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Contamination assessment, source apportionment and health risk assessment of heavy metals in paddy soils of Jiulong River Basin, Southeast China

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To trace the sources and evaluate the health risks of heavy metals in paddy soils of Jiulong River Basin, seventy-one samples of paddy soils were collected in July 2017. The heavy metals contents were determined using inductively coupled plasma mass spectrometry (ICP-MS) and atomic fluorescence spectrophotometry (AFS). The geo-accumulation index (I_{geo}) and potential ecological risk index (RI) methods were applied to evaluate the contamination of heavy metals, principal component analysis (PCA) and absolute principal component scores-multiple linear regression (APCS-MLR) were applied to trace the sources, and dose-response model was applied to assess the health risks to the human body. The results indicated that the paddy soils were moderately to heavily polluted by Cd and slightly polluted by Hg, Pb, As and Zn. Heavy metals in paddy soils presented considerable to high potential ecological risk, mostly contributed by Cd and Hg with contribution rates of 59.4% and 26.2%, respectively. The heavy metals contaminating paddy soils were derived from natural sources, agricultural activities, industrial discharge, coal combustion and unidentified sources, with source contribution rates of 31.37%, 24.87%, 19.65%, 18.05% and 6.06%, respectively. The heavy metals in paddy soils presented carcinogenic risks which humans can tolerate and no non-carcinogenic risks. The total non-carcinogenic risks mainly derived from agricultural activities and coal combustion, with contribution rates of 62.16% and 20.21%, respectively, while the total carcinogenic risks mainly derived from natural sources and industrial discharge, with contribution rates of 51.17% and 18.98%, respectively.

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1 Introduction

Heavy metals have drawn increasing attention from environmentalists because of their persistence, non-degradability and bioaccumulative characteristic.¹ The contents of heavy metals in the environment have increased with the rapid economic development in China in the past decades.² The soil can act as both a source and sink for heavy metals. Heavy metals accumulated in soils can cause adverse effects on the human body through direct routes, such as ingestion of soil, inhalation of dust particles and dermal absorption,³ and indirect routes, such as the food chain.⁴ Agricultural soil is the basis for the development of agricultural economy. It is of great significance to study the contamination characteristics, source appointment and health risk assessment of heavy metals in agricultural soils.

In the past decades, methods for evaluating heavy metals contamination have been developed by many environmental scientists.⁵ The I_{geo} method and RI method have been widely used to evaluate the contamination of heavy metals in soils and sediments.^{6–9} It is reported that the combination of I_{geo} method

and RI method can improve the relative accuracy of assessment results by considering the lithology, toxicity and comprehensive effect of heavy metals together.¹⁰ The dose-response model, recommended by USEPA, has been widely applied to soils to evaluate the human health risk (non-carcinogenic or carcinogenic) due to heavy metals.¹¹

It is important to identify the sources of heavy metals for prevention and control of heavy metal pollution. Multivariate statistical analyses have been widely used to trace the sources of heavy metals.^{12–16} Principal component analysis (PCA) is a commonly used tool. Absolute principal component scores-multiple linear regression (APCS-MLR) has been widely applied for quantitative analysis of pollution sources based on principal component analysis (PCA).^{17,18}

Jiulong River Basin is located in the southwest area of Fujian Province and includes the cities Longyan, Zhangzhou and Xiamen. The safety of the environment around Jiulong River Basin is important to the Western Taiwan Straits Economic Zone.¹⁹ It is reported that there are more than 3.8 million inhabitants in the basin.²⁰ It is also reported that Jiulong River has been polluted by heavy metals due to human activity and rapid development of industry and agriculture.^{19,21,22} Fujian Province is a major rice-producing province in southern China. The Jiulong River Basin plays an important role in the economic development of Fujian Province, contributing about a quarter of

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its GDP. Taking into account the importance of the Jiulong River Basin, it is necessary to study the contamination and effects of heavy metals in paddy soils of this area.

In this study, the contents of eight heavy metals in the paddy soils were analyzed with the following aims: (i) to assess the contamination of heavy metals in the paddy soils; (ii) to trace the potential sources of heavy metals and quantify the contribution rates of the identified sources; (iii) to assess the human health risks and quantify the contribution rates of the identified sources.

2 Materials and methods

2.1 Soil sampling and preparation

Surface paddy soil samples of depth 0–20 cm were collected from seventy-one sites in Jiulong River Basin, Southeast China (Fig. 1) in July 2017. Five sub-samples were taken randomly around the area (10 m × 10 m) of each sample site and mixed into a composite sample. The paddy soils (about 1 kg per sample) were taken to a clean laboratory and dried. They were then ground with an agate mortar and sieved with a 200 mesh nylon sieve to remove impurities.

2.2 Determination of heavy metals and quality control

Approximately 0.2 g of paddy soil was placed in a 30 mL Teflon digestion vessel and microwave digested with 2 mL HF, 2 mL HCl and 6 mL HNO₃. The contents of heavy metals Cr, Ni, Cu, Zn, Cd, and Pb were determined by ICP-MS (Agilent 7700x, Agilent Technologies, USA), while for Hg and As, AFS (AF-640, Ruili Analytical Instrument, China) was used. Blank and soil sample measurements were replicated 3 times. A standard reference (China GBW07405) was analyzed alongside the soil samples for quality control of the analytical method. The recovery rates of all heavy metals were 91.1–108.2% and the RSD values were all less than 5%.

2.3 Analytical method

2.3.1 Contamination assessment method. The I_{geo} method was proposed by Müller.²³ It is widely applied to evaluate the pollution level of a single heavy metal in soils and sediments.^{6,9} The value of I_{geo} was calculated by formula (1):

$$I_{\text{geo}} = \log_2 \left[\frac{C_n}{1.5 \times B_n} \right] \quad (1)$$

where I_{geo} was the geo-accumulation index of heavy metal n , C_n was the determined content of heavy metal n in paddy soil and B_n was the background value. The background value in Fujian soils was taken from a previous study.²⁴ The classifications of I_{geo} are listed in Table 1.

The RI method was proposed by Hakanson.²⁵ It is widely used to evaluate the potential ecological risk of heavy metals in soils and sediments.^{8,26} The values of E_r^i and RI were calculated by formulas (2) and (3):

$$E_r^i = E_r^i \times \frac{C_i}{C_b^i} \quad (2)$$

$$RI = \sum_{i=1}^n E_r^i \quad (3)$$

where E_r^i was the potential ecological risk index of heavy metal i , C_i was the determined content of heavy metal i in paddy soil and C_b^i was the background value²⁴ and T_r^i the biological toxic response factor of heavy metal i . The values of T_r^i were as follows: 1 for Zn; 2 for Cr; 5 for Cu, Ni and Pb; 10 for As; 30 for Cd; 40 for Hg.²⁶ RI is the comprehensive index of all heavy metals in this study. The RI standard was adjusted based on the species of examined heavy metal according to Yu *et al.*²⁶ The classifications of E_r^i and RI are listed in Table 1.

2.3.2 Source apportionment method. The correlation coefficients of heavy metals can be used to indicate the inter-relationship between them. It was reported that heavy metals which have significantly positive correlations may have similar sources and migration routes.²⁷ PCA is a useful tool for source appointment of heavy metals according the mathematical process of orthogonal transformation.²⁸

APCS-MLR was proposed by Thurston and Spengler.²⁹ It is widely used for quantitative analysis of identified sources based on PCA.^{17,18} The regression equation is shown as formula (4):

$$C_i = (r_0)_i + \sum_{k=1}^k (r_{ki} \times \text{APCS}_k) \quad (4)$$

where C_i was the determined content of the heavy metal i in paddy soils, $(r_0)_i$ is the constant term of multiple linear regressions, r is the regression coefficient and APCS is the absolute principle component score. The subscript i represents the heavy metal and k represents the potential source.

2.3.3 Health risk assessment method. Local residents can be exposed to heavy metals in soils through ingestion of soil, inhalation of dust particles and dermal absorption.³⁰ The health risk assessment estimates the adverse health effects on a human exposed to chemical contamination.¹¹ The average daily intake (ADI), hazard quotients of non-carcinogenic (HI and HQ) and carcinogenic risk (TCR and CR) through three exposure pathways were calculated by formulas (5)–(9).^{31–33}

$$\text{ADI}_{\text{ingestion}} = C_{\text{soil}} \times \frac{\text{IngR}_{\text{soil}} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times 10^{-6} \quad (5)$$

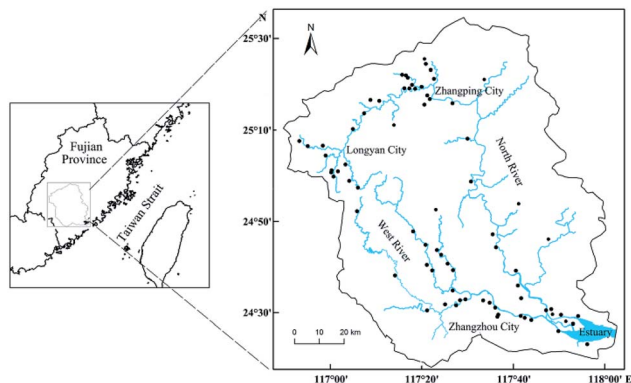


Fig. 1 Sampling locations of paddy soils from Jiulong River Basin.



Table 1 The classifications of geo-accumulation index (I_{geo}) and potential ecological risk index (RI)

| Index | Category | Degree |
|---|---|--|
| Geo-accumulation index (I_{geo}) | $I_{\text{geo}} < 0$ | Non-pollution |
| | $0 \leq I_{\text{geo}} < 1$ | Slight pollution |
| | $1 \leq I_{\text{geo}} < 2$ | Moderate pollution |
| | $2 \leq I_{\text{geo}} < 3$ | Moderate to heavy pollution |
| | $3 \leq I_{\text{geo}} < 4$ | Heavy pollution |
| | $4 \leq I_{\text{geo}} < 5$ | Heavy to extreme pollution |
| | $I_{\text{geo}} \geq 5$ | Extreme pollution |
| Potential ecological risk index (RI) | $E_r^i < 40$, $RI < 110$ | Low potential ecological risk |
| | $40 \leq E_r^i < 80$, $110 \leq RI < 220$ | Moderate potential ecological risk |
| | $80 \leq E_r^i < 160$, $220 \leq RI < 440$ | Considerable potential ecological risk |
| | $160 \leq E_r^i < 320$, $RI \geq 440$ | High potential ecological risk |
| | $E_r^i \geq 320$ | Extreme potential ecological risk |

$$ADI_{\text{inhalation}} = C_{\text{soil}} \times \frac{\text{InhR}_{\text{soil}} \times EF \times ED}{PEF \times BW \times AT} \quad (6)$$

$$ADI_{\text{dermal}} = C_{\text{soil}} \times \frac{SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (7)$$

$$HI = \sum_{i=1}^i HQ_i = \sum_{i=1}^i \frac{ADI_i}{RfD_i} \quad (8)$$

$$TCR = \sum_{i=1}^i CR_i = \sum_{i=1}^i (ADI_i \times SF_i) \quad (9)$$

where $AD_{\text{ingestion}}$, $AD_{\text{inhalation}}$ and AD_{dermal} were the average daily intakes through the three exposure pathways, $\text{IngR}_{\text{soil}}$ was the ingestion rate of soil, $\text{InhR}_{\text{soil}}$ was the inhalation rate of soil and C_{soil} was the determined content of the heavy metal n in paddy soils. EF was the exposure frequency, ED was the exposure duration, BW was the average body weight, AT was the average exposure time, PEF was the emission factor of soil, SA was the area of exposed skin, AF was the adherence factor of skin and ABS was dermal absorption factor. HI was the total

hazard index of several heavy metals; HQ was the hazard quotient of a single heavy metal. When the value of HI or HQ is lower than 1, there is no non-carcinogenic risk. RfD was the reference dose of non-carcinogenic heavy metals, TCR was the total cancer risk of several heavy metals, CR was the carcinogenic risk of a single heavy metal and SF was the carcinogenicity slope factor. When $10^{-6} < TCR$ (or CR) $< 10^{-4}$, there is carcinogenic risk which humans can tolerate, whereas when $10^{-4} < TCR$ (or CR), there is unacceptable carcinogenic risk. The selection of exposure parameters can affect the accuracy of the results. The parameters used in formulas (5)–(9) were taken from highly cited studies conducted in China and are listed in Tables 2 and 3.

3 Results and discussion

3.1 Contents and spatial distribution of heavy metals

The statistics parameters of heavy metals are listed in Table 4. The mean contents of heavy metals were Cr: 61.80 ± 21.79 , Ni: 12.85 ± 5.17 , Cu: 35.05 ± 15.56 , Zn: 151.71 ± 63.52 , As: 10.22 ± 2.22 , Cd: 0.34 ± 0.16 , Pb: 72.29 ± 27.64 , and Hg: 0.17 ± 0.04 mg

Table 2 The parameters used in the calculation of average daily intake (ADI)

| Parameter | Interpretation | Units | Values | | | Reference |
|-----------|---------------------------------|---|--------------------|--------------------|--------------------|-----------|
| | | | Adult male | Adult female | Children | |
| IngR | Ingestion rate | mg per day | 25 | 25 | 24 | 11 |
| EF | Exposure frequency | Day per year | 345 | 345 | 345 | |
| ED | Exposure duration | Year | 70 | 70 | 18 | |
| BW | Body weight | kg | 67.55 | 57.59 | 29.30 | |
| AT | Average time (non-carcinogenic) | Day | $ED \times 365$ | $ED \times 365$ | $ED \times 365$ | |
| AT | Average time (carcinogenic) | Day | 25 500 | 25 500 | 25 500 | |
| SA | Exposed skin area | m^2 | 0.169 | 0.153 | 0.086 | |
| AF | Adherence factor | $\text{mg} (\text{cm}^{-2} \text{ day}^{-1})$ | 0.49 | 0.49 | 0.65 | |
| ABS(Cd) | Absorption factor | | 0.14 | 0.14 | 0.14 | |
| ABS(Cr) | | | 0.04 | 0.04 | 0.04 | |
| ABS(As) | | | 0.03 | 0.03 | 0.03 | |
| ABS(Hg) | | | 0.05 | 0.05 | 0.05 | |
| ABS(Pb) | | | 0.006 | 0.006 | 0.006 | |
| ABS(Cu) | | | 0.1 | 0.1 | 0.1 | |
| ABS(Zn) | | | 0.02 | 0.02 | 0.02 | |
| ABS(Ni) | | | 0.35 | 0.35 | 0.35 | |
| InhR | Inhalation rate | $\text{m}^3 \text{ d}^{-1}$ | 16.57 | 12.80 | 7.63 | 34 |
| PEF | Particle emission factor | $\text{m}^3 \text{ kg}^{-1}$ | 1.36×10^9 | 1.36×10^9 | 1.36×10^9 | |



Table 3 The reference doses (RfD) and slope factors (SF) used in health risk assessment^a

| Elements | RfD/mg (kg d) ⁻¹ | | | SF/(kg d) mg ⁻¹ | | |
|----------|------------------------------------|------------------------------------|------------------------------------|----------------------------|--------------------|--------------------|
| | Ingestion | Dermal | Inhalation | Ingestion | Dermal | Inhalation |
| Cd | 1.00×10^{-3} ^a | 2.50×10^{-5} ^a | 5.71×10^{-5} ^b | — | — | 6.30 ^b |
| Cr | 1.50×10^{-0} ^a | 1.95×10^{-2} ^a | 2.86×10^{-5} ^b | 0.501 ^b | 0.20 ^b | 0.42 ^b |
| As | 3.00×10^{-4} ^a | 3.00×10^{-4} ^a | 3.00×10^{-4} ^b | 1.50 ^b | 3.66 ^b | 0.151 ^b |
| Hg | 1.60×10^{-4} ^a | 1.60×10^{-4} ^a | 8.57×10^{-5} ^c | — | — | — |
| Pb | 1.40×10^{-4} ^a | 1.40×10^{-4} ^a | — | — | — | — |
| Cu | 4.00×10^{-2} ^a | 4.00×10^{-2} ^a | — | — | — | — |
| Zn | 3.00×10^{-1} ^a | 3.00×10^{-1} ^a | 3.00×10^{-1} ^b | — | — | — |
| Ni | 2.00×10^{-2} ^a | 8.00×10^{-4} ^a | 2.06×10^{-2} ^b | 1.70 ^b | 0.425 ^b | 0.901 ^b |

^a The superscripts a, b and c indicate data cited from Li *et al.*,¹¹ Cao *et al.*,³⁵ and Chen *et al.*,³⁴ respectively.

Table 4 Statistics parameters (mg kg⁻¹) of heavy metals in paddy soils of Jiulong River Basin

| Element | Cr | Ni | Cu | Zn | As | Cd | Pb | Hg |
|------------|--------|-------|-------|--------|-------|------|--------|------|
| Max | 110.93 | 25.52 | 81.32 | 437.90 | 16.88 | 0.92 | 168.10 | 0.26 |
| Min | 41.36 | 5.85 | 19.32 | 83.16 | 6.21 | 0.12 | 40.16 | 0.11 |
| Mean | 61.80 | 12.85 | 35.05 | 151.71 | 10.22 | 0.34 | 72.29 | 0.17 |
| SD | 21.79 | 5.17 | 15.56 | 63.52 | 2.22 | 0.16 | 27.64 | 0.04 |
| CV | 0.35 | 0.40 | 0.44 | 0.42 | 0.22 | 0.48 | 0.38 | 0.24 |
| Background | 41.30 | 13.50 | 21.60 | 82.70 | 5.78 | 0.05 | 34.90 | 0.08 |

kg⁻¹. The background values of heavy metals in Fujian soils were taken from literature.²⁴ In this study, the mean contents of heavy metals in paddy soils were higher than the background values. Compared to the limit values of Chinese environmental quality standards for soils (GB15618-2018), the excess rates of Cu, Zn and Cd were 14.1%, 16.9% and 49.3%, respectively. The coefficient variances of all heavy metals were between 0.2 and 0.5, which indicated that all the heavy metals showed moderate variability.³⁶

Kriging interpolation was used to analyze the spatial distribution trend of heavy metals in paddy soils and the results are shown in Fig. 2. Higher contents of Cr, Ni, Cu, Zn and Cd appeared in North River (Longyan City); higher contents of Pb appeared in West River; higher contents of Hg and As appeared in Estuary. The spatial distributions of heavy metals may be the consequence of various sources of pollution, but more information about the pollution sources needs to be explored in depth using different statistical analysis.

3.2 Contamination assessment of heavy metals

The values of I_{geo} and E_r calculated by formulas (1) and (2) are shown in Fig. 3. The mean I_{geo} values followed a sequence of Cd > Hg > Pb > Cu > As > Co > Zn > Cr > V > Ni. The mean I_{geo} of Cd was 1.9, with 35.2% of the samples presenting moderate to heavy pollution ($2 \leq I_{\text{geo}} < 3$) and 54.9% of the samples presenting moderate pollution ($1 \leq I_{\text{geo}} < 2$). The mean I_{geo} of Hg was 0.42, with 7.0% of the samples presenting moderate pollution ($1 \leq I_{\text{geo}} < 2$) and 88.7% of the samples presenting slight pollution ($0 \leq I_{\text{geo}} < 1$). The mean I_{geo} of Pb was 0.38, with 11.3% of the samples presenting moderate pollution ($1 \leq I_{\text{geo}} < 2$) and 70.4% of the samples presenting slight pollution ($0 \leq I_{\text{geo}} < 1$). The mean I_{geo} of As and Zn were 0.21 and 0.19, respectively,

with most of the samples presenting slight pollution ($0 \leq I_{\text{geo}} < 1$). The mean I_{geo} of Cu, Cr and Ni were 0.00, -0.08 and -0.77, respectively, with most of the samples presenting non-pollution ($I_{\text{geo}} < 0$).

The mean E_r values followed a sequence of Cd > Hg > As > Pb > Cu > Co > Ni > Cr > V > Zn. The mean E_r of Cd was 187.6, with 14.1% of the samples presenting extreme risk, 35.2% of the samples presenting high risk and 46.5% of the samples presenting considerable risk. The mean E_r of Hg was 82.6, with 42.3% of the samples presenting considerable risk and 57.7% of the samples presenting moderate risk. All the E_r of As, Pb, Cu, Ni, Cr and Zn were lower than 40, presenting low risk. The comprehensive potential ecological risk index (RI) of eight heavy metals ranged from 169.0 to 688.9 with the mean value of 316.0. 12.7% of the samples presented high potential ecological risk ($RI \geq 440$) and 78.9% of the samples presented considerable potential ecological risk ($220 \leq E_r < 440$). The contribution rates of different heavy metals to the comprehensive potential ecological risk index were calculated and it was found that the comprehensive potential ecological risk was mostly contributed by Cd and Hg with contribution rates of 59.4% and 26.2%, respectively.

The assessment results of I_{geo} method and RI method were basically consistent, but some differences still exist. For example, Pb was assessed to be slight to moderate pollution by I_{geo} , while it was assessed to be low risk by RI. Hg was assessed to be slight to moderate pollution by I_{geo} , while it was assessed to be moderate to considerable risk by RI. These results may be attributed to the different toxicities of heavy metals.³⁷ The I_{geo} method focused on the lithology and a single heavy metal, while the RI method considered the toxicities and comprehensive effects of more than one heavy metal. The combination of I_{geo} method and RI method can make the evaluation results more accurate by considering the lithology, toxicity and comprehensive effect of heavy metals together.

3.3 Source apportionment of heavy metals

The Pearson's correlations matrix between the contents of heavy metals is listed in Table 5. There were significant correlations between Cr, Ni, Cu, and Zn and significant correlations between Cd, Zn and Pb. These results indicated that each group may have similar sources.



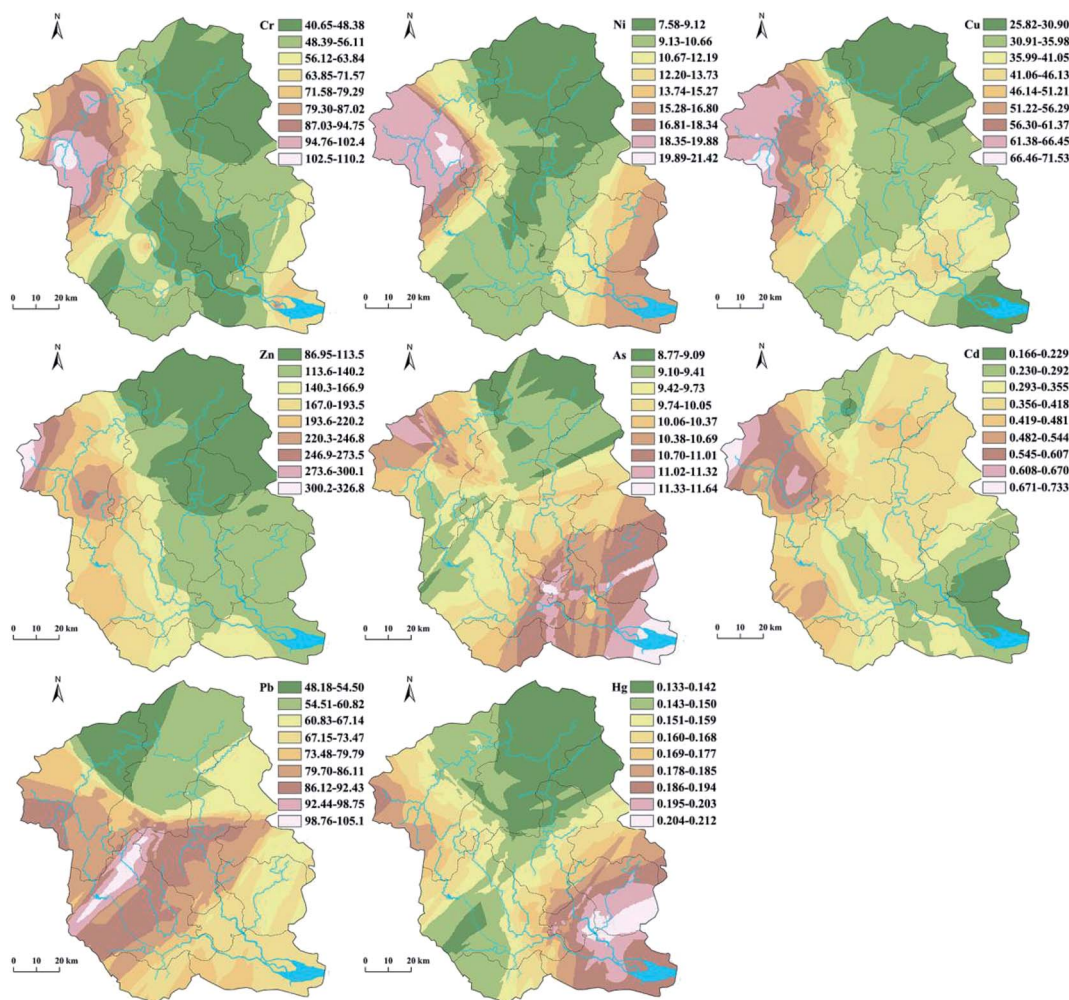


Fig. 2 Spatial distributions of heavy metals in paddy soils of Jiulong River Basin.

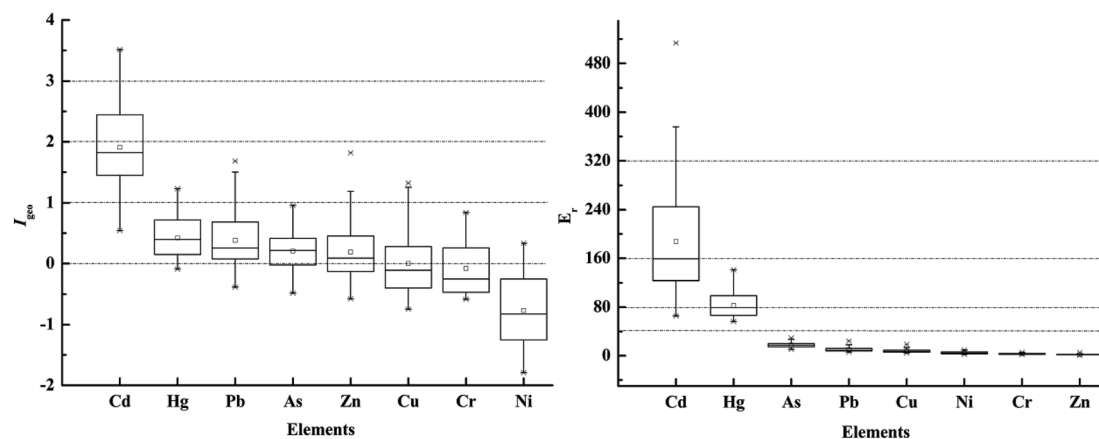


Fig. 3 Results of geo-accumulation index (I_{geo}) and potential ecological risk index (E_r) evaluations of heavy metals in paddy soils.

For further analysis, PCA was used to trace the sources of heavy metals and the results are listed in Table 6. The values of heavy metal content were suitable for PCA analysis, according to the values of KMO (0.643) and Bartlett's test (0.000). As shown in Table 6, four principal components, which comprise 83.55% of

the total variance, were extracted and they each explain 40.09%, 18.78%, 13.95 and 10.73% of the total variance. PC1 is heavily weighted by Cr, Ni and Cu, which indicated that these elements may be derived from the same sources. The contents of Cr, Ni and Cu were more similar to the background values of Fujian



Table 5 Pearson's correlations matrix between heavy metal concentrations^a

| | Cr | Ni | Cu | Zn | As | Cd | Pb | Hg |
|----|---------|---------|---------|---------|-------|---------|-------|----|
| Cr | 1 | | | | | | | |
| Ni | 0.801** | 1 | | | | | | |
| Cu | 0.562** | 0.476** | 1 | | | | | |
| Zn | 0.385** | 0.369** | 0.531** | 1 | | | | |
| As | 0.022 | 0.196 | 0.168 | 0.283* | 1 | | | |
| Cd | 0.393** | 0.302* | 0.438** | 0.783** | 0.229 | 1 | | |
| Pb | −0.001 | 0.058 | −0.035 | 0.468** | 0.133 | 0.487** | 1 | |
| Hg | −0.036 | 0.208 | 0.107 | 0.081 | 0.12 | −0.052 | 0.067 | 1 |

^a **significant correlation ($p < 0.01$); *significant correlation ($p < 0.05$).

Table 6 Rotated component matrix of principal component analysis for heavy metals

| Element | Principal components | | | |
|---------|----------------------|--------------|--------------|--------------|
| | PC1 | PC2 | PC3 | PC4 |
| Cr | 0.920 | 0.097 | −0.104 | −0.079 |
| Ni | 0.855 | 0.072 | 0.058 | 0.225 |
| Cu | 0.758 | 0.171 | 0.196 | −0.016 |
| Zn | 0.426 | 0.769 | 0.225 | −0.007 |
| As | 0.060 | 0.122 | 0.966 | 0.076 |
| Cd | 0.372 | 0.803 | 0.153 | −0.163 |
| Pb | −0.167 | 0.868 | −0.048 | 0.147 |
| Hg | 0.072 | 0.016 | 0.073 | 0.974 |

source, which indicated that PC1 may be related to natural sources. PC2 is heavily weighted by Zn, Cd and Pb, which indicated that these elements may be derived from the same sources. Zn, Cd and Pb are commonly found in fertilizers and pesticides and Cd can generally be used as a marker element for agricultural activities, such as pesticides and chemical fertilizers.^{38,39} Pb may also be derived from vehicle exhaust sources.⁴⁰ However, it has been reported that vehicle exhaust was not the main source of Pb in the sediments of Jiulong River Basin.¹⁹ Jiulong River Basin is an agricultural river network.⁴¹ The research of Li⁴² indicated that the large-scale use of pesticides and fertilizers is one of the main causes of water pollution in the Jiulong River Basin. Furthermore, Zhang *et al.*²¹ indicated that the contents of Cd, Pb and Zn in the water of Jiulong River were mainly affected by geochemistry and agricultural activities. Jiulong River is the main source of agricultural water for the basin. Based on the above discussion, PC2 may be related to agricultural activities. PC3 is heavily weighted by As. It has been reported that As may be related to industrial activities such as industrial discharge and sewage sludge.⁴³ It was reported that Xiamen City, located in the Jiulong River estuary area, has the third highest number of heavy metal enterprises.⁴⁴ There are paper mills, pharmaceutical factories, chemical plants and metal processing factories located in the downstream and estuary of Jiulong River. The discharges from these industrial factories could contribute to As pollution in paddy soils. In this study, the higher concentrations of As appeared in the downstream and estuary watershed areas (Fig. 2). Therefore, PC3 may

be related to industrial discharges. PC4 is heavily weighted by Hg. It was reported that coal combustion is an important source of Hg emission in China.⁴⁵ According to previous research, coal combustion is also an important source of Hg in the sediments of Jiulong River.⁴⁶ In this study, the higher concentrations of Hg appeared in the estuary watershed (Fig. 2), where a coal-fired power plant was located. Therefore, PC4 may be related to coal combustion.

Based on the results of PCA, APCS-MLR was used to quantify the contribution rates of each heavy metal source and the results are shown in Fig. 4. Natural sources contributed most to Cr, Ni and Cu, with contribution rates of 68.74%, 60.23% and 60.76%, respectively. Agricultural activities contributed most to Zn, Cd and Pb, with contribution rates of 47.43%, 54.63% and 66.33%, respectively. Industrial discharge contributed most to As with a contribution rate of 74.51% and coal combustion contributed most to Hg with a contribution rate of 89.03%. The unidentified sources may be a mixture of traffic sources, domestic sewage and other potential sources.

3.4 Health risk assessment of heavy metals

Heavy metals contaminating the soil can pose health risks to the human body through several pathways. One pathway is through the food chain (soil-crop-human body). There have been several previous studies of the health risks of heavy metals in rice grown in Fujian Province.^{47–49} The results indicated that the accumulation of Cd and Pb in rice posed potential health risks to consumers of some areas in Fujian Province. The other pathway is through direct exposure. Local residents can be exposed to heavy metals in soils through ingestion of soil, inhalation of dust particles and dermal absorption.

In this study, the objective is to evaluate the health risks of heavy metals through direct exposure pathways. The non-carcinogenic hazard index and carcinogenic risk index were calculated by formulas (5)–(9) and the results are presented in Table 7. The values of non-carcinogenic hazard index were all lower than 1, suggesting no non-carcinogenic risks to the

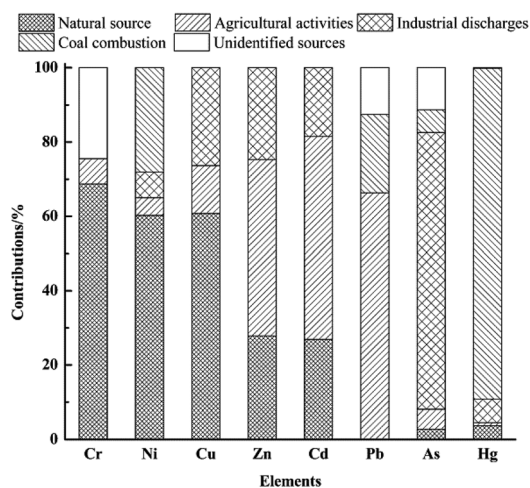
**Fig. 4** Contributions of each source to heavy metals in paddy soils.

Table 7 Health risks of heavy metals to populations through different pathways

| | Non-carcinogenic hazard index | | | Carcinogenic risk index | | |
|-------|----------------------------------|----------------------------------|----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| | Adult male | Adult female | Children | Adult male | Adult female | Children |
| Cr | $(3.83 \pm 1.35) \times 10^{-4}$ | $(3.51 \pm 1.24) \times 10^{-4}$ | $(4.23 \pm 1.49) \times 10^{-4}$ | $(1.08 \pm 0.38) \times 10^{-5}$ | $(1.27 \pm 0.45) \times 10^{-5}$ | $(6.17 \pm 2.17) \times 10^{-6}$ |
| Ni | $(2.31 \pm 0.93) \times 10^{-4}$ | $(2.71 \pm 1.09) \times 10^{-4}$ | $(5.08 \pm 2.04) \times 10^{-4}$ | $(7.65 \pm 3.07) \times 10^{-6}$ | $(8.97 \pm 3.61) \times 10^{-6}$ | $(4.35 \pm 1.75) \times 10^{-6}$ |
| Cu | $(3.07 \pm 1.36) \times 10^{-4}$ | $(3.60 \pm 1.60) \times 10^{-4}$ | $(6.79 \pm 3.01) \times 10^{-4}$ | | | |
| Zn | $(1.77 \pm 0.74) \times 10^{-4}$ | $(2.08 \pm 0.87) \times 10^{-4}$ | $(3.92 \pm 1.64) \times 10^{-4}$ | | | |
| As | $(1.19 \pm 0.26) \times 10^{-2}$ | $(1.40 \pm 0.30) \times 10^{-2}$ | $(2.64 \pm 0.57) \times 10^{-2}$ | $(5.37 \pm 1.16) \times 10^{-6}$ | $(6.29 \pm 1.37) \times 10^{-6}$ | $(3.05 \pm 0.66) \times 10^{-6}$ |
| Cd | $(1.21 \pm 0.59) \times 10^{-4}$ | $(1.42 \pm 0.69) \times 10^{-4}$ | $(2.66 \pm 1.29) \times 10^{-4}$ | $(3.63 \pm 1.75) \times 10^{-10}$ | $(3.29 \pm 1.59) \times 10^{-10}$ | $(9.90 \pm 4.79) \times 10^{-10}$ |
| Pb | $(1.81 \pm 0.69) \times 10^{-1}$ | $(2.12 \pm 0.81) \times 10^{-1}$ | $(4.00 \pm 1.53) \times 10^{-1}$ | | | |
| Hg | $(3.66 \pm 0.89) \times 10^{-4}$ | $(4.30 \pm 1.04) \times 10^{-4}$ | $(8.10 \pm 1.97) \times 10^{-4}$ | | | |
| Total | $(1.94 \pm 0.69) \times 10^{-1}$ | $(2.28 \pm 0.82) \times 10^{-1}$ | $(4.29 \pm 1.54) \times 10^{-1}$ | $(2.38 \pm 0.68) \times 10^{-5}$ | $(2.80 \pm 0.79) \times 10^{-5}$ | $(1.36 \pm 0.39) \times 10^{-5}$ |

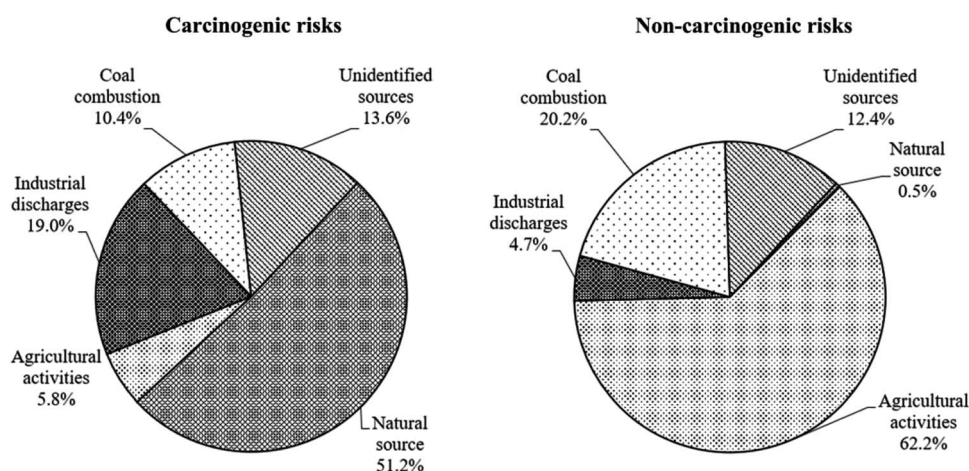


Fig. 5 Contributions of identified sources to the health risks of adult males.

human body. The values of carcinogenic risk index were all in the range of 10^{-6} to 10^{-4} which suggest carcinogenic risks that humans can tolerate. The total hazard index (HI) of eight heavy metals followed a sequence of children (0.429 ± 0.154) > adult female (0.228 ± 0.082) > adult male (0.194 ± 0.069). This result might be the reason that children are more sensitive to environmental pollutants which lead to higher non-carcinogenic risks.^{28,50}

The contribution rates of single metals to the total non-carcinogenic and total carcinogenic risks were calculated. According to the results, the total non-carcinogenic risks were comprised mostly by Pb and As with contribution rates of 93.04% and 6.14%, respectively. The total carcinogenic risks were mostly contributed by Cr, Ni and As with contribution rates of 45.44%, 32.06% and 22.50%, respectively.

Combining the results of APCS-MLR and the health risk assessment, the contributions of the identified sources to health risks of adult males were calculated and the results are shown in Fig. 5. The total non-carcinogenic risks were mainly derived from agricultural activities and coal combustion with contribution rates of 62.16% and 20.21%, respectively, while the total carcinogenic risks were mainly derived from natural sources and industrial discharge with contribution rates of 51.17% and 18.98%, respectively.

4 Conclusions

In this study, the concentrations of heavy metals in the paddy soils of Jiulong River Basin were analyzed to investigate the contamination, source apportionment and human health risks of heavy metals.

The results of this study showed that the mean contents of Cr, Cu, Zn, As, Cd, Pb and Hg were higher than the background value of Fujian soil and the contents of all the heavy metals showed moderate variability.

The I_{geo} method indicated that the paddy soils were moderately to heavily polluted by Cd and slightly polluted by Hg, Pb, As and Zn. The results of the RI method indicated that heavy metals in paddy soils presented considerable to high potential ecological risk, mostly contributed by Cd and Hg with contribution rates of 59.4% and 26.2%, respectively.

The source apportionment of heavy metals indicated that natural sources contributed most to Cr, Ni and Cu, with contribution rates of 68.74%, 60.23% and 60.76%, respectively. Agricultural activities contributed most to Zn, Cd and Pb, with contribution rates of 47.43%, 54.63% and 66.33%, respectively. Industrial discharge contributed most to As with a contribution rate of 74.51% and coal combustion contributed most to Hg with the rate of 89.03%.



The results of the health risk assessment indicated that heavy metals in paddy soils presented no non-carcinogenic risks, with all the HI values lower than 1. There were carcinogenic risks which humans can tolerate, with CR values falling in the range of 10^{-6} to 10^{-4} . According to the results of APCS-MLR and the health risk assessment, the total non-carcinogenic risks mainly derived from agricultural activities and coal combustion, with contribution rates of 62.16% and 20.21%, respectively, while the total carcinogenic risks mainly derived from natural sources and industrial discharge, with contribution rates of 51.17% and 18.98%, respectively.

These results can provide a reference for the prevention and control of heavy metals contamination.

Conflicts of interest

There are no conflicts to declare.

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