro- and micro-nutrients (Kaspari & Powers, 2016). Actually, despite recent efforts to model the nutrient status of soils worldwide (Aitkenhead & Black, 2018; Moreno-Jiménez et al., 2019; Shangguan et al., 2014), no study thus far has described the simultaneous bioavailability and spatial covariation (i.e., coupling *sensu* Ochoa-Hueso, Delgado-Baquerizo, et al., 2021; Ochoa-Hueso, Plaza, et al., 2021) of a wide range of chemical elements at the global scale; and even less so by using a standardized field-based methodology. Furthermore, few studies have investigated the role of atomic properties as drivers of global patterns in the bioavailability and coupling of

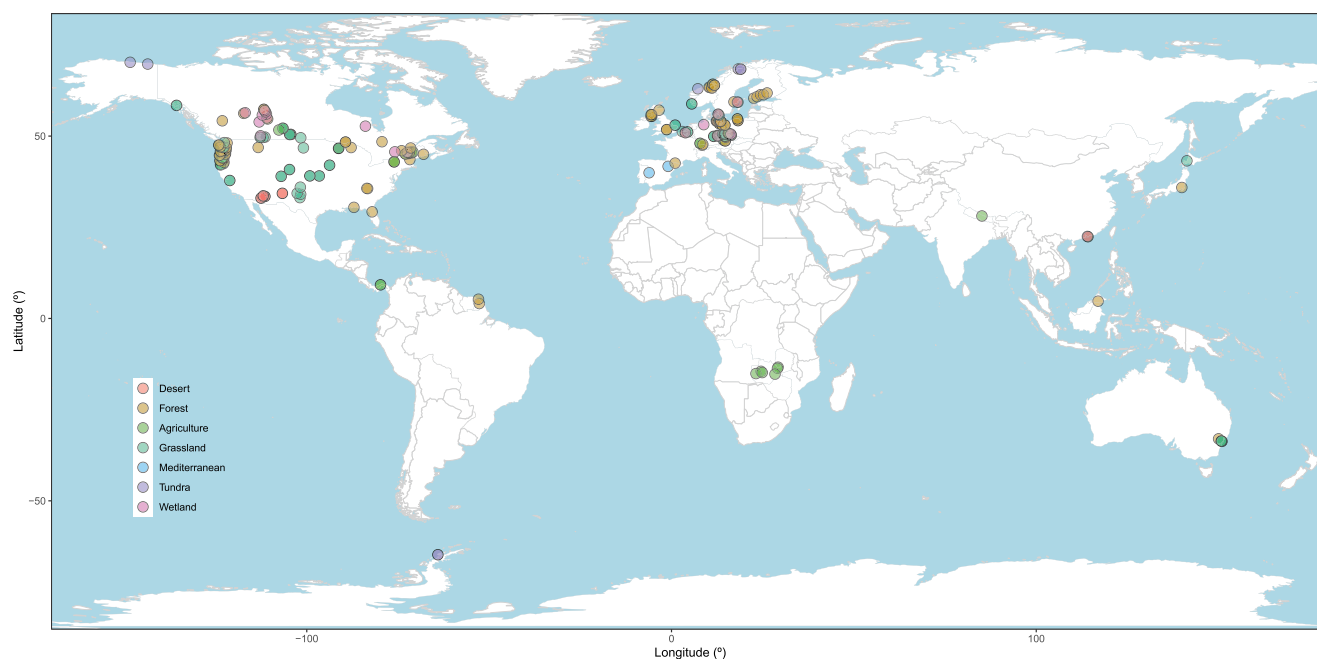


Figure 1. Geographic distribution of the 141 locations in which PRS® probes were buried. Locations are based on $0.1^\circ \times 0.1^\circ$ land tiles and biomes and represent an integrated measure of >15,000 individual observations (see Section 2 for a detailed description of burial procedure).

chemical elements in soils. This is highly surprising considering the well-known importance of atomic properties such as mass, ionization energy, valency, and mass to charge ratio as determinants of the reactivity and mobility of chemical elements (Ahrens, 1953; Burns, 1973; Kabata-Pendias, 2001; Ochoa-Hueso, Plaza, et al., 2021).

Here, we report results from a comprehensive global survey in which we assessed the bioavailability of thirteen soil chemical elements across >15,000 sampling sites distributed across all seven continents (Figure 1). We used this information to (a) describe the bioavailability and spatial coupling (*sensu* Ochoa-Hueso, Delgado-Baquerizo, et al., 2021; Ochoa-Hueso, Plaza, et al., 2021) of these thirteen soil elements across the globe and to (b) assess the main environmental drivers that determine their bioavailability, for which we used structural equation modeling (Lefcheck, 2015). Drivers considered included long-term precipitation and temperature, soil organic matter content, pH, texture (sand content), as well as long-term vegetation attributes (plant cover). We further evaluated (c) the impact of global change and agriculture on nutrient bioavailability and coupling. We also aimed to (d) study the role of the physical properties of atoms such as atomic mass, first and second ionization energy, valency, and mass to charge ratio as drivers of the bioavailability and coupling of chemical elements in soil. By characterizing the bioavailability and coupling of chemical elements in soils at the global scale and revealing the environmental and atomic factors driving them, we were able to assess the ubiquity of nutrient limitation and the vulnerability of the nutrient balance of ecosystems to global environmental change. Our study, thus, provides critical information to improve our understanding of the biogeochemical functioning of terrestrial ecosystems.

2. Methods

2.1. Measuring Bioavailable Chemical Elements

We measured the bioavailability of thirteen elements using the same field-based procedure and laboratory analytical approach. To do this, we deployed in the field almost 100,000 individual probes that contained ion exchange membranes (Plant Root Simulator® [PRS®] probes, Western Ag, Canada). Despite being highly concentrated across North America and Europe, sampling locations included a wide range of biomes, environmental conditions, and soil types, thus being representative of many kinds of terrestrial ecosystems found on Earth (Figure 1). Biomes considered included natural ecosystems such as forests (5,369 observations), grasslands (4,040 observations), deserts (1,745 observations), wetlands (1,023 observations), and tundra (263 observations), and managed ecosystems such as agricultural lands (2,454 observations). The assignment of the sites was done by the coauthors

who were involved in the data sampling. The study encompassed essential primary and secondary macronutrients (N, P, K, Ca, Mg, and S) (Chapin, 1980; Hawkesford et al., 2012; Kaspari & Powers, 2016), micronutrients (B, Fe, Zn, Cu, and Mn) (Broadley et al., 2012; Kaspari & Powers, 2016), and also two potentially phytotoxic metals (aluminum (Al), and lead (Pb)) (Hodson, 2012). Moreover, probes were incubated both under ambient conditions (>10,000 sampling points) and under experimentally manipulated conditions (>5,000 sampling points) simulating various global change scenarios such as warming, alterations of the hydrological cycle in terms of increased and reduced precipitation, and fertilization with only N, only P, or a combination of two or more nutrients.

At each location, we buried between 1 and 4 pairs (median 4) of anionic and cationic probes (49,577 and 48,059 individual cationic and anionic probes buried in total) for a mean period of approximately 53 days (first quartile = 27 days, median = 42 days, third quartile = 76 days). Plant root simulators consist of a plastic stake (15 × 3 cm) that holds an ion exchange membrane with an exchange surface of 17.5 cm² (Figure S1 in Supporting Information S1). Membranes were in close contact with the soil at a depth of 3–8 cm. Before use, the cation- and anion-exchange PRS® probes were saturated with sodium (Na⁺) and bicarbonate (HCO₃⁻), respectively. Anion probes were also treated with ethylenediaminetetraacetate (EDTA) to increase the adsorption of micronutrients, in particular polyvalent metal cations such as Al, Fe, Mn, Cu, and Zn (Hangs et al., 2004). After the burial, PRS® probes were retrieved and composited from each sampling location, then washed with deionized water to remove adhered soil particles and organic matter debris. All PRS® probe samples were shipped to Western Ag Innovations (Canada) for analysis. Samples were eluted with 0.5 M HCl and the eluant analyzed for nitrate (NO₃⁻) and ammonium (NH₄⁺) colorimetrically using an automated flow injection system and for all other elements (P, K, S, Ca, Mg, Fe, Mn, Cu, Zn, B, Al, and Pb) using inductively coupled plasma (ICP) spectrometry. Nitrate-N (NO₃⁻-N) and NH₄⁺-N were summed to estimate N availability. The ICP analyzer considers all forms of each element, but only ionic forms are mobile and adsorbed by ion-exchange membranes (e.g., PO₄³⁻, K⁺, SO₄²⁻, etc.). Given that an equilibrium is generally attained on ion-exchange membranes within a period of one to 2 weeks, PRS® probe values provide an integrated measure of bioavailability during the burial period that are comparable when expressed as mg of nutrient per m² of membrane over the burial period (Hartsock et al., 2020; Meason & Idol, 2008).

2.2. Extraction of Environmental Data: Climate, Soils, and Plant Cover

Mean annual temperature (BIO1) and precipitation (BIO12) were extracted from the WorldClim 2.0 database (Fick & Hijmans, 2017), a high resolution climate model (~1 km at equator). Plant cover (2001–2015) was obtained using remote sensing data from the Moderate Resolution Imaging Spectroradiometer at a ~1 km resolution (Filipponi et al., 2018). Soil C (%) and pH were obtained using standard lab methodologies for about 40% of samples. Sand content and the remaining soil C and pH data were extracted from SoilGrids250m 2.0, a system for digital soil mapping based on global compilation of soil profile data and environmental layers (250 m resolution; <https://soilgrids.org>).

2.3. Statistical and Numerical Analyses

2.3.1. Drivers of Nutrient Bioavailability

All numerical calculations and statistical analyses were carried out in R v4.3.0. We first explored variations in the bioavailability of soil elements across all samples and also the variability associated with specific biomes. We then evaluated the relationships between the bioavailability of soil elements and widely recognized drivers such as long-term mean annual precipitation and temperature, soil organic matter content, pH, texture (sand content), as well as long-term vegetation attributes (plant cover), for which we used Pearson correlations and structural equation modeling (Lefcheck, 2015). Mean annual precipitation and temperature were selected over other bioclimatic indicators because they are frequently considered as good surrogates for long-term climatic conditions of a given site, but we acknowledge that they do not necessarily represent soil and weather conditions during the sampling period. Previous to this, sampling points were grouped into 141 sampling locations that were defined based on land tiles of 0.1° × 0.1° (i.e., 11 km × 11 km) and biomes within those tiles. In our a priori model, we included the distance to the equator to account for potential spatial effects. Distance to the equator was predicted to affect all edaphoclimatic and plant variables. Climatic variables (long-term precipitation and temperature) were predicted to affect soil properties. Plant cover was predicted to be affected by soils and climate. Finally,

climate, soils, and plant cover were predicted to be direct drivers of soil element bioavailability. We ran separate models for each soil element, for a total of thirteen models. To test these models, we followed a d-sep approach using the piecewiseSEM package (Lefcheck, 2015), in which a set of linear structured equations are evaluated individually. To run the linear models, we used the “lm” function of the stats package. A good fit was assumed when Fisher's C values were non-significant ($P > 0.05$). We then carried out linear regressions between the bioavailability of individual elements and the percentage of the variance explained by the models concerning the different elements. We also correlated the bioavailability of soil elements to the total abundance of those elements in the Earth's crust reported by Rumble (2020).

2.3.2. Global Change Effects on Soil Element Bioavailability

We also evaluated the impact of global change on soil element bioavailability. For this, we used a subset of sites for which experimental data on global change drivers were available. We calculated effect sizes based on the natural logarithm of the response ratios and compared them against the null model assumption (i.e., no effect). We estimated the effects of specific drivers for which we had enough information, including warming, drought, irrigation, N addition, P addition, and multiple nutrient applications. Drought and irrigation were considered as two opposing aspects equally linked to the alteration of the hydrological cycle of a given location.

2.3.3. Soil Element Coupling

We developed a quantitative index of the degree of spatial coupling of the thirteen elemental cycles evaluated based on the mean of Spearman Rank correlation coefficients in absolute value (Ochoa-Hueso, Plaza, et al., 2021). In this index, the greater the mean correlation coefficient in absolute value, the greater the overall coupling of soil elements (Ochoa-Hueso, Plaza, et al., 2021). Greater correlation among elements may be indicative of common mechanisms connecting their cycles, including life-driven stoichiometric controls, similar organochemical interactions in the soil solution, and even ionic competition in base-exchange reactions. The average strength of coupling was then compared against randomly generated null models (95% confidence interval) derived from our same data set. Two-tailed statistical significance ($P < 0.05$) was based on 999 permutations. This coupling index was calculated separately for each element by considering correlations involving that specific element, and also separately for samples that either received or did not receive a global change treatment. The couplings of individual elements, both under control and global change conditions, were then correlated with the atomic properties of those elements, including atomic mass, first and second ionization energy, valency (we chose the most frequent one if more than one was possible), and mass to charge ratio, defined as the ratio between atomic mass and the most common valency of a given element. These properties are important determinants of the mobility and reactivity of elements across ecosystems, but their role has so far been primarily tested in aquatic, mostly marine, environments, while their role in determining the bioavailability of elements in soils is much less studied.

3. Results

3.1. General Patterns of Soil Element Bioavailability

The bioavailability of soil elements varied greatly across our global data set (Figure 2). These variations occurred mostly independently of burial duration, with only three elements or chemical forms, Mg, $\text{NH}_4^+\text{-N}$, and Al, showing slightly greater bioavailability with increasing burial duration (Table S1), thus demonstrating the inter-comparability of our data. Calcium, Mg, and K were the most abundant ions adsorbed by PRS® probes in soils across the globe, followed by S and N. Based on their mass-based abundance, Al, Fe, Mn, and P formed a group of elements with intermediate bioavailability. The least bioavailable elements in soils worldwide were Zn, B, Cu, and Pb. Moreover, nitrate-N dominated over ammonium-N across terrestrial ecosystems. Despite these general trends, the bioavailability of elements also varied greatly by biome (Figure 2 and Figures S2 and S3 in Supporting Information S1). Overall, macronutrient bioavailability was consistently highest in grasslands, and lowest in wetland ecosystems. Nitrate bioavailability was greatest in desert ecosystems and lowest in wetlands, while ammonium was the dominant form of bioavailable N in tundra and wetlands (Figure 2; Figure S3 in Supporting Information S1). Similar to nitrate, P bioavailability was lowest in wetlands and highest in grasslands and deserts (Figure 2; Figure S2 in Supporting Information S1). Wetlands were also characterized by greater bioavailability of Fe and S, while tundra ecosystems were particularly enriched in Cu and Zn but impoverished in B (Figure 2; Figure S2 in Supporting Information S1). In contrast, deserts were characterized by low Zn bioavailability (Figure 2; Figure S2 in Supporting Information S1). Forests and agricultural fields showed intermediate

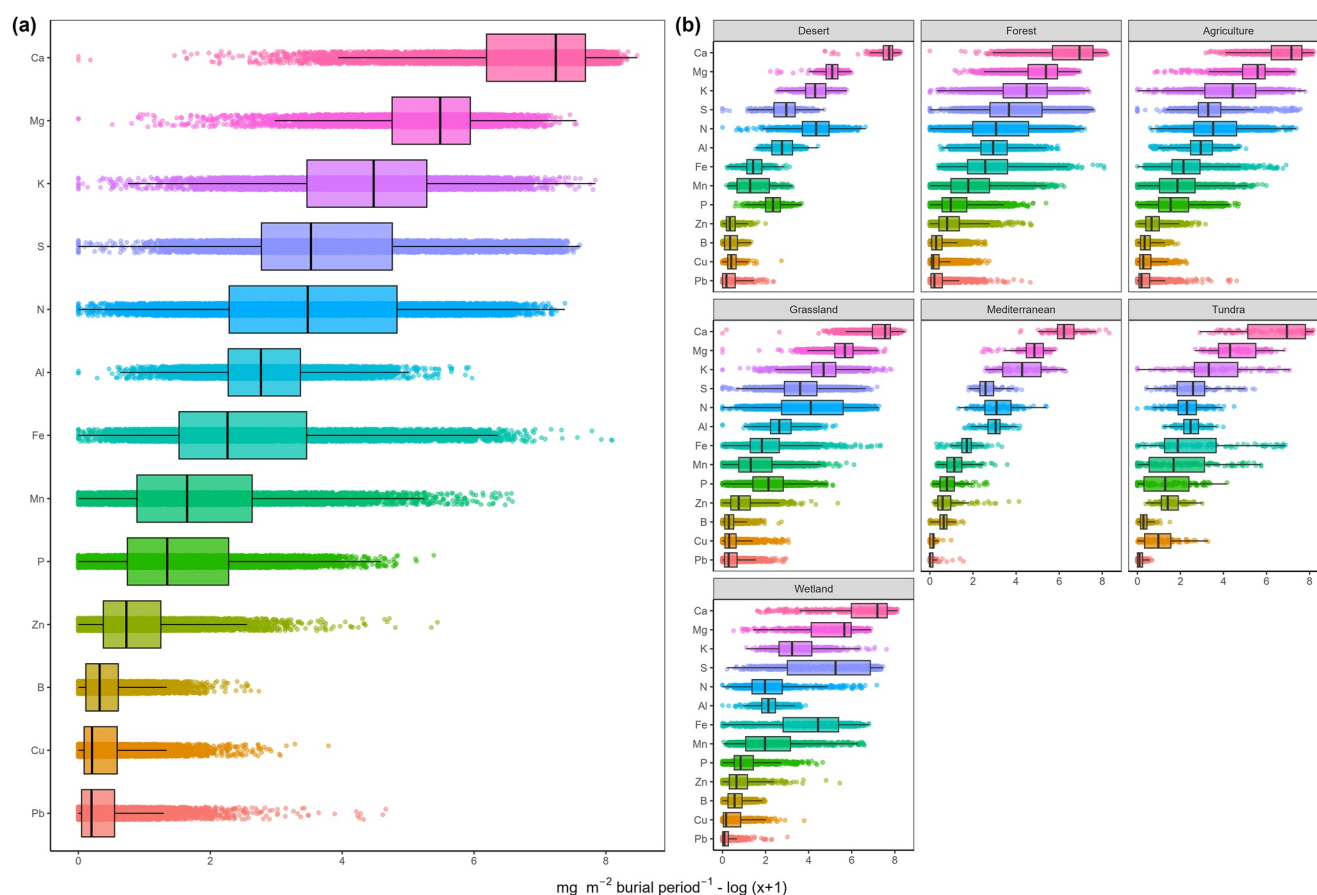


Figure 2. Soil element bioavailability across Earth ecosystems (a) and biomes (b), ordered based on their overall bioavailability in (a). Deviations in the bioavailability of chemical elements in (b) from the order in (a) may be indicative of biome-dependent controls over those elements.

bioavailability values for most soil chemical elements, although they showed consistently greater bioavailability of Mn as compared to other biomes (Figure 2; Figure S2 in Supporting Information S1).

3.2. Drivers of Soil Element Bioavailability

Structural equation models showed that the predictability of elemental bioavailability based on long-term climatic conditions, soil properties, and vegetation attributes ranged from 46% for Ca to 6% for Pb and Zn (Tables S2 and S3 in Supporting Information S1; Figure 3; Figure S4 in Supporting Information S1). The bioavailability of Ca and Mg increased with soil pH, whereas Al and Mn declined (Table S1; Table S2 in Supporting Information S1 and Figure 3a). Calcium bioavailability declined with increasing mean annual temperature and mean annual precipitation (Figure 3a). The bioavailability of Al, Ca, K, N, and P increased with declining soil C content, whereas Fe and Mn bioavailability increased with increasing soil C content (Figure 3a). Latitude was not a main driver of the bioavailability of elements, with only Cu and K being negatively correlated and Ca being positively correlated (Table S1). The ratio of ammonium-N to nitrate-N also increased along with latitude (Table S1 and Figure 4). We found a greater number of sites in which NH_4^+ -N dominated over NO_3^- -N from around 45° N–S, and particularly beyond 50° – 60° N–S (Figure 4).

Overall, the bioavailability of soil elements was directly related to the abundance of those elements in the Earth's crust reported in Rumble (2020) ($R^2 = 0.42$; $P < 0.01$; Figure 3b). This relationship was highly influenced by B. If B was removed from the analysis, then the association was only marginally significant ($P = 0.08$), but it remained statistically significant if any of the rest of elements was removed. Despite the positive relationship found between soil element bioavailability and the total concentration of elements in Earth's crust (Figure 3b), some elements deviated from this general pattern. In particular, the bioavailabilities of N, and to a lesser extent those of Ca and S, were higher than their predicted concentrations based on the fitted line. Those elements that

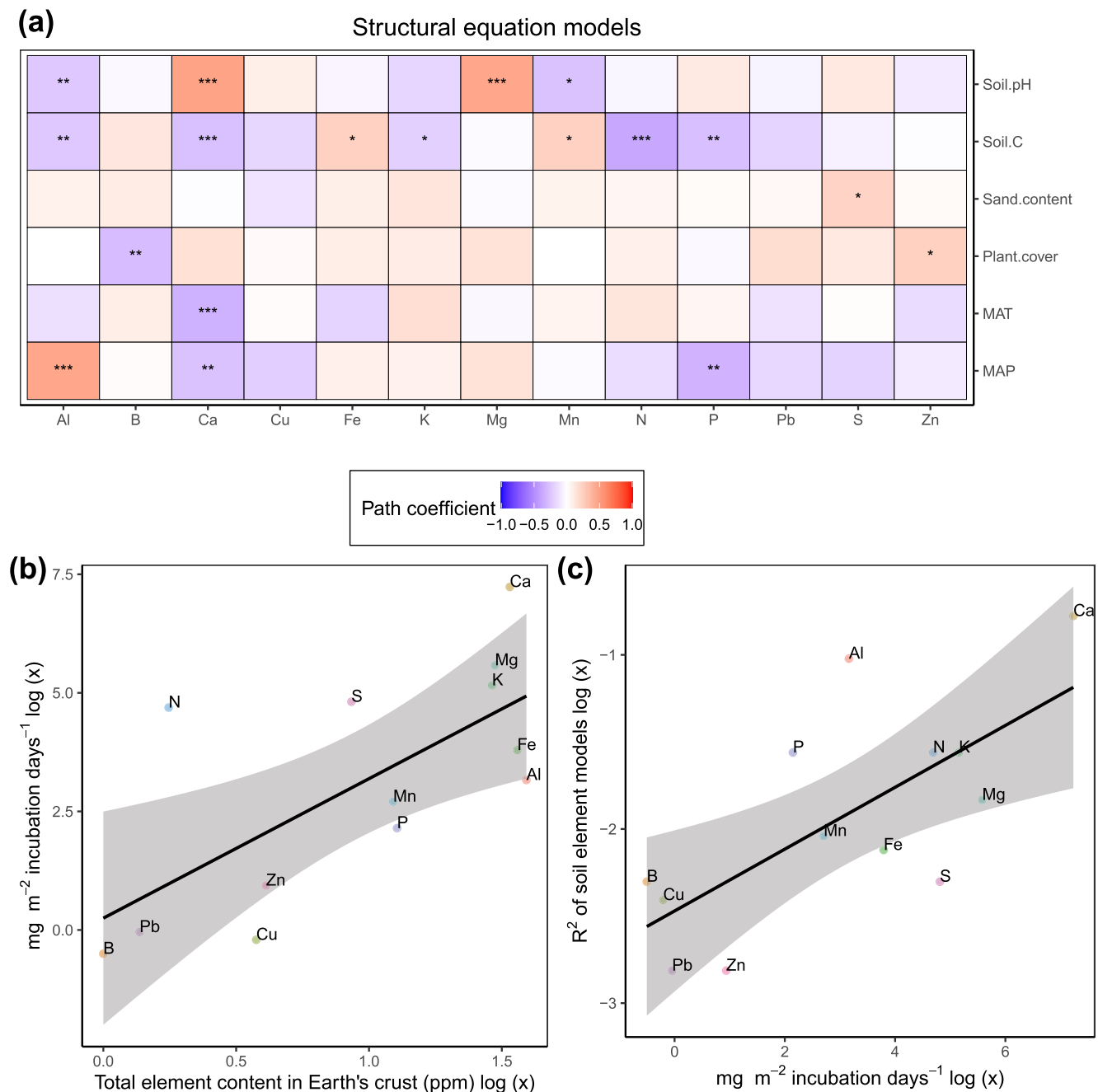


Figure 3. Environmental controls on soil element bioavailability based on (a) structural equation modeling. In (a) only direct paths connecting environmental drivers and soil element bioavailability are shown, while the representation of the a priori model tested, the significance of the intermediate paths, and the goodness of fit statistics are given in Figure S4 in Supporting Information S1. (b) Relationship between soil element bioavailability and total element content in the Earth's crust reported in Rumble (2020). (c) Relationship between soil element bioavailability and their predictability (R^2 coefficient) based on structural equation models from (a). * $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$.

were more bioavailable were also those that were better predicted by our SEMs ($R^2 = 0.35$; $P = 0.02$; Figure 3c; Figure S4 in Supporting Information S1).

3.3. Effects of Global Change on Soil Element Bioavailability

Global change drivers resulted in variations in the bioavailability of most elements, particularly N (Figure 5). Warming only had consistent effects on soil K bioavailability (Figure 5a), which increased, while multiple

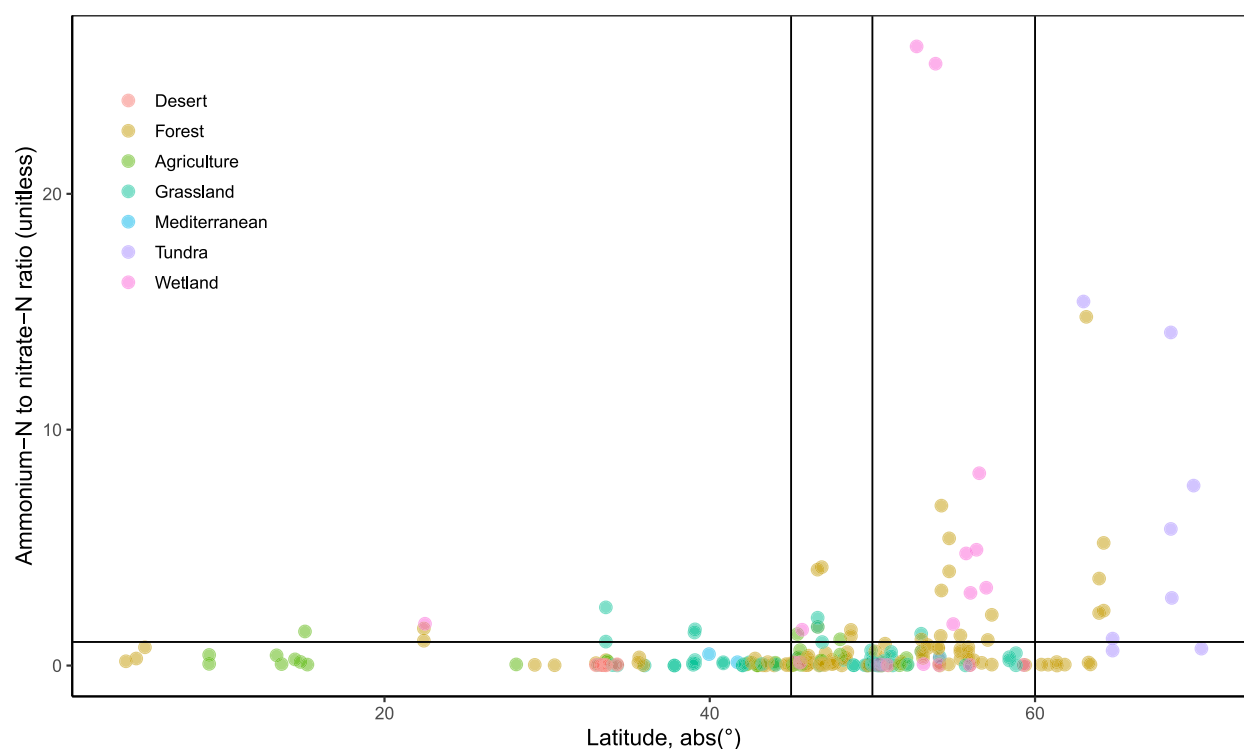


Figure 4. Distribution of reduced to oxidized N ratio based on absolute latitude.

nutrient additions resulted in greater bioavailability of all nutrients evaluated, except K (Figure 5f). Apart from increasing N, adding N resulted in greater Mn bioavailability (Figure 5e). Adding P also resulted in greater bioavailability of metals such as Al, Fe, Mn, Pb, and Zn (Figure 5e), and a concomitant reduction in the other two most important plant macronutrients (N and K). Irrigation resulted in greater bioavailability of Al and B and lower N and Pb (Figure 5c).

3.4. Coupling of Soil Elements and the Role of Atomic Properties

We then studied the coupling of topsoil chemical elements, for which we developed a quantitative index based on the mean of correlation coefficients, in absolute value, among all elements (Ochoa-Hueso, Plaza, et al., 2021). Using a null modeling approach based on >10,000 observations for which all elements were simultaneously bioavailable under unmanipulated conditions, we found that all soil elements were significantly more coupled than expected by chance ($P < 0.001$; two-tailed test) (Figure 6; Figure S5 in Supporting Information S1). Boron was the most decoupled element, whereas Cu was the most coupled one in soils across terrestrial ecosystems. Manganese, in turn, represented the median of coupling values.

Strikingly, the coupling of available soil elements was highly predictable based on the properties of their atoms such as their mass ($R^2 = 0.39$; $P = 0.01$; Figure 6a; Figures S5–S7 in Supporting Information S1), with heavier elements such as Cu and Pb being more tightly coupled to other elements. Elements with a greater mass to charge ratio, considered as an integrated proxy for the potential mobility and reactivity of atoms, were also more tightly coupled ($R^2 = 0.48$; $P < 0.01$; Figure S7 in Supporting Information S1). We also found an inverse relationship between soil element coupling and the second ionization energy, which is the energy needed to remove an electron from a $1+$ ion, and thus also linked to the reactivity of elements ($R^2 = 0.28$; $P = 0.04$; Figures S6 and S7 in Supporting Information S1). In contrast, the coupling of soil elements was not linked to their bioavailability or to their concentrations in the Earth's crust ($P > 0.05$ in both cases; Figure S7 in Supporting Information S1).

The relationships between soil element coupling and atomic mass, mass to charge ratio, or the second ionization energy were maintained across biomes, suggesting that these elemental properties are fundamental to the coupling of element cycling across terrestrial ecosystems (Figures S6 and S7 in Supporting Information S1).

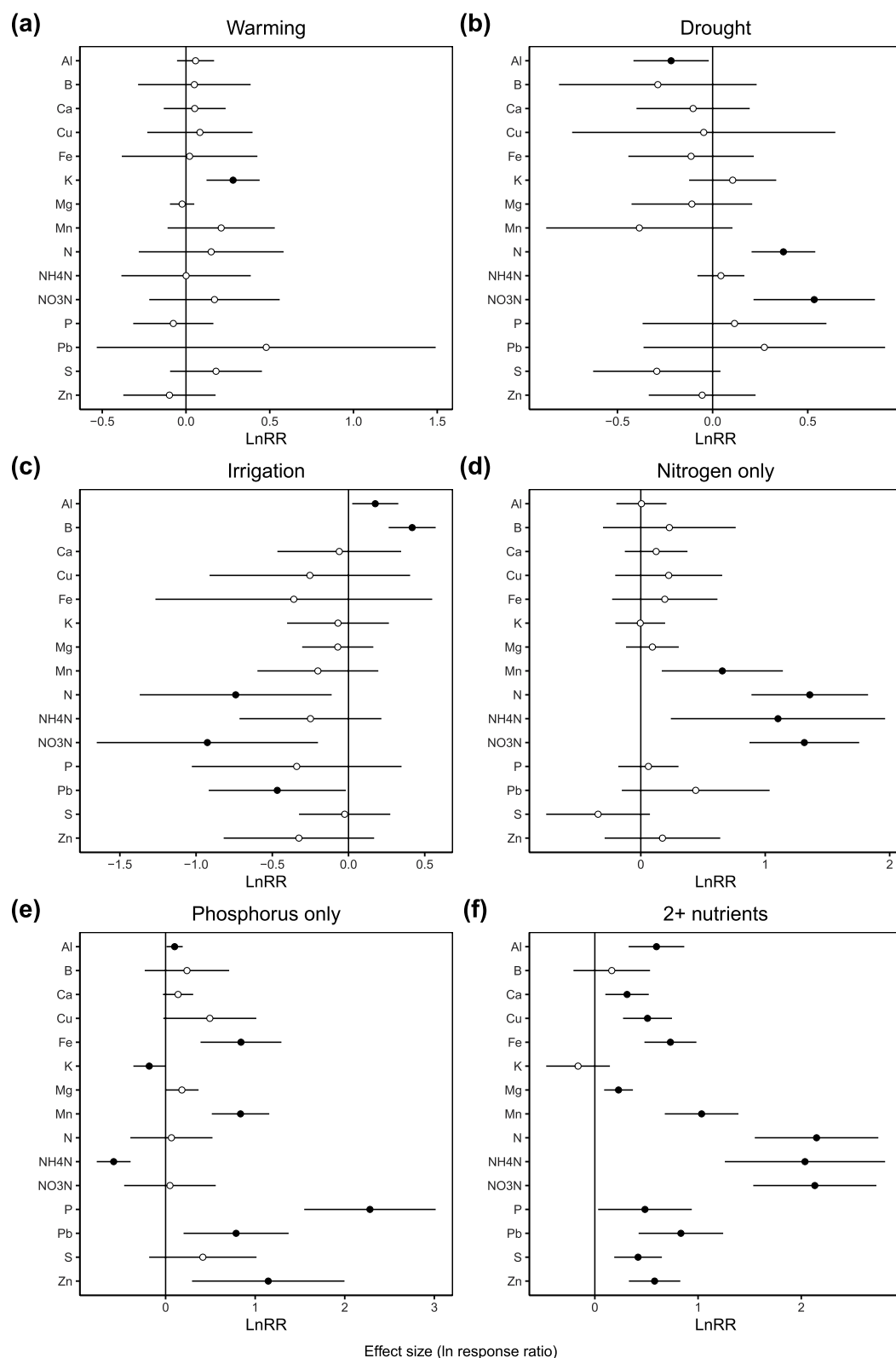


Figure 5. Soil element bioavailability in response to experimental manipulations of global change. 95% confidence interval bars that do not cross the zero line and black dots indicate soil chemical elements whose bioavailability is significantly different from the null expectation in response to global change at $P < 0.05$. LnRR = natural logarithm of the response ratio (i.e., effect size).

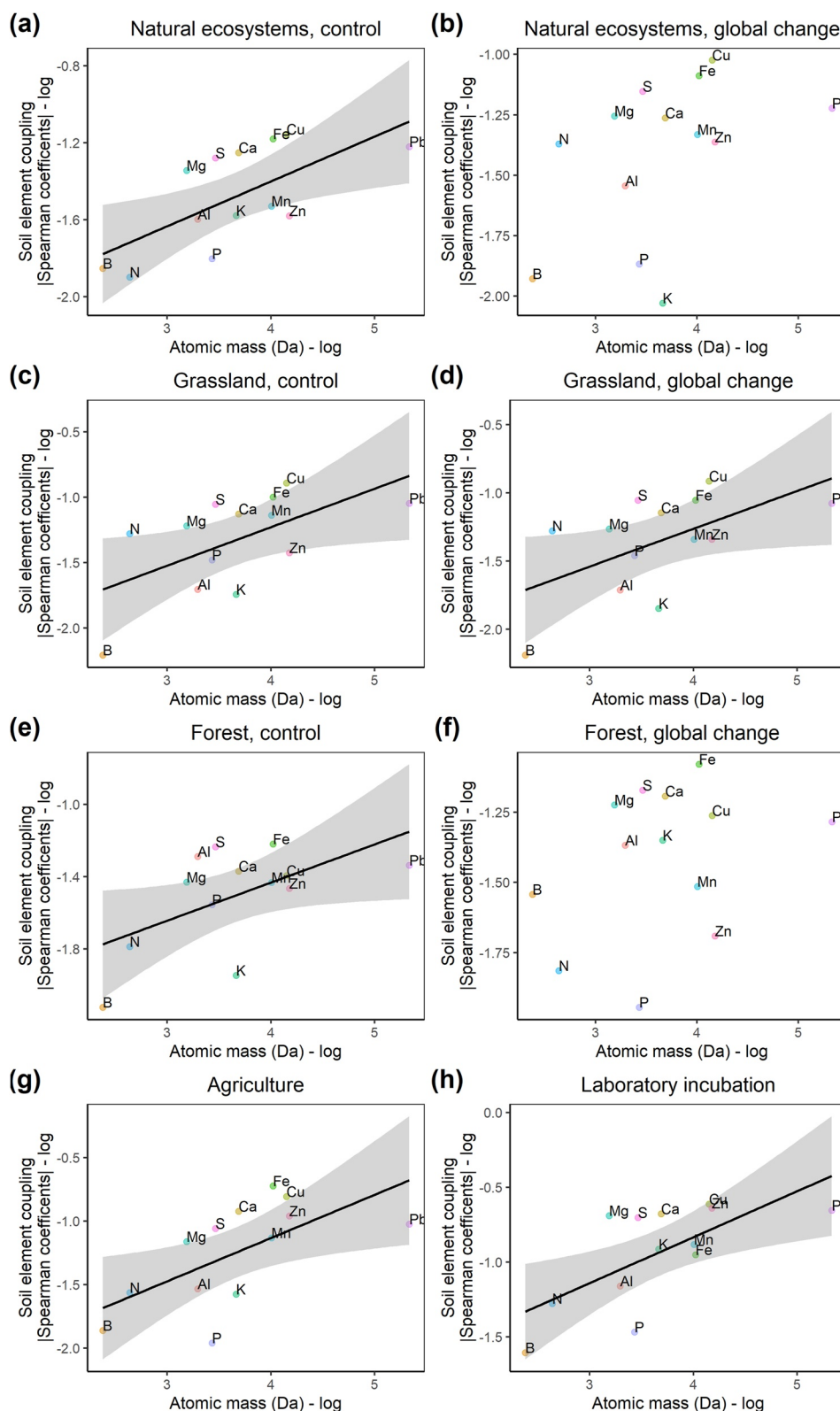


Figure 6.

However, some elements slightly deviated from this predictable pattern depending on biome. For example, K was more decoupled than predicted by its atomic mass in forests (Figure 6c), whereas P was more decoupled than expected based on its atomic mass in agricultural systems (Figure 6d). Global change drivers disrupted the predictable association between coupling and atomic mass (Figures 6e and 6g). Finally, we conducted the same analysis for a laboratory incubation experiment, which yielded highly comparable results to our global database (Figure 6h), thus strongly supporting the generality of our results.

4. Discussion

In our study, we found that the bioavailability of chemical elements in soils worldwide strongly mirrored the abundance of chemical elements in the Earth's crust, suggesting that parent material plays a fundamental role in driving global patterns of nutrient bioavailability. For example, feldspars are dominant in mineral soils worldwide (Haldar & Tišljarić, 2014; Huang & Wang, 2005) and contain high amounts of Ca, Mg, and K, which were the most abundant elements in our study. This also indicates the primary importance of chemical weathering processes as determinants of soil element bioavailability (Binkley & Vitousek, 1989; Schlesinger & Bernhardt, 2020). By contrast, elements that are cycled rapidly and are concentrated in biota and soil organic matter such as N, P, and S were in shorter supply worldwide. Despite this, the bioavailability of N was still higher than its predicted concentration based on its abundance in the crust. This may be attributed to the role of both biological and anthropogenic fixation of N, which contribute to increase the levels of bioavailable N in topsoils as compared to those naturally contained in rocks (Gruber & Galloway, 2008; Vitousek et al., 1997). In addition, climatic conditions, including MAT and MAP, were also important factors driving the bioavailability of elements, which is in agreement with previous studies (Moreno-Jiménez et al., 2022; Wu et al., 2021). This indicates that any alteration in climatic conditions, including those derived from climate change, may have important consequences for the bioavailability of chemical elements.

4.1. Drivers of Soil Element Bioavailability

Despite these consistent general patterns, the bioavailability of soil chemical elements also varied greatly across biomes, and chemical forms in the case of N. For example, consistent with the greater bioavailability of nitrate previously reported in desert soils, this form of N has frequently been shown to accumulate under water-limited conditions because at the levels at which both leaching and plant uptake are highly restricted, microbial N mineralization and nitrification still occur (Ochoa-Hueso et al., 2020; Yuan et al., 2017). Similarly, nitrate has been shown to accumulate in dry soils (Ochoa-Hueso et al., 2020; Yuan et al., 2017), which is also in agreement with our findings. Moreover, the greater number of sites in which NH_4^+ -N dominated over NO_3^- -N from around 45° N–S, and particularly beyond 50°–60° N–S, suggests that NH_4^+ -N is typically the dominant form of N in frequently water-logged ecosystems, including the upper distribution limit of deciduous temperate forests (45–50° N–S), taiga (50–70° N–S), and tundra (60–70° N–S). But, overall, the greater dominance of nitrate-N over ammonium-N across terrestrial ecosystems may be attributed to the fact that ammonium is readily nitrified in most soils and the high mobility of nitrate (Li et al., 2020; Schimel & Bennett, 2004). Wetlands, in turn, showed greater bioavailability of S, Fe, and Mn. The greater bioavailability of Fe and Mn may be linked to lower soil redox due to poorer oxygenation of this type of habitat (Pezeshki & DeLaune, 2012). In wetlands, these two elements are thus most likely abundantly found as reduced forms (i.e., Fe^{2+} and Mn^{2+}), which are highly mobile (Hartsock et al., 2020; Pezeshki & DeLaune, 2012; Ponnampetuma, 1972). Greater bioavailability of S, in turn, can be attributed to the high mobility of SO_4^{2-} in water and its accumulation in depressions and wetlands. We also showed that soil pH played a major role in the bioavailability of some elements, particularly Ca and Mg, which is highly compatible with the well-known dependence of soil nutrient bioavailability on pH (Binkley & Vitousek, 1989). Indeed, agricultural societies have taken advantage of this well-known relationship to increase nutrient bioavailability through pH-raising practices such as liming (Smith et al., 2015).

Figure 6. Coupling of soil chemical elements in relation to their atomic mass under unmanipulated conditions in natural ecosystems (a, c, e), in response to experimental global change simulation in natural ecosystems (b, d, f), in agricultural systems (g), and under laboratory incubation conditions (h). Scatterplots with regression lines depicted are significant at $P < 0.05$. See Figure S7 in Supporting Information S1 for detailed information on the relationship between coupling and atom properties. Coupling of elements was also determined in a lab study in which six agricultural soils varying in texture, pH, and nutrient levels were incubated with PRS® probes under lab conditions at three moisture levels: permanent wilting point, field capacity and saturation. Probes were removed after 1, 3, and 7 days. Coupling of elements was determined in the same way as global field studies.

4.2. Effects of Global Change on Soil Element Bioavailability

Global change drivers resulted in widespread changes in soil element bioavailability. However, not all manipulations were equally successful in altering soil element bioavailability, with multiple nutrient additions being the factor causing the most dramatic effects, as is clearly expected based on the type of manipulation. Moreover, not all elements responded in the same way to the different types of manipulations. For example, N addition resulted in consistently greater Mn bioavailability. This effect of N on soil Mn bioavailability has been associated with a decline in species richness and a shift in plant functional group dominance, from forb-dominated to graminoid-dominated communities, in grasslands (Tian et al., 2015). Phosphorus addition, in turn, caused widespread changes in macro- and micro-nutrient bioavailability. The fact that adding P resulted in greater bioavailability of metals may imply potential phytotoxic effects (Bolan et al., 2003), while the concomitant reduction in N and K, which together with P are the other two most important soil macronutrients, is most likely due to increased demand and uptake by plants. In addition, irrigation resulted in greater bioavailability of B and lower N. Boron is a very common element in irrigation waters, including natural, reclaimed, and desalinated waters, whose presence may cause potential toxic effects on plants and soil biota (Camacho-Cristóbal et al., 2008). In contrast, lower N under irrigation can be indicative of both greater plant uptake and leaching potential.

4.3. Coupling of Soil Elements and the Role of Atomic Properties

Our results also provide some of the first evidence that the bioavailability of topsoil chemical elements is more spatially coupled than what would be expected by chance across terrestrial ecosystems globally. Further, we found that coupling of individual chemical elements is highly predictable based on properties of their atoms or, in other words, on the fixed laws of particle physics. This may seem surprising at first, particularly in the context of environmental studies that, like ours, include a very wide range of conditions under which the PRS® probes were buried. However, we argue that the patterns that we found reflect the fact that all matter on Earth is formed by atoms (Ochoa-Hueso, Plaza, et al., 2021) whose properties, including atomic mass, mass to charge ratio, and second ionization energy, define their mobility and reactivity (Ahrens, 1953; Burns, 1973; Kabata-Pendias, 2001; Ochoa-Hueso, Plaza, et al., 2021). A study carried out across 16 chronosequences also showed that the coupling of chemical elements was also predicted by their atomic mass in topsoils (Ochoa-Hueso, Plaza, et al., 2021), but in contrast to our study, the relationship was negative. The discrepancy can be attributed to the distinct focus of the two studies; the chronosequence study assessed the total element content of topsoils (Ochoa-Hueso, Plaza, et al., 2021), whereas our PRS® probes measured bioavailability. Total elements represent an integrated measure of soil-forming processes that occur at temporal scales ranging from decades to thousands and millions of years, whereas bioavailable elements reflect processes that take place over much shorter timescales, that is, from minutes to days or months, including organic matter mineralization, sorption and desorption by clay minerals, and plant and microbial uptake and release. Moreover, Ochoa-Hueso, Plaza, et al. (2021) found that the three elements that are most critical to life on Earth (i.e., C, N, and P) deviated from the otherwise highly predictable pattern, constituting a fingerprint of life on Earth. Arguably, one of the most notable contributions of this framework is the generation of a relative reference state against which the coupling of chemical elements can be compared. This is achieved by first correlating all elements with one another and then ordering them based on their atomic mass.

Understanding how soil elements are coupled, regardless of the direction of the relationship, has important implications for the way in which we analyze, and measure, our world. Within this context, deviations from a relative reference state can be particularly informative because they may be indicative of reorganizational processes affecting terrestrial ecosystems that make them deviate from a predictable pattern. For example, in our study, K was more decoupled than predicted by its atomic mass in forests. This decoupling may be due to the substantial leaching of K from the canopy and soils (Hansen, 1996) and also to K limitation (Sardans & Peñuelas, 2015), which breaks the spatial stoichiometric congruence of forest soils. Interestingly, P was more decoupled than expected based on its atomic mass in agricultural systems. This points toward the important role of P in food production (Cordell et al., 2009; Elser, 2012), which has gained increased attention in recent years (Cordell et al., 2009; Elser, 2012). Phosphorus is needed for the energy metabolism of organisms (ATP), as well as in the formation of nucleic acids (DNA, RNA), but is typically both scarce and unavailable in many systems (Elser, 2012), which accounts for the high amounts of P that are usually added in the form of inorganic fertilizers or manure in agricultural systems (Cordell et al., 2009). We thus speculate that by analyzing how elements covary, first, and then finding deviations from the predictable coupling-atomic mass relationships may aid in determining elements that

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are critical controllers of plant production, and also to detect the effects of global change, even when those are subtle (Ochoa-Hueso, Delgado-Baquerizo et al., 2021).

5. Conclusions

In summary, our work provides new evidence that, despite the enormous variability in soil element bioavailability reported across sampling locations, Earth's biomes showed characteristic relative levels of soil elements. However, we acknowledge potential underestimations in the real bioavailability of some of the elements evaluated in this study due to, for example, the involvement of phytosiderophore-mediated uptake of nutrients by plants (e.g., for Fe), the role of organic chelates (e.g., Cu), and P-solubilizing enzymes, as well as competition between our probes and plant roots and microbes. Despite these potential uncertainties, we observed clear patterns in terms of soil element bioavailability, which was tightly linked to climatic, edaphic, and vegetation properties across global locations. These patterns are susceptible to alterations due to global change. Moreover, we found that soil elements were significantly more coupled (i.e., spatially correlated) than what is expected by chance, and that such coupling can be predicted based on the atomic mass, mass to charge ratio, and the second ionization energy of elements; or, in other words, based on the fixed laws of physics. We thus posit that deviations from this predictable pattern may indicate important reorganizational processes that may be traced back to destabilizing external forces, including agriculture and global change effects. Our work opens new and exciting research horizons that may have profound implications for our understanding of the biogeochemical links that define the functioning of our planet at different spatio-temporal scales.

Data Availability Statement

Raw data from this article can be found in Ochoa-Hueso and Bremer (2023) (<https://doi.org/10.6084/m9.figshare.22691767.v1>).

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