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Determining landscape-level drivers of variability for over fifty soil chemical elements

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HIGHLIGHTS

- 53 soil chemical elements from 9830 samples covering 39,000 km² in south-east China were analyzed.
- Longitude, pH, MAT, and MAP strongly affected soil element concentrations.
- Topsoil elements have structural and functional thresholds of climate and soil pH.
- The thresholds of topsoil elements response to climate were MAP = 1000–1500 mm, MAT = 17.8–18.0° and pH = 5.0–5.8.

GRAPHICAL ABSTRACT

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ABSTRACT

Syntheses of large datasets have allowed increased clarity of distribution patterns and variation in soil major and trace elements. However, the drivers of variation in topsoil elements across biogeographical scales are not well understood. Our aim was to (1) identify how landscape-scale climate, geographical features, and edaphic factors influence soil elements, and (2) determine key environmental thresholds for shifts in soil element concentration. We analyzed patterns of variation in topsoil elements using 9830 samples collected across 39,000 km² in subtropical land in southeast China. Canonical correlations and multiple linear regressions were used to model variations of each element across mean annual temperature (MAT), mean annual precipitation (MAP), land use, spatial topography, and soil pH. Element concentrations show significant latitudinal and longitudinal trends, and are significantly influenced by climate, land use, spatial topography, and soil pH. Longitude, pH, MAT, and MAP were the environmental factors most tightly correlated with element concentrations. Climate and soil pH drove positive or negative alterations in soil elements, with threshold indicators of MAP =

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Temperature
Precipitation
Soil elements
Soil pH

1000 mm/1500 mm, MAT = 17.8 °C/18.0 °C, and pH = 5.8/5.0, respectively. Our results indicate topsoil elements have structural and functional thresholds of climate and soil pH in relatively wet and acidic environments. Our findings can facilitate holistic soil element concentration predictions and help elucidate the specific influences of climate and soil pH, enabling development of more complete biogeochemical models.

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1. Introduction

Soil chemical elements are essential for plants; however, some elements may be toxic, potentially posing human health risks (Han et al., 2011; Hale et al., 2017; Tabatabaie et al., 2018). In general, moderate concentrations of essential nutrients are most beneficial for plant growth and overall environmental quality (Crutzen and Andreae, 1990; Seneviratne et al., 2010). Hence, it is imperative to understand biogeochemical cycles and how environmental factors influence soil elements (Sistla and Schimel, 2012; Thanh-Nho et al., 2018; Thouin et al., 2018), because a comprehensive understanding of the key drivers of variation in topsoil chemical elements is needed to improve predictive biogeochemical and ecological models. However, a comprehensive database encompassing landscape-scale field observations of soil elements is not currently available.

Plant-available N, P, and K are known as primary nutrients for plant growth, while Ca, Mg, S, Fe, Zn, Mn, Mo, Cu, and B are considered intermediate or micronutrients; the toxicity or deficiency of these nutrients can be detrimental for biochemical functions of entire terrestrial ecosystems (Lynch and St Clair, 2004; Thouin et al., 2018). Likewise, Mo and Fe can influence the N cycle (Colombo et al., 2014); Ca is able to modulate soil pH and cation exchange capacity (Reich, 2005); Si supports several benefits for plants, including increased uptake of key nutrients (Muhammad et al., 2016); eight heavy metals: Cd, Hg, Pb, Cr, Sb, Se, As, and Ba are important indicators of environmental contamination, and I and F, while not essential for plants, are crucial for human health. To quantify anthropogenic impact on plant-soil geochemistry, it is crucial to know the distribution and variability of the chemical elements (Reimann et al., 2018b). Biogeochemical redox processes control the bioavailability, chemical speciation, toxicity, and mobility of many of these elements, potentially improving our ability to predict environmental health and provide remediation strategies (Borch et al., 2010). Therefore, it is imperative to assess local and landscape patterns of soil elements and show the visibility and discoverability of these fundamental background datasets (Townsend et al., 2011; Reimann et al., 2018a).

Environmental factors have important long-term effects on soil elements (Sistla and Schimel, 2012; Thanh-Nho et al., 2018; Thouin et al., 2018). The biogeochemical cycles of most elements are shaped by soil parent material and soil weathering (Augusto et al., 2017; Yu et al., 2017), regulated by vegetation and microorganisms (Sinsabaugh et al., 2008; Vitousek et al., 2013), and influenced by climate (Delgado-Baquerizo et al., 2013; Simpson et al., 2016; Tan and Wang, 2016). In addition, land use and topography can affect soil elements (Chen et al., 2015; Ren et al., 2018). Climate change is likely to impact different soil elements in various ways, due in part to local soil properties (Seneviratne et al., 2010; Simpson et al., 2016). In addition, plant responses to soil fertility rely on climate (Wright et al., 2004; Han et al., 2011), and soil pH is used to measure the potential environmental and economic performance of soil, owing to its strong influence on element solubility and plant absorption (Laeuchli and Grattan, 2012; Luo et al., 2016; Meng et al., 2018). For both essential and toxic elements, site-specific environmental and edaphic factors can dictate concentrations and thresholds of biological tolerance, suggesting element distributions across a landscape are linked with ecological patterns. Understanding how these environmental gradients influence variations in element concentration may help elucidate ecological thresholds, which are abrupt shifts in ecological response to elements (Huggett,

2005; Li et al., 2017; Munson et al., 2018). Utilizing this ecological threshold concept, elements with detrimental impacts on the environment can be identified and potentially mitigated following assessments of element concentration patterns across a landscape (Lohmann et al., 2012; Colombo et al., 2014; Hale et al., 2017), as well as identifying breaks in cumulative probability distributions (Reimann and de Caritat, 2017).

We analyzed topsoil element field data spanning multiple environmental gradients, including geographic location, topography, temperature, precipitation, land use, and soil pH; our analyses provide representation of regional-scale biogeochemical cycles and can help illustrate how environmental and edaphic factors interact to drive soil chemistry and element distributions. We obtained nearly 10,000 soil samples across southeast China and performed comprehensive analysis of >50 elements. We explored biogeographic patterns of these elements across an area of 39,000 km² covering 26 districts/counties. Our aim was to identify how environmental (climate and edaphic) factors influence topsoil elements, assessing element concentrations as well as functional threshold indicators across a landscape. Multi-element regional geochemistry in the Eurasian continent tends to be sensitive to environmental impact. Our findings can improve identification of environmental health issues and provide information on *in situ* concentrations of elements at the regional scale, information that has been lacking for the development of comprehensive modeling (Maire et al., 2015).

2. Methods

2.1. Soil sampling and concentrations of soil elements

Soil sampling spanned 6 major land uses (forest, grassland, meadow, bare land, arable, urban area), along climate and pH gradients, covering 26 districts/counties (114°45'–117°55'E, 27°50'–30°10'N) in southeast China (Fig. 1) in 2010; bare land was completely void of vegetation; urban area included industrial areas. We collected soil samples rooting zone (0–20 cm) evenly across the study area with one composite sample in each 2 km × 2 km grid as a landscape average sampling density. Composite samples consisted of 5 subsamples collected from a 10-m² plot. Within each plot, soil cores (5 cm in diameter, 20 cm in depth) were collected, bulked, and homogenized in the field. Soil subsamples for elemental analysis were air-dried, sieved (2-mm mesh), and ground to a fine powder using a ball mill; for physiochemical (e.g. C, N, pH) analyses, subsamples were stored in portable refrigerator, transported to the lab and maintained at −20 °C prior to analyses (Luo et al., 2016; Rennert and Rinklebe, 2017).

We collected topsoil samples because soil microbes, nutrients, and plant productivity are primarily influenced by the topsoil environment (Delgado-Baquerizo et al., 2017). Concentrations of Ag, Al₂O₃, As, Au, B, Ba, Be, Bi, Br, CaO, Cd, Ce, Cl, Co, Cr, Cu, F, Fe₂O₃, Ga, Ge, Hg, I, K₂O, La, Li, MgO, Mn, Mo, Na₂O, Nb, Ni, P, Pb, Rb, S, Se, Sb, Sc, SiO₂, Sn, Sr, Th, Ti, Tl, U, V, W, Y, Zn, Zr, as well as total N, C, and organic C (hereafter all referred to as soil elements) were obtained. In total, 9830 topsoil samples were collected. Site-related information, including longitude, latitude, mean annual precipitation (MAP), mean annual temperature (MAT), slope, soil pH, land use and soil classification, were documented for each sample. These information were gathered from National Meteorological Bureau of China database (<http://cdc.cma.gov.cn/>,

Fig. 1. Geographical map of sampling site locations in southeast China.

data.cma.cn/en) and SRTM (Shuttle Radar Topography Mission) 90 m digital elevation data (<http://srtm.csi.cgiar.org>). Soil properties and topography related sampling distribution was listed in Table S1.

2.2. Soil elemental analyses

Soil pH was determined with a 1:2.5 soil-to-deionized water ratio using a pH meter (Thermo Orion-868). Atomic fluorescence spectroscopy was used for As, Bi, Sb, Hg, and Se analysis with a Varian SpectrAA-220FS, following leaching with molar ammonium acetate buffered to pH 7 (Rengel, 2011). X-Ray fluorescence spectroscopy with wavelength dispersion was used to measure Al_2O_3 , Ba, Br, CaO, Cl, Cr, Cu, F, Fe_2O_3 , Ga, K_2O , MgO, Mn, Na_2O , Nb, Ni, P, Pb, Rb, S, SiO_2 , Sr, Ti, V, Y, Zn, and Zr. Inductively coupled plasma mass spectrometry and atomic absorption spectrometry with a graphite oven and plasma emission spectrochemistry were used to measure Ag, Au, B, Be, Ce, Cd, Co, Ge, I, La, Li, Mo, Sc, Sn, Th, Tl, U, and W. Total N and organic C were measured via the potassium dichromate volumetric method (Xu et al., 2011). Total C was determined by X-ray fluorescence spectrometry analysis (Xu et al., 2012). Soil bulk density was measured using the cutting ring (volume of 100 cm^3) method. The detection limit of the method for each element was listed in the Table S2. When data were below the detection limit of the method, mean values was calculated with all results below detection limit set to 1/2 detection limit.

2.3. Climatic variables, soil pH, spatial topography and land use

Our analysis captured a substantial range of MAT, MAP, spatial geographical position, soil pH, and land use in Southeast China. Sampling sites represented 20 soil types (Harmonized World Soil Database, FAO Soil Taxonomic system) (Office, 1993; Shi et al., 2010) across an extensive area. The most widely distributed soils were Haplic Acrisols and Cumulic Anthrosols. The six land uses were not equally represented in the dataset: forest (3557), grassland (79), meadow (1624), bare land (Reich, 2005), arable (3612), and urban area (927). Slopes (topographic factor) of sampling sites were $0\text{--}41.46^\circ$, according to information obtained from SRTM (Shuttle Radar Topography Mission) 90 m digital elevation data (<http://srtm.csi.cgiar.org>) (See Table S1 for detail

description). Data for MAT and MAP were obtained from the National Meteorological Bureau of China database and compiled by interpolating information of monthly mean temperature and monthly precipitation records (resolution ratio: 1 km) for 40 years average (1970–2010) from 716 climate stations across China (<http://cdc.cma.gov.cn>). Sites ranged in MAT from 12 to 18°C , and in MAP from 500 to 1900 mm.

2.4. Statistical analysis

All data were $\log_{10}(x + 1)$ transformed before analyses, and the averages of all sites were calculated and standardized between 0 and 1 to improve data normality (average = 0 and SD = 1). Canonical correlation analysis and linear regression analyses were used to assess how MAT, MAP, land use, slope, and pH correlated with each soil element and the correlations between explanatory variables. The first canonical correlation is as large as the multiple correlations between any variable and the opposite set of variables. To demonstrate the relative effects of climate, spatial topography, and soil acidity, general linear model (GLM) analyses were applied. GLM can be used to separate the variance explained by different factors into the independent effects from each individual factor and interactive effects between these factors (Perdew et al., 1996).

To identify the concentration thresholds for each soil element along the gradient of MAT, MAP, and pH (these three factors were selected to further analysis because they contributed heavily to element canonical variables), we applied Threshold Indicator Taxa Analysis (TITAN) as an indicator value analysis (Baker and King, 2010). A soil element with a maximal indicator value score of 100% means that it was found in all sampling sites across an environment gradient value (MAT, MAP, or pH). Midpoints between two environmental gradient values were used as candidate thresholds (change points) to iteratively split observations into two groups, producing two indicator value scores at each split. The relative magnitude of value scores for groups on each side of a candidate threshold show whether a soil element exhibits greater association with the left sum z- (negatively responding to the environmental gradient) or with the right sum z+ (positively responding to the environmental gradient). Any value of an environmental gradient that resulted in a peak indicator score across all candidate splits was

identified as the observed environmental gradient threshold for that soil element. For each observed threshold, the indicator value scores were rescaled to z scores within TITAN according to the degree of departure from expected values by subtracting the mean of randomized permutations from the observed indicator value, and then divided by its permuted standard deviation (SD). Therefore, z scores distinguished each soil element response at the environmental gradient threshold: increasing (z+), decreasing (z-), or neutral. All z+ and z- scores were summed within different levels of each environmental gradient to assess the cumulative positive and negative responses in topsoil (Baker and King, 2010). If a threshold was observed, we calculated a 95% confidence interval. Threshold analyses were implemented using R package 'TITAN' (Baker and King, 2010). TITAN sum (z) across 500 bootstrap replicates was performed for both simulated and real data sets. From bootstrap replicates, two levels of reliability and indicator purity were also calculated (Baker and King, 2010). Ordinary least squares (OLS) regressions were used to assess potential correlations between environmental factors and ecological cluster abundance of soil chemical elements. All statistical analyses were performed using SAS/STAT version 9.4 (SAS Institute Inc., Cary, NC, USA) and R version 3.2.5 (R Foundation for Statistical Computing, Vienna, Austria, 2013).

3. Results

3.1. Spatial topography, soil pH, and land use effects on topsoil elements

The description of each of the 53 topsoil elements was listed in Table 1 for detail, including their mean value and standard deviation,

Table 1

Total concentrations of 53 elements as analyzed in the topsoil from a 39,000 km² area in southeast China (mean-standard deviation (Std)-maximum (Max)-minimum (Min) values).

Elements	Mean	Std	Max	Min	Elements	Mean	Std	Max	Min
Ag (μg/g)	0.036	0.020	0.690	0.005	Mn (μg/g)	2.566	0.238	3.744	1.049
Al ₂ O ₃ (μg/g)	1.156	0.090	1.430	0.593	Mo (μg/g)	0.254	0.097	1.806	0.068
As (μg/g)	1.006	0.180	2.716	0.142	Na ₂ O (μg/g)	3.132	0.171	3.628	1.512
Au (μg/g)	0.001	0.001	0.076	0.000	Nb (μg/g)	0.116	0.067	0.484	0.021
B (μg/g)	1.858	0.125	2.765	1.123	Ni (μg/g)	1.321	0.075	1.641	0.498
Ba (μg/g)	2.597	0.137	3.670	1.924	P (μg/g)	1.393	0.126	2.252	0.548
Be (μg/g)	0.508	0.110	1.666	0.182	Pb (μg/g)	2.760	0.116	3.378	2.137
Bi (μg/g)	0.194	0.110	1.382	0.030	Rb (μg/g)	1.506	0.116	2.672	1.024
Br (μg/g)	0.515	0.143	1.609	0.121	S (μg/g)	2.034	0.155	2.850	1.260
CaO (μg/g)	0.097	0.083	0.941	0.009	Sb (μg/g)	2.445	0.150	3.460	1.204
Cd (μg/g)	0.071	0.043	0.750	0.010	Sc (μg/g)	0.299	0.106	2.179	0.052
Ce (μg/g)	1.920	0.094	2.251	1.233	Se (μg/g)	1.081	0.105	1.535	0.017
Cl (μg/g)	1.751	0.143	2.997	1.041	SiO ₂ (μg/g)	0.115	0.040	0.671	0.012
Co (μg/g)	1.067	0.140	2.415	0.292	Sn (μg/g)	1.850	0.036	1.976	1.584
Corg (μg/g)	1.369	0.516	5.590	0.020	Sr (μg/g)	0.830	0.157	2.161	0.076
Cr (μg/g)	1.828	0.126	2.533	0.864	TC (μg/g)	1.680	0.141	2.350	1.061
Cu (μg/g)	1.415	0.143	3.030	0.528	Th (μg/g)	1.421	0.521	5.880	0.056
F (μg/g)	2.664	0.118	3.699	1.806	Ti (μg/g)	1.180	0.090	1.631	0.425
Fe ₂ O ₃ (μg/g)	0.723	0.092	1.374	0.215	Tl (μg/g)	3.724	0.093	4.148	2.458
Ga (μg/g)	1.233	0.102	1.746	0.762	TN (μg/g)	0.218	0.067	1.451	0.058
Ge (μg/g)	0.431	0.038	0.726	0.250	U (μg/g)	0.622	0.115	1.526	0.212
Hg (μg/g)	0.040	0.030	0.934	0.003	V (μg/g)	1.927	0.122	2.907	0.876
I (μg/g)	0.400	0.191	1.373	0.061	W (μg/g)	0.612	0.146	2.070	0.188
K ₂ O (μg/g)	0.488	0.094	0.784	0.146	Y (μg/g)	1.489	0.078	1.790	0.713
La (μg/g)	1.572	0.115	1.985	0.869	Zn (μg/g)	1.864	0.133	2.643	0.940
Li (μg/g)	1.629	0.140	2.764	0.756	Zr (μg/g)	2.495	0.102	3.043	1.556
MgO (μg/g)	0.212	0.067	0.658	0.021					

as well as maximum and minimum value. Multiple regression models that included each element and each environmental predictor illustrate slope, pH, land use, MAP, and MAT all had strong linear relationships with topsoil elements (Table 2, Table S3). A canonical correlation analysis showed that CaO, MgO, Mn, Na₂O, and Sr are most significantly influenced by several of these environmental factors (standardized canonical coefficient > 0.50) (Table S4–S6). In addition, land use significantly affected all elements (Table S4–S6). Slope (topographic factor) significantly affected one half (Penuelas et al., 2013) of the elements: Ag, Ba, Be, Br, Cd, Cl, Co, Cr, F, Ge, I, K₂O, Li, MgO, Mn, Mo, Na₂O, Rb, S, Sb, Se, Th, Ti, Tl, Zn, total N, total C, and organic C. Across the landscape, soil pH ranged 4.20–8.88; acidic soils (pH < 5.5) and alkaline soils (> 8) both pose challenges for vegetation such as low nutrient availability and ion toxicity. Overall, soil pH had the strongest correlation to soil elements (standardized canonical coefficient = 0.82, $p < 0.001$), although

Table 2

Results of F-values statistics from general linear models (GLM) where soil element were fitted as functions of environmental variables (** $p < 0.001$; * $p < 0.01$; $p < 0.05$; n.s.: not significant; TN: total nitrogen; TC: total C; Corg: soil organic C).

Elements	LUT	MAP	MAT	pH	Slope	R ²
Ag (μg/g)	88.8***	0.04 ns	7.11**	7.03**	6.31*	0.15***
Al ₂ O ₃ (μg/g)	148.38***	188.26***	335.22***	0 ns	0.61 ns	0.26***
As (μg/g)	50.28***	4.9*	1.84 ns	1.62 ns	0.9 ns	0.07***
Au (μg/g)	3.32**	14.78***	2.87 ns	1.05 ns	1.81 ns	0.04***
B (μg/g)	16.14***	10.62**	106.92***	0 ns	2.28 ns	0.17***
Ba (μg/g)	73.54***	55.66***	142.46***	151.49***	95.18***	0.28***
Be (μg/g)	162.07***	33.68***	3.55 ns	63.44***	12.22***	0.18***
Bi (μg/g)	191.44***	31.16***	38.01***	2.13 ns	3.6 ns	0.20***
Br (μg/g)	4.29***	59.8***	1028.31***	110.42***	105.18***	0.43***
CaO (μg/g)	5.44***	17.82***	27.38***	5307.12***	0.02 ns	0.69***
Cd (μg/g)	127.79***	3.2 ns	17.33**	439.44***	24.46***	0.32***
Ce (μg/g)	89.52***	20.19***	77.43***	143.71***	1.55 ns	0.24***
Cl (μg/g)	24.96***	42.46***	50.93***	33.43***	9.48**	0.14***
Co (μg/g)	48.21***	257.17***	81.01***	140.67***	10.81**	0.24***
Corg (μg/g)	224.61***	10.7*	10.78**	236.88***	5.8*	0.25***
Cr (μg/g)	11.93***	93.22***	1.43 ns	47.68***	14.05***	0.18***
Cu (μg/g)	68.26***	8.73*	0.03 ns	20.96***	0.17 ns	0.19***
F (μg/g)	78.61***	39.58***	46.63***	145.64***	38.79***	0.16***
Fe ₂ O ₃ (μg/g)	67.53***	144.26***	153.16***	20.72***	0 ns	0.15***
Ga (μg/g)	156.49***	227.66***	206.13***	0.08 ns	0.34 ns	0.19***
Ge (μg/g)	42.39***	11.97***	17.75***	31.31***	11.34***	0.13***
Hg (μg/g)	8.72***	5.56*	2.54 ns	41.43***	3.41 ns	0.15***
I (μg/g)	7.76***	37.77***	365.09***	129.82***	46.34***	0.24***
K ₂ O (μg/g)	81.94***	123.7***	210.44***	45.12***	59.58***	0.20***
La (μg/g)	125.58***	9.59**	50.68***	191.05***	0.49 ns	0.18***
Li (μg/g)	150.97***	20.35***	10.43**	3.96*	7.7**	0.18***
MgO (μg/g)	36.25***	33.06***	373.15***	732.88***	16.26***	0.40***
Mn (μg/g)	47.41***	52.11***	93.05***	421.66***	121.78***	0.40***
Mo (μg/g)	55.08***	1.99 ns	2.9 ns	0.16 ns	26.83***	0.09***
Na ₂ O (μg/g)	17.33***	21.33***	80.18***	77.39***	17.65***	0.41***
Nb (μg/g)	61.46***	31.15***	31.35***	9.01*	1.25 ns	0.15***
Ni (μg/g)	37.83***	23.59***	50.58***	189.89***	0 ns	0.20***
P (μg/g)	41.59***	53.05***	5.46*	1046.71***	0.28 ns	0.16***
Pb (μg/g)	169.45***	46.33***	69.05***	80***	0.25 ns	0.25***
Rb (μg/g)	142.5***	155.89***	163.48***	33.99***	34.44***	0.25***
S (μg/g)	7.29***	22.57***	3.66 ns	76.06***	22.48***	0.72***
Sb (μg/g)	4.38***	3.17 ns	102.84***	0.39 ns	23.98***	0.08***
Sc (μg/g)	78.93***	124.31***	137.17***	12.29***	0.32 ns	0.23***
Se (μg/g)	53.35***	0.26 ns	37.54***	9.99**	26.07***	0.15***
SiO ₂ (μg/g)	122.95***	95.87***	494.69***	61.09***	1.69 ns	0.26***
Sn (μg/g)	52***	191.66***	6.16*	9.61**	1.37 ns	0.21***
Sr (μg/g)	21.23***	130.33***	1.77 ns	624.42***	0.01 ns	0.38***
TC (μg/g)	224.69***	4.92*	7.25**	37.12***	4.77*	0.20***
Th (μg/g)	140.27***	47.23***	37.22***	17.52***	6.42*	0.14***
Ti (μg/g)	23.77***	82.6***	20.56***	0.22 ns	20.1***	0.27***
Tl (μg/g)	97.64***	42.35***	45***	16.6***	34.05***	0.21***
TN (μg/g)	212.51***	21.63***	12.4***	518.01***	8.7**	0.25***
U (μg/g)	126.51***	147.84***	36.62***	7.93**	0.13 ns	0.24***
V (μg/g)	29.81***	134.17***	11.8***	72.82***	0.77 ns	0.16***
W (μg/g)	168.09***	240.76***	24.79***	0.03 ns	0.64 ns	0.19***
Y (μg/g)	53.86***	125.8***	3.4 ns	105.81***	2.02 ns	0.25***
Zn (μg/g)	175.42***	99.05***	120.56***	141.21***	60.09***	0.29***
Zr (μg/g)	76.17***	0.79 ns	160.4***	41.15***	3.07 ns	0.19***

it did not significantly affect Al_2O_3 , As, Au, B, Bi, Ga, Mo, Sb, Ti or W (Table S4–S6).

3.2. Climatic effect on topsoil elements

Temperature (MAT) and precipitation (MAP) shape the distribution and concentrations of soil elements. We quantified the influence of MAT and MAP in landscape biogeographic patterns, and we found 32 soil elements were significantly correlated with both MAT and MAP (all $p < 0.05$; Table 2). MAP and MAT explained 10% and 6% of total variation among all soil elements, respectively. MAT played a significant role in determining the concentrations of all elements except Ag, Br, I, Mo, Ti, or Y, whereas MAP had no significant influence on As, Ba, Cr, Fe_2O_3 , or Li ($p > 0.05$) (Table 2). Six elements (Au, B, Co, Hg, Sb, Se) were not significantly influenced by either MAT or MAP. The standardized canonical coefficient of MAT and MAP to soil elements was 0.39 and -0.54 , respectively ($p < 0.001$) (Table S4–S6).

3.3. Threshold levels of soil pH, MAT, and MAP

Of all environmental factors, pH, longitude, MAT, and MAP showed the strongest correlations with soil elements, therefore, we further tested these thresholds, with the exception of longitude. Longitude ranged relatively low spatial scale in this study, it's not referential to figure out its threshold. For the whole topsoil system (pooled data), soil pH strongly influenced most elements positively (sum z^+), whereas few elements showed reduced concentration (sum z^-) due to soil pH (Fig. 2a, Fig. 3a). Cumulative z scores of the extended indicator value in TITAN analysis showed aggregated changes in element concentration and frequency, indicating the threshold pH value corresponding to maximal sum (z^+). Synchronous variations in concentration and frequency of soil elements was observed for more than half of the elements between pH = 5.0 and pH = 5.8 (Fig. 2a). A total of 17 elements declined in concentration along with soil pH and 26 increased along with soil pH (Fig. 3a). Among these elements, soil pH decreased total N and organic C around pH = 6.0, compared with more acidic or alkaline soils. In contrast, the concentration of Mn increased at pH = 5.5, Sr increased at pH = 6.0, and MgO at pH = 7.0 (Fig. 3a). Similarly, increases in MAT decreased most elements (sum z^-), (Fig. 2b, Fig. 3b). A total of 36 element elements decreased with greater MAT while 12 increased; Zr and S showed the greatest variation in their concentration at MAT = 16° and 18° , respectively (Fig. 3b). Overall, a sharp decrease in element concentrations was found around MAT = 18.0° (Fig. 2b). Between 16.5° – 18.5° , 85% of elements responded strongly to MAT (Fig. 3b). MAP had two different peak values (z^- and z^+) (Fig. 2c). A decrease in element concentration with MAP was observed around MAP = 1000 mm for z^+ and MAP = 1500 mm for z^- respectively (Fig. 2c), such that 23 elements declined with MAP and 21 increased (Fig. 2c). Relationships between the relative abundance of soil chemical elements assigned to each ecological cluster and their major environmental

predictors highlight soil chemical elements within each ecological cluster tend to co-occur (Fig. 4).

4. Discussion

4.1. Biogeographic patterns and environmental controls of chemical elements

Spatial topography slope, pH, land use, and climate all influence soil element biogeography in complex ways. A partial general linear model (GLM) combining these factors accounted for a wide range of variation (7%–72%) in soil element concentrations. The explanatory power of these environmental factors for different elements varied substantially. Our approach using partial GLM regressions with canonical correlations excludes collinearity between variables (Witten et al., 2009); therefore, we were able to distinguish independent effects of multiple factors when determining their contributions to element patterns across the landscape. In general, soil pH and climate explained the majority of all soil element variances. These likely reflect pervasive geographic patterns in soil development and likely relate to soil element variations (Barron et al., 2009; Colombo et al., 2014; Hale et al., 2017). These soil element responses to climate variability across a range of pH showed concentrations increased in acidic cool and dry environments and decreased in alkaline warm and moist environments. These results agree with previous work showing MAT and MAP are crucial factors that influence soil element distribution and concentration (Han et al., 2011). In acidic, cool, and dry environments, some soil elements exist in ionic forms. For example, oxidized iron (Fe^{3+}) is soluble under acidic soil conditions, but precipitates as Fe^{3+} (hydr)oxides in close to neutral pH. In alkaline, warm, and moist environments, some soil elements, such as S, are more likely influenced by oxidation-reduction processes, and decline in concentration (Borch et al., 2010). In addition, denitrification combined with pyrite oxidation is an important N removal pathway in soil (Borch et al., 2010). We found Mn, an essential plant nutrient, had the highest concentration among all trace elements. We also found Sr, which can improve bone density in humans, was widely distributed. Concentration and distribution of both Mn and Sr tended to increase in less acidic soil. Our results strongly indicate soil pH must be included in interpretation of bivariate relationships between elements and climate because variation of soil elements in a given climate is driven by soil pH. The influences of increased temperatures and reduced precipitation are not strong enough to offset the effects of soil pH extremes (Luo et al., 2016; Meng et al., 2018). Our findings suggest predictions of the influence of environmental change on soil elements will improve significantly by incorporating local-scale pH into comprehensive models.

In previous studies, the effects of multiple environmental factors on such a diverse set of soil elements have not been explored. As soil properties can feed back to influence vegetation composition and community structure (Hobbie, 2015), the effects of climate and edaphic

Fig. 2. Effect of environmental factors on accumulative negative (sum z^-) and positive (sum z^+) responses of soil elements along (a) soil pH, (b) MAT, and (c) MAP gradients, based on data from 9830 samples. Blue and red circles represent sum (z^+) and sum (z^-), respectively. Vertical dashed lines indicate environmental gradient thresholds corresponding to maximal sum (z). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Threshold Indicator Taxa Analysis (TITAN) of soil element thresholds, integrating responses to environmental factors based on data from 9830 samples. Blue and red circles represent negative (z-) and positive (z+) responses to environmental factors, respectively. Symbol size is in proportion to z scores, and elements with a larger symbol represent greater changes in concentration ($\mu\text{g/g}$). For each element, solid lines indicate the 95% bootstrap confidence interval. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

gradients on soil elements, as shown in our study, can have implications for entire terrestrial ecosystems. Warm and moderately wet climates with soils containing high pools of element nutrients and higher pH are most beneficial for vegetation and human health (Coomes et al., 2014). Policy aiming to protect human health and mitigate contamination requires a comprehensive understanding of the interactions between soil elements and multiple environmental gradients. Our results indicate complex interactions between climate and edaphic factors may explain element variations across entire landscapes.

4.2. Thresholds of soil elements changes to climate and pH

Our assessment of landscape scale topsoil elements determined ecological thresholds of element concentration, distribution, and variation due to climate and pH. The majority of soil elements increased or decreased along pH, MAT, or MAP gradients, with key tipping points at $\text{pH} = 5.0$ and 5.8 , $\text{MAT} = 17.8^\circ$ and 18.0° and $\text{MAP} = 1000$ mm and 1500 mm. Our results also showed that $>65\%$ of the assessed soil elements decreased at high MAT. Elements such as B, Co, Cr, Fe_2O_3 , Mn, Ni, Sc, V, and Y are more sensitive and declined sharply at $\text{MAT} = 18.0^\circ$. These elements had similar threshold temperatures and may react to temperature stress synchronously. However, those same elements displayed different precipitation thresholds and responded to MAP asynchronously. Increased MAP is likely to change soil redox conditions and intensification of precipitation could have crucial impacts on biogeochemical processes and ecosystem services.

Future changes in climate will likely exert idiosyncratic effects on biogeochemical cycles, modifying nutrient biogeography by altering spatial patterns of soil element composition across landscapes. For example, experimental imposition of warming, and reduced precipitation, on Mediterranean vegetation led to species-specific differences in response to a range of soil macro- and micronutrients (Sardans et al., 2008; Penuelas et al., 2013). Climate and soil acidity have been acknowledged as simultaneous drivers of vegetation distribution (Han et al., 2011; Simpson et al., 2016; Yu et al., 2017), but by analyzing topsoil elements from a wide range of land use and soil types, we have shown that soil-climate interactions predict the distributions of heterogeneous chemical elements. As a wide-range of *in situ* data has not been available until recently, our study enhances the availability of high-resolution soil data across biogeographical scales to improve predictions

of ecological responses to current and future climate variations. Notably, our work shows the responses of soil elements to temperature and precipitation regimes are contingent on local soil pH and therefore, soil pH should be included in comprehensive models. Climatic factors and soil pH are often highly correlated with observed differences in overall soil microbial community composition (Lauber et al., 2009; Maestre et al., 2015). Therefore, in future research there is an exciting opportunity to overlay our soil chemical element findings with a regional atlas of dominant soil microbial functional groups to further explore the biotic drivers of soil chemical element distribution patterns and environmental predictors. Due to the overwhelming diversity of soil microbial communities, it has been difficult to characterize individual taxa and document their regional distributions. Our analyses of soil chemical elements set an important foundation to enable future integration of abiotic and biotic edaphic factors. For example, clustering relatively few dominant microbial taxa into ecological groups may further elaborate the complex interacting factors shaping the distribution of soil elements. We propose a promising opportunity involves narrowing the immense number of microbial taxa to a “most wanted” list to better interpret soil biological contributions to soil chemical element distribution patterns and ecosystem functioning.

5. Conclusion

Our study is the first to comprehensively document the topsoil concentration and distribution of multiple elements and quantify the potential influences and variability at a landscape scale. Across all factors correlated with biogeographic distributions of soil elements, longitude, MAP, MAT, and pH had the greatest direct influences, with climate and soil pH substantially shaping the distribution of chemical elements. Our results showed that the key thresholds were around $\text{MAP} = 1000$ – 1500 mm, $\text{MAT} = 17.8$ – 18.0° and $\text{pH} = 5.0$ – 5.8 , suggesting that soil element thresholds can be used as predictors of topsoil element responses to future climate changes with the incorporation of local soil pH. In addition, monitoring toxic element concentrations can indicate environmental condition thresholds are being approached so actions can be taken prior to deleterious outcomes. Our findings broaden the knowledge of biogeochemical cycling in topsoil and the fundamental constraints on soil stoichiometry across wide environmental gradients. We also provide synthetic data compilation

Fig. 4. Identified habitat preferences for clustered soil chemical elements. Relationships between relative abundance of phylotypes assigned to each ecological cluster and their major environmental predictors (Identity of phylotypes within each cluster are presented in Figs. 2 and 3). Red lines are fitted lines from OLS regressions. Regression analyses highlight that soil chemical elements within each ecological cluster tend to co-occur. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and analyses that can be used to better parameterize complex multi-element biogeochemical models, crucial for predictive accuracy (Morel and Price, 2003; Wright et al., 2004; Yu et al., 2017). Our findings demonstrate how complex interactions of climate, geographical features, and edaphic factors shape element variability across a landscape, potentially influencing plant community composition, production, and nutrient quality. Building on our results, future efforts should include a regional map of dominant microbial taxa in soil, further elucidating the predictors of soil chemical element distribution across environmental predictors.

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Author contributions

Haiyan Ren, Quanping Zhou designed the research; Haiyan Ren, Quanping Zhou performed the research; Haiyan Ren, Jianbo He, Ying Hou analyzed the data; and all coauthors contributed to the writing of the manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.12.024>.

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