Allocation and source attribution of lead and cadmium in maize (*Zea mays L.*) impacted by smelting emissions

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The sources and pathways of Pb and Cd accumulated in maize were assessed using Pb isotopes and Pb/Cd ratios.

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Abstract

Plants grown in contaminated areas may accumulate trace metals to a toxic level via their roots and/or leaves. In the present study, we investigated the distribution and sources of Pb and Cd in maize plants (*Zea mays L.*) grown in a typical zinc smelting impacted area of southwestern China. Results showed that the smelting activities caused significantly elevated concentrations of Pb and Cd in the surrounding soils and maize plants. Pb isotope data revealed that the foliar uptake of atmospheric Pb was the dominant pathway for Pb to the leaf and grain tissues of maize, while Pb in the stalk and root tissues was mainly derived from root uptake. The ratio of Pb to Cd concentrations in the plants indicated that Cd had a different behavior from Pb, with most Cd in the maize plants coming from the soil via root uptake.

Keywords: Lead; Cadmium; Pb isotopes; Maize; Atmospheric deposition; Soil; Zinc smelting; China

1. Introduction

Environmental contamination by trace metals is a global problem and has been intensively studied (Nriagu and Pacyna, 1988). Metal accumulation in crop plants represents an important route of toxic metals into the human food chain (Mclaughlin et al., 1999). Pb and Cd are of particular concern because of their high toxicity and long biological half-life in humans (Komarnicki, 2005). Therefore, a better understanding of the transfer and accumulation of these metals from the environment into crop plants is critical for the protection of human health.

Pb and Cd exhibit different behaviors in biological systems. Generally, Pb is hardly taken up from soil into plants even at high concentrations because of its low solubility and strong interactions with soil particles (Clemens, 2006). However, Cd is generally a very labile trace metal in soil, and can be readily taken up by plant roots (Sauerbeck, 1991; Wagner, 1993). Besides soil, plants can also take up metals directly from the atmosphere. Some airborne pollutants that deposit on leaf surfaces can be absorbed by leaves and subsequently be translocated to unexposed parts. This pathway can contribute significantly to the accumulation of metals in plants, depending on the type of metal and plant species. Harrison and Chirgawi (1989) used growth cabinets with filtered air to demonstrate the impact of airborne metals on several vegetables. The atmospheric contribution to the contamination of spinach was up to 85% for Pb, but only 23% for Cd. Dollard (1986) using ^{210}Pb to examine the foliar uptake and redistribution of lead in several plant species, found that foliar absorption of lead could account for about 35% of the internal lead burden of radish root tissues, but only for 3% of the Pb in carrots. The translocation of foliar absorbed metals to non-exposed parts of plants is not well documented. Some studies found that the translocation of foliar absorbed Pb to fruits or seeds of plants was very slight

(Chamberlain, 1983; Haar, 1970), while other literature reported that cereal grains could accumulate substantial amounts of Pb via foliar absorption (CCFAC, 1995).

More studies of metal uptake by plants have been based on the quantitative measurement of concentrations and total amounts, but the Pb isotopic compositions can increase our knowledge on the cycling and pathways of Pb in the environment. As a general rule, Pb derived from anthropogenic sources is less radiogenic than the geogenic Pb, and different inputs may contain Pb with characteristic ratios (Sangster et al., 2000). It is, therefore, possible to trace various Pb sources in a plant based on Pb isotope composition analyses (e.g. Watmough and Hutchinson, 2004; Klaminder et al., 2005; Komárek et al., 2008).

Zinc smelting areas in southwestern China are seriously contaminated by Pb and Cd due to the smelting emissions (Shen et al., 1991; Feng et al., 2004, 2006; Bi et al., 2006a, 2006b, 2007; Yang et al., 2006), but Pb isotope ratios in soils and plants to identify the anthropogenic metal sources and burdens have not been conducted. The objective of the present study was to estimate the contributions of the smelting originated Pb and Cd to the total burdens of the two metals in soil and maize plants. For this purpose, we analyzed total metal concentrations and $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios. We expected that the maize plant take up metals from both the polluted soils and atmosphere via roots and leaves, respectively, but that the contribution and translocation of of Pb and Cd from these two sources to different tissues of the maize plants varied.

2. Materials and methods

Soil and maize samples were collected within a range of about 3 km from a typical zinc smelting site located in Hezhang, southwestern China (Figure 1). Previous studies had identified the smelting emissions as the major source of Pb and Cd contamination in soils and plants (Bi et al., 2006a, b). The feeding zinc ore samples were collected simultaneously from the smelting workshop during the sampling period. Each maize sample consisted of at least five individual plants collected from an area of about 1 m^2, and the corresponding soil samples were collected from the root zone of these plants. Reference soil and maize samples were also collected from control sites with the similar geological and geographical conditions as the smelting sites but far away (> 100 km) from smelting sites.

Soil samples were air dried at room temperature, and ground to <100 μm. About 250 mg of sample was digested with 6 ml of HCl (30%, v/v), 2 ml of HNO_3 (65%, v/v) and 2 ml of HF (40%, v/v) in a microwave digestion system for 26 min. The digested solution was diluted to 25 ml with Milli-Q water. Each maize sample was separated into root, stalk, leaf and grain sub-samples. All sub-samples were thoroughly cleaned with tap water and Milli-Q water to remove adhering particles, then air-dried, and ground to fine powder. The samples (500 mg) were then digested with 6 ml of HNO_3 (65%, v/v) and 2 ml of H_2O_2 (30%, v/v) in a microwave digestion system for 30 min, and the digested solution was diluted to 25 ml with Milli-Q water.

The concentrations of Pb and Cd of the sample solutions were determined using flame or graphite furnace atomic absorption spectrometry (AAS 5100, Perkin-Elmer Inc.). For quality assurance and quality control (QA/QC), we analyzed duplicates, method blanks and standard reference materials (SRM 2710, GBW 07404 and GBW 07602). The recoveries ((measured value / certified value)×100%) for the metals in standard reference materials were in the range of 87-114%, and the relative difference between sample duplicates was < 13%. Soil pH was determined in a 3:1 water/soil suspension, and organic matter content of the soil was estimated by loss on ignition (LOI) (Yang et al., 2006).

The Pb isotopic composition was analysed for selected ore, soil and maize samples by ICP-MS (Perkin-Elmer Elan 6100 DRC^{plus}). The details of the procedure were reported by Lee et al. (2006). The analytical parameters were set as 190 sweeps/reading, one reading/replicate, and 10 replicates per sample solution. Dwell times of 40, 25, 25, and 25 ms were used for ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb, respectively. Procedural blanks, duplicates and reference material (NIST SRM981 Common Pb Isotopic Standard) were used for quality control. The analysis was repeated when the differences between the measured and certified values of the standard reference material exceeded 0.5%. The Pb counts of the procedural blank were < 0.5% of the samples, and the precision (% RSD) of the Pb isotope ratios of ten replicates were typically < 0.5%. The average Pb ratios of ^{204}Pb/^{207}Pb, ^{206}Pb/^{207}Pb, and ^{208}Pb/^{207}Pb were 0.0645 ± 0.0001, 1.0938 ± 0.0011, and 2.3710 ± 0.0030, which were in good agreement with the standard reference values of 0.0645, 1.0933, and 2.3704, respectively.

3. Results

3.1. Metal concentrations

Lead and Cd concentrations in the soils from the smelting area exhibited wide ranges (69-2300 μg g^{-1} and 7.4-55 μg g^{-1}, respectively) and depended on the distance of the sampling locations to the smelting site (Fig. 1, Table 1). In comparison, reference soils sampled at the control sites showed much lower concentrations of Pb and Cd (40-45 μg g^{-1} and 0.22-0.27 μg g^{-1}, respectively). The maximum allowable concentrations (MAC) of Pb and Cd in agricultural soils (pH < 6.5) of China are 250 μg g^{-1} and 0.3 μg g^{-1}, respectively (National Environmental Protection Agency of China, 1995). Thus most soils from the smelting area had Pb and Cd concentrations exceeding the respective MAC value. These results indicate that these soils at the smelting area had been seriously contaminated by Pb and Cd.

Metal concentrations varied among different parts of the sampled maize plants. The concentration of Pb decreased in the order leaves > roots > stalks > grains, whereas the order was roots > leaves > stalks > grains for Cd (Table 1). Both Pb and Cd concentrations in the maize roots and leaves significantly exceeded those of the samples from the control sites (Table 1). In the present study, we were unable to collect maize grain samples from the control sites, but a previous study (Zhang et al., 1998) showed that the concentrations of Pb and Cd (0.007-0.616 μg g^{-1} and 0.002-0.006 μg g^{-1}, respectively) in maize grains from an uncontaminated area in China were much lower than in our samples from the smelting area. In addition, most grain samples in this study had higher concentrations of Pb and Cd than the national guidance limit for foods of China (0.2 μg Pb g^{-1} and 0.1 μg Cd g^{-1}, respectively) (Ministry of Health of the People's Republic of China, 2005), indicating that the grains were contaminated with these two metals, and may not be suitable for human consumption.

3.2. Lead isotopes

The Pb isotope compositions of various ore, gasoline, coal, soil and plant samples are presented in Fig. 2. In general, the local background soils were characterized by relatively high $^{206}Pb/^{207}Pb$ (1.244-1.249) and low $^{208}Pb/^{206}Pb$ (1.198-1.199) ratios. In contrast, zinc ores used in the smelting operations exhibited a rather low radiogenic signature ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios were 1.176-1.188 and 2.103-2.112, respectively), which corresponded to a previous study (1.174-1.187 and 2.103-2.127 for $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$, respectively) (Fig. 2) (Zheng, 1994). Soils from the smelting area had intermediate $^{206}Pb/^{207}Pb$ (1.181-1.238) and $^{208}Pb/^{206}Pb$ (1.994-

2.098) ratios. All samples formed a single line (Fig. 2), suggesting that their isotope ratios derived from a simple binary mixing process between smelting emissions and local geogenic background. Gasoline Pb and coal Pb are the most common anthropogenic source of Pb to the environment in southwestern China (Mukai et al., 1997, 2001; Zhu et al., 2001; Gao et al., 2004), but their impact on the soils and maize plants in the present study were not important (see Fig. 2).

Representative maize plant samples grown on those soils with different Pb concentrations (site 1, 7 and 11) were selected for Pb isotope analyses. Pb isotope ratios were very similar in the three leaf (^{206}Pb/^{207}Pb, 1.185-1.186; ^{208}Pb/^{206}Pb, 2.090-2.094) and grain (^{206}Pb/^{207}Pb, 1.180-1.181; ^{208}Pb/^{206}Pb, 2.091-2.104) tissues, but differed greatly in the roots (^{206}Pb/^{207}Pb, 1.182-1.209; ^{208}Pb/^{206}Pb, 2.050-2.098) and stalks (^{206}Pb/^{207}Pb, 1.172-1.193; ^{208}Pb/^{206}Pb, 2.080-2.114). In Fig. 2, the maize samples were distributed along a line, which is similar to that defined by the soils and ores, indicating the mixed origins of Pb in the maize samples from zinc smelting emissions and local natural background.

3.3. Lead/Cadmium ratios

The ratio of Pb to Cd concentration was calculated for all samples, and the results are listed in Table 1. The Pb/Cd ratios of the soil samples ranged from 9.3 to 52 with a mean value of 28, while the root samples had a mean value of 3.1 only. The stalks had slightly higher Pb/Cd ratios (mean 3.9) than the roots, and the average Pb/Cd ratios further increased to 5.7 in leaves and to 9.1 in grains.

3.4. Correlations

Correlation analyses between Pb and Cd concentrations in soils and in maize tissues showed that soil Pb concentrations were significantly correlated to the Pb concentrations in the maize root and stalk tissues, while leaf Pb was significantly correlated only to grain Pb (Table 2). The correlations were much stronger for Cd than for Pb, and the Cd concentrations correlated significantly among all type of sampled materials (Table 2).

4. Discussion

4.1. Source attribution of lead in maize plants

The main pathways of Pb accumulation in plants are the root uptake of soil Pb and the leaf uptake of atmospheric Pb. In the present study, the soil Pb is itself predominantly derived from atmospheric deposition of the zinc smelting flue gas dusts, therefore, the soil derived Pb and the foliar Pb uptake direct from the atmosphere in the maize tissues should have similar isotopic signatures. However, this was not the case as shown by the large variation of Pb isotope ratios among maize tissues (Fig. 3). Despite the large differences in Pb concentrations and isotope ratios of the soils, the maize leaves and grains sampled from different sites had similar $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios (Fig. 3), which differed greatly to their corresponding stalks, indicating the same origin of Pb in these tissues, but not from the stalk transport of the root uptake Pb. In this zinc smelting area, zinc ores were divided into two categories, one was sulfide ore and the other was oxide ore. The ratio of sulfide ore and oxide ore used in the smelting was 9:1 (Feng et al., 2004) during the sampling period. Based on this ratio and Pb isotopic compositions of the ores, we estimated that the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios of the atmospheric particle emitted from the zinc smelting operations were about 1.187 and 2.104, respectively. These ratios were very similar to those of the maize leaf samples, and thus demonstrated that Pb in the maize leaves may have mainly originated from the atmospheric deposition of the smelting flue gas dust. This is consistent with the reported results that plant leaves can uptake substantial amount of Pb direct from atmosphere (Haar, 1970; Buchauer, 1973; Harrison and Chirgawi, 1989; Dollard, 1986; Klaminder et al., 2005).

The surface of the grains in the present study was unlikely contaminated by airborne/soil particle because all the grains were wrapped by the husk when sampling. Therefore, the Pb accumulated in the grain samples refers to that of tissue absorption instead of surface adsorption. Metals accumulated in grain (seed) are mainly transported from the leaves via phloem (Patrick, 1997; Patrick and Offler, 2001; Grusak, 1994; Pearson et al., 1995). Previous study has proved that the foliar Pb can be translocated towards the actively growing regions (Watmough et al., 1999), including grains (CCFAC, 1995). Hence, it is possible that the Pb in the grains in our study was mainly derived from the leaves since they had the similar isotope ratios (Fig. 3).

The difference of Pb isotope ratios between leaves and stalks also indicates that the Pb stored in the root and stalk tissues is unlikely derived from the transport of the foliar Pb, and it can be derived only from the soil Pb. However, our current data are unable to explain the relatively lower ^{206}Pb$^{/207}$Pb ratios (and higher ^{208}Pb$^{/206}$Pb ratios) in the maize stalks and roots (sample 11) compare to their corresponding soils (Fig. 3). A possible explanation is that the soil Pb isotopes exhibit fractionation with less radiogenic Pb concentrating in the phyto-available fractions (e.g. the soluble or exchangeable fraction) (Klaminder et al., 2005; Wong et al., 2002; Wong and Li, 2004; Bacon and Hewitt, 2005). Of course more work is needed to test this hypothesis.

It can be summarized from the above discussion that maize plants from the zinc smelting emission impacted area had Pb in their roots and stalks mainly derived from the soil, while Pb in leaves and grains appeared to have originated mostly from the atmosphere. Besides the isotopic evidence, the significant positive correlation of total

Pb concentrations between leaves and grains, and between soils, roots and stalks further supports this conclusion (Table 2). Our result is in good agreement with previous studies that atmospheric Pb is an important source of Pb in plants (Buchauer, 1973; Haar, 1970; Harrison and Chirgawi, 1989; Dollard, 1986; Klaminder et al., 2005).

4.2 Source attribution of cadmium in maize plants

Based on the total metal concentrations, it is not easy to distinguish the Cd origins in the maize tissues. But the Pb/Cd ratios calculated in the present study may provide some insights on the Cd cycling and pathways in plants, which differ to those of Pb. The decrease of Pb/Cd ratios from soils to maize roots (Table 1) indicates a much higher bioavailability of Cd than Pb in soil, a finding that is consistent with other reports (Clemens, 2006; Sauerbeck, 1991; Wagner, 1993; Voutsa, 1996). While in the aboveground tissues of the maize plants (especially grains) the Pb/Cd ratios were higher than those of the roots (Table 1), this can be explained by two possible reasons. One is that Pb is preferentially transferred in comparison with to Cd from root to shoot of the maize plants. An alternative explanation is that an additional source (atmospheric origin) with relatively higher Pb/Cd ratios was involved in these aboveground tissues. The former explanation is less likely because Pb binds to the cell wall of plants more strongly than Cd, and the rate of Pb movement along the apoplast is lower than that of Cd (Seregin and Ivanov, 1998). Previous studies have proved that the accumulation of Pb in maize shoot is lower than Cd (Makowski et al., 2005; Cui et al., 2004).The Pb/Cd ratios of the ambient air in the smelting area were reported to be 18-26 with a mean value of 23 (Shen et al., 1991). A similar mean ratio of 24 in the moss samples collected from the same smelting site was reported by Bi et al. (2006b). Hence, it is possible that the relative higher Pb/Cd ratios in the aboveground tissues of the maize were resulted from the atmospheric deposition. This is consistent to the above discussion that atmospheric Pb had dominant contribution to the total Pb burden in the maize leaves and grains.

It is worthy to note that Pb/Cd ratios of the maize leaves were much lower than those of the ambient air (Shen et al., 1991) and the mosses (Bi, et al., 2006b). Many studies argue that atmospheric Pb may be more readily transferred to plant leaves than other metals (Harrison and Chirgawi, 1986; Watmough et al., 1999; Watt et al., 2007), especially in acid environment (Watmough et al., 1999). Watmough et al. (1999) found that foliar uptake of Pb may be enhanced at low pH values because of the increased mobility of deposited metals and an increase in membrane permeability. Greger et al. (1993), however, reported that low pH decreases the net uptake of Cd, probably by an exchange reaction in the cutin and pectin of the cuticular membranes. The studied area is located in a serious acid deposition region in China (Feng et al., 2002). We, therefore, expect that the decrease of Pb/Cd ratios from atmosphere deposition to leaves of the maize is not due to the preferential absorption/adsorption of atmospheric Cd to the maize leaves in comparison with Pb, but a significant contribution of soil Cd to the leaves. Previous study also found that maize plants grown on heavily contaminated soils accumulated substantial amounts of Cd in their leaf tissues (Liu et al., 2005). Therefore, we may conclude from the above observationsthat the Cd burden in the maize was probably dominated by soil Cd. The significant correlation between Cd concentrations in maize tissues and soils supports this statement (Table 2).

5. Conclusion

This field investigation was conducted to obtain insights on Pb and Cd behaviors in maize plants from a typical area with soil and atmosphere being heavily contaminated.

Results showed that Pb in the maize leaves and grains were dominated by atmospheric inputs, while Cd in the whole plant seemed to be mainly derived from soil. Hence, the atmospheric contamination by Pb is more important than that of the soil in terms of the impact of Pb on human health through food chain. However, more work is needed to further confirm the significant contribution of atmospheric Pb to the grains, and factors (e.g. humidity and pH) that influence the absorption/adsorption of atmospheric Pb by leaves are also required to be extensively studied.

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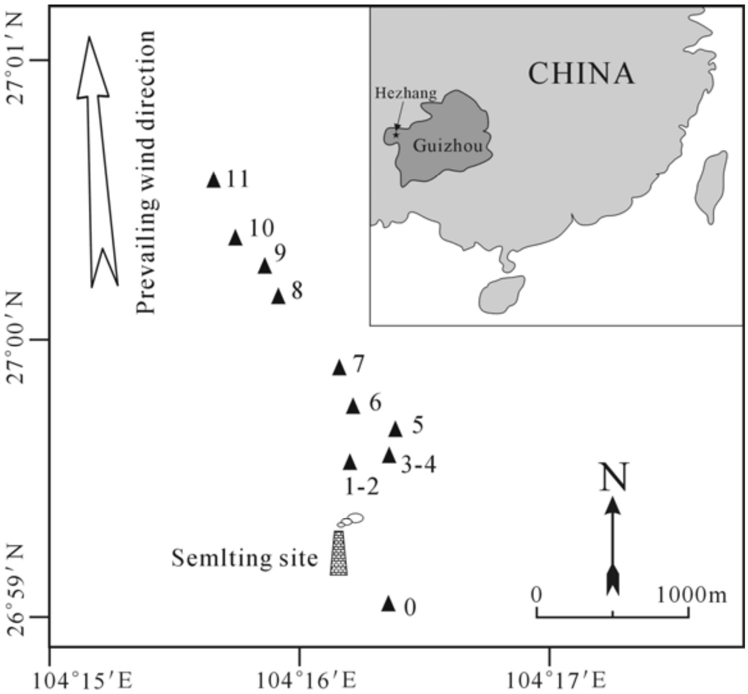


Figure 1. Study area and sampling locations

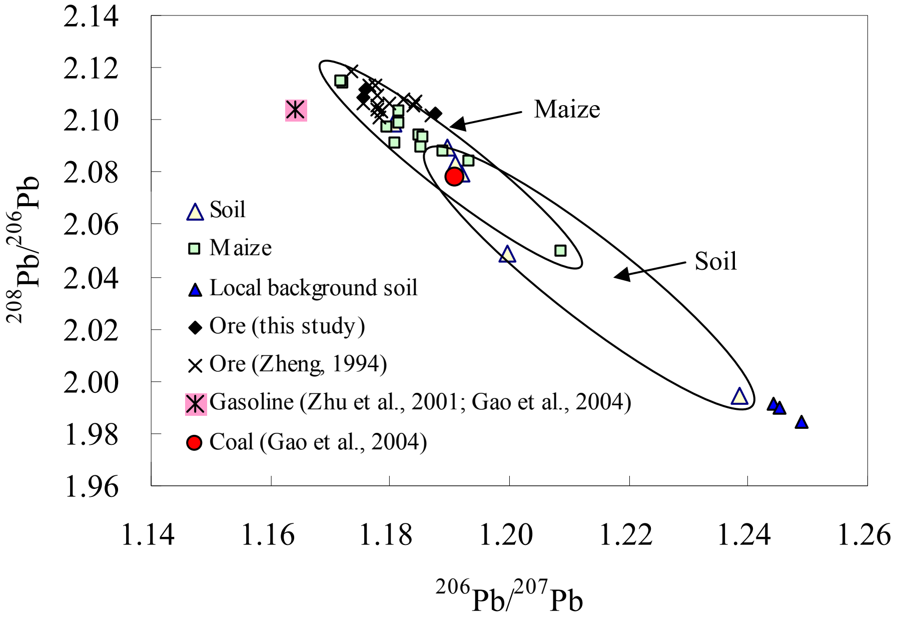
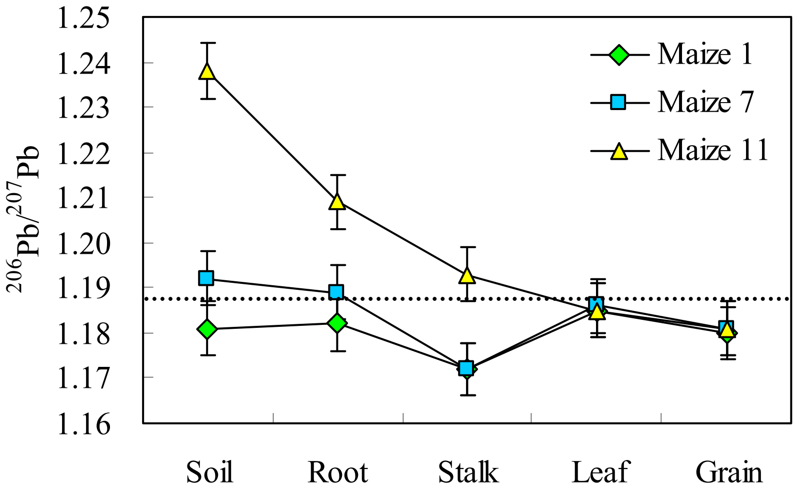


Figure 2. A plot of ^{206}Pb/^{207}Pb versus ^{208}Pb/^{206}Pb for the analysed samples. The ellipses have been added manually to indicate the groups.



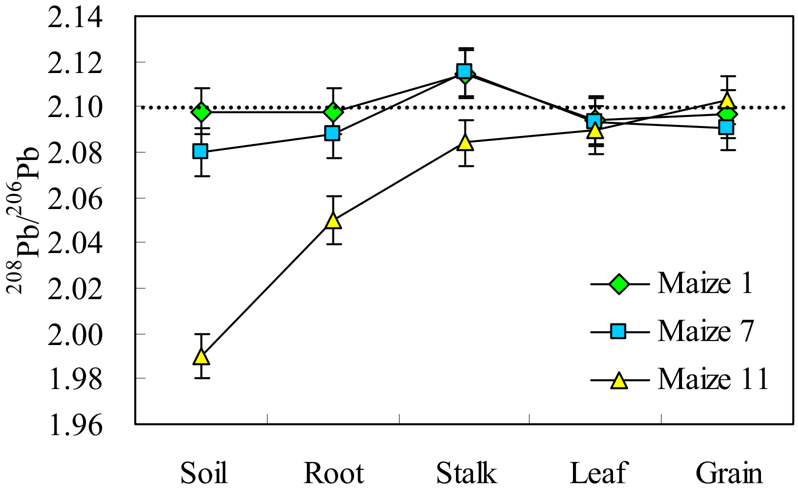


Figure 3. A plot of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios in different maize tissues and the soils where they grown. The dashed represents the average $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios of the feeding ores used during the sampling period.

Table 1. Lead and cadmium concentrations and Pb/Cd ratios of soils, maize roots, stalks, leaves and grains with soil pH and LOI .

Sample site	Distance from the smelting site (m)	Lead concentration (μg g^{-1})					Cadmium concentration (μg g^{-1})					Lead/cadmium ratios					pH	LOI[a] (%)
		soil	maize				soil	maize				soil	maize					
			root	stalk	leaf	grain		root	stalk	leaf	grain		root	stalk	leaf	grain		
0	-600[b]	400	17	2.1	47	1.0	19	4.4	0.23	4.1	0.09	21	3.8	9.3	11	12	4.8	15
1	500	2300	140	2.9	57	1.2	55	37	5.8	31	0.43	42	3.8	0.5	1.8	2.7	6.5	13
2	510	2300	220	2.9	57	1.2	44	40	1.6	30	0.33	52	5.5	1.8	1.9	3.5	6.5	13
3	600	320	29	1.8	78	1.1	18	15	1.0	12	0.15	18	2.0	1.8	6.7	7.2	4.8	16
4	610	220	16	2.2	130	1.4	17	7.5	0.73	17	0.13	13	2.2	3.0	7.8	11	5.3	15
5	700	320	24	1.8	40	1.1	29	19	0.47	7.4	0.15	11	1.3	3.8	5.5	7.1	6.0	14
6	900	370	31	2.8	51	1.0	15	9.6	1.2	11	0.11	25	3.2	2.3	4.7	9.3	5.0	16
7	1200	400	25	2.0	79	1.0	13	5.7	0.32	14	0.10	32	4.4	6.3	5.8	11	6.4	13
8	1700	250	13	1.9	56	0.92	13	6.5	0.52	16	0.09	19	2.0	3.6	3.4	11	5.8	14
9	1900	500	10	2.3	25	1.0	12	3.6	1.0	4.6	0.12	43	2.9	2.3	5.4	8.7	5.6	13
10	2200	330	16	1.9	50	1.2	7.4	2.9	0.17	4.9	0.05	44	5.5	12	10	21	5.8	6.3
11	2600	69	8.1	2.1	38	0.85	7.4	25	2.3	8.8	0.18	9.3	0.32	0.9	4.3	4.7	4.0	11
Control site																		
1		40	5.2		1.7		0.25	0.62		0.08							6.5	14
2		45	1.9		1.3		0.22	0.40		0.10							6.2	14
3		40	4.8		2.1		0.27	0.16		0.17							6.4	13

[a] Loss on ignition; [b] upwind direction

Table 2. Pearson correlation matrix between Pb and Cd concentrations in soils and maize tissues.

	Lead				Cadmium			
	grain	leaf	stalk	root	grain	leaf	stalk	root
leaf	0.649*				0.846**			
stalk	0.224	-0.065			0.876**	0.663*		
root	0.371	-0.007	0.737**		0.925**	0.765**	0.730**	
soil	0.370	-0.067	0.769**	0.955**	0.910**	0.806**	0.705*	0.812**

* Significant level at P <0.05, ** P <0.01 (two-tailed)