Environ Sci Pollut Res (2017) 24:19816–19826
DOI 10.1007/s11356-017-9516-1

RESEARCH ARTICLE

Assessment of the potential health risks of heavy metals in soils in a coastal industrial region of the Yangtze River Delta

Bifeng Hu[1] · Jiayu Wang[1] · Bin Jin[2] · Yan Li[3,4] · Zhou Shi[1]

Received: 30 November 2016 / Accepted: 12 June 2017 / Published online: 7 July 2017

Abstract Soil heavy metal contamination is a serious environmental problem. Human beings may be directly exposed to heavy metals in soils through the inhalation of soil particles, dermal contact, and oral ingestion, which can seriously threaten health. This study assesses the health risks associated with heavy metals in soils by determining the concentrations of eight heavy metals (Cr, Pb, Cd, Hg, As, Cu, Zn, and Ni) based on 2051 surface-soil samples collected from the southern Yangtze River Delta of China. The mean concentrations were higher than the corresponding background values in Zhejiang Province and China as a whole, indicating an accumulation of heavy metals. The health risk assessment suggests that the non-carcinogenic and carcinogenic risks in the study area were not significant. The non-carcinogenic risk for children was the highest, followed by those for adults and seniors; the non-carcinogenic risk for the entire population was less than 1.0, the predetermined threshold. Carcinogenic risk for adults was the highest, followed by those for seniors and children; a few sample points had a value larger than the threshold of 1.0E−04. Arsenic represented the greatest contribution to non-carcinogenic and carcinogenic risk. Meanwhile, ingestion of heavy metals in soil was the main exposure pathway for carcinogenic risk, followed by inhalation and dermal exposure. The spatial method of Getis-Ord was used to identify hot spots of health risk. Hot spots with high hazard index (HI) and total carcinogenic risk (TCR) for children, adults, and seniors were mainly distributed in core urban areas, such as Jiangbei, Haishu, Yinzhou, Jiangdong, and the urban areas of some other counties, which coincided with industrial, mining, and urban areas of the study area and were strongly influenced by anthropogenic activities. These results provide a basis for heavy metal control in soil, source identification, and environment management in the Yangtze River Delta and other rapidly developing industrial regions in China.

Keywords Heavy metals · Health risk assessment · Spatial variability · Hot spot · Cold spot

Responsible editor: Zhihong Xu

Electronic supplementary material The online version of this article (doi:10.1007/s11356-017-9516-1) contains supplementary material, which is available to authorized users.

✉ Yan Li
liyan522@zju.edu.cn

1 Institute of Agricultural Remote Sensing and Information Technology Application, Zhejiang University, Hangzhou 310029, China

2 Ningbo agricultural food safety Management Station, Ningbo 315000, China

3 Institute of Land Science and Property Management, School of Public Affairs, Zhejiang University, Hangzhou 310058, China

4 School of Public Affairs, Zhejiang University, No. 866 Yuhangtang Road, Xihu District, Hangzhou 310058, China

Introduction

Heavy metal contamination and accumulation in soil have attracted worldwide attention due to their wide sources, toxicity, non-biodegradable properties, and accumulative behaviors (Nriagu, 1990; Liu and Diamond, 2005). In the last few decades, with continuous industrialization and urbanization, heavy metal contamination, which is caused by industrial and domestic wastewater emissions, sewage irrigation, vehicle exhaust, and overuse of pesticides and fertilizers, has become more serious in China (Cai et al., 2015; Wu et al., 2016). According to a national survey of soil pollution released by the Ministry of Land and Resources and the Ministry of

Environmental Protection of the People's Republic of China, the concentration of heavy metal in 16.1% of soil samples was higher than the maximum safe concentration in China (NSPCIR, 2014). The soil heavy metal contamination degree in some areas, such as the Yangtze River Delta, the Pearl River Delta, and an old industrial base in the northeast of China, are more prominent (Hang et al., 2013). Therefore, it is significant to investigate heavy metal contamination in soil and identify the health threat it poses to citizens.

Heavy metals, especially trace metals, such as chromium (Cr), lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), copper (Cu), zinc (Zn), and nickel (Ni), are found in most soils in China. Unlike many organics, heavy metals are highly resistant to environmental degradation, and tend to bioaccumulate, sequentially posing a great threat to microbiota, flora, and fauna once they have been transformed from solid form into ionic moieties or through biomethylation to organometallic moieties (Wei and Yang, 2010;Chen et al., 2015). Furthermore, trace metals in soils can threaten human health through consumption of infected animals, and the chronic low-level intake of soil metals through ingestion or inhalation has a seriously negative effect on human health (Qu et al., 2012; Tsai and Lee, 2013). Previous studies also revealed that chronic exposure to Cd can have harmful effects, such as lung cancer, prostatic proliferative lesions, bone fractures, kidney dysfunction, and hypertension (Satarug et al., 2003), while chronic effects of As consist of bladder cancer, kidney cancer, skin cancer, lung cancer, and liver cancer (Chen et al., 1985; Smith et al., 1998). Exposure to Pb may cause plumbism, anemia, nephropathy, gastrointestinal colic, and central nervous system symptoms (Li et al., 2014). Moreover, there is no known medical treatment that is able to reverse these health effects (Huang et al., 2007), so soil contamination caused by trace metals and the health risk it causes to human beings has attracted attention worldwide (Giller and McGrath, 1988; Cheng et al., 2007; Ha et al., 2014; Hu et al., 2017). The US Environmental Protection Agency (USEPA) lists some trace metals, such as Cd, Cr, As, Hg, Pb, Cu, Zn, and Ni, as priority control pollutants, according to their toxicity, bioaccumulation, and low degradability (Giller and McGrath, 1988; Abrahams, 2002).

In recent years, health risk assessment of heavy metals in contaminated soil has been carried out, but most of it was concentrated on local urban, industrial, or mining areas and focused on statistical analysis, ignoring the spatial pattern of health risk assessment of heavy metals in contaminated soil (Cao et al., 2010; Qu et al., 2012; Lu et al., 2015). It will be of great significance to explore spatial patterns and conduct spatial analysis of health risk assessment in an administrative region and then compare the results among different land use types. In this study, a detailed investigation was conducted to assess the health risk of trace metals in surface soils to make an informed decision on approaches to reduce contamination, minimize human exposure, and protect populations from risk. This article combines spatial interpolation and spatial statistical analysis to identify the spatial features and potential health risks of selected heavy metals in different land use types in the southern Yangtze River Delta of China.

The main objectives of this study were to (1) establish a general understanding of the concentrations of eight heavy metals (Cr, Pb, Cd, Hg, As, Cu, Zn, and Ni) in surface soils and assess the potential health risk for different age groups, (2) investigate the contribution of different exposure pathways to non-carcinogenic and carcinogenic risks and characterize their spatial patterns for different age groups, and (3) identify areas of non-carcinogenic and carcinogenic health risk in the study area.

Materials and methods

Study area

The selected study area is an important typical coastal industrial city, located on a typical flat alluvial plain in the Yangtze River Delta (YRD) region of China (28°51′–30°33′ N, 120°55′–122°16′ E). The YRD is one of the most developed economic districts in China. It is located in eastern China (Fig. 1). The study area has an area of 9816 km^2 and a population of 7.81 million. It enjoys a warm and humid subtropical climate, with an annual average temperature of 16.4 °C, and the annual precipitation is 1480 mm (Bai et al., 2010; Qin et al., 2015). The selected study area is the starting port of the "Marine Silk Road" and is the fourth biggest harbor in the world. It is also a transportation hub of the YRD, with large amounts of traffic on highways G1501, G92, G15, G1512, G9211, and G15W3. Moreover, it is an important chemical industrial base in China. The chemical, textile and garment, and machinery industries are the three industrial pillars. It is one of 14 cities that implemented the reform and opening policy early in 1984 and has developed petrochemical, electronic, metallurgy, engineering, building materials and textile industries since then. However, with dramatically increased industrial operations and rapid urban expansion over the past three decades, the soil environment of the selected study area is faced with heavy metal contamination due to increasing pollutant inputs from anthropogenic sources (Song et al., 2009). To protect and improve the soil environment, it is necessary to identify the concentration level and spatial characteristics of trace metals in soils. Understanding the exposure risk of trace metals via different paths is the basic precondition for soil pollution prevention and control.

Sampling and chemical analysis

A total of 2051 topsoil samples were collected from the study area, which was first divided into strata according to land use

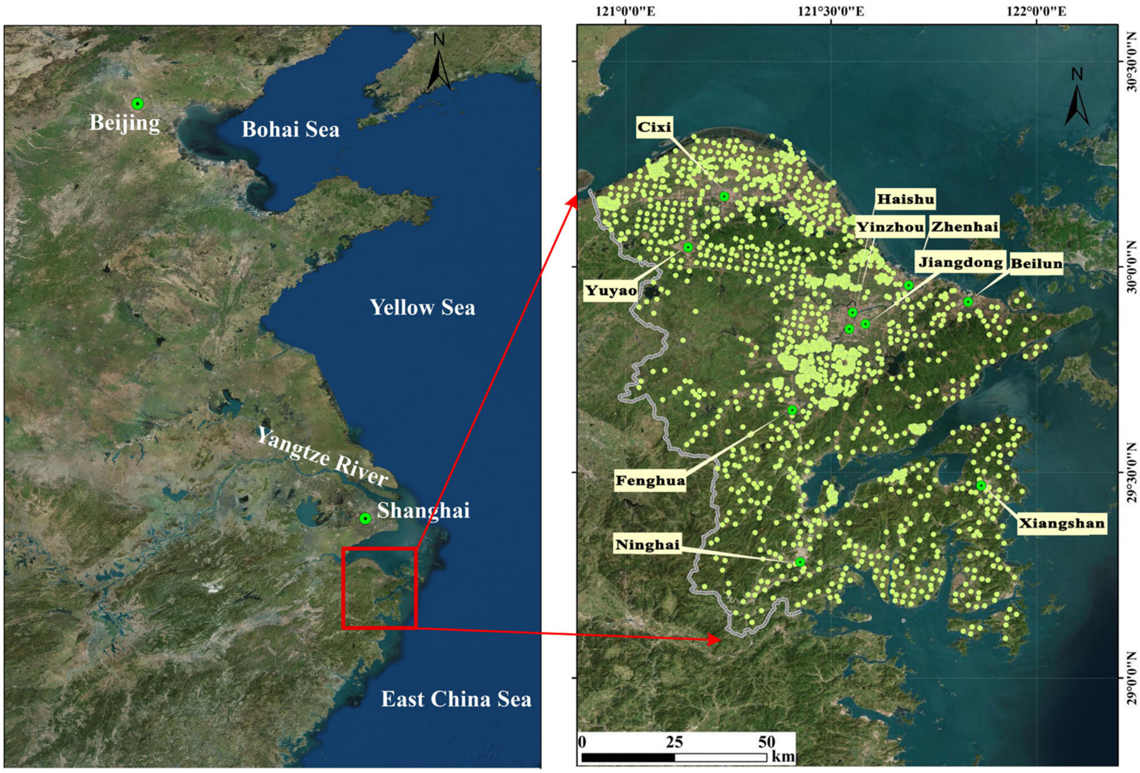


Fig. 1 Location of study area and sampling points

type, and systematic grid sampling was applied. At some of the grid nodes, grid sampling was augmented by sampling nearby areas (Fig. 1). A total of 261 topsoil samples were collected from the suburbs, 722 from mining and industrial areas, and 1068 from basic farmland. The sampling density in the suburbs and farmland was one sample per two square kilometers, while the sampling density in mining and industrial areas was two samples per square kilometer. The sample points were distributed as evenly as possible. Each sample was combined with five subsamples collected from five locations within 5 m. All soil subsamples were collected at a depth of 0–20 cm using a stainless steel shovel.

Fresh soil samples (about 1 kg) were transported to the laboratory in polyethylene zip-lock bags, lyophilized and sieved through a 2-mm mesh. All samples were stored at room temperature until analysis. A portion of the soil samples were passed through 0.149-mm sieves to completely dissolve the soil particles for heavy metal analysis (CNEMC, 1990). Soils (0.5 g) were digested with a mixture of concentrated HF–$HClO_4$–HNO_3 on a hot plate (CEPA, 1995). The digested solution was cooled, filtered, and finally diluted to 25 mL. The concentrations of Cd, Cr, Pb, Cu, Zn, and Ni were measured using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, iCAP6300DUO, Thermo Electron Corporation), while the concentrations of As and Hg were measured using atomic fluorescence spectrometry (AFS; Beijing Jitian Instruments Co., Ltd. production, AFS-820) after the soil samples were microwave digested using aqua regia (Hu et al., 2016). Reagent blanks and standard reference materials were used in the analysis for quality assurance and quality control. The recoveries of the elements ranged from 90 to 110%.

Health risk assessment of heavy metals in soils

Human health risk assessment is used to determine probabilistic non-carcinogenic and carcinogenic risks to the public after chemical exposure. Due to their behavioral and physiological differences, in this study, the population was divided into three groups—children, adults, and seniors—and the exposure paths were divided into three paths: inhalation, dermal, and ingestion.

Exposure analysis Chronic daily intake (CDI, mg/kg/day) was used to evaluate exposure to heavy metals in the soils. The direct exposure to the soil was estimated by three pathways: (1) inhalation of particulates emitted from the soil, (2) dermal contact with the soil, and (3) incidental ingestion of the soil. The CDI of the three exposure pathways was defined using USEPA methodology (SEPAC 2009; USEPA 2010). The three equations are as follows:

$$\mathrm{CDI}_{Inhalation} = \frac{PM_{10} \times M_{PM} \times ET \times IR_{air} \times EF \times ED}{BW \times AT \times PEF} \quad (1)$$

$$\mathrm{CDI}_{Dermal} = \frac{C_{soil} \times SA \times PE \times AF \times ABS \times ED}{BW \times AT \times 10^6} \quad (2)$$

$$\mathrm{CDI}_{Ingestion} = \frac{C_{soil} \times IR_{soil} \times EF \times ED}{BW \times AT \times 10^6} \quad (3)$$

where C_{soil} is the concentration of heavy metals in the soil (mg/kg); PM_{10} is ambient particulate matter in a similar area in the YRD region (0.146 mg/m^3) (Shen et al., 2014); M_{PM} is the heavy metal concentration of airborne particulate matter, assumed to be equal to C_{soil}, where dust is derived from the soils (Wang, 2010); ET is exposure time (24 h/day); IR_{air} is inhalation rate of air (m^3/day); EF is exposure frequency (days/year); ED is exposure duration (year); SA is the skin surface area for the soil contact (cm^2/day); FE is the fraction of dermal exposure ratio to the soil; AF is the soil adherence factor (mg/cm); ABS is the fraction of applied dose absorbed across skin; and 10^6 is the conversion factor from kg to mg. Body-function parameters, such as body weight (BW), came from China's Health Statistical Yearbook (CHSY, 2006). Other exposure variables are from the USEPA Integrated Risk Information System. The CDI of heavy metals for children (3–12 years old), adults (18–45 years old), and seniors (>45 years old) were calculated separately. The parameters are provided by USEPA (USEPA 2002; USEPA 2010).

Non-carcinogenic risk assessment The hazard quotient (HQ) represents potential non-carcinogenic risk for an individual heavy metal. HQ is defined as the ratio of CDI (mg/kg/day) to the reference dose (RfD, mg/kg/day), which is an estimation of daily exposure to the human population and is likely to be without an appreciable risk of deleterious effects during a lifetime (USEPA, 2010):

$$\mathrm{HQ} = \frac{CDI}{RfD} \quad (4)$$

$$\mathrm{HI} = \sum_{i=1}^{n} HQ_i = HQ_{Inhalation} + HQ_{Dermal} + HQ_{Ingestion} \quad (5)$$

The values of RfD for the selected heavy metals in different exposure pathways are provided by USEPA (USEPA 2002; USEPA 2010). With respect to the assessment of the overall potential risk posed by more than one heavy metal, HQs can be added to generate a hazard index (HI) to estimate the combination of risks (Eq. 5) (Risk Assessment Guidance for Superfund, 1989). If HI exceeds one, there is a chance that non-carcinogenic effects will occur, and the probability tends to increase with the value. Otherwise, there are likely to be no non-carcinogenic effect.

Carcinogenic risk assessment For carcinogens, risk is estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to the potential carcinogenic risk (Luo et al., 2012). Potential carcinogenic risk can be evaluated from the following equations:

$$\mathrm{CR} = \mathrm{CDI} \times \mathrm{CSF} \quad (6)$$

$$\mathrm{TCR} = \sum_{i=1}^{n} \mathrm{CDI}_i \times \mathrm{CSF}_i \quad (7)$$

where CR is the probability of carcinogenic risk (unitless), TCR is the total probability of carcinogenic risk, and CSF is the carcinogenic slope factor of each metal (1/mg/kg/day). Total carcinogenic risk is equal to the sum of the risk from all exposure pathways from all individual metals. The values of CSF for the selected heavy metals in different exposure pathways are provided by USEPA (USEPA 2010). The range of acceptable total risk for regulatory purposes is 1E−06 to 1E−04 (USEPA, 2010; Park and Choi, 2013). In regulatory terms, when TCR is less than or equal to 1E−06, it denotes virtual safety and when TCR is equal to or greater than 1E−04, it indicates a potentially great risk (USEPA, 2002).

Hot spot analysis

Getis-Ord is a spatial statistics method used for hot spot analysis. It can identify statistically significant spatial clusters of high values (hot spots) and low values (cold spots). The general G statistic of overall spatial association is given as

$$G = \frac{\sum_{i=1}^{n}\sum_{j=1}^{n} W_{i,j}X_iX_j}{\sum_{i=1}^{n}\sum_{j=1}^{n} X_iX_j}, \forall j \neq i \quad (8)$$

where X_i and X_j are attribute values for features i and j, and $W_{i,j}$ is the spatial weight between features i and j. The ZG-score for the statistic is computed as

$$ZG = \frac{G - E[G]}{\sqrt{V[G]}} \quad (9)$$

where

$$G = \frac{\sum_{i=1}^{n}\sum_{j=1}^{n} W_{i,j}}{n(\mathrm{n}-1)}, \forall j \neq i \quad (10)$$

$$V[G] = E\left[G^2\right] - E[G]^2 \quad (11)$$

Data analysis

Statistical analysis of the data was performed using Origin8 and Microsoft Excel 2010. ArcGIS10.2 software (ESRI, USA) was used to map the sampling sites and the hot spot map. Ordinary Kriging was used to construct the spatial maps of heavy metal health risk for the study area. The Getis-Ord Gi index was used to investigate the hot spots and cold spots of heavy metal health risk for the study area. The map of land use type was provided by the Data Center for Resources and Environmental Sciences, Chinese Academy of Sciences (RESDC) (http://www.resdc.cn). Due to the lack of the carcinogenic slope factor for Hg, Cu, Ni, and Zn, only the carcinogenic hazard indices for Cr, Pb, Cd, and As were estimated.

Results and discussion

Descriptive statistics of heavy metals in soils

The statistics of the total concentrations of the elements in the soils are shown in Table 1. The coefficient of variation (CV) indicates the degree of variability for the concentrations of metal in the soil. CV ≤20% is regarded as low variability, 21% < CV ≤ 50% is moderate variability, 50% < CV ≤ 100% is high variability, and CV above 100% is exceptionally intense variability (Karim Nezhad et al., 2015). The CV of metals in research area soils in decreasing order are Hg (104.55%) > Ni (56.96%) > Cd (50.68%)> Cu (47.99%) >As (45.20%) > Cr (43.41%) > Pb (37.23%) > Zn (33.00%). Hg showed exceptionally intense variability. Ni and Cd showed high variability while Cr, Pb, As, Cu, and Zn showed moderate variability. The skewness values of all metals were greater than one, and the concentration after log-transferred still deviate the Gaussian distribution evidently. This indicates that these metals positively skew towards lower concentrations compared with the mean concentration.

According to the statistical results, the concentrations of Cr, Pb, Cd, Hg, Cu, Zn, and Ni were higher than their background values in Zhejiang Province and China (CNEMS, 1990). Specifically, the mean concentrations of Cr, Pb, Cd, Hg, Cu, Zn, and Ni were 1.28, 1.81, 2.86, 3.37, 1.98, 1.57, and 1.19 times their background values in Zhejiang Province and 1.11, 1.60, 2.06, 4.46, 153, 1.49, and 1.09 times their background values in China, respectively. In contrast, the mean concentration of As was lower than its background value in Zhejiang Province and China. The concentrations of Hg and Cd for some sampling sites were higher than the second grade of the national soil quality guideline value of China (CNEPA, 1995), where 6.92% of samples exceeded the standard value of Cd concentration in soil and 31.15% samples exceeded the standard value of Hg concentration in soil. The results indicate that Cd and Hg have accumulated to a serious degree compared with the relatively low concentrations of Cr, Pb, Cu, Zn, and Ni. The concentration level of As remained at a safe level.

Human health risk assessment of heavy metals in soils

As shown in Table 2, the mean non-carcinogenic risk (HQ) of all eight heavy metals for children was the largest among the different age groups. That means that children experienced the most serious non-carcinogenic risk. Among the eight trace metals, people were most exposed to As and Pb, mainly due to relatively strong toxicity and low RfD values. Though the mean HQs of different age groups were less than 1.0, the maximum non-carcinogenic risk of As for children reached 2.03E+00. This suggests that in some places, non-carcinogenic risk has reached a dangerous level, and measures need to be taken to protect children from the non-carcinogenic risk of As. For example, parents should avoid exposing their children to contaminated soil, and schools should be built in sites that are far from mining or industrial companies.

As the Table 2 suggested, the mean hazard index (HI) for children was the largest. This indicates that children experience the greatest non-carcinogenic combination risks. Adults had the next highest mean HI, followed by seniors, but the mean HI values of children, adults, and seniors were all less than 1.0, which means that citizens in the study area are

Table 1 Descriptive statistics for heavy metal concentrations in soils (mg/kg)

Items	Cr	Pb	Cd	Hg	As	Cu	Zn	Ni
Mean	67.72	43.11	0.20	0.29	6.61	34.77	110.67	29.22
Median	69.70	42.40	0.18	0.19	6.26	33.00	106.00	29.80
Std	29.40	16.05	0.10	0.30	2.99	16.69	36.52	16.64
Skewness	1.47	2.44	7.17	2.34	5.11	4.56	5.16	5.33
Kurtosis	10.23	21.63	99.19	6.72	97.26	51.17	62.49	62.08
Min	6.04	8.13	0.03	0.02	0.87	4.28	34.30	2.89
Max	326.00	263.00	1.84	2.26	69.80	315.00	714.00	293.00
CV(%)	43.41	37.23	50.68	104.55	45.20	47.99	33.00	56.96
BV1	52.9	23.7	0.07	0.086	9.2	17.6	70.6	24.6
BV2	61	26.9	0.097	0.065	11.2	22.6	74.2	26.9

Number of samples is 2051 (CNEMC, 1990)

BV1 background value of Zhejiang Province, *BV2* background value of China

Table 2 Descriptive statistics for non-carcinogenic risk in soils

Item	Ages	HQ (non-carcinogenic risk)								
		Cr	Pb	Cd	Hg	As	Cu	Zn	Ni	HI
Mean	Child	*3.91E−03*	*9.36E−02*	*8.34E−03*	*1.69E−02*	*1.92E−01*	*7.55E−03*	*3.20E−03*	*4.22E−03*	3.30E−01
	Adults	3.82E−03	2.76E−02	7.98E−03	1.44E−02	5.67E−02	2.23E−03	9.45E−04	2.06E−03	1.16E−01
	Senior	1.65E−03	2.11E−02	3.05E−03	5.79E−03	4.34E−02	1.70E−03	7.23E−04	1.15E−03	7.86E−02
Min	Child	3.49E−04	1.77E−02	1.27E−03	2.46E−03	2.52E−02	9.30E−04	9.93E−04	1.36E−03	1.18E−01
	Adults	3.40E−04	5.20E−03	1.21E−03	1.37E−03	7.44E−03	2.74E−04	2.93E−04	5.34E−04	4.06E−02
	Senior	1.47E−04	3.98E−03	4.64E−04	7.06E−04	5.70E−03	2.10E−04	2.24E−04	3.77E−04	2.80E−02
Max	Child	1.88E−02	5.71E−01	7.78E−02	9.82E−02	2.03E + 00	6.84E−02	2.07E−02	2.06E−02	2.16E + 00
	Adults	1.84E−02	1.68E−01	7.44E−02	1.06E−01	5.98E−01	2.02E−02	6.09E−03	1.53E−02	6.60E−01
	Senior	7.93E−03	1.29E−01	2.84E−02	3.83E−02	4.58E−01	1.54E−02	4.66E−03	6.13E−03	4.94E−01

unlikely to experience obvious adverse health effects. However, we still need to note that the mean HI for children was 0.33 and the HI of all sample points was bigger than 0.1. The total exposure hazard index of 4.6% of sample points was between 0.5 and 1.0.

It was found that the HQ of all age groups due to different exposure routes occurred in the following decreasing order: ingestion > dermal > inhalation (Fig. 2). This is in accordance with previous studies (Wang, 2010; Hu et al. 2016). The risk of soil ingestion was more than 10 times higher than that of inhalation and dermal exposure, which must receive more attention during health risk assessment. This suggests that ingestion poses the highest risk to citizens in the study area, and more attention should be paid to the food chain.

The mean carcinogenic risks due to Cd and As among children, adults, and seniors exceeded 1.0E−06 but were less than 1.0E−04 (Table 3), which means that concentrations of Cd and As have posed carcinogenic hazard risks to all people; fortunately, it is not a great risk (USEPA 2010). The mean carcinogenic risks due to Cr and Pb among children, adults, and seniors were less than 1.0E−06. This indicates that concentrations of Cr and Pb are at a safe level.

The TCR for children, adults, and seniors were 1.18E−05, 2.77E−05, and 1.63E−05, respectively, which are all within the acceptable limit. However, both the maximum carcinogenic risk due to Cd and the maximum carcinogenic risk for adults exceeded the safe threshold of 1.0E−04 and were up to 2.0E−04. This indicates that though the mean value of carcinogenic risk due to each kind of heavy metal and TCR are at a relatively low risk level, some areas are still confronted with serious carcinogenic risk caused by heavy metals in soil, especially that caused by Cd pollution. Cd accumulation had been shown to be related to anthropogenic activities (e.g., industrial activities) (Hu and Cheng, 2013; Sun et al., 2013). In this study, we only considered the total concentration of heavy metals, but the bioaccessibility values of these heavy metals are lower than their total concentration, so the health risk we calculated may be larger than its actual value. Bioaccessibility concentration should be taken into consideration in future work (Luo et al., 2012; Niu et al., 2013).

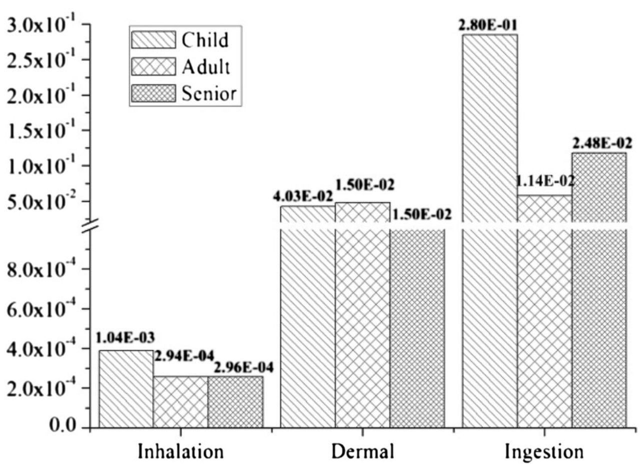


Fig. 2 Mean HQ of different exposure paths of different ages

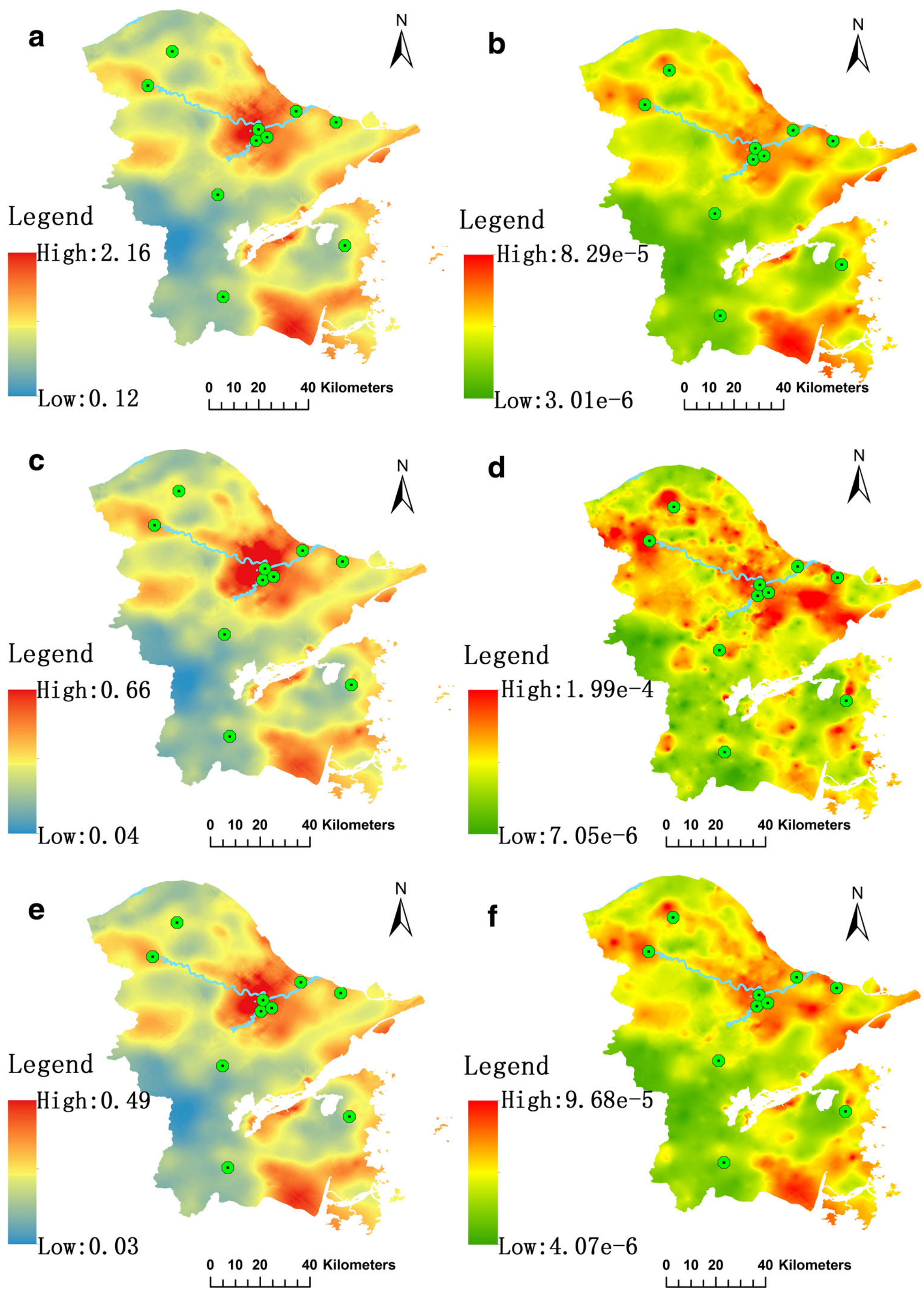
Table 3 Descriptive statistics for carcinogenic risk (CR) and HI in soils

		CR				
		Cr	Pb	Cd	As	TCR
Mean	Child	5.89E−08	2.77E−09	4.36E−06	7.40E−06	1.18E−05
	Adults	1.94E−07	2.81E−09	2.04E−05	7.28E−06	2.77E−05
	Senior	1.95E−07	3.21E−09	7.96E−06	8.35E−06	1.63E−05
Min	Child	5.25E−09	5.23E−10	6.63E−07	9.72E−07	3.28E−06
	Adults	1.73E−08	5.30E−10	3.10E−06	9.56E−07	7.07E−06
	Senior	1.74E−08	6.05E−10	1.21E−06	1.10E−06	4.48E−06
Max	Child	2.84E−07	1.69E−08	4.07E−05	7.81E−05	8.28E−05
	Adults	9.33E−07	1.72E−08	1.90E−04	7.69E−05	2.00E−04
	Senior	9.39E−07	1.96E−08	7.42E−05	8.81E−05	9.66E−05

Spatial distribution and hot spot of human health risk

According to the spatial distribution pattern of HI and total TCR for children, adults, and seniors (Fig. 3), children had the greatest non-carcinogenic risk, followed by adults and seniors. The maximum HI for adults and seniors was less than 1, which indicates that adults and seniors were confronted with low potential non-carcinogenic risk caused by heavy metals in soil. The maximum HI for children was larger than 1.0, indicating a potential human health risk in the corresponding areas. High values of HI for children, adults, and seniors were found in the central and southern parts of the study area, such as Yinzhou, Haishu, Jiangdong, Jiangbei, and Zhenhai and the urban area of Ninghai. These are the core urban areas in the study and witness much industrial, commercial, and transportation activities. Most industrial and mining factories in the study area are located in these sites. The TCRs for children, adults, and seniors presented a similar spatial pattern. The TCR values were relatively high in Yinzhou, Haishu, Jiangdong, Jiangbei, and Zhenhai and the urban areas of

Fig. 3 Spatial distribution patterns of HI for **a** children, **c** adults, and **e** seniors and TCR for **b** children, **d** adults, and **f** seniors



Ninghai, Xiangshan, and Yuyao. The TCRs for children and seniors in the study area were less than 1E−04, indicating that the carcinogenic risks for children and seniors remain at a safe level throughout the study area. However, in some places, such as Beilun, TCR for the adults was higher than 1E−04, which suggests that the adults in this area are potentially exposed to great carcinogenic risk. Beilun is famous for its foreign trade industry, construction industry, small- and medium-sized enterprises, and the first giant coal-fired power plant, which has an installed capacity of five million kilowatts, all of which may lead to the accumulation of heavy metals in soil.

The hot spots of HI for children, adults, and seniors had similar spatial distributions (Fig. 4). The hotspots were mainly distributed in core urban areas, such as Jiangbei, Haishu, Yinzhou, and Ninghai, which means people there are faced with a significantly high non-carcinogenic risk compared with other places. Cold spots of HI for children, adults, and seniors were mainly distributed in the north and west, such as Cixi,

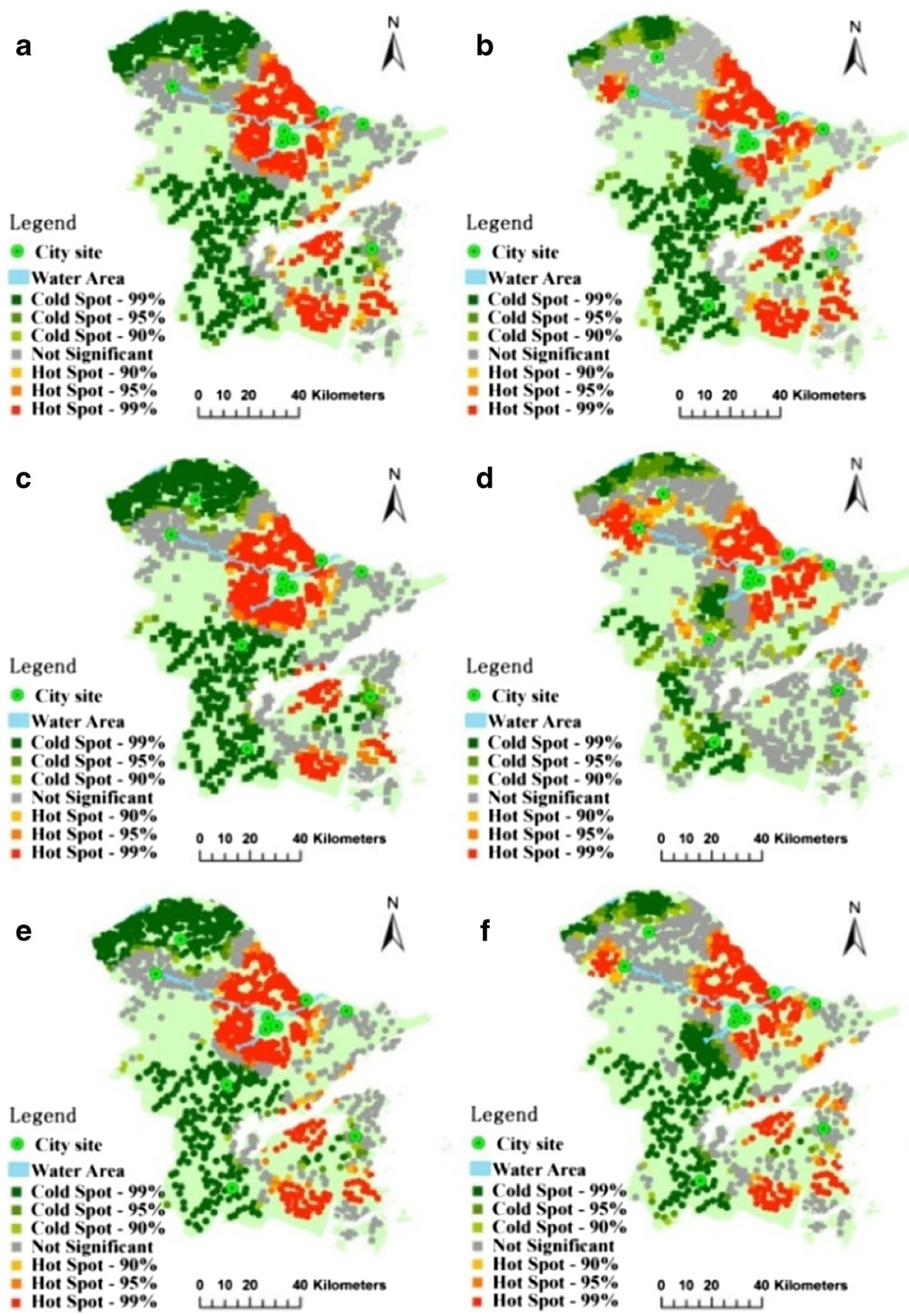


Fig. 4 Hot spots of HI for **a** children, **c** adults, and **e** seniors and TCR for **b** child, **d** adults, and **f** seniors

Yuyao, Fenghua, and Ninghai. Compared with Fig. 3, the spatial pattern of hot spots of HI and TCR among different age groups was similar to that of non-carcinogenic and carcinogenic risk among different age groups (Fig. 4).

The spatial pattern of TCR had similar hot spots for children and seniors (Fig. 4b, d, f), and the hot spots mainly located in the northeast part of the study area, like Jiangbei, Jiangdong, Haishu, Yinzhou, Ninghai, and Beilun, which indicates that the citizens in these places are confronted with a serious carcinogenic risk, although the TCR was still below the threshold of 1.0E−4. The hot spots of TCR for adults located in the northwest and northeast parts of the study area, e.g., Jiangbei, Jiangdong, and Yinzhou, also the urban areas in Yuyao.

Land use and heavy metal pollution

Land use cover change (LUCC) is one of the most important human activities that drives the evolution of the environment. It has great effect on the accumulation, distribution, and migration of heavy metals in the environment (Imperato et al., 2003; De Vries et al., 2007). Many studies have found that land use and land use cover change control soil heavy metal accumulation and spatial distribution. Vegetation can absorb heavy metals directly, and it can also change the physical, chemical, and biological properties of soil and then control the mobility and activity of heavy metals in soil, which will eventually cause pollution of heavy metals in soil (Satsananan, 2012).

Land used for industry and transportation usually is at high risk for heavy metal pollution because industry and transportation are important sources of heavy metals and therefore have great influence on the spatial distribution and accumulation characteristics of heavy metals in soil (Hoehun H et al., 2014; Mohammed AH et al., 2015).

Land use mode determines the type and intensity of industrial activities as well as fertilization, pesticide application, and the cultivation management system used in agricultural land. These factors then lead to spatial variation of heavy metals in soil for a certain land use type (Zhao and Chen, 2011).

The core urban area of the study area includes Haishu, Yinzhou, Haishu, Jiangbei, and Jiangdong. Most electronics factories, battery factories, plastics factories, metallurgy factories, and textile factories in the study area are distributed in these areas and discharge waste water and waste residue that contain heavy metals. Therefore, the topsoil in these places may be significantly affected by heavy metals due to the emissions from industry, transport, commercial, and life activities. Zhenhai is famous for its petrochemical industry, and it has a petrochemical economic and technological development zone at the national level. Beilun district is an important chemical industry base and has two economic and technological development zones at the provincial level, and many chemical factories are located there. In contrast, the cold spots are mainly distributed outside the cities, where the main land use types are forest and arable land. These areas are the main agricultural production base of the study area and have less industrial activities. The spatial patterns of the hot and cold spots implies that anthropogenic activities, especially industrial activities, have caused significant accumulation of heavy metals in the soil, which has threatened the health of local citizens.

HI and TCR hot spots are mainly observed in urban areas, along Yuyao River and Fenghua River, including Haishu, Yinzhou, Jiangbei, Zhenhai, and Jiangdong. These areas are the core urban industrial and commercial regions in the study area. They also have many factories and undertake business activities. There are more than 21,000 enterprises related to mining, metallurgy, electronics, construction, plastics, etc. Among them, 89 enterprises are severe pollution enterprises monitored by the Ministry of Environmental Protection of the People's Republic of China.

Therefore, we can take some corresponding measures to prevent and control soil heavy metal pollution and health risk caused by it: (1) establishing a spatial buffer for industrial land—improper utilization of industrial land can lead to serious negative influence on the ecological environment in the surrounding areas. This is also a main source of spatial pollution of soil heavy metals. Therefore, it is necessary to set up a buffer zone between industrial areas and residential areas to keep a safe distance between polluted land and residents. (2) Beginning special rectification work in polluted land area—soil heavy metals caused by industrial production can reside in the soil for a long time (Kasassi et al., 2008). This poses great health risk to citizens living in and attending schools in these areas. The government should pay more attention to industrial discarded land and take measures to govern it. (3) Regulating the usage of farmland polluted by heavy metals—we should establish a reasonable monitoring network for soil pollution and assess the pollution condition of farmland. If the soil in farmland is compromised, the farmland should be converted to another use type.

Conclusion

This article assessed the potential health risk of heavy metals in soils, taking an important coastal industrial region in the YRD as an example. The concentrations of eight heavy metals were first investigated; non-carcinogenic and carcinogenic risks were then assessed for different age groups, and their spatial distribution pattern was characterized. Finally, the hot and cold spots of non-carcinogenic and carcinogenic health risks were identified.

The mean concentrations of the eight heavy metals were all higher than the corresponding background values in Zhejiang Province and China. The mean HIs for children, adults, and seniors were less than 1; among these, the HI for children was the largest, which means children are experiencing the greatest non-carcinogenic combination risks. HQs for different exposure pathways witnessed the following decreasing order: ingestion > dermal > inhalation. The mean carcinogenic risks of Cd and As for children, adults, and seniors all exceeded 1.0E−06 but were less than 1.0E−04. The mean carcinogenic risk of Cr and Pb for children, adults, and seniors were all less than 1.0E−06. The total carcinogenic risks for children, adults, and seniors were 1.18E−05, 2.77E−05, and 1.63E−05, all lower than the corresponding threshold values. The hot spots of HI and TCR for children, adults, and seniors were mainly distributed in core urban areas, such as Jiangbei, Haishu, Jiangdong, and Yinzhou, while the cold spots were distributed in the north and west parts of the study area, such as Cixi, Yuyao, Fenghua, and Ninghai.

The results suggest that trace heavy metals in the study area represent a certain degree of enrichment caused by anthropogenic activities. In general, the potential health risk from heavy metals in soils for children, adults, and seniors are still at a safe level, but some of the samples exceeded the threshold of safe concentrations, so effective measures should be taken to protect the citizens, especially children, from exposure to heavy metals. The study results provide a basis for policy makers and regulators.

Some issues still need to be considered, however. In this study, we only considered the impact of total concentrations of heavy metals on human health risk. Future studies should involve a calculation of the available heavy metal content and combine the bioavailability and bio-accessibility of heavy metals, as well as toxicity, into the health risk assessment to acquire more rigorous results. Furthermore, the processes by which heavy metals are transported from food to human beings are not clearly understood. Additionally, the lack of the slope factor of some heavy metals made it impossible to calculate the carcinogenic risk, which negatively affected the final result. Finally, in this study, we used some parameters like SA, AF, ABS, and EF provided by USEPA because there is still no specified value of these parameters for Chinese people. In the future, we should replace these parameters for Chinese population, which can help us get more reasonable results.

Acknowledgements This work was supported by the National Key Research and Development Program of China (2016YFD0201200) and the Key Research and Development Project of Zhejiang Province (2015C02G1320007; 2015C02G4010045).

References

Abrahams PW (2002) Soils: their implications to human health. Sci Total Environ 291:1–32

Bai X, Wang WJ, Wang W, Wu H (2010) Spatio-temporal variability characteristics of soil organic matter in Ningbo City, Zhejiang Province. Res Environ Sci 23(2):191–197

Cai LM, Xu ZC, Bao P, He M, Dou L, Chen LG, Zhou YZ, Zhu YG (2015) Multivariate and geostatistical analyses of the spatial distribution and source of arsenic and heavy metals in the agricultural soils in Shunde, Southeast China. J Geochem Explor 148:189–195

Cao HB, Chen JJ, Zhang J, Zhang H, Qiao L, Men Y (2010) Heavy metals in rice and garden vegetables and their potential health risks to inhabitants in the vicinity of an industrial zone in Jiangsu, China. J Environ Sci 22(11):1792–1799

Chen CJ, Chuang YC, Lin TM, Wu HY (1985) Malignant neoplasms among residents of a Blackfoot disease endemic area in Taiwan: high-arsenic artesian well water and cancers. Cancer Res 45:5895–5899

Cheng J, Zhou S, Zhu Y (2007) Assessment and mapping of environmental quality in agricultural soils of Zhejiang Province, China. J Environ Sci 19(1):50–54

China National Environmental Protection Agency. 1995. Environmental quality standard for soils. Report No. GB15618–1995 (in Chinese)

CNEMC (China National Environmental Monitoring Center) (1990) The background concentrations of soil elements of China. China Environmental Science Press, Beijing **(In Chinese)**

De Vries W, Lofts S, Tipping E, Meili M, Groenenberg JE, Schütze G (2007) Impact of soil properties on critical concentrations of cadmium, lead, copper, zinc, and mercury in soil and soil solution in view of ecotoxicological effects. Rev Environ Contam Toxicol 191:47–89

Giller KE, McGrath SP (1988) Pollution by toxic metals on agricultural soils. Nature 335(6192):676

Ha H, Olson JR, Bian L, Rogerson PA (2014) Analysis of heavy metal sources in soil using Kriging interpolation on principal components. Environ Sci Technol 48:4999–5007

Hang XS, Wang HY, Zhou JM (2013) Prevention and regulation countermeasures of soil heavy metal contamination in Yangtze River Delta. Chin J Soil Sci 44(1):245–251 **(In Chinese)**

Hoehun H, James RO, Ling B, Peter AR (2014) Analysis of heavy metal sources in soil using Kriging interpolation on principal components. Environ Sci Technol 48:4999–5007

Hu YN, Cheng HF (2013) Application of stochastic models in identification and apportionment of heavy metal pollution sources in the surface soils of a large-scale region. Environ Sci Technol 47:3752–3760

Hu WY, Huang B, He Y, Yusef KK (2016) Assessment of potential health risk of heavy metals in soils from a rapidly developing region of China. Hum Ecol Risk Assess: Int J 22(1):211–225

Hu BF, Chen SC, Hu J, Xia F, Xu JF, Li Y, Shi Z (2017) Application of portable XRF and VNIR sensors for rapid assessment of soil heavy metal pollution. PLoS One 12(2):e0172438

Huang SS, Liao QL, Hua M, Wu XM, Bi KS, Yan CY, Chen B, Zhang XY (2007) Survey of heavy metal pollution and assessment of agricultural soil in Yangzhong district, Jiangsu Province, China. Chemosphere 67:2148–2155

Imperato M, Adamo P, Naimo D, Arienzo M, Stanzione D, Violante P (2003) Spatial distribution of heavy metals in urban soils of Naples city(Italy). Environ Pollut 124(2):247–256

Karim Nezhad MT, Tabatabaii SM, Gholami A (2015) Geochemical assessment of steel smelter-impacted urban soils, Ahvaz, Iran. J Geochem Explor 152:91–109

Kasassi A, Rakimbei P, Karagiannidis A, Zabaniotou A, Tsiouvaras K, Nastis A, Tzfeiropoulou K (2008) Soil contamination by heavy metals: measurements from a closed unlined landfill. Bioresour Technol 99(18):8578–8584. doi:10.1016/j.biortech.2008.04.010

Li ZY, Ma ZW, Kuijp TJ, Yuan ZW, Huang L (2014) A review of soil heavy metal pollution from mines in China: pollution and health risk assessment. Sci Total Environ 468–469:843–853

Liu J, Diamond J (2005) China's environment in a globalizing world. Nature 435:1179–1186

Lu SJ, Wang YY, Teng YG, Yu X (2015) Heavy metal pollution and ecological risk assessment of the paddy soils near a zinc-lead mining area in Hunan. Environ Monit Assess 187:627–638

Luo XS, Ding J, Xu B, Wang YJ, Li HB, Yu S (2012) Incorporating bioaccessibility into human health risk assessments of heavy metals in urban park soils. Sci Total Environ 424:88–96

Mohammed AH, Nasly MA, Mir SI, Zakir Hossain HM (2015) Spatial distribution and source apportionment of heavy metals in soils of Gebeng industrial city, Malaysia. Environ Earth Sci 73:115–126

Niu LL, Yang FX, Xu C, Yang HY, Liu WP (2013) Status of metal accumulation in farmland soils across China: from distribution to risk assessment. Environ Pollut 176:55–62

Nriagu JO (1990) A history of global metal pollution. Science 272:223–224

NSPCIR, 2014. Ministry of Environmental Protection, Ministry of Land and Resources. 2014, The National Soil Pollution Condition Investigation Report[EB/OL], http://www.zhb.gov.cn/gk ml/hbb/qt/201404/t20140417_270670.htm. 17th April 2014

Park JH, Choi KK (2013) Risk assessment of the abandoned Jukjeon metal mine in South Korea following the Korean guidelines. Hum Ecol Risk Assess 19:754–766

Qin FJ, Wang F, Lu HB, Zhuang YQ, Wang B, Cen TX, Han HX, Zhang H (2015) Temporal-spatial variation of organic matter in cultivated soils in Ningbo City over 50 years. Acta Agriculturae Zhejiangensis 27(1):92–96 **(in Chinese)**

Qu CS, Ma ZW, Yang J, Liu Y, Bi J, Huang L (2012) Human exposure pathways of heavy metals in a lead-zinc mining area, Jiangsu Province, China. PLoS One 7(11):1–11

Risk Assessment Guidance for Superfund. 1989 Human health evaluation manual, (Part A) [R]. Once of Emergency and Remedial Response [EPA/540/1–89/002], Washington, DC vol. 1

Satarug S, Baker JR, Urbenjapol S, Haswell-Elkins M, Reilly PE, Williams DJ, Moore MR (2003) A global perspective on cadmium pollution and toxicity in non- occupationally exposed population. Toxicol Lett 137(1–2):65–83

Satsananan C (2012) The determination of heavy metals in homegrown vegetable [dissertation]. Suan Sunandha Rajabhat University, Thailand

SEPAC (State Environment Protection Administration of China) (2009) Technical guidelines for risk assessment of contaminated sites. Beijing, China. Available at www.mep.gov.cn/gkml/hbb/bgth/200910/W020091009550671751947 .pdf

Shen GF, Yuan SY, Xie YN, Xia SJ, Li L, Yao YY, Qiao YZ, Zhang J, Zhao QY, Ding AJ, Li B, Wu HS (2014) Ambient levels and temporal variations of PM2.5 and PM10 at a residential site in the mega-city, Nanjing, in the western Yangtze River Delta, China. J Environ Sci Heal Part A 49:171–178

Smith AH, Goycolea M, Haque R, Biggs ML (1998) Marked increase in bladder and lung cancer mortality in a region of northern Chile due to arsenic in water. Am Jour Epidemiol 147:660–669

Song MY, Liu JB, Zhou TF, Zhou ZY (2009) Chemical speciation of some heavy metals in Ningbo urban soil and ecological effects. Chin J Soil Sci 40(6):1426–1143

Sun CY, Liu JS, Wang Y, Sun LQ, Yu HQ (2013) Multivariate and geostatistical analyses of the spatial distribution and sources of heavy metals in agricultural soil in Dehui, Northeast China. Chemosphere 92:517–523

Tsai CP, Lee CTC (2013) Multiple sclerosis incidence associated with the soil lead and arsenic concentrations in Taiwan. PLoS One 8(6): e65911. doi:10.1371/journal.pone.0065911

USEPA. 2010. Integrated Risk Information System (IRIS). United States Environmental Protection Agency, Washington, DC, USA. Available at www.epa.gov/ncea/iris/index.html (accessed July 15, 2010)

USEPA (United States Environmental Protection Agency) (2002) Supplemental guidance for developing soil screening levels for superfund sites OSWER 9355.4–24. United States Environmental Protection Agency, Washington, DC

Wang Z (2010) Identifying sources and assessing potential risk of heavy metals in soils from direct exposure to children in a mine-impacted city, Changsha, China. Jour Environ Qual 39:1616–1623

Wei BG, Yang LS (2010) A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. Microchem J 94:99–107

Wu JS, Song J, Li WF, Zhang MK (2016) The accumulation of heavy metals in agricultural land and the associated potential ecological risks in Shenzhen, China. Environ Sci Pollut Res 23:1428–1440

Zhao SP, Chen LX (2011) Soil heavy content analysis and ecological risk assessment of different landuse types in Daqing region. J Soil Water Conserv 25(5):195–199