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Controlling factors of soil selenium distribution in a watershed in Se-enriched and longevity region of South China

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Abstract

Selenium (Se) is an essential nutritional element for human beings. Many studies have been conducted on concentration and distribution patterns of soil Se in low Se, Se-enriched, and selenosis areas; however, soil Se has not been systematically studied in a watershed, especially in Se-enriched longevity region and karst area in South China. This study is carried out to explore the controlling factors of Se-enriched soils in Baishou river tributary watershed, where soils are Se-enriched, and local people have the phenomenon of longevity. The area-weighted average rock Se concentration in the watershed is 0.054 mg/kg, and there are no significant differences in rock Se concentration between different strata and between different lithological rocks. The area-weighted average concentration of Se in soils (0–20 cm) is 0.80 mg/kg, and the soil Se concentration is of high level in the watershed. Soil Se concentration decreases from upstream to downstream in the watershed, and significantly correlated with elevation. Climate is the main factor causing high content of soil Se in the watershed which lacks black rock series. The difference of clastic and carbonate parent materials in soil forming process and the physical and chemical properties (pH, OM, etc.) are the main reasons for the spatial variation of Se distribution in the watershed. The research will be beneficial to the development and utilization of Se-enriched soil in Se-enriched area.

Keywords Selenium · Se-enriched soil · Controlling factors · Longevity region · Watershed · South China

Introduction

In 1957, Schwarz and Foltz proved that selenium (Se) is an essential nutritional element for animals (Schwarz and Foltz 1957). Moderate Se shows positive biological function, while deficient and excessive Se can cause adverse effects on human health (Fordyce 2013; Li et al. 2013; Liu et al. 2013; Zhu et al. 2008). Increasing human health and longevity is of global interest (Lv et al. 2011). The research by Liu et al. (2013)

reported that concentration of Se in soils has a significant positive correlation with longevity index in China.

The Se contents varies markedly in different places due to its extremely uneven distribution in the environment (Li et al. 2008; Luo et al. 2004; Ni et al. 2016; Tan et al. 2002; Zhu et al. 2008). Many studies have been conducted on concentration and distribution patterns of soil Se in low Se, Se-enriched, and selenosis area (Yu et al. 2014; Luo et al. 2004; Zhu et al. 2008; Xing et al. 2015; Pérez-Sirvent 2010); however, soil Se has not been systematically studied in a watershed, especially in Se-enriched and longevity and karst area in South China. The study of soil Se in a watershed in Se-enriched, longevity and karst area will be beneficial to researching mechanism of longevity of residents and the difference of chemical behaviors of selenium in karst area.

In China, there are lots of Se deficiency areas, which account for approximately 72% of the national land area (Yu et al. 2014). The soils developed under tropic and subtropic conditions have higher total Se (> 0.3 mg/kg) than those under temperate humid conditions (Tan et al. 2002). However, there are also selenosis areas in China. One of the typical selenosis areas is located in Naore Village, Ziyang

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Country, Shannxi Province, and the soil Se concentration can be higher than 20 mg/kg (Luo et al. 2004); Yutangba is another typical selenosis area with very high Se content in Enshi Prefecture (Zhu et al. 2008); those two selenosis areas are very small (< 1km^2). The study by Luo et al. (2004) in Daba Region, South Qinling Mountain found that variation of soil Se contents results from variation of bedrocks from which the soils were developed. Extensive studies showed that excessive Se contents (> 3 mg/kg) in soils are mainly related to black rock series (Feng et al. 2012; Luo et al. 2004; Park et al. 2010; Zhu et al. 2008), especially related to Lower Cambrian and Ediacaran black rock series in China (Fan et al. 2011; Luo et al. 2004; Ni et al. 2016). In addition, the research by Xing et al. (2015) in Dashan region which is a Se-enriched area in China reported that the concentrations of total Se are correlated with content of clay, soil organic matter, and pH. Pérez-Sirvent (2010) also found that concentration of Se is correlated with the soil physicochemical properties and the mineralogical composition, particularly, positively with quartz percentage but negatively with calcite percentage in Murcia Region (SE, Spain). In summary, soil is a complicated historical natural continuum, and the geological setting (strata and lithology), pedogenic factors and processes, physical and chemical properties, and element geochemical behaviors are likely to affect soil Se concentration and distribution (Li et al. 2008).

Since 1999, the National Multi-Purpose Regional Geochemical Survey, the Eco-geochemical Assessment, and the Geochemical Evaluation of Land Quality have been carrying out in China (Li et al. 2014; Yang et al. 2014). As a result, a large number of Se-enriched soils have been found in South China, especially in Guangxi Zhuang Autonomous Region (Guangxi). Percentages of aging population are highest in South China (Hainan, Guangxi and Guangdong province) based on the sixth population census data of China (Liu et al. 2013), and there are the most longevity counties in Guangxi. According to the report of Guangxi geochemical evaluation of land quality (2016), 1.3453 million hm^2 Se-enriched soils were found in 21 countries, accounting for 70% of evaluation areas. The strata from Proterozoic to Quaternary in Guangxi are well developed, and the Devonian is distributed mostly widely where carbonate rocks, clastic rocks, argillaceous rocks, and siliceous rocks are marine deposits and dominated by carbonate rocks (Bureau of Geology and Mineral Resources Guangxi Zhuang Autonomous Region 1985). Some strata in the Devonian are located in regions where karst are widely developed. In addition, there are many watersheds in Guangxi. The study of soil Se content and distribution in the watershed is useful for the development of precision agriculture and Se-enriched soil resources.

In this study, we chose a watershed in Yongfu county, Guangxi, China as the study area, analyzed soil properties,

total Se in rocks, and total Se in soils, and we investigated geological setting (strata and lithology), soil-forming factors, and processes for the following purposes: (1) to understand origin and formation mechanism of Se-enriched soil and (2) to explore factors influencing the concentration and distribution of soil Se in a watershed in Se-enriched, longevity, and karst area.

Materials and methods

Geographical and geological setting

The research area is located in Baishou town (alias: longevity town), west of Yongfu county, where soils are Se-enriched, and it was granted as "Longevity Town of China" by the National Committee of Support and Nursing for the Elderly in 2007. Its central coordinate is N 25° 05′ 26″, E 109° 49′ 17″. The area is of continental mid-subtropical humid monsoon climate. According to observation data of Guilin meteorological station, with 1536.3 h sunshine per year, the area has annual average solar radiation of 41.1675 J/m^2, annual average temperature of 18.8 °C (− 3.8~38.8 °C), and annual average precipitation of 2001.2 mm. Affected by monsoon climate, the region shows distinct seasonal characteristics of dry in autumn and winter and wet in spring and summer. With respect to vegetation, the research area is of typical evergreen broad-leaved forest belt in mid-subtropical zone. According to Chinese soil genetic classification, soil types in the study area include red soil, limestone soil, and alluvium soil.

In the research area, from east to west, strata outcrops are exposed in the following order: Lianhuashan Formation (D$_1$L), Nagaoling Formation (D$_1$n), Yujiang Formation Lower (D$_2$y^1), Yujiang Formation Upper (D$_2$y^2), Donggangling Formation (D$_2$d), Rongxian Formation (D$_3$), and Holocene (Q$_h$). Early Devonian Lianhuashan Formation to Yujiang Formation are geological formations of littoral facies terrigenous clastic rocks and neritic facies sandstone and claystone. In the Middle Devonian Donggangling Formation, the seawater widely expanded due to regional transgression. The mechanical sedimentation of neritic environment in this area was replaced by biological and chemical sedimentation, leading to neritic environment carbonate formations. Late Devonian inherited the sedimentary environment of Middle Devonian. At the terminal of the watershed, there is a small Quaternary sediment distribution area (see Fig. 1).

Determining the boundary of watershed

The digital elevation model was established with vector 1:50,000 topographic maps. The boundary of Baishou river
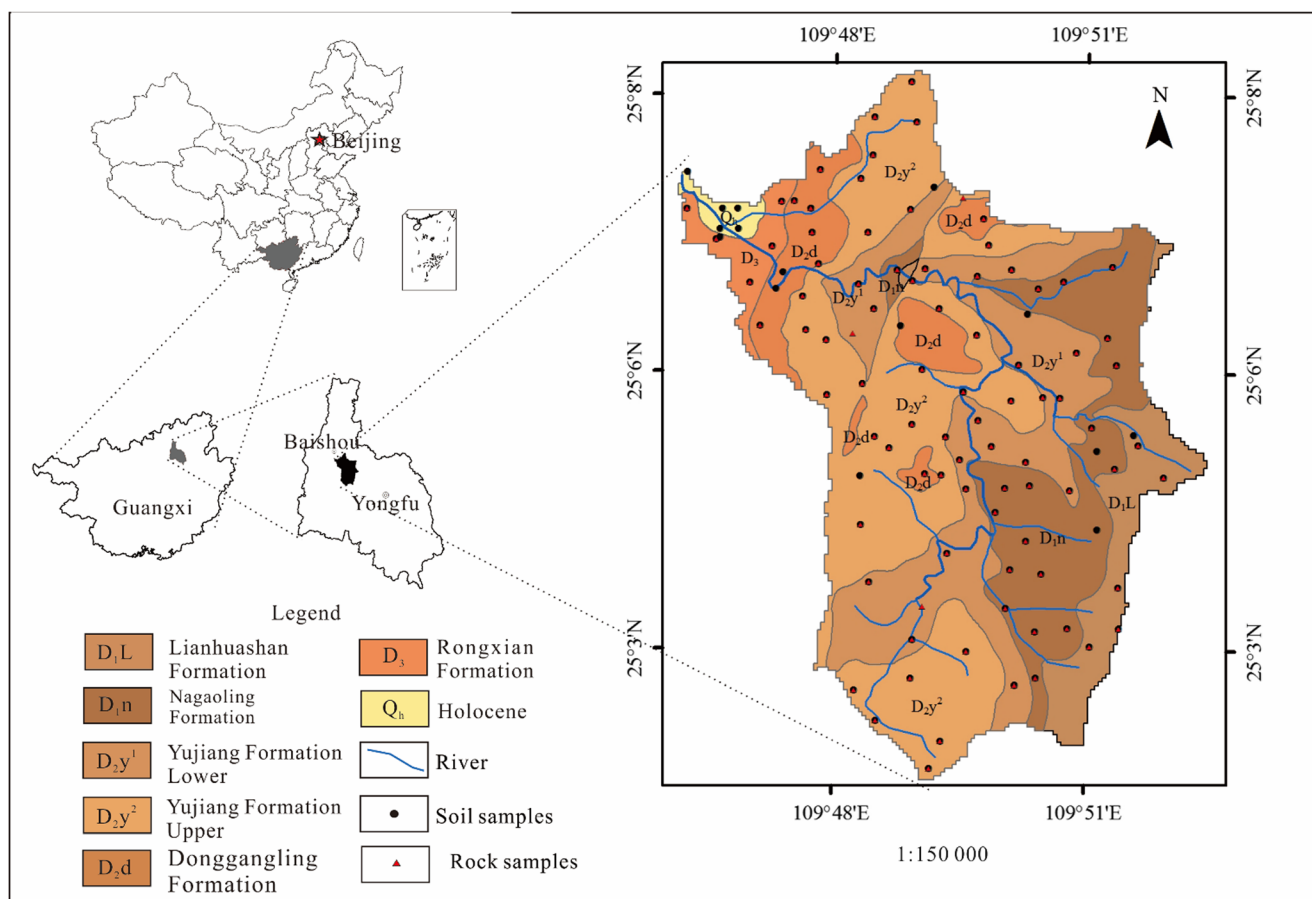
Fig. 1 The study area in Baishou river tributary watershed, Guilin City, Guangxi Zhuang Autonomous Region, China

tributary watershed was determined by hydrological analysis tool with ArcSWAT.

Sampling method and preparation

Totally, 104 top soil (0–20 cm) samples, and 89 rock samples were collected in the Baishou river tributary watershed in 2016. Soil samples were collected from various geological regions at a density of one sample per km², and fresh rock samples were collected below the same positions where soil samples were taken. The sampling sites were located far away from potential interfered areas, such as villages, roads, and garbage dumps. Coordinates and elevation of sample sites were recorded using a Garmin GPS. The spatial distribution of data points is shown in Fig. 1. The collected soil samples were loaded into a clean sack and kept in a cool, dry place; and then, dried samples were sieved by 10, 20, 60, 100, and 200 mesh nylon sieves for testing their different physical and chemical properties. The collected rock samples were washed clean with deionized water, and then they were dried at room temperature. The dried rocks were crushed and sieved by 200 mesh nylon sieve. The sieved rock and soil samples were kept in plastic automatic sealing bags for the following analysis.

Chemical analysis

Soil properties

The pH was measured in a 1:2.5 suspension of soils in non-carbon dioxide distilled water (Lu 2000). The soil organic matter (OM) was processed with heated $k_2Cr_2O_7$ oxidation and measured by $FeSO_4$ titration (Lu 2000). The physical clay (< 0.01 mm) in soils was determined by water sedimentation analysis method (Lu 2000). Major elements (CaO, MgO, Fe_2O_3, K_2O, Na_2O, SiO_2, Al_2O_3, and MnO) in soil were analyzed by X Ray Fluorescence (XRF).

Total Se in soils and rocks

The soil and rock samples were dissolved using a mixture of HF, HNO_3, and aqua regia until the solution became clear (Yu et al. 2014). After Se (VI) was reduced to Se (IV), Se concentration in solution was measured by an automated continuous flow hydride generation spectrometer (HG-AFS, AFS-9700, Beijing Kechuang Haiguang Instrument Co., Ltd., Beijing, China).

Quality control

The certified reference materials analyzed along with each batch of samples in this study included GBW-07404 (GSS-4, calcareous soil, China), GBW-07405 (GSS-5, yellow-red soil, China), GBW-07106 (GSR-4, quartz sandstone, China), GBW-07107 (GSR-5, shale, China), and GBW-07120 (GSR-13, quartz sandstone, China). The measured values for GBW-07404, GBW-07405, GBW-07106, GBW-07107, and GBW-07120 were 0.66 ± 0.01 mg/kg (certified value 0.64 ± 0.14 mg kg − 1), 1.61 ± 0.07 mg/kg (certified value 1.6 ± 0.2 mg/kg), 0.08 ± 0.02 mg/kg (certified value 0.08 ± 0.03 mg/kg), 0.078 ± 0.02 mg/kg (certified value 0.078 ± 0.023 mg/kg), and 0.021 ± 0.003 mg/kg (certified value 0.021 ± 0.004 mg/kg), respectively. The relative standard deviation in duplicated samples was < 8%, and Se recovery rate was 95~102% for soil.

CIA calculation

The soil weathering degree can be estimated by the chemical index of alteration (CIA), which is calculated using following formula (Nesbitt and Young 1982):

$$CIA = \frac{n(Al_2O_3)}{n(Al_2O_3) + n(CaO^*) + n(Na_2O) + n(K_2O)} \times 100$$

Where CaO* is the amount of CaO incorporated in silicate fraction (Nesbitt and Young 1982).

$n(CaO^*) = \min\{n(CaO^*) - [10/3\ n\ (P_2O_5)], n(Na_2O)\}$(Mclennan 1993).

Statistic and spatial analysis

A multivariate analysis was made for variables, including correlation analysis, variance analysis, and principle component analysis (PCA) using spss18.0. In this study, geostatistics and GIS technology were used to predict spatial distribution of Se in soils at unsampled locations. Co-kriging (COK) method was selected to accurately map spatial distribution of soil Se using ArcGIS10.1. For the research area containing complicated geological background, predicting Se distribution in soil using COK can produce a better approximation of the actual concentrations (Shao et al. 2016). The abnormal values were rejected using Pauta criterion method.

Results

Se concentrations and distribution of rocks in the watershed

The concentrations of rock Se vary between 0.041 and 0.093 mg/kg according to the type and age of the rock

(Table 1). The area-weighted average rock Se concentration in the watershed is 0.054 mg/kg, which is closed to the crustal and mantle values (0.05 mg/kg; Liu et al. 1984). The Se concentration of rocks in the research area is much less than that in Ziyang Naore village (pyritic black carbonaceous slate and volcanic tuff of the Early Cambrian Lujiaping Formation 22 mg/kg; Luo et al. 2004) and Yutangba (carbonaceous chert and carbonaceous shale of the Lower Permian Makou and Wujiaping Formation 6471~83,124 mg/kg; Zhu et al. 2008). One-factor Analysis of Variance was made for rock Se variance in different strata. The results show that there are neither significant differences in rock Se concentration between different strata, nor significant differences between various lithological rocks at the same stratum. The distribution of rock Se is shown in Fig. 2a.

Se concentrations and distribution of soils in the watershed

The Se contents in soils vary between 0.27 and 1.40 mg/kg, with an area-weighted average value of 0.80 mg/kg in the watershed (Table 1). According to soil Se grading system (Tan et al. 2002), the soil Se concentration is in high-Se level (0.4~3.0 mg/kg). The average concentration of Se there is 1.0 and 2.3 times higher than average soil Se values in the world (0.40 mg/kg; Fordyce 2013) and in China (0.239 mg/kg; Tan et al. 2002), respectively. The Se concentrations are also higher than the average soil Se content in Rugao (0.13 ± 0.02 mg/kg; Sun et al. 2009) which is a famous longevity town in the world.

The Co-kriging (COK) method is used to accurately map the spatial distribution of soil Se using ArcGIS10.1, and the distribution of soil Se in the watershed is shown in Fig. 2b. The result indicates that Se concentrations decrease from upstream to downstream in the watershed. The highest soil Se concentration is in the upper reaches of the tributary of Baishou river, where littoral facies terrigenous clastic rocks and neritic facies sandstone and claystone are distributed, and the area-weighted average concentrations of soil Se in clastic rock area (D_1L, D_1n, D_2y^1, D_2y^2) is 0.83 mg/kg (Table 1). Soils with medium Se concentrations are in the middle and down reaches, where the neritic environment carbonate formations are distributed, and the area-weighted average concentrations of soil Se in carbonate area (D_2d, D_3) is 0.62 mg/kg (Table 1). The Lowest Se concentration in soils is in the tributary terminus, where there are Quaternary sedimentary facies (Qh) outcrops, and the area-weighted average concentrations of soil Se is 0.45 mg/kg (Table 1). One-factor Analysis of Variance (One-Way ANOVA) and multiple comparisons were made for Se variance in clastic rock area and carbonate rock area (Table 1). The result shows, in the watershed, there are no significant differences between soil Se concentration in clastic rock area (D_1L, D_1n, D_2y^1, D_2y^1) and that

Table 1 Selenium content in rocks, soils (mg/kg) of different strata

Chron	Stratum		Relative area (%)	Lithology	Rock		Soil		
Devonian	Lianhuashan Formation (D_1L)		8	Sandstone	0.093 ± 0.032; $n = 5$	0.093	0.47–1.40 0.83 ± 0.33 A $n = 6$	0.83 A	0.81 A
	Nagaoling Formation (D_1n)		19	Claystone Sandstone Shale	0.063 ± 0.040; $n = 6$ 0.054 ± 0.018; $n = 9$ 0.074 ± 0.034; $n = 3$	0.060	0.27–1.30 0.91 ± 0.29 A $n = 20$		
	Yujiang Formation	Lower (D_2y^1)	24	Claystone Sandstone Shale	0.039 ± 0.018; $n = 7$ 0.049 ± 0.033; $n = 9$ 0.076 ± 0.056; $n = 5$	0.052	0.52–1.11 0.84 ± 0.18 A $n = 20$		
		Upper (D_2y^2)	36	Claystone Sandstone Shale	0.067 ± 0.039; $n = 2$ 0.052 ± 0.032; $n = 27$ 0.050 ± 0.014; $n = 2$	0.053	0.28–1.16 0.79 ± 0.22 A $n = 32$		
	Donggangling Formation (D_2d)		9	Dolomite Limestone	0.036 ± 0.023; $n = 5$ 0.053 ± 0.001; $n = 2$	0.041	0.42–1.01 0.67 ± 0.22 AB $n = 12$	0.62 B	
	Rongxian Formation (D_3)		3	Limestone	0.071 ± 0.049; $n = 5$	0.071	0.29–0.75 0.48 ± 0.17 B $n = 6$		
Quaternary	Holocene (Q_h)		1				0.30–0.77 0.45 ± 0.19 B $n = 5$	0.45 B	0.45 B
Average						0.054			0.80

Se concentration refers to means ± standard deviation. Average separation with columns by Duncan's multiple range test at $p < 0.01$. The uppercase letters A and B represent extremely significant levels ($\alpha = 0.01$).

in carbonate rock area (D_2d, D_3). However, there are significant differences in soil Se content between clastic rock area (0.83 mg/kg) and carbonate area (0.62 mg/kg) ($p < 0.01$).

In addition, Fig. 2b also shows that content of selenium in soils gradually decreases with the decrease of elevation, and some regions of relative low Se content appear in low-lying
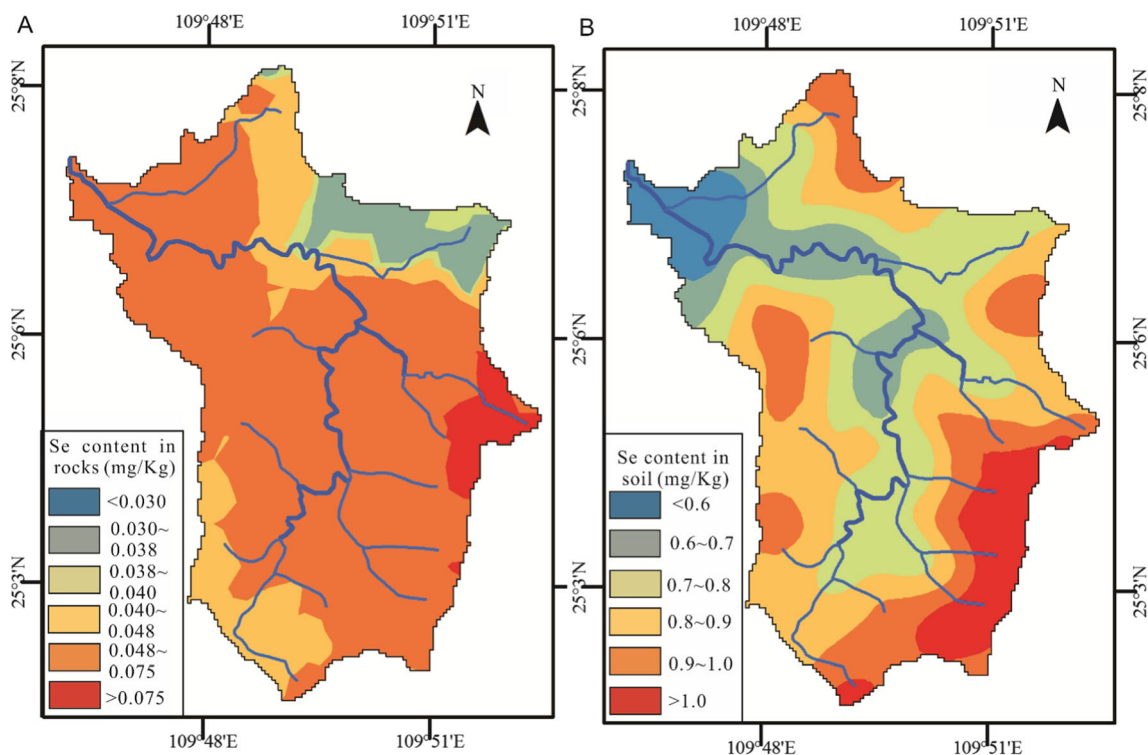

Fig. 2 The distribution map of **a** Se concentration in rocks and **b** Se concentration in soils

Table 2 Correlation coefficients between concentrations of selenium and other elements in the surface soils ($n = 101$)

Variables	pH H_2O	OM	Clay	Fe_2O_3	Al_2O_3	CaO	K_2O	MgO	Na_2O	P_2O_5	SiO_2	TiO_2	MnO
Se	−0.41**	0.30**	0.45*	0.22*	0.24*	−0.19	−0.17	−0.18	0.01	−0.29**	−0.13	0.62**	−0.37**

*Significant correlation ($p < 0.05$). **Significant correlation ($p < 0.01$).

land near the river. Pearson's correlation coefficient shows that elevation is significantly correlated with Se concentration ($r = 0.44**$, $n = 101$) in soils.

Discussion

Influence of strata and rock Se concentration on soil Se in the watershed

In the watershed, rock Se concentration is relatively low (0.054 mg/kg), which is closed to crustal and mantle values (0.05 mg/kg; Liu et al. 1984), as shown in Table 1. Previous studies showed that excessive Se concentrations(> 3.0 mg/kg) in China were mainly found in black rock series, especially in Lower Cambrain and Ediacaran black rock series, including black shale, cherts, black siliceous rock, etc. (Fan et al. 2011; Luo et al. 2004; Ni et al. 2016). The most of black shale formed under anoxic environments (Fan et al. 2011) and were characterized by high content of organic carbon. In the watershed, the major types of rocks are littoral facies terrigenous clastic rocks, neritic facies sandstone, claystone, and carbonate rock. Analysis of Variance (ANOVA) and multiple comparisons also shows that there are no significant differences in rock Se concentration in different strata and lithology in the watershed. With the process of soil formation, the impact of parent material on Se concentration gradually decreases, while the role of physical characteristic tends to increase (Matos et al. 2017). As the source of parent material, the impact of rock on soil Se concentration may become weaker, there is no

significant relationship between rock and soil Se concentrations.

However, there are significant differences in soil Se content between clastic rock area (0.83 mg/kg) and carbonate area (0.62 mg/kg) ($p < 0.01$). The result suggests that factors other than Se in rocks are responsible for Se distribution in soils in the watershed.

The effects of soil factors, soil-forming process, and physical and chemical properties on the soil Se in the watershed

With regard to climate factor, the research area is of the mid-subtropical humid monsoon climate, the zonal soil is red soil, and the major soil-forming processes are desilicification, allitization, and bioaccumulation (Zhao and Huang 2014). With emendation of CaO, the results of soils in the research area show that the average CIA is 84.38 (± 1.95). The high CIA values indicate the weathering under hot and rainy conditions, in which the degree of chemical alteration is relatively high. Under high temperature and rainy weather conditions, the clay fraction is dominated by kaolinite and sesquioxides (Fe and Al) (Matos et al. 2017). Table 2 shows that the Se concentration is significantly correlated with Al_2O_3 ($r = 0.24*$, $n = 101$), Fe_2O_3 ($r = 0.22*$, $n = 101$), and clay ($r = 0.45*$, $n = 101$). Fe and Al oxides play an important role in Se adsorption due to their being positively charged in a wide pH and their relatively high surface areas (Matos et al. 2017); meanwhile, Se can be strongly absorbed on Al and Fe oxides as inner-sphere surface complexes (Gabos et al. 2014).

Fig. 3 Box plot of **a** pH in soils developed from different parent materials and **b** content of organic matter in soils developed from different parent materials
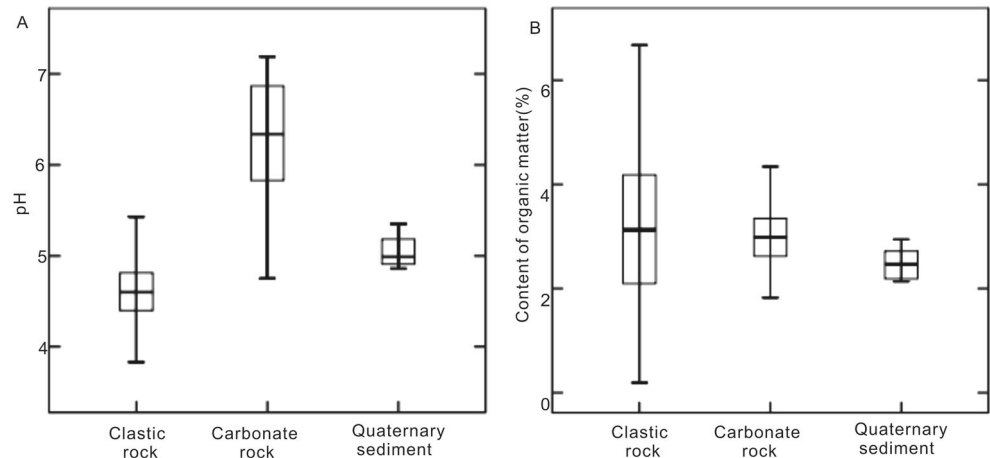
Table 3 Loading values for four main components for PCA

| Variables	PC1	PC2	PC3	PC4
Clay	0.490	− 0.584	0.082	− 0.354
Al_2O_3	0.838	− 0.473	0.025	− 0.054
CaO	0.214	0.821	0.334	− 0.246
Fe_2O_3	0.844	− 0.333	0.139	0.033
K_2O	0.775	− 0.148	0.011	0.380
MgO	0.382	0.781	0.361	− 0.234
Na_2O	0.545	− 0.412	− 0.327	0.248
P_2O_5	0.466	0.594	− 0.231	0.167
SiO_2	− 0.924	− 0.091	− 0.315	0.065
TiO_2	0.192	− 0.613	0.120	− 0.527
Elevation	− 0.317	− 0.401	0.538	0.412
pH	0.381	0.721	− 0.152	− 0.127
OM	− 0.006	0.094	0.675	0.413
MnO	0.502	0.367	− 0.382	0.336
Eigenvalue	4.350	3.711	1.456	1.230
Explained variance	31.075	26.510	10.402	8.789
Explained variance accumulated (%)	31.075	57.585	67.987	76.776

Previous study also reported that oxy-hydroxides of Al or Fe absorbed Se fraction were regarded as plant available Se in acidic non-flooded soil (Nakamaru and Altansuvd 2014). Climate factor should be responsible for the high content of soil Se in the watershed.

With regard to parent materials, Table 1 shows that soils developed from clastic rock (sandstone, claystone, and shale) have higher Se concentrations than those from carbonate (dolomite, limestone) and Quaternary sediment in the watershed. Soils developed from carbonate have a higher pH (Fig. 3a). During dissolution of carbonate rock, due to the repetition of decalcification and recalcification, the process of desilicification and allitization is delayed, leading to higher

Fig. 4 Loadings of variables in main components 1, 2, and 3 obtained in determinations made in soil sample

pH. According to Pearson's correlation coefficient, pH is significantly negatively correlated with Se concentration ($r = − 0.41**$, $n = 101$) in soils (Table 2). With decreasing of pH, selenite [Se(IV)] becomes stronger than [Se(VI)] in adsorption by amorphous iron oxyhydroxide (Balistrieri and Chao 1990). The negative charges on soil particles surface increase with rise of pH, causing electrostatic repulsion of anionic Se species and decrease of adsorption (Fontes and Alleoni 2006; Goh and Lim 2004). Parent material is the main cause of difference in soil Se concentrations between clastic and carbonate areas.

Biology is one of the important factors for the formation of soil. Although the annual yield of fresh organic matter in soil is very high under the high temperature and rainy weather conditions, the activity of microorganisms is very strong, resulting in little accumulation of soil organic matter and humus (Zhao and Huang 2014). The relatively low contents of OM is observed in Quaternary sediment distribution area (Fig. 3b). According to Pearson's correlation coefficient, OM is significantly correlated with Se concentration ($r = 0.30**$, $n = 101$) in soils (Table 2). OM is an important component that retains Se in soils, immobilizes Se by both biotic and abiotic mechanisms, and reduces its bioavailability (Li et al. 2017). The low contents of OM should be responsible for low Se concentration in soils in Quaternary sediments distribution area.

With regard to topography, Fig. 2b shows that the content of selenium in soils gradually decreases with the decrease of elevation in the watershed, and elevation is significantly correlated with the Se concentration ($r = 0.44**$, $n = 101$) in soils. The topography can indirectly affect soil formation by causing
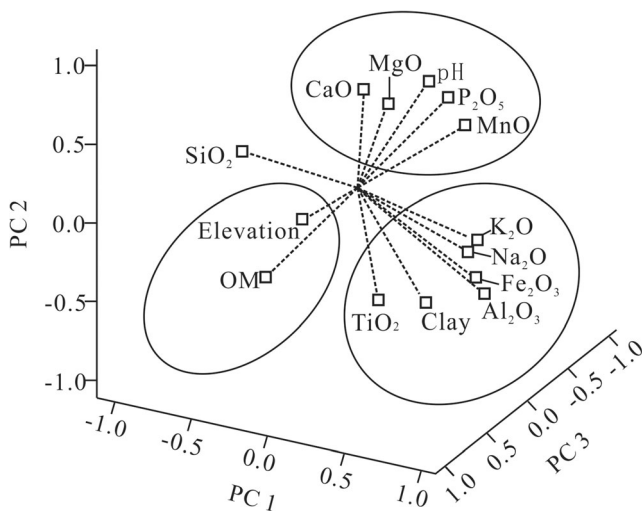
redistribution of matter and energy (Tan et al. 2002). Pearson's correlation coefficient also shows that elevation is significantly negatively correlated with the pH ($r = -0.54$**, $n = 101$), and significantly correlated with the OM ($r = 0.27$**, $n = 101$). So the topography indirectly affects soil Se concentration in the watershed.

In order to achieve a better description and interpretation of the analytical information, PCA has been performed, and the results are presented in Table 3 and Fig. 4. The results showed accumulative variance of 76.78% up to the fourth principal component with values of PC1, PC2, PC3, and PC4 equal to 31.08, 26.51, 10.40, and 8.79%, respectively (Table 3). PC1, PC2, and PC3 described the variation of all attributes satisfactorily. The loading plot for PC1, PC2, and PC3 (Fig. 4) presented three distinct clusters, in which the one formed by Al_2O_3, Fe_2O_3, TiO_2, Clay, K_2O, and Na_2O is closely related to pedogenic processes. According to the coefficient of aqueous migration (Kx, Перельман А.M. 1955), Ti is an element of weak migration. Due to surface soil is influenced by precipitation input and leaching, the positive correlation between Se and TiO_2 shows that the content of Se is related to retention of soil Se. CaO, MgO, P_2O_5, and MnO, which are closely related to pH, compose the second cluster. The third cluster is formed by elevation and OM which are of Se significantly positive correlation series. SiO_2, which is the major component of clastic rocks, shows no correlation. Those results corroborate with Pearson's correlation coefficients, as previously presented. Pearson's correlation and PCA confirmed that pedogenic factors (climate, terrain) and processes, soil physical and chemical characteristic (pH, OM), and geochemical behaviors of Se impacted soil Se distribution in the watershed.

Conclusion

This study has found that area-weighted average Se concentrations in rocks and soils in Guilin Yongfu Baishou river tributary watershed are 0.054 and 0.80 mg/kg, respectively. Soil Se concentration decreases from upstream to downstream, and it is significantly correlated with elevation in the watershed. Due to lack of high-Se rock black series, rock Se concentration is not the main factor affecting spatial variability of soil Se in the watershed. Climate is the main factor causing high content of soil Se in the watershed which lacks black rock series. The difference of clastic and carbonate parent materials in soil forming process and the physical and chemical properties (pH, OM, etc.) are the main reason for the spatial variation of Se distribution in the watershed. Due to total Se in soils may not exactly reflect the level of Se that enters food chain, the bioavailable Se and influencing factors need further study at the watershed.

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