Tracing sources of pollution in soils from the Jinding Pb–Zn mining district in China using cadmium and lead isotopes

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ABSTRACT

Systematic variations in the Cd and Pb isotope ratios in polluted topsoils surrounding the Jinding Pb–Zn mine in China were measured so that the sources of the metals could be traced. The average $\delta^{114/110}$Cd value and ^{206}Pb/^{207}Pb isotope ratio in background soils from the region were +0.41‰ and 1.1902, respectively, whereas the contaminated soil samples had different values, with the $\delta^{114/110}$Cd values varying between −0.59‰ and +0.33‰ and the ^{206}Pb/^{207}Pb isotope ratios varying between 1.1764 and 1.1896. We also measured the Cd and Pb isotopic compositions in oxide ores, sulfide ores, and slags, and found that binary mixing between ores and background soils could explain almost all of the variations in the Cd and Pb isotope ratios in the contaminated soils. This suggests that Cd and Pb pollution in the soils was mainly caused by the deposition of dust emitted during anthropogenic activities (mining and refining). The Pb and Cd isotope ratios clearly showed that contamination in soils in the northeastern part of the area was caused by surface mines and zinc smelters and their slagheaps, while contamination in soils in the southwestern part of the area also came from tailing ponds and underground mines. The main area of soil polluted by dust from Pb–Zn mining processes roughly extended for up to 5 km from the mine itself.

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1. Introduction

Anthropogenically emitted chemical elements, including environmentally toxic metals (Hg, Pb, Cd, etc.), can accumulate in relatively large amounts in soils and plants and in the bodies of animals and humans. They can cause a number of diseases in humans and animals, and subsequently result in serious biological and ecological problems (Lin and Pehkonen, 1999; Schroeder and Munthe, 1998; Saratug et al., 2010; Strady et al., 2011). Following rapid social and economic development over the past several decades, soil pollution by metals has become more serious and widespread in developing countries, including China (Wei and Yang, 2010; Li et al., 2014). A six-year soil pollution study conducted by the Chinese government found that the country's soil had been vastly polluted by human activities in the industrial, mining, and farming sectors (CSC, China State Council, 2012). Among these, mining is considered to be one of the most significant sources of metal contamination (Liu et al., 2005; Acosta et al., 2011).

As a result, tracing the sources of metals in the environment is critical to understand their pollution level and fate. The first way to determine pollution metal's sources is to use metal concentration gradients and relative enrichment factors (EF). However, this approach has some limitations particularly in complex, multiple sources environment (Hansmann and Köppel, 2000; Sun et al., 2011). In order to better constrain and to better distinguish sources, other tools has to be used in addition to concentration and EF. For example, Lead (Pb) has four naturally occurring isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb). Of these, only ^{204}Pb is non radiogenic, whereas ^{206}Pb, ^{207}Pb, and ^{208}Pb are the end products of the radioactive decay of ^{238}U, ^{235}U, and ^{232}Th, respectively (Dickin, 1995). Therefore, different Pb sources may have characteristic isotopic compositions, so that variations of Pb isotope ratios (IRs) in environmental media can be used to determine the origins of Pb and contributions of natural or anthropogenic sources, such as sediments (Farmer et al., 1996; Brännvall et al., 1999; Bindler et al., 2001; Ettler et al., 2006; Townsend and Seen, 2012), topsoils (Klaminder et al., 2011; Morton-Bermea et al., 2011), plants (Bacon et al., 1996; Weiss et al., 1999; Bindler et al., 2004), and aerosols (Hopper et al., 1991; Monna et al., 1997). New geochemical proxies, such as Cd and Zn isotopes, can potentially also be used to help determine the sources of metals in the environment.

Cadmium has eight stable isotopes (^{106}Cd, ^{108}Cd, ^{110}Cd, ^{111}Cd, ^{112}Cd, ^{113}Cd, ^{114}Cd, and ^{116}Cd), and the relative molar proportions

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vary between 0.89% for [108]Cd and 28.17% for [114]Cd (Cloquet et al., 2005). Significant variations have also been observed in natural terrestrial samples with a total fractionation of about 1.5‰ in $\delta^{114/110}$Cd values for samples from MORB and OIB rocks, loess, sediments, and sulfides (Wombacher et al., 2003; Schmitt et al., 2009; Zhu et al., 2013). Rosman and de Laeter (1976, 1988), Rosman et al. (1980a, 1980b), and Wombacher et al. (2003, 2008) showed that evaporation and condensation processes can yield larger Cd isotopic fractionation in meteorite samples, ranging from −8‰ to +16‰ in $\delta^{114/110}$Cd value. Large Cd isotopic fractionations were also reported for industrially partly evaporated Cd metal (Wombacher et al., 2004; Cloquet et al., 2005, 2006; Shiel et al., 2010; Gao et al., 2013). For example, Cloquet et al. (2005, 2006) found that dust and slag produced by smelters have distinctly different Cd isotopic compositions with $\delta^{114/110}$Cd of −0.64‰ in dust (vapor phase) and 0.36‰‰ in slag (residue phase). Significant fractionation of Cd isotopes has also been found to occur during the metallurgical processing of Zn and Pb ores, giving a total $\delta^{114/110}$Cd range of 1.04‰ (0.39–0.52‰ in $\delta^{114/110}$Cd in the refined Cd metal and −0.52‰ in the fume (Shiel et al., 2010), which strongly indicated that Cd isotopes in vapor phases are usually significantly enriched in light isotopes leading residues enriched in heavier. Therefore, it is reasonably believed that Cd isotopes proportion varies according to different reactions particularly during anthropogenic processes, and such fractionated Cd can been used to trace the sources of metals in the environment.

As one of the few lead–zinc deposits with over 10-million-ton reserves across the world, Jinding lead–zinc mine is currently the largest lead–zinc deposit proved in China (Xue et al., 2007; Ye et al., 2010). Its total mining area amounts to 6.8 km², of which more than 80% can be open-pit mining. Large-scale mining of the Jinding Pb–Zn deposit began in the 1980s and has caused serious environmental problems in the area (Zu et al., 2004; Yi et al., 2012). Therefore, in the study presented her, we evaluated the potential of Pb and Cd to trace anthropogenic impact on soils near the Jinding Pb–Zn deposits in China. For that, we determined metals concentrations as well as Pb and Cd isotope ratios in soils and effluents from mining/smelting activities. We expected to better constrain the pollution sources and to distinguish the natural versus anthropogenic sources.

2. Materials and methods

2.1. Study area

The Jinding Pb–Zn deposit, in Lanping County, Yunnan Province, southwestern China, has a surface area of about 8 km². The deposit was discovered in 1960, and it is the largest Zn–Pb deposit in sandstone in China and one of 17 super-large Pb–Zn deposits (defined as containing more than 10 Mt of metal reserves) in the world (Xue et al., 2007; Ye et al., 2010). The Jinding Pb–Zn deposit contains ∼200 Mt of ore reserves that contain 6.08% Zn and 1.29% Pb, and the total metal reserves are ∼15 Mt. A number of other metals accompany Pb and Zn in the ores, and these include Tl (8167 t at between 6 and 20 μg/g), Cd (170,000 t at between 0.01 and 0.2%), Ag (1722 t typically at between 1 and 20 g/t, but reaching 156 g/t), and Sr (1.47 Mt at between 13% and 18%) (Xue et al., 2007). The deposit occurs as tabular ore bodies that are hosted within Early Cretaceous and Tertiary terrestrial clastic rocks in the Lanping–Simao Basin. The deposit contains six ore zones, which are the Jiayashan, Beichang, Xipo, Baicaoping, Paomaping, and Fengzishan zones. More than 30 primary minerals have been identified in this deposit, and these have included sulfides, oxides, carbonates, sulfates, bitumen, and native metals. The most common minerals in the primary ores are sphalerite, galena, and pyrite.

However, the main minerals in the oxidized ores are smithsonite, hydrozincite, anglesite, and gypsum. Almost all of the Cd occurs in Zn minerals (sphalerite, smithsonite, and hydrozincite).

Since 1980s, large-scale mining of the Jinding Pb–Zn deposit began. Up to now, about 80% of ores come from surface mining, including primary (sulfide) ores and secondary (oxidized) ores. Other come from underground mining, mainly including primary (sulfide) ores. Pb and Zn metals are major productions for smelter, and Cd is recovered from soot produced by Pb and Zn refining. As shown in Fig. 1, a town (Jinding) and agricultural fields are very close to the mine, and Bijiang River runs through the mining area. Long-term anthropogenic activities have resulted in serious environmental problems around this area. Contaminant mainly derived from dust dispersion produced by mining and refining or river transport and deposition of metal contaminated particles by erosion. Possible sources of contamination in the Jinding Pb–Zn mining area include (a) surface mining (in the Jiayashan and Beichang ore zones), (b) smelting, (c) slagheaps, (d) the tailings dam, and (e) underground mining (in the Xipo and Fengzishan ore zones). All of these sources may have contributed to serious metal pollution in the soils surrounding the mining area.

2.2. Sampling

In order to discriminate possible sources of the contaminants, samples used in this study are agricultural soils, sulfide/oxide ores and slag. Soil samples from a depth of 10–20 cm were collected along the road marked in Fig. 1. Six soil samples were collected from the northeastern part of the study area and seven soil samples were collected from the southwestern part. Two soil samples were collected from woods about 20 km northeast of the mine and treated as background unpolluted soil samples. Two primary (sulfide) ore samples and two secondary (oxidized) ore samples were collected from the open-pit mining area, and two slag samples were collected from the smelter slagheap, and these were used to represent the potential sources of contaminants in the study area.

The soil samples were air-dried naturally (which took about 8 d), and then each sample was crushed and passed through an 80 mesh sieve. Each sieved sample was ground further in an agate mortar and passed through a 200 mesh sieve so that the most homogeneous powder possible was obtained for isotopic analysis. Each ore and slag sample was also dried, crushed, and passed through a 200 mesh sieve.

2.3. Element and isotope analysis

2.3.1. Trace element analysis

Briefly, a 50 mg aliquot of a sample was weighed into a high pressure digestion vessel and digested using a 1:2 mixture of HF and HNO_3 at 180 °C for at least 24 h, until the sample was completed dissolved. The Cd, Pb, and Zn concentrations in the digested samples were determined by inductively coupled plasma–mass spectrometry (ICP-MS; PE ElAN DRC-e) at the State Key Laboratory of Ore Deposit Geochemistry, at the Institute of Geochemistry, Chinese Academy of Sciences. The concentrations were determined with satisfactory precision for most of the elements, and the relative standard deviations were typically lower than 5%. The sample preparation and calibration procedures and the operating conditions used for the instrument were established previously and have been published by Qi and Grégoire (2000). The international reference materials AGV-2, AMH-1, and GBPG-1 and the Chinese National reference material GSR-1 were analyzed so that the quality of the data could be controlled.
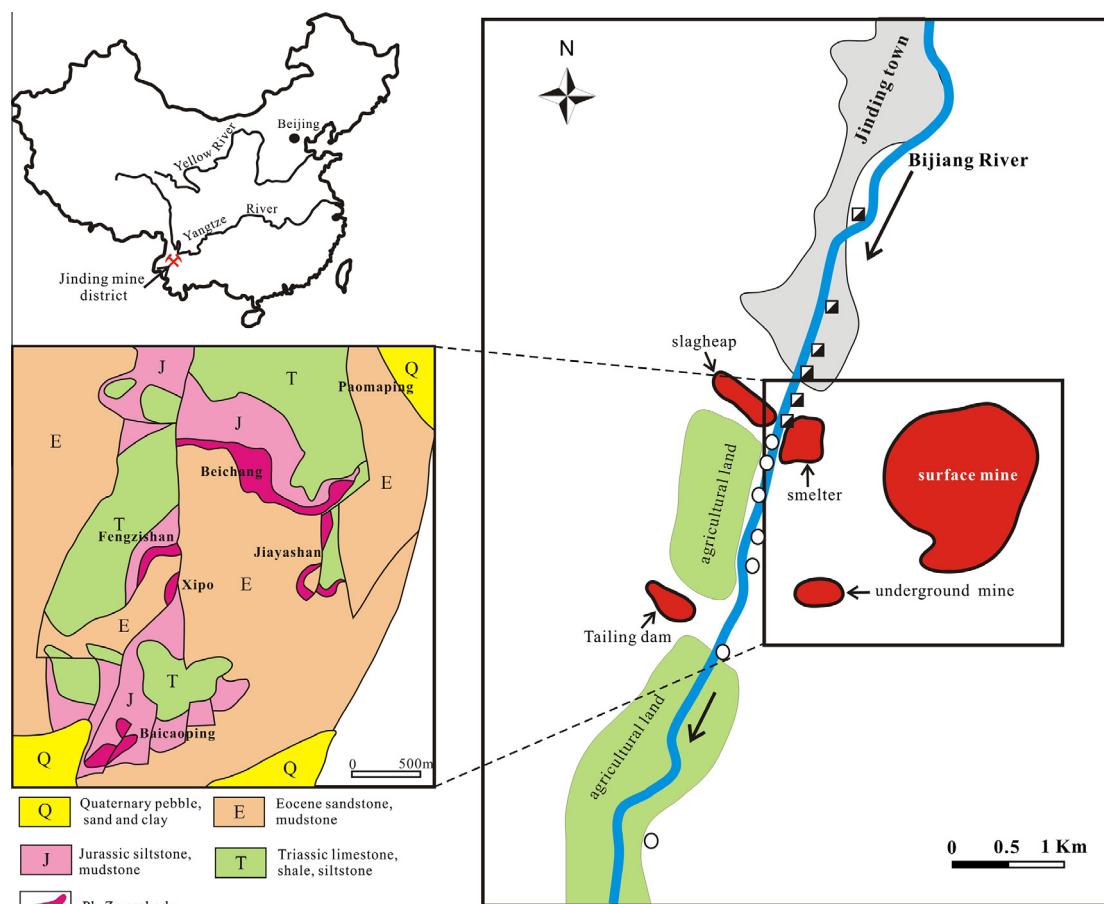
Fig. 1. Potential sources of pollution in the study area and the locations of the sampling sites.

2.3.2. Pb isotope analysis

An aliquot of a prepared sample powder was dissolved in a mixture of concentrated HF and concentrated $HClO_4$ for 72 h. The Pb in the digested sample was separated and purified using conventional anion exchange techniques (using 200–400 mesh AG1 × 8 resin) with dilute HBr. The Pb IRs were measured using an Isoprobe-T mass spectrometer at the Analytical Laboratory Beijing Research Institute of Uranium Geology, China. The ^{207}Pb–^{204}Pb double spike method has been employed to correct the mass fractionation effects for Pb isotopic analysis of samples. The within-run analytical precision of the $^{208}Pb/^{206}Pb$ IR when 1 µg of Pb was analyzed was below 0.005%. Repeat analyses of reference material NBS981 gave a $^{208}Pb/^{206}Pb$ IR of 2.1652465 ± 0.000069, a $^{207}Pb/^{206}Pb$ IR of 0.9145100 ± 0.000056, and a $^{204}Pb/^{206}Pb$ IR of 0.0591995 ± 0.000013.

2.3.3. Cd isotope analysis

After the Cd concentrations in the powder samples were determined, an aliquot that would have contained more than 100 ng Cd was taken from each sample and oxidized using a 1:2 mixture of HF and HNO_3 at 100 °C for at least 16 h, until the sample was completely dissolved. A procedure using an anion exchange resin column, which has been described by Cloquet et al. (2005) and Zhang et al. (2010), was used to separate the Cd from the matrix. The procedure that was used to separate the Cd from the matrix is shown in Table 1. The method gave a mean Cd recovery of 99.8%. Elements that could potentially interfere with the determination of the Cd isotopes, such as Sn, In, Zn, and Pb, were found at concentrations that were negligible relative to the Cd concentrations.

Table 1
Summary of Cd separation chemistry.

Procedure	Reagent	Volume (ml)
Resin	AG-MP-1 M (100–200 mesh)	3
Clean	0.0012 mol/L HCl	25
Condition	2 mol/L HCl	20
Load sample	2 mol/L HCl	2
Wash	2 mol/L HCl	10
Wash	0.3 mol/L HCl	30
Wash	0.06 mol/L HCl	20
Wash	0.012 mol/L HCl	10
Collect Cd	0.0012 mol/L HCl	20

The Cd isotope measurements were performed at the State Key Laboratory of Marine Environmental Science, at Xiamen University, using a Nu multi collector ICP-MS instrument. Aliquots of the digested samples were introduced into the instrument using a cyclonic chamber system with a perfluoroalkoxy alkane pneumatic nebulizer in free aspiration mode. The samples and bracketing reference solutions were run in two blocks of 15 measurement cycles for each m/z ratio. The system typically generated a total Cd signal of about 57 V/ppm at an uptake rate of about 100 µL/min, which corresponded to ca. 75 ng Cd analyzed. The nebulizer and spray chamber were rinsed after each run with 0.6 M HNO_3 until the signal intensity reached the original background level (generally after 3 min).

The standard–sample bracketing method was used to calculate delta values. The concentrations in the samples and reference Cd samples (the bracketing Cd reference was obtained from Spex)

were matched to within 10%. The analyses were conducted in static mode. The blank solution signal was subtracted from each of the measured masses. Instrumental drift was corrected by averaging the ratios measured in the bracketing reference solutions. Only sections with linear or smooth drifts for the reference solution were considered and used to calculate the delta values for the samples. A Cd solution (Spex) was used as an internal reference standard. A fractionated Cd metal sample (a Münster Cd solution from Nancy University) was used as a second reference material. Repeated measurements of the Münster Cd solution gave a $\delta^{114/110}$Cd value of 4.47‰ ± 0.08‰ (mean ± 2σ), which was identical to the previously recommended Cd isotopic value for the solution, 4.48‰ (Cloquet et al., 2005). The relationship between the two delta values reported indicates mass dependent fractionation, suggesting that all measurements were free of or corrected for any possible isobaric interference. δ notation, as defined by the relationship shown below, was used to present the results.

$$\delta^{x/110}Cd(‰) = [(^{x}Cd/^{110}Cd)_{sample}/(^{x}Cd/^{110}Cd)_{std} - 1] \times 1000‰,$$

where ^{x}Cd means the ^{111}Cd, ^{112}Cd, ^{113}Cd, or ^{114}Cd isotope.

3. Results

The results are shown in Table 2. The average Cd, Pb, and Zn concentrations in the background topsoil samples were 0.99 µg/g, 28.7 µg/g, and 57.8 µg/g, respectively. The Pb and Zn concentrations in the background topsoil were below the Chinese national first grade standards for soil (Pb < 35 µg/g and Zn < 100 µg/g), and the Cd concentration was below the third grade standard for soil (Cd < 1.0 µg/g) according to the Soil Environmental Quality Standards of China (GB15618-1995). This indicated that the background Cd concentration in the soil in the study region was relatively high. The average concentrations in the contaminated soil samples were 175 µg/g (with a range of 1.61–531 µg/g) for Cd, 1270 µg/g (with a range of 15.8–3060 µg/g) for Pb, and 7140 µg/g (with a range of 103–15,300 µg/g) for Zn. The Cd, Pb, and Zn concentrations were far higher in the contaminated soil samples than in the background soil samples, indicating that the study area suffered extremely

serious metal pollution. The average Cd, Pb, and Zn concentrations in the sulfide ore and oxidized ore samples were 2944 µg/g, 37,740 µg/g, and 104,225 µg/g, respectively, and the mean Cd, Pb, and Zn concentrations in the smelter slag samples were 727 µg/g, 14,550 µg/g, and 29,250 µg/g, respectively. As shown in Fig. 2, Cd concentrations were positively correlated with both Zn and Pb concentrations in soils, ores, slag and background soil samples. Although this binary mixture exhibited suggests that the major pollution source may be the Pb–Zn mine production, the relative contribution from five possible sources of contamination in the Jinding Pb–Zn mine as mentioned above still need to better constrain.

The background soil samples had higher $\delta^{114/110}$Cd values (0.41‰ ± 0.01‰; mean ± 2σ, which will be used subsequently) than any of the other samples, and the mean ^{206}Pb/^{207}Pb IR was 1.1902 ± 0.0004. The $\delta^{114/110}$Cd value in the contaminated soil samples ranged from −0.59‰ to +0.33‰, with a mean of −0.39‰ ± 0.24‰, and the ^{206}Pb/^{207}Pb IRs ranged from 1.1764 to 1.1896, with a mean of 1.180 ± 0.004. The mean $\delta^{114/110}$Cd value in the oxidized ore was −0.64‰ and the mean ^{206}Pb/^{207}Pb IR was 1.1769, while the mean $\delta^{114/110}$Cd value in the primary ore was −0.37‰ and the mean ^{206}Pb/^{207}Pb IR was 1.1770. The smelter slag samples (from smelting the oxidized ore) had a mean $\delta^{114/110}$Cd value of −0.48‰ and a mean ^{206}Pb/^{207}Pb IR of 1.1758.

The spatial distributions of Pb and Cd are shown in Fig. 3. The Pb and Cd concentrations in the soil samples decreased to the background concentrations at a point about 2.5 km from the center of the sampling area to the northeast and at a point about 5 km from the center of the sampling area to the southwest. The Pb and Cd concentrations in the surface soil samples from the northeastern part of the study area decreased as the distance from the center of the sampling area increased. However, the Pb and Cd concentrations in the soil samples from the southwestern part of the study area did not follow a similar trend, and this was possibly caused by there being additional pollution sources in the southwestern part of the study area (Fig. 3A and B). The Pb and Cd IRs followed similar trends to the Pb and Cd concentrations, as illustrated in Fig. 3C and D.

Table 2
Metal concentrations and the Cd and Pb isotopic compositions in the samples.

| Sample	Cd (µg/g)	Zn (µg/g)	Pb (µg/g)	$\delta^{114/110}$Cd (2 sd, ‰)	$\delta^{112/110}$Cd (2 sd, ‰)	^{208}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{206}Pb/^{204}Pb	^{206}Pb/^{207}Pb	Description	Distance from smelter (m)
BJ-1	0.81	52.8	27.1	0.40 ± 0.05	0.22 ± 0.05	38.848	15.650	18.631	1.1905	Soil background	20Km
BJ-2	1.17	62.7	30.2	0.41 ± 0.05	0.24 ± 0.05	38.776	15.603	18.566	1.1899	Soil background	20Km
YH-1	3870	123,000	55,600	−0.58 ± 0.10	−0.29 ± 0.08	38.723	15.668	18.450	1.1776	Oxide ore	
YH-2	4910	151,000	72,400	−0.70 ± 0.13	−0.35 ± 0.09	38.878	15.715	18.484	1.1762	Oxide ore	
YS-1	727	48,400	6660	−0.35 ± 0.09	−0.17 ± 0.08	38.752	15.677	18.464	1.1778	Primary ore	
YS-2	2270	94,500	16,300	−0.39 ± 0.18	−0.17 ± 0.11	39.042	15.764	18.540	1.1761	Primary ore	
YNZ-1	765	29,800	15,500	−0.52 ± 0.11	−0.26 ± 0.09	38.990	15.753	18.522	1.1758	Metallurgical slag	
YNZ-2	689	28,700	13,600	−0.44 ± 0.12	−0.21 ± 0.10	38.958	15.741	18.507	1.1757	Metallurgical slag	
D-1	531	15,300	3060	−0.56 ± 0.13	−0.29 ± 0.10	38.933	15.728	18.505	1.1766	Topsoil, NE	100
D-2	161	6850	1100	−0.59 ± 0.10	−0.31 ± 0.08	38.773	15.682	18.472	1.1779	Topsoil, NE	300
D-3	55.8	2400	832	−0.57 ± 0.12	−0.28 ± 0.09	38.767	15.678	18.481	1.1788	Topsoil, NE	600
D-4	34.7	1150	428	−0.38 ± 0.14	−0.17 ± 0.09	38.858	15.697	18.553	1.1819	Topsoil, NE	1000
D-5	17.6	1110	65.1	−0.35 ± 0.10	−0.16 ± 0.07	38.863	15.671	18.575	1.1853	Topsoil, NE	1500
D-6	1.61	117	44.7	0.33 ± 0.10	0.15 ± 0.08	38.883	15.658	18.585	1.1869	Topsoil, NE	2500
X-1	390	18,500	2340	−0.48 ± 0.13	−0.25 ± 0.10	38.982	15.742	18.522	1.1766	Topsoil, SW	100
X-2	499	20,900	3450	−0.35 ± 0.16	−0.18 ± 0.11	38.984	15.747	18.524	1.1764	Topsoil, SW	300
X-3	66.9	2750	722	−0.42 ± 0.09	−0.20 ± 0.07	38.933	15.730	18.525	1.1777	Topsoil, SW	600
X-4	134	6350	1530	−0.49 ± 0.13	−0.22 ± 0.09	38.954	15.738	18.518	1.1766	Topsoil, SW	1000
X-5	92.5	4230	942	−0.34 ± 0.10	−0.15 ± 0.08	38.888	15.719	18.499	1.1769	Topsoil, SW	1500
X-6	286	13,100	1990	−0.55 ± 0.11	−0.27 ± 0.09	38.490	15.595	18.388	1.1791	Topsoil, SW	2500
X-7	2.69	103	15.8	−0.27 ± 0.15	−0.13 ± 0.09	38.588	15.588	18.543	1.1896	Topsoil, SW	5000
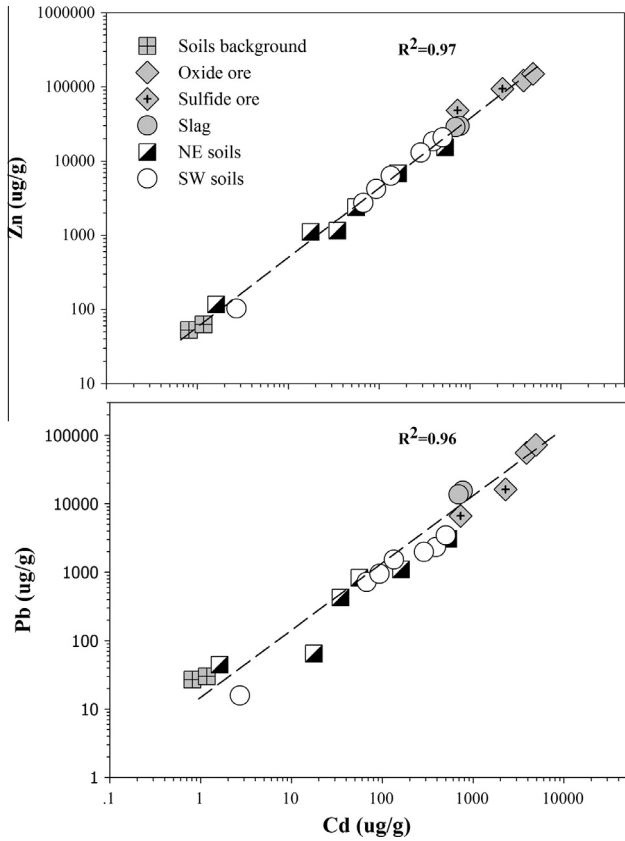
Fig. 2. Correlations between the Cd, Pb, and Zn concentrations in different samples.

4. Discussion

4.1. Pb isotopes

The spatial distributions of the metal concentrations in the polluted soils clearly demonstrated that the Jinding Pb–Zn mining district is the main source of Cd and Pb to the soils in the area. The Pb isotopes also indicated that Pb in the polluted topsoils was a mixture of Pb emissions from at least two isotopically distinct sources.

As a whole, the Pb isotopic composition was very similar in all of the ore and slag samples, and this composition was comparable to compositions that have previously been found in similar types of samples (Zeng et al., 2005; Xue et al., 2007). For example, the mean $^{206}Pb/^{207}Pb$ IR was 1.177 ± 0.001 from samples in this study, which were comparable to the $^{206}Pb/^{207}Pb$ IR of 1.178 ± 0.001 in sulfide samples found (e.g., galena, sphalerite, and pyrite) (Zeng et al., 2005). The similar Pb isotopic compositions in ore and slag samples and in sulfide samples analyzed by others suggest that the melting process did not cause significant amounts of Pb isotopic fractionation.

Almost all of the samples fitted a binary mixing model for the combination of Pb from the pollution sources caused by the mining and smelting activities and the background Pb in the soil, as can be seen from Fig. 4. This indicates that the Pb in the contaminated soil came from two different sources with different isotopic compositions. From the tri-isotope plot shown in Fig. 5, it can also be seen that most of the spatial variation in the Pb isotopic compositions could be explained using different mixing proportions for two different end-members, background soils at one end and ores and slags at the other. However, one point (sample X-7, from southwest of the center of the sampling area) was not explained by these end-members. This point was quite distant from the smelter (5 km
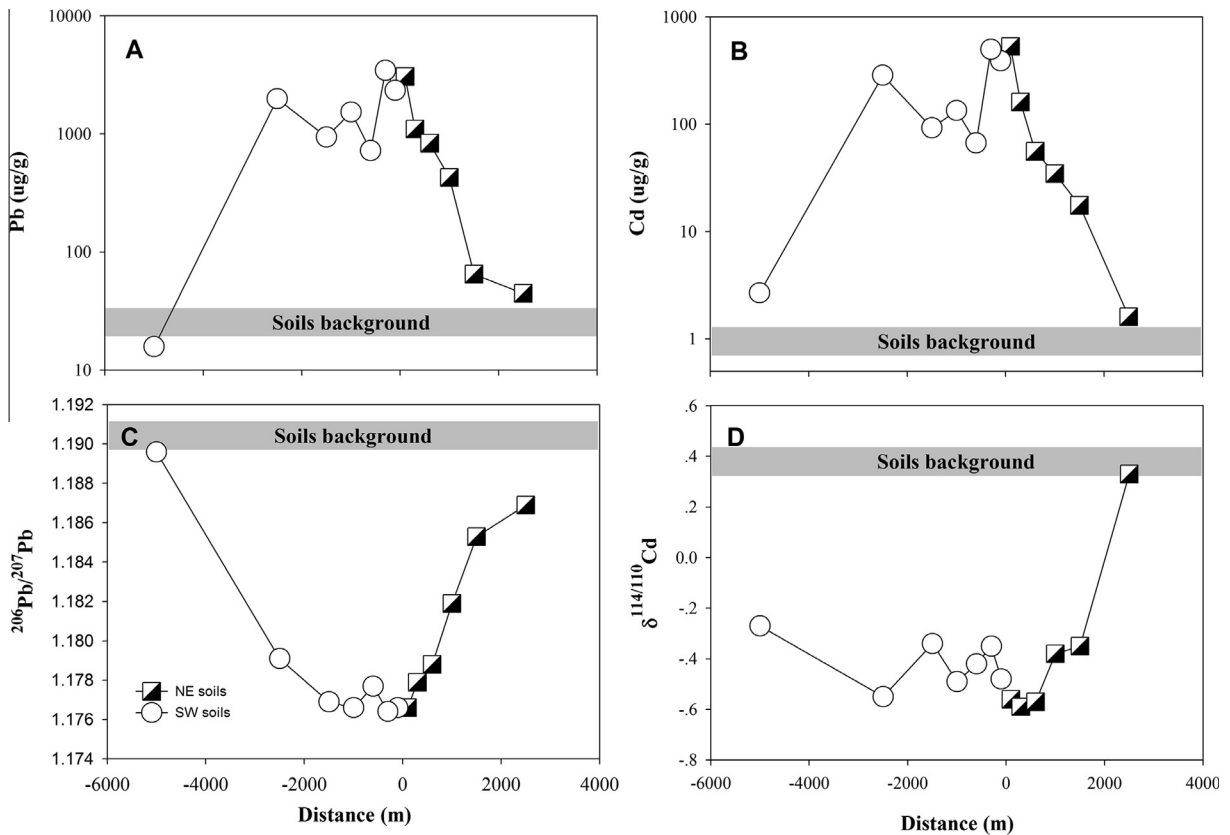

Fig. 3. Variations in the Cd and Pb concentrations and isotopic compositions with the distance from the pollution sources.
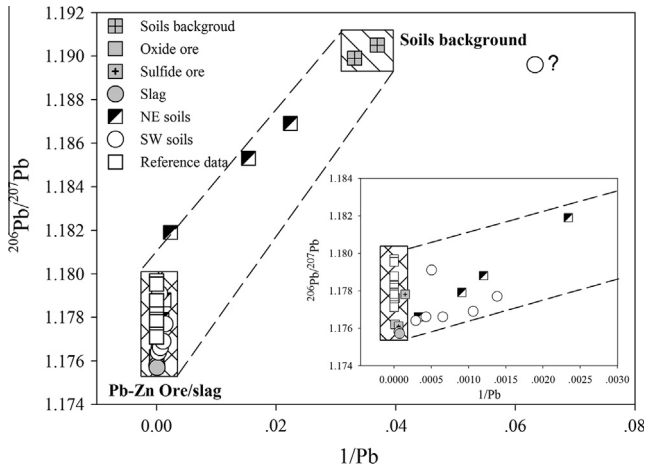
Fig. 4. Correlation between the Pb concentrations and isotope ratios in different samples, reference data from and Zeng et al. (2005) and Xue et al. (2007).
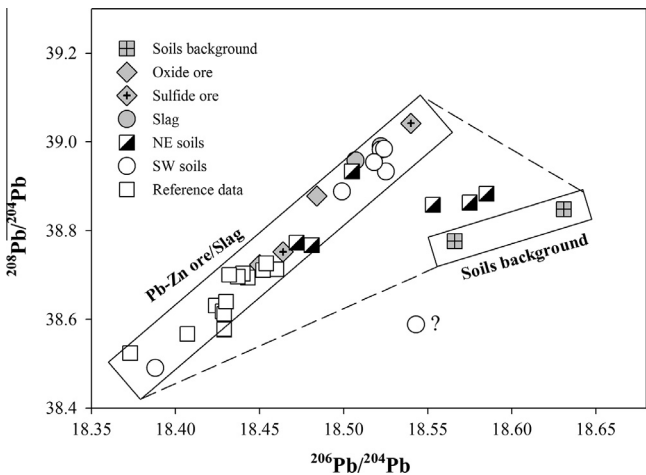

Fig. 5. Differences between the ^{208}Pb/^{204}Pb isotope ratios and the ^{206}Pb/^{204}Pb isotope ratios in different samples, reference data from and Zeng et al. (2005) and Xue et al. (2007).

southwest), and contained a very low Pb concentration (15.8 μg/g, which is below the concentrations found in the background soils and below the Chinese national first grade standard for soil) but the sample was slightly contaminated with Zn and Cd. This means that at least one more end-member was required to fully explain the Pb isotopic compositions that were found in the soil samples. The most likely explanation for this anomalous result is that the Pb concentrations of the background soils in the south may be different from those in the north because the underlying geology is different in the two areas.

4.2. Cd isotopes

The δ$^{114/110}$Cd values for the ore samples ranged between −0.35‰ and −0.70‰. A similar range (−0.35‰ to −0.70‰) was found by Zhu et al. (2013). The lighter Cd isotope was significantly enriched in ore samples compared with δ$^{114/110}$Cd values (−0.13‰ to 0.18‰) that have previously been found for other Pb–Zn ores (Shiel et al., 2010), which suggests that the genesis of ore deposit in our study area should be studied further. Although there is only limited amount of samples available, an offset among different type of samples still can be found. For example, the mean fractionation of 0.27‰ in the δ$^{114/110}$Cd value between primary (sulfide)

ores and secondary (oxidized) ores can been observed, which may indicate that heavy isotopes are preferentially removed, and residual is enriched in lighter isotopes during secondary alteration.

In general, the Cd concentrations and the δ$^{114/110}$Cd values in the soil samples from both the northeastern and southwestern parts of the study area decreased and approached the values of the background soil samples as the distance from the center of the sampling area increased. Although the trend was more irregular in the southwestern part than in the northeastern part of the study area (Fig. 3C and D), the Cd concentrations and the δ$^{114/110}$Cd values found in the soil samples from both the northeastern and southwestern parts of the study area fitted a binary mixing model in which the pollution sources from the mining activities and the background soil values were used, as shown in Fig. 6.

The evaporation and condensation processes involved in the industrial processing of ore could cause a relatively large degree of Cd isotopic fractionation. Cloquet et al. (2006) reported that the δ$^{114/110}$Cd values in slag and soot from a smelter in northern France were 1.0‰ different because of fractionation. The soot representing the vapor phase formed during the hot processing of ore is enriched in the lighter Cd isotopes (−0.64‰ in δ$^{114/110}$Cd), while the slag representing the final residue after the evaporative processes are complete is enriched in the heavier Cd isotopes (0.36‰ in δ$^{114/110}$Cd). Soot samples were not collected in our study. However, we estimated that the δ$^{114/110}$Cd value for the soot produced in the smelter was −1.48‰, based on the 1.0‰ offset between smelting slag and soot from results of Cloquet et al. (2006) and the mean δ$^{114/110}$Cd value of −0.48‰ for samples of slag in this study. Using the isotope mass conservation law, we estimated that about 16% of Cd in the ores entered the smoke and dust produced during the smelting process, matching the value of about 15% that was calculated by Cloquet et al. (2006). However, as mentioned above, the majority of the Cd in soot produced by Pb and Zn refining is recovered as a byproduct. Therefore, Compared with the large amounts of dust generated during the mining and ore transportation processes, the amounts of Cd released into the environment by soot is very small. As shown in Fig. 6, the results did not show that an end-member enriched in the lighter isotope occurred, indicating that dust fallouts produced by the reduction and evaporation of Cd is less important in this area.

Thus, the conclusions that we have drawn from the Cd concentrations and δ$^{114/110}$Cd values also fitted the Pb concentrations and Pb IRs that were found, confirming that (a) surface mining (in the Jiayashan and Beichang ore zones), (b) the smelter, and (c) the
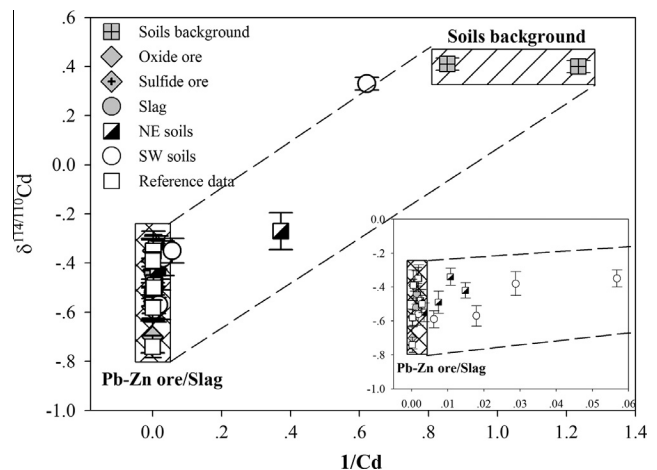

Fig. 6. Correlation between the Cd concentrations and isotope ratios in different samples, Reference data from Zhu et al. (2013).

slagheap were major sources of pollution to the soil samples from both the northeastern and southwestern parts of the study area. The other two pollution sources, (d) the tailings dam and (e) underground mining (in the Xipo and Fengzishan ore zones), that occur in the southwestern part of the study area are additional sources of pollution to the soil samples from the southwestern part of the study area. The Cd and Pb isotope data therefore corroborated each other, showing that the Pb–Zn mining activities taking place in the study area were the sources of Cd and Pb contamination in the soils in the study area.

The Bijiang River runs through the mining area that we studied, as shown in Fig. 1. Studies by Yi et al. (2012) have shown that the Bijiang River water quality has been significantly affected by mining activities (relative to the background water quality for the Bijiang River). The principal pollutants in the Bijiang River are currently As, Pb, and Zn, and no Cd pollution has been detected. The metal concentrations in the Bijiang River have been found to decrease gradually as the distance from the Jinding mining area increases (Yi et al., 2012). Contamination of soils caused by agricultural irrigation should, therefore, be considered. In comparison with the Cd and Pb concentrations that have been found in those water samples (tens to several tens of nanograms of Cd and Pb per gram of water), the extraordinarily high metal concentrations (several tens to thousands of micrograms of Cd and Pb per gram of soil) that were found in the soils around 5 km from the mining area are difficult to explain by river-borne transport rather than dust transport. Therefore, according to the Cd and Pb concentrations and isotopic compositions that were found, we conclude that the transportation of dust generated through anthropogenic activities (the mining and refining of ore) is responsible for the serious pollution that we found in the area within about 5 km of the Jinding mine. Contamination beyond the Jinding mine district may, of course, be caused by the transport of metals by the Bijiang River.

5. Conclusions

The Cd and Pb isotopes compositions that were found in this study clearly demonstrated that binary mixing between emissions from the ores and slags and the background Cd and Pb concentrations in the soil could explain almost all of the variations. This suggested that Cd and Pb soil pollution was mainly related to anthropogenic activities (mining and refining of ores) in the study area. Furthermore, variations in the Cd and Pb concentrations and isotope compositions confirmed that the emission and deposition of dust produced by surface mining, the smelter, the slagheap, the tailings dam, and underground mining were responsible for polluting the nearby soil. The most serious pollution occurred in soils within around 5 km of the pollution sources. The effect of the transportation of Cd and Pb in the waters of the Bijiang River remain unclear, and further study will be required to determine the importance of that source to the Cd and Pb concentrations and isotope compositions in the study area.

Acknowledgments

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