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Spatial distribution, risk and potential sources of lead in soils in the vicinity of a historic industrial site

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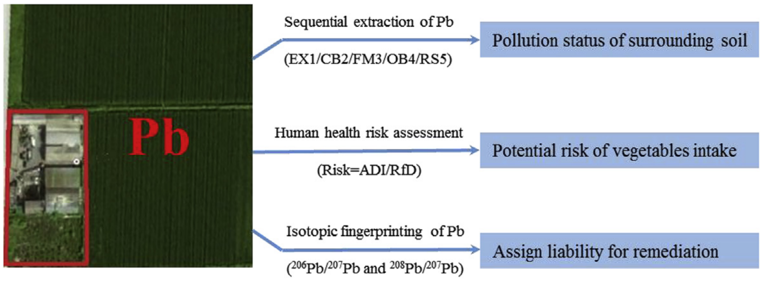
HIGHLIGHTS

- Surface soils near a site where historically, lead oxide was produced, were contaminated with Pb.
- Results of sequential extractions showed that predominant form of Pb was that bounds to Fe/Mn-oxides.
- Predicted, daily intake of Pb by local inhabitants, via consuming home-grown vegetables, exceeded benchmark doses.
- The isotopic patterns of Pb in soil and vegetables resembled that of lead oxide previously processed at the industrial site.
- Source tracing will have critical implications for future measures to reduce risks posed by Pb.

GRAPHICAL ABSTRACT



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ABSTRACT

Because of measures taken by local and national government agencies to control releases of metals, former industrial sites in China that are contaminated with lead (Pb) in soils have been abandoned. Compared with historic sites themselves, little attention has been paid to contamination with Pb in areas surrounding these sites. In this study, a method by integrating sequential extraction and isotopic fingerprinting was proposed to reveal the key fractions of Pb contaminants in soils, trace their sources and determine the subject of liability for remediation. Topsoils from near a historic site, where lead oxide was produced, were found to be contaminated. Concentrations of Pb in soils were inversely proportional to distances from the industrial site and depth in soils. The predominant form of Pb was the Fe/Mn-oxide-bound fraction (FM3), which accounted for from 53.39% to 82.07% of total concentrations of Pb. Concentrations of Pb in vegetables produced on contaminated soils exceeded those allowed in food for consumption by humans. An assessment of hazards and risks posed by consumption of vegetables grown on these soils indicated relatively high potential for adverse effects on local residents around the closed plant. By use of isotopic finger printing for Pb, the abandoned factory was determined to be the most likely source of Pb in topsoils, especially fraction FM3. To mitigate exposures of people to Pb via

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consumption of locally produced food, recommended strategies should target legacy sources of Pb to soils in the vicinity of this historic industrial site.

1. Introduction

Lead (Pb) is an important raw material for various industries. Production and consumption of Pb in industrial processes affects concentrations of Pb globally with the major producers being China, Australia, United States, Peru, Canada, Mexico, Sweden, Morocco and South Africa (Qu et al., 2014). However, Pb is a toxic metal that can affect almost every organ and system in the human body (Adrian et al., 1982). Furthermore, children are more vulnerable to exposure to Pb than adults (Sciarillo et al., 1992). Chronic, low-level exposure to Pb during childhood can result in adverse health effects, such as deficits in IQ and attention spans that can lead to reading and learning disorders (Landrigan et al., 2004). In a number of countries, concentrations of Pb in blood of children have decreased significantly since the 1990s (Al-Othman et al., 2012). However, poisoning with Pb during childhood continues to be a major public health concern for certain at-risk groups (Koller et al., 2004).

Rapid industrialization of China has resulted in contamination of some environments (Chen et al., 2016; Shi et al., 2012a; b; Shi et al., 2017) and Pb is one of the contaminants of greatest concern. It has caused more than 40 publicly reported poisoning incidents in 16 provinces of China since 2005 (Qu et al., 2014). Children have been the main victims, and thus poisoning by Pb is considered to be an important pediatric environmental health problem in China. Accordingly, since 2011 controlling contamination of the environment with Pb has been listed as a priority for protection of the environment by the Chinese central government. A large number of polluting factories that historically discharged Pb to the environment have been phased out and closed down by local governments. Consequently, in recent years large numbers of these former industrial sites have been abandoned. Some of the sites may be reclassified for urban development, whereas various Pb components in the environment can still pose risks to future residents or workers (Stiber et al., 1998). In America, Pb-containing compounds have been identified as a major hazardous chemical at 46.8% of the 1343 Superfund sites currently on the National Priorities List (USEPA, 2017). According to China's legal requirements, in order to protect the safety of residential environments, previous industrial sites have to be investigated and remediated before being redeveloped.

Besides Pb at industrial sites, emissions of Pb-containing smoke, dust and wastewater during various industrial processes could also affect surrounding environments and communities. Results of previous studies have demonstrated significant amounts of Pb in soils adjacent to non-ferrous metal smelting (Mackay et al., 2013), lead-acid battery manufacturing (Chen et al., 2012) and mining and smelters (Qu et al., 2012). However, even after the industrial activities of these factories are stopped, Pb that accumulated in soil during operations are still present and can be difficult to eliminate so that they can have long-term effects on people and the environment (Pelfrêne et al., 2013). Nevertheless, when compared with active industrial sites and historical sites themselves, little attention has been given to areas surrounding historical sites. Pollution indexes or geostatistical analyses based on total concentrations have routinely been used to assess both the degree of Pb pollution and the area of contaminated soil (Liu et al., 2014; Mcgrath et al., 2004). Risks associated with the presence of Pb, however, are varied and depend on its chemical forms (Luthy et al., 2003). Lead is present in soil in various fractions, which can affect behavior of Pb and its toxicity in soils, depending on its chemical interactions, mobility and bioavailability (Arenas-Lago et al., 2014). Since total concentrations of metals provide limited information on their chemical behavior and availability, fractioning methods based on sequential extractions have been developed to determine forms of Pb in soil and their availability and possible toxicity.

Risk alleviation or remediation of soils in vicinities of historic industrial sites requires capital support. In general, such costs should be paid by the polluters (Qu et al., 2016). Normally, the previous factory can be determined as the subject of liability of the historical site itself. However, it is less easy to determine sources of Pb in surrounding areas which could be influenced by multiple sources of Pb, including atmospheric deposition from long-range transport. Knowing only the total concentrations and chemical forms of Pb is insufficient for an accurate evaluation of contamination sources.

Lead has a number of stable isotopes that can be used for forensic determination of sources associated with particular bodies of ore. Industrial activities that bring Pb from more remote sources to factories can alter the natural isotopic composition in its vicinity. It is sometimes possible to use these unique isotopic ratios to distinguish "anthropogenic" from local, ambient Pb. Isotopic compositions of Pb, are commonly expressed as ratios of isotopes, including: $^{206}Pb/^{204}Pb$, $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ and $^{208}Pb/^{207}Pb$. These ratios are not significantly affected by physic-chemical fractionation processes. Therefore, patterns of relative proportions and ratios of stable isotopes of Pb have been used as "fingerprints" of environmental pollution to determine sources of contamination of soils by Pb (Komárek et al., 2008).

The present study was conducted to assess risk of Pb contained in soils of the area surrounding a historic industrial site in Jiangsu, China. Specific objectives were to: (1) evaluate the current status of contamination of soils with lead and potential effects in the vicinity of a closed facility that released Pb to the environment; (2) provide a better understanding of chemical forms and locations of Pb in soils; (3) determine likely sources of Pb pollution and assign liability for remediation and (4) help local governments prioritize pollution control and health intervention policies to protect the local population.

2. Materials and methods

2.1. Site description

The study area is located in Jing County, Jiangsu Province, China (Fig. 1). The climate is subtropical monsoon with mean annual temperature of 15.1 °C and mean, annual precipitation of 1038 mm. The prevailing wind directions are northwest in winter and southeast in summer. The factory of concern, which had produced lead oxides, including $3PbO \cdot PbSO_4 \cdot H_2O$, $2PbO \cdot PbSO_4$ and Pb_3O_4. In 2011, the facility was shut down by the local government. There is an irrigation ditch and residential district which lies to the west and

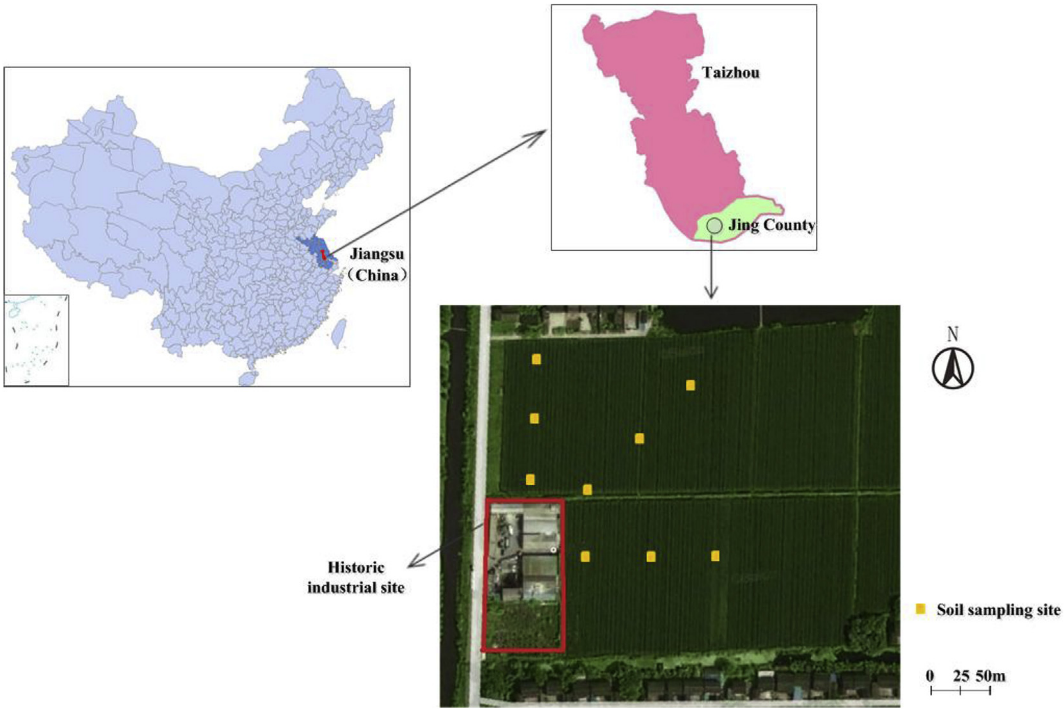

Fig. 1. Locations from which samples of representative soils were collected.

south of the lead processing plant, respectively. The research was conducted on about 55, 000 m^2 of farmland to the north and east of the vicinity of this closed plant (Fig. 1).

2.2. Sampling and quantification of total Pb

Sampling sites were distributed on 5, 50, and 100 m circles around the closed plant in the direction of north, northeast, and east (Fig. 1). Typically 250 g soil was collected at depths of 0, 15, 30 or 50 cm at each sampling site by use of a hollow stem auger. In total, 36 samples of soils were collected in December 2015. These samples were dried, hand crushed, and sieved with a 1-mm mesh stainless steel screen.

Since the rice cultivation period was over, three species of local planted and commonly consumed vegetables (asparagus lettuce, pakchoi and turnip) were collected to estimate human exposure to Pb. The vegetables were within 5 m of the boundary of the abandoned Pb processing plant. Edible portions of 20 samples of vegetables were washed with double distilled water to get rid of air born pollutants. Vegetables were then freeze-dried and ground to a powder prior to analysis without cooking.

The samples were digested according to U.S. EPA Method 3050B using a Hot Block digestion system (Environmental Express, Mt. Pleasant, SC). Total concentrations of Pb were measured using ICP-MS. For QA/QC, blank control, duplicate samples and standard reference soils (Center for Certified Reference Materials, China) were used. Recoveries of analyzed Pb in standard reference materials were 100 ± 5% of recommended values and the relative standard deviations (RSDs) of duplicates were less than 3%. 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.

2.3. Sequential extraction of soils

Chemical forms of Pb in soils can vary significantly. In an attempt to identify forms of Pb in soils, a sequential extraction procedure (Tessier et al., 1979) was applied. Each sample of soil (1 g) was weighed into a 40-mL polyethylene centrifuge tube and conducted at room temperature with successive extractions (For details, see Supporting Information). Concentrations of Pb in fraction 1 (EX1, exchangeable), fraction 2 (CB2, carbonate-bound), fraction 3 (FM3, Fe/Mn-oxide-bound), fraction 4 (OB4, organic matter-bound) and fraction 5 (RS5, residual) were determined by inductively coupled plasma mass spectrometry (ICP-MS). Overall recovery of Pb using the chemical fractionation procedure, as determined by comparing the sum of Pb determined in all five fractions with a single total Pb determination, was 87.3–113.2%.

2.4. Quantification of isotopes of Pb

With the aim of determining sources of Pb in soils and vegetables, in addition to total concentrations and each fraction of Pb, stable isotopes ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb were measured. Representative samples from possible sources of Pb, including a sample of product (Pb_3O_4) collected from the closed factory's warehouse, which was thought to be consistent with previous emissions from the factory, and a sample of coal collected from a local power station, thought to represent likely Pb in atmospheric deposition, were collected and their isotope ratios of Pb were measured. Following dilution of digests and extracts to concentrations of 1–15 μg of Pb L^{-1} using 0.1 M HNO_3, isotopes of Pb were quantified by use of ICP-MS. To assure accuracy and assess precision, and update ratio correction factors, NIST (National Institute of Standards and Testing) standard reference material #981 was analyzed every five samples. Recoveries of analyzed Pb in standard reference materials were 96–105%. The measured values for ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios of reference material

(1.0930 ± 0.0016 and 2.3702 ± 0.0019, respectively) were in close agreement with the certified values of 1.0933 and 2.3704, respectively. The relative standard deviation (RSD) of the replicates was generally less than 0.5% for ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios.

Furthermore, source apportionment can be accomplished by analyzing the Pb isotopic signatures in the samples and major sources with a linear mixing model. The following equations can be employed for such analysis:

$$\left(\frac{^{206}Pb}{^{207}Pb}\right)_s = f_1\left(\frac{^{206}Pb}{^{207}Pb}\right)_1 + f_2\left(\frac{^{206}Pb}{^{207}Pb}\right)_2 \tag{1}$$

$$f_1 + f_2 = 1 \tag{2}$$

where the subscript S represents the sample, the subscripts 1 and 2 represent the two major sources, and f_1 and f_2 are their relative contributions, respectively.

2.5. Estimation of risks to health

Risk assessment has been recognized as an important tool for identifying potential risks in human activities and presenting risk information for the decision maker (Bai et al., 2011; Chen et al., 2013; Guo et al., 2017; Shi et al., 2012a; b). To estimate the risk posed by Pb in vegetables to humans, daily intake of Pb via consuming vegetables was quantified by the following equation (USEPA, 1989). The equation links the time-averaged dose to concentrations in the vegetables.

$$ADI = \frac{C \times IR \times EF \times ED}{BW \times AT} \tag{3}$$

The potential health risk can be characterized as the quotient of daily intake of Pb and the reference dose by the following equation (USEPA, 1989). To assess exposures of various groups' dietary intake, individuals were stratified into three age groups classified as children (3-<10 years), adolescents (10-<18 years) and adults (>18 years).

$$\mathrm{Risk} = \mathrm{ADI} / \mathrm{RfD} \tag{4}$$

where: ADI is the average daily intake or dose through ingestion (mg kg^{-1} day^{-1}); C is the concentration of Pb in the exposure medium (mg kg^{-1}, dm); IR is the ingestion rate of vegetables (kg d^{-1}); EF is the exposure frequency (d y^{-1}); ED is the exposure duration (y); BW is the body weight (kg) and AT is the time period over which the dose is averaged (d). RfD is the reference dose of Pb. The values of parameters for exposure estimation were listed in Table S1.

2.6. Statistical analyses

Statistical analyses were performed with SPSS 16.0 software and Origin 9.0. Homogeneity of variances and normality of data were tested by use of Levene's test and the Shapiro-Wilks normality test, respectively. When necessary, data were log-transformed to obtain homogeneity of variances and normality. When these assumptions were met, significant differences among different groups of soil samples were analyzed by one-way analysis of variance. The probability value of $p < 0.05$ was set as the level for statistical significance. Pearson correlation analysis was used to evaluate associations between and among single and combined Pb fraction/isotope(s) of soil samples, vegetable samples and product sample.

3. Results and discussion

3.1. Total concentrations of Pb in soils

Frequency distributions of total concentrations of Pb in soils near the closed plant were strongly, positively skewed (Fig. S1). The cumulative probability function of concentrations of Pb was not normally distributed. Total concentrations of Pb in soils varied 100-fold among samples, ranging from 22.1 to 2230 mg kg^{-1}, dm at various distances from the former industrial site. There were four samples for which concentrations of Pb exceeded the level for protection of agricultural plants (300 mg kg^{-1}, dm soil) from direct effects of Pb on their growth (Environmental Quality Standard for Soils of China; GB15618-1995). However, in comparison with Farmland Environmental Quality Evaluation Standards for Edible Agricultural Products (HJ/T332-2006), there were 14 samples that exceeded 50 mg kg^{-1}, dm soil, which are set to protect health of humans when consuming vegetables. Although the industrial site has been abandoned for several years, soils with concentrations of Pb that were greater than the standards were observed. This result is due to immobility and persistence of Pb in soils (Chaney et al., 1989).

It can been seen from Fig. 2 that concentrations of Pb in soils with a distance of 5 m exceeded the criterion value greatly and were apparently higher than that in soils with a distance of 50 m and 100 m. This result indicated that area with short-distances to the closed factory were heavily polluted by Pb. All samples of top soils collected from within the 5 m circle were contaminated with Pb, with a maximum concentration of 2230 mg kg^{-1}, dm, which was observed in soil from the east side of the facility. Concentrations of Pb in soils 50 or 100 m from the site were less than the criterion value (GB15618-1995), which indicated that the zone in need of active remediation was within a circle 50 m from the borders of the site. Furthermore, concentrations of Pb in surface soils in east were greater than that in north and northeast. This spatial pattern may be related with the influence of wind, which would alter Pb pollutants' diffusion in air and their accumulation in soil.

Concentrations of Pb decreased significantly with depth of soils ($p < 0.05$). Mean concentrations of Pb at depth of 30 and 50 cm which were 29.5 and 28.3 mg kg^{-1}, dm, respectively, were both less than the criterion for protection of health of humans as well as being near to the background concentration of 26.2 mg kg^{-1}, dm for soils in Jiangsu Province (NEMC, 1990). However, mean concentrations of Pb in surface soil and at depth of 15 cm were much higher, with the value of 172.6 and 76.0 mg kg^{-1}, dm, respectively. These results indicate slow vertical movement of Pb in soil. Furthermore, greater concentrations of Pb in surface soils, relative to that in subsoils, indicated that sources of Pb might have come via transport from external environments, rather than from in situ, parent materials (Chang et al., 2009). Patterns of distribution of concentrations of Pb were typical of those observed for dispersion of point-source air pollutants. Usually, smaller particles from industrial sites, that can be carried by the wind, and deposited by dry fall and rainfall on soils where they can accumulate (Jin et al., 2015; Ren et al., 2006). In some neighboring environments, concentrations of Pb in aerosols and fugitive dust in vicinities of factories involved in processing Pb-containing materials, were greater than those in more remote reference areas (Chen et al., 2012; Qu et al., 2012).

3.2. Pb partitioning based on sequential extraction

In addition to variation in total concentrations of Pb in soils, relative proportions of Pb in various fractions varied among locations (Fig. 3). When sequential extraction was used to partition Pb

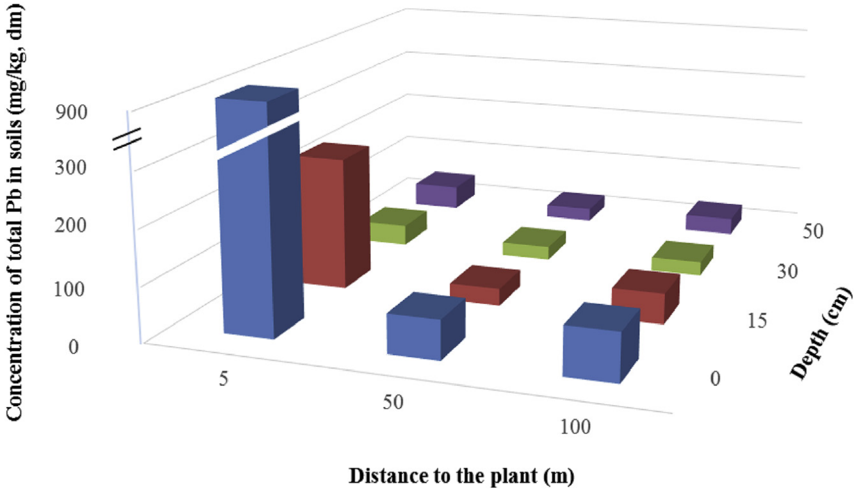

Fig. 2. Spatial distribution of concentrations of Pb in soils in the vicinity of the closed factory.

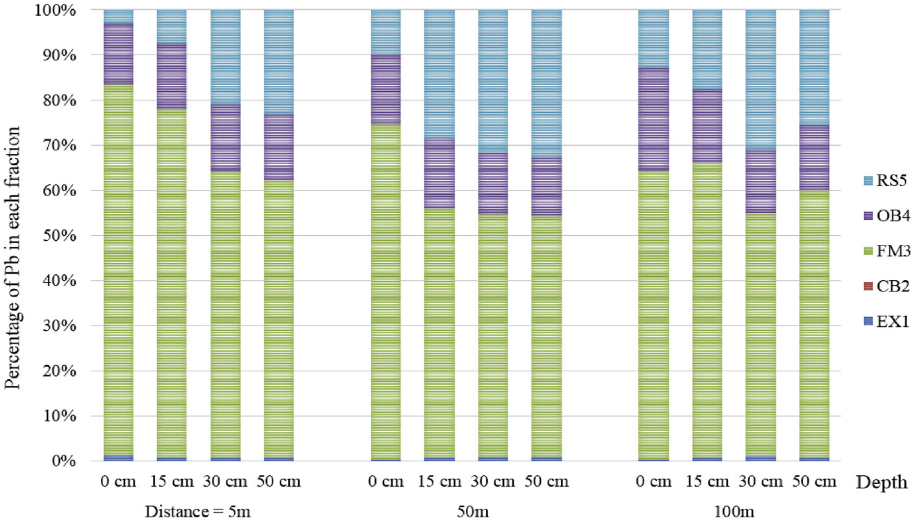

Fig. 3. Fractionation of Pb expressed as % of the sum of five fractions.

into five, operationally defined chemical fractions, those extracted in the first steps can be regarded as the active or biologically available fractions that are more soluble, whereas Pb extracted in the subsequent steps are less active and less available. The predominant form of Pb was the third fraction (Fe/Mn oxides, FM3), which was in the range from 53.4 to 82%. The residual fraction (2.97–32.47%), contained fractions in which Pb was associated with organic matter- (13.18–22.76%), carbonate (0–0.11%) or freely exchangeable (0.39–1.33%), but contained significantly less Pb, compared with the fraction representing Pb bound to surfaces of Fe/Mn-oxides. The decreasing order of proportions of Pb in the fractions was FM3>RS5>OB4>EX1>CB2. Similar distributions of Pb among fractions was observed in soils of the Gejiu mining district of Yunnan (Li et al., 2015a), which was FM3>RS5>OB4>CB2>EX1. However, previous studies also found that fractionation of Pb varies greatly among soils. In soils from some farming and smelting areas, Pb was mainly associated with exchangeable and carbonate fractions (20–51%), whereas they accounted for much less (3.4–9.3%) in soils from mining areas (Li et al., 2015a). Thus it can be seen that it is necessary to partition Pb based on sequential extraction in different areas and it is conceivable that the concentration of bioavailable part will be much useful in contaminated soil assessment rather than total metal.

Greater total concentrations of Pb in soils in the vicinity of the former Pb processing plant were associated with the Fe/Mn-oxide-bound fraction (Fig. 4). The presence of Fe/Mn oxides, the most important bearing phases for Pb in the study area, was probably due to the original source of the Pb used in the facility. Results of previous studies revealed that Fe and Mn would tend to accumulate quickly as Fe/Mn oxides under oxic conditions and when pH was greater than 6 (Han et al., 2005; Macleod and Lester, 1997). The pH of soils in this study ranged from 7.0 to 8.4 with a mean of 7.9. Fe/Mn oxides exist as nodules, concretions, cement between particles or simply as a coating on surfaces of particles, and are thus excellent scavengers for metals. Some studies have reported the importance of Fe/Mn oxides in retention of Pb in soil (Schneider et al., 2016). Moreover, biotic manganese oxides are more reactive than abiotic manganese oxides and adsorption of Pb on biogenic manganese oxide was 500- to 5000-fold greater than that on chemically precipitated abiotic manganese oxide (Nelson et al., 2002). Relatively large concentrations of Pb associated with Fe/Mn-oxide in this area might have been associated with the effect of biotic

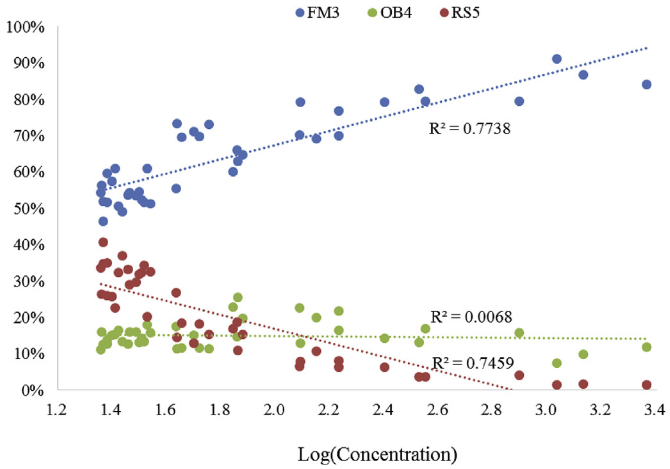

Fig. 4. Percentage of three major phases of Pb.

manganese oxides, while characterization of biotic manganese oxides is however difficult and requires additional techniques, including transmission electron microscopy (TEM) extended X-ray absorption fine structure (EXAFS) and UV Raman spectroscopy (Kim et al., 2006). It was also found that the trend of relative proportions of Pb in the Fe/Mn-oxide-bound fraction was opposite to that of Pb in the residual fraction (Fig. 4). Alternatively, relative proportions of Pb associated with organic matter varied little among different locations. In more contaminated topsoil within 5 m of the boundary of the abandoned Pb processing plant, 82.1% of Pb was associated with the Fe/Mn-oxides, while only 2.97% of Pb was in the residual fraction. This may occur because pollutant emissions generated from products and by-products of the former plant were lead oxides, not lead metal that distributed in crystal lattice or lead carbonate that distributed in carbonate-bound fraction. Accordingly, the greater total concentrations of Pb in contaminated soils were, the more proportions of Pb in the Fe/Mn-oxide-bound fraction occupied and the fewer proportions of Pb in the residual fraction occupied.

In these sequential extractions, residual metals are held in crystal structures, and metals are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature (Tessier et al., 1979). Compared with the residual fraction, Pb in the Fe/Mn-oxide-bound is thermodynamically unstable, especially under anoxic and acidic conditions. This indicates the relatively greater mobility and bioavailability of Pb in the studied soil, especially in more contaminated soils. Accumulation of Pb in the mobile and bioavailable forms would likely result in greater concentrations of Pb in plants that grow in contaminated soils.

3.3. *Accumulation of Pb in vegetables and its risk to health of humans*

Mean concentrations of Pb in vegetables, cabbage, radish and pakchoi, expressed on a fresh weight basis, were 1.25, 1.90 and 4.08 mg kg^{-1}, wm, respectively. When concentrations of Pb in vegetables were compared to guidance values, 100% of the vegetables examined exceeded the maximum allowed concentration (0.1 mg kg^{-1}) set by China. Furthermore, concentrations in vegetables grown on contaminated soils in the vicinity of the facility exceeded the guidance value (0.3 mg kg^{-1}, wm) for leafy vegetables set by the EU (EC, 2006) by an order of magnitude. Compared with the results from other studies (Table S2), concentrations of Pb associated with vegetables in the vicinity of this historic industrial site was comparable to, or even greater than, those vegetables from gardens irrigated with wastewater, or contaminated by e-waste processing, mining or smelting activities (Luo et al., 2011; Ferri et al., 2015; Mcbride et al., 2014; Pope et al., 2005; Zheng et al., 2007). In the study, results of which are reported here, the greatest concentration of 4.25 mg kg^{-1} was found in pakchoi. Only aubergine near a zinc plant in Huludao (5.47 mg kg^{-1}) (Zheng et al., 2007) and spring onions near a copper smelter in Zlatna (9.1 mg kg^{-1}) (Pope et al., 2005) contained such large concentrations of Pb.

Vegetables were collected from the most polluted soils nearest the closed lead oxide plant. The above results indicated that Pb pollution of soil indeed had adverse implications for planting vegetables. Concentrations of Pb in edible parts of these vegetables could be attributed to sorption from soil. However, processes such as splash and wind can also contaminate plant surfaces with soil particles and aerosols containing Pb. Results of previous studies have indicated that the extent of physical contamination of plant tissue by soil particles adherence/incorporation was even more important than uptake via roots in transferring Pb (Mcbride et al., 2014).

Since the people in Jing County rely heavily on locally grown vegetables as a food source, it would appear from the above results that there may be a risk of Pb intake. In comparison to most other environmental toxicants, a number of critical health effects can occur at small concentrations of Pb in blood even without a threshold. Thus, it is not possible to establish a Tolerable Daily Intake (TDI) that would be considered protective of health (FAO/WHO, 2017). The European Food Safety Authority (EFSA) has established a mean lifetime dietary Pb exposure of 0.96 μg kg^{-1} d^{-1} for children, 0.55 μg kg^{-1} d^{-1} for adolescents and 0.50 μg kg^{-1} d^{-1} for adults (EFSA, 2012). Since the Pb TDI has not yet been established, EFSA benchmark doses were used as a reference dose to which to compare calculated individual daily intakes of Pb. Calculated, mean daily intake of Pb through ingestion of vegetables was 11.5, 8.7 and 7.1 μg kg^{-1} d^{-1} for children, adolescents and adults, respectively. All predicted exposures exceeded the EFSA benchmark dose by more than ten-fold (Table S3). These results showed that there were relatively large hazards for local residents living around the closed plant through consumption of locally grown vegetables that are contaminated with Pb.

There have been several studies in which risks associated with long-term exposure to Pb have been assessed for humans consuming vegetables grown in waste water irrigated areas (Amin et al., 2013), waste-incinerator site (Li et al., 2015b), urban gardens (Mcbride et al., 2014) and mining areas (Roba et al., 2016). Results of this study will supplement more information with data on vegetables grown in contaminated farmlands around closed industrial sites. However, there might still be differences between calculated risks and actual effects. When determining risk, it was assumed that intake was equal to the absorbed dose (USEPA, 1989), which might over estimate exposure and thus risk. Alternatively, the total dietary intake also involves crops and other food. The rice produced in the study area is also consumed by local residents, while accumulation of Pb in crops was not quantified in the current research. In the future, it is necessary to collect rice samples and more vegetable samples in other seasons to fully assess the potential risk of Pb contamination in local produced food. In addition to vegetable ingestion, in areas of industrial activity, children might also obtain exposure through ingestion of soil via hand-mouth pathway (Qu et al., 2012). Children are particularly vulnerable to consequences of exposure to Pb since increased absorption of Pb during development period leads to adverse outcomes. From this point of view, it is necessary to conduct further investigation of human health in this area to clarify the health effects.

3.4. Isotopes of Pb and identification and apportioning of sources

In environmental studies, isotopes (^{206}Pb, ^{207}Pb, ^{208}Pb) are prevalent due to natural abundances. Fingerprinting of Pb based on isotopes has been used previously and contamination of the environment by human activities can be linked to inputs of ^{207}Pb from anthropogenic sources (Cheng and Hu, 2010; Kumar et al., 2013). Therefore, in the present study, ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios were used for identification of anthropogenic signals. Dependence of isotopic ratios on concentrations of Pb were investigated by plotting ^{206}Pb/^{207}Pb ratio against total concentrations of Pb (Fig. S2), which illustrated that ^{206}Pb/^{207}Pb ratios of all soils ranged from 1.11 to 1.17, and isotopic ratios were almost independent of concentrations of Pb. However, a clear difference between lesser and greater concentrations of Pb were observed ($p < 0.05$). The ^{206}Pb/^{207}Pb ratios varied greatly and can be divided into two groups in general. For the cleaner soil samples, the ratios were concentrated from 1.14 to 1.17, while for the polluted soil samples with higher Pb concentrations, the ratios were concentrated from 1.11 to 1.13. This result indicated that the sources of Pb in clean soils were different from that of polluted soils. Besides Pb in background, there were Pb from extraneous sources.

Furthermore, attributions of sources of Pb can be revealed by plots of ^{206}Pb/^{207}Pb versus ^{208}Pb/^{207}Pb. Placement of samples and markers in the joint domain of ^{206}Pb/^{207}Pb versus ^{208}Pb/^{207}Pb ratio were shown in Fig. 5. Considerable variation can be seen on the plot and a demarcation between different sample types was illustrated using circles depending on their location. All the soil samples could be divided into two groups mainly, which can be classified as either “background” or “contaminated”. Most of the deeper soil samples with lesser concentrations of Pb were higher on the plot. At the same time, most of the surface samples, which were heavily polluted, were in the lower position on the plot. Moreover, Pb in the polluted surface soils had an isotope signature similar to that from the former product sample, indicating Pb pollution in the farmland was indeed caused by the closed plant's previous anthropogenic Pb discharge, not from the natural formation or the atmospheric deposition of coal burning. Since the Pb contents in soil varied greatly both vertically and horizontally, the contribution ratios of soil background and human activities are considerably different for each sampling site. By applying equations (1) and (2), it was found that former industrial emission contributed about 77.2% in average to the total Pb concentration of contaminated surface soils.

As expected, most of the vegetables exhibited patterns of isotopic ratios of Pb that were different from background soils, but patterns of ratios of isotopes were more similar to that of contaminated surface soils (Fig. 6). This result demonstrates that most of the Pb in vegetables was from former industrial activities and there was potential for adverse effects due to eating vegetables grown on contaminated soils in the region.

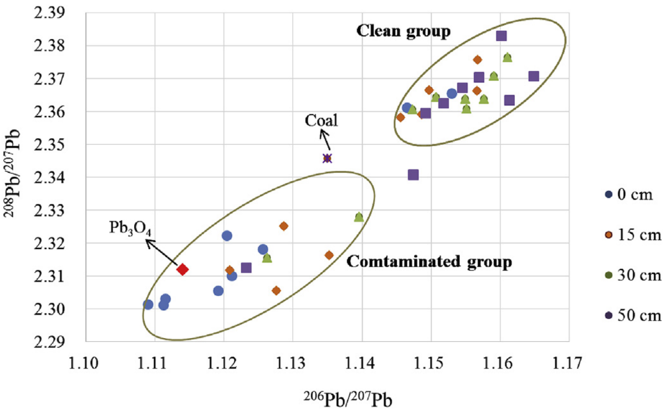

Fig. 5. Scatter plot of ratios of isotopes of Pb in soil and samples of Pb_3O_4 product and coal.

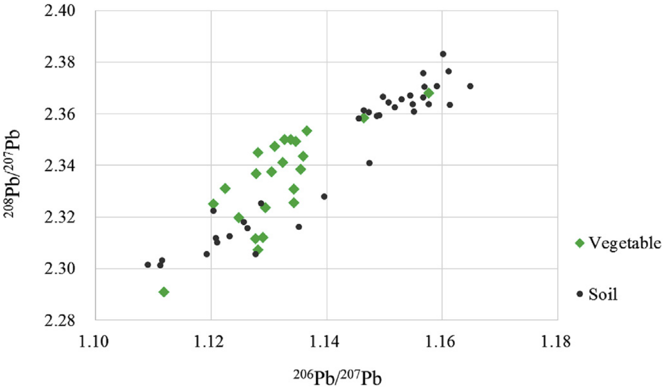

Fig. 6. Scatter plot of ratios of isotopes of Pb in vegetables and soils.

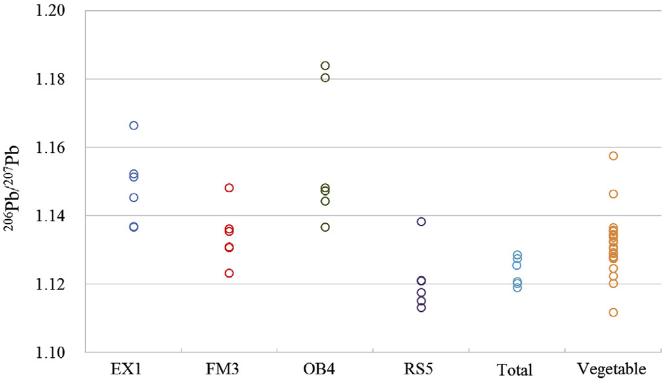

Fig. 7. ^{206}Pb/^{207}Pb ratios in various fractions of Pb in farming soil and vegetable.

Pb in vegetables were mainly from the more transferable fractions of that in soils. Pb isotope fractionation can occur over geological time as a consequence of parent isotope disequilibrium, and cannot occur in physical, chemical and biological processes, including sequential extraction (Cheng and Hu, 2010; Komárek et al., 2008). In this study, ^{206}Pb/^{207}Pb ratios in both vegetables and various fractions of Pb in soil samples collected from the farming layer (0–15 cm) were compared (Fig. 7). It was found that ^{206}Pb/^{207}Pb ratios of Pb in vegetables ranged from 1.12 to 1.14, which closely resembled that of total Pb and FM3 in the soil of farming layer. This result is consistent with the result of sequential extraction, which demonstrated that FM3 makes up the greatest proportion of Pb in soils, especially the heavily polluted surface soils. This ability to use lead isotopes as an inherent tracer to follow the chemical forms, dispersion and uptake of Pb has been proven useful.

4. Conclusions

Although the industrial site has been dormant for several years, samples of soils that contained high concentrations of Pb were observed. Concentrations of Pb in surface soils near the site were greater than those from farther away and exceeded a number of soil guideline values, while the degree of pollution tended to decline significantly with distance from the site and depth of sampling. Sequential extraction showed that the predominant form of Pb was that bound to the Fe/Mn-oxide fraction and certain conditions might cause it to be rapidly displaced to even more mobile forms. It is noteworthy that, locally produced vegetables did not comply with the legislation on the concentrations of Pb allowed for human consumption. Comparison with the EFSA values still indicated that consumption of homegrown vegetables by local inhabitants themselves resulted in high Pb intakes, which exceeded the benchmark dose levels by more than 10-fold. This result reflected that the soil near the historic site is not suitable for planting vegetables. Furthermore, the isotopic patterns of Pb in vegetables were consistent with that in the polluted surface soils, which were isotopically close to anthropogenic Pb discharged from the closed plant previously.

Results of the study reveal the pollution status of Pb in the vicinity of this historic industrial site and its potential risk to public health if used for production of food. Isotopic fingerprinting successfully determines the previous plant, who should afford the liability of pollution control and remediation, as polluter of the pollution in its surrounding area. It is also suggested that further studies in this area should be performed to assess human exposure and relevant human health risks from living close to the closed plant. The study results increase the decision-making value of soil pollution control and can help to reduce the information asymmetry that may be an obstacle to redevelopment.

Declarations of interest

The authors declare that they have no conflict of interest.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2018.04.119.

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Supporting information

Details of successive extractions:

•Fraction 1 (EX1, exchangeable): the residue from fraction 1 was extracted for 1 h with 8 mL of 1 M $MgCl_2$ (pH 7.0).

•Fraction 2 (CB2, carbonate-bound): the residue from fraction 2 was extracted for 5 h with 8 mL of 1M NaOAc adjusted to pH 5.0 with acetic acid (HOAc).

•Fraction 3 (FM3, Fe/Mn-oxide-bound): the residue from fraction 3 was extracted with 20 mL of 0.04M $NH_2OH \cdot HCl$ in 25% (v/v) HOAc at 96 ◦C with occasional agitation for 6 h.

•Fraction 4 (OB4, organic matter-bound): the residue from fraction 4 was extracted with 3 mL of 0.02M HNO_3 and 5 mL of 30% (v/v) H_2O_2 (adjusted to pH 2 with HNO_3). The mixture was heated to 85 ˚C for 2 h, with occasional agitation. A second 3-mL aliquot of H_2O_2 (pH 2 with HNO_3) was added, and the mixture was heated again to 85 ˚C for 2 h with intermittent agitation. After cooling, 5 mL of 3.2MNH_4OAc in 20% (v/v) HNO_3 was added and the sample was diluted to 20 mL and agitated continuously for 30 min.

•Fraction 5 (RS5, residual): the residue from fraction 5 was digested with aqua regia and perchloric acid at 160 ˚C.

After each successive extraction, separation was performed by centrifuging at 7000×g for 10 min. The supernatant was decanted and filtered to remove plant debris. Before the next extraction, the residue was washed with deionized water by vigorous manual shaking, and the supernatant was then discarded after 10 min of centrifugation.

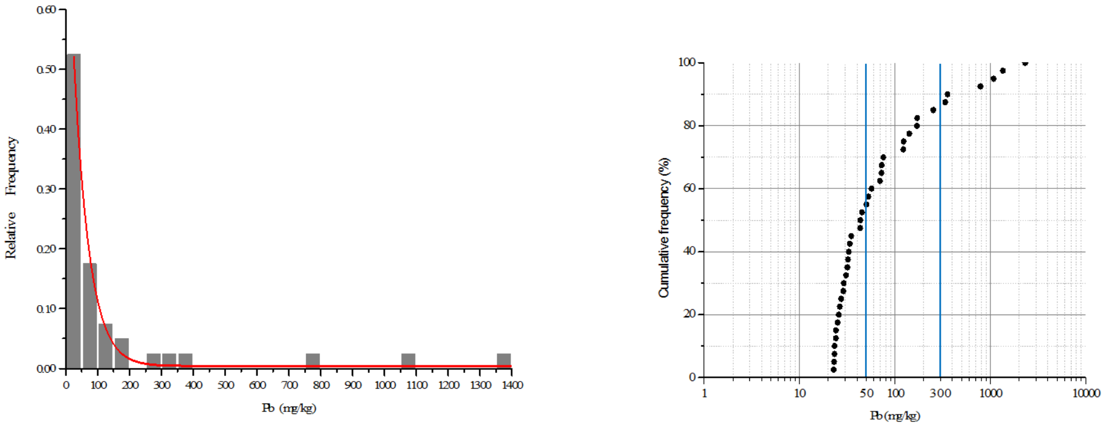

Fig. S1. Relative (left) and cumulative (right) frequency of total concentrations of Pb in soils.

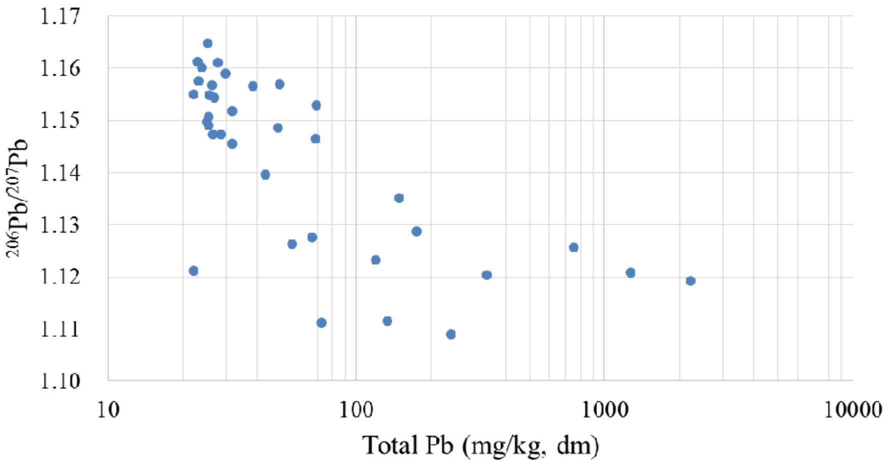

Fig. S2. Plot of ^{206}Pb/^{207}Pb ratio against total concentrations of Pb in soil.

Table S1

Parameters for exposure estimation.

Age groups	Body weight (kg)	Ingestion rate of vegetables (g d^{-1})	Data source
Children (3-9 years)	22.1	156.3	Derived from [6-7]
Adolescents (10-17 years)	46.3	247.3	Derived from [7]
Adults (>18 years)	61.8	270.3	Derived from [8]

Table S2

Comparison with other reports of Pb concentrations (mg kg^{-1} FW) in vegetables.

Region	Sampling site description	Pb concentrations		References
		Range	Mean	
This study	Near historic industrial site	0.53-4.25	1.63	
New York and Buffalo, USA	Urban gardens	0.09-2.1	0.44	[1]
Longtang, China	Near an e-waste incineration site	0.11-1.3	0.52	[2]
Huludao, China	Near zinc plant	0.07-5.47	1.60	[3]
Zlatna, Romania	Near copper smelter	0.19-9.1	0.55	[4]
Brescia, Italy	Near ferroalloy plant	0.08-3.3	0.89	[5]

Table S3

Daily intake of Pb by each group.

	ADI ($\mu g\ kg^{-1}\ d^{-1}$)	RfD ($\mu g\ kg^{-1}\ d^{-1}$)	ADI/ RfD
Children	11.5	0.96	12.0
Adolescents	8.7	0.55	15.8
Adults	7.1	0.50	14.3

Table S4

Pb partitioning in soil from different distances and depths (in average).

Distance from site	Depth	Total Pb±SD ($mg\ kg^{-1}$)	EX1	CB2	FM3	OB4	RS5
5 m	0 cm	849.40±813.21	1.33%	0.11%	82.07%	13.53%	2.97%
	15 cm	278.02±543.56	0.84%	0.02%	77.19%	14.44%	7.51%
	30 cm	43.56±12.16	0.74%	0	63.38%	14.91%	20.98%
	50 cm	45.08±43.32	0.80%	0	61.40%	14.66%	23.14%
50 m	0 cm	133.01±93.65	0.39%	0	74.26%	15.55%	9.80%
	15 cm	32.30±4.92	0.76%	0	55.18%	15.47%	28.58%
	30 cm	26.66±2.40	0.92%	0	53.87%	13.60%	31.62%
	50 cm	24.83±1.19	0.95%	0	53.39%	13.18%	32.47%
100 m	0 cm	89.41±29.68	0.53%	0	63.93%	22.76%	12.78%
	15 cm	59.12±53.60	0.78%	0	65.35%	16.40%	17.47%
	30 cm	26.91±2.66	1.25%	0	53.78%	13.97%	30.99%
	50 cm	32.77±11.21	0.91%	0	59.05%	14.56%	25.48%

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