Assessment of Heavy Metal Contents in Surface Soil in the Lhasa–Shigatse–Nam Co Area of the Tibetan Plateau, China

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Abstract Eight important heavy metals (As, Cr, Cu, Ni, Pb, Zn, Mn, and Hg) were investigated in surface soil samples collected from the Lhasa–Shigatse–Nam Co region, Tibetan Plateau, China. The mean contents of As, Cr, Cu, Ni, Pb, Zn, Mn, and Hg in the samples were 39.5, 57.4, 28.5, 48.2, 15.7, 79.2, 637 and 0.0175 mg/kg, respectively. All metals were divided into three clusters by cluster analysis. The results of geoaccumulation index indicated that no samples were polluted by Cr, Pb, Zn, and Mn, and samples were polluted with As, Cu, Ni, and Hg to different degrees. All surface soils had a low ecological risk with potential ecological risk index below 150, indicating a low ecological risk. As, Pb, and Hg were the primary contributors to potential ecological risk.

Keywords Heavy metal · Cluster analysis · Geoaccumulation index · Potential ecological risk index

The Tibetan Plateau is bordered to the south by the Himalayan mountain range. At an average altitude of more than 4,500 m above sea level (m.a.s.l.), and encompassing an area of about 2.5 million km², it is the highest and one of the largest plateaus in the world. Because of its special geographical location, and for sociohistorical reasons, the exploration and use of its natural resources has remained very low. The ecological environment of the Plateau has

basically retained its original state. To date, Tibet is still one of the places least affected by human activities and pollution in the world. Because of its unique landform, fragile ecosystem, and special monsoon circulation, the Tibetan Plateau has been regarded as a region sensitive to the impacts of global contaminants (Huang et al. 2012). More recently, this fragile ecological environment has been subject to stressors in recent years as a result of rapid economic development, urbanization, and the completion of the Qinghai–Tibet railway, which has led to an influx of visitors to Tibet.

The soil environment in this region is interfacial, heterogeneous, and changing. Basic characteristics of soil contamination differ from those of air and water, such as concealment and hysteresis, accumulation, and irreversibility (Sun et al. 2010). The soil plays an important environmental role and acts as a reservoir or sink for many kinds of pollutants. Pollutants stored in soil can be transferred to other ecosystems such as groundwater or crops, and can consequently affect human health (Sheng et al. 2012). Heavy metals have attracted much attention (Li et al. 2008, 2012; Ma et al. 2009; Sheng et al. 2012; Rizo et al. 2011) because of their toxicity and persistence in the environment. Contents of heavy metals in soils, which are determined on the basis of the total metal content of soil samples, are widely used in many countries as a criterion of soil pollution (Sheppard et al. 1992).

For the present study, we collected surface soil samples from an area of the Tibetan Plateau to determinate the contents of some important heavy metals, to explore the possible sources, and to assess the ecological risk of metal contaminants. Acquiring these data at such high elevations enabled us to conduct an assessment of the behavior of these metals in the pristine environment of the Tibetan Plateau.

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Materials and Methods

The soil samples were collected during a scientific expedition to the Lhasa–Shigatse–Nam Co area of Tibet. This area is a famous tourist route and there are some residents along the road. The locations of the sample sites, between 28°52′47.11″N and 30°34′12.88″N, and between 89°30′35.29″E and 91°5′11.73″E, are shown in Fig. 1.

Sample S1 was located near Nam Co, which is the highest salt lake in the world. S2 and S3 were located near Yamdrok Tso, which is another high plateau lake. S4 and S5 were situated near a village along highway S307, and S6, S7, and S8 were located along highway G318. S9 was located in Norbulingka, Lhasa. Most of the area is contained in a well-preserved ecosystem, where the environment is sensitive to outside influences.

Five surface soil samples (0–10 cm deep) were collected at each site, and the samples were combined to form a mixed sample for the site. The samples were then sealed in clean polyethylene bags, transported to the laboratory, and stored at −20°C until analysis. After the samples had been dried to a constant weight at room temperature, they were ground and homogenized through a 100-mesh sieve before being analyzed.

To determine contents of Cr, Cu, Pb, Zn, Ni, Mn, and As, about 0.5 g of milled soil from each sample was digested with aqua regia ($\text{HNO}_3/\text{HCl} = 1:3$) and HClO_4 (Qiao et al. 2011). The mineral residues were then diluted with deionized water to a final volume of 25 mL in a volumetric flask, and were stored in the fridge at 4°C before being placed in an inductively coupled plasma-optical emission spectrometer (ICP-OES, Teledyne Leeman Labs, Hudson, NH, USA).

For the analysis of Hg, 0.1 g of soil was weighed and added to a 20 mL ampule, to which 2 mL of HNO_3 and 1 mL of deionized water were added. After allowing 30 min of predigestion, the ampule was sealed using an

RFJ model manual ampule sealer. The ampule was heated for 2 h in boiling water (Shi et al. 2013). After the solution had cooled to room temperature, the ampule was opened and the digested solution was diluted with water to a volume of 10 mL in a 15 mL polyethylene terephthalate vial. The solution was mixed to homogeneity, then analyzed using AF-610B atomic fluorescence spectrometry (AFS, Beijing Rayleigh Analytical Instrument Co., China).

Each sample was analyzed three times. The blank reagent and standard reference materials (GBW08302 soil, China National Center for Standard Materials) were included for quality assurance and control. The percentage recovery for the eight metals ranged from 85 % to 105 %. The total organic carbon (TOC) concentration ranged from 9.1 to 22 mg C/g, with an average of 15.6 ± 3.77 mg C/g, as determined by a TOC analyzer (OI Analyzer, College Station, TX, USA).

A number of calculation methods have been put forward for quantifying the degree of metal enrichment or pollution in soils (Borgese et al. 2013; Sun et al. 2010; Cao et al. 2009; Chen et al. 2005). We calculated the geoaccumulation index (I_{geo}) to assess the level of heavy metal contamination in the soil. The I_{geo} enables assessment of contamination by comparing current and pre-industrial contents, although it is not always easy to obtain pre-industrial sediment layers (Ji et al. 2008; Caeiro et al. 2005). It was computed using the following equation:

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n},$$

where C_n represents the measured content of element n , and B_n is the background content of element n in Tibetan soil. The constant, 1.5, allows us to analyze natural fluctuations in the content of a given substance in the environment, and to detect very small anthropogenic influences (Faiz et al. 2009).

Fig. 1 Distribution of sampling sites

Table 1 Metal contents (mg/kg) at different sampling sites (n = 3)

Sites	As	Cr	Cu	Ni	Pb	Zn	Mn	Hg	TOC/(mg C/g)
S1	23.3	32.4	6.4	19.0	15.1	59.9	477	0.0127	22.00
S2	14.3	37.3	19.3	23.7	15.7	80.6	584	0.0187	16.50
S3	160.1	80.1	41.5	57.1	28.2	84.9	581	0.0119	18.40
S4	65.4	80.8	76.0	56.7	11.4	94.2	833	0.0031	16.90
S5	19.6	55.4	26.2	33.6	10.2	75.1	631	0.0400	12.00
S6	21.6	73.4	19.1	113	12.3	79.1	628	0.0168	16.10
S7	19.4	65.6	18.9	73.9	14.8	81.0	611	0.0133	16.30
S8	11.0	53.9	31.3	32.9	17.8	88.6	778	0.0134	9.10
S9	20.7	37.9	17.8	24.0	16.2	69.8	614	0.0281	13.10
Mean	39.5 ± 48.0	57.4 ± 18.8	28.5 ± 20.3	48.2 ± 30.5	15.7 ± 5.3	79.2 ± 10.2	637 ± 107	0.0175 ± 0.0107	15.6 ± 3.77
Background value ^a	16.8	68.1	19.6	28.7	27.9	71.1	565	0.0203	
Nam Co basin ^b	12.9	91.3	12.9	19.5	29.1	42.8	428	–	
Tibetan top soils ^c	19.3	156	24.3	55.9	32.1	75.6	617	0.037	

^a Background values of Tibetan soils from a survey in Chinese soil (Wei 1990)^b Metal contents in the Nam Co basin (Li et al. 2009)^c Metal contents of Tibetan top soils (Sheng et al. 2012)

Fig. 2 Dendrogram obtained by cluster analysis for heavy metal contents in soil samples

Fig. 3 I_{geo} of metals in soil samples

The potential ecological risk index method of assessing the risk of heavy metals is the only method that considers both the content and toxic response factors of heavy metals, and is the most commonly employed (Huang et al. 2009). The potential ecological risk index is calculated using the following equation (Li et al. 2013):

$$RI = \sum_{i=1}^m E_r^i = \sum_{i=1}^m \left(T_r^i \times \frac{C_D^i}{C_B^i} \right),$$

where C_D^i is the measured content of the sample; C_B^i is the background content of Tibetan soil; E_r^i is the potential ecological risk factor of a single metal; T_r^i is the biological toxicity factor of different metals; and RI is the potential ecological risk index of many metals. The commonly adopted T_r^i of Cr, Cu, Ni, Pb, Zn, Mn, Hg, and As are 2, 5, 5, 5, 1, 1, 40, and 10, respectively (Yan et al. 2013; Li et al. 2013; Xu et al. 2008). Assessment of E_r^i of a given substance was made according to five grades, while the RI of a given region was assessed according to four grades (Hakanson 1980).

The data were analyzed using SPSS 18.0 for windows (Chicago, IL, USA). Pearson correlation analysis was calculated to discuss the correlation between heavy metals. A level of $p < 0.05$ was considered to be statistically significant. Cluster analysis (CA) was also used to identify

similarities between different metals. Eight heavy metal contents and TOC in the soil samples were selected as the analysis factors. The Means of within-groups linkage and squared Euclidean distances were utilized to perform the CA. Meanwhile, the results are represented in a dendrogram.

Results and Discussion

The metal contents in the soil at different sampling sites, as well as the background values of Tibetan soils from a survey in Chinese soil (Wei 1990), are presented in Table 1. The data of each sample in the table are the average of three parallel analyses. For comparison, the results of Li et al. (2008) for the Nam Co basin and the results of Sheng et al. (2012) for Tibetan top soils are also presented in Table 1.

The average contents of Cu, Ni, Zn, and Mn in the soil samples were slightly higher than the background values, and the average content of As was twice the background value. Maximum values of As and Pb were found at site S3 near Yamdrok Tso, surrounded by rapeseed; the content of As was 9.5 times higher than the background value. Maximum contents of Cr, Cu, Zn, and Mn occurred at site S4, which is located at the foot of the Karuola glacier. These elements were likely inherited from soil parent material.

Compared with the mean contents observed in the Nam Co basin, the contents of As, Cu, and Ni in soils were higher, while the contents of other metals were lower or similar. Compared with Sheng et al. (2012), a significant increase in only the contents of As was observed. The presence of shale, schist, and phyllite in the soil, as well as the influence of traditional agriculture, may contribute to the high contents of As in the soil samples (Li et al. 2009).

Significant correlations were observed between As and Pb (Pearson correlation coefficient was 0.752, $p < 0.05$);

Table 2 E_r^i of eight heavy metals and RI in soil samples

Sites	E_r^i of As	E_r^i of Cr	E_r^i of Cu	E_r^i of Ni	E_r^i of Pb	E_r^i of Zn	E_r^i of Mn	E_r^i of Hg	RI	Altitude(m.a.s.l.)
S1	13.9	0.95	1.62	3.31	2.71	0.84	0.84	25.1	49.2	4,758
S2	8.51	1.10	4.91	4.14	2.82	1.13	1.03	36.8	60.4	4,480
S3	95.3	2.35	10.6	9.94	5.05	1.19	1.03	23.4	149	4,472
S4	38.9	2.37	19.4	9.88	2.04	1.33	1.47	6.15	81.6	5,035
S5	11.7	1.63	6.68	5.86	1.82	1.06	1.12	78.8	109	4,095
S6	12.8	2.16	4.87	19.6	2.20	1.11	1.11	33.1	77.0	3,823
S7	11.6	1.93	4.82	12.9	2.65	1.14	1.08	26.2	62.2	3,792
S8	6.56	1.58	7.97	5.74	3.20	1.25	1.38	26.4	54.1	3,594
S9	12.4	1.11	4.54	4.18	2.90	0.98	1.09	55.5	82.6	3,654
Mean	23.5 ± 28.6	1.69 ± 0.551	7.27 ± 5.19	8.39 ± 5.31	2.82 ± 0.946	1.11 ± 0.143	1.13 ± 0.189	34.6 ± 21.1	80.5 ± 31.4	4,189 ± 518

Cr and Cu, Ni, and Zn were also correlated with each other (Pearson correlation coefficients were 0.695, 0.748, and 0.724, respectively, $p < 0.05$); between Cu and Zn (0.798, $p < 0.01$); between Mn and Cu (0.783, $p < 0.05$); and between Mn and Zn (0.824, $p < 0.01$). Hg was not correlated with any other trace element.

The dendrogram obtained by cluster analysis is shown in Fig. 2, grouping the eight elements and TOC into three clusters.

Cr, Cu, Ni, Zn, and Mn were associated in the first cluster. Cu, Zn, Mn show a strong similarity. Ni and Cr are usually enriched in soils developed from ultramafic rocks, and the ultramafic rocks have a wide distribution in the Tibetan Plateau (Sheng et al. 2012). Meanwhile, their mean values are close to soil background values. These five elements may exist together in soil parent material as products of weathering of the exposed bedrock. The second cluster consisted of As, Pb, and TOC. This indicates that the TOC concentration may influence contents of As and Pb in soils, probably in wet or nutrition-enriched areas, which implies that As and Pb contents are probably related to soil organic matter. Previous studies have shown that Pb is particularly strongly bound to humic matter in organic rich soil (Alloway 2013).

Hg was isolated in the third cluster, implying that Hg may have a different origin from other metals. Hg in the soil may originate from minerals, diffuse air pollution, and local pollution sources, as well as from the use of sewage sludge and organic Hg compounds in agriculture (Alloway 2013). The results of the cluster matched well with the results of the Pearson correlation analysis.

To evaluate which elements show relatively higher risks in Tibetan soils, the I_{geo} was calculated for each site (Fig. 3).

All of the samples had a value of $I_{geo} \leq 0$ for Cr, Pb, Zn, and Mn, indicating that the environment is unpolluted by these elements. Environmental pollution by As was found in two samples: one sample from S4 had a value of $1 < I_{geo} \leq 2$, indicating a moderately polluted environment, and a second sample, from S3, had a value of $2 < I_{geo} \leq 3$, indicating a moderately to strongly polluted environment. The presence of Cu in two samples indicated an unpolluted to moderately polluted environment, whereas one sample indicated a moderately polluted environment. The values for Ni in three samples indicated an unpolluted to moderately polluted environment, and in one sample, a moderately polluted environment (S6). Regarding the index for Hg, only one sample (S5) indicated an unpolluted to moderately polluted environment; the other samples indicated an unpolluted environment.

A potential ecological risk assessment was performed to detect the potential ecological risk levels of heavy metals in the soil. Table 2 shows calculations of the potential

Fig. 4 Relationship between RI' and RI

ecological risk factors of individual elements (E_r^i), and a comprehensive potential ecological index (RI).

The calculated means of the E_r^i occurred in the following order: $Hg > As > Ni > Cu > Pb > Cr > Mn > Zn$. The highest degrees of risk caused by individual heavy metals at each site were as follows: As at S3, Cr, and Cu at S4, Ni at S6, Pb at S3, Zn and Mn at S4, and Hg at S5. The calculated E_r^i values of As at S3 indicated a considerable level of risk, and site S3 near the Yamdrok Tso has a higher content of TOC. According to the cluster analysis, As content is probably related to soil organic matter. Sheng et al. (2012) also reported that soils may have higher As risks in some areas of Tibetan which is caused by its higher natural origin. The calculated E_r^i values of Hg in S5 and S9 indicated a moderate level of risk. S5 was situated near a village and S9 was located in Lhasa, which possibly affected by human activities. Sheng et al. (2012) found that contamination of Hg possibly occurred in some areas of the Plateau that may have a human-influenced source. The E_r^i values of other metals indicated a low level of risk.

All of the RI values were lower than 150, indicating a low ecological risk in the present study. Based on RI values, the risk posed by heavy metals at the different sampling sites were, in descending order, S3, S5, S9, S4, S6, S7, S2, S8, and S1. However, the RI value of S3 is close to 150, so this site requires some attention.

Both Pearson correlation analysis and cluster analysis indicate that soil contamination by As, Pb, and Hg are different from other metals. To reveal the influence of the three metals on soil contents, a comparison between RI' (sum of E_r^i values of As, Pb, and Hg) and RI is shown in Fig. 4.

As, Pb, and Hg are the primary contributors to potential ecological risk, and the RI' and RI display the same trend. The ratios of RI' to RI range from 59 % to 87 %, especially in the three relatively high RI sites (S3, S5, and S9), where ratios of RI' to RI were 84 %, 86 %, and 87 %, respectively.

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