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Aridity and reduced soil micronutrient availability in global drylands

Eduardo Moreno-Jiménez[1,*], **César Plaza**[2,3], **Hugo Saiz**[2], **Rebeca Manzano**[1,4], **Maren Flagmeier**[1,5], and **Fernando T. Maestre**[2]

[1]Department of Agricultural and Food Sciences, Faculty of Sciences, Universidad Autónoma de Madrid. Avda. Fco. Tomás y Valiente 7, 28049 Madrid, Spain

[2]Departamento de Biología y Geología, Física y Química Inorgánica, Universidad Rey Juan Carlos. C/ Tulipán s/n, 28933 Móstoles, Spain

[3]Instituto de Ciencias Agrarias, Consejo Superior de Investigaciones Científicas. C/ Serrano 115 bis, 28006 Madrid, Spain

[4]Dipartamento di Agraria, Sezione di Scienze e Tecnologie Ambientali e Alimentari, Universita' degli Studi di Sassari. Viale Italia 39, 07100 Sassari, Italy

[5]Department of Biology (Botany), Faculty of Sciences, Universidad Autónoma de Madrid. C/ Darwin 2, 28049 Madrid, Spain

Abstract

Drylands cover more than 40% of terrestrial surface, and their global extent and socio-ecological importance will increase in the future due to the forecasted increases in aridity driven by climate change. Despite the essential role of metallic micronutrients in life chemistry and ecosystem functioning, it is virtually unknown how their bioavailability changes along aridity gradients at the global scale. Here we analysed soil total and available Cu, Fe, Mn, and Zn in 143 drylands from all continents, except Antarctica, covering a broad range of aridity and soil conditions. We found that total and available micronutrient concentrations in dryland soils were low compared to averages commonly found in soils of natural and agricultural ecosystems globally. Aridity negatively affected the availability of all micronutrients evaluated, mainly indirectly by increasing soil pH and decreasing soil organic matter. Remarkably, the available Fe:Zn ratio decreased exponentially as aridity increased, pointing to stoichiometric alterations. Our findings suggest that

[*]To whom correspondence should be addressed: Eduardo.moreno@uam.es.

Data availability

The data that support the findings of this study and the R codes are available in Figshare (https://figshare.com/s/6fd77aaad01c0fa55051). The R codes for the statistical models are provided in a supplementary file.

Author Contributions

E.M.J, C.P. and F.T.M designed the study. F. T. M. coordinated the global dryland survey. E.M.J. and R.M. prepared, processed and analyzed soil samples for metals. E.M.J., M.F., H.S., C.P. and F.T.M. contributed to data analysis and interpretation. E.M.J. drafted the manuscript and all the co-authors contributed significantly to the writing. All authors commented on and approved the final manuscript.

Competing interests

The authors declare no competing financial interests

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increased aridity conditions due to climate change will limit the availability of essential micronutrients for organisms, particularly that of Fe and Zn, which together with other adverse effects (e.g., reduced water availability) may pose serious threats to key ecological processes and services, such as food production, in drylands worldwide.

Currently 45% of the Earth's terrestrial surface is estimated to be occupied by dryland ecosystems[1], which collectively constitute the Earth's largest biome[2]. Drylands are areas where water is scarce and primary productivity is limited because water evapotranspiration exceeds precipitation. Climatic predictions forecast widespread increases in aridity of terrestrial ecosystems worldwide[3], which will lead to a 11-23% increase in the global extent of drylands by the end of this century[4]. While the impacts of aridity on above-ground organisms have been widely investigated in drylands[5], there are important gaps in our knowledge regarding its impacts on soil processes and nutrients[6], and on micronutrients in particular[7]. Soil metal micronutrients have essential biological functions[8,9] as they are critical for cell growth and redox homeostasis, act as enzyme cofactors in photosynthesis and other common biochemical pathways, and participate in the synthesis of biomolecules and in animal immunocompetence[10–12]. Micronutrient malnutrition is also a major animal and human health concern[13–15]. For all these reasons, small changes in metal availability may substantially affect the performance of individual organisms, with cascading effects on communities and ecosystems[7].

The solubility of soil metals, and thus their biological availability and activity in terrestrial ecosystems, depends on soil properties such as pH, organic matter and clay content and composition[16,17]. Independently of the parent material, aridity limits soil weathering, base cation leaching and plant production[5,18]. This impedes the formation of reactive clay minerals, soil acidification and soil organic matter accumulation and preservation[18]. Therefore, forecasted increases in aridity due to climate change may strongly affect metal bioavailability indirectly through its effects on soil properties. Given the importance of element stoichiometry within living organisms as a driver of the functioning and dynamics of terrestrial ecosystems[19,20], aridity-induced changes in metal bioavailability may ultimately affect the functioning of drylands.

The need to increase food production worldwide, especially staple food and meat, will require the intensification of agricultural practices in many drylands, both through more intensive grazing and through the cropping of areas that are currently under low human pressure[21]. However, no previous study has evaluated how changes in aridity, such as those forecasted by climatic models, affect the availability of soil metals in drylands globally. We aimed to do so by examining the abundance and availability (extractability with diethylenetriaminepentaacetic acid, DTPA) of Cu, Fe, Mn, and Zn in soils from 143 dryland ecosystems from all continents except Antarctica covering a broad range of aridity, soil pH, organic C, and clay content conditions. How aridity affects the abundance and availability of soil metals need to be known to fully understand climate change impacts on soil stoichiometry and fertility, as well as on plant productivity and nutritional content. These aspects are key for ensuring the living and wellbeing of ~40% of the global population living in drylands[22,23], particularly in developing countries (which account for 90% of this

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population4). We hypothesise that aridity impacts the availability of metals in drylands indirectly through its effects on soil properties such as soil pH, organic matter, and clay content24.

Results and Discussion

Total and available metals in dryland soils

Total soil metallic micronutrient concentrations in the drylands evaluated were below global averages commonly reported for natural and agricultural soils, especially for Fe and Zn25,26 (Fig. 1 and Supplementary Figure 1). In all cases, total metal concentration was negatively correlated with aridity (Supplementary Table 1). This relationship was irrespective of the parent material, as suggested by the lack of differences in aridity between the major lithological classes (sedimentary, metamorphic, and igneous rocks) of the parent material of the soil samples used in this study (Supplementary Figure 2). We also found that median available micronutrient concentrations decreased as aridity increased (Fig. 1). Aridity was strongly inversely correlated with both available Fe and available Mn ($P < 0.001$, Supplementary Table 1), but was not related with available Zn or Cu. The strong negative correlations observed between aridity and available Fe suggest that this element may become less available in the future due to climate change. While none of the ecosystems studied were used for agriculture at the time of sampling (see Methods), the increasing demand to convert marginal lands into croplands make drylands such as those studied here susceptible to being converted into agriculture, particularly in developing countries27. Decreasing micronutrient availability associated with increasing aridity, together with other adverse effects such as water limitation, may threat the provision of ecosystem services by drylands (e.g. quality crops/food). Furthermore, many of the ecosystems studied here are used for livestock production, and it is well documented that animals feeding on forage derived from micronutrient poor soils are more vulnerable to malnutrition28,29.

Changes in available Fe:Zn ratio

The decoupling in the availability of soil nutrients has been widely studied for C, N, P, K, S, Ca, and Mg, and has been linked to unbalanced geochemical and biological processes in terrestrial ecosystems7,24,30,31. Here we examined changes in the stoichiometric ratios of available micronutrients in soils at the global scale (Supplementary Figure 3), and found that the available Fe:Zn ratio decreased exponentially with increasing aridity (Fig. 2). Iron is intimately linked to primary productivity because it has an essential role in photosynthesis, is a cofactor of many enzymes, regulates cell homeostasis and participates in vital processes such as oxygen transport in many animals32. Zinc is an essential micronutrient for life because it is involved in cell growth, cellular homeostasis and enzyme production10, and therefore key biological processes, such as photosynthesis and reproduction, can be limited by low Zn availability. In general, Zn concentrations in dryland soils were low, but the availability of Fe decreased more rapidly than that of Zn as aridity increased. Under future scenarios of rising aridity and decreasing Fe and Zn availability, plant competition for both micronutrients may be expected to increase, and the species-dependent strategies adopted to increase Fe uptake from the rhizosphere may be crucial for plant survival. In particular, gramineous species are known to release phytosiderophores, chelating compounds that

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solubilize and increase the availability of Fe in the rhizosphere, whereas non-gramineous species adopt strategies based on soil acidification and reduction for Fe acquisition33. Under soil conditions of metal deficiency, gramineous plants might outcompete non-gramineous species because the chelation strategy is believed to be more efficient than the acidification-reduction strategy34. In our study, we found a significant, albeit weak (adjusted $R^2 = 0.030$; $P = 0.017$), positive relationship between available Fe and the cover of gramineous species (Supplementary Figure 4), a response that was not observed in the case of Zn ($P = 0.24$). Although we cannot establish a cause and effect relationship using our data, these results suggest that soil Fe availability could be related to the dominance of gramineous species within dryland vegetation. These effects would add to other consequences of aridity already observed, such as shifts in the composition of dryland vegetation beyond a rainfall threshold around 180 mm35.

Drivers of soil metals in drylands

We used confirmatory path analysis (CPA)36 to better understand how aridity and other drivers (pH, organic matter, clay content and total metal concentration) affected the availability of metals. Our *a priori* models provided a good fit to our data (Fisher's C P-value > 0.65 for all metals; Figs. 3 and 4). Our model explained 13% and 55% of the variability observed in total and available Fe concentrations, respectively (Fig. 3). Available Fe was positively influenced by soil organic C content and total Fe, and negatively influenced by pH and aridity. Our model explained 14% and 40% of the variability observed in total and available Zn concentrations, respectively. Total Zn was positively affected by soil organic C, while available Zn was positively influenced by total Zn and organic C, and was negatively correlated to pH (Fig. 3). Our model explained 10% and 66% of the variability observed in total and available Cu concentrations, respectively. Available Cu was positively correlated to total Cu and soil organic C (Fig. 4). Our model explained 10% and 44% of the variability in total and available Mn, respectively. Total Mn concentration and organic C had positive effects on available Mn, while pH was negatively related to the concentration of this metal (Fig. 4).

By examining the direct, indirect, and total sum of effects provided by our CPAs, we were able to disentangle the most influential drivers on metal availability (Fig. 5). The total effect of aridity on the availability of the metals studied was negative, and was stronger for Fe and Mn than for Zn and Cu. This finding is consistent with the exponential decrease observed for the available Fe: Zn ratio with increasing aridity (Fig. 2). The effects of aridity on the metals studied were mostly indirect. Among the geochemical drivers examined, soil organic C and pH were found to exert the greatest direct effects on the availability of Zn, Cu, and Mn. For Fe, the direct and total effects of soil organic C and pH were also substantial and similar to each other. The relatively minor role of clay content, compared to organic C and pH, may be attributed to the coarse texture and low soil development typical of drylands37. Low moisture conditions may impede soil weathering and the formation of reactive sites on minerals38, thus reducing their influence on metal availability.

Our results provide the first empirical evidence that aridity indirectly decreases metal availability, probably by decreasing soil organic C and increasing pH, in global dryland soils. It is well documented that drylands, compared to wetter regions, tend to have smaller soil organic matter stocks because of lower plant C inputs[5] and higher pH because of higher accumulation of soluble salts and carbonates into the soil[39,40]. Single-site studies have shown that organic matter enhances metal concentration and bioavailability in soils [7,8,41,42], and a significant body of research reports that plants growing in organic-matter-poor soils are prone to micronutrient deficiency symptoms[18,43,44]. The direct and positive effects of organic C on Cu, Fe, Mn and Zn availability may be attributed to the capacity of soil organic matter to form soluble complexes with metals, thus decreasing their sorption and increasing their mobility[45–47]. The direct and negative influence of increasing soil pH on metal availability is also consistent with previous studies[17,44,48], and may be attributed to several geochemical reactions that change metal speciation from soluble free metal ions (e.g. Fe^{3+}, Zn^{2+} and Mn^{2+}) to insoluble recalcitrant phases[49] (e.g. Fe and Mn hydroxides, Zn-Al layered double hydroxide, and carbonates[50]). A smaller effect of soil pH on the availability of Cu than on that of Zn or Mn has been previously observed[51]. Aridity may trigger additional geochemical changes in Fe speciation that could explain the stronger effects of aridity on Fe than Zn availability. In particular, water scarcity and high temperature may favor the transformation of ferrihydrite ($Fe(OH)_3$) and goethite (α-FeOOH) to hematite (α-Fe_2O_3), a Fe form more recalcitrant and less mobile in soils[52]. Insoluble phases of Zn are dominated by Zn-Al layered double hydroxides[53], which have a lower variety of exchangeable stable phases in soils than Fe.

Outlook

Our results suggest that increases of aridity such as those forecasted with climate change may limit the availability of essential micronutrients, particularly Fe and Zn, through indirect effects on soil pH and soil organic matter. Rising temperatures and less rainfall are expected to increase soil pH[54] and reduce soil organic matter[4] in drylands, but high uncertainty persists concerning the extent and rate of these effects. Although providing strong empirical evidence for the direction of the response, our analyses do not account for time, and thus the pace of the aridity-induced changes in soil micronutrient availability needs to be addressed in future research. Further experimental *in-situ* and greenhouse studies could be based on our results to account for time-delayed effects of aridity on soil metal abundance and availability.

The implications of our findings for key ecological processes and services related to primary production also remain uncertain, especially because micronutrient availability may not be the only and main limiting factor for plant growth and development in drylands[55]. Despite current uncertainties, our results suggest that detrimental impacts of reduced Fe and Zn availability in dryland soils may be exacerbated under climate change. Together with further limitations to primary production caused by increased aridity and reduced water availability, this process may limit the suitability of many dryland soils for farming and/or grazing, and limit their capacity to maintain healthy plant and animal populations. Our findings also have important implications for human health, as Fe and Zn deficiencies are ranked among the most important health risk factors worldwide. It has been estimated that Fe and Zn deficiencies already affect to 70% and 30% of the world's human population, respectively[48,56,57], and the population subjected to micronutrient deficiency has increased over the last four decades[58]. In a scenario of widespread increases in aridity conditions and high population growth rates –typical of most developing countries[59]–, marginal soils such as those from drylands will be critical to provide ecosystem services such as food and bioenergy crop production[18], and to ensure the global sustainability of our planet. Our data, therefore, indicate that the detrimental impacts of aridity on the availability of micronutrients in soils, and of Fe and Zn in particular, should be taken into account when forecasting climate change impacts on the production of food, particularly staple food and meat, similar to those forecasted for Se and other micronutrients in a recent studies[15,60]. These impacts must be considered when designing management and policy actions to achieve the UN Sustainable Development Goals, and to fully understand how forecasted scenarios of increased aridity will affect the functioning and agricultural/rangeland potential of drylands worldwide.

Materials and Methods

Description of the survey

Field data were collected from 143 dryland ecosystems located in 18 countries (Argentina, Australia, Botswana, Burkina Faso, Brazil, Chile, China, Ecuador, Ghana, Iran, Israel, Kenya, Mexico, Morocco, Peru, Spain, Tunisia, United States of America and Venezuela) (Supplementary Figure 1). These sites are a subset of the global network of 224 sites from Maestre et al. (2012), plus some additional sites surveyed in Botswana, Ghana and Burkina Faso. The study sites were selected to capture a wide variety of the abiotic (climatic, soil type, slope) and biotic (vegetation type, vegetative cover, species richness) features found in drylands worldwide. Also, selected sites encompassed multiple land uses, ranging from those with very low human impacts over recent time scales (e.g. National Parks and other protected areas) to those where human activities such as grazing, grass fiber/wood collection and game hunting are currently, or have been recently carried out. However, we excluded areas devoted to agriculture, occupied by riparian/coastal ecosystems, recently engineered (e.g. planted or recently restored areas) or used for other human activities that have completely removed their vegetation and altered their geomorphologic characteristics (e.g. infrastructure/mining). Mean annual precipitation and temperature of the study sites varied from 66 mm to 1219 mm, and from -1.8ºC to 27.8ºC, respectively. All the sites studied experience high seasonal variability in rainfall and seasonal drought, and were located at an elevation between 69 m and 4668 m a.s.l. The range of soil types present at the studied sites is also large, including more than 25 categories from the FAO classification and encompassing all major soil types present in drylands (Maestre et al. 2012). A summary of climatic and chemical properties of the soils included in this work are shown in Supplementary Figure 6. The studied sites cover a wide gradient in aridity conditions (1 – precipitation/evapotranspiration[24]), as well as soil pH, organic C and clay content (see Supplementary Figure 6).

Sample collection took place between February 2006 and December 2013 using a standardized sampling protocol (see Maestre et al, 2012 for details). In brief, samples were collected during the dry season in most of the sites from five randomly selected bare ground areas (i.e. devoid of vascular vegetation). From each of these areas, a composite sample consisting of five 145 cm^3 soil cores (0-7.5 cm depth) was collected, bulked and homogenized in the field. After field collection, the soil samples were taken to the laboratory, where they were sieved (2 mm mesh), air-dried for one month and stored for laboratory analyses. For this study, a single sample per site was composed by mixing single plot subsamples in equal amounts and homogenizing the sample.

Environmental parameters and soil chemical analysis

The coordinates of each site were recorded *in situ* with a portable Global Positioning System, and were standardized to the WGS84 ellipsoid for visualization and analyses. Aridity (1 - aridity index, where aridity index is the ratio of precipitation to potential evapotranspiration) was estimated using the Global Aridity Index dataset (http://www.cgiar-csi.org/data/global-aridity-and-pet-database61), which is based on the interpolations provided by the Worldclim climatic database62.

To avoid any potential effects associated with the use of multiple laboratories when analyzing the soils collected, all the soil samples were shipped to Spain and the analyses were performed in the same laboratory (laboratories of Rey Juan Carlos University, Autonomous University of Madrid, and Spanish National Research Council). Soil pH was determined in a 1:5 suspension (soil to distilled water), organic C was determined colorimetrically after oxidation with a mixture of potassium dichromate and sulphuric acid63, and clay content was determined by a simplified sieving- and sedimentation-based method.64

We quantified total and available metal concentrations by inductively coupled plasma atomic emission spectroscopy (ICP-OES, Iris Intrepid II XDL, Thermo Scientific) after digestion with HNO_3/H_2O_2 mixture65 and extraction with diethylenetriaminepentaacetic acid (DTPA)28, respectively. We limited this analysis to Cu, Fe, Mn, and Zn because these are the metals for which the DTPA extraction is standardized28. Briefly, for total metal concentrations, 6.0 mL of HNO_3, 4.0 mL of H_2O_2 and 6.0 mL of miliQ water was added to 0.5 g of soil; the mixture was heated at 125 ºC for 30 min, filtered through a #42 Whatmann filter and brought to 50.0 mL with miliQ water. Total metal recovery calculated relative to that for a certified reference material (CMR048-050G, sandy soil supplied by Sigma Aldrich®) was 92% for Cu, 90% for Fe, 81% for Mn and 97% for Zn. The metal fraction determined after digestion with HNO_3/H_2O_2 is sometimes referred to as "pseudototal", as a small fraction of the total may remain undissolved; here we used the term "total" for simplicity and consistency with previous studies66–68. Limits of detection (LD) and quantification (LQ) calculated according to the IUPAC and were 1 and 4 mg kg-1 for total Cu, 8 and 22 mg kg-1 for total Fe, 0.8 and 2 mg kg-1 for total Mn, 3 and 7 mg kg-1 for total Zn. For available metal concentrations, 12 mL of a solution containing 0.005 M DTPA, 0.01 M $CaCl_2$ and 0.1 M triethanolamine (TEA) at a pH of 7.30 was added to 6 g of soil; the mixture was shaken for 2 h at room temperature (20ºC), and the supernatant filtered through a 42 Whatmann filter prior to analysis by ICP-OES. We used the DTPA method as indicator of available pool of metals in soils because this technique is extensively used for these purposes in neutral to basic soils, as is the case of most of the soils studied69–71. The LD and LQ were 0.04 and 0.1 mg kg^{-1} for available Cu, 0.2 and 0.5 mg Fe kg^{-1} for available, 0.02 and 0.05 mg Mn kg^{-1} for available Mn, 0.04 and 0.1 mg kg^{-1} for available Zn. Matrix effects were negligible. Calibration curves prepared with multielemental standards had regression coefficients greater than 0.99, and standard solutions of known concentration were included every 40 samples as quality control.

Data processing and statistical analyses

We checked the normality of all variables without transformation and after log- and square-root transformations. Then, for each variable we selected the case that better fitted to a normal distribution. Finally, all variables were centered and standardized before inclusion in the models.

We first explored the relationship between aridity and total and DTPA-extractable metals using correlations to evaluate the independent effect of climate in soil metal concentrations. Linear and non-linear regressions were used to explore the relationship between available metal ratios and aridity. Furthermore, we also explored the effect of available Fe and Zn on the cover of gramineous plants (including the families *Juncaceae*, *Cyperaceae* and *Poaceae*) because such species have efficient metal uptake mechanisms33. We then used confirmatory path analysis (CPA) to examine the relative importance of aridity and other soil parameters for each soil metal. This technique allows the analysis of several variables that can present complex dependencies among them, enabling the evaluation of direct and indirect of variables simultaneously36. As soil parameters we included pH, clay content, organic matter and total metal, which are well-recognized modulators of metal geochemistry and can have a direct effect on soil metal concentration/availability16,49. Human activity is also known to affect metals in soils, but in our study we found no or very weak correlations between total and available metals and human activity indexes related to distance to towns, cities or roads and to population size and density (Supplementary Table 1). Furthermore, as variables included in the CPA presented a significant spatial clustering (*P*-value for Moran´s I < 0.05 for all variables), we included in each CPA a spatial autocorrelation random effect based on the geographical distance between all study sites to remove confounding effects due to spatial autocorrelation. We built our CPA considering an *a-priori* model that included all the potential relationships between the variables (Supplementary Figure 5). We then simplified the model for each metal doing a stepwise variable selection by removing at each step the path with less explanatory power. Finally, we selected the best model based on Akaike and Bayesian information criteria36. To evaluate the influence of each factor (driver) in the abundance and availability of metals in soils, we calculated the direct effects of each variable (clay, organic matter, pH and total metal concentration) and the indirect effects mediated through direct effects on other variables affecting metal availability (e.g. the effect of aridity on decreasing organic matter in soils). Finally, we calculated the total effect for each variable (summing direct and indirect effects) to identify the predominant drivers for each metal. All data processing and statistical analyses were conducted with the piecewise*SEM* package72 for R.3.5.173.

Supplementary Material

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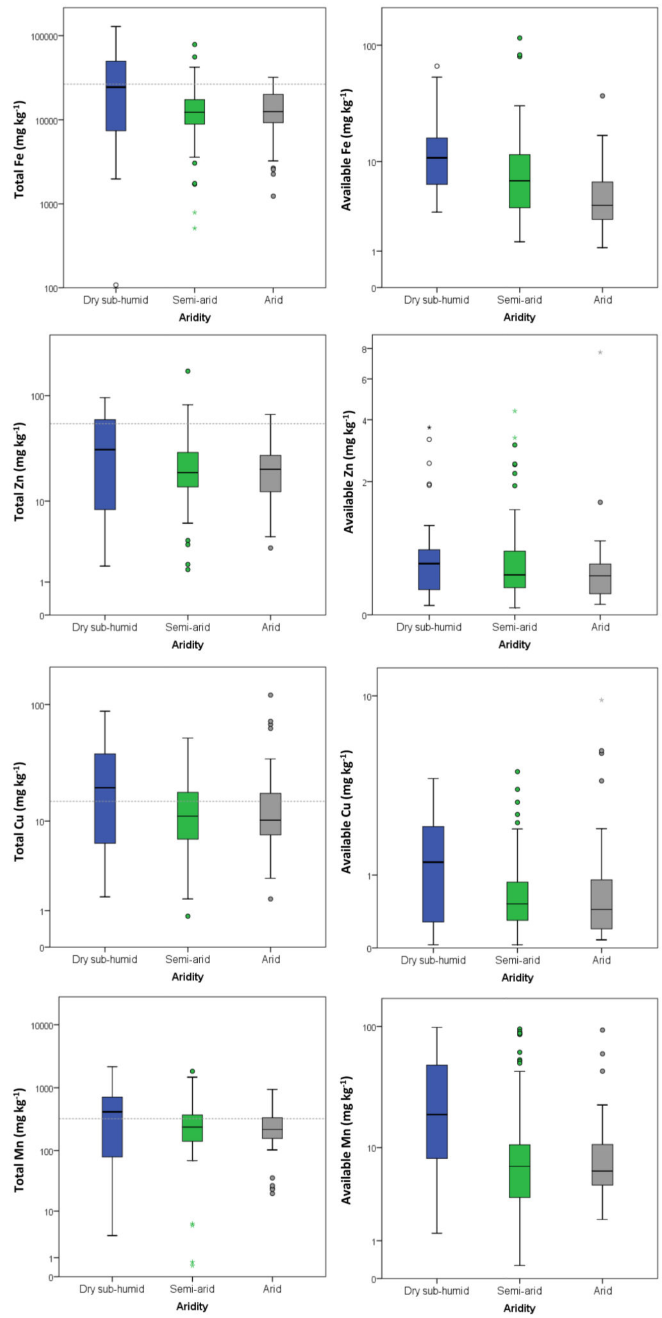

Figure 1.

Boxplots of total and available (DTPA-extractable) Cu, Fe, Mn and Cu concentrations in soils from global drylands grouped by aridity (1 – precipitation/evapotranspiration) classes. Grey dashed lines indicate averages of metal concentration commonly found in soils globally25,26.

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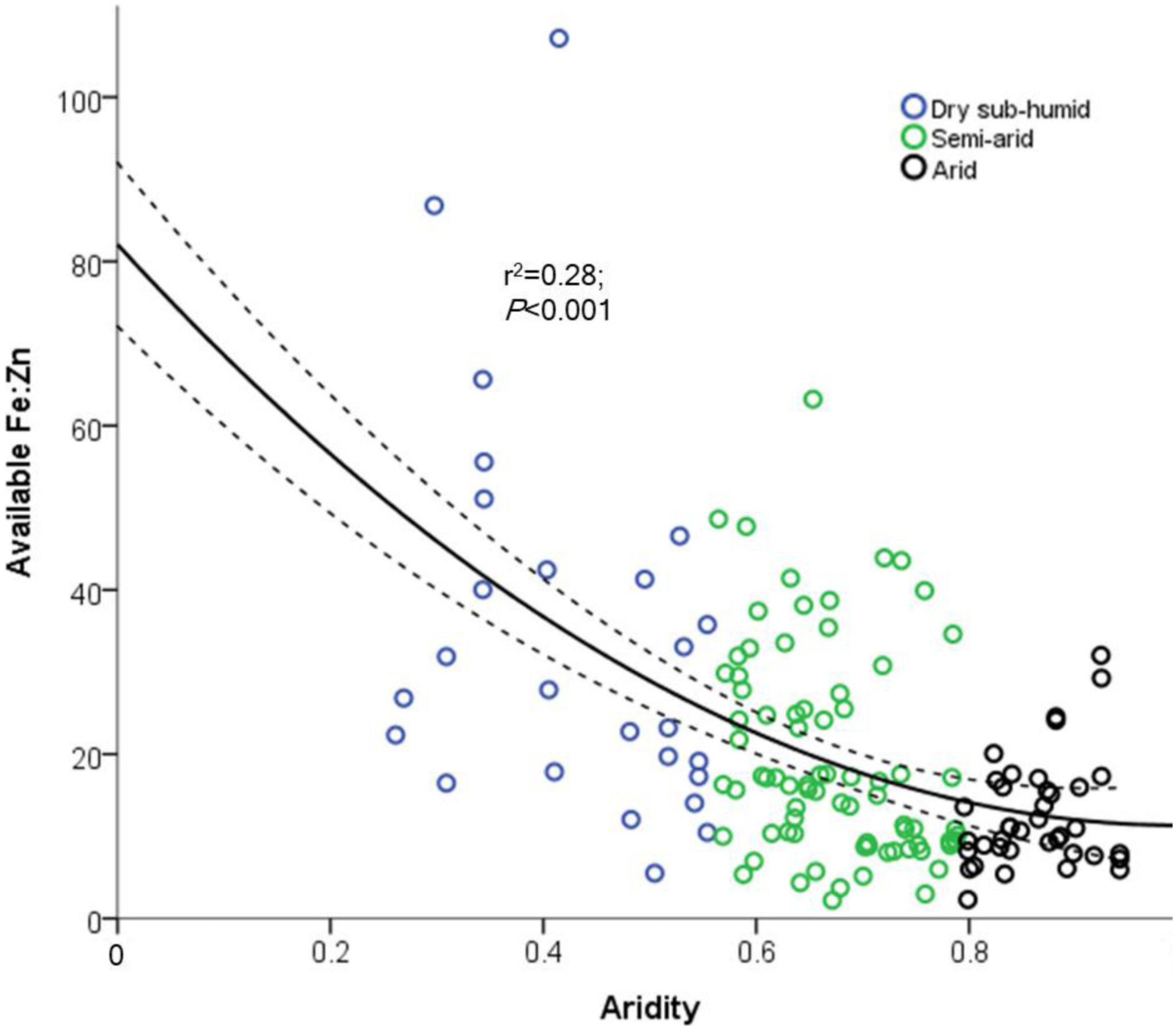

Figure 2.
Changes in the Fe:Zn ratio as a function of aridity (1 – precipitation/evapotranspiration).

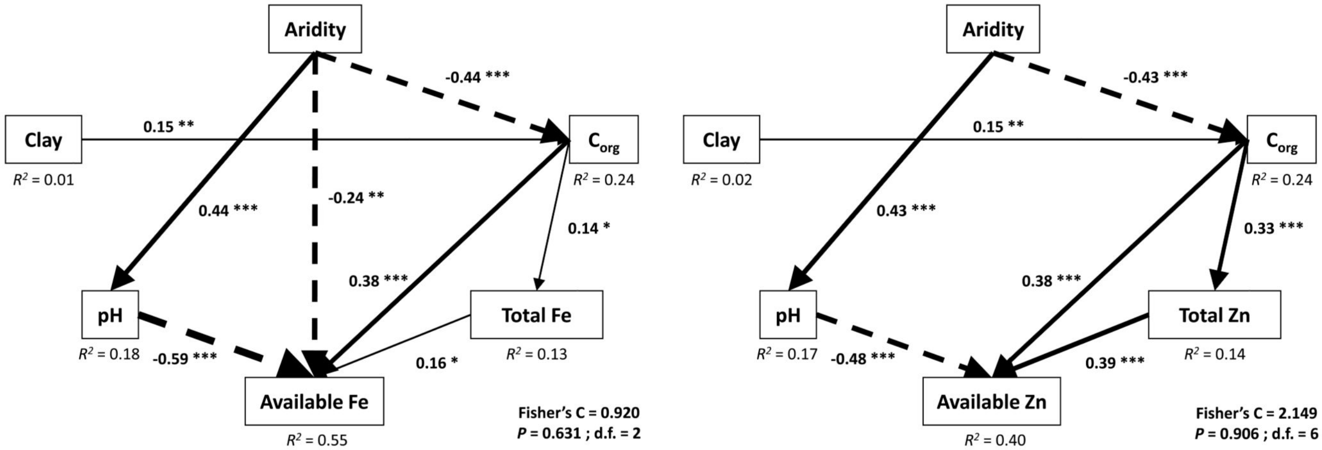

Figure 3.

Effects of aridity, clay percentage, pH, and organic C on total and available Fe (left) and Zn (right). Numbers adjacent to arrows are standardized path coefficients (analogous to relative regression weights) and indicative of the effect of the relationship. Continuous arrows show positive and dashed arrows negative relationships, with arrow thicknesses proportional to the strength of the relationship. The proportion of variance explained (R^2) is shown besides each response variable in the model. Goodness-of-fit statistics are shown in the lower right corner as the Fischer's C value, the *P*-value, and the degrees of freedom (d.f.) for each model. The *a-priori* model was refined by removing paths with non-significant relationships (see the *a priori* model in Supplementary Figure 5). *$P < 0.05$; **$P < 0.01$; ***$P < 0.001$.

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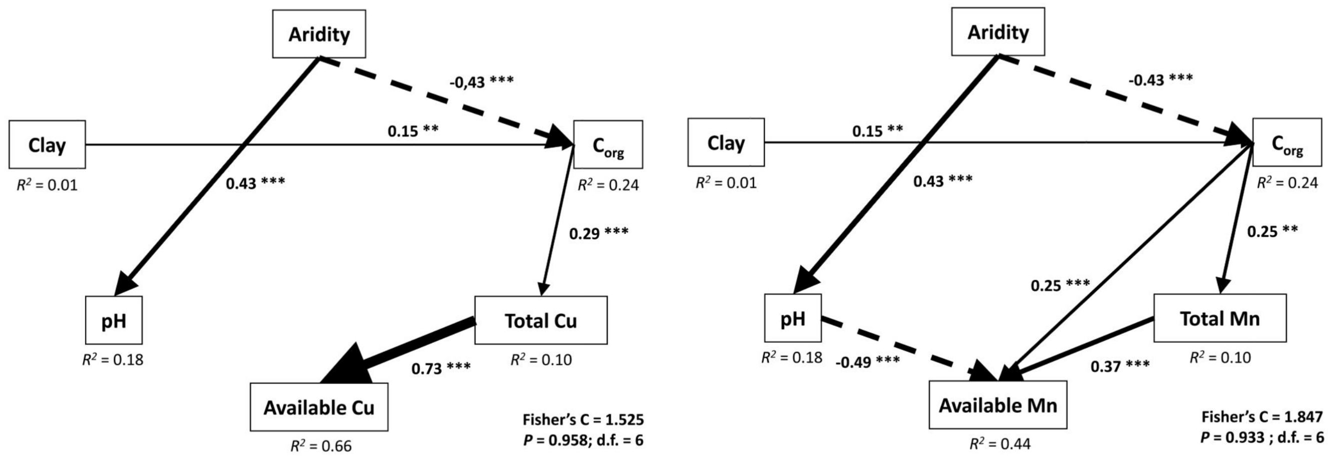

Figure 4.

Effects of aridity, clay percentage, pH, and organic C on total and available Cu (left) and Mn (right). Numbers adjacent to arrows are standardized path coefficients (analogous to relative regression weights) and indicative of the effect of the relationship. Continuous arrows show positive and dashed arrows negative relationships, with arrow thicknesses proportional to the strength of the relationship. The proportion of variance explained (R^2) is shown besides each response variable in the model. Goodness-of-fit statistics are shown in the lower right corner as the Fischer's C value, the *P*-value, and the degrees of freedom (d.f.) for each model. The *a-priori* model was refined by removing paths with non-significant relationships (see the *a priori* model in Supplementary Figure 5). *$P < 0.05$; **$P < 0.01$; ***$P < 0.001$.

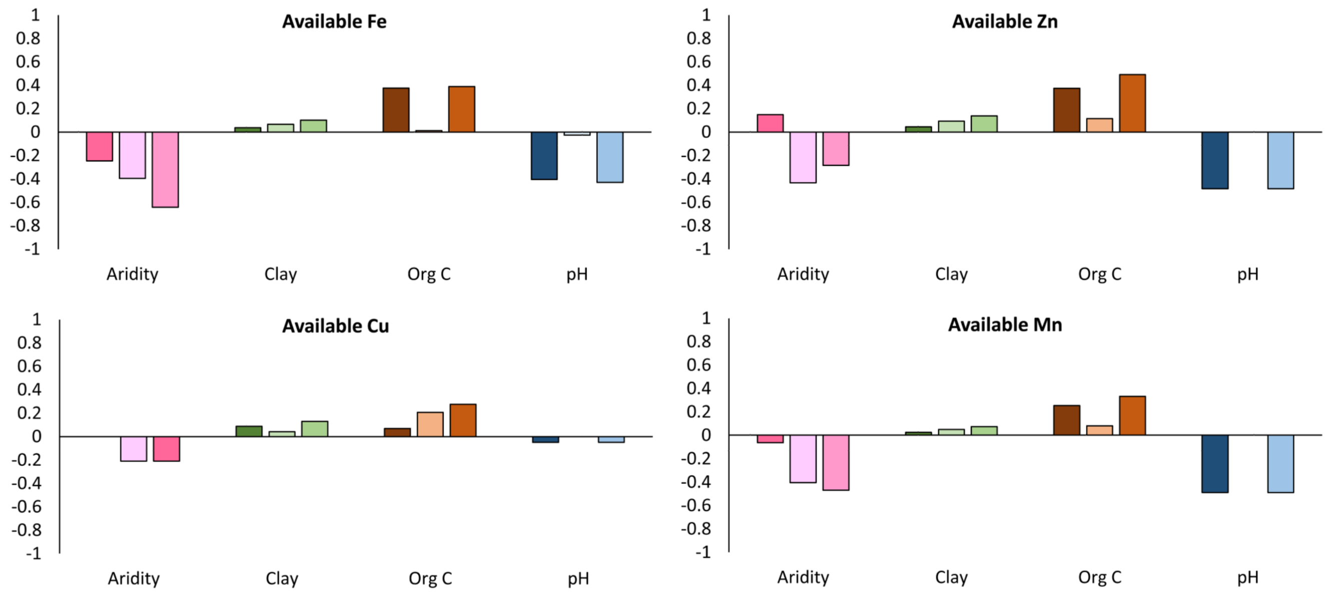

Figure 5.

Standardized direct (dark), indirect (light), and total sum effects (intermediate) of aridity (pink), clay (green), organic C (brown) and pH (blue) on available metal concentrations derived from confirmatory path analysis.