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Speciation, risks and isotope-based source apportionment of trace elements in soils of the northeastern Qinghai–Tibet Plateau



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Abstract: Trace elements in soils might cause contamination and ecological risks to the environment with increasing anthropogenic disturbance. This study investigated the distribution, speciation, risks and possible sources of 28 target trace elements in soils of the northeastern Qinghai–Tibet Plateau. The average concentrations of trace elements in soils of the study area ranged from 0.25 (Hg) to 697.38 mg kg⁻¹ (Cr). The residual fraction was the dominant host of V, Cr, Cu, Sn, Sb Hg and REEs, while Co, Ni, Zn, Mo, Cd and Pb had large proportions in the non-residual fractions. Risk assessment code analysis showed that Cd should be recognized as a priority pollutant in the study area. Correlation analysis indicated that Pb, Cu, Zn, Cd and Sn might originate from the same or similar source. The ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb ratios of the soils were in the range of 1.166–1.224 and 2.031–2.122, respectively. The anthropogenic Pb contribution proportion was in the range of 0–53.92% for the study area. The anthropogenic Pb contribution was higher in the areas with more intensive anthropogenic activities. Heavy metals and excessive anthropogenic disturbance should be effectively controlled in the northeastern Qinghai–Tibet Plateau to maintain the ecological sustainability and human health of this fragile area.

Keywords: trace element; speciation; risk assessment; Pb isotopic fingerprint; the Qinghai–Tibet Plateau

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Soil pollution induced by trace elements has attracted wide attention in recent decades. Trace elements originating from natural or anthropogenic sources ubiquitously exist in various environments including soils, sediments and water (Seshan et al. 2010; Lee et al. 2011; Li & Ji 2017). Weathering of minerals is one important natural source for trace elements in soils. Anthropogenic sources of trace elements in soils mainly include industrial/mining wastes and non-point pollution sources (Wu et al. 2016, 2018b). Trace elements do not decompose through natural processes, whereas they might be easily transformed to organic complexes with higher toxicity and accumulate in organisms. Speciation of trace elements has significant impacts on the mobility, bioavailability and potential risks of these elements (Dessai & Nayak 2009; Fernandes et al. 2014). The mobility of soil trace elements with different chemical forms follows the order of exchangeable > carbonate > Fe-Mn oxide bound > organic bound > residual (Fernandes & Nayak 2015). Therefore, chemical speciation will provide more comprehensive information to evaluate the potential impacts, mobility and bioavailability of trace elements (Ke et al. 2017; Liang et al. 2017; Meng et al. 2018). Moreover, application of a risk assessment code (RAC) using chemical speciation of trace elements will also provide more accurate information on potential risks of these elements (Zhu et al. 2012).

Source identification is critical for pollution control and prevention. The traditional approaches of source identification rely on statistically analysing numerous data (Han *et al.* 2018). However, these methods exhibit some shortcomings such as the need to employ indirect inference and the requirement of large

amounts of data. Stable isotopes, which can be considered as the 'signature' of elements, have shown advantages for source apportionment of trace elements in soil (Zhang *et al.* 2017; G. Li *et al.* 2018). Pb isotope ratios have been increasingly applied to yield information on geochemical origins, to determine the principal sources of anthropogenic Pb, to identify the transport pathways of Pb and to calculate the contribution percentage of anthropogenic sources (Yu *et al.* 2013; Kong *et al.* 2018).

The northeastern Qinghai–Tibet Plateau is more populated and industrialized than the other parts of this plateau (Wu *et al.* 2016, 2018*a*; L. Li *et al.* 2018). Therefore, the objective of this study is to identify the speciation, risks and possible sources of trace elements in soils of the northeastern Qinghai–Tibet Plateau. The final goal is to provide useful information on soil quality maintenance in the high-elevation areas.

Materials and methods

Study area and sampling strategy

The study area is located in the northeastern Qinghai–Tibet Plateau. A total of 17 topsoil (0–20 cm) samples were collected in June 2017 to represent the typical soil of the agricultural and pastoral zone (APA-1, APA-2, APA-3 and APA-4), industrial zone (IA-1, IA-2, IA-3 and IA-4), mining zone (MA-1, MA-2, MA-3 and MA-4), and salt-lake zone (SLA-1, SLA-2, SLA-3, SLA-4 and SLA-5) of the study area (Fig. 1). The topsoil samples were stored in polyethylene bags and taken back to the laboratory as soon as possible.

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Fig. 1. Study area, sampling sites and distribution of trace elements in soils. APA, IA, MA and SLA refer to the agricultural and pastoral area, industrial area, mining area, and salt-lake area, respectively.

Sequential extraction procedures

The sequential extraction procedure proposed by Tessier *et al.* (1979) was proved to be effective for analysing speciation of trace elements in soils or sediments (Fernandes & Nayak 2015). Therefore, this method was selected to determine the fraction of trace elements in soil samples from the study area. Following the sequential extraction procedure (Tessier *et al.* 1979), five fractions were analysed for trace elements including the exchangeable fraction (F1), the carbonates fraction (F2), the Fe–Mn oxide fraction (F3), the organic matter fraction (F4) and the residual fraction (F5).

The supernatants from each sequential extraction step were filtered through a 0.45 μ m cellulose acetate syringe filter, and then stored in the fridge at -4° C until analysis. The concentrations of trace element in each step were determined using an Agilent7900 inductively coupled plasma mass spectrometer (ICP-MS: Agilent Inc., USA). The soil digestion procedure and the determination of the total content of trace elements in soils are described in previous reports (Wu *et al.* 2018*a*, *b*). The trace elements included 12 typical heavy metals (Pb, Cd, Cr, Ni, Zn, Mo, Cu, Sn, Hg, Co, Sb and V) and 16 rare earth elements (REEs: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y). The determination of soil physicochemical properties are described in previous studies (L. Li *et al.* 2018; Wu *et al.* 2018*a*, *b*)

Risk assessment of trace elements

The risk assessment code (RAC) was used to determine the potential ecological risks of trace elements in soils of the study area. The RAC was calculated as the percentage sum of exchangeable and carbonate forms. Ecological risk was categorized into five levels including safe (RAC <1%), low (RAC in the range 1–10%),

medium (RAC in the range 11-30%), high (RAC in the range 31-50%) and dangerous/very high risk (RAC > 50%) according to a previous report (Chen *et al.* 2018).

Source identification by Pb isotopes

The combination of measurable and unique characteristics of Pb isotopes that are preserved during transport, processing and degradation of the original materials have provided a useful tool for source apportionment of Pb pollution. Lead isotopic determination is based on the principle that Pb has four natural isotopes. Different types of anthropogenic sources and ore deposits of Pb have different isotope ratios and signatures. Lead isotopic fractionation does not occur during environmental or industrial processes (Zhang *et al.* 2007; Cheng & Hu 2010; G. Li *et al.* 2018). Therefore, this study used a binary model to make an arbitrary calculation for anthropogenic source:

$$(^{206}\text{Pb}/^{207}\text{Pb})_{\text{nat}}f_1 + (^{206}\text{Pb}/^{207}\text{Pb})_{\text{ant}}f_2 = (^{206}\text{Pb}/^{207}\text{Pb})_{\text{sample}}$$

 $f_1 + f_2 = 100\%$

where 'ant' and 'nat' refer to the anthropogenic and natural fractions, respectively; f_1 and f_2 are the fractional contributions of the natural and anthropogenic sources, respectively. The isotopic ratio of ²⁰⁶Pb/²⁰⁷Pb in unpolluted soils was about 1.20. The ²⁰⁶Pb/²⁰⁷Pb background value for soils of the Qinghai–Tibet Plateau was set as 1.2004 by averaging the results of soils (J.-Z. Feng *et al.* 2010; X. Feng *et al.* 2010) and local dust (Cong *et al.* 2011). Lead in soil was considered to originate from natural sources when the ²⁰⁶Pb/²⁰⁷Pb value was higher than 1.2004. The ²⁰⁶Pb/²⁰⁷Pb of anthropogenic sources for western China was simplified and roughly estimated as 1.1365, which was calculated

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from an aerosol from Russia (Bollhöfer & Rosman 2001; Mukai *et al.* 2001; Yu *et al.* 2013). Lead in soil was considered to originate from the anthropogenic sources if 206 Pb/ 207 Pb value was less than 1.1365.

Analyses of Pb isotopic compositions were conducted at Beijing Research Institute of Uranium Geology. Lead isotopic ratios were measured using a mass spectrometer (IsoProbe-T) based on the 'Standard for Determination of Trace Lead Isotopic Composition in Rocks and Minerals (DZ/T 0184.12-997). A certified reference material (NBS981, USA) was used for quality control/assurance with the certified 208 Pb/ 206 Pb, 207 Pb/ 206 Pb and 204 Pb/ 206 Pb values of 2.1684 ± 0.0008, 0.91464 ± 0.00033 and 0.059042 ± 0.000037, respectively. The Pb isotopic ratios of 17 soil samples in this study were measured in duplicate with relative standard deviations of less than 0.5%.

Pearson's correlation matrix (PCM) was adopted to discuss the relationship between trace elements. PCM was performed using SPSS 22.0 (IBM, New York, USA).

Results and discussion

Soil characteristics

The major type of 17 soil samples in the study area was sandy clay loam based on soil texture analysis. The average pH of soils in the study area was 8.50 with a range of 7.96–9.28, indicating that soils in the study area are alkaline. The cation exchange capacity of the soils showed the significant spatial variation to range from 1.43 to 42.02 cmol kg⁻¹ (centimoles of positive charge per kg of soil) with an average value of 9.53 cmol kg⁻¹. The contents of soil total organic carbon also significantly varied with a range of 0.13–3.85 g kg⁻¹.

Distribution of trace elements in soils of the study area

The distribution of heavy metals in soils of the study area showed significant spatial variation (Fig. 1). The average concentration of target heavy metals in soils of the northeastern Qinghai-Tibet Plateau ranged from 0.25 (Hg) to 697 mg kg^{-1} (Cr) by following the order Cr > Pb > Zn > V > Ni > Cu > Co > Sn > Sb > Cd > Mo > Hg.The average concentration of Cr was about 10 times its background value, while the average concentration of Pb/Zn was about 26/6 times its corresponding background value. Soil samples collected from site IA-1 near a chemical factory in the eastern study area possessed the highest concentration of Cr with $10\,818 \text{ mg kg}^{-1}$, while soil samples collected from site MA-2 near a lead-zinc mine in the middle of the study area showed the highest concentration of Pb and Zn with values of 8258 and 6874 mg kg^{-1} , respectively. The mean concentration of Cd/Hg was about 27/13 times its background value, while the average concentrations of Sb and Sn were about 3 and 2 times the corresponding background value, respectively. Site IA-3, located at an oilfield in the western study area, exhibited the maximal concentration of Hg (0.80 mg kg⁻¹) in soil, while site MA-2 near a lead-zinc mine in the middle of the study area showed the highest concentration of Cd with 50 mg kg⁻¹. The mean concentrations of V/Co/N/Cu/Mo were similar to their corresponding background values. The concentrations of heavy metals in the soils were similar to those in the soils of the Huangshui watershed and the Karuola Glacier in the Qinghai-Tibet Plateau (Dai et al. 2019; Zhang et al. 2019).

The content of total REEs in soil samples collected from the study area ranged from 97 to 307 mg kg⁻¹, with an average value of 178 mg kg⁻¹ (Fig. 1). Light REEs (LREEs) were the main components of the REEs in soils of the study area. LREEs including Ce, La and Nd were the most abundant REEs in the soils, with average concentrations of 63, 31 and 27 mg kg⁻¹, respectively.

Three main heavy REEs (HREEs) including Y, Sc and Gd accounted for 11, 6 and 3% of the total REEs, respectively. The average concentrations of individual REEs followed the order Ce > La > Nd > Y > Sc > Pr > Sm > Gd > Dy > Er > Yb > Eu > Ho > Tb > Lu > Tm.

Speciation of trace elements in soils of the study area

The toxicity and bioavailability of trace elements can be ascertained based on the speciation of these elements. Anthropogenic trace elements exist in the exchangeable and adsorptive fractions, while the carbonate fraction is considered to weakly and easily equilibrate with the aqueous phase to become more bioavailable (Guo *et al.* 2011; Lin *et al.* 2014).

The chemical speciation of heavy metals in soils showed element-dependent features with significant spatial variation (Fig. 2). The residual fraction of each heavy metal in soils on average accounted for 29.9-99.7% of its total content. The residual fraction percentage of V, Cr, Cu, Sn, Sb and Hg in soils exceeded 50% on average, suggesting that it was not easy for these metals to become mobile in soils of the study area. Chromium existed in soils bound to the residual fraction (93.9%), with the remaining four fraction contents ranging from 1.0 to 2.5%. Copper existed in soils bound to the residual fraction (71.6%) and the organic fraction (18.4%). The chemical speciation of Cu in soils of the study area was significantly different from that in the tailing samples (Chen et al. 2018). Tin and Sb existed mostly bound to the residual fraction (99.7 and 93.0%, respectively), with the rest of the four chemical forms occurring in the range of 0.0–0.2 and 0.4–4.0%. It is generally difficult for heavy metals existing in the organic matter fraction to be released under normal moderately reducing or weakly oxidizing environments (Lin et al. 2014). Therefore, Cr, Cu, Sn and Sb in soils of the study area might be relatively safe since they possessed weak release potential. Vanadium existed in soils as 83.7% bound in the residual fraction and 14.8% in the exchangeable fraction. The heavy metals in the exchangeable fraction are generally sensitive to environmental changes, and easy to migrate and transform (Lin et al. 2014). As a result, V might exhibit some bioavailability and toxicity. Mercury, on average, existed at 56.9% in soils in the residual fraction, 20.4% in the organic matter fraction, 9.8% in the exchangeable fraction, 8.7% in the Fe–Mn oxide fraction and 4.2%in the carbonate fraction (4.2%). The trace metals contained in the Fe-Mn oxide or hydroxide fraction might be released if the oxidation-reduction potential decreases (Guo et al. 2011). Heavy metals bound to carbonate are easily released under acidic conditions (Guo et al. 2011). This indicated that Hg might represent some potential ecological risk.

The fractional profiles for Co, Ni, Zn, Mo, Cd and Pb were totally different from those for the other heavy metals because the nonresidual fractions were the main components for these metals. The dominant speciation of Co was the residual form with an average proportion of 39.3%. However, the sum of the exchangeable, carbonate and Fe-Mn oxide fractions reached 48.3% on average. The sum of the exchangeable, carbonate and Fe-Mn oxide fractions of Ni was 47.3% on average, exceeding the proportion of the residual form (44.4%). These results indicated that Co and Ni in the soils of the study area were generally sensitive to environmental changes and could readily migrate and transform. Zinc existed in soils bound to the residue (40.3%), Fe-Mn oxide (26.8%), organic matter (22.3%) and carbonate (9.6%) fractions. The average proportions of the exchangeable, carbonate and Fe-Mn oxide fractions for Mo in soils reached 14.2, 5.3 and 24.4%, respectively. Cadmium existed in soils mainly in the exchangeable (6.3%), carbonate (25.7%) and Fe-Mn oxide (16.7%) fractions. The results indicated that Mo and Cd had a potential ecological risk to the environment. Contrary to the other heavy metals, Pb existed in soils L. Li et al.



Fig. 2. Chemical speciation of heavy metals in soils of the study area. APA, IA, MA and SLA refer to the agricultural and pastoral area, industrial area, mining area, and salt-lake area, respectively.

mainly bound to the Fe–Mn oxide (38.7%) and the residue (29.9%) fraction. Most of the Pb also existed in the Fe–Mn oxide fraction in the Huogeqi Copper Mine in Mongolia (Chen *et al.* 2018). The exchangeable Pb content in the soils was very low. If the oxidation–reduction potential decreases, the Fe–Mn oxide fraction may be deoxidized and Pb released. Therefore, Pb had a high potential ecological risk under reducing conditions.

Different REEs in soils showed different chemical speciation (Fig. 3). The percentage of REEs (except for Gd) in the residual fraction of the soils was in the range 50-92.1%, on average, while the average percentage of the residual form of Gd reached 39.1%. The organic matter fraction of REEs ranged from 4.8 to 29.8% on average, while the Fe-Mn oxide fraction of REEs ranged from 2.0 to 19.3%. The carbonate fraction of REEs ranged from 1.5 to 12.1% on average, while the average exchangeable fraction of REEs was less than 0.2%. Speciation of Ce, Sm, Gd, Tb, Er, Tm, Yb and Lu followed the order residual > organic > Fe-Mn oxide > carbonate > exchangeable, while speciation of Y, La, Pr, Nd, Eu, Tb and Ho followed the order residual > organic > carbonate > Fe-Mn oxide > exchangeable. Chemical speciation of Sc was different to that of the other REEs, following the order residual > Fe-Mn oxide > organic > carbonate > exchangeable. These results illustrated that REEs might show relatively low bioavailability, toxicity and potential ecological risk.

Ecological risks posed by trace elements in soils of the study area

Ecological risks posed by trace elements in soils were evaluated using the RAC method (Fig. 4). RAC values of Cd were in the range 13.02–65.92%, showing that Cd poses a medium–high ecological risk in 47.1% of sampling sites. Mercury in site APA-1 and Cd in site MA-3 represent very high ecological risks, illustrating that effective control of Hg and Cd is necessary to maintain safe ecosystems in the study area. Heavy metals including Co, Mo, Pb, Ni, V, Hg and Zn pose a medium ecological risk in 21.0, 19.5, 19.0,

16.1, 15.3, 14.0 and 10.6% of the sampling sites, respectively. The average RAC values of REEs Cu, Cr, Sb and Sn ranged from 0.10 to 7.39%, suggesting that these trace elements pose low ecological risks. Lead, Mo, Co, Hg, Zn and V pose high ecological risks in 23.5, 29.4, 17.6, 5.9, 5.9 and 5.9% of sampling sites, respectively. Heavy metals including Cd, Hg, Pb, Mo, Co, Zn and V should be paid special attention to in soils of the study area due to their relatively high potential ecological risk.

Source identification of trace elements in soils of the study area

Correlation analysis was used to determine the relationship between the target trace elements of this study (Table 1). Positive correlation existed between the pairs Sn–Zn, Sn–Cd, Cd–Cu, Cd–Zn, Zn–Cu, Ni–Cr, Ni–Co and Co–Cr at a significance level of P < 0.01. Lead showed a significant positive relationship with Cu, Zn, Cd and Sn at a significance level of P < 0.01, suggesting that these heavy metals might originate from the same or similar source.

Lead isotopic ratios were effective indicators to determine the possible sources of heavy metals in the environment. Lead isotopic ratios of different functional areas of this study and previous reports have been summarized in Table 2. The average $^{206}Pb/^{207}Pb$ value of the agricultural and pastoral area was the highest of four areas, followed by the salt-lake area and the industrial area. The average $^{206}Pb/^{207}Pb$ value of the mining area was the lowest, indicating that this area had more anthropogenic Pb. The $^{206}Pb/^{207}Pb$ values of all four areas were higher than those of vehicle emissions and cement. Moreover, the $^{206}Pb/^{207}Pb$ values of all four areas partially overlapped with those of natural sources, aerosols and coal.

The Pb isotopic compositions of all four areas have been plotted in Figure 5a and b. A characteristic line ($R^2 = 0.7963$) made by Pb isotopic ratios of all reported sources (coal, aerosol, vehicle exhaust, cement and metallurgical dust) was used to determine the possible sources of Pb in the soils. Overall, the ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb isotope ratios were similar to those of natural sources, aerosols and Speciation and source of trace elements in soils



Fig. 3. Chemical speciation of rare earth elements (REEs) in soils of the study area. APA, IA, MA and SLA refer to the agricultural and pastoral area, industrial area, mining area, and salt-lake area, respectively.



Fig. 4. Risk assessment code (RAC) of trace elements in soils of the study area. APA, IA, MA and SLA refer to the agricultural and pastoral area, industrial area, mining area, and salt-lake area, respectively.

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	V	Cr	Co	Ni	Cu	Zn	Мо	Cd	Sn	Sb	Hg	Pb	REEs
V	1												
Cr	0.227	1											
Co	0.560*	0.843 [†]	1										
Ni	0.266	0.996 [†]	0.877^{\dagger}	1									
Cu	-0.258	-0.237	-0.106	-0.233	1								
Zn	-0.173	-0.063	0.044	-0.055	0.645 [†]	1							
Mo	0.120	0.452	0.539*	0.509*	-0.224	-0.103	1						
Cd	-0.178	-0.072	-0.064	-0.064	0.660†	0.999 [†]	-0.093	1					
Sn	0.127	-0.238	-0.225	-0.225	0.505*	0.795 [†]	-0.190	0.798^{+}	1				
Sb	0.303	0.058	0.097	0.097	0.023	0.226	0.313	0.228	0.270	1			
Hg	0.459	-0.137	-0.131	-0.131	0.076	0.301	-0.296	0.299	0.540*	0.373	1		
Pb	-0.177	-0.065	-0.058	-0.058	0.642^{+}	1.000^{+}	-0.116	0.999 [†]	0.794 [†]	0.219	0.301	1	
REEs	0.473	-0.370	-0.352	-0.352	-0.249	-0.235	-0.120	-0.232	0.314	0.368	0.420	-0.237	1

Table 1. Pearson correlation coefficients of trace elements in soil of the study area

Note: *P < 0.05; $^{\dagger}P < 0.01$.

coal, while they were significantly distinct from those of metallurgical dust, cement and vehicle emissions (Fig. 5a). This analysis provided the evidence that soil Pb from many sampling sites (except APA-1, APA-4, IA-3 and SLA-5) in the northeastern Qinghai–Tibet Plateau was from mixed sources (Fig. 5b).

The results showed that less than 53.92% of Pb in soils of the study area was contributed by anthropogenic activities (Fig. 5c). The anthropogenic contribution proportions for Pb were in the range of 0-21.52% with a mean value of 7.57% in the agricultural and pastoral area, 0-52.04% with a mean value of 23.32% in the industrial area, 4.93-53.92% with a mean value of 27.56% in the mining area, and 0-25.87% with a mean value of 13.44% for the salt-lake area. Copper, Zn, Cd and Sn might have the same natural and anthropogenic contributions as Pb, Cu, Zn, Cd and Sn might originate from the same or similar source based on the correlation analysis. Moreover, anthropogenic contributions in the industrial and mining area were higher in comparison with the other areas. Anthropogenic Pb contribution was low in the agricultural and pastoral area, as well as the salt-lake area, with relatively less anthropogenic disturbance.

Importance and application of this study

Total concentrations of trace elements in soils have been widely used to evaluate pollution and potential ecological risks (Wu *et al.* 2016, 2018*a*; L. Li *et al.* 2018). However, information to determine the critical element with stronger mobility and bioavailability cannot be obtained through the use of total concentration data alone. Thus, speciation analysis provides useful information on different fractions of these elements hosted in soils or other materials. Moreover, studies on speciation and ecological risk of trace

elements including REEs in soils of the Qinghai–Tibet Plateau and other high-elevation areas are limited. Therefore, this study will provide the theoretical basis for soil quality management in the high-elevation areas.

Trace elements generally include heavy metals, REEs, and some other elements such as radium and barium. However, many studies have paid more attention to the distribution of heavy metals in the environments since heavy metals have harmful effects on ecosystems and humans (Tan *et al.* 2006; Lin *et al.* 2014; Wu *et al.* 2018*a*). This study provides comprehensive information on the distribution, speciation, risks and possible sources of heavy metals and REEs in soils of the Qinghai–Tibet Plateau, and provides thorough insight into the soil quality with respect to trace elements.

Source apportionment is important for pollution control and prevention (Wu *et al.* 2016, 2018*a*). Isotope-based source apportionment generally provides more direct evidence for determining the contribution proportions of different sources. However, this method has not been widely used to identify the possible sources of trace elements in the Qinghai–Tibet Plateau. Therefore, this study discussed the contribution proportions of natural and anthropogenic lead sources, and addressed new information on the source apportionment of trace elements in soils of the high-elevation areas. Trace element isotopes of some trace elements such as Hg, Sr, Cd, Cr, Cu and Zn can also be used for source identification and apportionment (J.-Z. Feng *et al.* 2010; X. Feng *et al.* 2010; Sun *et al.* 2017). It will be more accurate to determine different pollution sources and contribution proportions by using multiple isotopes in the future.

The Qinghai–Tibet Plateau is a unique geological feature in the world which attracts global attention. This study, focused on trace

Table 2. Pb isotopic compositions from four areas, natural sources and pollution sources

Sample	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb	Reference
Agricultural and pastoral area	1.187-1.208	2.054-2.078	This study
Industrial area	1.167-1.224	2.031-2.099	This study
Mining area	1.166-1.197	2.059-2.122	This study
Salt-lake area	1.184-1.201	2.065-2.089	This study
Natural source	1.183-1.200	2.077-2.096	Zhu (1995), Zhu et al. (1998, 2001), Millot et al. (2004) and Lee et al. (2007)
Coal	1.140-1.192	2.057-2.117	Mukai et al. (1993), Mukai et al. (2001) and Tan et al. (2006)
Vehicle exhaust (leaded and unleaded)	1.110-1.147	2.123-2.193	Chen et al. (2005)
Cement	1.163	2.104	Tan <i>et al.</i> (2006)
Metallurgical dust	1.172	2.078	Tan <i>et al.</i> (2006)
Aerosol	1.131–1.189	2.100-2.133	Bollhöfer & Rosman (2001), Mukai <i>et al.</i> (2001), Chen <i>et al.</i> (2005), Hsu <i>et al.</i> (2006), Lee <i>et al.</i> (2007), Liu <i>et al.</i> (2014) and Zhu <i>et al.</i> (2010)



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Fig. 5. (a) Correlation between ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁶Pb/²⁰⁷Pb of the samples (this work) and reference source samples. (b) Correlation between ²⁰⁶Pb/²⁰⁷Pb and 1/Pb in soil samples of this study. (c) Pb isotopic compositions in soil samples of this study. APA, IA, MA and SLA refer to the agricultural and pastoral area, industrial area, mining area, and salt-lake area, respectively.

elements in the soils of this region, will provide some useful information on soil pollution control and environmental management in similar high-elevation areas of the world.

Conclusions

The distribution of heavy metals in soils of the study area showed a significant spatial variation. The average concentrations of Cd, Pb, Hg, Cr and Zn were over 6 times their corresponding background values. The highest concentration of Cr and Hg occurred in soils of the eastern and western study area, respectively. The maximal concentration of Pb, Zn and Cd occurred in soils of the middle study area. REEs in soils were mostly derived from natural origins with an average content of 178 mg kg^{-1} . The residual fraction was the dominant form of V, Cr, Cu, Sn, Sb, Hg and REEs. RAC analysis showed that Cd should be recognized as a priority pollutant in the study area. Correlation analysis indicated that Pb, Cu, Zn, Cd and Sn might originate from the same or similar source. The lead isotopic compositions exhibited by Pb in the soils were influenced by a mixed contribution of natural and anthropogenic sources. The anthropogenic Pb contribution proportion was in the range 0-53.92%. The average percentages of anthropogenic Pb in the four types of areas showed a positive correlation with the intensity of anthropogenic activities.

Heavy metals including Pb, Zn and Cd should be paid more attention, in line with the speciation and source identification

results. Effective management of the anthropogenic activities in the northeastern Qinghai–Tibet Plateau is needed to control the heavy metal pollution in this area.

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Author contributions LL: Data curation (Lead), Formal analysis (Lead), Writing - Original Draft (Equal); JW: Conceptualization (Lead), Funding acquisition (Equal), Investigation (Lead), Project administration (Lead), Supervision (Lead), Writing - Original Draft (Equal), Writing - Review & Editing (Lead); JL: Conceptualization (Equal), Funding acquisition (Equal), Investigation (Equal), Project administration (Equal), Supervision (Equal), Writing - Review & Editing (Equal), Project administration (Equal), Supervision (Equal), Writing - Review & Editing (Equal); JX: Data curation (Supporting), Formal analysis (Equal).

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