1 **Thresholds in decoupled soil-plant elements under changing climatic conditions**

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This document is the accepted manuscript version of the following article:
Luo, W., Sardans, J., Dijkstra, F. A., Peñuelas, J., Lü, X. T., Wu, H., ...
Jiang, Y. (2016). Thresholds in decoupled soil-plant elements under
changing climatic conditions. *Plant and Soil*, 409(1-2), 159-173.
<https://doi.org/10.1007/s11104-016-2955-5>

14 **Abstract**

15 *Background and aims* Aridity has increased in the past decades and will probably
16 continue to increase in arid and semiarid regions. To decipher plant and soil capacity
17 to retain metal cations when climate evolves to more arid conditions.

18 *Methods* We analyzed K, Na, Ca, Mg, Fe, Mn, Zn and Cu concentrations in 580 soil
19 samples and 666 plant (shoot and root) samples along a 3600 km aridity gradient in
20 northern China.

21 *Results* The concentrations of soil exchangeable K, Mg, Mn, Fe and Cu clearly
22 decreased with increasing aridity due to the relationships of aridity with soil clay
23 content and soil pH. Increases in exchangeable Na and Ca concentrations at mid- and
24 high-aridity levels are probably due to the soil salinization, whereas increased
25 exchangeable Fe concentrations at extreme aridity level may be more related to a
26 reduced pH at very high aridity. Element concentrations in both plant shoots and roots
27 were unrelated to soil exchangeable element concentrations; instead they increased
28 monotonously with increasing aridity, corresponding with decreases in plant size and
29 shoot/root ratios. The shoot/root mineralomasses ratios in general increased with
30 increasing aridity. The proportional higher element contents in shoots than in roots
31 with increasing aridity is related to increased water uptake and/or use efficiency.

32 *Conclusions* The extractability of soil elements in response to changing climate varied
33 with the nature of specific elements and to the extent these elements are controlled by
34 biological and geochemical processes, i.e., some decreased linearly with increasing
35 aridity, whereas others first decreased and then increased with different thresholds.
36 These contrasting effects of aridity on nutrient availability could further constrain
37 plant growth and should be incorporated into biogeochemical models. The prevailing
38 paradigm of a positive relationship between concentrations of plant and soil elements

39 needs to be reconsidered under changing climatic conditions.

40 **Keywords** Aridity; Biogeochemical cycles; Clay; Climate change; Soil pH;

41 Threshold.

42

Introduction

Aridity has increased in the past decades and will probably continue to increase in arid and semiarid regions (Dai 2013). Such climatic changes have considerable influences on global biogeochemical cycles and ecosystem development (Sardans and Peñuelas 2007). Studies of the variations of concentrations of elements in the soil-plant system in relation to changes in aridity could enhance our ability to understand and predict how ecological processes and biota will respond to global climate change (Han et al. 2011; Vicente-Serrano et al. 2012; Zhang et al. 2012). To date such knowledge is largely limited to essential elements such as nitrogen (N), phosphorus (P) and sulfur (S) (Duval et al. 2013; Luo et al. 2016; Peñuelas et al. 2012; Sardans et al. 2015). However, other elements, which are also important to ecosystem functions and services, are rarely studied (Duval et al. 2013; van Groenigen et al. 2006). For example, potassium (K) plays an important role in stomatal behavior, osmoregulation, enzyme activity and cell expansion (Wang et al. 2004) and despite this it is an understudied element in global change scenarios (Sardans and Peñuelas 2015). Magnesium (Mg) and calcium (Ca), two major intracellular divalent cations, are important cofactors in more than 300 enzymatic reactions such as energy metabolism and protein and nucleic acid synthesis (Whitehead, 2000). Copper (Cu) is an essential nutrient for plant growth and development and is a component of proteins involved in electron transfer and oxygen transport (Hansch and Mendel 2009). Manganese (Mn) is an essential element in plants for many functions including electron transport during photosynthesis and for riboflavin, ascorbic acid and carotene formation (Whitehead 2000). Zinc (Zn) is also essential for plants, e.g., for the production of auxins and root development (Whitehead 2000).

Biogeochemical cycles of multiple elements are traditionally biologically coupled due to preservation of elemental ratios in the plants, animals and microorganisms that drive them (Elser et al. 2011; Falkowski et al. 2008; Howarth et al. 2011). However, soil carbon (C) and N cycles were found to be decoupled from P and S cycles in such situations as increasing aridity in dryland ecosystems (Delgado-Baquerizo et al. 2013; Luo et al. 2016) and changing environments (Yang et al. 2014). This is because C and N cycles are most likely driven by biological processes such as photosynthesis and biological N-fixation, whereas P and S cycles are most likely driven by physical processes because P and S are rock-derived elements (Luo et al. 2016). Other macro- and micro-elements, such as K, sodium (Na), Ca, iron (Fe) and Cu, can enter terrestrial ecosystems through a number of sources including biological processes (e.g., organic matter decomposition), geochemical processes (e.g., chemical weathering, salinization or changes in soil pH) and various human activities (e.g., fertility inputs) (Austin 2011; Whitehead, 2000; Ramezani, 2013). Yet, little attention has been paid to the responses of the cycles of other elements, especially micro-elements, to a changing environment in arid and semiarid regions. In arid and semiarid regions drought can be accompanied by increases in salinity causing the precipitation and immobilization of elements such as Fe, Mn and Zn. This effect can be even greater when salinity coincides with increases in soil pH (Elamin and Hussein, 2000). Moreover, some studies have observed that drought can be related to changes in soil pH, causing either decreases (Clark et al. 2005) or increases in micro-element concentrations (Kopittke et al. 2012) depending on soil type and drought intensity and timing, highlighting other possible indirect impacts of drought on microelements and trace element plant-soil cycles.

91 Increasing aridity may affect not only biogeochemical cycles but also the extent to
92 which elements are coupled by biological processes. Increases in aridity limit the soil
93 diffusion capacity, and thus reduce the availability of elements in soils, soil microbial
94 activities, and plant uptake; such modifications may lead to a reduction in the
95 concentrations of elements in plant tissues (Han et al. 2011). On the other hand, it has
96 been widely reported that plants tend to accumulate some elements such as K^+ and
97 Ca^{2+} to enhance cell osmotic potential under drought stress, an important adaptation
98 strategy for maintaining water use efficiency (Chaves et al. 2003; Xoconostle-Cazares
99 et al. 2010). These processes illustrate how aridity can affect the biological coupling
100 of element cycles in terrestrial ecosystems.

101 Aridity is a fundamental driver of biotic and abiotic processes in arid and semiarid
102 areas, and hence, variations in patterns of elements in the soil-plant system may be
103 more sensitive to changes in aridity in these regions compared to other regions with
104 abundant rainfall (Austin 2011; Delgado-Baquerizo et al. 2013; Schroter et al. 2005).
105 Our previous study has showed that the plant N and P concentrations would not co-
106 develop with soil N and P availability under changing climatic conditions (Luo et al.
107 2015). In the present study, to examine how elements in the soil-plant system respond
108 to aridity, the concentrations of eight mineral elements in soils and plants were studied
109 along a 3600 km long transect representing a considerable precipitation gradient
110 across the arid and semiarid regions in northern China. Specifically, the present study
111 aims to demonstrate spatial patterns of metal cations in relation to climatic variables
112 and to explore the relationships between the concentrations of these elements in plants
113 and in top soils.

Material and methods

Transect and site description

In early August 2012, a field sampling campaign was conducted in 58 locations with a mean interval of 65 km between them along a 3600 km transect (West-East) in northern China (Fig. 1). The topography of the study area consists of gently rolling hills and tablelands, with elevations varying from 1500 m in the west to 700 m above sea level in the east. The sampling sites were randomly selected with an interval of 50-100 km. The geographic ranges for the data set are 39.9° N to 50.1° N (latitude) and 90.5° E to 120.4° E (longitude) (Fig. 1). Over this area, the climate is predominantly continental arid and semiarid; the annual potential evapotranspiration (PET) varies from 1229 mm (West) to 751 mm (East) and the mean annual precipitation (MAP) increases from 38 mm (West) to 436 mm (East) (see Fig. S1). The main vegetation types were shrublands, desert grasslands, typical steppe grasslands and meadow grasslands progressing from West to East. The plant species richness increased from west to east ranging from 5 to >25 species per m². The dominant plant species were *Reaumuria* spp. and *Salsola* spp. in the western region and *Stipa* spp., *Aropyron* spp., and *Cleistogenes* spp. in the eastern region. Soil types were predominantly arid, sandy, brown *loessials* rich in Ca, and belong to the chestnut brown and gray-brown desert soil group. Sampling sites were selected 500-1000 m away from major roads and human habitation, subjected to minimal grazing or other anthropogenic disturbances. The latitude, longitude and elevation for each sampling site were recorded with a GPS device (eTrex Venture, Garmin, USA). For more details on the sampling sites were refer to Luo et al. (2013) and Wang et al. (2014)

Sampling

At each site, two parallel 50 m × 50 m plots with a distance of approximately 1 km were selected and five 1 m × 1 m subplots were set within each plot (see Fig. 1). The five subplots were located at the four corners and in the center of the plot. In each subplot, after removing surface litter, soil samples (to 10 cm depth) were collected from ten randomly selected locations, using a soil core (2.5 cm diameter). We therefore collected a total of 580 bulk soil samples from 58 sampling sites along the large-scale transect. Soil samples were homogenized by hand mixing and then separated into two subsamples: one was stored in a plastic bag in a refrigerator at 4 °C for incubation experiments; the other was stored in a cloth bag at room temperature for soil chemical analyses.

In each subplot, the maximum height (cm) of plants belonging to each of the three dominant genera, *Stipa*, *Cleistogenes*, and *Agropyron*, was measured with a ruler. Then five to ten mature and healthy individuals of each genus were selected and extracted by pushing a soil cylinder (25 cm in diameter and 30 cm in depth) into the soil surrounding an individual plant sample and digging the plant out with a spade (Luo et al. 2013; 2015). Above- and below-ground tissues were carefully separated and then stored in paper bags separately. We collected a total of 666 plant samples (shoot and root) across the aridity gradient. The aboveground parts of the three genera in each plot were harvested and separated to calculate the aboveground biomass of each genus (g m^{-2}). Within the same day, plant material sampled was dried at 105 °C for 30 min in order to minimize respirations and decomposition, and then stored at 4 °C until further processing and analyses in the laboratory. More details can be found in Luo et al. (2013) and Wang et al. (2014).

Measurements

Soils were passed through a 2 mm sieve, and fine roots and plant debris were removed. Microbial biomass C (MBC) and N (MBN) contents were analyzed with the fumigation-extraction method (Vance *et al.*, 1987). An aliquot of 10 g fresh soils (<2.0 mm) were used to measure soil pH in water (1:2.5 soil to solution).

The exchangeable K, Na, Ca and Mg concentrations were measured by extracting air-dried soils (2.5 g; <2.0 mm) with 50 ml NH₄OAc (1 M; pH=7.0), and the exchangeable Fe, Mn, Cu and Zn concentrations were measured by extracting air-dried soils (10 g; <2.0 mm) with 20 ml diethylene triamine penlaacetic acid (DTPA; pH=7.3). Concentrations of all eight elements in the soil extracts were measured by atomic absorption spectrometry (AA6800, Shimadzu, Japan). Soil inorganic C (SIC) concentrations were measured by measuring the volume of CO₂ released from air-dried soil (10 g; <2.0 mm) after treatment with 8 ml HCl (2 M) at room temperature. The SIC content was used to represent the carbonate content in our study. Soil available sulfur (SAS) concentrations were measured by extracting air-dried soils (10 g; <2.0 mm) with 50 ml CaCl₂ (0.15 %) and the contents in the soil extracts were determined using the turbidimetric method.

Soils (10 g) were fractionated into sand (particle size, 50-300 μ m), silt (2-50 μ m) and clay (<2.0 μ m) using the ultrasonic energy method (Roscoe *et al.*, 2000). Clay content was expressed as a weight percentage of the oven-dried soil.

Soils were air-dried and ground to pass through a 1 mm sieve. Then SOC and STN concentrations were analyzed using an elemental analyzer (2400II CHN elemental analyzer; Perkin-Elmer, USA) at the Stable Isotope Facility of the University of California, Davis after removing carbonates using HCl (0.5 M).

Plant shoot and root samples were washed with deionized water and dried at 65 °C

to constant weight, and then ratios of shoot to root were measured as the dry root biomass (g) divided by the dry shoot biomass (g). Root samples were cleaned of excess soil by sonicating 3-5 g roots in 15 ml centrifuge tubes for 30 minutes in ultrapure (18 MV) water. The washed roots were again oven-dried at 65 °C to a constant weight. All plant materials were then ground and passed through a 1 mm sieve for measurement of elements.

Dried soil samples (100-150 mg; <1.0 mm) and plant samples (150-200 mg; <1.0 mm) were both acid digested with a mixture of acids (HNO₃, HClO₄ and HF, in a proportion of 5:1:2 (v/v/v) for soil samples and 5:1:0 for plant samples) in a microwave oven. Microwave digestion was performed until the sample was dissolved into the solution. The concentrations of K, Na, Ca, Mg, Fe, Mn, Zn and Cu were then measured either using inductively coupled plasma mass spectrometry (Perkin Elmer, ELAN-6000) or inductively coupled plasma emission spectroscopy (Perkin Elmer, OPTIMA 3000 DV).

Climate data

MAP and PET were extracted from a global climate dataset from <http://www.worldclim.org/>. Aridity was defined as 1-AI, where AI, the ratio of precipitation to potential evapotranspiration, is the aridity index (Delgado-Baquerizo et al. 2013).

Statistical analysis

Before numerical and statistical analysis, all variables (K, Na, Ca, Mg, Fe, Mn, Zn and Cu concentrations in soils and plants) were averaged at the site level. Some of these dataset were log₁₀-transformed to meet distributional assumptions underlying the statistical modeling. To demonstrate the effects of soil parent materials on the

patterns of soil exchangeable elements, ordinary least squares (OLS) linear regressions were explored between soil total elemental concentrations and the corresponding exchangeable concentrations along the transect. In addition, linear regressions were used to explore relationships between aridity and the ratios between soil exchangeable- and total elemental concentrations.

Linear or curvilinear (quadratic) regressions were used to relate each soil exchangeable element to aridity to explore the effects of climate regimes on patterns of soil exchangeable elements in the present study. We found that the relationships between soil exchangeable concentrations of K, Mg, Mn, Zn and Cu and aridity were well described by linear regressions. Then OLS regressions were used to relate exchangeable concentrations of these five elements to soil pH value and contents of SIC, clay, SOC, STN, MBC and MBN. We found that the relationships between soil exchangeable Ca, Na and Fe concentrations and aridity were well described by a second-order polynomial, with thresholds at aridity being 0.65 for Ca, 0.63 for Na and 0.83 for Fe. Therefore, OLS linear regressions were used to relate soil exchangeable Ca, Na and Fe concentrations to soil pH value and contents of SIC, clay, SOC, STN, MBC and MBN above and below their thresholds. We further explored the relationships of aridity with soil pH value, and with concentrations of SIC, SAS and STN using linear regressions.

To show the effects of climatic variables on plant element patterns, OLS linear regressions were used to relate aridity to the contents of plant elements in shoots and roots for the three genera. Maximum plant height and plant shoot/root ratios in relation to aridity were also explored with linear regressions. Total site mineralomasses were defined as the total contents of the eight studied elements (K, Na, Ca, Mg, Fe, Mn, Zn and Cu) in the biomass of each site by adding the contents in

the plants of the three main genera per plot. Linear regressions were used to relate the total site mineralomasses and shoot/root mineralomasses ratios with aridity.

All statistical univariate analyses were carried out with SPSS11.0 (SPSS, Inc., USA, 2001).

The aridity, soil clay content and soil pH were analyzed as factors explaining the maximum variability of soil exchangeable concentrations and soil exchangeable/total soil concentrations ratio of K, Na, Ca, Mg, Fe, Mn, Zn and Cu by structural equation modeling (SEM). This analysis provided information for the direct, indirect and total effects of the exogenous variables on the endogenous variables. We fitted the different models using the sem R package and determined the minimum adequate model using the Akaike information criterion. Standard errors and the significance level (*P* value) of the total, direct and indirect effects were calculated using bootstrapping (1200 repetitions).

Results

Soil and plant elements in relation to environmental variables

There were no significant relationships between total and exchangeable soil element concentrations ($P>0.05$, Fig. S3) except for Ca ($R^2=0.72$; $P<0.001$, Fig. S3B) and Cu ($R^2=0.12$; $P<0.01$, Fig. S3H). The ratios of soil exchangeable to total elements in surface soils decreased from wetter to intermediate aridity sites; thereafter, K, Na and Fe increased whereas the other elements continued to decline (Fig. S4).

The concentrations of soil exchangeable K, Mg, Mn and Cu decreased with increasing aridity (all $P<0.01$, Fig. 2). The concentrations of these four elements were positively correlated with MBC, MBN, SOC, STN, and soil clay contents, but negatively correlated with soil pH and SIC (Table 1).

The concentrations of soil exchangeable Ca, Na and Fe showed a concave-shaped trend with aridity, i.e., they first decreased and then increased with aridity thresholds of 0.65 for Ca, 0.63 for Na and 0.83 for Fe (all $P<0.05$, Fig. 2). When the aridity was lower than these thresholds, Ca, Na and Fe concentrations were all found to be positively correlated with MBC, MBN, SOC, STN and soil clay (all $P<0.05$, Table 1). Exchangeable Ca and Na were also positively correlated with SIC when the aridity was above their thresholds ($P<0.05$, Table 1). When aridity was higher than their thresholds, Ca, Na and Fe concentrations were all negatively correlated with MBC and MBN concentrations, SOC and STN concentrations and soil clay ($P<0.05$, Table 1). Fe concentrations were negatively correlated with soil pH and SIC below the threshold aridity of 0.83 (both $P<0.05$, Table 1).

Unlike the patterns of exchangeable elements in soils, the concentrations of the eight elements in both plant shoots and roots increased consistently with increasing

aridity along the aridity transect (Fig. 3).

When the total contents of the eight studied elements in the biomass of each site were analyzed, we observed that the total site mineralomasses of K, Na, Zn and Cu decreased with aridity (Fig. S5). Thus, as a general rule and notwithstanding the high concentrations in shoots and roots, with increasing aridity the total contents in stand biomass tend to decrease. Interestingly, the shoot/root ratio of the total site mineralomasses did not change with aridity (data not shown). When these correlations were studied at the genus level, the patterns of mineralomass with aridity were different than those observed with whole stand biomass. Aridity was not related with total content of any of the eight studied elements in any of the three dominant genera throughout the sites, but aridity was positively related with Na, Fe, Mn and Zn shoot/root mineralomass ratios in *Stipa* spp, with Ca, Na, Mg and Mn shoot/root mineralomass ratios of *Cleistogenes* spp., and with Mn shoot/root mineralomass ratios of *Agropyron* spp. (Fig. S6).

Multivariate soil analyses

The SEM showed that aridity had indirect significant relationships with soil exchangeable concentrations of K, Na, Ca, Fe, Mn and Cu by way of its negative relationship with soil clay contents and positive relationship with soil pH (Fig. 4 and 5). Aridity had also a significant positive relationship (direct, not related to previously commented indirect relationships) on soil Na and Ca. Thus, aridity affected soil exchangeable concentrations of the studied elements mainly due to its relationships with soil clay content and soil pH. The total linear relationship of aridity with soil exchangeable K, Mg, Mn, Fe, Cu and Zn concentrations was negative, and was positive with soil exchangeable Na and Ca concentrations (Fig. 4 and 5).

The SEM showed that exchangeable/total concentration ratios were indirectly affected by aridity through its own indirect relationships with soil clay content and soil pH (Fig. 6 and 7). Aridity had also a direct effect on concentrations not related with those indirect effects. The total relationships of aridity with ratios were negative for all elements except for Na, which had a positive relationship (Fig. 6 and 7).

Discussion

Effects of element pool on element availability

Soil available concentrations of mineral nutrients are almost entirely derived from parent materials in terrestrial ecosystems (Foulds 1993). Hence, soil total element pools play a critical role in availability. However, we found that most soil exchangeable element patterns were unrelated to total element patterns along the climatic gradient (Fig. S3), implying that the exchangeable fractions were not directly correlated with element pool size in the parent materials. The lack of relationships of soil total and exchangeable element contents may be attributed to variations in weathering rates from parent material (and hydrologic controls on such rates) across climate and soil gradients, which might have masked the effects of soil parent materials on element availability. In arid areas succession can be viewed as a process through which biota accumulate enough nutrients (West, 1981). This would be related to the drop in mineral weathering with aridity rise (West, 1981). The lack of weathering as a result of the short wet periods complements the salt neo-formation during the intense and long dry periods (Verhge, 2009). Consistently, previous studies have shown that soil element availability in dry ecosystems was also determined by weathering rates, which releases exchangeable forms of elements from the

lithosphere, as opposed to being determined by the pool size of elements in the parent materials (Schlesinger and Bernhardt 2013). A more detailed information on the parent material (geology) and its depth is warranted for a better understanding of the mechanism underlying the absence of relationship between soil total and extractable mineral content (Vitousek and Chadwick 2013). The mineralization of organic matter is other source of available bio-elements. In arid and semi-arid environments the mineralization rates of organic matter decays by several processes such a decrease in soil microbial activity and soil enzyme activity (Sardans & Peñuelas, 2005, 2013), which is frequently associated to the production of more recalcitrant litter and soil accumulation of some bio-elements (Sardans & Peñuelas, 2007; 2013; Sardans et al., 2008). However, there was no information regarding these factors along the large-scale soil transect in our study. **Climatic controls on element availability**

Soil exchangeable K, Mg, Mn and Cu concentrations were found to be negatively correlated with aridity across the climatic gradient ($0.4 < \text{aridity} < 1$), whereas Ca, Na and Fe concentrations were only negatively correlated with aridity in regions when the aridity was below a certain level (i.e., aridity=0.65 for Ca, 0.62 for Na and 0.83 for Fe) (Fig. 2). There are various controlling mechanisms that could explain these patterns. Firstly, biological mineralization releasing exchangeable element forms from organic matter is generally considered as a major limiting factor determining exchangeable element contents (Schlesinger and Bernhardt 2013). Hence, patterns of soil exchangeable elements mainly depend on soil biological mineralization rates associated with microbial activity. This hypothesis was partly supported in our study by the positive relationships between soil exchangeable elements and MBC and MBN along the climatic gradient (Table 1). Moreover, our results also showed that when aridity rises SOC decreases with aridity. Therefore the lower rates of mineralization

with higher aridity could be related to less organic carbon in soil to be mineralized and/or less microbial biomass to produce enzymes and to mineralize. Secondly, biological cycling shaping the vertical distributions of rock-derived elements can move micronutrients upwards because most rock-derived elements are taken up by plant roots, transported into aboveground biomass and recycled to the soil surface through litterfall (Jobbágy and Jackson 2004). Biological cycling processes decrease with increasing aridity (Moyano et al. 2013, Wang et al. 2014), which can to some extent explain the decreased rock-derived minerals with decreasing precipitation in our study. Thirdly, soil organic matter complexation is considered to be a major process in the preservation of soil elements in most temperate soils (Oades 1988). Soil organic matter can absorb many soil minerals and protect them from being lost. Hence, the declines in exchangeable element concentrations in the surface soils with increasing aridity were partly associated with decreasing organic matter. The importance of soil organic matter in this regard can be further evidenced by the positive relationships between the concentrations of most exchangeable elements and soil organic matter content along the transect in our study (Table 1). Fourthly, soil clay content also plays an important role in the retention of soil elements at the soil surface (Tiller et al. 1984). We found that the concentrations of most soil elements increased with increased soil clay content, the latter of which was inversely related with aridity. Lastly, soil pH has an effect on the solubility or retention of minerals in soils, with a greater retention rate and lower solubility of metal cations occurring at high soil pH (Martinez and Motto 2000). SEM analyses showed that drought had indirect, negative relationships with soil availability of the eight studied elements by way of its negative relationships with soil clay content and its positive relationship with soil pH (Table 1). Thus, taken together, the combined effects of these

environmental variables result in an ultimate decline of the availability of the considered soil elements with increasing aridity along the transect. Moreover, as commented previously, previous studies have shown that soil element availability decreases with aridity because of the decreases in minerals weathering (West, 1981; Schlesinger and Bernhardt 2013).

Our results showed that soil exchangeable concentrations of Ca, Na and Fe increased in the extreme range of aridity (mainly Ca and Na) (Fig. 2) and decoupled from K, Mg, Mn and Cu concentrations (opposite trend) when the aridity was higher than a certain threshold (i.e., aridity=0.65 for Ca, 0.62 for Na and 0.83 for Fe) (Fig. 2). We did not find evidence for a clear positive relationship between soil exchangeable concentrations of Ca, Na and Fe and biological variables such as MBC, MBN, SOC, and STN (Table 1), which indicated that patterns of soil exchangeable Ca, Na and Fe shifted from biologically-controlled factors (microbial activities and soil fertility) to geochemically- and geophysically-controlled factors (evaporation and carbonate equilibrium) with increasing aridity. Relatively high aridity can generally promote soil drying and alter hydrological transport processes, increasing salinity. Calcium (Ca) and Na in particular as relatively mobile and abundant elements in soils can be transported from soil depths and redistributed to the top soil layers as a result of hydraulic redistribution. Higher evapotranspiration can transport minerals passively to the aboveground tissues, from which minerals will be deposited to the soils. In addition, increases in aridity can produce large areas of bare soil, enhancing wind erosion and physical weathering in drylands. In support of this explanation, concentrations of soil SO_4^{2-} and CO_3^{2-} were found to accumulate under such dry conditions along our transect (see Fig. S7). In dry conditions Na and Ca accumulate in the soil surface forming salt crystals and carbonates, which in turn contribute to the

production of rock debris and thereby contributing to the release of more rock-derived elements (Rodriguez-Navarro and Doehne 1999). A decrease in soil pH at extremely dry sites (at aridity above 0.78) (see Fig. S8) can increase the solubility of Fe through pH buffering by equilibria of H_2CO_3 , HCO_3^- , and CO_3^{2-} (Bloom, 2000). This may be one plausible reason for abruptly higher Fe concentrations at the driest sites of the present study. Moreover, dry climatic conditions favor the formation and accumulation of these compounds due to low effective precipitation, since precipitation can dissolve and leach these compounds from the soil profile.

Soil properties and processes may change suddenly and/or nonlinearly in response to extrinsic differences in environmental forcing such as precipitation and temperature; such responses have been characterized as “pedogenic thresholds” in a variety of complex ecosystems (Vitousek and Chadwick 2013). Our results showed that Na and Ca in soil extracts decreased to an intermediate aridity and Fe concentrations in soil extracts decreased to the end of the studied range of aridity and then increased at greater aridity, forming thresholds (i.e., aridity=0.62 for Na, 0.65 for Ca and 0.83 for Fe) marking a minimum of a concave curve. Similarly, along a climatic gradient in the Sierra Nevada Range, Dahlgren et al. (1997) found that primary mineral weathering and clay mineral formation increased abruptly within a relatively narrow climatic zone due to a favorable combination of temperature and precipitation. Chadwick et al. (2003) analyzed soil properties and processes along an arid to humid climosequence on Kohala Mountain, Hawaii and identified pedogenic thresholds where mineral weathering and soil properties changed greatly with increased rainfall. Vitousek and Chadwick (2013) demonstrated that concentrations of silicon (Si), aluminum (Al), and Fe in surface soils along a rainfall gradient in Hawaii declined with increasing precipitation from 260 mm yr^{-1} to approximately 1700 mm

yr⁻¹, thereafter, Fe concentrations were enhanced abruptly whereas Si and Al concentrations continued to decrease.

Minor environmental forcing at pedogenic thresholds could have profound and long-term consequences on ecosystem functions (Lenton et al. 2008; Scheffer et al. 2009; Scheffer et al. 2012). Identifying changes in the relationships between aridity and ecosystem element cycles can reveal critical vulnerability of arid and semiarid ecosystems to global climate change (Scheffer et al. 2009). Due to the profound influence of elements on plant growth and maintenance and reproduction of terrestrial ecosystems, the cycles of multiple elements are at the core of ecosystem functions. The present study has indicated that a small climate change can affect ecosystem processes by differently impacting on distinct elements and this can be even greater at specific aridity thresholds (aridity=0.62 for Na; 0.65 for Ca and 0.83 for Fe); once local aridity passes beyond these turning points, the decoupling among different elements can be larger. This would force into a long process of recovery (Scheffer et al. 2009). Based on our results, a conceptual model was proposed to show the effects of environmental factors on soil exchangeable element concentrations along the aridity gradient (Fig. S10). This simple model may be applied to other dryland ecosystems, but possibly with different aridity scales of change in the different elements in response to aridity and changes in the slope responses of some of the elements because of differences in soil chemical and physical properties, vegetation types, and atmospheric deposition rates across scales. Our study provides robust, direct evidence for improvement of the process-based modeling of biogeochemical cycling in arid and semi-arid areas.

The decoupling of biogeochemical cycles of multiple elements in drylands when

aridity rises and the different responses of the different element cycles in plant-soil system when aridity reaches certain levels may also have profound consequences on ecosystem structures, functions, and productivity by the stoichiometry shifts (Peñuelas and Sardans 2009). For instance, when aridity is above 0.62 (as observed in the present study) for Na this would cause a rise in the accumulation of Na in the soil surface and enhance osmotic stress. Plant would necessarily consume a lot of energy in the osmoregulation, which may cause them serious injuries, resulting in losses of many plant species and a reduction of vegetation cover (Chaves et al. 2003). These stoichiometrical changes linked to the different rates of change in some elements when aridity reaches certain levels may exacerbate the negative effects of aridity on food production and the photosynthetic capacity of ecosystems increasing processes of degradation of the arid and semiarid ecosystems, with feed-back effects worsening the plant community capacity to retain nutrients, such as observed in this study. Moreover, this decoupling of biogeochemical cycles with changes in aridity necessarily implies an ecosystem stoichiometry shift. For example, we have observed a positive relationship between aridity and the soil exchangeable Ca/Mg ratio ($R^2=0.26$, $P<0.0001$). Soil Ca/Mg ratios have been associated with variations in several cellular structures and functions in terrestrial plants (Stael et al. 2012).

Effects of climate and soil on plant elements

In the present study, we found that plant shoot and root element concentrations increased with increasing aridity for the three genera but were not correlated with exchangeable element concentrations in soils along the transect (Fig. 3). One of the

possible reasons for this lack of relationship is the “dilution effect” of plant size (i.e., biomass) with increasing water availability (Jarrell and Beverly 1981). Higher precipitation significantly increased plant size in this water-limited ecosystem (see Fig. S9), which, in turn, could dilute element concentrations in plant tissues. Another reason for this lack of correlation between plant element and soil exchangeable element concentrations is the significantly decreased plant shoot/root ratios with increasing aridity (see Fig. S9), which may increase the ratios of plant mineral uptake to mineral demand, reducing the dependence of plant mineral content on soil mineral availability. Further, such uncoupling of soil nutrient element availability and plant nutrient content may also be attributed to the decreased vegetative cover and biomass with increased aridity (Wang et al. 2014), which may decrease resource competition pressure among plants, partly compensating for the reduced soil nutrient availability. In fact, when we analyzed total element contents in community biomass as the product between concentrations and biomasses in the species of the three dominant genera, we observed some increase of total K, Na, Zn and Mg at the beginning of the aridity gradient with a further change in the slope sign, with decreased in biomass contents of these elements. Thus, the results showed that the effects of aridity on total biomass is proportionally higher than the concentration effect under enhanced drought for these four elements. This trend was also observed for the other four elements but was insignificant. Moreover, and interestingly, the shoot/root mineralmass ratios of several studied elements (Fe, Na, Zn, Mg and Mn) increased with aridity in several species (Fig. S6). These results have at least three consequences for ecological stoichiometry. First, the fact that each plant taxon tends to allocate these elements more to shoots than roots with increasing aridity, thereby increasing favorable osmotic conditions, suggests a possible strategy for the improvement of water uptake and use

efficiency, related with K (and other highly soluble elements such as Na) contents and concentrations (Fig. 3). Second, as this aridity-related trend affects elements differently, it generates a shift in plant organ stoichiometry. Third, changes in shoot/root allocation associated with drought can be distinct at the community and species-specific levels. In the case of this study we did not observe a shift in community shoot/root ratios along the gradient but this was observed for some elements at the species level. While species-specific increases in shoot/root ratio were related with increasing aridity, increasing aridity also diminished the presence of the *Agropyron* spp. and *Cleistogenes* spp. which had the lowest shoot/root ratios. Thus, the former effect was counteracted by the latter.

In conclusions, In general the concentrations of exchangeable elements in soils decreased with increasing aridity, but with three exceptions: Na and Ca in soil extracts decreased only up to a threshold of intermediate aridity, and Fe decreased up to a point close to the end of the studied range of aridity, but thereafter increased with greater aridity. The biogeochemical cycles of these elements, normally coupled in less arid regions, were decoupled in more arid regions at aridity values of 0.62 for Na, 0.65 for Ca and 0.83 for Fe. The decoupling appeared to be most directly associated with the balance between biological and geochemical controlling mechanisms of element cycles. Both linear and nonlinear relationships between element cycles and climate change can greatly influence the plant growth and ecology functions, especially for arid and semiarid ecosystems where climate regimes play a profound role in plant and ecosystem functions. The multiplicity of thresholds of different mineral elements may also imply that ecosystem functions such as biogeochemical processes could abruptly change at multiple points along an environmental gradient. Plant element concentrations decreased with increases in plant size and shoot/root

ratios, both associated with increasing rainfall, but concentrations had no relationships with soil element availability. Thus, in a general sense the results describe lower soil availability of elements and lower plant element stocks, resulting in a decrease in the amount of elements involved in the plant-soil cycle with increasing aridity. Depending on the element, this outcome manifested with differing intensities, and for three of the eight elements there were also interrupted or inverse patterns. The results also showed a decoupling among the studied elements with increasing aridity, which is relevant for other areas and biogeochemical and ecosystem models. Overall, our findings advance our understanding of the unique nature of cycles of multiple elements in soil-plant systems across wide gradients of environmental factors and make it possible to better parameterize complex multi-element biogeochemical models included in Earth system models.

527 **Acknowledgments**

528 We thank all members of the Field Expedition Team from the Institute of Applied
529 Ecology, Chinese Academy of Sciences for assistance with field data collection. We
530 also thank the Erguna Forest-Steppe Ecotone Research Station, Institute of Applied
531 Ecology, Chinese Academy of Sciences. This work was financially supported by the
532 National Natural Science Foundation of China (41371251), by the National Basic
533 Research Program of China (2011CB403204), and State Key Laboratory of Forest
534 and Soil Ecology (LFSE2013-01). JP and JS acknowledge funding from the European
535 Research Council Synergy grant ERC-2013-SyG-610028 IMBALANCE-P, the
536 Spanish Government grant CGL2013-48074-P and the Catalan Government grant
537 SGR 2014-274.
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Table 1 Relationships between soil exchangeable element concentrations and soil properties (soil pH, soil inorganic carbon (SIC), clay, soil organic carbon (SOC), soil total nitrogen (STN), and microbial biomass carbon (MBC) and nitrogen (MBN)) along the climatic gradient. Pearson correlation coefficients are shown.

		pH	Clay	SIC	SOC	STN	MBC	MBN
K		-0.447***	0.723***	-0.313**	0.772***	0.790***	0.674***	0.614***
Ca	Above threshold	-0.066	-0.006	0.838***	-0.560**	-0.512**	-0.562**	-0.576**
	Below threshold	0.048	0.948***	0.129	0.875***	0.916***	0.654**	0.586*
Na	Above threshold	-0.066	-0.097	0.750**	-0.458**	-0.476**	-0.515**	-0.516**
	Below threshold	-0.098	0.786**	0.145	0.634*	0.662*	0.267	0.353
Mg		-0.311*	0.650***	-0.286*	0.579***	0.590***	0.449***	0.411**
Fe	Above threshold	-0.163	-0.490**	0.231	-0.379*	-0.435*	-0.536**	-0.505**
	Below threshold	-0.645**	0.685*	-0.406**	0.835***	0.826***	0.627***	0.596**
Mn		-0.643**	0.681***	-0.417**	0.895***	0.885***	0.752***	0.700***
Zn		-0.258	0.356**	-0.051	0.406**	0.409**	0.213	0.23
Cu		-0.450***	0.654***	-0.321*	0.721***	0.699***	0.515***	0.467***

Note: 'Above threshold' represents the regions with aridity which is higher than the element specific-threshold, and 'below threshold' represents the regions with aridity which is lower than the element specific-threshold (aridity=0.65 for Ca, 0.62 for Na and 0.83 for Fe; see Fig. 2). For more details of the soil properties along the transect, refer to Fig. S9 in the supporting information section. *, $P<0.05$; **, $P<0.01$; ***, $P<0.001$.

Figure legends

Fig. 1 A 3600 km transect in northern China. A total of 58 sampling points from West to East were selected along the transect. Two 50 m × 50 m plots were selected and five 1 m × 1 m sampling subplots were placed within each plot at the four corners and the center at each site. Aridity is defined as 1-AI, where AI, the ratio of precipitation to potential evapotranspiration, is the aridity index.

Fig. 2 Relationships between eight soil element concentrations and aridity across 58 sampling sites in northern China's arid and semiarid areas. Aridity is defined as 1-AI, where AI, the ratio of precipitation to potential evapotranspiration, is the aridity index.

Fig. 3 Relationships between eight plant element concentrations and aridity in northern China's arid and semiarid areas. Data for the three graminoid genera sampled are distinguished by color and symbol. Regression R^2 values are given in the Fig. Aridity is defined as 1-AI, where AI, the ratio of precipitation to potential evapotranspiration, is the aridity index.

Fig. 4 Diagrams of the structural equation models that best explained the maximum variance of the soil exchangeable concentrations of the eight studied elements and aridity, soil clay content and soil pH as exogenous factors. Black and red arrows indicate negative and positive relationships, respectively.

Fig. 5 Total, direct and indirect effects of aridity, soil clay content and soil pH on soil exchangeable concentrations of the eight studied elements. Data obtained by using the bootstrap technique (with 1200 repetitions). Aridity is defined as 1-AI, where AI, the ratio of precipitation to potential evapotranspiration, is the aridity index.

Fig. 6 Diagrams of the structural equation models that best explained the maximum variance of the soil exchangeable/total concentration ratios of the eight studied elements and aridity, soil clay content and soil pH as exogenous factors. Black and red

731 arrows indicate negative and positive relationships respectively.

732 **Fig. 7** Total, direct and indirect effects of aridity, soil clay content and soil pH on soil
733 exchangeable/total concentration ratios of the eight studied elements. Data obtained
734 by using the bootstrap technique (with 1200 repetitions). Aridity is defined as $1-AI$,
735 where AI , the ratio of precipitation to potential evapotranspiration, is the aridity index.

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Fig. 1

Fig. 2

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746 **Fig. 3**

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Fig. 4

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Fig. 5

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Fig. 6

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764 Fig. 7
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