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Credit authorship contribution statement

Shiyu Wang: Experiment, Methodology, Formal analysis, Investigation, Writing, Original draft. **Yusef Kianpoor Kalkhajeh:** Writing - review & editing, Supervision, Grammar check. **Zhirui Qin**: Methodology, Writing - review & editing. **Wentao Jiao**: Resources, Writing - review & editing. Funding acquisition, Project administration, Supervision.

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Spatial distribution and assessment of the human health risks of heavy metals in a retired petrochemical industrial area, South China

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Abstract: Petrochemical industries are widely distributed in China. As a negative consequence, heavy metals in petrochemical area can result in soil contamination. However, the relevant research of heavy metals contamination in petrochemical area was few. In this study, a total of 103 topsoil samples (< 20 cm) and 25 profile soil samples were collected and examined in a retired petrochemical industrial area, South China. The results showed the mean contents of Hg, Cd, As, Pb, Ni and Cu were 0.18, 0.69, 16.22, 47.24, 31.62 and 93.06 mg·kg^{-1}, respectively. The spatial distribution of six metals in topsoil was largely attributed to the industrial activities during the petroleum refining and transshipment process. Ni was the main pollutant in the petroleum refining process. While, the contamination of other metals mainly were caused by the leakage of the oil during transshipment. The migration of six metals to subsoil layers was also observable. In accordance, Hg, Cd, As, Pb, Cu, and Ni dropped by 95.02, 71.91, 89.45, 90.88, 99.22, and 65.07%, respectively, compared to their contents in topsoil. The contamination of the heavy metals was mainly caused during the process of petroleum refining and transshipment. The distribution of heavy metals in the factory was mainly affected by the industrial activities or the lateral infiltration of Lianhuashan River. Soil ingestion was the primary pathway for children and adults exposure to heavy metals. The total non-cancer human health risk induced by heavy metals was within the limit of USEPA

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(10^{-6} a^{-1}). While the cancer risks alone induced by As through soil ingestion to children was 1.14×10^{-6} a^{-1}, which exceeded the limit of USEPA. This study indicated that not only petroleum hydrocarbon but also heavy metals can cause soil contamination in a retired petrochemical industrial area, which provides a novel cognition. Altogether, measures should be taken in practice to substantially improve the soil quality in petrochemical industrial area.

Keywords: Heavy metals; petrochemical industry; spatial distribution; vertical migration; human health risks

1 Introduction

Heavy metals' pollution has become one of the main environmental soil problems worldwide (Asgari and Cornelis et al., 2015; Hossein et al., 2019). Anthropogenic activities such as agriculture, urbanization and industrialization are the main driving forces of soil heavy metal contamination rather than occurring from soils naturally (e.g., due to the erosion of parent rocks, atmospheric deposition, and volcanic activities) in recent years (Wu et al., 2013; Latare et al., 2014; Özkul et al., 2016; Wang et al., 2019). Industrialization has been noted as the primary source of heavy metal contamination (Martín et al., 2014; Meisam et al., 2017; Hossein et al., 2019). This pollution not only affects the quality of soil, but also poses serious health risks to individuals (Chabukdhara et al., 2013; Asgari and Cornelis, 2015). Human exposure to heavy metals takes place through soil ingestion, dermal contact, and inhalation (Mungai et al., 2016). Upon exposure, heavy metals can damage the body's immune, reproductive and nervous systems (USEPA 2004).

More studies have focused on soil pollution of heavy metals in relation to industrial activities in China due to the rapid development (Fiedler et al., 2009; Rachwał et al., 2017; Yang et al., 2018). Especially, mining and electroplating factories have been drawn much attention (Guo et al., 2015; Xiao et al., 2017; Cao et al., 2019). However, the impact of petrochemical industry on soil heavy metals' pollution remained relatively unknown. Nevertheless, petrochemical industries are

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important to the contribution of energy production all over the world including China. Petrochemical industries account for 20% of China's total industrial economy and it is an essential economic pillar for many developed areas (Lin 2016; Peng, 2016; Hu et al., 2018; Zhang 2019). But it has been proved that heavy metals have existed in the crude petroleum. The pollution of heavy metals in the process of refining is becoming unavoidable (Shen et al., 2011; Zhao et al., 2012; Yi 2013). Some refining or transshipment processes have caused the metals contamination (Yuan et al., 2017; Huang et al., 2018). It has been reported that the mean contents of Cu, Zn, Cd, Pb, As and Ni in topsoil (<20cm) samples in a petrochemical industry in Xinjiang ranged 0.07-126.61 mg·kg^{-1} (Wang et al., 2016). The contents of Hg, As, Cd, Pb, Cu and Ni in an oil refinery in the city of Hangzhou were up to 0.201-47.9 mg·kg^{-1} (Zhou et al., 2019). These investigations provided some advantageous reference that the refining process of raw oil can cause soil heavy metal pollution, but we still do not know which section is the main driver to produce the heavy metal. While production process was an indispensable aspect to the soil contamination that cannot be ignored (Ren 2007; Sun 2019). It’s necessary to dig the real origin of these heavy metals.

Petrochemical industry is one of the pillar industries in Guangdong Province and the output value accounts for 6.7% of the total industrial output in the whole province (Feng and Zhou, 2018). Panlong is one of the typical petrochemical industries in this area and was in business from 2000-2007. It was an idle land and no exogenous pollution since 2007. So it was an ideal area for the investigation of soil heavy metal contamination and origin relating to petroleum industry. But after this industry was dismantled, the residual heavy metals may induce health risks to the local humans. According to the United States Environmental Protection Agency (USEPA) (2014), cadmium (Cd), arsenic (As), mercury (Hg), lead (Pb), copper (Cu) and nickel (Ni) are priority pollutants. In accordance, this study aimed to: (1) address the spatial distribution of heavy metals in topsoil associated with the industrial production process; (2) study the migration of the heavy metals versus the soil depth; (3)

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speculate the possible sources of soil heavy metals; and (4) assess the potential health risks of human exposure to the heavy metals.

2 Material and Methods

2.1 Sample collection and treatment

This investigation was carried out in the inner of Panlong petrochemical factory in Guangzhou City, Guangdong Province, South China. The study area has a longitude of 113°14′～113°34′E and a latitude of 22°45′～23°05′N, and it covers an area of 130000 km^2. This region has a subtropical climate with an average annual temperature between 21.4 and 21.9 °C and average annual rainfall from 1620 to 1900 mm. During the crude petroleum processing, the oil is transported into the storage tank firstly, and then into the refinery. After physical and chemical purification, the gasoline and diesel oils are transported back to the storage tanks. Finally, the separated oil, mainly the light and heavy oil are pumped into the transfer room and sold as the factory's products. The soil heavy metals in the different part of the industry may have a different distribution. To facilitate analysis, the factory area is divided into several sections, mainly including refinery area, tank storage area, office, and residence area (Fig. 1).

A total of 103 topsoil samples numbered from S1 to S103 were collected via the random sampling method of 40m by 40m (0-20cm), ensuring that each divided section has enough samples. Locations of sampling sites were recorded accurately by a Global Positioning System (GPS) (Trimble 5700, America). The second time for sampling was taken according to the results of the contents of the metals. Additional profile samples were taken at sites S46, S76, S79, S95 and S103 due to their high metal contents. The depth of each sampling site was 0-5.7 m covering plough layer and subsoil. For each profile sampling site, 5 subsamples at 5 soil profiles were collected at different depths. The sampling depths at each site are shown in Support Information of Table 1. At the same time, the geotechnical experiment was carried out to test the soil particle size and other properties.

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Soil samples at each sampling site were taken using a stainless steel spade and mixed thoroughly. Afterwards the soil samples were chosen by quartation, plants' debris and residues were removed. After that, 0.5 kg of each soil sample was taken and stored in a self-sealing plastic bag at 4 °C. One gram of soil was placed in a Teflon autoclave and treated by adding 22 mL acid mixture (3.0 mL of HCl, 9.0 mL of HNO_3, 2.0 mL of HF, and 8.0 mL of $HClO_4$) at 80 °C until a clear solution was acquired. Filtration of digested samples were done by Whatman No.42 filter papers ($<$ 2.5 um). The digested soil samples were stored at 4 °C for determination of metals (Mahmood et al., 2019).

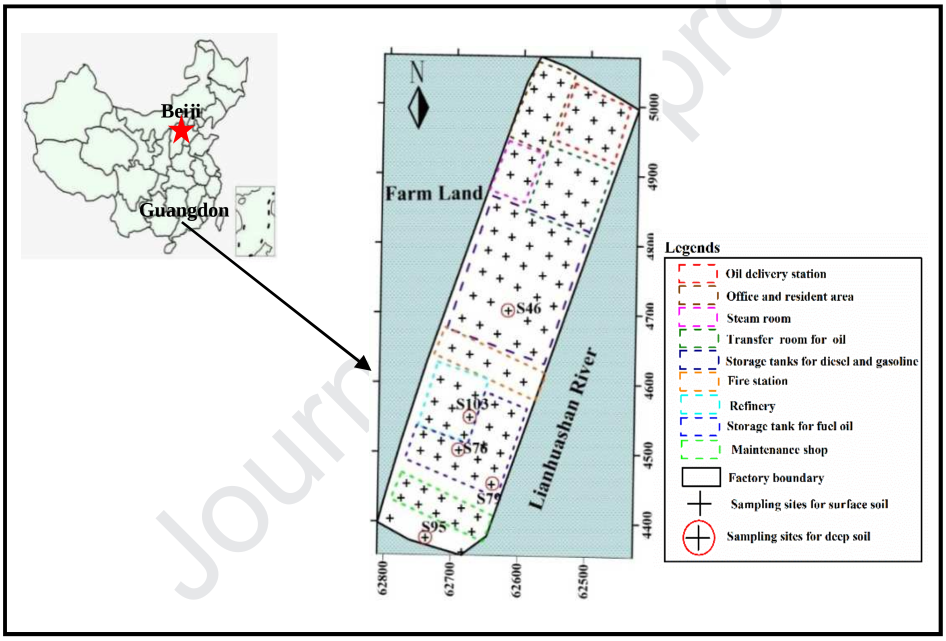

Fig1. A schematic diagram of the location of Panlong petrochemical industrial area and the sampling scheme

2.2 Sample detection and quality assurance/quality control (QA/QC)

Hg and As were determined using cold vapor atomic absorption spectrometry by Atomic Fluorescence Photometer (AFS-8220) with the method detection limit (MDL) of 0.002 mg·kg^{-1} and 0.01 mg·kg^{-1}, respectively; Pb, Ni and Cu were detected using flame by Atomic Absorption Spectrophotometer (AFX-210) with MDLs of 0.1 mg·kg^{-1}, 5 mg·kg^{-1}, and 1 mg·kg^{-1}, respectively; Cd was measured using a graphite

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furnace by Atomic Absorption Spectrophotometer (AFX-200) with a MDL of 0.01 $\text{mg}\cdot\text{kg}^{-1}$. Controlled measurements on internal reference material, reagent blanks, and duplicated soil samples were randomly selected from the sample sets to ensure the quality assurance/quality control (QA/QC). The average deviation between duplicate samples was 15%. The method recovery of the metals ranged from 91.4 to 108%. All the blank samples were all below the MDLs.

2.3 Data analysis

2.3.1 Principal component analysis

Principal Component Analysis (PCA) is a mathematical procedure that uses an orthogonal transformation to convert a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables (Ha et al., 2014). In this study, canoco 5.0 software was used to identify the potential sources of heavy metals.

2.3.2 Human health risk models

From the perspective of soil heavy metals' pollution, the current international human health risk assessment model is divided into two parts: cancer and non-cancer chemical models. According to the classification system of the World Health Organization (WHO), the International Agency for Research on Cancer (IARC) and the Integrated Risk Information System (IRIS) database of EPA, Cd and As are considered as cancer chemicals; Cu, Ni, Pb, and Hg are considered as non-cancer or less cancer chemicals.

The cancer risk assessment model is as follows:

$$R^C = \sum_{i=1}^{l} R_i^c \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$R_i^c = \left[1 - \exp\left(- ADD \times Q_i\right)\right] / 70 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where R^C is the total health risks of the cancer chemicals annually, a^{-1}; R_i^C is the health risk of the cancer-chemical *i* annually, a^{-1}; ADD is the average daily exposure dose, $\text{mg}\cdot(\text{kg}\cdot\text{d})^{-1}$; and Q_i is the carcinogenic coefficient of the chemical, $\text{mg}\cdot(\text{kg}\cdot\text{d})^{-1}$

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(Table 1).

The non-cancer risk assessment model is as follows:

$$R^n = \sum_{i=1}^{l} R_i^n \quad \text{.........(3)}$$

$$R_i^n = \left(ADD \times 10^{-6}\right)/(RfD \times 70) \quad \text{.........(4)}$$

where R^n is the total health risk for the non-cancer chemicals annually, a^{-1}; R_i^n is the health risk of the non-carcinogenic chemical *i* annually, a^{-1}; *ADD* is the average daily exposure dose, $\text{mg}\cdot(\text{kg}\cdot\text{d})^{-1}$; *RfD* is the reference dose of the non-cancer chemical, $\text{mg}\cdot(\text{kg}\cdot\text{d})^{-1}$ (Table 1); 70 is the average life time, a^{-1}.

Table 1. Toxicity parameters of heavy metals

Heavy metals	*RfD*[mg·(kg·d)$^{-1}$]			*Q*$_i$[mg·(kg·d)$^{-1}$]		
	Ingestion	Dermal	Inhalation	Ingestion	Dermal	Inhalation
As	3×10^{-4}	3×10^{-4}	3×10^{-4}	1.5	3.66	15.1
Cd	0.001	0.001	0.001	6.1	0.38	6.3
Hg	0.0003	2.1×10^{-5}	8.57×10^{-5}			
Pb	3.5×10^{-3}	5.25×10^{-4}	3.52×10^{-3}			
Ni	0.02	0.0054	0.0206			
Cu	3×10^{-3}	0.005	2.86×10^{-5}			

In the present study, ingestion of soil (s-ing), dermal contact of soil (s-der) and inhalation of soil (s-inh) were taken into account as the main three pathways of human exposure to heavy metals. Using IARC, WHO, and US EPA-IRIS approaches, the age groups are divided into two subgroups: children (0-6 years) and adults (>18 years). The *ADD* of heavy metals from various exposure pathways was calculated using the formulas (5-7). The parameters of the human health risk assessment models are summarized in Table 2, derived from USEPA (2004), US Department of Energy (USDoE) (2011), and China Environmental Protection Department (Duan, 2017).

$$ADD_{s-ing} = (C \times IR_1 \times \text{CF} \times EF \times ED) / \left(BW \times AT\right) \quad \text{.........(5)}$$

$$ADD_{s-der} = (C \times CF \times SA \times AF \times ABS \times EF \times ED) / \left(BW \times AT\right) \quad \text{.........(6)}$$

$$ADD_{s-inh} = (C \times IR_2 \times EF \times ED) / \left(PEF \times BW \times AT\right) \quad \text{.........(7)}$$

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Table 2. Parameters of human health risk assessment models

Exposure parameters	Description	Values	
		Adults	Children
BW	Body weight (kg)	60	18
ED	Exposure duration to soil (a)	25	10
AF	Skin adherence factor for soil (mg(cm^2·d)$^{-1}$)	0.1595	0.1595
EF	Exposure frequency to soil(d·a^{-1})	225	225
SA	Skin surface available for daily contact(cm^2)	5000	2500
IR$_1$	Ingestion rate of soil(mg·d^{-1})	100	200
IR$_2$	Ingestion rate of air(m^3·d^{-1})	8	20
AT	Average time on soil(d)	70×365(cancer） ED$_2$×365(non-cancer）	70×365(cancer） ED$_2$×365(non-cancer）
ABS	Dermal absorption factor	0.03 for As; 0.001 for Hg, Pb, Cd, Cu, Ni	
PEF	Particle emission factor(m^3·kg^{-1})	1.36×10^9	
CF	Conversion factor for unit (kg·mg^{-1})	1×10^{-6}	
C	Content of heavy metal in soil(mg·kg^{-1})	-	

2.3.3 Human health risk assessment

Overall, $R<10^{-6}$ a^{-1}, 10^{-4} a$^{-1}>R>10^{-6}$ a^{-1}, and $R>10^{-4}$ a^{-1} represent no health risks, no obvious health risk, and very high risk of human exposure to heavy metals (US EPA, 2004). The International Commission on Radiological Protection (ICRP) recommended 5×10^{-5} a^{-1} as the acceptable level of human health risks.

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3. Results and discussion

3.1 Heavy metals in topsoil

The contents of the six heavy metals of 103 topsoil samples are shown in Fig. 2. As can be seen, the contents of Hg, Cd, As, Pb, Ni and Cu ranged from 0.004-5.62, 0.11-7.69, 1.78-54.6, 5.1-454, 10-335 and 16-1030 mg·kg^{-1}, respectively, with mean values of 0.18, 0.69, 16.22, 47.24, 31.62 and 93.06 mg·kg^{-1}, respectively. The contents of heavy metals at some sampling sites exceed the background values of Guangzhou **(**Support Information of Table 2**)**. The exceeding sampling sites accounted for 24.27%, 100%, 11.65%, 17.48%, 43.69% and 79.61% of the total ones, respectively for Hg, Cd, As, Pb, Ni, and Cu. Likewise, the highest contents were 43.23, 69.91, 2.18, 7.57, 11.96 and 32.19 times of the background values for Hg, Cd, As, Pb, Ni, and Cu,

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respectively. This indicated that the industrial activities caused the accumulation of heavy metals in the factory. The highest contents of Ni and Pb exceeded the standards of Category Ⅰ of Land Use of Chinese National Standards (GB36600-2018), which was the soil quality for residential construction in China (Support Information of Table 3**)**. These metals were accumulated for 8 years in this industrial area and if it goes on like this, the contents of other four metals would reach the CategoryⅠvalues in 3.45, 13.96, 9.365, 7.78 years for Hg, Cd, As and Cu, respectively. The results indicated that heavy metals were also contaminations that can't be ignored besides organic pollutants in a petrochemical area that should cause attention.

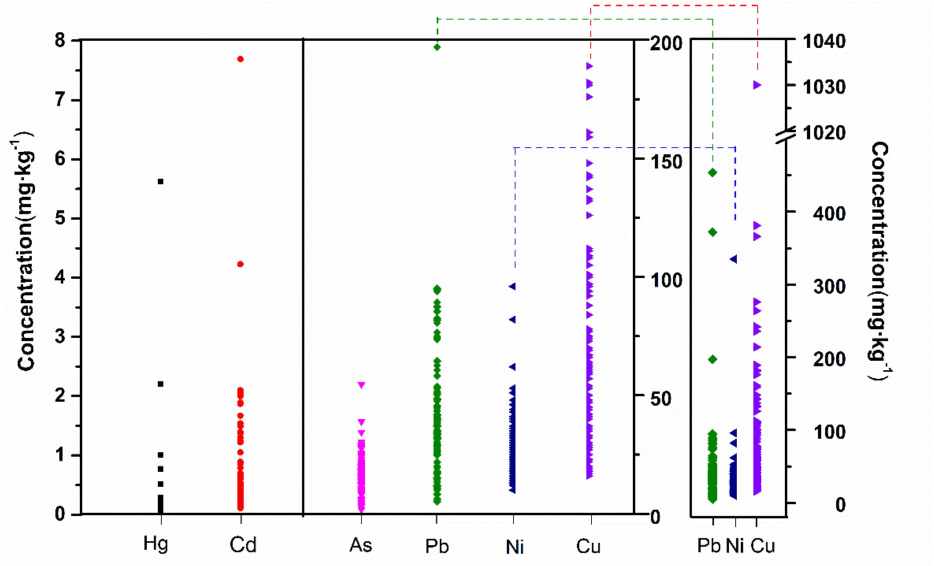

Fig. 2. Contents of heavy metals in topsoil in Panlong petrochemical industrial area

Likewise, numerous research about the heavy metal contamination in soils have been reported around the world including China (Xia et al., 2011; Asgari et al., 2015; Meisam et al., 2017; Yang et al., 2018; Cao et al., 2019; Hossein et al., 2019). The contents of Hg, As, Cd, Pb and Cu in Nanhongmen agricultural soils in China were 0.099, 10.72, 0.168, 25.04 and 25.58 $mg\cdot kg^{-1}$, respectively, of which the contents were relatively low compared with this study (Wu et al., 2013). Because Nanhongmen is a typical reclaimed water irrigation area in China, and the majority of the heavy metals are from the secondary effluent of the sewage treatment plant. Hence, soil contents of heavy metals are much lower than the soils from petrochemical industrial

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areas. Although Pb in agricultural topsoils in Ebro basin (Spain), ranging from 4 to 147 mg•kg^{-1} (average 17.54 mg•kg^{-1}), was 10-25 times higher than the background level in Spain (Martín et al., 2006), while it was much lower than that of this study. Some previous reports have suggested more serious soil contamination of heavy metals in industrial areas than agricultural areas (Wang et al., 2015b). For instance, the contents of As, Cd and Pb in the topsoil (<20cm) in Veles of Macedonia were 7.8, 6.1 and 170 mg·kg^{-1}, respectively, which were within the content ranges of this study. The contents of As, Cd and Pb in Iberian Peninsula were 68.86, 4.36 and 2147.40 mg·kg^{-1}, respectively. Except for Cd, other two metals far exceeded that of this study, especially for Pb. This is attributed to the large Pb production in Macedonia in 19th century (Conesa et al., 2006). Therefore, high Pb values in this region were closely related to the historical mining activities (Martín et al., 2014). Comparing with the contents of the heavy metals in different areas, the contamination levels of metals in this study are relatively higher than the agricultural areas and similar with other industrial areas.

3.2 Spatial distribution of heavy metals in topsoil

Fig. 3 illustrates the spatial distribution of heavy metals in the study area. The highest contents of Hg (5.62 mg·kg^{-1}) and Cd (7.69 mg·kg^{-1}) were detected in the middle of the petrochemical industrial area (S46). The highest contents of Pb and As were found at S76 (454 mg·kg^{-1}), S79 (54.6 mg·kg^{-1}), respectively. These two sites were in the tank storage area for diesel, gasoline and fuel oil. Therefore, high contents of Pb and As in these two sites might be related to the leakage of diesel, gasoline and fuel oil when transshipment. In addition, the high Pb contents may also be attributed to the heavy motor vehicle traffic, because the industry area is very close to the road (Yao et al., 2016). The highest content of Ni (335 mg·kg^{-1}) was found at S103, located in the refinery area. It may come from the process of catalytic cracking of crude oil during refining and it has been verified by Jin (2003) in China, who reported that the crude oil became heavier after Fluidized Catalytic Cracking process due to the increasing contents of heavy metals such as Ni and vanadium (V). Likewise, Ma

(2014) found that in the eight petroleum refineries in Fujian, Luoyang, Jinxi and Yanchang, the contents of Ni in soils ranged from 170 to 1420 mg·kg^{-1}, which was the highest content among other heavy metals, indicating that Ni was the main pollutant in the petroleum refineries in China. Zhang et al. (2005) drew the similar conclusion by comparing different kinds of industries, including coking plants, phosphate fertilizer plants, refineries, aromatics plants and steel plants in Nanjing.

The highest contents of Cu (1030 mg·kg^{-1}) was at S95 which was very close to the maintenance workshop. Electric welding was the main task in the maintenance workshop. Cu is the most commonly used metal in the process of electric welding due to its good thermal conductivity, ductility, and corrosion resistance ranking second to aluminum (Sun and Ion., 1995; Ololade 2014). Therefore, long term welding can cause high Cu contents in the factory.

Nevertheless, the contents of six metals in the office and residence areas in the northwest parts were relatively low, ranging from 0.004 to 57 mg·kg^{-1}. This was because there were no industrial activities in this area. On the other hand, it illustrated the contribution of industrial activities to soil contamination. Similar to our results, Liu (2016) found that the contents of Cu, Ni, Pb and Cd ranged between 0.47 and 49 mg·kg^{-1} in Luoyang residence area, North China. Likewise, the contents of As, Cd, Cu, Hg, Ni and Pb were 0.09-49.4 mg·kg^{-1} in residence area in Baiyin of Northwest China (Li et al., 2008). These values were within the range of residence area of this study, but much lower than in oil refining and storage areas. The results indicated the heterogeneity of spatial distribution of heavy metals in topsoil of this petrochemical industrial area.

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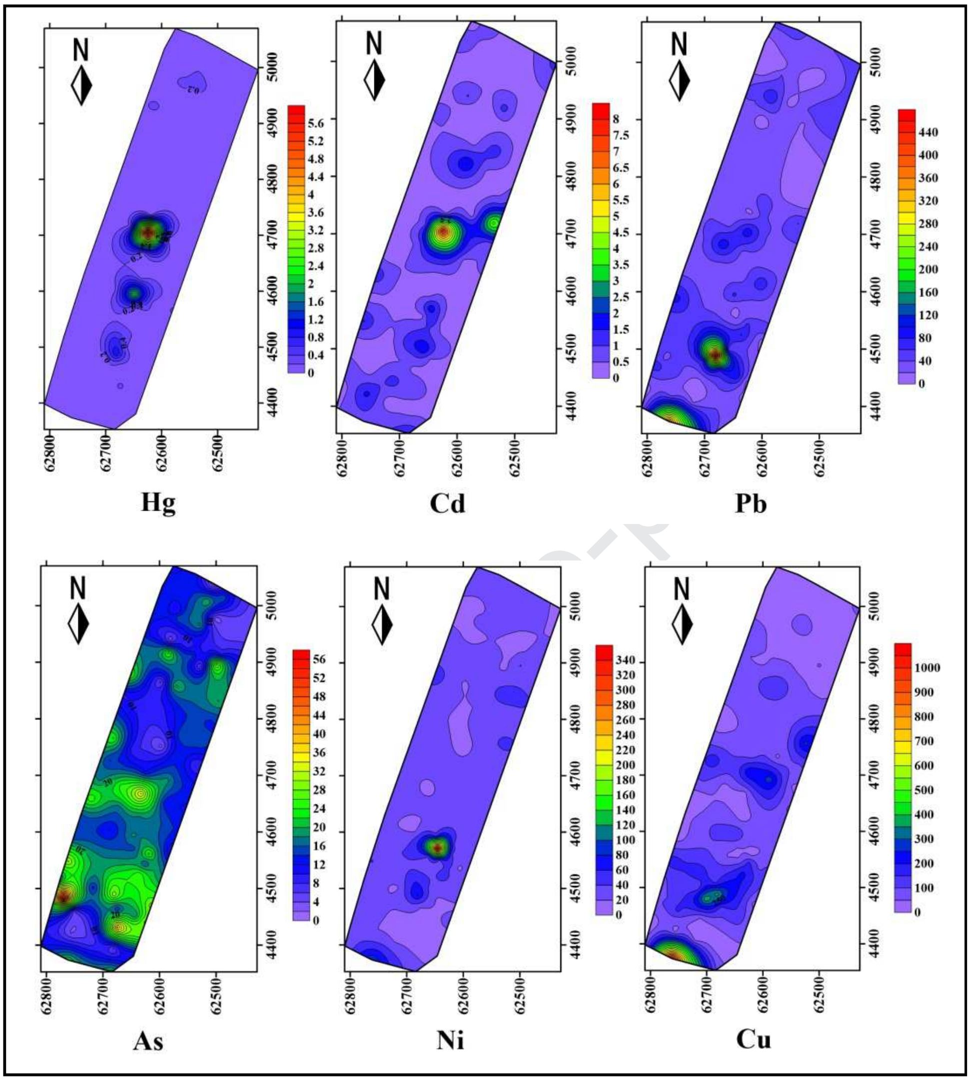

Fig.3. Spatial distribution of heavy metals in topsoil (<20cm) in Panlong petrochemical industrial area (mg·kg^{-1})

3.3 Migration of the heavy metals versus soil depths

In general, the heavy metals mainly accumulated in topsoil. In the topsoil, the contents of Hg, Cd, As, Pb, Cu and Ni were 5.62, 7.69, 54.6, 454, 1030 and 335 mg·kg^{-1}, respectively. The metals decreased with soil depth, particularly from the topsoil to the second soil layer (Fig. 4). In the second soil layer, the contents of heavy metals ranged from 0.28 to 117 mg·kg^{-1}, which 65.07-99.22% decreased comparing with that in the topsoil. But below the second soil layer, the contents of metals became stable except As. This indicated that the migration of the metals to deeper soil was in low quantities. This was mainly attributed to the short working time of the industry (from 2000 to 2007). Although the rainfall in Guangdong was heavy, the migration of the metals to deep soil with the flushing was weak. On the other hand, soil textures also affected the migration of the metals. It were coarse and fine sand- textures in top and second soil layers, which leads to the migration of metals in high quantities. Below the second soil layer, there was no obvious change for Hg (S46), Cd (S46), Pb (S76), Cu (S95) and Ni (S103). This was because of the fine sand-texture of the second layer versus muddy silt and silt-textures of the third and fourth layers. The permeability coefficient of muddy silt and silt were relatively small, prohibiting metals from migrating to the deeper soil layers. But for As (S79), the content in the third soil layer was 3.67 higher than that in the second layer which was different from other metals. This may be affected by the lateral infiltration of Lianhuashan River, which was quite close S79. The groundwater at S79 site was partly from Lianhuashan River with a level of 1.72 m. There were six wells in the factory. As was detected with a high concentration of 110 ug·L^{-1} in Well#2 adjacent to S79, while the concentration of As in other wells were relatively low (Support Information Table 4).

However, the migration of the heavy metals to the deep soil layers is affected by various environmental factors, such as the redox conditions, pH, contents of ions, and organic matters content of soil (Gutiérrez et al., 2016). Some of metals may form complexes with the soil particles (He et al., 2014; Gregory et al., 2018). Furthermore, competition for adsorption sites between complexes and metals might affect the adsorption of metals on soil particles. Therefore, the future study will consider all these factors to achieve a better understanding of the metals' migration versus soil depth.

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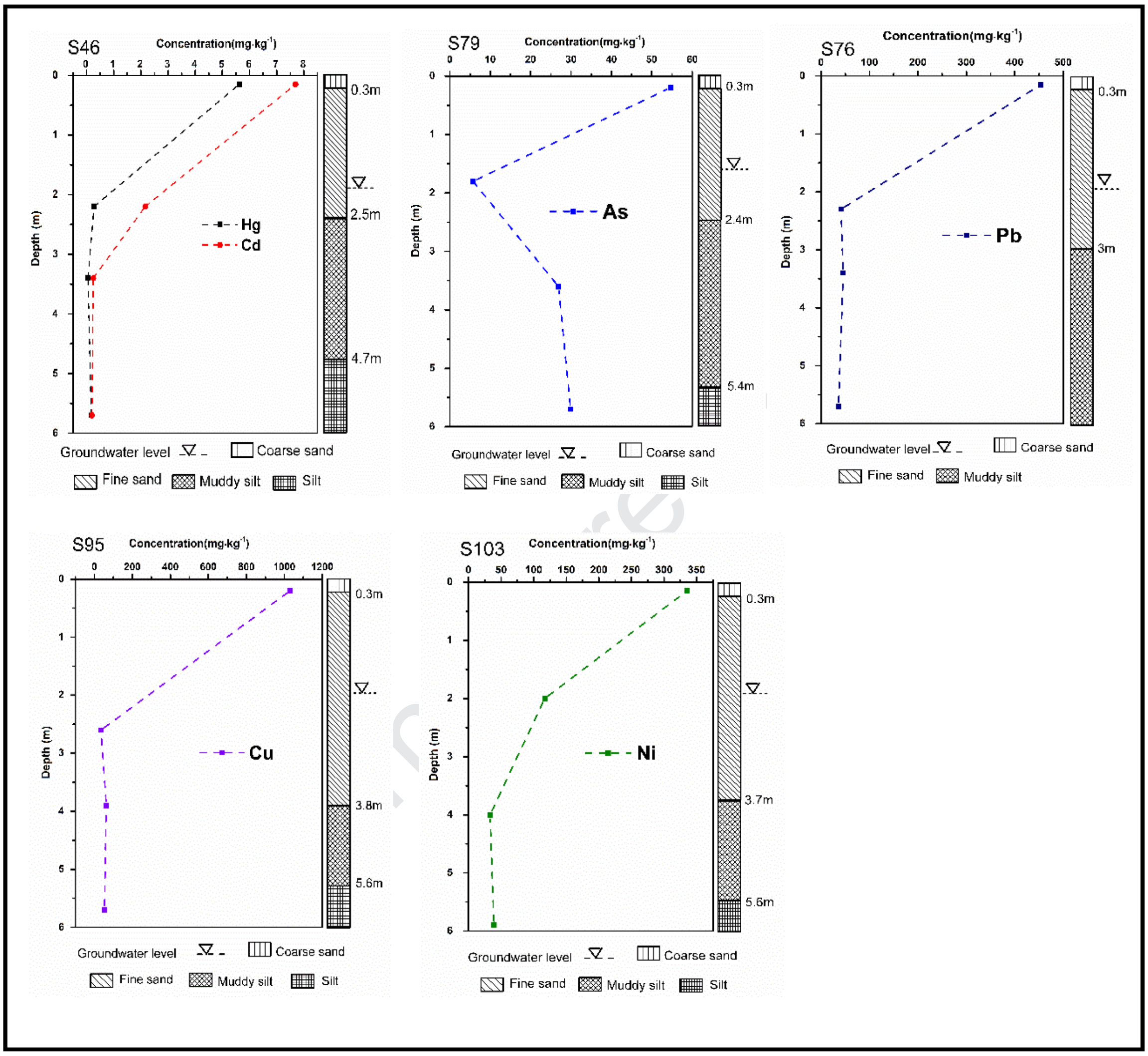

Fig.4. Contents of heavy metals versus soil depth in Panlong petrochemical industrial area

3.4 Source speculation of heavy metals

Basically, the potential sources of the metals at the 5 profiles, where the metals contents were highest, can be reflected by PCA. The two principal components together accounted for 77.82% of the total variation. The contribution of the first principal component (PC1) was 62.09% (Fig.5). Based on the coordinate axis, PC1 was mainly associated with the topsoil layers of S46-1, S76-1, and S95-1. In other

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words, these soils had significant positive loads on PC1, indicating that they likely originated from the same source. These sampling sites were located within the area of the storage tanks, thus the metals may come from the leakage of diesel, gasoline, and fuel oil when transported. However, S79-1 was very close to the sampling sites which were at the third and the second soil layers (except S103-2), indicating the metals at these sampling sites may have a similar source. As shown in Fig.4, the groundwater levels were shallow for all the 5 sampling sites. It indicated that the metals at these sites may be affected by the lateral infiltration of Lianhuashan River. Hence, it can be speculated that the source of heavy metals at S79-1 site may not only related to the industrial activities in the factory but also related to Lianhuashan River as well. The second principal component (PC2) explained 15.7% of the total variation and showed a significant loading of S103-1 and S103-2. S103 located in the refinery area. Refinery production processes involved the producing and distilling of diesel and gasoline, and the catalyzing, cracking or hydrofining of crude oil. Therefore, heavy metals in the topsoil of S103 may probably come from these production processes. Hence, petrochemical industry should be focused on heavy metal pollution in the aspect of crude oil leakage and the industrial production process.

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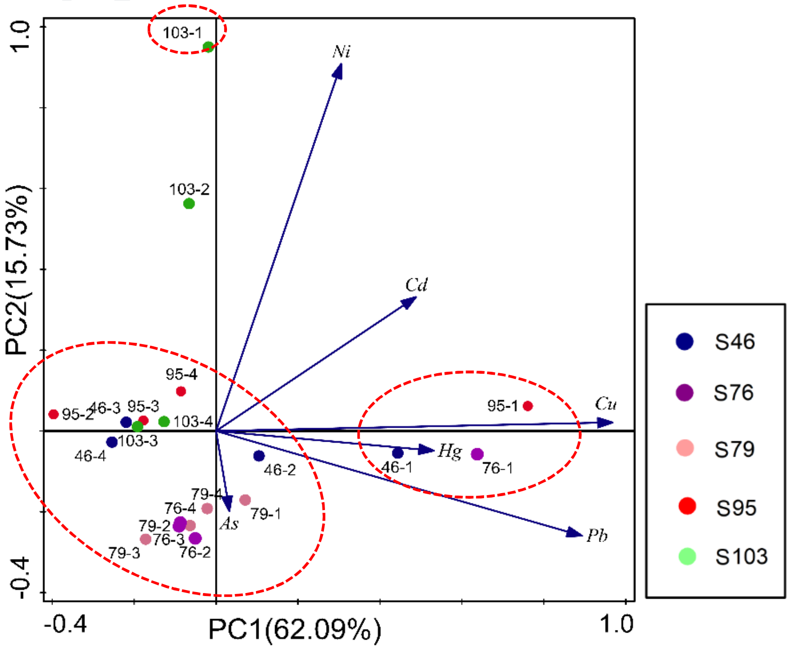

Fig. 5. Principal component analysis of the heavy metals in Panlong petrochemical industrial area

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Note: 46-1, 46-2, 46-3, 46-4 indicated the sampling sites at the first, second, third and the fourth soil layer, respectively. Likewise, 76-, 79-, 95- and 103- indicated the same meanings. In case of confusion, S was omitted before every sampling number.

3.5 Assessment of human health risks

The human health risks of the metals, which have the highest contents in the study area were assessed. As shown in Table 3, the total non-cancer human health risks of the metals induced through soil ingestion, soil dermal, and soil inhalation were 1.02×10^{-8}, 1.86×10^{-10}, and 3.14×10^{-11} a^{-1}, respectively, to adults and 6.82×10^{-8}, 3.10×10^{-10}, and $2.62\times10^{-10}a^{-1}$, respectively, to children. While, the total cancer health risks induced through soil ingestion, soil dermal, and soil inhalation were 6.75×10^{-7}, 2.51×10^{-7}, and 2.69×10^{-10} a^{-1} respectively for adults, and 1.80×10^{-6}, 1.67×10^{-7} and 8.97×10^{-10} a^{-1}, respectively for children. The total non-cancer health risks of the metals induced through the three exposure pathways were 1.05×10^{-8} $a^{-1}$and 6.88×10^{-8} a^{-1} for adults and children respectively, which were within the limit of USEPA (2004). However, the cancer risks for children induced by Cd (1.97×10^{-6} a^{-1}) exceeded the limit of USEPA (2004). Furthermore, the cancer risks induced solely through soil ingestion for children ($1.8\times10^{-6}a^{-1}$) also exceeded the limit of USEPA (2004), but not ICRP ($5\times10^{-5}a^{-1}$). For the cancer metals, the health risk induced by As was greater than that induced by Cd. The non-cancer health risks to children were 6.69 (soil ingestion), 1.67 (soil derma), and 8.33 (soil inhalation) times higher than those to adults, while the cancer health risks induced by As and Cd to children were 2.67 (soil ingestion), 6.67 (soil derma) and 3.33 (soil inhalation) times higher than those to adults. This finding may be attributed to the fact that children have higher likelihood to expose to heavy metals through hand-finger sucking. This is regarded as one of the critical exposure pathways of soil heavy metals to children (White and Marcus, 1998). Similar findings were reported by Rasmussen et al. (2001) and Chen et al. (2015).

In terms of the total risks of human’ exposure to heavy metals, the exposure pathways were ordered as: ingestion>derma>inhalation. The non-cancer risks induced by soil ingestion accounted for the highest proportion of the total risks, which were

89.76-99.2% and 97.21-99.79%, for adults and children, respectively. The cancer-risks induced by soil ingestion accounted for 63.12-99.94% and 89.21-99.98%, for adults and children, respectively. This finding was consistent with the results of previous researches (Chabukdhara and Nema, 2013; Wang et al., 2019). Similarly, Olawoyin et al. (2012) found that the human risks induced through ingestion was 23 times greater than soil inhalation in Niger delta. These authors also pointed that the human risks induced through dermal contact was 3 times greater than ingestion of soil. Likewise, Boban et al. (2015) found that the dermal absorption was the most important exposure pathway for As, Cd, Cu, and Ni for children. These difference might be attributed to different calculation formulas. For instance, Olawoyin et al. (2012) employed hazard index (HI) to assess the health risks.

Table 3. Human health risks to heavy metals' exposure through different pathways in Panlong petrochemical industrial area

		Ingestion		Derma		Inhalation		Health Risks	
		Adults	Children	Adults	Children	Adults	Children	Adults	Children
Non-cancer risks（R^n）	Cd	1.13E-10	7.52E-10	9.00E-13	1.50E-12	6.64E-15	5.53E-14	1.14E-10	7.54E-10
	As	2.67E-09	1.78E-08	2.13E-11	3.55E-11	1.57E-13	1.31E-12	2.69E-09	1.78E-08
	Hg	2.75E-10	1.83E-09	3.13E-11	5.22E-11	5.66E-14	4.72E-13	3.06E-10	1.89E-09
	Pb	1.89E-09	1.26E-08	1.01E-10	1.69E-10	1.11E-13	9.28E-13	1.99E-09	1.28E-08
	Ni	2.46E-10	1.64E-09	7.26E-12	1.21E-11	1.40E-14	1.17E-13	2.53E-10	1.65E-09
	Cu	5.04E-09	3.36E-08	2.41E-11	4.02E-11	3.11E-11	2.59E-10	5.09E-09	3.39E-08
	Total	1.02E-08	6.82E-08	1.86E-10	3.10E-10	3.14E-11	2.62E-10	1.05E-08	6.88E-08
Cancer-risks（R^C）	Cd	2.46E-07	6.56E-07	1.22E-10	8.14E-11	1.49E-11	4.98E-11	2.46E-07	6.56E-07
	As	4.29E-07	1.14E-06	2.51E-07	1.67E-07	2.54E-10	8.47E-10	6.80E-07	1.31E-06
	Total	6.75E-07	1.80E-06	2.51E-07	1.67E-07	2.69E-10	8.97E-10	9.26E-07	1.97E-06

4. Conclusions

This study investigated the spatial distribution of heavy metals and the related potential health risks to humans in a retired petrochemical industrial area in Guangzhou, South China. Based on our study, the contents of heavy metals in topsoil were all below the limits of Land use of Category Ⅰ of China's national standards (GB36600-2018). The spatial distribution of heavy metals in topsoil was obviously heterogeneous and largely attributed to the industrial activities involving in refining of

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the crude oil and leakage of the oil. Lateral infiltration of Lianhuashan River may also have an influence on the distribution of the metals. The cancer risk solely induced through soil ingestion for children exceeded the limit of USEPA (10^{-6} a^{-1}). This study indicated that not only petroleum hydrocarbon but also heavy metals can cause soil contamination in an industrial area. It provides a novel cognition for the study of contamination in petrochemical industries. Therefore, appropriate measures have to be taken to substantially improve the soil quality and reduce the health risks to the local humans. It is worth mentioning that the total risks from a sum of single metals in this study might be lower than the actual risks, considering some unknown synergy effects among various heavy metals. Consequently, the synergy effects of the metals need further attention in terms of the assessment of human health risks in the future.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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1. The spatial distribution of heavy metals was related to the industrial production process.
2. Petroleum refining and transshipment were the main processes that cause contamination of soil heavy metals.
3. The migration of heavy metals versus soil was not only related to the industrial activities but also affected by the lateral infiltration of the river.
4. Cancer risks solely induced by As through soil ingestion to children exceeded the limit of USEPA.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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