Factors affecting trace element content in periurban market garden subsoil in Yunnan Province, China

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Abstract

Field investigations were conducted to measure subsoil trace element content and factors influencing content in an intensive periurban market garden in Chenggong County, Yunnan Province, South-West China. The area was divided into three different geomorphological units: specifically, mountain (M), transition (T) and lacustrine (L). Mean trace element content in subsoil were determined for Pb (58.2 mg/kg), Cd (0.89 mg/kg), Cu (129.2 mg/kg), and Zn (97.0 mg/kg). Strong significant relationships between trace element content in topsoil and subsoil were observed. Both Pb and Zn were accumulated in topsoil (RTS (ratio of mean trace element in topsoil to subsoil) of Pb and Zn $\geqslant 1.0$) and Cd and Cu in subsoil (RTS of Cd and Cu $\leqslant 1.0$). Subsoil trace element content was related to relief, stoniness, soil color, clay content, and cation exchange capacity. Except for 7.5 YR (yellow-red) color, trace element content increased with color intensity from brown to reddish brown. Significant positive relationships were observed between Fe content and that of Pb and Cu. Trace element content in mountain unit subsoil was higher than in transition and lacustrine units (M > T > L), except for Cu (T > M > L). Mean trace element content in calcareous subsoil was higher than in sandstone and shale. Mean trace element content in clay texture subsoil was higher than in sandy and sandy loam subsoil, and higher Cu and Zn content in subsoil with few mottles. It is possible to model Pb, Cd, Cu, and Zn distribution in subsoil physico-chemical characteristics to help improve agricultural practice.

Key words: trace elements; subsoil; topsoil; relationships

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Introduction

Knowledge of trace element (TE) content in subsoil and the factors governing their spatial distribution is of interest to (1) help diagnose soil contamination by potentially toxic elements due to human activities, and (2) map risks of soil micronutrient deficiencies for crops (Sterckeman et al., 2004). Biological availability of TE and risk to environmental and ecological systems are related to TE transformation ability. Distribution of TEs is linked to variability in soil characteristics, including TE fractions, environmental factors, distribution of human activities, and land use. Soil characteristics are related to geomorphology, soil formation processes, and climate (Wu and Wang, 1998; Zhang et al., 1994; Koretsky et al., 2007).

Trace elements in soil parent materials become active and mobile during soil weathering and formation. Because of vertical variation in influencing factors, TE content varies among soil profiles. Trace elements are transported from topsoil to subsoil through leaching and are then deposited in certain layers. Trace elements can also be returned to the topsoil via certain biological cycles or adsorbed by organic matter or clay. Therefore, subsoil TE content reflects soil formation processes and elemental cycles, and may indicate degree of contamination from anthropogenic activities. Koretsky et al. (2007) reported subsoil Zn, Co, Cr, Ni, Cu, and Pb contents were related to sulphides and organic matter content. Previous studies have also demonstrated that the vertical distributions of Cu, Zn, Cr, Pb, Cd, As, Mo, and Hg are influenced by land use, organic matter, iron oxides, and pH (McCray et al., 2001; Kabala and Szerszen, 2002; Bellett et al., 1991). Additionally, Pb and Zn contents in subsoil can be bound with iron colloids and clay-iron coatings (Van Oort et al., 2006).

In China, the most important source of trace elements in agricultural soil are wastewater irrigation, pesticides, phosphorus fertilizers, and metal-rich organic fertilizers (Zhou and Song, 2004; Guo et al., 2006; Chen et al., 2008). Approximately 25×10^6 ha of agricultural soil is contaminated by trace elements in China (Wei et al., 1999; Cheng, 2003). Most TE contamination is related to

Pb, Cd, Cu, and Hg pollution in soil. Recently, there has been growing concern regarding TE soil contamination in China, including in the Yunnan Province (Zhou and Song, 2004). Chengong County, located south-east of Kunming City and bordering Dianchi Lake, is one of the most important vegetable production areas in Yunnan Province. Agricultural production has occurred in the area for more than 2000 years, with current crops mainly consisting of rice, fruits, vegetables, and flowers. Topsoil content of trace elements such as Pb, Cd, Cu and Zn were higher in the research area than the mean TE content of soils in China (Zu et al., 2003). Very few studies have been conducted in regards to subsoil TE content in the area, however, which is important for understanding trace element sources and its consequences for crops. Our research aimed to: (1) measure TE content in subsoil, (2) trace the anthropogenic effects on subsoil TE content, and (3) assess the factors influencing the content of subsoil TEs.

1 Materials and methods

1.1 Soil samples

The general orientation of Chenggong County, Kunming Prefecture, Yunnan Province, China, is north-east to south-west. The eastern and the northern areas are the transitional or hilly middle-mountain areas, and the western area is the lakeside, forming a relief gradient from the north-east to south-west. There are three geomorphological units: lacustrine (L), transition (T) and mountain (M). Where possible, hand augering down to 80–120 cm was conducted in 2006. The research area is one of the most important areas of vegetable production in Yunnan Province, China ($24°52'00''$N–$24°54'24''$N; $102°46'20''$N–$102°52'20''$E). Field observations for soil volumes included texture by hand analysis, color (based on Munsell soil color charts), stoniness, and pH with a test kit. When the horizon at this depth was significantly different from the surface horizon, samples from the same parent material were taken. A total of 32 pairs of top/subsoil samples were collected. Topsoil samples were collected from a depth of 0 to 15 cm and the horizon of subsoil samples ranged between 40 and 60 cm in the lacustrine unit and 60 and 80 cm in the transition and mountain units. Elementary soil samples were collected to evaluate vertical differences in soil characteristics, trace element content, and the origin of contamination.

The 32 pairs were chosen as follows: 8 pairs in the lacustrine unit, 21 pairs in the transition unit, and 3 pairs in the mountain unit. In the lacustrine unit, lake sediments were clearly identified in the lakeside and subsoil. From the end of the tertiary to the early quaternary, the land in the eastern lakeside rose up and Dianchi Lake level fell, resulting in gradual de-swamping of soils. In the samples, texture varied from loam or sandy clay (clay content 23.4%–44.3%, FAO texture particle size limits: clay <0.002 mm, silt: 0.002–0.05 mm and sand: 0.05–2 mm) in topsoil to clay or sandy clay (clay content 18.8%–54.0%) in subsoil. The color of the subsoil was usually brown (10 YR (yellow-red) based on Munsell codes) and

darker than in topsoil (5–10 YR). In the transition unit, samples presented loam to loamy clay texture (clay content 44.2%–76.0%) in topsoil and clay texture (clay content 45.5%–76.0%) in subsoil, therefore, clay content was not different between top and subsoil. Color was brown (5–10 YR) in topsoil and reddish brown (2.5–5 YR) or brown (7.5–10 YR) in subsoil. Colluvium and lacustrine-alluvial mixed deposits characterized soil parent material. The texture in the mountain unit was mainly clay in topsoil (clay content 68.7%–81.0%) and subsoil (clay content 56.0%–68.3%) as a result of limestone and marlstone weathering. Color was reddish brown (2.5 YR) in both horizons.

1.2 Soil analysis

Air-dried samples were gently broken up in a porcelain mortar and passed through a 2.0 mm sieve for soil property analysis. A sub-sample was then crushed to 0.25 mm in the same mortar for carbon, total TE (Pb, Cd, Cu and Zn), and total Fe analyses.

Soil pH_{H_2O} was measured in deionized water by potentiometry (soil-solution ration 1:2.5) (Lao, 1988). Cation exchange capacity (CEC) was measured with 1 mol/L of NH_4OAC at pH 7.0 to replace cations at the soil exchange sites with NH_4^+ (Lao, 1988). Soil organic carbon (SOC) was measured after $K_2Cr_2O_7$ + H_2SO_4 digestion and titration of the excess oxidant with Mohr's salt. Trace elements (Pb, Cd, Cu and Zn) and Fe were extracted with aqua regia (3/4 HCl + 1/4 HNO_3) in a digester block and measured with an atomic absorption spectrophotometer (TAS-990, Beijing Purkinje General Instrument Co. Ltd., China).

1.3 Statistical analysis

Data were analyzed with descriptive statistics (Excel 2003). Regression analysis was used for models of trace element contents with variable soil and other factors using SPSS (13.0) at $P < 0.05$ or $P < 0.01$ levels. Only significant relationships are reported here. Boxplots of data distribution were analyzed using Statistica 6.0.

2 Results

2.1 Trace element contents in topsoil and subsoil

The TE contents in topsoil, shown as mean ± SE (standard errors) (range) were Pb: (85.1 ± 13.1) mg/kg (30.9–212.4 mg/kg), Cd: (1.01 ± 0.97) mg/kg (trace–4.0 mg/kg), Cu: (129.1 ± 54.5) mg/kg (25.0–217.5 mg/kg), and Zn: (113.3 ± 36.8) mg/kg (43.1–220.3 mg/kg). Mean contents of Pb and Zn in topsoil were higher than in subsoil, and mean contents of Cd and Cu were similar in topsoil and subsoil.

Subsoil trace element contents are shown in Fig. 1. Content of Pb was (58.2 ± 20.8) mg/kg and ranged from 33.4 to 116.8 mg/kg. In 50.1% of samples, Pb content was between 50 and 100 mg/kg. In 9.4% of samples (located in the mountain unit), Pb content was >150 mg/kg. Content of Cd was (0.89 ± 0.80) mg/kg and ranged from trace
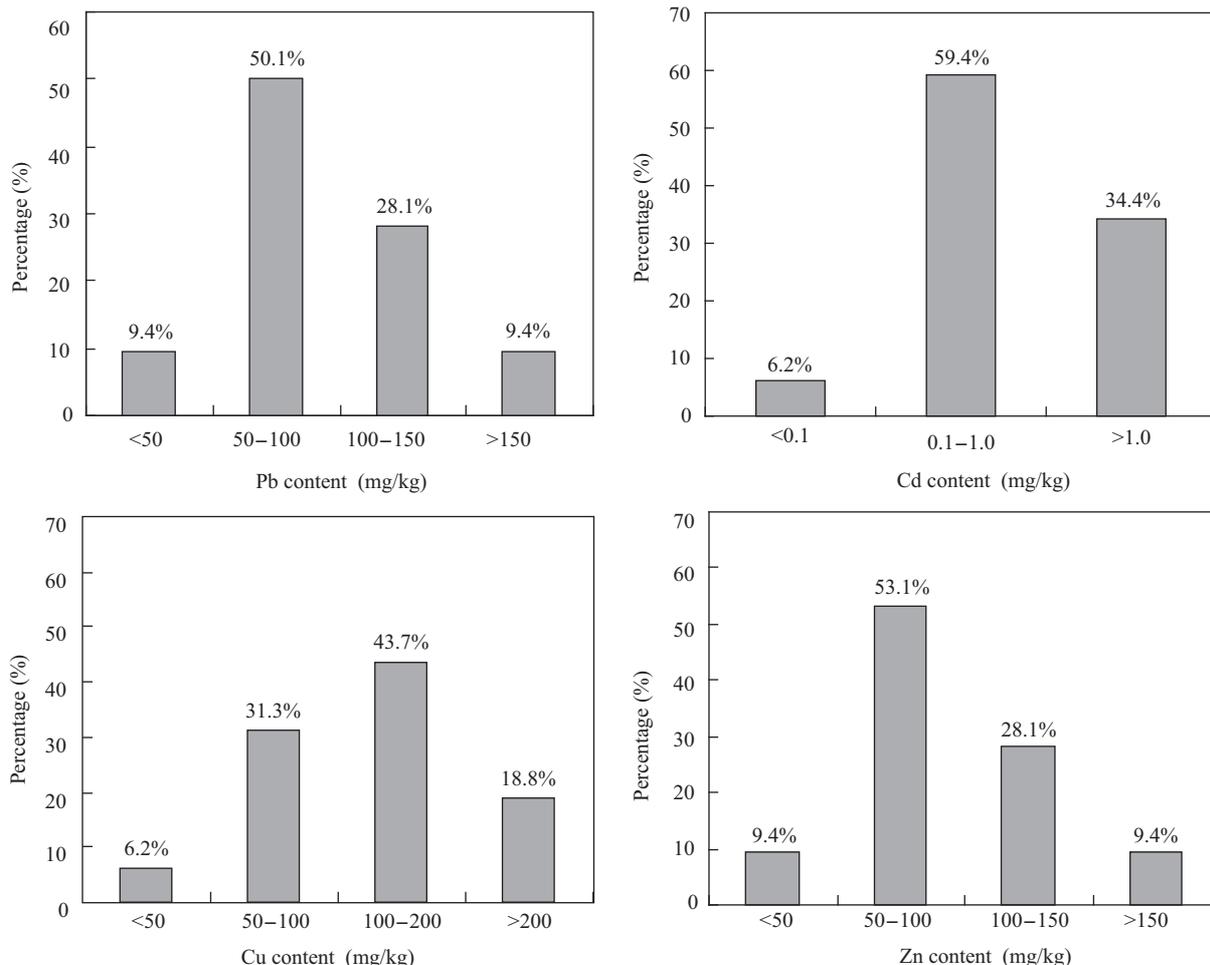
Fig. 1 Frequency distributions of Pb, Cd, Cu, and Zn content for subsoil samples in the research area.

to 2.30 mg/kg. In 59.4% of samples, Cd content was between 0.1 and 1.0 mg/kg and was ⩾ 1.0 mg/kg in of 34.4% samples, distributed in all three units. Content of Cu was (129.2 ± 65.9) mg/kg and ranged from 26.8 to 218.2 mg/kg. In 43.7% of samples, Cu content was between 100 and 200 mg/kg, and in 31.3% of samples was between 50 and 100 mg/kg. In 18.8% of samples, located in the transition unit, Cu content was > 200 mg/kg. Content of Zn was (97.0 ± 36.6) mg/kg and ranged from 15.7 to 176.3 mg/kg. In 53.1% of samples, Zn content was between 50 and 100 mg/kg, and in 28.1% of samples was between 100 and 150 mg/kg. In 9.4% of samples, Zn content was >150 mg/kg.

2.2 Relationship of trace element contents between top-soil and subsoil

The ratio of mean trace element content in top-soil/subsoil (RTS) was determined. Mean RTS of Pb and Zn were 1.47 (0.74–11.51) and 1.38 (0.76–8.13), respectively. The RTS of Pb and Zn in 84.4% of samples were ⩾1.0. Mean RTS ratios of Cd and Cu were 1.30 (0.70–8.43) and 1.03 (0.73–1.65), respectively. Approximately 71.9% of Cd samples had RTS ⩽ 1.0, while 78.3% of Cu samples had RTS ⩽1.0 (Fig. 2).

Strong significant positive correlations were found between Cd, Cu, and Zn contents in topsoil and subsoil (Table 1). No significant relationship between Pb content
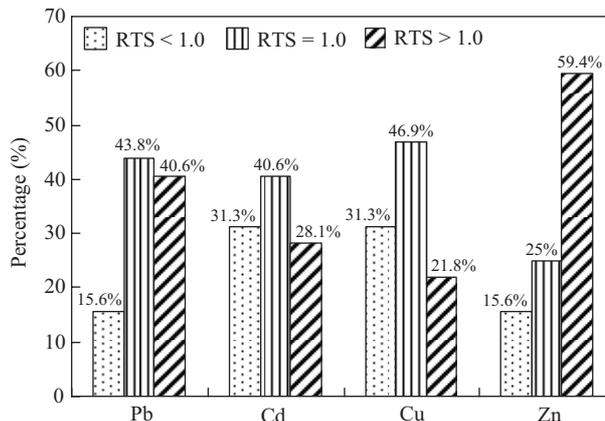

Fig. 2 Frequency distributions of relative topsoil/subsoil (RTS) for Pb, Cd, Cu, and Zn.

Table 1　Relationships between trace element (TE) contents in topsoil and subsoil

TE	Equation	R^2	F	P	N
Pb*	$y = 17.09 + 0.67x$	0.745	81.83	<0.001	31
Cd	$y = 0.04 + 1.10x$	0.816	137.06	<0.001	32
Cu	$y = 12.17 + 0.91x$	0.895	262.95	<0.001	32
Zn	$y = 37.63 + 0.78x$	0.605	45.86	<0.001	32

* Outlier sample when Pb 212.4 mg/kg in topsoil was excluded.

in topsoil and subsoil was observed. A significant positive relationship between Pb content in topsoil and subsoil
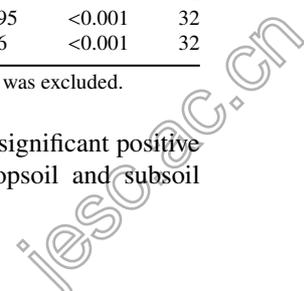
was observed, however, when outlier samples (Pb: 212.4 mg/kg) were excluded.

2.3 Effect of soil morphological properties on subsoil trace element contents

2.3.1 Relief

In the lacustrine unit, mean TE content in subsoil was Pb: 4l.55 mg/kg, Cd: 0.72 mg/kg, Cu: 82.4 mg/kg, and Zn: 69.4 mg/kg. In three out of eight samples closer to Dianchi Lake, mean TE content (Pb: 45.7 mg/kg, Cd: 0.81 mg/kg, Cu: 83.2 mg/kg, and Zn: 79.1 mg/kg) was higher than samples located further from the Lake (Pb: 43.2 mg/kg, Cd: 0.57 mg/kg, Cu: 80.2 mg/kg, and Zn: 65.2 mg/kg).

Mean TE content in the transition unit was Pb: 53.4 mg/kg, Cd: 0.74 mg/kg, Cu: 160.8 mg/kg, and Zn: 94.8 mg/kg. Mean TE content in samples originating from two hilltops were lower than samples originating from the intermediate foot slope.

Mean TE content in the mountain unit was Pb: 108.20 mg/kg, Cd: 2.1 mg/kg, Cu: 114.8 mg/kg, and Zn: 155.00 mg/kg. The TE content in the mountain unit was higher than in the lacustrine and transition units (M > T > L), except for Cu (T > M > L) (Fig. 3).

2.3.2 Parent materials and stoniness

Stoniness was < 15% in subsoil. The Pb and Cd contents (45.8 and 0.45 mg/kg, respectively) were lower with no stones than with a stone charge (59.5 and 0.94 mg/kg, respectively). For Cu and Zn, however, the opposite result was found, with Cu (174.9 mg/kg) and Zn (118.6 mg/kg) content higher with no stones than with a stone change (Cu: 124.3 mg/kg and Zn: 94.8 mg/kg).

Sandstone and limestone were the main types of stones found in the subsoil. Mean TE content in samples with sandstone were lower than in samples with limestone, except for Cu. The other "stoniness" was shale, in which mean TE content of subsoil was lower than with sandstone and limestone, except for Zn (Fig. 4).

2.3.3 Color

According to field observations, color of subsoil was brown or reddish brown, including 10, 7.5, 5, and 2.5 YR based on Munsell Color Codes. In 28.1% of samples, color was 10 YR with mean Pb: 46.8 mg/kg, Cd: 0.7 mg/kg, Cu: 102.5 mg/kg, and Zn: 79.9 mg/kg. Color in 12.5% of samples was 7.5 YR with mean Pb: 51.6 mg/kg, Cd: 0.88 mg/kg, Cu: 160.3 mg/kg, and Zn: 118.6 mg/kg. Color in 12.5% of samples was 5 YR, with mean Pb: 54.3 mg/kg, Cd: 0.72 mg/kg, Cu: 132.8 mg/kg, and Zn: 93.4 mg/kg. In
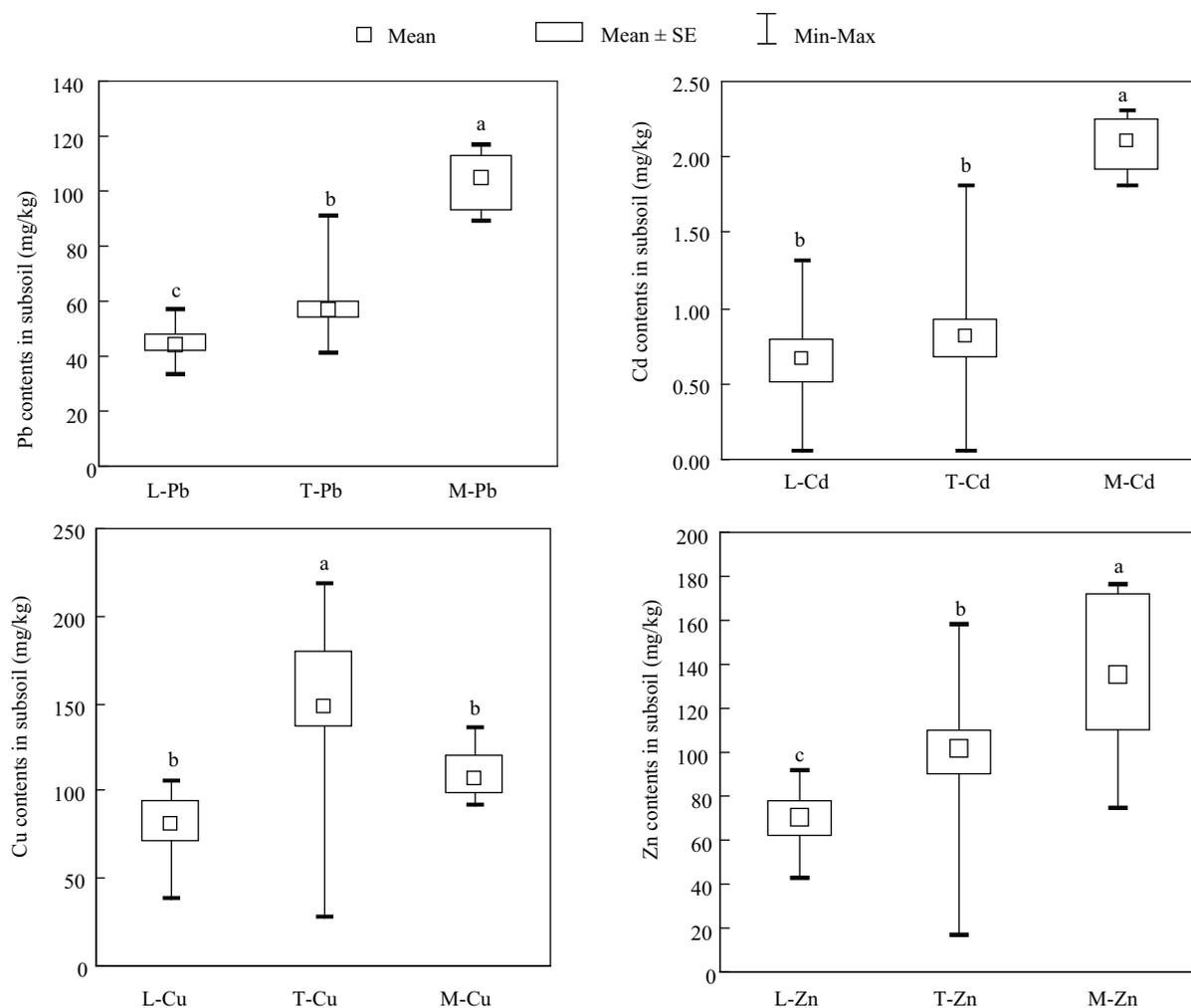

Fig. 3 Mean Pb, Cd, Cu, and Zn content in subsoil among physiographic units (L: lacustrine; T: transition; M: mountain). a, b and c refer to statistical tests on the means.
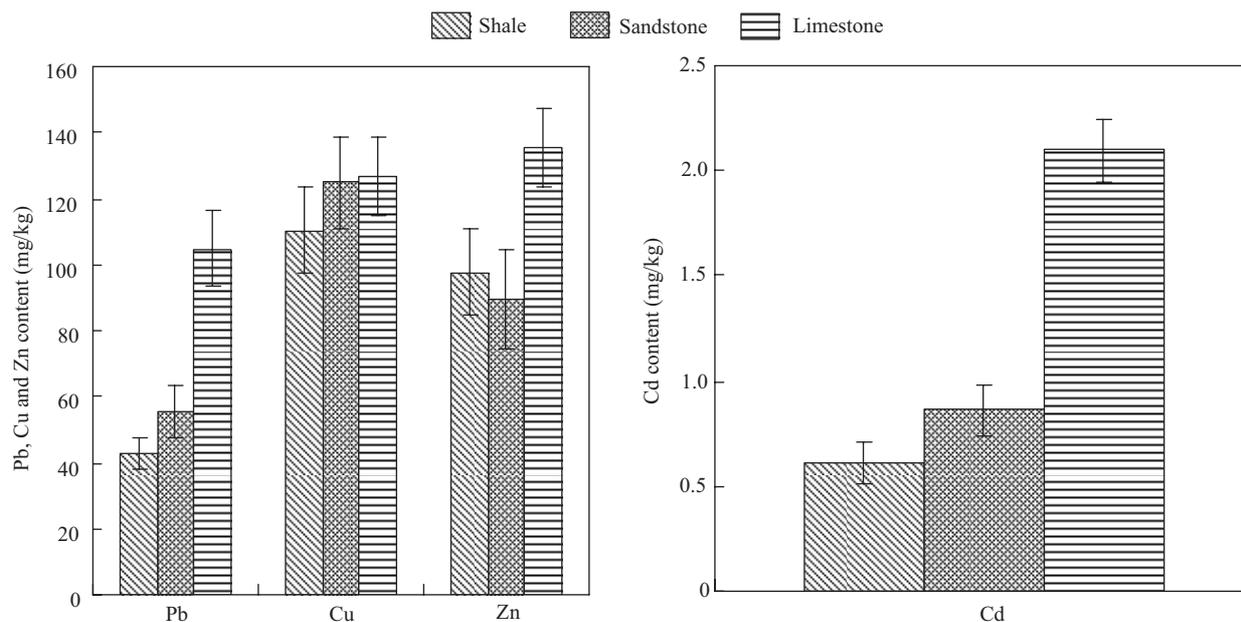
Fig. 4   Mean Pb, Cd, Cu, and Zn content in subsoil according to nature of stone lithology.
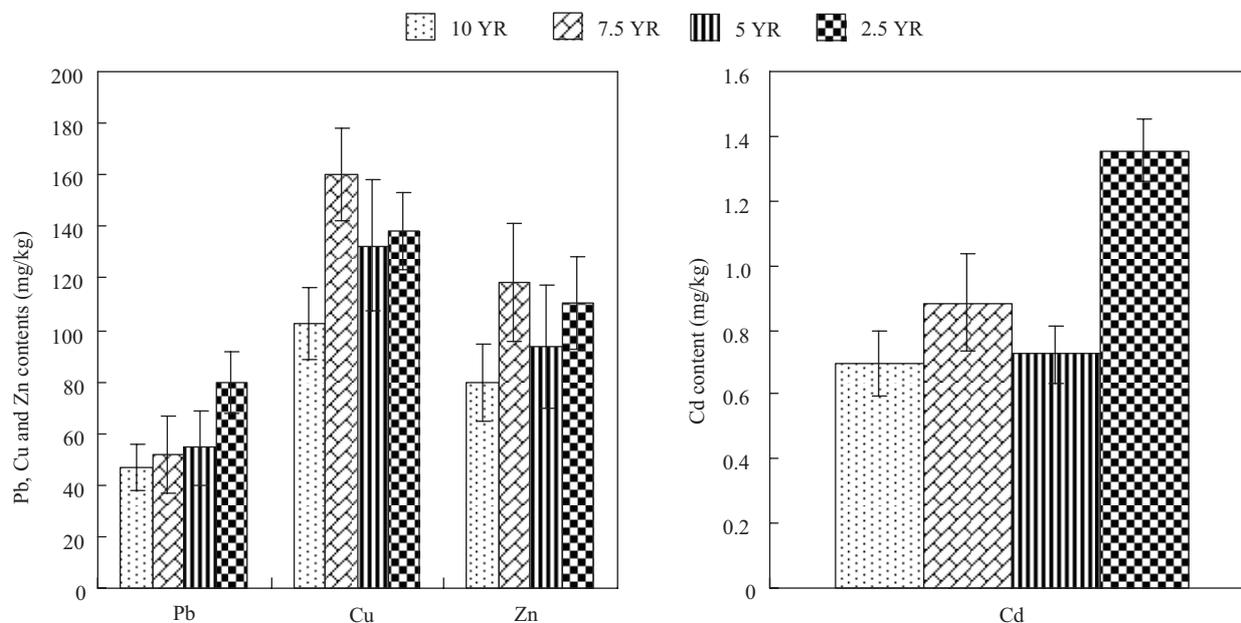

Fig. 5   Mean Pb, Cd, Cu, and Zn content in subsoil according to soil color.

25% of samples, color was 2.5 YR, with mean Pb: 79.9 mg/kg, Cd: 1.36 mg/kg, Cu: 138.2 mg/kg, and Zn: 110.3 mg/kg.

Relationships between TE content and color showed that 10 YR samples had the lowest TE content, 2.5 YR samples had the highest Pb and Cd contents, and 7.5 YR samples had the highest Cu and Zn contents. Except for 7.5 YR samples, TE content increased with color from brown to reddish brown (Fig. 5). The TE contents in subsoil samples with intense colors (7.5 YR + 10 YR) (Pb 48.3 mg/kg, Cd 0.76 mg/kg, Cu: 120.3 mg/kg, and Zn: 91.8 mg/kg) were lower than with pallid colors (5 YR + 2.5 YR) (Pb: 65.0 mg/kg, Cd: 0.99 mg/kg, Cu: 135.09 mg/kg, and Zn: 100.5 mg/kg).

As red color is related to soil Fe_2O_3 content, the relationships between TE content and Fe_2O_3 content were

analyzed. The Fe contents in topsoil and subsoil were (8.93 ± 2.65)% and (9.09 ± 3.31)%, respectively. Significant positive relationships were observed between Fe content and Pb ($Y_{Pb} = 25.54 + 3.60X_{Fe}$, $F = 14.6$, $R^2 = 0.327$, $P < 0.01$, $n = 32$) and Cu ($Y_{Cu} = 48.68 + 8.85X_{Fe}$, $F = 10.86$, $R^2 = 0.266$, $P < 0.01$, $n = 32$) content.

2.3.4 Texture

In 20 out of 32 samples (62.5%), subsoil texture was clay. Mean TE content in samples with clay texture were Pb: 59.7 mg/kg, Cd: 0.85 mg/kg, Cu: 129.2 mg/kg, and Zn: 93.2 mg/kg, which were higher than in samples with sandy texture (Pb: 42.6 mg/kg, Cd: 0.55 mg/kg, Cu: 82.1 mg/kg, and Zn: 71.0 mg/kg) and in samples with sandy loam texture (Pb: 37.6 mg/kg, Cd: 0.68 mg/kg, Cu: 85.8 mg/kg, and Zn: 91.7 mg/kg).

2.3.5 Mottles

According to subsoil mottles, samples were classified into two groups, one with many black, red, or yellow mottles due to organic matter and redox reactions, and the other with few mottles. Mean TE content for the mottles groups were Pb: 52.6 mg/kg, Cd: 0.70 mg/kg, Cu: 142.1 mg/kg, and Zn: 97.4 mg/kg, which were lower than for Cu (161.5 mg/kg) and Zn (108.8 mg/kg) in samples with few mottles and higher than for Cd (0.57 mg/kg) and similar for Pb (52.8 mg/kg).

2.4 Effect of chemical properties on subsoil trace element content

Subsoil mean pH was 6.4 and ranged from 4.3 to 8.2. The CEC and SOC in subsoil were 20.22 cmol/kg (7.87–30.50 cmol/kg) and 0.6 mg/kg (0.1–1.6 mg/kg), respectively. Positive linear relationships were observed between CEC and TE content (Fig. 6).

No significant relationships between TE, pH, and SOC were observed. Mean TE contents in subsoils with pH ⩽ 6.5 were Pb: 60.3 mg/kg, Cd: 0.91 mg/kg, Cu: 142.2 mg/kg, and Zn: 101.1 mg/kg, which were higher than in samples with pH >6.5 (Pb: 52.9 mg/kg, Cd: 0.87 mg/kg, Cu: 95.5 mg/kg, and Zn: 86.5 mg/kg). Mean TE content in subsoil with SOC ⩽ 0.5 were Pb: 65.3 mg/kg, Cd: 0.96 mg/kg, Cu: 126.0 mg/kg, and Zn: 91.7 mg/kg, which were higher than in samples with SOC > 0.5 for Cu (133.8 mg/kg) and Zn (104.7 mg/kg), lower than for Pb (65.3 mg/kg), and similar for Cd (0.96 mg/kg).

3 Discussion

Variety and distribution of TE in soils mainly depend on pedological factors (relief, soil parent materials, soil texture and soil types) and land-use practices (irrigation, cultivation, fertilizer and pesticide rates, and urban and industrial deposits) (Romic and Romic, 2003; Panichayapichet et al., 2007; Fan, 2007). Consequently, subsoil TE content is influenced by soil parent materials, climate, clay content, pH, organic matter, agricultural practices, and exogenous TE.

Background values of TE in Kunming Prefecture are Pb: 43.3 mg/kg, Cd: 0.18 mg/kg, Cu: 44.6 mg/kg and Zn: 99.2 mg/kg (Duan et al., 2006). Compared with these values, Pb, Cd, and Cu contents in subsoil from the present study were higher and Zn was similar. It has been suggested that TE content in subsoil is related to anthropogenic activities in addition to parent materials. Accumulation of TE in topsoil widely exists in cultivated soil, which is linked to climate, anthropogenic activities, and organic matter accumulation in topsoil (Heinrich, 2007). In arid zones, exogenous TE mainly accumulates in topsoil and leaching is weak, due to the dry climate and the draw up of TE to topsoil by biological cycles. Organic matter is also a crucial factor in TE binding in topsoil (Kabala and Scerszen, 2002).

$Y = 37.76 + 1.02X,\ F = 3.70, R = 0.352, P < 0.05$

$Y = -0.039 + 0.047X,\ F = 3.70,\ R = 0.352, P < 0.01$

$Y = 55.49 + 3.68X,\ F = 6.18, R = 0.414, P < 0.05$

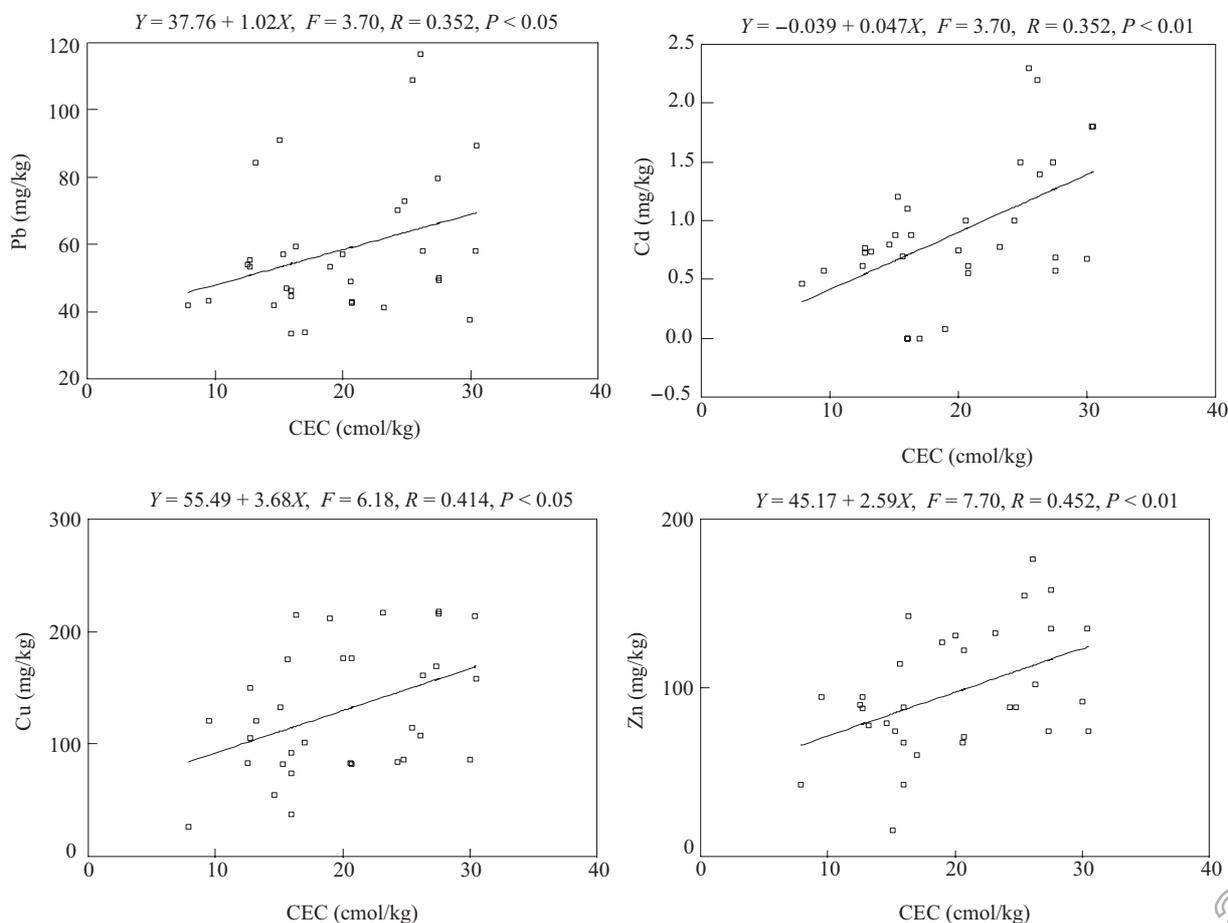$Y = 45.17 + 2.59X,\ F = 7.70, R = 0.452, P < 0.01$

Fig. 6   Relationships between CEC and Pb, Cd, Cu, and Zn content in subsoil.

Significant positive relationships between TE content in topsoil and subsoil were observed within the research area. Accumulation of TE content in subsoil depended on TE content to a certain extent, although this was dependent on TE mobility (Sterckeman et al., 2004). Mean RTS of Pb and Zn were 1.47 and 1.38, respectively. Compared with the ratio of TE content to Fe content (TE/Fe), the ratios of Pb/Fe and Zn/Fe in topsoil were higher than in subsoil. Ratios of Pb/Fe and Zn/Fe in topsoil to subsoil were 1.57 and 1.41. Exogenous Pb and Zn are considered TE sources in topsoil. Previous research has indicated that TE content decreases with soil depth increase (Wang et al., 2005) and that most TE accumulation occurs at a depth of 0–50 cm in topsoil, depending on land-use (Zhang and Gong, 1996). On the other hand, however, TE content in subsoil is mainly related to background values (Xu et al., 1999). Mean content of Cd and Cu were almost the same in topsoil and subsoil. Ratios of Cd/Fe and Cu/Fe in topsoil were also similar to that in subsoil and ratios of Cd/Fe and Cu/Fe in topsoil to subsoil were 1.16 and 1.08, respectively. The TE content in parent material was one of the most important factors influencing soil TE in this area. Both Cd and Cu were easily transferred under the influence of precipitation and anthropogenic activities. In particular, Cu and Cd were more readily transferable in soil with high moisture and ground water in the lacustrine unit. These trace elements have strong affinity with organic matter and accompany organic matter distributing along the profile. It has been suggested that Cd and Cu can be leached with soil colloids and solubilize and migrate in soil solution (Sterckeman et al., 2004; Zu, 2008).

Subsoil TE content has relationships with soil properties, such as relief, stoniness, parent materials, color, texture, and mottles. Results from our study showed that TE content increased with color intensity from brown to reddish brown, except for 7.5 YR. Reddish brown soils have abundant Fe_2O_3 to fix TE and low pH, which should be linked to high TE content. The observed positive relationships between Fe and Pb and Cu could explain the color, which was a suitable indicator for redox conditions and TE mobility. Soil pH significantly influences mobility and release of TE in soils, as well as vertical distribution in soil profiles (Zhao et al., 2001; Bellett et al., 1991). The relationship between pH and trace elements might be an indirect expression of colloids on proton activity (Sterckeman et al., 2004). The adsorption and desorption of TE can be affected by pH (Guo et al., 2003; Rautengarten et al., 2004). Available TE content (soluble, exchangeable and carbonate bound contents) decreases with pH increase, and the Fe-Mn oxide bound TE fraction has a significant positive relationship with soil pH (Wang and Zhou, 2003; Zhang et al., 2003). Although no significant relationships between TE content and pH were observed in the current study, TE content in soils at pH ⩽6.5 were higher than that at pH >6.5. Soil pH can affect organic matter constituents and oxide colloids, which cause variability in TE fractions (Kirkham, 1977). When pH is low, the ratio of fulvic acid content in organic matter is high, which can result in TE leaching to subsoil and TE content decreasing in topsoil

(Wang et al., 2005).

Considering the relief, changes in TE content in subsoil were linked to sample sites, parent materials, textures, and stoniness. For example, TE content in samples close to Dianchi Lake was higher than those far from the lake in the lacustrine unit. Mean TE content in samples located on the hilltop were lower than those located on the foothills in the transition unit (except for Pb), which was likely related to human activities and soil erosion from hilltop to foot slope. Geographic setting also influenced vertical TE distribution. Previous research has shown that TEs are mainly distributed at a depth of 0–50 cm due to wastewater irrigation, sludge application, and atmospheric deposits in Fujian Province (Wang et al., 1996). Studies have also demonstrated that TE distribution in vegetable soil is influenced by transportation (Pb), municipal domestic wastewater (Zn), wastewater irrigation (Zn), organic matter application (Cu), and geomorphology (Cd) in Nanjing (Zhang et al., 2005). Cao (2004) described vertical distribution characteristics of TE contamination in soil profiles for eight landscape units in Tianjin City, with TE (As, Pb, Mo, Hg and Cd) content varying in soil profiles heavily contaminated by Cd, Hg, Cu and Pb.

Parent material was the key factor controlling TE distribution in Tianjian City (Xu et al., 1999; Cao, 2004). The TE in soils derived from colluvial deposits of igneous, granite, and sedimentary rock parent materials are easily leached, and TE content in C layers are higher than in A layers because of strong weathering. The TE content in soils derived from alluvial parent materials are 1–1.5 times higher than from residual parent materials (Cao, 2004). In the present research area, sandstone and limestone were the main types of stones in subsoil, besides shale. The TE content was in the order of limestone > sandstone > shale, with high Pb and Cd contents in subsoil with stoniness <15%, and high Cu and Zn contents in subsoil with no stones. Similarly, Cu and Zn in subsoil with few mottles were higher than in the group with many mottles. Therefore, Cu and Zn exhibited different behavior in subsoil than Pb and Cd, and were linked to stoniness and mottles. In addition, Pb and Cd were maintained more strongly with weathering products.

Significant positive relationships between CEC and TE content were observed. CEC is influenced by soil clay content and SOC (Sterckeman et al., 2004). Mean TE content in subsoil with clay texture was higher than in subsoil with sandy or sandy loam texture, which was relative to TE fixed to clay. The distribution of particle size in soil affects adsorption, mobility, and transportation of TE, especially clay content in soil (Sterckeman et al., 2004; Voegelin et al., 2003). Additionally, physical and chemical adsorptions increase with clay content in soil. Physical clay (< 0.01 mm) content have significant negative relationships with organic and Fe-Mn oxide bound TE in Fluvio-aquic soils (Liu et al., 2003). In addition, TE content in different profile layers increases with clay content. The varying tendency of Co, Cr, and Ni content in the profile layer is associated with the fine (< 20 μm) mineral fraction, Sn, Ti and Zn with the fine mineral fraction and organic

Table 2   Summary for factors influencing subsoil TE content in the research area

Factors	Pb	Cd	Cu	Zn
Pedological factors	M > T(L);	M > T > L;	T > M > L;	M > T > L;
	High on hilltop;	High on hilltop;	High on hilltop;	High on hilltop;
	2.5 YR >10 YR;	2.5 YR > 10 YR;	2.5 YR > 10 YR;	2.5 YR > 10 YR;
	Stoniness > no stoniness	Stoniness > no stoniness		
	Limestone > sandstone > shale;	Limestone > sandstone > shale;	Limestone sandstone > shale;	Limestone > sandstone > shale;
	Clay > sandy (loam).	Clay > sandy (loam);	Clay > sandy (loam);	Clay > sandy (loam).
		Many mottles > few mottles;		
		RTS < 1.	RTS < 1.	
Land-use practice factors	Positive relationship with CEC;	Positive relationship with CEC;	Positive relationship with CEC;	Positive relationship with CEC;
	Accumulation near Lake;	Accumulation near Lake.	Accumulation near Lake.	Accumulation near Lake;
	RTS > 1.			RTS > 1.

L: lacustrine unit; T: transition unit; M: mountain unit.
CEC is a pedological characteristic partly due to soil genesis and partly influenced by inputs (organic matter).

matter, and Cd, Cu and Pb with organic matter in France. The higher TE content was due to their higher content in alumino-silicates (clay) and Fe oxides and hydroxides (Sterckeman et al., 2004). Additionally, because TEs have affinity with organic matter, they may move down the profile accompanying organic matter (Kabala and Scerszen, 2002). Tessier extractions indicate most non-residual Pb, Zn, Cu, Cr, Co and Cd are associated with the organic fraction of the sediments at all profile depths (Tessier et al., 1979; Koretsky et al., 2006). In the current research area, excessive organic manure has been applied to soil during recent years (Zu, 2008). Although no significant positive relationships between SOC and TE content were observed, Cu and Zn content in soils with SOC $\geqslant$ 0.5 g/kg were higher than in samples with SOC < 0.5 g/kg. The effect of SOC on TE content plays an important role, including ion exchange adsorption and chelation. Organic matter is an adsorbent, which decreases or changes the activity and transportation of TE in soil (Kabala and Scerszen, 2002; Chen and Chen, 1996) and TE can be absorbed on organic colloids. Voegelin et al. (2003) determined that organic matter may modify the activity of TE in soil, depending on adsorption of humic acid and solubility of TE-humic acid chelated substances. High molecular organic compounds (humins) adsorb TE and decrease the mobility and biological activity of TE.

In summary, the factors influencing subsoil TE content in the research area were pedological factors (relief and soil parent materials) and land-use practices (anthropogenic activities) (Table 2).

4 Conclusions

Mean TE content in subsoil was determined for Pb: 58.2 mg/kg, Cd: 0.89 mg/kg, Cu: 129.2 mg/kg, and Zn: 97.0 mg/kg. Strong significant relationships between TE contents in topsoil and subsoil were observed, mean Pb and Zn contents in topsoil were higher than in subsoil, and most RTS of Pb and Zn were $\geqslant$1.0. Mean Cd and Cu contents were similar in topsoil and subsoil, and most RTS ratios of Cd and Cu were $\leqslant$1.0.

Except for 7.5 YR, TE content increased with color from brown to reddish brown. The TE contents in subsoil in the mountain unit was higher than in the lacustrine and transition units (M > T > L), except for Cu (T > M > L). Mean TE contents in subsoil samples with limestone were higher than samples with sandstone and shale. Mean TE contents in subsoil samples with clay texture were higher than in samples with sandy or sandy loam texture. Both Cu and Zn contents in subsoil with few mottles were higher than with many mottles, while Pb was similar and Cd was lower.

Pedological factors, land-use practices, wastewater irrigation, sludge application, city dust precipitation, and other anthropogenic activities were the predominant sources of subsoil TE content. Therefore, relief and soil parent materials in land use management and anthropogenic activities in agricultural production should be considered as they all influence trace element content in soil. Although many models exist for assessing TE mobility in soil, it is important to pay attention to their food chain transfer considering their effect on human health.

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