Assessment of lead bioaccessibility in soils around lead battery plants in East China

Zan-fang Jin [a], Zhuo-jun Zhang [b], Hui Zhang [a], Cong-qiang Liu [b], Fei-li Li [a,*]

[a] College of Biological and Environmental Engineering, Zhejiang University of Technology, Hangzhou, 310032, China
[b] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, 550002, China

HIGHLIGHTS

- 70 Soil samples were collected surrounding five battery plants in China.
- An *in vitro* method mimicking gastric and intestinal environment was applied.
- Pb bioaccessibility of soils was ranged from 4.12% to 66.9% in gastric phases.
- Pb isotopic ratios showed the battery dust was the main anthropogenic source.
- Two modes of bioaccessible Pb had been established based on soil properties.

ARTICLE INFO

ABSTRACT

Soil ingestion is an important human exposure pathway for lead (Pb). A modified physiologically based extraction test was applied to 70 soil samples from five battery plants in East China. The mean values for soil pH, soil organic matter, Fe and Mn concentrations ranged from 5.9% to 8.1, 0.37% to 2.2%, 2.78% to 3.75%, and 507–577 mg kg^{-1}, respectively, while Pb concentrations ranged widely in 14.3–2000 mg kg^{-1}. The isotopic ratios of 14 soils from one of the five battery plants formed a straight line in the plot of ^{208}Pb/^{206}Pb vs. ^{207}Pb/^{206}Pb, indicating Pb emissions from the lead battery plant as the dominant anthropogenic source within 200 m. Lead bioaccessibility in the soils ranged from 4.1% to 66.9% in the gastric phase and from 0.28% to 9.29% in the gastrointestinal phase. Multiple step regressions identified modes as $BA_{gastric} = -106.8 + 0.627[Pb] + 19.1[Fe] + 11.3[SOM]$, and $BA_{gastrointestinal} = -2.852 + 0.078[Pb]$.

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1. Introduction

Lead (Pb) is a poison element of multiple affinities, which is ubiquitous in the soil environment. There is considerable concern regarding human exposure to soil Pb because of negative health effects, particularly with neurological development and the hematopoietic system in young children (Washam, 2002; Lanphear et al., 2005). Human exposure to soil Pb occurs through inhalation, ingestion, and dermal contact (Van Wijnen et al., 1990; Cui and Chen, 2011). Ingestion of soil is considered an important exposure pathway for Pb in children through outdoor hand-to-mouth activities (Rodriguez and Basta, 1999; Patinha et al., 2012), which causes an average of 50–200 mg ingestion of soil/day for a child

(Oomen et al., 2003). However, only those Pb could be released from soil into solution in the gastrointestinal tract, existing in a form that can be absorbed into blood stream, were bioaccessible (Cave et al., 2011), and could cause toxic effects (Lu et al., 2011).

During the digestion process, Pb was released from soil and become bioaccessible. However for this exposure route the degree of Pb release is dependent on the degree of dissociation of Pb from soil solids. The oral bioaccessibility is the fraction of Pb dissolved from a solid sample (e.g. soil, dust) under simulated gastrointestinal conditions (Ruby et al., 1999). Oral bioaccessibility, rather than total Pb content, provides a more realistic estimate during health risk assessments. Presently, bioaccessible Pb is considered to represent the maximum amount of Pb available for absorption (Tang et al., 2004; Bosso and Enzweiler, 2008).

Pb bioaccessibility is mainly controlled by soil and pollutant properties. Soil properties, such as soil pH, texture, soil organic

* Corresponding author. Tel.: +86 13868092159; fax: +86 571 88320745.
  E-mail address: lifeili@zjut.edu.cn (F.-l. Li).

matter (SOM), Fe and Mn oxides (Cui and Chen, 2011), and pollutant solubilities and chemical forms, are specific to the contaminated environment and cannot be controlled. As a result, the bioaccessibility of Pb varies greatly with the type of sample. For example, Pb bioaccessibility in peri-urban soils ranged from 26.8% to 105.2% and from 5.5% to 102.6% in the gastric and gastrointestinal phase extractions, respectively (Smith et al., 2011), while in lead mine wastes Pb bioaccessibility was only 1–6% of the total Pb in the gastrointestinal tract (Ruby et al., 1993). Pb from industrial area soil was more bioaccessible than that from residential yard and farm soil (Ren et al., 2006). A detailed understanding of Pb accessibility in soils from different environments is needed.

During the development and urbanization process in China, some polluting enterprises have moved to suburban and rural areas. These lead battery factories, whose production covered about one-third of total output in the world, are a significant source of pollution and much higher Pb concentrations have been reported close to lead battery facilities (Chen et al., 2012). Lead concentrations ranged from 50.2 to 9140 mg kg^{-1} within 500 m of a lead-acid battery factory in Guangdong, China (Chen et al., 2012), and ranged from 304 to 602 mg kg^{-1} in the vicinity of a lead battery plant in the city of Gaziantep, Turkey (Kaya and Yaman, 2012). Xue et al. (2014) using the positive matrix factorization and geo-statistical approach, partitioned the variances into sources related to lead battery plants, soil background, and agronomic practices, and the lead battery plant was estimated contributing 55.37% for Pb of the total source within a 1-km radius of a lead battery plant. A study with lead isotope ratios showed that lead from industrial activity was present in the thin top layer (Díaz-Somoano et al., 2007). Children in suburban and countryside areas, who have poorer self-protection awareness, more hand-to-mouth activities, and sensitivity to nutrient deficiency, are more likely to be susceptible to Pb absorption from the environment (Wang and Zhang, 2006; He et al., 2009), but few assessments of Pb absorption in children have been carried out in suburban and rural areas.

Environmental research was carried out around five lead battery plants of different ages in China. The aims of this study were: (1) to investigate Pb bioaccessibility from soils around selected battery plants using a modified physiologically based extraction test (PBET) and its distribution characteristics; (2) to discuss the relationship between soil properties and Pb bioaccessibility in soils around battery plants by means of Pb isotopic compositions analysis; and (3) to provide researchers with more detailed information for understanding Pb exposure from battery pollutant.

2. Materials and Methods

2.1. Soil sampling and pretreatment

70 topsoil samples were collected in July 2011 from five lead-acid battery plants that had been established from 0.5 to 7 years ago in China. For each battery plant site, 12 soil samples were collected at three distances (50, 100 and 200 m) in four directions (N, S, E and W) from the battery plant, and two soil samples were collected inside the battery plant. Soil samples were placed in nylon woven bags under room temperature and transported back to the laboratory as quickly as possible. After being air-dried at room temperature, soil samples were crushed and sieved to pass through a 2-mm sieve. Each soil sample was then divided into three subsamples: two were further ground with an agate mortar and pestle and sieved to 150 µm (100-mesh sieve) and 250 µm (60-mesh sieve) for determination of total elements and the bioaccessibility test, respectively, and the left was stored in plastic bags for analysis of the soil physicochemical properties. The soils samples (14

soils) of HN battery plant were selected from the 70 samples to determine their Pb isotopic compositions additionally.

2.2. Determination of total elements and soil physicochemical properties

The physicochemical properties of the soils were determined according to standard methods of soil analysis. Soil pH values were measured in distilled water (1:2.5 w/v)(Lu et al., 2011). SOM was determined by the hot hydration method (Jackson, 1958). Particle-size distribution was assessed using the hydrometer method. Cationic exchange capacity (CEC) was obtained by the BaCl$_2$–H$_2$SO$_4$ forcing exchange method (ISO 11260-2008). Total P was measured by H$_2$SO$_4$–HClO$_4$ digestion and Mo–Sb colorimetry methods (Lu et al., 2011).

The total concentrations of metals in the soils were determined using flame atomic absorption spectrometry (PE AA800, PerkinElmer Inc., Waltham, USA) after being microwave digested 0.1 g soil with 8 mL HNO$_3$ + 2 mL H$_2$O$_2$ + 3 mL HF. The condition for flame atomic absorption spectrometer for Pb, Fe and Mn were as follows, wavelengths at 283.3, 248.3, and 249.5 nm, lamp current at 10, 30, and 20 mA, and slit width at 0.7, 0.2, and 0.2 nm, respectively.

2.3. Determination of Pb isotope composition

For determination of Pb isotopes under a minimal blank value of Pb, soil samples (0.05 g) were digested in a mixture of concentrated HNO$_3$ (65%, v/v) and concentrated HF (40%, v/v) in Teflon vessels on a hotplate at 200 °C. High-purity acids were used throughout the analysis. The digested solution was purified using a Dowex AG50 1X8 (200–400 mesh) anion exchange resin column as previously described (Li et al., 2012). Measurements of Pb isotope ratios were executed on a multi-collector Inductively Coupled Plasma-Mass Spectrometer (MC-ICP-MS, Nu Plasma, Nu Instruments Ltd., Wrexham, UK) after purification (Li and Niu, 2003).

2.4. In vitro Pb bioaccessibility test

In vitro bioaccessibility was determined with a physiologically based extraction test (PBET) performed on a < 250-µm soil subsample, which is the upper limit of particle size for adhering to fingers and becoming available for incidental ingestion during hand-to-mouth activity (Rodriguez and Basta, 1999; Lu et al., 2011).

Gastric solution (0.15 M NaCl) for the test was prepared by adjusting 4 L of deionized water to pH 1.5 with concentrated HCl (12 M) and adding 2 g citrate, 2 g malate, 1.68 mL lactic acid, 2 mL acetic acid, and 5 g pepsin (P7000, Sigma Chemical Co.). Gastric solution (600 mL) was combined with 6 g test soil in the glass reactor vessel. The reactor vessel was approximately three-quarters submerged in a temperature-controlled water bath maintained at 37 °C. Anaerobic conditions were created by constantly bubbling argon gas at 1 L min^{-1} from the solution bottom. Gastric mixing was simulated using paddle stirrers at a speed of 100 rpm. The solution pH was checked after 10 min and intervals of 20 min thereafter, adjusting pH with concentrated HCl as necessary to maintain a pH of 1.5. After 1 h, a 20-mL sample was collected by a syringe.

The reactor vessel was topped up to 600 mL with another 20 mL of freshly prepared gastric solution. The conditions of the extraction solution were modified to mimic intestinal solution by raising the pH to 7.8 by adding NaHCO$_3$ powder (Oomen et al., 2003), then adding 1.2 g pig bile powder (P333010, Dibai Chemical Co.) and 0.36 g porcine pancreatin (P1500, Sigma Chemical Co.) to each reactor vessel, then keep pH value of 7.0 with all other conditions remaining unchanged. The solution pH was checked every 20 min and adjusted with concentrated HCl or NaHCO$_3$ powder as

necessary. After 4 h, a 20-mL sample for the gastrointestinal phase was obtained for analysis (Tang et al., 2008).

The sampled gastric and intestinal solution samples were centrifuged at 4000g for 15 min, filtered through a 0.45-µm fiber filter and stored in a refrigerator at 4 °C until analysis. The samples were acidified to pH 2 using HCl. Pb in the solution was determined using a graphite furnace atomic absorption spectrophotometer (Tüzen, 2003).

The reference soil, GBW07429, was used to validate the accuracy of the *in vitro* bioaccessibility tests ($n = 20$), with recoveries ranging from 96.4% to 105% and a relative standard deviation of less than 15%. A duplicate was extracted in every 5 samples. The mean standard deviations of 14 duplicates were 0.74% and 0.29% for gastric and gastrointestinal bioaccessibilities, respectively. Blank extraction was conducted in each batch of extraction, and 10 blank tests were obtained. Pb concentrations in blank extraction were averaged at 6.4 µg (ranged in 5.32–7.38 µg) and 1.15 µg (range in 0.88–1.32 µg) for gastric and gastrointestinal phases, respectively.

2.5. Bioaccessible Pb concentration and its bioaccessibility

Bioaccessible Pb in the gastric and gastrointestinal phases was calculated as Eq. (1). Pb bioaccessibility was defined as the percentage of bioaccessible Pb in the gastric and gastrointestinal phases of total Pb in the soil, as expressed in Eq. (2).

$$\text{Bioaccessible Pb} = \frac{C_{sol}V_{sol}}{m_{soil}} \qquad (1)$$

$$\text{Bioaccessible} = \frac{C_{sol}V_{sol}}{m_{soil}c_{soil}} \times 100\% \qquad (2)$$

where C_{sol} (mg L^{-1}) indicates Pb concentration in the gastric or the gastrointestinal solution from the PBET, V_{sol} is the reaction solution volume in the reaction vessel (L), C_{soil} is the Pb concentration in soil (mg kg^{-1}), and m_{soil} is the soil mass in the reaction vessel (kg).

2.6. Quality control and statistical analysis

The standard solutions of Pb, Mn and Fe (1000 µg L^{-1}; provided by the National Institute of Metrology, China) for the calibration of atomic absorption spectroscopy determinations were diluted to appropriate concentrations using 2% HNO$_3$. Standard reference materials (GBW07429 and GBW07415; China National Analysis Centre for Iron and Steel, Beijing, China) were used as quality assurance and quality control for heavy metal analyses. The recoveries of analyzed metals in standard reference materials were within 100 ± 5% of recommended values, and the relative standard deviation of duplicate tests was less than 10%. Reagent blanks were used to correct the entire analysis procedure. Reagents used in the experiment were guaranteed or of analytical grade. Milli-Q water was used for preparation and dilution of all solutions (Millipore, USA). Prior to use, all glassware and plastic containers were soaked in 20% (v/v) HNO$_3$ for at least 24 h, thoroughly washed with tap water, and then rinsed with Milli-Q water three times.

Instrumental mass fractionation of Pb was corrected by adding ^{205}Tl/^{203}Tl = 2.3872 as an internal isotopic standard. During the MC-ICP-MS measurements, the NIST-SRM 981 standard was analyzed after each batch of five samples to monitor mass fractionation. The average measured Pb ratios of ^{208}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, and ^{206}Pb/^{204}Pb in NIST-SRM 981 were 36.6853, 15.4852, and 16.9325, in close agreement with the reference values of 36.722, 15.4963, and 16.9405, respectively. These results indicate that mass fractionation was very small and could be ignored in our analyses. The background Pb during the whole procedure was < 50 pg.

Data processing was performed using Sigmaplot 10.0 and Excel 2010. Statistical analyses were performed with SPSS 16.0. Soil Pb mean separation statistics were tested for significant differences using Student's t-Test and were separated using Duncan's multiple range test ($p < 0.05$). To test the relationships between the bioaccessible Pb and soil total Pb concentrations, Spearman correlation analyses were performed. Furthermore, to investigate the principal factors determining soil bioaccessible Pb, a multiple linear regression was applied to correlate the measured gastric and gastrointestinal bioaccessible Pb with soil physicochemical parameters. Before including one of these variables in the model, their linear relationship was tested. Only if linearity was observed was the variable included in the model.

3. Results and discussion

3.1. Physicochemical properties of soils

Soil physicochemical properties from five battery plant sites are shown in Table 1. Soil pH at most battery plant sites was slightly alkaline, ranging from 7.9 to 8.1, except for site SD-1, which had a weakly acidic pH of 5.9. The maximum (2.20%) and the minimum (0.37%) SOM contents were obtained at AH and HN battery plants, respectively, while the SOM contents of the other battery plant sites were in the range 1.10–1.50%. Soil CEC was significantly higher at the JS battery plant site (47.5 cmol kg^{-1}) than at the other battery plant sites (19.8–37.7 cmol kg^{-1}). Total Mn and Fe ranged from 507 to 577 mg kg^{-1} and 2.78% to 3.75%, respectively, and were both divided into three levels. Significant differences were also seen in the soil texture of sampled battery plants. Sands, silts and clays ranged from 13.3% to 60.0%, 29.4% to 67.0%, and 10.5% to 19.8%, respectively.

3.2. Distribution of total Pb concentration and Pb isotope composition

Table 2 shows the total Pb concentration in soils inside and outside the battery plants. Inside the battery plants, total Pb concentration in soils varied from 51.4 to 2000 mg kg^{-1}. Outside the battery plants, total Pb in soils ranged from 14.3 to 200 mg kg^{-1} at all distances from the plant. There were 6 samples exceeded the value of the secondary level of 80 mg kg^{-1} in paddy or dry field of the Environmental Quality Standard for Soils of China (GB15618-2008), which level is for preliminarily screening the degrees of soil pollution.

The impacts of the age of the battery plant and the local prevailing wind direction were very important in determining the distribution of Pb in soils. Inside the battery plants, total Pb in soils increased with the age of the battery plant (Table 2). For samples taken outside the battery plants, more recently established battery

Table 1
Soil properties around five battery plants.

Plant sites	SD-1	JS	SD-2	AH	HN
pH	6.2a	8.1b	8.0b	8.0b	7.9b
SOM (%)	1.42b	1.10b	1.43b	0.37a	2.20c
CEC (cmol kg^{-1})	23.8a	47.5c	37.7bc	35.1ab	27.1ab
Fe (%)	3.74b	3.72b	2.78a	3.59b	3.13a
Mn (mg kg^{-1})	634bc	676c	515a	507a	563ab
Particle size composition (%)					
Sand (>50 µm)	51.3%bc	13.2%a	59.0%c	46.4%b	22.7%ab
Silt (2–50 µm)	34.7%a	67.0%b	30.6%a	38.2%a	62.7%b
Clay (<2 µm)	14.0%ab	19.8%c	10.4%a	15.3%b	14.6%b

SOM, soil organic matter; CEC, cationic exchange capacity.
Means in the same row followed by different letters are significantly different among plant sites at $p < 0.05$, tested with One-way ANOVA of Duncan's multiple range tests.

Table 2
Total Pb concentration in soils around five lead–acid battery plants.

Distance, direction		Battery plants				
		Total Pb concentration (mg kg^{-1})				
		SD-1	JS	SD-2	AH	HN
The age of the battery plant (y)		1	3	5	6	7
Inside	East side	51.4	267	70.0	1480	2000
	West side	73.1	65.8	796	353	1350
50 m	East	24.5	20.5	23.6	31.7	107
	South	22.6	24.1	29.0	144	157
	West	18.6	34.6	200	24.1	63.3
	North	18.3	23.2	33.9	33.7	70.8
100 m	East	22.6	21.5	22.6	107	152
	South	19.5	23.8	64.3	36.6	74.9
	West	14.3	28.3	53.2	35.1	51.6
	North	23.1	24.7	40.3	33.9	64.5
200 m	East	24.5	23.4	25.0	34.1	45.6
	South	19.4	27.5	59.0	33.7	73.9
	West	20.9	25.6	43.4	20.8	58.7
	North	19.2	23.8	29.9	24.9	47.2
Standard values[a]		80				

[a] The level preliminarily screening the degrees of soil pollution for Pb in paddy or dry field in China, GB15618-2008.

plants (SD-1 and JS, with running times of 1 and 3 years, respectively) displayed similar Pb concentrations at 50, 100, and 200-m circles, indicating minimal effects on the spatial distribution of Pb concentrations (Fig. 1a and b). When battery plants were more than 3 years old, the patterns of Pb distribution were typical of the dispersion of point-source air pollutants. For example, Pb concentrations were significantly higher at sampling sites highly consistent with the local prevailing wind direction at the site i.e. 50 m W of SD-2 (Fig. 1c), 100 m E and 50 m S of AH and HN (Fig. 1d and e). Usually, small particles from battery plant sites may be carried by the wind, and they are later washed into the soil by rainfall (Ren et al., 2006). In this study, the maximum Pb concentrations we had observed appeared in the soil samples at 50 m, then 100 m, indicating that most of the lead emissions were contained within the scope of the surrounding 200 m.

The ratios of $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{206}Pb/^{204}Pb$ of 14 samples ranged from 38.0734 to 38.6269, 15.5710 to 15.6276, and 17.9333 to 18.4706, respectively. The Pb isotope ratios of $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}$ Pb were commonly used as tracers (Tommasini et al., 2000) for distinguishing anthropogenic Pb inputs from those of natural origin (Walraven et al., 1997). In our case, the ratios of $^{208}Pb/^{206}Pb$ vs. $^{207}Pb/^{206}Pb$ of soil samples formed a straight line (R^2 = 0.9954; Fig. 2) in the plot, showing a binary mixing system. In a binary mixing system, there are only two lead sources, lead from anthropogenic source and natural lead from the soil, whose isotope ratios fall at the ends of the line (Díaz-Somoano et al., 2007). Usually, the natural origin characterized by lower ratio values of $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$, in this case, they should be lower than 2.0913 and 0.8461, respectively. The other anthropogenic endmember, characterized by higher ratio values of $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$, should be higher than 2.1231 and 0.8683, respectively. Since the soil of the two highest Pb isotopic ratios had Pb concentrations of 1350 and 2000 mg kg^{-1}, respectively, which were sampled inside of HN battery plant and were much higher than the lowest concentration of 47.2 mg kg^{-1}, they were supposed to be close to the Pb isotopic ratios of the real endmember of anthropogenic sources. The Pb isotopic ratios from Chinese coal and vehicle exhaust, as the most common anthropogenic sources, lying off the plotted line (Fig. 2), however they had greater values of Pb ratios than 2.1231 and 0.8681, they possibly contributed Pb characterized with high values of Pb ratios to all the values on the plotted line of Fig. 2. On the other hand, in the rural area of a 200-m radius around the lead battery plant, Chinese coal and

vehicle exhaust, as atmospheric pollutants, seemed to have similar contributions to all soil samples. This would not give rise to the values on the line to the right-hand side of Fig. 2, instead it elevates or moves right the plotted line, like system errors. This excluded the two anthropogenic sources from the endmember of the binary mixing system, and indicated that the Pb dust from the lead battery plant was the dominant anthropogenic Pb pollutant contributing Pb to these soils in the peripheral 200-m area.

3.3. Pb bioaccessibility of soils around battery plant

Pb bioaccessibility in soils around battery plants are shown in Table 3. In the soils inside these lead-acid battery plants, Pb bioaccessibility in the gastric phase ranged from 4.12% to 66.9%, with an average of 31.4%, while in the gastrointestinal phase, Pb bioaccessibility ranged from 1.02% to 9.29% with a mean of 4.4%. Pb bioaccessibility in the gastric phase of soils in the study was lower than the reported values in peri-urban contaminated soils, such as 50.0–105% in shooting range soil, 60.9–64.1% in incinerator soil, and the values in urban soils of 23–77% (mean 52%) (Farmer et al., 2011), and close to the value of 0.5–85.7% (mean 25.3%) in an old mining site (Navarro et al., 2006), but much higher than those in mine wastes (1–6%) (Juhasz et al., 2011). The average Pb bioaccessibilities in the gastrointestinal phase in this study were close to the average value of 4.4% found in the peri-urban soils, and were within the range of 0.6–11.1% as reported (Smith et al., 2011). The decrease in Pb bioaccessibility in the gastrointestinal phase was due to its alkaline extraction solution (pH 7.0) compared with the strongly acidic solution (pH 1.5) in the gastric phase (Ren et al., 2006). However, the results outlined in this paper and those from other in vitro test studies (Roussel et al., 2010; Cui and Chen, 2011) clearly indicate that Pb bioaccessibility in soil is mostly less than 100%. The assumption that 100% of soil-bound Pb is bioavailable overestimates the potential risk of Pb exposure in soil, which may impact on remediation or management decisions.

In the soils within 200 m of the battery plants, Pb bioaccessibility ranged from 4.20% to 31.8% and 0.28% to 5.88% in the gastric and the gastrointestinal phases, with means of 13.0% and 2.30%, respectively (Table 3). Pb bioaccessibilities outside the battery plants were significantly lower than those inside the plants ($p < 0.01$). However, within the outside samples, Pb bioaccessibilities near the battery plant were not higher than those further away from the battery plant as we supposed. These results went against
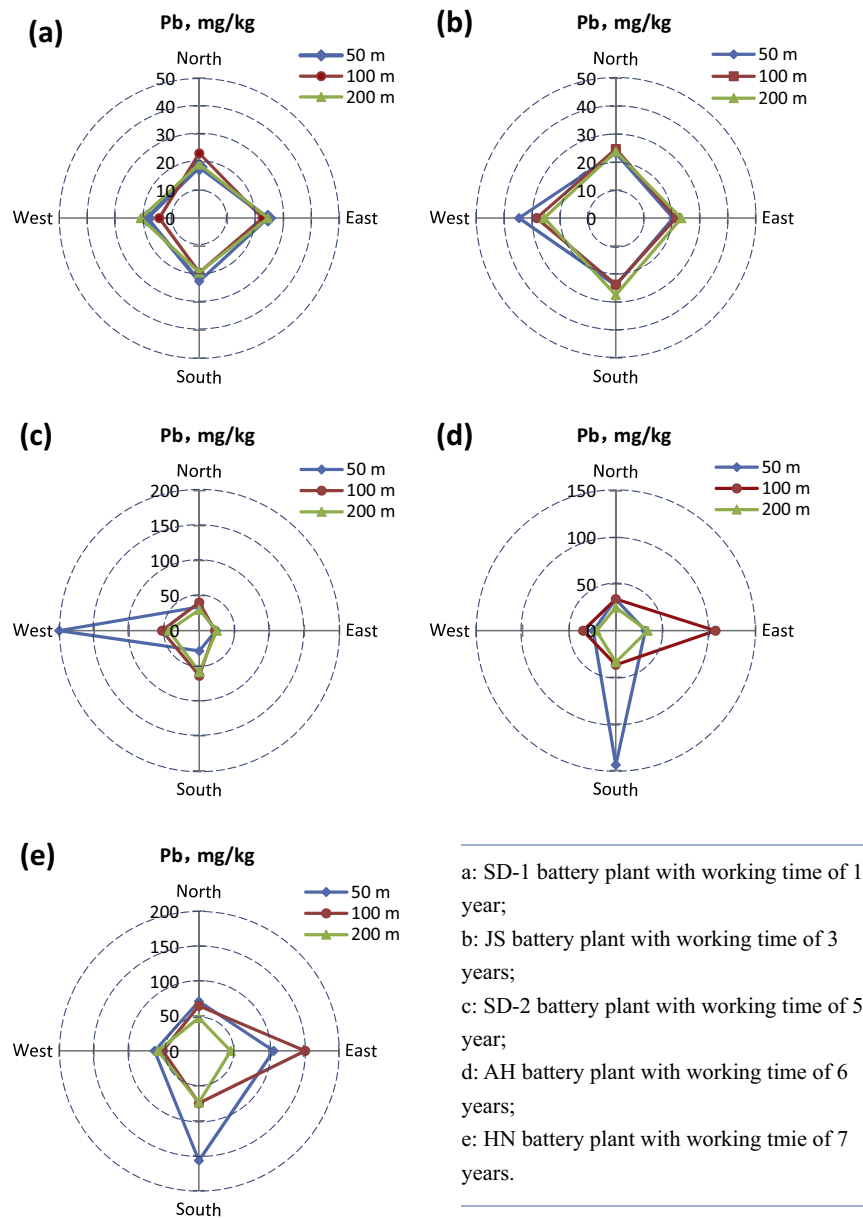
Fig. 1. The spatial distribution of Pb around battery plants.

a: SD-1 battery plant with working time of 1 year;

b: JS battery plant with working time of 3 years;

c: SD-2 battery plant with working time of 5 year;

d: AH battery plant with working time of 6 years;

e: HN battery plant with working tmie of 7 years.

the rule that the impact of Pb dust decreased with increase of distance from the battery plant. This suggested that the artificially added Pb had a similar bioaccessibility as indigenous Pb. So we determined the bioaccessibility of Pb dust collected from the bag filter (Table 3) in one of the battery plants. As we deduced, the bioaccessibility of Pb dust ranged from 15.2% to 25.0% in the gastric phase. These values were greater than the mean of Pb bioaccessibility of soils outside battery plants, but lower than those inside the plants. This was possibly because of the application of recycled wastewater inside the plants.

The soil Pb bioaccessibility of outside soils in both the gastric and the gastrointestinal phase for the JS battery plant site (with the mean of 6.94% and 0.78%, respectively) were significantly different from those of the other four battery plant sites (Table 3). These results may be because of the soil texture at the JS battery plant site, which was characterized by high clay and silt content and low sand content (Table 1). Clay and silt are better sorbents for Pb than sand. Poggio et al. (2009) concluded that Pb bioaccessibility in Grugliasco urban soil was negatively correlated with silt
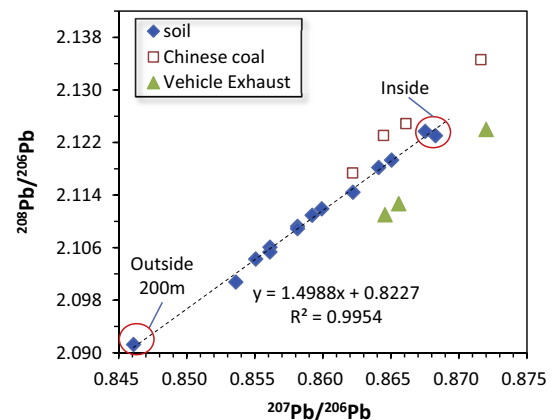

Fig. 2. Comparison of the Pb isotopic ratios in soils around the battery plant in Henan, China and Chinese coal from references (Chen et al., 1998; Díaz-Somoano et al., 2009), vehicle exhaust and dust (Duzgoren-Aydina et al., 2004; Zhu et al., 2010).

Table 3
Pb bioaccessibility with a modified PBET tests in soils around battery plants.

Distance, direction		Battery plant									
		Pb Bioaccessibility in gastric phase (%)					Pb Bioaccessibility in gastro-intestinal phase (%)				
		SD-1	JS	SD-2	AH	HN	SD-1	JS	SD-2	AH	HN
Inside	East side	4.12	14.4	18.1	59.3	65.4	1.90	1.02	1.52	8.04	7.16
	West side	23.1	5.16	33.3	24.3	66.9	1.79	1.20	6.30	5.53	9.29
50 m	East	11.8	6.70	11.0	9.24	17.1	2.61	0.91	3.82	1.56	2.55
	South	17.4	8.21	19.9	10.5	15.6	3.91	1.19	4.65	0.56	2.15
	West	18.3	8.66	27.0	11.9	12.2	2.59	0.85	1.77	2.87	1.86
	North	16.9	8.69	11.8	10.7	9.60	2.10	1.08	4.67	3.85	1.95
100 m	East	12.3	7.68	19.1	17.9	13.8	2.10	0.54	2.65	0.68	1.65
	South	10.5	7.68	18.0	6.77	15.2	1.72	0.28	1.87	1.36	3.18
	West	23.4	6.71	19.2	13.1	13.9	2.25	0.33	1.21	3.79	5.87
	North	17.1	8.89	12.9	11.9	13.1	2.42	0.57	4.87	2.20	1.88
200 m	East	14.9	4.20	19.8	10.7	12.8	1.67	0.86	3.84	1.52	3.47
	South	15.6	4.48	11.7	7.40	17.3	2.84	0.29	2.38	1.54	2.49
	West	17.6	5.06	12.6	31.8	9.80	3.11	1.15	5.88	2.77	2.69
	North	13.3	6.30	8.63	14.6	11.2	1.36	1.25	4.16	2.20	3.85
Means of outside soil		15.8b	6.94a	16.0b	13.0b	13.5b	2.39b	0.78a	3.48c	2.08b	2.80bc
Lead dust collected from bag dust filter (n = 3)		15.2–25.0					0.37–0.94				

Means in the same row followed by different letters are significantly different among plant sites at $p < 0.05$, tested with using One-way ANOVA of Duncan's multiple range tests.

and clay contents. Madrid et al., 2008 showed that the clay fraction had the lowest Pb bioaccessibility in every sample from Torino and Seville city and that Pb bioaccessibility in the clay fraction was lower than in the whole soil.

Because the lead battery plant dust was the main source of anthropogenic Pb, the pollutant properties at the five battery plants were essentially the same, predominantly in the form of lead oxide (Rooney et al., 2007), and the impact of the lead pollutant source and properties need not be discussed. The mixed bioaccessibility of Pb was dominated by the amount of Pb dust and the local soil environment, and a quantitative relationship existed among the amount of bioaccessible Pb, the total amount of Pb and the soil properties. Although Pb bioaccessibility ranged between 8.63 and 33.83% for all 70 soil samples, linear relationships between the total Pb concentration and bioaccessible Pb concentrations in the gastric phase and the intestinal phases were obtained, with correlation coefficients (R^2) of 0.97 in both cases ($n = 70$, Fig. 3), as findings of Farmer (2011) that total Pb concentration was the best indicator of the bioaccessible Pb concentration. The spatial decay curves of the three forms of Pb concentrations (total Pb, bioaccessible Pb in stomach and intestinal) around the battery plants are shown in Fig. 4. Slow decreases in the concentrations of the bioaccessible Pb in both gastric and gastrointestinal phases of soils with distance from the battery plant were found.

Pb dust from the battery plant might react with soil and cause changes to the bioaccessibility of Pb after entering the soil. The bioaccessibility of Pb is known to be influenced by metal speciation and soil physicochemical parameters (Roussel et al., 2010). From the Pb isotope composition analysis, we verified that the main anthropogenic source was Pb emission from battery plants, which meant that lead pollutants entering the soils had very similar metal speciation. This enabled us to isolate the relationship between soil physicochemical properties and Pb bioaccessibility of Pb dust.

We examined the relationships between bioaccessible Pb concentrations and soil physicochemical properties further by stepwise multiple linear regression analysis. Those soil properties that failed to explain significant linear relationships in the variation, such as CEC, were not used as independent variables in the multiple regression equation (Romero et al., 2008; Tang et al., 2008).

Multiple stepwise regressions identified a mode based on total Pb, and total Fe, and SOM that could explain 98.6% of the variation in bioaccessible Pb in the stomach phase, expressed as Eq. (3); and a mode based on total Pb that could explain 98.6% of the variation in bioaccessible Pb in the stomach-intestinal phase, expressed as Eq. (4).

$$BA_{gastric} = -106.8 + 0.627[Pb] + 19.1[Fe] + 11.3[SOM],$$
$$R^2 = 0.972, p < 0.0001 \tag{3}$$

$$BA_{gastrointestinal} = -2.852 + 0.078[Pb], \quad R^2 = 0.971, p < 0.0001 \tag{4}$$

Where $BA_{gastric}$ (mg kg^{-1}), and $BA_{gastrointestinal}$ (mg kg^{-1}) are the bioaccessible Pb concentrations in the gastric phase and in the gastro-intestinal phase, respectively, [Pb] (mg kg^{-1}) is total concentration of Pb in soil, [Fe] (%) is total iron concentration in soil, [SOM] (%) is content of soil organic matter.

In other words, in the gastric phase, Pb bioaccessibility was mainly controlled by soil total Pb concentrations, contents of Fe, and SOM, while in the gastrointestinal phase, it was mainly controlled by soil total Pb concentrations. However, total Pb concentration was still a best indicator of the bioaccessible Pb concentration.

The soil pH had no significant relationship with the amount of bioaccessible Pb extracted in the small intestinal and the gastric phases. This result agreed with the previous report about the relationship between Pb bioaccessibility and soil pH (Roussel et al., 2010), which might be because of the strong acid environment in the stomach concealing the effect of soil pH. Ruby et al. concluded that Pb in soils with neutral or higher soil pH appeared to have greater solubility in the gastric environment (Ruby et al., 1996), because the predominant forms in alkaline soils are lead carbonate ($PbCO_3$) and lead hydroxide ($PbOH^+$). Lead combined with these minerals appears to be soluble in the gastric environment, regardless of the local pH levels (neutral or higher soil pH).

The soil bioaccessibility of Pb was positively correlated with SOM for the gastric phase (Eq. (3)), in accordance with the conclusion that Pb bioaccessibility increased with higher SOM in the PBET test (Ruby et al., 1996). The presence of SOM reduced Pb leaching during weathering but allowed bound Pb to be released by cation
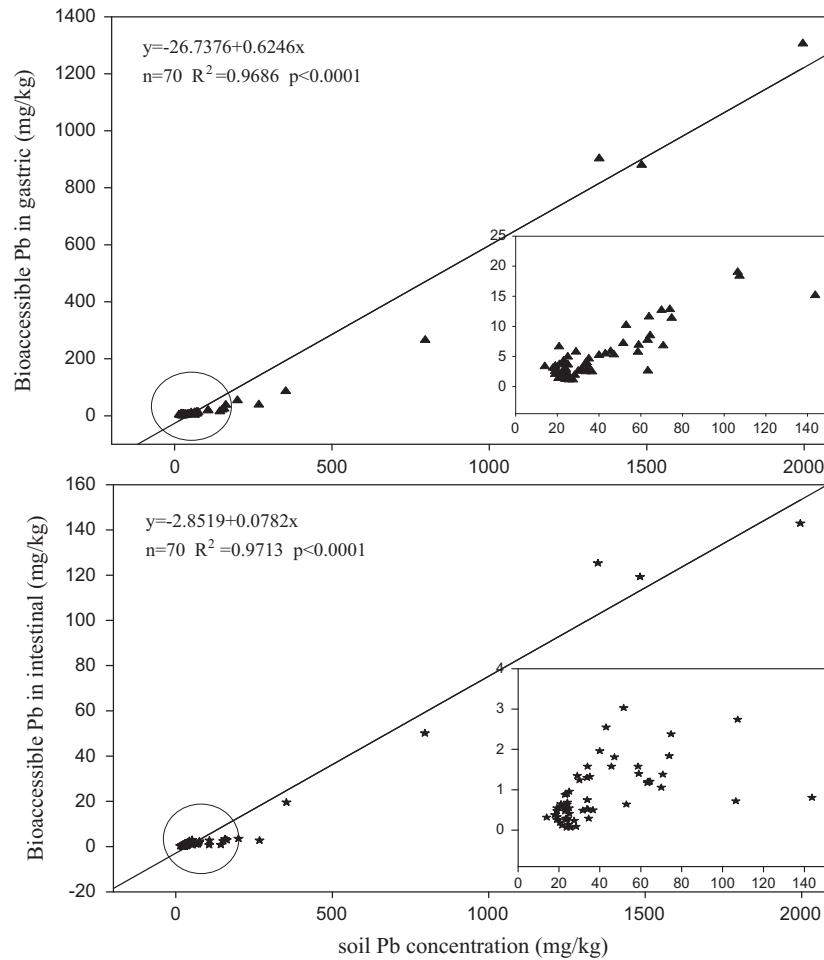
Fig. 3. A Linear regression between the bioaccessible Pb concentration and total Pb in soils around battery plants.
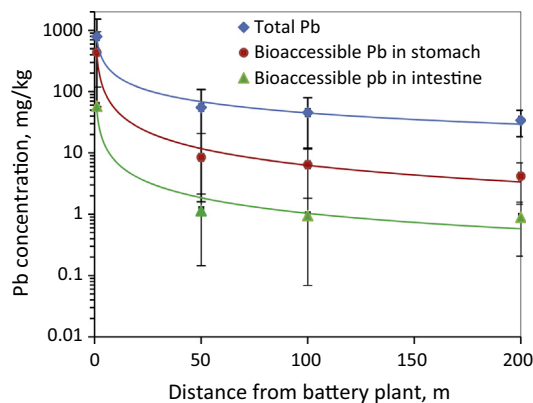

Fig. 4. The spatial decay curve of Pb concentration around battery plants. Vertical bars represent means + S.D. of twenty and eight replicates for outside and inside points, respectively.

exchange in the acidic stomach simulation, whereas the Pb species formed in the absence of organic matter was less acid-soluble.

In the present study, soil Fe content played an important role in controlling the soil bioaccessibility of Pb, with higher Pb bioaccessibility associated with higher Fe content in the selected soil samples. No significant relationship was obtained between Pb bioaccessibility and soil Mn content. A number of studies have demonstrated that Fe/Mn oxides are very efficient sorbents and control solubility of Pb at pH 5.5 (O'Reilly and Hochella, 2003),

and $Fe(OH)_3$ and ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$) were very effective in reducing bioaccessible Pb (Beak et al., 2006).

4. Conclusions

The distribution and bioaccessibility of Pb in soil around five lead battery plants in China were studied. The influence of the prevailing wind direction gradually took effect with the increased age of the battery plant, leaving a higher concentration of Pb downwind of the prevailing wind direction. The ratio of $^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$ of soils from one battery plant in the plot formed a straight line, indicating that Pb emitted from the battery plant was the dominant anthropogenic lead pollutant in the peripheral 200-m area.

The bioaccessibility of Pb in these soil samples, obtained by a modified PBET method, ranged from 4.2% to 66.9% in the gastric phase and from 0.28% to 9.29% in the gastrointestinal phase. A significant positive correlation was observed between bioaccessible Pb and total Pb concentrations. Bioaccessible Pb was also affected by soil physicochemical properties. Multiple stepwise regressions identified a mode based on total Pb, SOM, and total Fe with the variation of bioaccessible Pb in the stomach, expressed as $BA_{gastric} = -106.8 + 0.627[Pb] + 19.1[Fe] + 11.3[SOM]$; and a mode based on total Pb with the bioaccessible Pb in the stomach-intestinal, expressed as $BA_{gastrointestinal} = -2.852 + 0.078[Pb]$, indicating that total Pb concentration was still a best indicator of the bioaccessible Pb concentration. It is necessary to confirm the general soil contamination–human bioaccessibility relationships by

carrying out investigations in other areas, if possible with different soils and land use conditions.

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