Journal of Geochemical Exploration 179 (2017) 1–8

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/gexplo

# Spatial patterns and correlations of lead concentrations in soil, leaf vegetables and human hair in the Pearl River Delta region, South China

Huihua Zhang[a,*], Junjian Chen[a,*], Tailong Guo[a], Li Zhu[b], Dingqiang Li[a]

[a] Guangdong Key Laboratory of Agricultural Environment Pollution Integrated Control, Guangdong, Institute of Eco-Environmental and Soil Sciences, Guangzhou 510650, China
[b] Management School, Jinan University, Guangzhou 510632, China

ARTICLE INFO

*Keywords:*
Lead
Soil
Leaf vegetable
Human hair
Pearl River Delta

ABSTRACT

A total of 924 soil samples, 170 leaf vegetable samples and 53 human hair samples were collected to evaluate the regional lead (Pb) concentration levels in soil, leaf vegetables and human hair across the Pearl River Delta (PRD) area. Soil Pb concentrations were greater than the risk screening value of Pb (80 mg $kg^{-1}$) in 3.5% of the vegetable planting area; about 8% vegetable Pb concentrations were exceeded the national standard of the maximum level of contaminants of 0.3 mg $kg^{-1}$. Pearson correlations indicated that there was no correlation between soil Pb and vegetable Pb in the study area. Pb concentrations of 12 hair samples were higher than the upper limit of the normal value of 10.0 mg $kg^{-1}$, and lower than the high-exposure risk value of 25 mg $kg^{-1}$. Therefore, the young residents in the PRD area had not suffered a high exposure to Pb, but still had a potential health risk. This health risk did not directly come from local leaf vegetable consumption.

## 1. Introduction

Lead (Pb) is one of toxic metals commonly found in soils. The natural Pb content in soils originates from parent rocks. The overall mean value of natural Pb for different soils has been calculated to be 25 mg $kg^{-1}$ (Kabata-Pendias and Mukherjee, 2007). The major anthropogenic sources of soil Pb pollution include sewage irrigation, application of pesticides and inorganic fertilizers, some mining operations, leaded gasoline, lead-based paint and atmospheric deposition(Zhu et al., 2001; Li et al., 2006; Lee et al., 2007; Niu et al., 2013; Laidlaw et al., 2016). Pb in soils can enter into livestock and human through the food chain (Nabulo et al., 2010; Luo et al., 2012; Li et al., 2012; Chang et al., 2014). Moreover, direct ingestion or inhalation of dust or soil is an important pathway in humans (Kamenov and Gulson, 2014; Laidlaw et al., 2016). Excessive intake of Pb can pose potential adverse health effects to human especially children (Zheng et al., 2007; Norton et al., 2014; Yu et al., 2015).

The Pearl River Delta (PRD) area is the largest industrial center and fastest development area in South China. Due to rapid development of industrialization and urbanization, and lack of effective pollution control measures, the decline of the region's environmental quality has been obvious since the late 1980s. Many studies have reported that the level of Pb contamination in the PRD area was more severe than that of most other trace metals (Li et al., 2000; Zhu et al., 2001; Wong et al., 2002, 2003; Ip et al., 2005; Duzgoren-Aydin, 2007), and pointed out that the Pb concentrations in surface soils were dominantly affected by the anthropogenic activities(Wong et al., 2002; Zhang et al., 2006), which included the mining and smelter operation (e.g. the Fankou Pb ore and Shaoguan smelter, located in the north of the PRD), industrial and vehicular emissions and other sources (Li et al., 2000; Zhu et al., 2001; Wong et al., 2002, 2003; Ip et al., 2005; Zhang et al., 2006; Duzgoren-Aydin, 2007; Luo et al., 2012). The Pb contaminant from these nonpoint sources can elevate the overall background concentrations of surface soils through atmospheric deposition (Zhang et al., 2006).

Although some authors have confirmed that atmospheric deposition was the major pathway for Pb entering the soil environment (Bi et al., 2009; Luo et al., 2012), and the long-range transport of atmospheric Pb is an important external source (Hsu et al., 2006; Witt et al., 2006; Lee et al., 2007), present research around the environmental influence of Pb mainly focused on the assessment of Pb exposure near specific Pb-related locations such as Pb-acid battery factories (Luo et al., 2011) and e-waste processing sites (Chen et al., 2012). Few studies about spatial pattern of Pb in soils, vegetables, and human hair, were conducted at a large regional scale. The aims of this study were to: (1) obtain information on Pb concentrations and spatial patterns in soils and leaf vegetables across the PRD area; and (2) determine relationships between Pb concentrations in soil, leaf vegetables and human hair at

* Corresponding authors.
*E-mail addresses:* hhzhang@soil.cn (H. Zhang), jjchen@soil.gd.cn (J. Chen).

http://dx.doi.org/10.1016/j.gexplo.2017.04.002
Received 5 December 2016; Received in revised form 7 April 2017; Accepted 25 April 2017
Available online 01 May 2017
0375-6742/ 

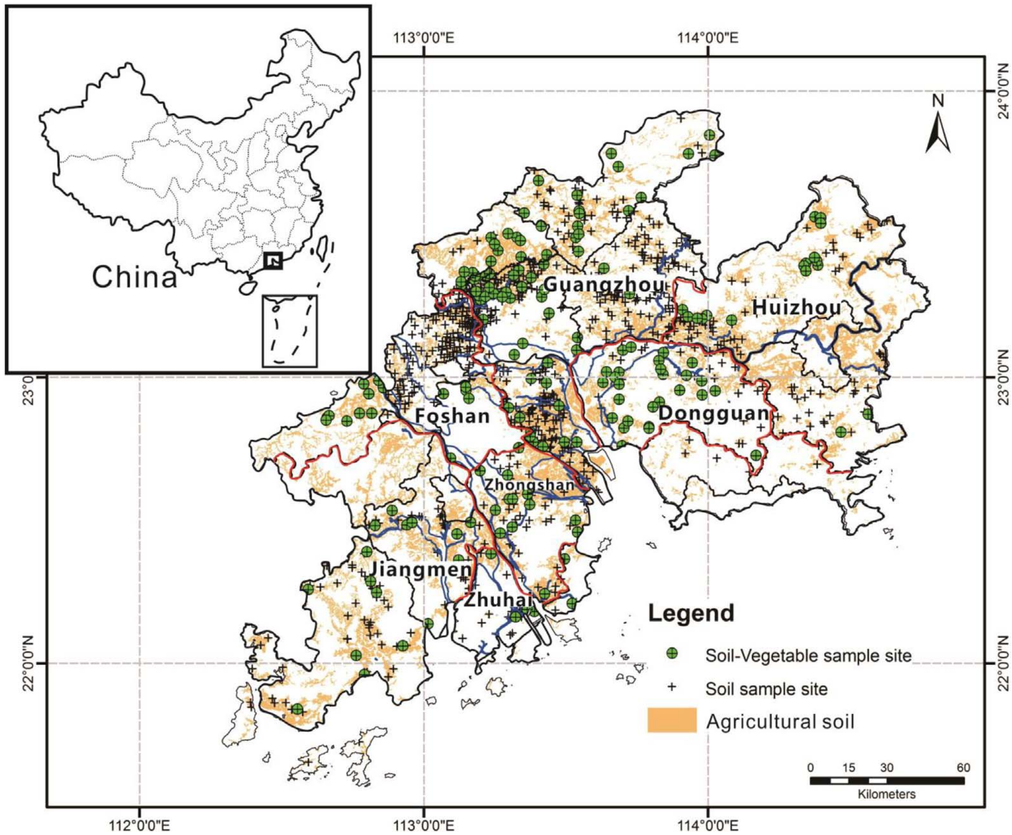


**Figure 1.** Locations of soil and vegetable samples in the Pearl River Delta area, Guangdong, China (The yellow areas represent the agricultural soils and the red line shows the city boundaries). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

a regional scale. The results of the present study may be used to assess the influence of soil Pb contamination on vegetable quality and human health at a large regional scale.

## 2. Materials and methods

### 2.1. Study area

The PRD area is located in the south of Guangdong Province, and covers 41,698 km$^2$, geographic coordinates is 21.5°–23.0°(N), 112°–115°(E).(Fig. 1). The climate in the study area is subtropical--tropical monsoon with average annual temperature of 21–22 °C and average annual rainfall of 1600–2000 mm (GSGIO, 1993). The main soil types in the PRD area are ferralsols, mostly developed on the parent material of acid igneous rocks in local hills, and paddy soils developed on the fluvial sediments (GSGIO, 1993). In the study area, 10–15 vegetable crops or three rice crops were planted annually, and a rotation of vegetable and rice was usually applied in paddy soils. In the PRD area, the vegetable planting area is about 4830 km$^2$. The vegetable production was 1129.2 × 10$^4$ tons in 2011. The leaf vegetables is the dominant consumption for local residents; their planting areas are about 33% of the total planting area (Wan, 2013). The Statistics Bureau of Guangdong Province reported that the export of fresh vegetables were up to 78.3 × 10$^4$ tons in 2012 (SBG, 2012).

### 2.2. Soil, vegetable and human hair sampling

A total of 924 soil samples were collected at 0–15-cm soil depth to investigate the spatial distribution of Pb concentrations in the study area during 2009–2010 (Fig. 1). All sample sites were located far away from obvious point source polluted areas such as industries, feedlots, and wastewater stations. Each soil sample consisted of five subsamples, and each subsample was about 1 kg.

One hundred and seventy leaf vegetable samples (corresponding with the soil sample locations) were collected on September 1st to 10th to reveal the correlation between soil Pb and vegetable Pb (Fig. 1). The vegetable species included pakchoi, Chinese flowering cabbage, leaf mustard, Romaine lettuce, Chinese lettuce, water spinach, celery, Chinese chives, spinach, amaranth, and watercress. Each vegetable sample consisted of five subsamples.

We collected 53 hair samples from local young people, 18–25 years old, of both genders (Male: 30 persons; Female: 23 persons), without dyed or treated hair. Hair samples 1–2 cm long were cut with stainless steel scissors from the nape of the neck, close to the occipital region of the scalp, and stored in plastic bags.

### 2.3. Analytical methods

Soil samples were air-dried at room temperature (25 °C) and ground to pass through a 150-μm nylon sieve. These samples were then digested to dryness using an acid mixture of 10 ml HF, 5 ml $HClO_4$, 2.5 ml HCl, and 2.5 ml $HNO_3$ (Luo et al., 2012).

The vegetable samples were thoroughly cleaned with tap water and ultrapure water to remove adhering particles, and then the edible parts were separated, weighed (fresh weight), and dried in an oven at 60 °C. The dry samples were ground to fine powder for chemical analysis. The dry samples were ashed in a muffle furnace for 16 h at 500 °C, dissolved in 0.5 M $HNO_3$, and diluted to 25 ml with deionized water (Luo et al., 2012).

Each hair sample was washed with a solution of 1% of Triton X-100 in ultrapure water for 5 min in an ultrasonic bath. This was repeated with a second wash with ultrapure water and no detergent. Then each hair sample was rinsed with ultrapure water and dried at 50 °C to a constant weight (GRANERO et al., 1998). Three ml of $HNO_3$ (Merck, Darmstadt, Germany) was added to about 150 mg of washed hair sample and digested for 24 h in Teflon vessels at room temperature. Digestion was then completed by adding 500 μL of $H_2O_2$ (Alfa Aesar, USA) for an additional 24 h. After digestion, the solutions were diluted by the addition of high-purity deionized water to reach a volume of 25 ml.

The Pb concentrations in soil, vegetable and human hair samples were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES; Model PS 1000, AT, USA). The National standard reference materials (ESS-4 for soils, GSV-1 for plants and GSH-1 for hairs) were used for the QA/QC protocol. The recovered Pb concentration of ESS-4 (Beijing, China; Standard value: 22.6 ± 1.7 mg $kg^{-1}$), GSV-01(Beijing, China; Standard value: 7.1 ± 0.9 mg $kg^{-1}$) and GSH-01 (Beijing, China; Standard value: 8.8 ± 1.1 mg $kg^{-1}$) were 23.1 ± 1.6 mg $kg^{-1}$ ($n$ = 32), 7.3 ± 0.6 mg $kg^{-1}$ ($n$ = 10) and 9.0 ± 0.5 mg $kg^{-1}$ ($n$ = 4), respectively. The analytical precision was about 2.2% for soils, 2.8% for plants and 2.3% for hairs, respectively.

The pH of the soil was measured by adding 10 g of sample into 25 ml of deionized water (Chinese National Standard Agency, 1988). The soil organic matter content was measured using the potassium bichromate oxidation process (Yu and Wang, 1988).

### 2.4. Data analysis

The data descriptive statistics, normal probability plot and Pearson correlation analysis were performed using the Minitab 16 statistical software (Minitab Inc., USA). The spatial interpolation and distribution pattern maps were produced using the ArcGIS 10.0 for Desktop software (Esri Inc. USA).

## 3. Results

### 3.1. Pb concentrations in soils

Soil Pb concentrations are presented in Table 1 and ranged from 7.06 to 232 mg $kg^{-1}$. These values generally fitted a log normal distribution (Fig. 2); therefore, the geometric mean value of 45.10 mg $kg^{-1}$ and geometric standard deviations of 1.02 were used to represent the central tendency and variations of the data in the study area. The geometric mean concentrations of soil Pb decreased in the following order: Dongguan > Zhongshan > Foshan > Zhuhai > Guangzhou > Jiangmen > Shengzhen. The highest Pb concentration in soils was observed in Guangzhou.

### 3.2. Pb in leaf vegetables

Vegetable Pb concentrations are shown in Table 2 and ranged from 0.01 to 0.79 mg $kg^{-1}$. These data generally fitted the log normal distribution (Fig. 3). The arithmetic mean is 0.11 mg $kg^{-1}$. The geometric mean is 0.07 mg $kg^{-1}$ with a large geometric standard deviation of 1.08. The highest value was observed in Guangzhou. The mean concentrations of Pb in leaf vegetables decreased in the following order: Dongguan > Guangzhou > Foshan > Huizhou > Jiangmen > Zhongshan > Zhuhai (Table 2).

### 3.3. Pb in human hair

The Pb concentrations in human hair Pb are shown in Table 3 and ranged from 2.27 to 20.23 mg $kg^{-1}$. These data generally fitted a log normal distribution (Fig. 4). The arithmetic and geometric means were 7.26 and 6.14 mg $kg^{-1}$, respectively (Table 3). The highest value (20.23 mg $kg^{-1}$) was observed in Jiangmen. The mean concentrations of hair Pb decreased in the following order: Zhuhai > Foshan > Huizhou > Guangzhou > Jiangmen > Dongguan (Table 3).

### 3.4. Comparison of Pb concentration of soil, leaf vegetable and human hair between regions

The scatter plot of soil vs. vegetable Pb concentrations in the PRD area showed that there were no linear correlations between soil and vegetable Pb concentrations in both the whole PRD area and in individual cities (Fig. 5). The Pb-polluted vegetables were not grown in soils with high Pb concentrations. Moreover, the average concentrations of Pb in soil, leaf vegetable and human hair in different cities in the PRD area (Fig. 6) indicate little relationship between the Pb concentrations in soils, vegetables and human hairs in each city. For example, in Dongguan, there were high Pb concentrations in soils and vegetables but low Pb concentrations in human hair. However, in Zhuhai, there were low Pb concentrations in vegetables and high Pb concentrations in hair.

## 4. Discussion

### 4.1. Pb in vegetable soils

In the PRD area, soil Pb had a high baseline value of 57.5 mg $kg^{-1}$, which represents the historical level about 30 years ago (Zhang et al., 2006). Moreover, previous studies have indicated that the soil Pb concentration had been strongly influenced by atmospheric input from

**Table 1**
Descriptive statistics of Pb concentrations (mg $kg^{-1}$) in soils.

| Sample site | n | AM ± SD[a] | Range | Median | Skew | GM (GSD)[b] | pH ($H_2O$) | OM[c] (%) |
|---|---|---|---|---|---|---|---|---|
| Dongguan | 61 | 65.32 ± 24.75 | 20.36–139.50 | 58.22 | 1.2[d] – 0.01[e] | 61.20 (1.43) | 5.76 ± 0.87 | 2.58 ± 0.70 |
| Foshan | 145 | 51.95 ± 21.39 | 23.22–229.90 | 48.90 | 4.3,0.6 | 49.02 (1.38) | 5.84 ± 1.12 | 2.61 ± 1.01 |
| Guangzhou | 450 | 49.47 ± 24.95 | 8.40–232.00 | 45.95 | 2.4, – 0.4 | 44.30 (1.61) | 6.34 ± 0.96 | 2.44 ± 0.66 |
| Huizhou | 97 | 37.90 ± 17.93 | 8.93–127.00 | 35.30 | 1.7, – 0.2 | 34.22 (1.58) | 6.69 ± 0.43 | 2.41 ± 0.62 |
| Jiangmen | 91 | 46.05 ± 18.67 | 7.06–116.70 | 44.80 | 1.3, – 0.9 | 42.43 (1.53) | 5.49 ± 0.67 | 2.28 ± 0.90 |
| Shengzhen | 6 | 25.40 ± 11.96 | 13.72–42.18 | 19.34 | 0.9,0.6 | 23.29 (1.51) | 5.96 ± 1.36 | 2.44 ± 0.91 |
| Zhongshan | 50 | 60.01 ± 14.87 | 26.39–92.28 | 60.31 | 0.3, – 0.5 | 58.14 (1.29) | 6.02 ± 0.97 | 2.45 ± 0.90 |
| Zhuhai | 24 | 48.56 ± 13.66 | 26.09–90.72 | 47.84 | 1.1, – 0.02 | 46.84 (1.31) | 6.11 ± 0.99 | 2.34 ± 0.63 |
| Total | 924 | 49.74 ± 23.26 | 7.06–232.00 | 46.9 | 2.3, – 0.5 | 45.10 (1.57) | 6.12 ± 0.96 | 2.42 ± 0.74 |
| Threshold | | | | | | 50[f], 80[g] | | |

[a] AM ± SD, arithmetic mean ± standard deviation).
[b] GM (GSD), geometric mean (geometric standard deviation).
[c] OM, organic matter.
[d] Untransformed data.
[e] Ln-transformed data.
[f] The maximum permissible concentration of Pb for green food production areas (MOH, 2012).
[g] The health risk screening value of Pb for vegetable soils (AQTSGP, 2014).

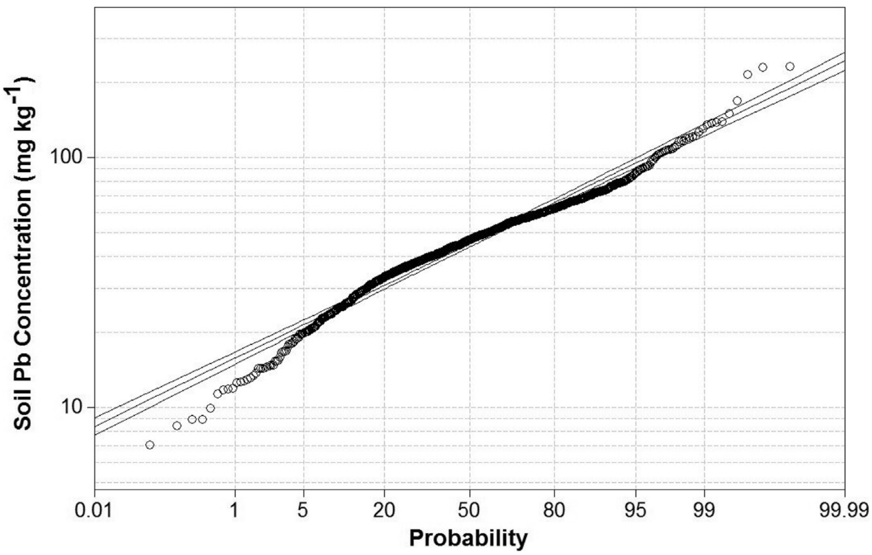


**Fig. 2.** Lognormal probability plot for total Pb concentrations of soils in the Pearl River Delta area.

**Table 2**
Descriptive statistics of Pb concentrations (mg $kg^{-1}$ FW) in leaf vegetables.

| Sample site | n | Mean ± SD | Range | Median | C.V. (%) |
|---|---|---|---|---|---|
| Dongguan | 27 | 0.19 ± 0.07 | 0.12–0.37 | 0.16 | 36.8 |
| Foshan | 16 | 0.07 ± 0.02 | 0.04–0.10 | 0.08 | 29.0 |
| Guangzhou | 74 | 0.15 ± 0.18 | 0.05–0.79 | 0.08 | 119.8 |
| Huizhou | 18 | 0.05 ± 0.07 | 0.01–0.26 | 0.03 | 140.2 |
| Jiangmen | 17 | 0.04 ± 0.01 | 0.03–0.04 | 0.04 | 15.1 |
| Zhongshan | 13 | 0.02 ± 0.01 | 0.01–0.03 | 0.02 | 25.1 |
| Zhuhai | 6 | 0.01 ± 0.003 | 0.01–0.02 | 0.01 | 62 |
| Total | 171 | 0.11 ± 0.14 | 0.01–0.79 | 0.07 | 121.6 |
| | | 0.07(1.08)[a] | | | |
| Threshold | | 0.2[b], 0.3[c] | | | |

[a] Geometric mean (geometric standard deviation).
[b] Maximum permissible concentration for non-environmentally polluted vegetables (AQSIQ, 2001).
[c] Maximum level of contaminants in leaf vegetables for food security (MOH, 2012).

**Table 3**
Descriptive statistics of Pb concentrations (mg $kg^{-1}$) in human hair.

| Sample site | n | Mean ± SD | Range | Median | C.V. (%) |
|---|---|---|---|---|---|
| Dongguan | 3 | 3.74 ± 0.82 | 3.19–4.68 | 3.35 | 21.9 |
| Foshan | 2 | 12.09 ± 8.56 | 6.03–18.14 | 12.09 | 70.9 |
| Guangzhou | 17 | 7.23 ± 3.25 | 2.96–13.87 | 6.54 | 45.0 |
| Huizhou | 11 | 7.80 ± 4.96 | 2.27–15.94 | 6.37 | 58.6 |
| Jiangmen | 17 | 6.08 ± 4.91 | 2.49–20.23 | 4.67 | 80.8 |
| Zhuhai | 3 | 12.48 ± 4.07 | 8.14–16.20 | 13.10 | 32.6 |
| Total | 53 | 7.26 ± 4.60 | 2.27–20.23 | 5.83 | 62.3 |
| | | 6.14(1.76)[a] | | | |
| Threshold | | 10[b], 25[c] | | | |

[a] Geometric mean (geometric standard deviation).
[b] The upper limit of normal value for Chinese residents(Qin, 2004).
[c] High exposure risk value (Furman and Laleli, 2000).

rapid urbanization and industrialization, primarily as a result of coal burning activities (Li et al., 2000), automobile exhaust and industrial sources (Wong et al., 2003).

The results of the current study show that the geometric mean concentration of Pb in vegetable soils was 45.1 mg $kg^{-1}$. Though it was much higher than the background value of 29.4 mg $kg^{-1}$ in Guangdong Province, it was considerably lower than the historical level of 57.5 mg $kg^{-1}$ (Zhang et al., 2006). This suggests that soil Pb derived from anthropogenic activities was decreasing, perhaps because of increasingly strict environmental protection measures such as the use of

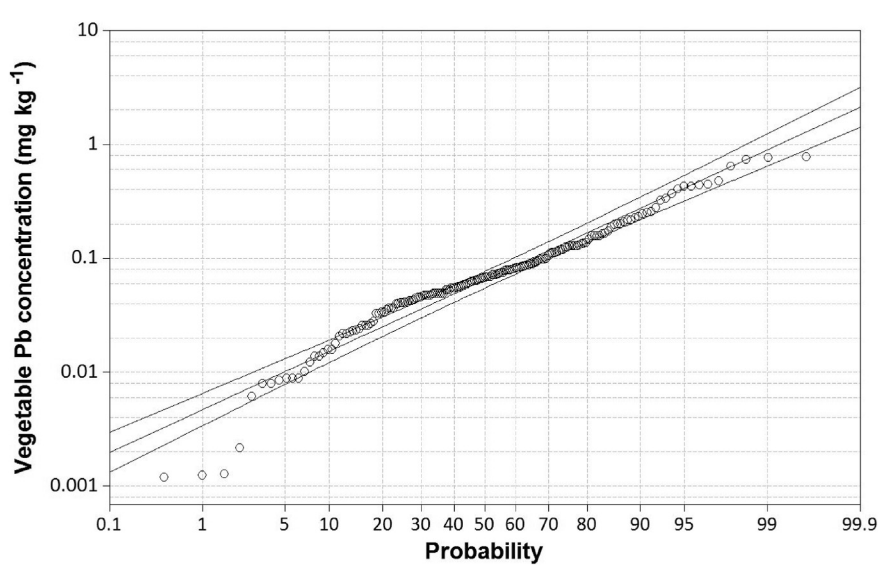


**Fig. 3.** Lognormal probability plot for vegetable concentrations in the Pearl River Delta area.

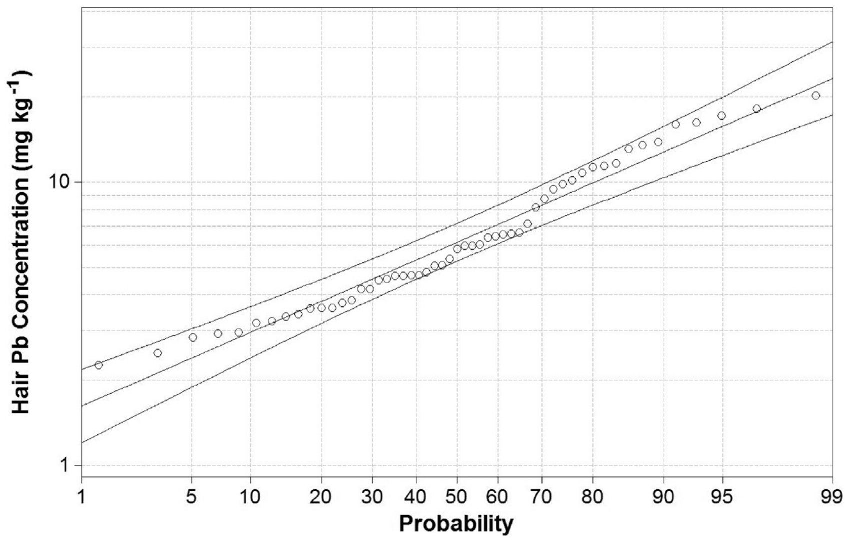


**Fig. 4.** Lognormal probability plot for human hair Pb concentrations in the Pearl River Delta area.

unleaded rather than leaded gasoline. Moreover, vegetables can take up Pb from soils continually because of the shorter planting cycle and higher yields than non-vegetable crops or natural vegetation.

In this study, Pb concentrations of 60 soil samples were greater than the risk screening value of Pb (80 mg $kg^{-1}$) (AQTSGP, 2014), and soil Pb concentrations of 400 soil samples were greater than the standard for green food production areas (50 mg $kg^{-1}$) (MAPRC, 2013). The spatial distribution pattern of soil Pb concentrations showed that soil Pb concentrations were higher than the risk screening value in about 3.5% of the vegetable planted area (Fig. 7). In about 40% of the vegetable planted area (Fig. 7), soil Pb concentrations were beyond the standard for green food production areas.

In the PRD area soils with a high Pb concentration were generally distributed in the Guangzhou, Dongguan and Fosan cities (Fig. 7). Previous researches have indicated that concentrations of soil Pb have been strongly influenced by atmospheric inputs, primarily from coal burning activities (Li et al., 2000), automobile exhaust, and industrial sources (Wong et al., 2002) in these cities. The spatial distribution patterns of soil Pb may be related to the prevailing wind direction of Guangdong Province (Zhang et al., 2006), Moreover, in this study soil Pb has an obviously similar spatial distribution pattern with yearly average $PM_{10}$ concentrations reported by Li et al. (2015), Which may further confirm that Pb concentrations in surface soils had a close relationship with the annual regional atmospheric deposition in the PRD area.

### 4.2. Pb in leaf vegetables

The present study showed that the geometric mean concentration of Pb in vegetables was 0.07 mg $kg^{-1}$ (FW). The Pb concentrations of 13 leaf vegetable samples were higher than the maximum level of contaminants of 0.3 mg $kg^{-1}$ (FW) for food security (MOH, 2012); and Pb concentrations of 25 leaf vegetable samples were beyond the maximum permissible concentration of Pb of 0.2 mg $kg^{-1}$ (FW) for non-environmental polluted vegetables (AQSIQ, 2001). In our study area, 85% of leaf vegetable Pb concentrations were lower than 0.2 mg $kg^{-1}$ (FW). These may thus be considered non-environmentally polluted vegetables.

The present results showed that there was no linear correlation between soil Pb and vegetable Pb in both the whole PRD area and in

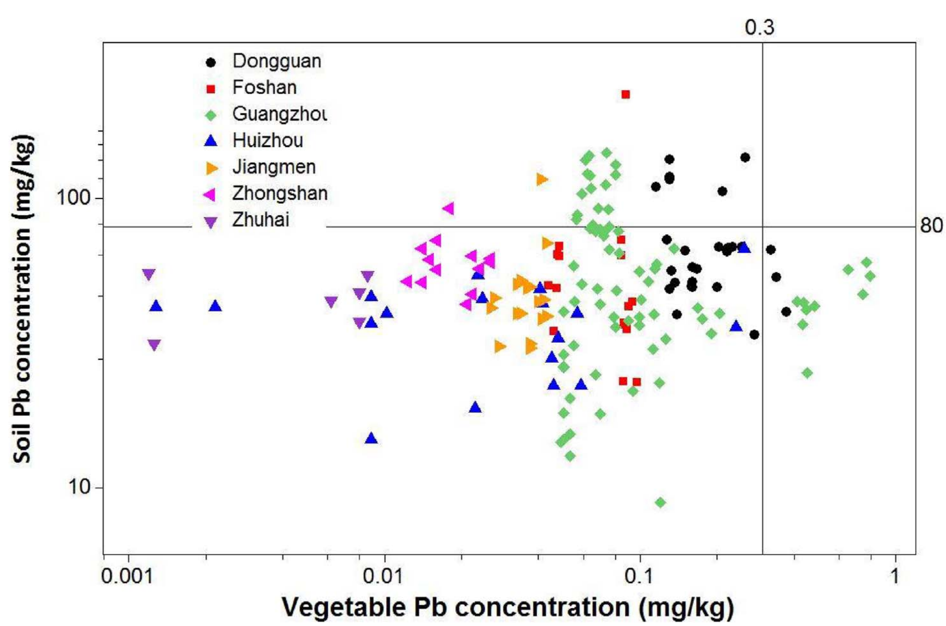


**Fig. 5.** Scatter plot of log-transformed soil concentrations vs. log-transformed vegetable Pb concentrations in the Pearl River Delta area.

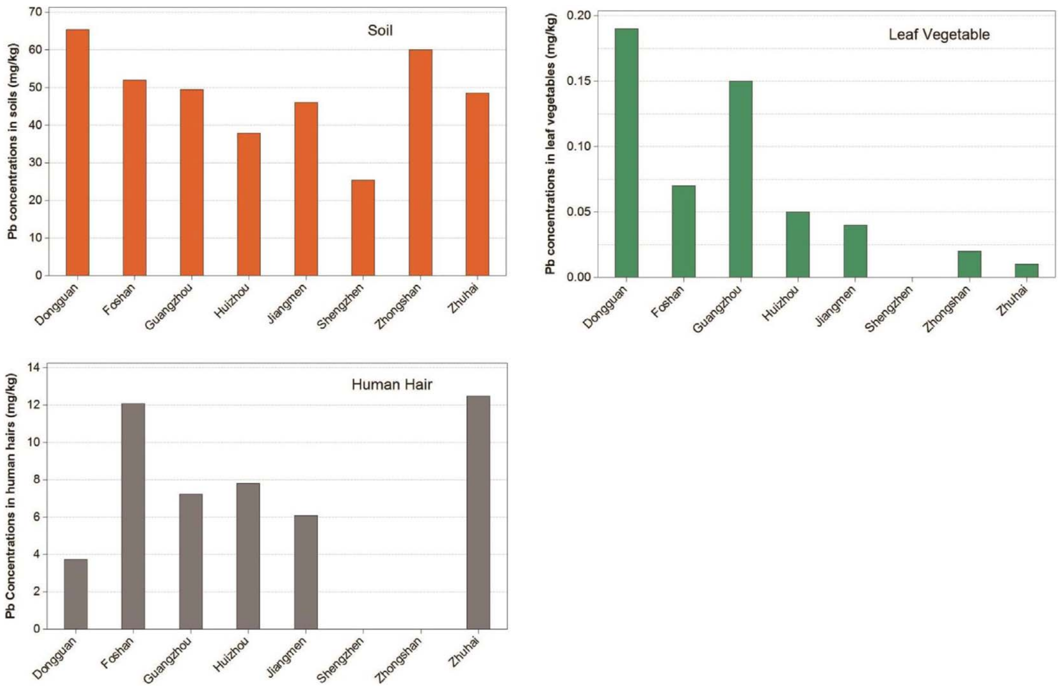


**Fig. 6.** Bar charts for Pb concentrations in soil, leaf vegetable, and human hair in different cities in the PRD area.

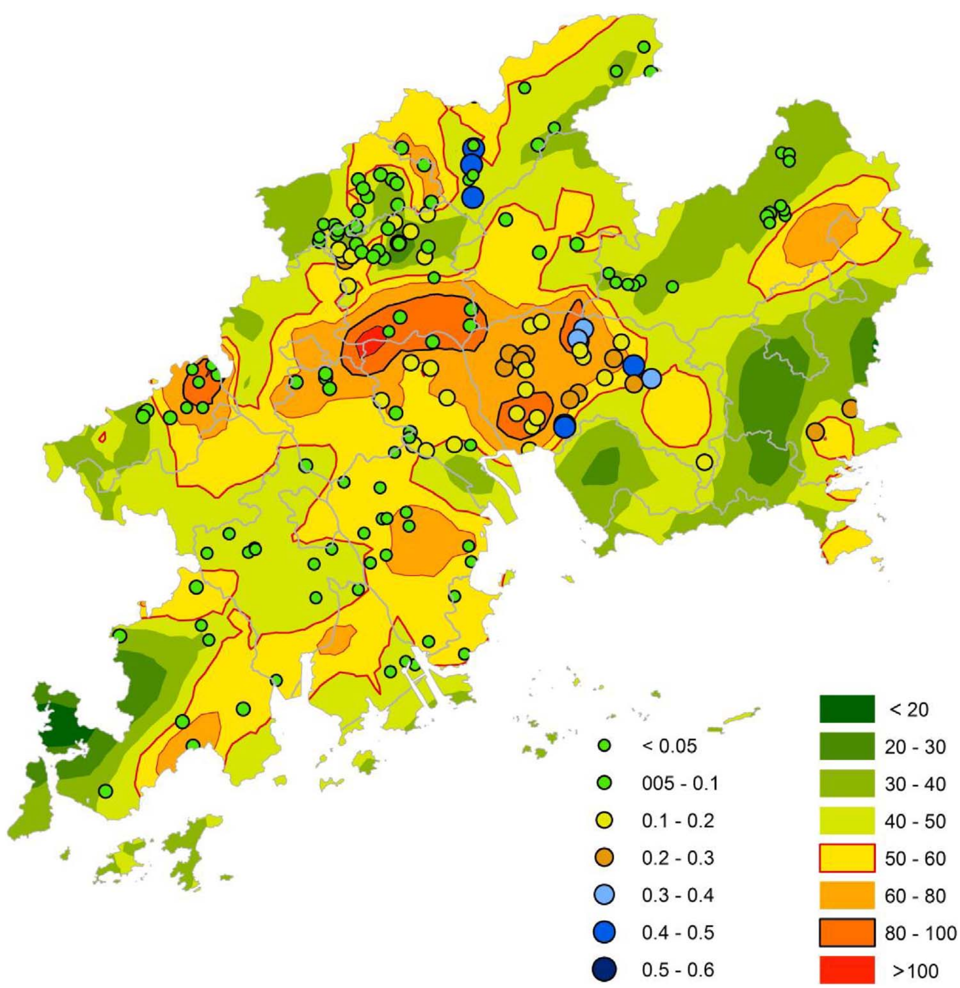


**Fig. 7.** Spatial pattern of Pb concentration (mg $kg^{-1}$, dry weight) in soils. The circles indicate the Pb concentration levels of leaf vegetables (mg $kg^{-1}$, fresh weight) in the Pearl River Delta area. The red line and black lines represent the area in which soil Pb concentrations were higher than 50 mg $kg^{-1}$ and 80 mg $kg^{-1}$, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Table 4**
Pearson correlations of soil Pb, leaf vegetable Pb, soil pH and soil organic matter content.

| | Soil Pb | Leaf vegetable Pb | Soil pH | SOM |
|---|---|---|---|---|
| Soil Pb (*p*-value) | 1 | | | |
| Leaf vegetable Pb (*p*-value) | 0.083 (0.454) | 1 | | |
| Soil pH (*p*-value) | − 0.117 (0.288) | − 0.159 (0.149) | 1 | |
| SOM (*p*-value) | 0.177 (0.108) | − 0.022 (0.841) | 0.035 (0.749) | 1 |

different cities (Fig. 5), and there was also no spatial correlation between soil and vegetable Pb (Fig. 7), which should indicate that soil Pb was not the major Pb source for leaf vegetables. Furthermore, there was no significant Pearson correlation between leaf vegetable Pb, soil Pb, soil pH and soil organic matter content (Table 4). These results suggested that elevated vegetable Pb concentrations were likely coming from Pb in dust particles adhering to vegetable leaves.

Some studies have revealed that atmospheric deposition of Pb may be the most major Pb source in above-ground tissues of plants in Pb-polluted areas (Bi et al., 2009; Luo et al., 2012). Yang and Appleby (2016) pointed out that the leaves of some plants can absorbed a significant proportion of their Pb directly from the atmosphere based data of unsupported $^{210}$Pb of the leaves. In this study, Pb-polluted vegetable sites were mainly distributed in Guangzhou and Dongguan (Fig. 7). The polluted vegetable species were pakchoi, Romaine lettuce, and Chinese lettuce. These leaf vegetables with larger leaf surface area can intercept more atmospheric deposition, and more atmospheric Pb thus enters the plant by foliar uptake. Particles contained Pb might be found on the surface of the leaves in a strongly agglomerated form. They might be trapped by the cuticular wax and then diffused in the leaf tissue (Schreck et al., 2012). Now though atmospheric deposition of Pb was the major Pb source for both surface soils and leaf vegetables, there was no any correlation between them. The main reason was that the spatial distribution of soil Pb was similar to the annual atmospheric deposition (Li et al., 2015), but the Pb concentrations in these leaf vegetables were mainly affected by monthly atmospheric deposition. Liao et al. (2015) showed that air quality improves in the wet season (April to September) relative to the dry season (October to March) in the PRD area, based on the air quality monitoring network during 2006–2012. Vegetable growing seasons are mainly during the wet season with better air quality. Therefore, the difference between annual atmospheric depositions and seasonal depositions may be why we found no spatial correlation between soil Pb and vegetable Pb in the study area.

### 4.3. Pb in human hair

The most common matrices used in human biomonitoring are blood, urine and hair. Hair is a biological specimen that is much more easily and non-invasively collected, inexpensive, and easily stored and transported to the laboratory for analysis than blood specimens (Rodrigues et al., 2008). Blood and urine samples offer only a short time window for analysis, being subject to fluctuations in response to changes in physiological conditions. Thus although some studies indicated that hair analysis results do not always match other biological indicators because of gender, skin color, eating habits, age and lifestyle (Chojnacka et al., 2005, 2010), hair Pb concentrations provide a more reliable way of assessing past and ongoing exposure to Pb pollution (Gellein et al., 2008; Gil et al., 2011).

The average concentration (7.26 ± 4.6 mg kg$^{-1}$) of hair Pb in this study was much higher than the historical value of 2.3 mg kg$^{-1}$ in Guangzhou and close to the average level of Chinese residents (7.14 ± 3.25 mg kg$^{-1}$) (Qin, 2004). Furman and Laleli (2000) reported that human hair usually contains less than 5 mg kg$^{-1}$ of Pb, and concentrations above 25 mg kg$^{-1}$ indicate a high exposure. Qin (2004) provided the upper limit of normal value of 10.0 mg kg$^{-1}$ for hair Pb for Chinese residents based on 2466 hair samples.

The present results showed that hair Pb concentrations were lower than 25 mg kg$^{-1}$, with a range of 2.27–20.23 mg kg$^{-1}$; 12 hair samples were beyond the 10.0 mg kg$^{-1}$ limit, distributed in most study areas, except Dongguan. Therefore, it can be concluded that the young residents had not suffered a high exposure to Pb in the study area, but in some cases still had a potential health risk. Previous studies have indicated that the consumption of vegetables and rice does not cause a health risk to local populations in the PRD area (Li et al., 2012; Chang et al., 2014). Moreover, Ip et al. (2005) revealed that in the Pearl River Estuary, high concentrations of Pb were found in fish; the mean concentration was 2.2 mg kg$^{-1}$ with a highest value of 30.7 mg kg$^{-1}$. Thus, the health risk found in our study did not directly originate from local leaf vegetable consumption. Though some researches had indicated that presence of food in the stomach prevents adsorption of Pb so food was not a major source of Pb to humans (Gulson et al., 2006; Kamenov and Gulson, 2014), the consumption of fish contained high Pb also should be paid much more attention in the PRD area.

## 5. Conclusions

The present results showed that the geometric mean of soil Pb concentration (45 mg kg$^{-1}$) was lower than historical level (57 mg kg$^{-1}$), and 85% of leaf vegetables Pb concentrations were lower the standard of 0.2 mg kg$^{-1}$ for non-environmentally polluted vegetables. Both soils and atmospheric depositions were the primary Pb sources for vegetables. Atmospheric deposition of Pb may be the main source of polluted vegetables, which should be mainly affected by monthly atmospheric deposition patterns. The difference between annual atmospheric depositions and seasonal depositions may explain the lack of any spatial correlation between soil Pb and vegetable Pb in the study area. The health risk of higher Pb concentrations in human hair did not come directly from local leaf vegetable consumption in the PRD area.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 31270516 and 41171387), the Natural Science Foundation of Guangdong Province, China (No·S2012030006144), the Science and Technology Planning Project of Guangdong Province, China (No. 2012A020100003), Pearl River S & T Nova Program of Guangzhou (No. 2013 J2200003).

## References

AQSIQ, 2001. Safety qualification for agricultural product – safety requirements for non-environmental pollution vegetable (GB 18406.1 - 2001). In: General Administration of Quality Supervision, Inspection and quarantine of China, Beijing, China.
AQTSGP, 2014. Risk Screening Values for Soil Heavy Metal The Pearl River Delta Area (DB 44/T1415–2014). (Administration of Quality and Technology Supervision of Guangdong Province).
Bi, X., Feng, X., Yang, Y., Li, X., Shin, G.P.Y., Li, F., Qiu, G., Li, G., Liu, T., Fu, Z., 2009. Allocation and source attribution of lead and cadmium in maize (*Zea mays* L.) impacted by smelting emissions. Environ. Pollut. 157 (Barking, Essex:1987). (834–9).
Chang, C.Y., Yu, H.Y., Chen, J.J., Li, F.B., Zhang, H.H., Liu, C.P., 2014. Accumulation of heavy metals in leaf vegetables from agricultural soils and associated potential health risks in the Pearl River Delta, South China. Environ. Monit. Assess. 186, 1547–1560.
Chen, L., Xu, Z., Liu, M., Huang, Y., Fan, R., Su, Y., Hu, G., Peng, X., Peng, X., 2012. Lead exposure assessment from study near a lead-acid battery factory in China. Sci. Total Environ. 429, 191–198.
Chinese National Standard Agency, 1988. Determination of pH Value in Forest Soil. GB 7859-87, UDC 634.0.114:631.422.
Chojnacka, K., Górecka, H., Chojnacki, A., Górecki, H., 2005. Inter-element interactions in human hair. Environ. Toxicol. Pharmacol. 20, 368–374.
Chojnacka, K., Michalak, I., Zielińska, A., Górecka, H., Górecki, H., 2010. Inter-relationship between elements in human hair: the effect of gender. Ecotoxicol. Environ. Saf. 73, 2022–2028.
Duzgoren-Aydin, N.S., 2007. Sources and characteristics of lead pollution in the urban

environment of Guangzhou. Sci. Total Environ. 385, 182–195.
Furman, A., Laleli, M., 2000. Semi-occupational exposure to lead: a case study of child and adolescent street vendors in Istanbul. Environ. Res. 83, 41–45.
Gellein, K., Lierhagen, S., Brevik, P.S., Teigen, M., Kaur, P., Singh, T., Flaten, T.P., Syversen, T., 2008. Trace element profiles in single strands of human hair determined by HR-ICP-MS. Biol. Trace Elem. Res. 123, 250–260.
Gil, F., Hernández, A.F., Márquez, C., Femia, P., Olmedo, P., López-Guarnido, O., Pla, A., 2011. Biomonitorization of cadmium, chromium, manganese, nickel and lead in whole blood, urine, axillary hair and saliva in an occupationally exposed population. Sci. Total Environ. 409, 1172–1180.
Granero, S., Llobet, J.M., Schuhmacher, M., Corbella, J., Domingo, J.L., 1998. Biological monitoring of environmental pollution and human exposure to metals in Tarragona, Spain. I. Levels in hair of school children. Trace Elem. Electrolytes 15, 39–43.
GSGIO, 1993. Guangdong soil. In: Liu, A.S. (Ed.), Science Publish House, Guangdong Soil General Investigation Office.
Gulson, B., Mizon, K., Korsch, M., Taylor, A., 2006. Changes in the lead isotopic composition of blood, diet and air in Australia over a decade: globalization and implications for future isotopic studies. Environ. Res. 100 (1), 130–138.
Hsu, S.-C., Chen Liu, S., Jeng, W.-L., Chou, C.C.K., Hsu, R.-T., Huang, Y.-T., Chen, Y.-W., 2006. Lead isotope ratios in ambient aerosols from Taipei, Taiwan: identifying long-range transport of airborne Pb from the Yangtze Delta. Atmos. Environ. 40, 5393–5404.
Ip, C.C.M., Li, X.D., Zhang, G., Wong, C.S.C., Zhang, W.L., 2005. Heavy metal and Pb isotopic compositions of aquatic organisms in the Pearl River Estuary, South China. Environ. Pollut. 138, 494–504.
Kabata-Pendias, A., Mukherjee, A.B., 2007. Trace Elements from Soil to Human. Springer, Berlin Heidelberg.
Kamenov, G.D., Gulson, B.L., 2014. The pb isotopic record of historical to modern human lead exposure. Sci. Total Environ. 490, 861–870.
Laidlaw, M.A.S., Filippelli, G.M., Sadler, R.C., Gonzales, C.R., Ball, A.S., Mielke, H.W., 2016. Children's blood lead seasonality in flint, Michigan (USA), and soil-sourced lead hazard risks. Int. J. Environ. Res. Public Health 13 (4), 358.
Lee, C.S.L., Li, X.-D., Zhang, G., Li, J., Ding, A.-J., Wang, T., 2007. Heavy metals and Pb isotopic composition of aerosols in urban and suburban areas of Hong Kong and Guangzhou, South China—Evidence of the long-range transport of air contaminants. Atmos. Environ. 41, 432–447.
Li, X., Wai, O.W.H., Li, Y.S., Coles, B.J., Ramsey, M.H., Thornton, I., 2000. Heavy metal distribution in sediment profiles of the Pearl River estuary, South China. Appl. Geochem. 15, 567–581.
Li, J., Xie, Z.M., Xu, J.M., Sun, Y.F., 2006. Risk assessment for safety of soils and vegetables around a lead/zinc mine. Environ. Geochem. Health 28, 37–44.
Li, Q., Chen, Y., Fu, H., Cui, Z., Shi, L., Wang, L., Liu, Z., 2012. Health risk of heavy metals in food crops grown on reclaimed tidal flat soil in the Pearl River Estuary, China. J. Hazard. Mater. 227-228, 148–154.
Li, L., Yang, J., Wang, Y., 2015. Retrieval of high-resolution atmospheric particulate matter concentrations from satellite-based aerosol optical thickness over the Pearl River Delta area, China. Remote Sens. 7, 7914–7937.
Liao, Z., Sun, J., Fan, S., Wu, D., Ren, M., Zhou, J., 2015. Variation characteristics and influencing factors of air pollution in Pearl River Delta area from 2006 to 2012. China Environ. Sci. 35, 329–336.
Luo, C., Liu, C., Wang, Y., Liu, X., Li, F., Zhang, G., Li, X., 2011. Heavy metal contamination in soils and vegetables near an e-waste processing site, South China. J. Hazard. Mater. 186, 481–490.
Luo, C., Yang, R., Wang, Y., Li, J., Zhang, G., Li, X., 2012. Influence of agricultural practice on trace metals in soils and vegetation in the water conservation area along the East River (Dongjiang River), South China. Sci. Total Environ. 431 (5), 26–32.
MAPRC, 2013. Green Food – Environmental Quality for Production Area (NY/T 391–2013). MInistry of Agriculture of the People's Republic of China.
MOH, 2012. Maximum Levels of Contaminants in Foods (GB 2762–2012). Ministry of Health of the People's Republic of China.
Nabulo, G., Young, S.D., Black, C.R., 2010. Assessing risk to human health from tropical leafy vegetables grown on contaminated urban soils. Sci. Total Environ. 408, 5338–5351.
Niu, L., Yang, F., Xu, C., Yang, H., Liu, W., 2013. Status of metal accumulation in farmland soils across China: from distribution to risk assessment. Environ. Pollut. 176, 55–62.
Norton, G.J., Williams, P.N., Adomako, E.E., Price, A.H., Zhu, Y., Zhao, F.J., 2014. Lead in rice: analysis of baseline lead levels in market and field collected rice grains. Sci. Total Environ. 485-486C (1), 428–434.
Qin, J., 2004. The upper limit of normal value of hair Pb,Cd,As,Hg in Chinese resident. Guangdong Weiliang Yuanshu Kexue 11, 26–37.
Rodrigues, J.L., Batista, B.L., Nunes, J.a., Passos, C.J.S., Barbosa, F., 2008. Evaluation of the use of human hair for biomonitoring the deficiency of essential and exposure to toxic elements. Sci. Total Environ. 405, 370–376.
SBG, 2012. Guangdong Statistical Yearbook – 2012. Statistics Bureau of Guangdong Province. China Statistic Press, Beijing.
Schreck, E., Foucault, Y., Sarret, G., Sobanska, S., Cécillon, L., Castrec-Rouelle, M., Castrec-Rouelle, M., Uzu, G., Dumat, C., 2012. Metal and metalloid foliar uptake by various plant species exposed to atmospheric industrial fallout: mechanisms involved for lead. Sci. Total Environ. 427–428, 253–262.
Wan, Z., 2013. The Development Report of Guangdong Vegetables Industry. pp. 2012.
Witt, M., Baker, A.R., Jickells, T.D., 2006. Atmospheric trace metals over the Atlantic and South Indian Oceans: investigation of metal concentrations and lead isotope ratios in coastal and remote marine aerosols. Atmos. Environ. 40, 5435–5451.
Wong, S., Liu, X., Zhang, G., Qi, S., Min, Y., 2002. Heavy metals in agricultural soils of the Pearl River Delta, South China. Environ. Pollut. 119, 33–44.
Wong, C.S.C., Li, X.D., Zhang, G., Qi, S.H., Peng, X.Z., 2003. Atmospheric deposition of heavy metals in the Pearl River Delta, China. Atmos. Environ. 37, 767–776.
Yang, H., Appleby, P.G., 2016. Use of lead-210 as a novel tracer for lead (Pb) sources in plants. Sci. Rep. 6 (21707), 1–9.
Yu, T., Wang, Z., 1988. Soil Analytical Chemistry. Science Press, Beijing.
Yu, Y., Li, Q., Wang, H., Wang, B., Lu, Q., Yan, Z., 2015. Exposure risk of young population to lead: a case study in Le'an river basin in Jiangxi province, China. Environ. Pollut. 209, 140–146.
Zhang, H.H., Li, F.B., Wu, Z.F., Li, D.Q., Xu, D.R., Yuan, H.X., 2006. Baseline concentrations and spatial distribution of trace metals in surface soils of Guangdong province, China. J. Environ. Qual. 37, 1752–1760.
Zheng, N., Wang, Q., Zhang, X., Zheng, D., Zhang, Z., Zhang, S., 2007. Population health risk due to dietary intake of heavy metals in the industrial area of Huludao city, China. Sci. Total Environ. 387 (1–3), 96–104.
Zhu, B.-Q., Chen, Y.-W., Peng, J.-H., 2001. Lead isotope geochemistry of the urban environment in the Pearl River Delta. Appl. Geochem. 16, 409–417.