



Spatial distribution, sources, and risks of heavy metals in soil from industrial areas of Hangzhou, eastern China

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Abstract

Heavy metal (HM) pollution in soil is an inevitable outcome of industrialization. Quantitating the distribution of this pollution—on, e.g., local and regional scales—is an important step in remediation and prevention. The present study investigated HM pollution in the soil of the industrial zone of Hangzhou, Zhejiang Province; specifically, analyzed the HM concentrations, spatial distribution, sources, and potential ecological and health risks. A total of 2651 soil samples were collected; and the levels of As, Cr, Cu, Pb, Hg, Ni, Cd, and Sb were determined. The average concentrations of these HMs were all lower than the national construction land soil pollution risk screening values; but the average levels of As, Cu, Pb, Ni, and Cd exceeded the background values of soil HMs in Zhejiang Province. By analyses of the spatial distribution in combination with a positive matrix factorization model, 84.6% of soil HM pollution in the study area was related to human activities, and 15.6% was from natural sources. Affected by human activities, there were large differences in the spatial distribution characteristics of various HMs. The potential ecological hazard index method and a health risk model were adopted to assess the ecological and human health hazards in Hangzhou. The mean value of the potential ecological risk index (PERI) of HMs was 407.54, indicating a high ecological risk; Cd (PERI: 323.4) might be the main pollution risk element of soil in this area. The carcinogenic and noncarcinogenic risk indices were typically within an acceptable range.

Keywords Heavy metal pollution · Health risk assessment · Positive matrix factorization · Spatial distribution · Urban soil

Introduction

As a key part of the earth's terrestrial ecosystem, soil acts as an extremely important mediator in various life activities. Heavy metals (HMs) in soil have the characteristics of biotoxicity, accumulation and non-degradability, which make it easy to accumulate in soil (Li et al. 2019; Zwolak et al. 2019). Although the soil has a certain ability to absorb and accommodate HMs, due to the unreasonable production activities of human beings, a large amount of HMs are continuously released into the surface soil of the surrounding

environment through wastewater and atmospheric deposition (Sorme and Lagerkvist 2002; Zhao et al. 2015). Numerous studies have confirmed that the accumulation of HMs reduces soil quality, and threatens the environment and human health (Yang et al. 2008; Bo et al. 2009; Sun et al. 2019); the problem of HM pollution in soil is an active area of global research (Zhong et al. 2014). In recent decades, as China undergoes rapid urbanization and industrialization, discharge of HMs into soil ecosystems continues to increase (Chen 2007; Li et al. 2020; Wu et al. 2021). The China soil pollution survey bulletin (2005–2013) shows that soil pollution is substantial, and HMs are the main pollutants (MEP 2014). Therefore, the situation of soil HM pollution in China is still very serious.

In general, HMs are naturally present in soil, so the natural concentration of HMs in soil is determined by weathering and pedogenesis processes (Osman 2014). Nevertheless, with the development of human society and economy, more and

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more regional HMs are released into the environment mainly through industrial processes, waste treatment, application of agrochemicals, and wastewater irrigation (Sun et al. 2019). The above-mentioned human activities and natural inputs both affect the distribution of HMs in topsoil (Alloway 2013; Liu et al. 2015; Lu et al. 2012), and thus identifying the specific sources of HMs is critical to pollution prevention and control (Jie et al. 2017; Hu et al. 2013). Many previous studies used multivariate statistics (e.g., principal component analysis, cluster analysis) in combination with geostatistical methods to identify the sources of HMs in soil (Liang et al. 2017; Maas et al. 2010). In recent years, positive matrix factorization (PMF) model has also been successfully applied to quantify the sources of soil HMs (Hu et al. 2018; Paatero and Tapper 1994). Due to the advantages and disadvantages of each method, combining multiple methods to analyze the source of HMs in soil is the current trend.

The ecological and health risk assessment of HMs in soil can provide important scientific references for regional determination of pollution levels and formulation of environmental protection policies (Jiang et al. 2017; Liu et al. 2020). Evaluation indicators such as enrichment factor (EF), potential ecological risk index (RI), and geoaccumulation index (Igeo) have been widely used in many studies in the ecological risk assessment of soil HMs. In addition, the human health risk assessment, including non-cancer risk and cancer risk, developed by the US Environmental Protection Agency can provide information on the potential harm of HMs to the human body and now is one of the most widely used methods in this field. These indices can be used to compare the HM pollution and environmental risks caused by various human activities (Long et al. 2021).

Hangzhou is the provincial capital of Zhejiang Province. In the process of promoting Hangzhou's urbanization development strategy and pattern, the layout of land use and coverage is also undergoing unprecedented rapid changes. Many industrial enterprises, especially those with substantial pollution, have left behind major soil environmental pollution problems after their relocation (Yu and Qiang 2011). The problem of HMs in soil is particularly prominent (Fei et al. 2018). Therefore, this paper reports research on soil HMs in the regions of fractional major industrial enterprises (e.g., the chemical, pharmaceutical, and equipment manufacturing industries) in Hangzhou. Three primary objectives of this research were as follows: (1) analyze the concentrations and spatial distribution of HMs in soil, (2) quantitatively identify possible sources of HMs in soil by PMF, and (3) estimate ecological and human health risks by probabilistic statistical methodology.

Materials and methods

Study area description and sampling

The study areas are located in Hangzhou city, eastern China (118°21' to 120°30'E, 29°11' to 30°33'N; Fig. 1). Hangzhou has a subtropical monsoon climate, and the mean annual temperature, average relative humidity, and precipitation are 17.8 °C, 70.3%, and 1454 mm, respectively. The annual acid rain rate of Hangzhou is 54.7%; and the annual mean pH of precipitation is 5.19, ranging from 3.43 to 8.82. Thus, acid rain is at a moderate level. Hangzhou has relatively large topographic changes. It is in the plain of northern Zhejiang; and the geomorphologic features consist of mountains, hills, and plains. The southeast of the soil-forming parent material is mainly shallow marine sediment, and the northwest is fluvio-lacustrine sediment. The soil formation time is relatively short, ranging from thousands of years to > 10 y; and the main natural soil type is moisture soil. Although tertiary industry with low pollution risk dominates the industrial structure of Hangzhou, there are many industrial enterprises that emit substantial pollution. Electronics, the chemical industry, energy, and metal manufacturing constitute a large proportion of emission sources; yet their contributions to soil HM pollution remain insufficiently quantitated. The production activities of these industries will accumulate HMs in the soil through sewage and fumes. Therefore, the focus of this study was key industrial enterprises, including the original areas of relocated enterprises.

A total of 2658 soil surface samples were collected in Hangzhou from October–November 2018. These soil samples were collected from 180 enterprises in different industries; including chemical engineering, pharmacy, printing and dyeing, electroplating, and papermaking. As shown in Fig. 1, these samples were mainly concentrated in the east of Hangzhou, and spread all over the main urban area. The soil in the areas where these key enterprises and industries are located is an ideal place to monitor whether the regional HMs exceed the standard, and thus it has important indicative significance for regional environmental control. Moreover, the areas where these key enterprises are located often gather a large number of people, and it is also of good reference significance to evaluate the ecological and health risks by exploring the concentration of HMs in the soil of these areas. When collecting samples, the longitude and latitude were recorded in accordance with the Global Positioning System. A 2-mm sieve was used to remove plant debris and other impurities from air-dried soil samples, and the treated samples were stored at room temperature.

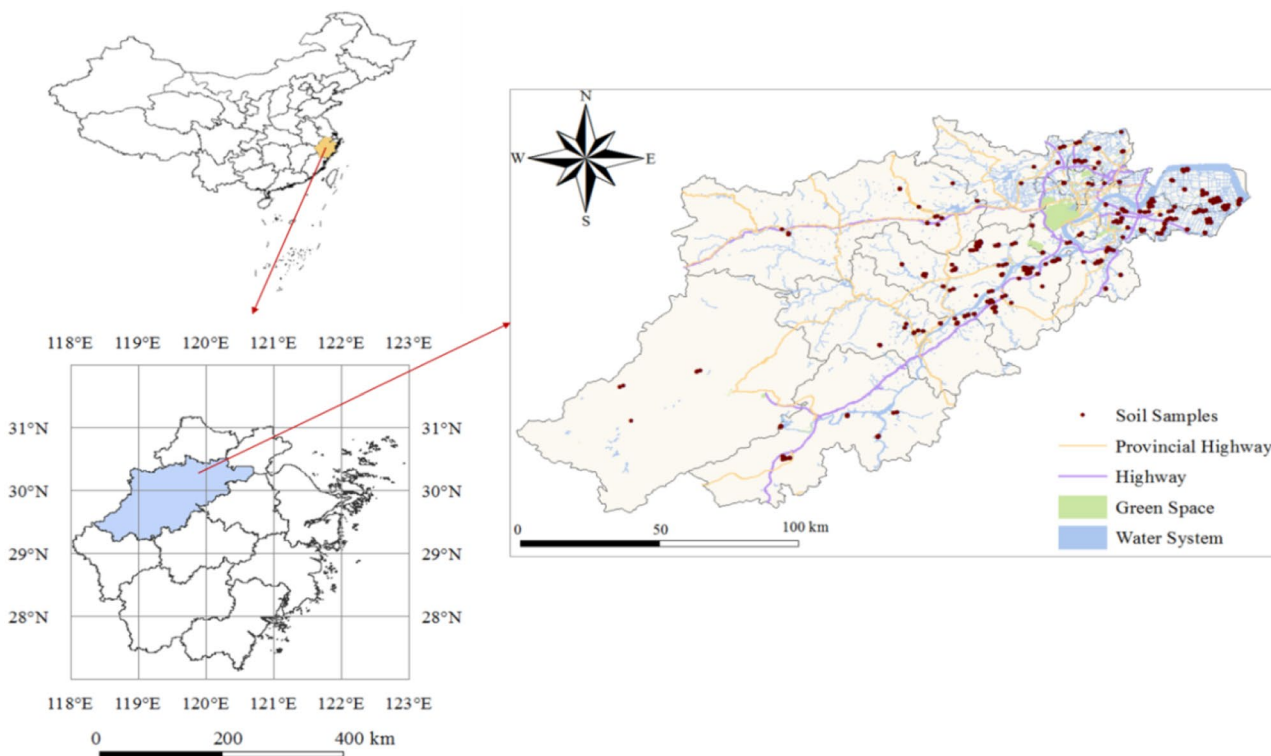


Fig. 1 Distribution of sampling sites in the study area

Heavy metal analysis

The HNO₃–HClO₄–HF method was used to digest samples (Fei et al. 2018, Li et al. 2016). The levels of Cr, Cu, Pb, Cd, and Ni were determined by inductively coupled plasma mass spectrometry (Agilent 7850, Palo Alto, CA, USA). Portions of the soil samples were digested with HNO₃/HCl (1:3 by volume); and then the levels of As, Sb, and Hg in the digested samples were analyzed by atomic fluorescence spectrometry (Lin et al. 2010). GSS-1 and GSS-4 were used as standard reference materials for verifying the accuracy of the elemental analyses. The recoveries of these elements ranged from 85 to 110%.

Data analysis and PMF model

Statistical analysis of the data was conducted with SPSS 22.0. ArcGIS 10.2 was used to display the spatial distribution of soil HM. A PMF model was adopted to determine the sources of HMs in soil (Paatero and Tapper 1994. This model utilizes nonnegative constraints to obtain physically realistic meanings (Wang et al. 2015), and the equation is as follows:

$$x_{ij} = \sum_{k=1}^p g_{ik}f_{kj} + e_{ij} \tag{1}$$

where x_{ij} is the content of the metals in the soil sample, g_{ik} is the contribution rate, f_{kj} is the content of the metals in source, and e_{ij} is the residual.

The PMF model is limited and iteratively calculated based on the weighted least-squares method. The concentration and uncertainty data of the sample are used to weight each sampling point, and minimize the objective function Q , and the equation is as follows:

$$Q = \sum_{i=1}^m \sum_{j=1}^n \left(\frac{e_{ij}}{u_{ij}} \right)^2 \tag{2}$$

where e_{ij} represents each residual item, and u_{ij} is the uncertainty of the data x_{ij} . Here, if HM level < method detection limit (MDL), the uncertainty u was calculated as:

$$u = \frac{5}{6} \times \text{MDL} \tag{3}$$

and if HM level > MDL, u was calculated as:

$$U_{nc} = \sqrt{(\sigma \times c)^2 + (\text{MDL})^2} \quad (4)$$

where c is the measured value, and σ is the standard deviation (SD). Data analysis was conducted in PMF 5.0 model (USEPA 2014).

Risk analysis

Potential ecological risk analysis of heavy metals

One can use the potential ecological hazard index (PEHI) method, developed by Håkanson (1980), to evaluate the potential impact of HM on ecosystems. The potential ecological risk index involves four parameters, including pollutant type, pollutant concentration, toxicity level, and sensitivity of media to pollutant pollution. The equations are as follows:

$$f_i = \frac{C_i}{B_i} \quad (5)$$

$$E_r^i = T_r^i \times f_i \quad (6)$$

$$RI = \sum_{i=1}^n E_r^i \quad (7)$$

where f_i is the pollution index of soil HM i , C_i is the measured level of soil HM i , B_i is the background value of soil HM i , E_r^i is the potential ecological risk index (PERI) of a single HM i , T_r^i is the toxic response factor of HM i (the toxicity response factors were normalized; Cd=30, As=10, Cu=Pb=5, Ni=Cr=2, Hg=40, and Sb=7), RI is the PERI of multiple HMs, and n is the number of the HM. Table S1 shows the classification of ecological risk.

Health risk assessment of heavy metals

The health risk model developed by the USEPA was adopted to evaluate the health risks of soil HMs to humans, including carcinogenic and noncarcinogenic risk models. Exposure risk assessment was performed by exposure dose calculations through exposure pathways. Generally, the exposure routes of HMs in soil include oral ingestion, dermal contact, and inhalation. Among them, oral ingestion and dermal contact are usually considered to be the main ways for HMs in soil to come into contact with human body (Qu et al. 2012). Therefore, we chosen these two pathways for assessing the health risk and the equations are as follows:

$$\text{CDI}_o = \frac{c \times \text{InhR} \times \text{CF} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (8)$$

where CDI_o is the mean daily intake via oral ingestion (mg/kg-d), c is the soil HM content (mg/kg), InhR is the

respiratory rate, CF is conversion factor (10^{-6} kg/mg), EF is the exposure frequency, ED is the exposure duration (y), BW is average body weight (kg), and AT is mean exposure time to HMs (y).

$$\text{CDI}_{\text{der}} = \frac{c \times \text{SA} \times \text{AF} \times \text{CF} \times \text{ABS} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (9)$$

where CDI_{der} is the mean daily exposure through skin-to-skin contact (mg/kg-d), SA is the exposed skin surface area, AF is the skin adhesion, and ABS is the skin absorption factor. The corresponding coefficients are different when evaluating adults and children.

The cancer risk was evaluated by the total cancer risk (*risk*) values of HMs, and the *risk* was calculated as follows:

$$\text{risk} = \text{CDI} \times \text{SF} \quad (10)$$

where CDI is the daily exposure doses, and SF is the corresponding slope factors. The USEPA suggests that the acceptable risk level of humans to HM pollution is 10^{-6} to 10^{-4} (Wang et al. 2020). Thus, if the values are $< 10^{-6}$, the risk to human health is not obvious; and if the values are $> 10^{-4}$, there is substantial risk.

The noncarcinogenic risk was calculated using the sum of the hazard quotient (HQ) by various exposure pathways. The HQ was calculated by the equation is as follows:

$$\text{HI} = \sum \text{HQ}_i = \sum \frac{\text{CDI}_i}{\text{RfD}_i} \quad (11)$$

where HI is the total hazard index, and RfD is the reference dose. If HI is < 1 , the risk is small or negligible; and if HI is > 1 , there are possible adverse health effects (Qing et al. 2015). Table S3 shows the parameters of the human health risk assessment model, and Table S4 shows the reference dose for noncarcinogenic HMs and the slope factor for carcinogens.

Results and discussion

Concentrations of heavy metals in soil

Table 1 shows the descriptive statistics of HM concentrations in the soil. The levels of As, Cr, Cu, Pb, Hg, Ni, Cd, and Sb in the soil were 13.2, 2.35, 39.6, 46.1, 0.12, 36.7, 1.66, and 0.28 mg/kg, respectively. Thus, the order of the average values of HMs was Ni > Cu > Pb > As > Cr > Cd > Sb > Hg. One can use the SD and coefficient of variation (CV) as indicators of the degree of dispersion and variation of HMs in soil. The SD of As, Cr, Cu, Pb, Ni, and Cd were large (especially Cu, Pb, and Ni; there were large concentration differences of these elements). The reason for this irregular distribution might be that different industries emit

Table 1 Descriptive statistics of heavy metal concentrations in the study soils (mg/kg)

Elements	Min	Max	Mean	SD	CV	BG	RSV	Mean CF
As	0.72	1320	13.2	57	4.32	5.93	60	2.34
Cr	ND	585	2.35	16.9	7.20	53.7	5.7	0.04
Cu	1.70	4300	39.6	149	3.76	22.5	18,000	1.76
Pb	4.2	6470	46.1	276	5.98	28.3	800	1.63
Hg	0.002	16.4	0.12	0.48	3.86	0.128	38	0.94
Ni	1.10	2370	36.7	87.2	2.38	23.7	900	1.55
Cd	ND	889	1.66	25.7	15.4	0.154	65	10.8
Sb	ND	34.7	0.28	1.31	4.63	0.69	180	0.41

CF is the ratio of the particular metal concentration in soil to its background value. CF classes: < 1 (low contamination), 1–3 (moderate contamination), 3–6 (high contamination), and > 6 (very high contamination)

Min minimum, *Max* maximum, *SD* standard deviation, *CV* coefficient of variation, *BG* background values of Hangzhou, in accordance with the soil geochemical background in Zhejiang; *RSV* risk screening values of the soil heavy metals, in accordance with the soil environmental quality–risk control standard for soil contamination of development land (GB36600-2018), *Mean CF* contamination factor of the heavy metals

different distributions of pollutants (discussed in the subsequent section). The CVs of As, Cr, Cu, Pb, Ni, Cd, and Sb were $\gg 1$; which indicates a strong degree of variation, and that anthropogenic activities are a main source of these HMs (Daniela et al. 2002). In the study of Sun et al. (2019), Zn, Cu, Ni, Pb, Cr, Cd, and As showed a moderate degree of variability with CV (< 0.5), while Hg had higher CV (> 0.5). Their results differed from ours, possibly due to stronger human activity in our study area.

The soil background values are the fundamental basis for comprehensive evaluations of soil pollution. In this research, the average levels of As, Cu, Pb, Ni, and Cd exceeded their background levels by ca 1.42 \times to 10.78 \times ; indicating that these elements were substantially enriched in the soil. In contrast, the average levels of Cr, Hg, and Sb in the soil were lower than their background values. In addition, the concentrations of As, Cu, Pb, Hg, Ni, Cd, and Sb were mostly lower than their risk screening values for soil contamination of development land (MEEC 1998); whereas around 4.9% of the samples had a total Cr level that was higher than the risk screening value. Compared with industrial areas in other areas, the mean levels of Cr and Sb in the soil of Hangzhou were lower than the reported values for soil from Lianyuan, China and four major cities of Nepal (Liang et al. 2017; Yadav et al. 2019); whereas other elements were higher than the levels in Tangshan and Puning, China (Sun et al. 2019; Wang et al. 2019). Therefore, although the HM levels in most sample sites did not exceed the national risk screening values, the substantial accumulation of these metals in the soils is noteworthy.

Spatial distribution of heavy metals in soils

As shown in Fig. 2, places with higher levels of As, Cu, Pb, Hg, and Cd were in the southwest and northeast regions of

Hangzhou. Cr and Ni were in high concentrations in the central area, whereas the hot spots for Sb were located in a small part of the north of the study area. As mentioned in the previous section, different industries probably emit different distributions of pollutants. For example, the HM pollution from mineral exploitation, metal processing, and mineral transportation enterprises is often a substantial hazard. In this research, the levels of As, Cr, Cu, Pb, Hg, and Cd in the soil of a mining company in the southwest area of Hangzhou were higher than those of other enterprises. Furthermore, regional nonpoint source pollution and agricultural production activities might also affect the spatial distribution of HMs in soil.

A copper mining area has exploited its location in the south–southwest of the study area since the 1960s. Long-term mining and smelting can produce large quantities of waste ore and tailings, which might lead to enrichment of Cu in the surrounding area. Additional main reasons for the enrichment of copper in the eastern region are the exploitation of coal mines and the surrounding steel factories. Furthermore, Pb and As in the ore are oxidized into Pb and As oxide particles under oxygen-rich and high-temperature environments, and are discharged into the air and soil in the form of waste smoke—leading to accumulation of Pb and As in the soil. Pb and As were also more enriched in the north-eastern region, located in the main urban area of Hangzhou; a high-density population and busy traffic area. In addition, there are several major vegetable production bases in the northeast; application of pesticides and chemical fertilizers will lead to accumulation of HMs such as Cu, Pb, and Hg in the soil (Gimeno-García et al. 1996).

The high level area of Cr was in the east–central part of the study area: Tonglu county of Hangzhou. Tonglu county has many large and small factories; mostly tanneries, electroplating, and textiles. Therefore, enrichment of Cr in this

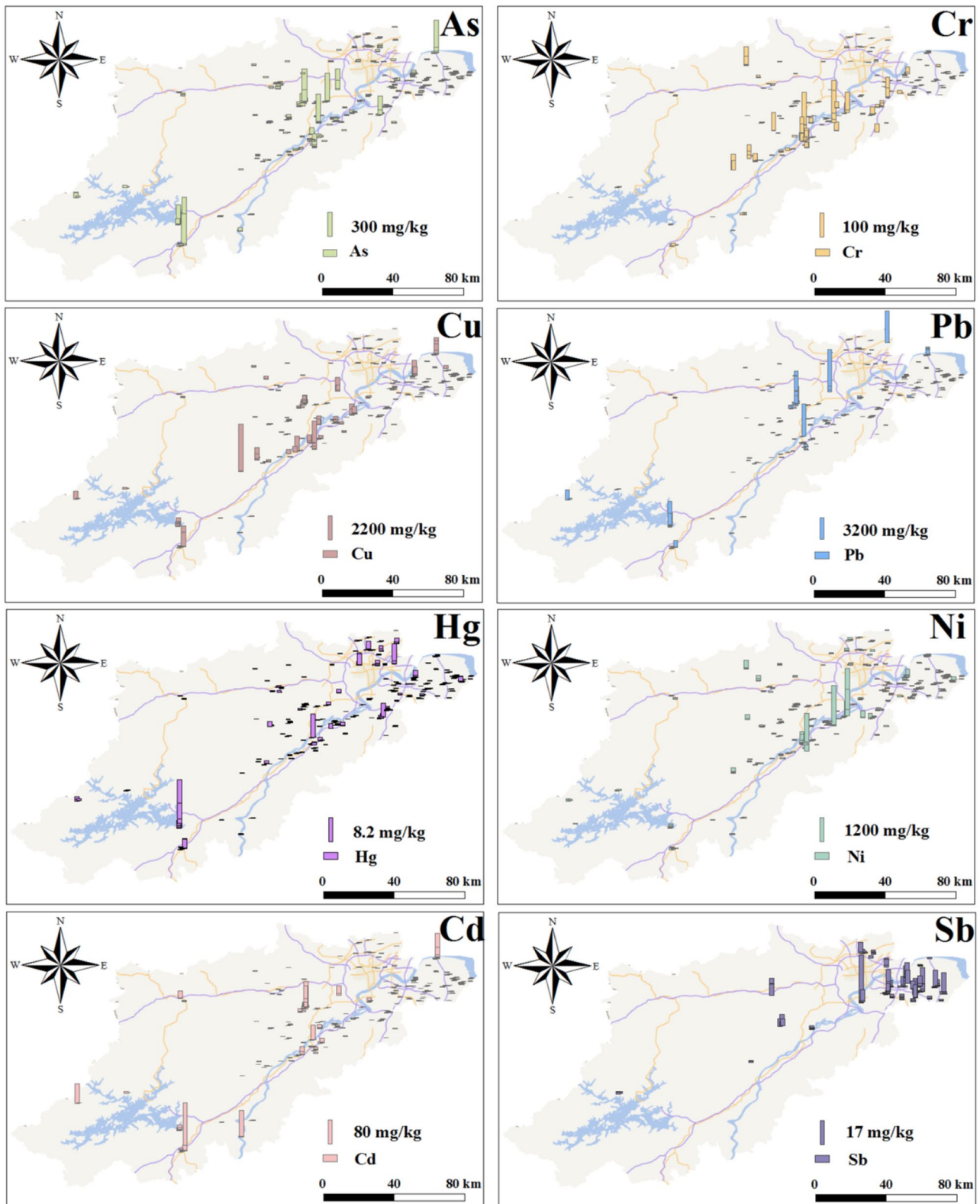


Fig. 2 Spatial distributions of heavy metals in soil

area may be due to direct or indirect accumulation in the soil during operation of these enterprises (Testa et al. 2004). The high concentration of Hg in soil was similar to the distribution characteristics of As, Cu, and Pb in the southwest. Mineral mining, metallurgical electroplating, and similar industries might be a source of Hg pollution. The difference between Cd and Hg was that the distribution of Cd in the soil of the study area covered nearly the entire southwest (Chun'an county and Jiande city of Hangzhou). The copper mine area mentioned previously is in Jiande city; where there are also stone coal, iron, and uranium mines. Chun'an County also has many mineral resources; mining metallurgy might be the cause of Cd accumulation in soil.

The spatial distributions of Ni and Sb were considerably different from those of the other metals. The main high-concentration areas of Ni were through the north and south of Hangzhou; mostly including Fuyang district, Tonglu county, and Chun'an county. These are areas with mineral smelting industries, which might be pertinent to the Ni enrichment (Fry et al. 2021). The high Sb concentration area was mainly in the north, where there are many industrial enterprises (such as printing and dyeing enterprises, electronic machinery, and equipment manufacturers) that are also important sources of Sb pollution.

Source analysis of heavy metals

In this study, PMF 5.0 software was adopted to quantify the sources of HMs in the soil. By continuously changing the number of factors to perform model fitting calculations, it was determined that when there are three factors, the difference between Qrobust and Qtrue in the model was smallest; indicating that the scheme can optimally explain the information contained in the original data. Among them, factor 1 contains higher contribution rates of Cu and Hg (Fig. 3 and Table S2). The contribution rate of Hg was > 90%; thus, one can infer that Hg was the identifying element of factor 1. Discharge of untreated industrial wastewater is the main source of Hg pollution in soil (Hu et al. 2018). Generally, industrial activities such as mineral mining and metallurgical electroplating contribute to the enrichment of mercury; and they are also an important source of copper pollution in soil. Thus, factor 1 was identified as a source of industrial activity. The main loads of factor 2 were Cr, Ni, and Sb, which indicated that these elements came from the same pollution source. Many studies suggest that the soil parent material might be the source of Cr and Ni in soil (Mikkonen et al. 2018; Zhou et al. 2016). In accordance with a descriptive statistical analysis of soil HMs, the mean level of Cr and

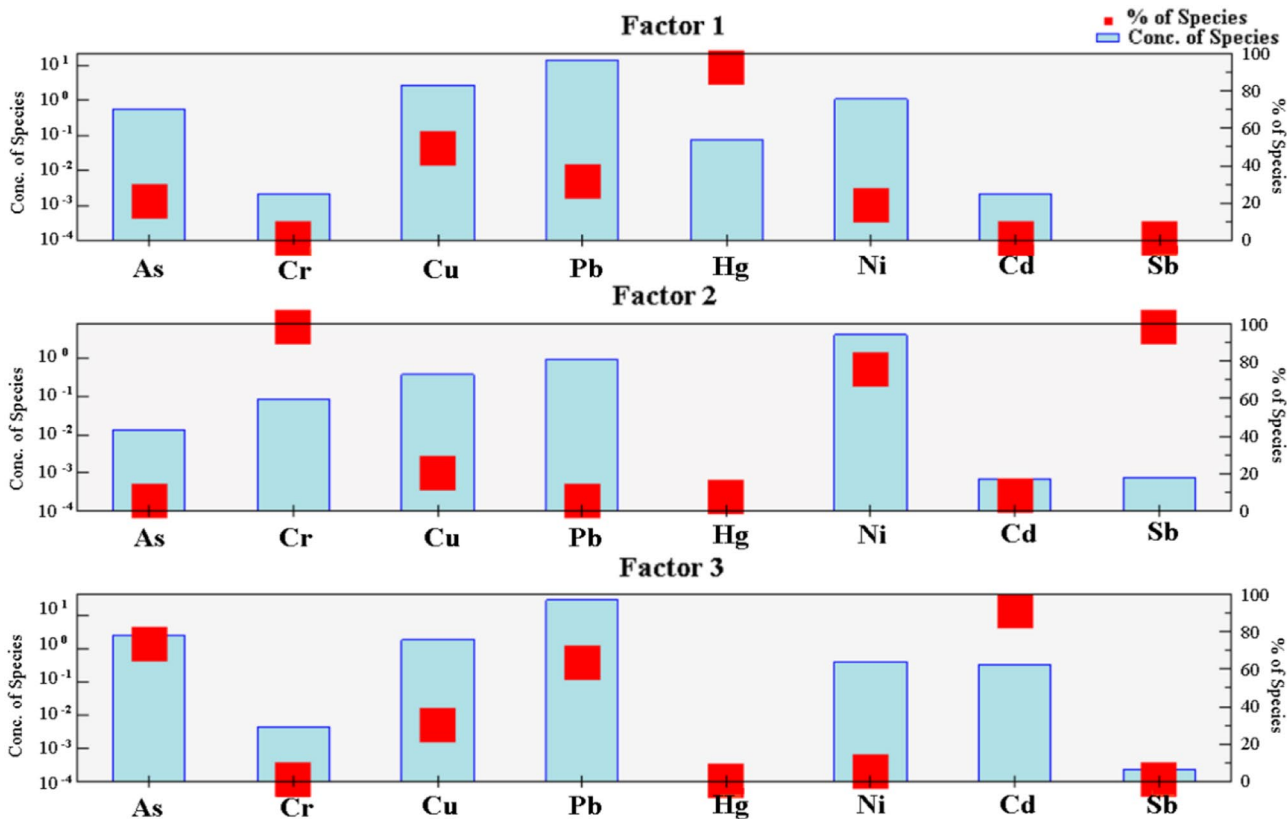


Fig. 3 Source profiles of soil heavy metals, calculated by the PMF method

Sb in the soil was lower than the background value of Zhejiang Province, whereas Ni exceeded the background value of Zhejiang Province but was lower than the national soil environmental value. Therefore, pedogenesis—originating from natural weathering of the parent material—might be the main factor that affected Cr, Ni, and Sb in the study area. From a comprehensive analysis, factor 2 represented natural sources and the main indicator of soil parent material. As, Pb, and Cd exhibited high contribution rates in factor 3: 73.7%, 63.6%, and 90.9%, respectively; the accumulation of these metals in the soil is through atmospheric deposition and airborne dust adsorption of automobile exhaust gas (Pardjak et al. 2008; Zhang et al. 2015). Based on the above analysis, factor 3 was identified as traffic activity.

In addition, the PMF model quantified the overall contribution of each source to the total HM concentration (Table S2). Traffic activity made the greatest contribution (53.5%), followed by industrial activity (31.1%) and natural source (15.4%). Therefore, the main source of HMs in soil of this study area was anthropogenic sources, accounting for 84.6% of total. Compared to other studies, Sun et al. (2019) also identified and quantified the sources and contributions of HMs in soils by PMF model, and their results indicated that anthropogenic sources were the main contribution, which were consistent with ours. In a study by Wu et al. (2021), PMF model was also employed to identify the source and contributions of HMs in soil, and found that the industrial emissions/atmospheric deposition and agricultural sources are the main contributions, and followed by natural sources. These studies further demonstrate the important impact of human activities on soil HM accumulation.

Health and ecological risks of heavy metals

Potential ecological risk

The potential ecological risks of HMs in the soil were assessed by the PEHI method (Table 2). In accordance with the classification of potential ecological risk (Table S1), except for Cd, the single-factor PERI E_r^i of the other seven HMs were all slight ecological risks; the average value was < 40. However, the average PERI of Cd was 323.4, much larger than that of the other metals, and was in hazard level III (considerable potential ecological risk). In addition, some sample points in the study area were substantially high ecological risk based on the maximum PERI of HMs. The mean value of the PERI of the total HMs in the study area was 407.54, which indicated a high ecological risk. Therefore, Cd might be the main pollution risk element in this area, and harm the local environment and human health. Our findings are the similar with the results of Wu et al. (2021). Previous studies have also found that soil Cd concentration is generally higher throughout the Yangtze River Delta region,

Table 2 Ecological risk index of soil heavy metals in the study area

Heavy metal	E_r^i		
	Min	Mean	Max
As	7.2	23.4	13,200
Cr	–	0.08	1170
Cu	8.5	8.8	21,500
Pb	21	8.15	32,300
Hg	0.08	37.6	655
Ni	2.2	3.1	4740
Cd	–	323	26,700
Sb	–	3.01	243
Total	39	408	101,000

China (Hu et al. 2016; Shao et al. 2016). Therefore, it may be related to the geochemical background of the region.

Human health noncarcinogenic risk assessment

Table 3 shows the noncarcinogenic risk index of soil HMs. The HQ values of both adults and children were as follows: oral ingestion > skin contact; indicating that the main route of noncarcinogenic risk in the study area was oral ingestion. The average noncarcinogenic risk factors of various HMs and the total noncarcinogenic risk index HI for were < 1, which indicates that the eight HMs in the study area had no noncarcinogenic risk to human health on average. However, the maximum value of the noncarcinogenic risk index was > 1 for children, indicating that there were some areas that have potential health hazards to children. For the reasons, children do not necessarily have good health awareness, such as inhaling HM by sucking their fingers (Rasmussen et al. 2001). Furthermore, the absorption rate, digestibility and hemoglobin sensitivity of children to HMs are higher than that of adults (Bacigalupo and Hale 2012). Therefore, many studies have shown that children face higher health risks than adults (Rehman et al. 2017; Zheng et al. 2020). Overall, the noncarcinogenic risk of HMs in Hangzhou soil to human health is low.

Because of the lack of carcinogenic slope factors for copper, mercury, and antimony, only the carcinogenic risks of arsenic, chromium, lead, nickel, and cadmium were estimated in this study. Table 4 shows the carcinogenic risk indices of As, Cr, Pb, Ni, and Cd under oral intake and skin contact. The risk size and noncarcinogenic risk of the same element in different exposure routes of adults and children were the same, and the risk of the oral intake route was higher than that of skin contact; but the carcinogenic risk to children was higher than that to adults. The reasons for this are similar to the noncarcinogenic risks we discussed above. In the oral intake route, the carcinogenic risk of HMs was as follows: Ni > As > Cd > Cr > Pb; and the risk mean value

Table 3 Noncarcinogenic risk index of soil heavy metals in the study area

	Metal	Minimum			Mean			Maximum		
		HQ _o	HQ _{der}	Total	HQ _o	HQ _{der}	Total	HQ _o	HQ _{der}	Total
Adults	As	3.59E-03	3.49E-05	3.62E-03	6.57E-02	6.40E-04	6.64E-02	6.58E+00	6.41E-02	6.65E+00
	Cr	–	–	–	1.17E-03	4.67E-06	1.18E-03	2.91E-01	1.16E-03	2.93E-01
	Cu	6.35E-05	8.45E-07	6.43E-05	1.48E-03	1.97E-05	1.50E-03	1.61E-01	2.14E-03	1.63E-01
	Pb	1.79E-03	4.78E-05	1.84E-03	1.97E-02	5.25E-04	2.02E-02	2.76E+00	7.36E-02	2.83E+00
	Hg	9.96E-06	5.57E-07	1.05E-05	5.98E-04	3.34E-05	6.31E-04	8.17E-02	4.57E-03	8.62E-02
	Ni	8.22E-05	1.21E-06	8.34E-05	2.74E-03	4.05E-05	2.78E-03	1.77E-01	2.62E-03	1.80E-01
	Cd	–	–	–	2.48E-03	3.96E-04	2.88E-03	1.33E+00	2.12E-01	1.54E+00
	Sb	–	–	–	1.05E-03	–	1.05E-03	1.30E-01	–	–
	HI	5.53E-03	8.53E-05	5.62E-03	9.49E-02	1.66E-03	9.66E-02	1.15E+01	3.60E-01	1.19E+01
Children	As	2.37E-02	4.90E-05	2.38E-02	4.35E-01	8.98E-04	4.36E-01	4.36E+01	8.99E-02	4.37E+01
	Cr	/	/	/	7.74E-03	6.55E-06	7.75E-03	1.93E+00	1.63E-03	1.93E+00
	Cu	4.20E-04	1.19E-06	4.21E-04	9.78E-03	2.76E-05	9.80E-03	1.06E+00	3.00E-03	1.07E+00
	Pb	1.19E-02	6.71E-05	1.19E-02	1.30E-01	7.36E-04	1.31E-01	1.83E+01	1.03E-01	1.84E+01
	Hg	6.59E-05	7.82E-07	6.67E-05	3.95E-03	4.69E-05	4.00E-03	5.40E-01	6.41E-03	5.47E-01
	Ni	5.44E-04	1.70E-06	5.45E-04	1.81E-02	5.68E-05	1.82E-02	1.17E+00	3.67E-03	1.17E+00
	Cd	–	–	–	1.64E-02	5.56E-04	1.70E-02	8.79E+00	2.98E-01	9.09E+00
	Sb	–	–	–	6.92E-03	–	–	8.59E-01	–	–
	HI	3.66E-02	1.20E-04	3.67E-02	6.28E-01	2.33E-03	6.30E-01	7.62E+01	5.05E-01	7.67E+01

Table 4 Carcinogenic risk index of soil heavy metals in the study area

	Metal	Risk _o	Risk _{der}	Risk _{total}
Adults	As	1.01E-05	9.87E-08	1.02E-05
	Cr	6.03E-07	9.61E-08	6.99E-07
	Pb	2.01E-07	1.60E-09	2.02E-07
	Ni	3.19E-05	3.19E-06	3.51E-05
	Cd	5.19E-06	2.07E-08	5.21E-06
	Total	4.81E-05	3.40E-06	5.15E-05
Children	As	1.68E-05	3.46E-08	1.68E-05
	Cr	9.98E-07	3.37E-08	1.03E-06
	Pb	3.32E-07	5.62E-10	3.33E-07
	Ni	5.28E-05	1.12E-06	5.39E-05
	Cd	8.58E-06	1.60E-07	8.74E-06
	Total	7.95E-05	1.35E-06	8.09E-05

was in the acceptable range—indicating that a single HM had no carcinogenic risk to human health. From the overall carcinogenic risk index, the average risk values of adults and children were all < 10⁻⁴, which indicated that the overall carcinogenic risk of soil HMs was also within the acceptable range in the research area.

In conclusion, oral intake was the main route of harm, and the health risk to children was substantially higher than that to adults. As and Pb, and As and Ni, in soil were the main factors of noncarcinogenic and carcinogenic health risk, respectively. Therefore, As pollution in soil warrants

the attention and management of relevant departments. In Long’s study, there was no carcinogenic risk of As for adults but significant risk for children, and indicated that various industrial activities can lead to different kinds of soil HM pollution (2021).

Conclusions

The concentrations, sources, spatial distribution, and risks of HMs from industrial areas of Hangzhou were analyzed. The mean concentrations of the eight HMs were all less than the soil pollution risk screening value; but the mean contamination factors of As, Cu, Pb, Ni, and Cd were all > 1 (indicating that they all had different degrees of pollution in the soil). Based on the spatial distribution and PMF analysis, human activities were the main source of HM pollution, which accounted for 84.6% of the total pollution sources. Industrial activities such as metallurgical electroplating and mineral mining were the main pollution sources of Hg and Cu; the main sources of Cr, Ni, and Sb were natural weathering of soil-forming parent materials; and the sources of As, Pb, and Cd were the main contributions provided by traffic. The analysis of the PEHI method indicates that Cd substantially harms the ecological environment. In accordance with the health risk analyses of HMs in soil, the average index of carcinogenic and noncarcinogenic risk of these HMs was within the acceptable range. Thus, human activities substantially contribute to the soil HM pollution in Hangzhou and

might be ecologically hazardous. Relevant departments can take corresponding measures to prevent further pollution.

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Data availability Upon request, the data will be made available to readers.

Code availability Not applicable.

Declarations

Conflict of interest The authors declare that there is no conflict of interest.

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