



Research article

Spatial distribution and ecological risk assessment of soil heavy metals in a typical volcanic area: Influence of parent materials

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ABSTRACT

To understand the distribution characteristics and potential ecological risks of heavy metals in soils in the typical volcanic area, 2,592 soil samples were collected from the surface layer (0–20 cm) and 269 samples were collected from the middle (80–100 cm) and deep layers (180–200 cm) in northeast of Hainan province, China. Accordingly, eight heavy metals (Cu, Pb, Zn, Cr, Ni, Cd, As, and Hg) were analyzed and determined. The effects of different parent materials and land use types on the accumulation of heavy metals in soils were compared, and the primary heavy metal sources were analyzed. The pollution level and ecological risk of heavy metals in soils in the study area were evaluated using the geo-accumulation index (I_{geo}) and potential ecological risk indices (E_i & RI). The results showed that, except that of Pb, the median concentrations of the analyzed heavy metals in the surface soils were higher than the background concentrations in the Hainan Island soils, indicating varying degrees of accumulation. The influence of land use type on the accumulation of heavy metals in surface soils varied from that of the parent materials. Anthropogenic activities highly influenced As, Cd, Hg, and Pb concentrations, whereas geological conditions primarily influenced Cr, Cu, Ni, and Zn concentrations. The I_{geo} results showed that the mean value of the eight metal elements were greater than zero, except for Pb. In the surface soils, the I_{geo} values of As, Cd, Hg, and Zn mostly fell into the light to moderate pollution class, and those of Cr, Cu, and Ni fell into the medium and heavy pollution class. The RI of the study area showed a high to significantly high ecological risk because of the Cd, Hg, and Ni concentrations. The results give a new insight in the parent material's geochemical control on the heavy metal elements in soils, and it can serve as a reference for the background value of local soil heavy metals and provide a scientific basis for controlling the potential ecological risk of heavy metals and reasonable land use plans.

1. Introduction

Excessive accumulation of heavy metals in soil leads to their entry into the human body through the digestive system, respiratory system, or skin, thereby causing various diseases [1, 2]. In addition to human activities, many factors, such as total concentration,

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parent rock, land use type, and soil properties, affect the mobility and bioavailability of heavy metals in soil. However, since the industrial revolution, the direct release of heavy metals through human activities and changes in the surface environment caused by human activities have substantially affected the natural cycle of heavy metals in soils. Therefore, with intensifying soil pollution and related health problems, heavy metal pollution of soils has become one of the crucial ecological and environmental problems limiting human development.

Owing to its unique geographical location, Hainan Island is one of the provinces in China with relatively high environmental quality. However, with continuous modernization on Hainan Island, the influx of foreign people and vehicles, extensive local enterprise production, and uncontrolled use of fertilizers and pesticides by farmers have damaged the environment in some areas. Since the anthropogenic contamination of urban soils on northern Hainan Island has been first reported [3], numerous studies have assessed heavy metal pollution in Hainan recent decades. Agriculture and aquaculture make the heavy metals accumulated in Hainan mangrove sediments [4] and emissions from industrial sewage and shipping activities has threatened the offshore ecosystem [5]. Ecological risk assessment shows that there is a moderate to strong ecological risk of Hg in agricultural land of Qiongzong located in central Hainan which is a relatively backward city [6]. In the industry-oriented western region, even groundwater is undergoing generally low pollution level by heavy metals [7]. Thus, to protect the environment of Hainan, further investigations on heavy metal pollution of agricultural land are required, and appropriate plans should be developed.

Numerous volcanoes are present north of Hainan Island, which represent Quaternary volcanoes in China [8]. A considerable amount of magma was transported to the surface of the Earth as a result of intense volcanic activity forming basalt [9]. Basalt-based soils reportedly contain high background levels of heavy metals [10]. However, reports on the distribution of heavy metals in these high background levels of Hainan and the interactions between land use types and parent materials are lacking. The Shishan–Yongxing and Yunlong areas of Haikou contain basalt deposits and sedimentary rocks, including Quaternary sediments. Several anthropogenic activities are prevalent in the region, most of which are related to agricultural production. Therefore, the Shishan–Yongxing and Yunlong areas were selected as the study areas. The sampling units were divided according to soil parent materials and land use types. The concentrations of heavy metals in the soil were analyzed to determine the heavy metal pollution of the local agricultural land.

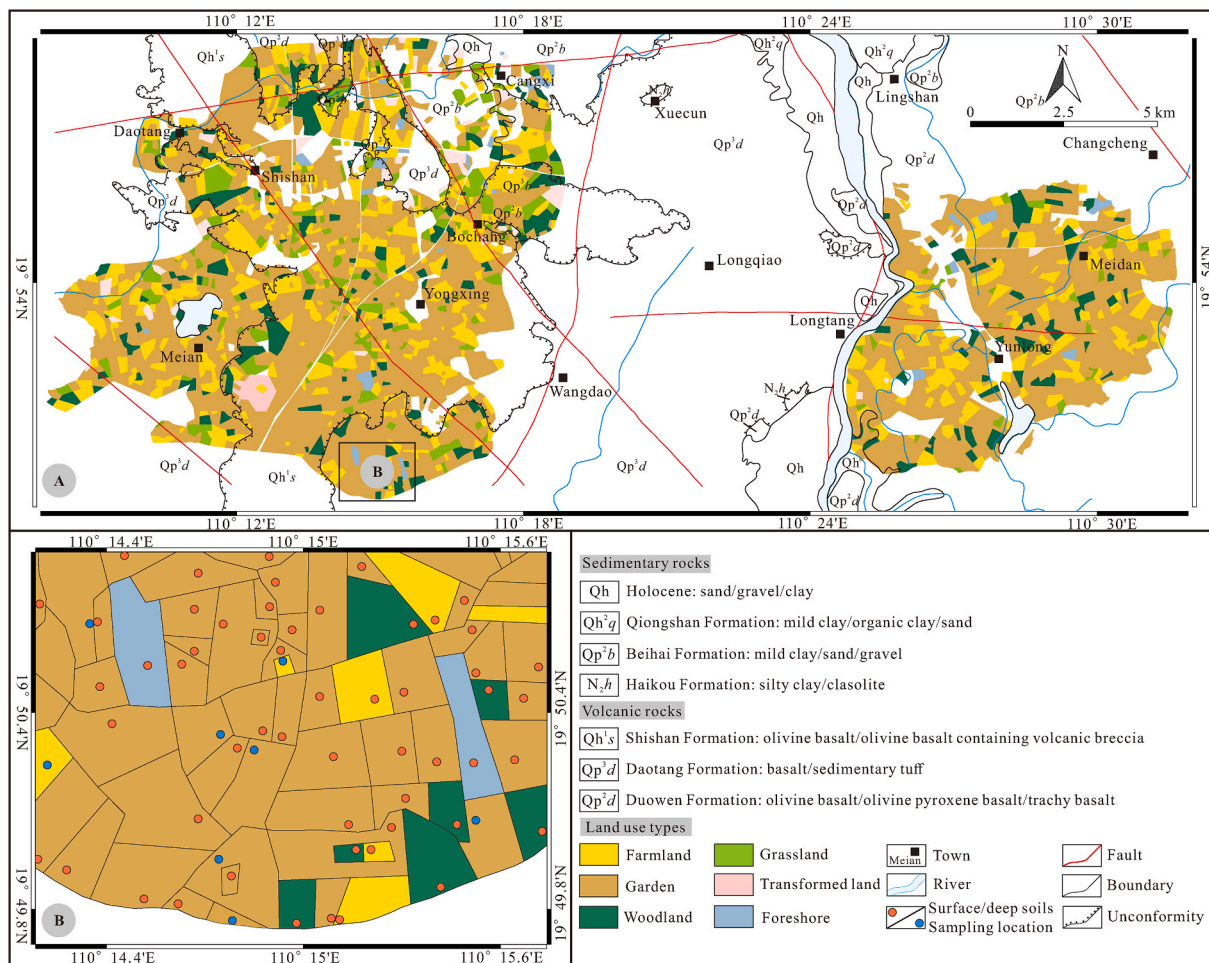


Fig. 1. Geological background and land use types of study area (A. geological map [8] and land use types of study area. B. sampling sites).

Moreover, the status of heavy metal pollution of soil in a typical area with high heavy metal concentrations and other areas with basalt-derived soils and the accumulation characteristics of heavy metals under different land use types were compared. The sources of heavy metals in the soil were analyzed, and the potential ecological risks of heavy metals were evaluated. The present results can serve as a reference basis for the baseline levels of local soil heavy metals and provide a scientific basis for the prevention of ecological risks, control of soil heavy metals, and the prudent use of land resources.

Shishan–Yongxing and Yunlong are located in the northeast of Hainan Island within the Meilan and Qiongsan districts of Haikou City, respectively. The average annual temperature is 24.3 °C, and the average annual precipitation is 2,067 mm. The geology of the study area comprises the Douwes (Qp^{2d}), Beipiao (Qp^{2b}), Daotang (Qp^{3d}), and Shishan (Qh^{1s}) formations, as well as Quaternary loose sediments (Qh), indicated from bottom to top in Fig. 1A.

The land use types in the study area are farmland, garden, woodland, grassland, transformed land, and foreshore (see Fig. 1A). Gardens with fruit orchards, such as that of litchi, accounted for 60.14% of the study area (158.18 km²). Farmland, primarily comprising vegetable crops, occupied 19.27% (50.69 km²) of the study area. Woodland covered 9.63% (25.32 km²) of the study area and primarily included shrubs and mixed forests. Grassland, transformed land, and foreshore covered 8.59% (22.61 km²), 1.41% (3.71 km²), and 0.96% (2.53 km²) of the total study area, respectively. Transformed land primarily comprised paved areas, an artificial accumulation of land; however, foreshore comprised the areas surrounding ponds, typically used for poultry farming or livestock grazing. These two types of land uses are closely associated with human activities.

2. Materials and methods

2.1. Sampling and analysis

Three subsamples at a depth of 0–20 cm were combined as surface soil samples based on land use type and geological background (Fig. 1B). Additional soils at depths of 80–100 cm and 180–200 cm were sampled at a density of 1 sample/km². Disturbed or evidently contaminated soils were avoided during sample collection to achieve better representativeness.

In total, 2,592 surface soil samples were collected in this study, and 269 middle and deep soil samples were collected from suitable surface soil sampling locations. Before chemical analysis, all samples were subjected to shade drying, and a soil particle size of <2 mm was reserved.

Geochemical data for the analyzed samples were provided by the Central Laboratory of the North China Geological Exploration Bureau, Langfang, Hebei Province, China. The analytical methods and detection limits for various indicators are listed in Table 1. Quality control during the analysis and testing process was conducted according to the following standards: 1) multi-objective regional geochemical survey specification (1:250000) (DZ/T 0258-2014) [11], 2) sample analysis methods and technical requirements for ecological geochemical evaluation (DD 2005-03) [12], and 3) technical requirements for sample analysis and testing of geochemical assessment of land quality (Trial) (DD2008-06) [13].

2.2. Geo-accumulation index (I_{geo})

The geo-accumulation index method (I_{geo}), also called the Muller Index [14], has been widely applied in the assessment of soil pollution [15, 16, 17, 18]. The calculation formula for I_{geo} is as shown in Equation (1):

$$I_{geo} = \log_2 \left[\frac{C_i}{k \times S_i} \right] \tag{1}$$

where C_i is the measured concentration of heavy metals in the soils, and S_i is the geochemical background concentration value of the corresponding measured heavy metals in China. The constant k is a background matrix correction value to accommodate anthropogenic effects and to make provision for potential fluctuations and variations in the reference background concentrations (typically specified as 1.5). In this study, the background concentrations of heavy metals in the Hainan Island soil were referenced, and the

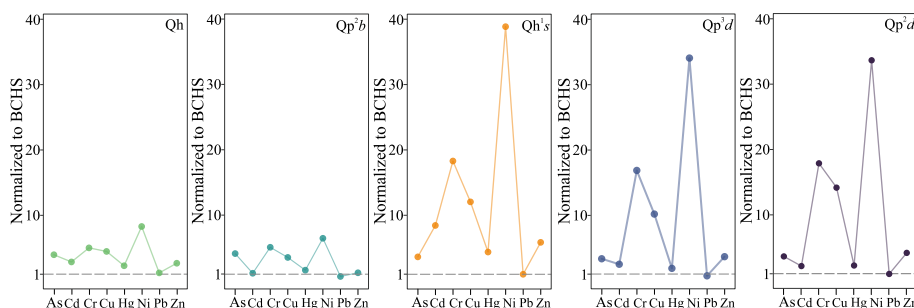


Fig. 2. Normalized patterns for the heavy metal elements contents in surface soils (Qp^{2d}: Duowen Formation, Qp^{2b}: Beipiao Formation, Qp^{3d}: Daotang Formation, and Qh^{1s}: Shishan Formation, Qh: Quaternary loose sediments).

Table 1
Analytical methods and detection limits for various indicators.

Heavy metals	Analytical methods	Detection limits	Units
Cu	ICP	0.5	mg·kg ⁻¹
Pb	ICP-MS	2	mg·kg ⁻¹
Zn	XRF	2	mg·kg ⁻¹
Cr	XRF	2	mg·kg ⁻¹
Ni	ICP-MS	0.3	mg·kg ⁻¹
Cd	ICP-MS	0.02	mg·kg ⁻¹
As	AFS	0.2	mg·kg ⁻¹
Hg	AFS	0.0005	mg·kg ⁻¹
Zn	XRF	2	mg·kg ⁻¹

concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn were 1.14, 0.05, 15.24, 4.95, 0.03, 4.12, 22.34, and 35.11 mg kg⁻¹, respectively [19]. The Igeo can be generally divided into seven classes [20], representing different degrees of pollution (Table 2).

2.3. Potential ecological risk assessment

The potential ecological risk index (RI) [21], which is commonly used in ecological environment studies [22, 23, 24], was applied to identify the ecological risks caused by heavy metals. The toxicity and environmental response of different heavy metals were considered based on the toxicity response factor (Kundu et al., 2017). The RI can be defined as shown in Equation (2):

$$RI = \sum_{i=1}^n E_r^i = \sum_{i=1}^n (T_r^i \times C_f^i) = \sum_{i=1}^n \left(T_r^i \times \frac{C_i}{C_n^i} \right) \tag{2}$$

where E_rⁱ is the ecological risk index for a given heavy metal, C_fⁱ is the contamination factor (the ratio between the measured concentration, C_i, and the background concentration, C_nⁱ, in the Hainan Island soil), and T_rⁱ is the toxic response factor for the different metals, that can be expressed as shown in Equation (3):

$$T_r^i(\text{Hg}) = 40 > T_r^i(\text{Cd}) = 30 > T_r^i(\text{As}) = 10 > T_r^i(\text{Cu}) = T_r^i(\text{Ni}) = T_r^i(\text{Pb}) = 5 > T_r^i(\text{Cr}) = 2 > T_r^i(\text{Zn}) = 1 \tag{3}$$

[25]. Criteria for the assessment of the potential ecological risk status with E_rⁱ & RI are presented in Table 3.

3. Results and discussion

3.1. Statistical characteristics

The statistical parameters of heavy metals in the surface soils are listed in Table 4. The median concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in surface soils in the study area were 4.09, 0.15, 267.22, 58.38, 0.08, 140.66, 19.41, and 139.31 mg kg⁻¹, respectively. Compared with the background concentrations of Hainan Island soils (BCHS), the median concentrations of heavy metals, except Pb, in surface soils were several times higher, particularly Cr and Ni concentrations. For example, the Cr content in surface soils was approximately 20 times higher than BCHS content, and the Ni content in surface soils was 30 times higher than BCHS content (Figure 2).

The heavy metal concentrations in surface soils of other provinces in southwest and southeast of China (which had the same geological background) [26, 27], whole China [28, 29], Conterminous U.S.A [30], and Europe [31] were listed in Table 4. The concentrations of Cr, Ni and Zn in the surface soil of Haikou showed extremely high enrichment, which was much higher than other areas, but there was a good soil Pb status. Compared with Ludian in southwestern China and Xuyi in southeastern China, the concentrations of Hg in surface soil of Haikou is also higher.

Normalized to the BCHS, the concentrations of heavy metals in surface soils derived from different geological formations greatly varied. The line plots were similar for median heavy metal concentrations in soils derived from sedimentary and volcanic rocks, respectively. Therefore, two types of parent rock, sedimentary and volcanic, were considered in the analysis.

Table 2
Criteria for the assessment of soil pollution with geo-accumulation index (Igeo).

Igeo	Classification	Pollution degree
Igeo ≤ 0	0	Free
0 < Igeo ≤ 1	1	Light
1 < Igeo ≤ 2	2	Moderate
2 < Igeo ≤ 3	3	Moderate–heavy
3 < Igeo ≤ 4	4	Heavy
4 < Igeo ≤ 5	5	Heavy–extreme
Igeo > 5	6	Extreme

Table 3
Criteria for the assessment of the potential ecological risk index (E_r^i & RI).

	Criteria				
	Light	Moderate	High	Significantly high	Extremely high
E_r^i	< 40	40–80	80–160	160–320	≥320
RI	< 150	150–300	300–600	600–1200	≥1200

Table 4
Statistical parameters of heavy metals in surface soils in the study area ($\text{mg}\cdot\text{kg}^{-1}$).

Parameter	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Min	0.05	0.02	5.60	3.26	0.01	4.99	4.91	15.38
Max	39.49	11.49	625.50	516.29	2.11	417.52	562.93	798.90
Mean	4.17	0.24	255.45	57.03	0.11	140.32	21.73	140.82
Median	4.09	0.15	267.22	58.38	0.08	140.66	19.41	139.31
Standard deviation	2.20	0.29	93.55	26.83	0.12	68.70	17.05	63.87
Kurtosis	67.14	896.55	0.11	42.85	83.57	0.07	566.10	9.56
Skewness	5.08	23.35	-0.37	3.02	7.07	0.29	20.37	1.22
Coefficient of variation	0.53	1.21	0.37	0.47	1.06	0.49	0.78	0.45
BCHS	1.14	0.05	15.24	4.95	0.03	4.12	22.34	35.11
Xuyi, Jiangsu Province, Southwest China	7.64	0.14	165	42	0.03	107	22	88
Ludian, Yunnan Province, Southeast China	2.99	0.38	72	206	0.06	44.1	22.8	124
China	11.5	0.097	61	23	0.065	27	25	71
Conterminous U.S.A	7.2	-	54	25	0.089	19	19	60
Europe	11.6	0.284	95	17	0.061	34	33	68

Parent rocks had little influence on As, Hg, and Pb concentrations in surface soils but greatly influenced the Cr, Cu, Ni, and Zn concentrations. In addition, the Cd content in the surface soils developed from the Shishan Formation (QH¹s) was significantly higher than in the other soils.

3.2. Concentrations of heavy metals in surface soils based on different parent rocks with different land use types

Previous studies have revealed that different land use types affect heavy metal concentrations in surface soil [32, 33]; however, they did not consider the geological background. Therefore, our study further compared the effects of different land use types on soil heavy metals against different geological backgrounds (Fig. 3). Because most of the analysis results of the samples used in this study did not pass the normal distribution test, the non-parametric statistical test method (Kruskal–Wallis tests) was applied. Notably, the effects

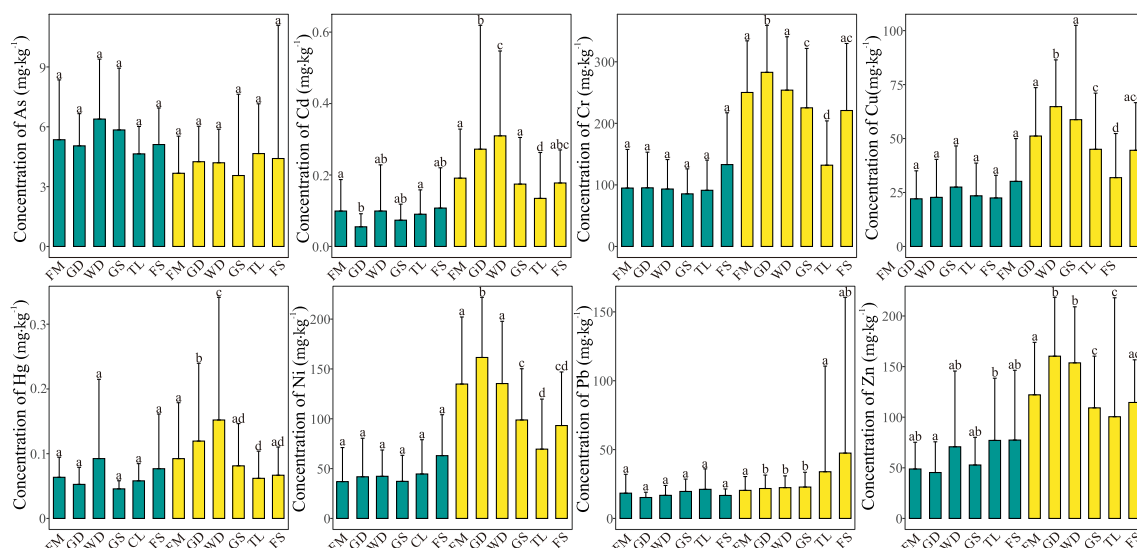


Fig. 3. Comparison of the contents of soils in different land uses and different parent rocks (the soils derived from sedimentary rocks are identified as green, the soils derived from volcanic rocks are identified as yellow; FM: farmland, GD: garden, WD: woodland, GS: grassland, CL: construction land, FS: foreshore; Significant differences are denoted by different letters ($P < 0.05$)). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

of land use type on heavy metals varied depending on the soil parent materials.

In the soils with sedimentary rock parent material, different land use types had little effect on the heavy metal contents. The differences in the concentrations of As, Cr, Cu, Hg, Ni, and Pb under different land use types were not significant. In contrast, land use types influenced the Cd and Zn concentrations in the soil. However, in the soils derived from volcanic rocks, the concentrations of the remaining elements, except As, were significantly affected by land use type.

This could be related to the variations in major elements, organic matter, and pH under different geological conditions. In addition, the synergy and antagonism between elements affect the absorption of heavy metals by plants. For example, P can effectively react with Pb in soil solutions, precipitate insoluble minerals, and increase the efficiency of As [34]. Studies have revealed that the types and levels of microorganisms in soils with different soil parent materials are also significantly different (another work in progress), which can further change the bioavailability of heavy metals [35, 36]. This may also be a reason for this phenomenon that the effects of land use types on soil heavy metal accumulation varied with parent materials. However, the crucial influencing factor for this phenomenon requires further investigation.

3.3. Vertical distribution characteristics of heavy metals

The vertical distribution of the eight heavy metals in the soils also showed significant differences (Fig. 4). The eight heavy metals can be divided into two categories based on their concentrations in the surface, middle, and deep soils. The first category has higher concentrations in the surface soil than in the middle and deep soils and includes As, Cd, Hg, and Pb. The second category comprises Cr, Cu, Ni, and Zn, whose contents in surface soils slightly changes or is slightly lower than those in deep soils. The vertical distribution characteristics of soil suggest that the influence of the surface environment of the Earth is higher than that of inheritance from the parent materials. Heavy metals entering environmental media through human activities are primarily introduced through soluble exchange platforms, adsorption, and other active components. These are readily adsorbed by surface organic matter and typically accumulate in surface media [37]. Therefore, the higher concentrations of As, Cd, Hg, and Pb in surface soils may indicate that they are significantly affected by exogenous factors.

Because anthropogenic activities have little effect on the Sc concentration in the crust [37], it has been used as a reference element for calculating the concentration enrichment factor [38] of potentially toxic elements on Hainan Island [39] and in other regions worldwide [40, 41]. Therefore, assessing whether the elements are affected by anthropogenic activities based on the correlation between heavy metal and Sc concentrations in the soil is reasonable. Therefore, we compared the relationships between the eight heavy metals and Sc at different depths, as shown in Fig. 5.

The relationship between the eight heavy metals and Sc was divided into two categories. The first category included Cr (Fig. 5C), Cu (Fig. 5D), Ni (Fig. 5F), and Zn (Fig. 5H), which exhibited good and stable correlations with Sc at different depths. The second category included As (Fig. 5A), Cd (Fig. 5B), Hg (Fig. 5E), and Pb (Fig. 5G), which exhibited poor correlations with Sc (almost no stable correlation). The stable correlation from deep to shallow indicated that Cr, Cu, Ni, and Zn have a good inheritance of parent materials, suggesting that the parent material is the primary source.

3.4. Pearson correlation analysis

The correlation matrix for the eight heavy metals is shown in Fig. 6. Highly positive correlations were observed between Cr, Cu, Ni,

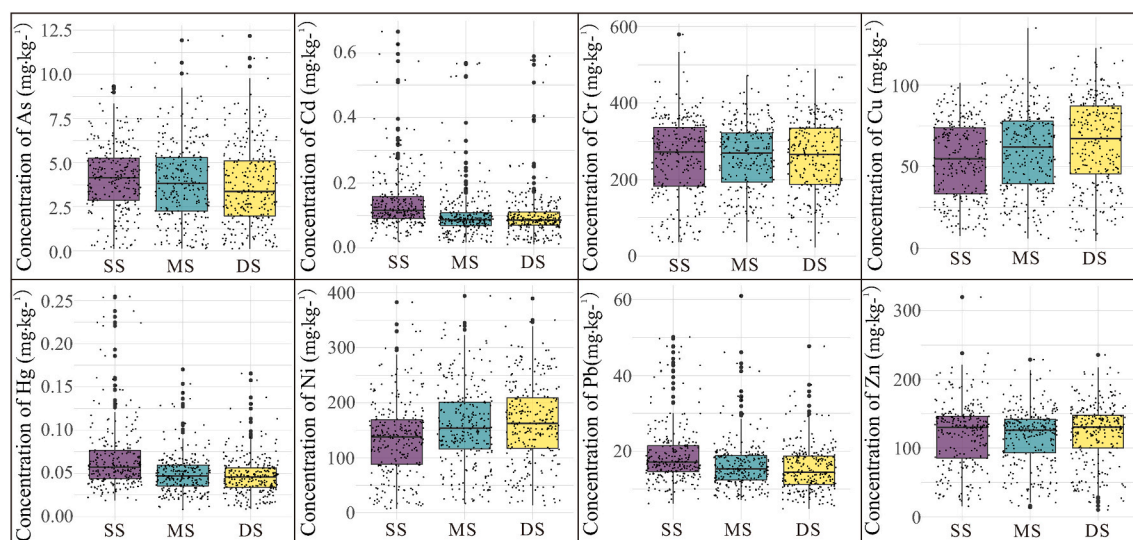


Fig. 4. Box plot of soil heavy metals' content at different depths (SS: surface soils, MS: middle-layer soils, DS: deep-layer soils).

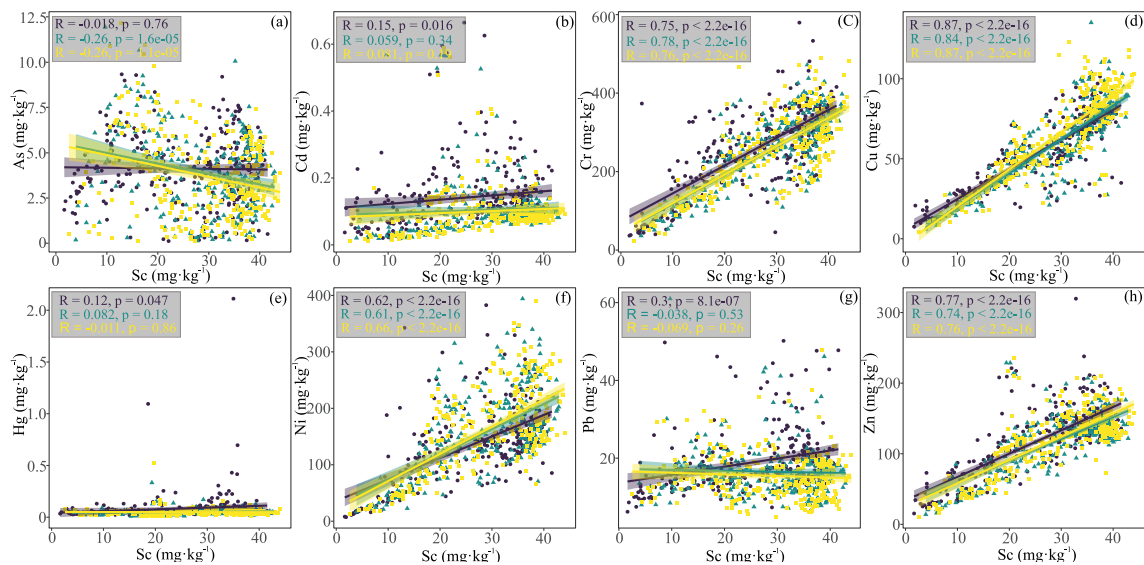


Fig. 5. Correlation between contents of soil heavy metals and Sc in different depth (the surface soils are marked purple, middle-layer soils are marked green, deep-layer soils are marked yellow). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

and Zn, with correlation coefficients of 0.55–0.77 ($p < 0.05$), indicating the same source. In contrast, Pb, As, Cr, Cu, Ni, and Zn exhibited weak correlations or did not correlate, indicating that the source was not entirely consistent. Although the correlations between Hg, Cd, and six other elements were also significantly positive, the correlations were relatively weak compared with those of Cr, Cu, Ni, and Zn, indicating complex Cd and Hg sources.

3.5. Principal component analysis

Principal component analysis (PCA) was performed to identify the major influencing factors of heavy metals in the surface soils. There were two principal components when eigenvalues were >1 . The biplots for the principal component scores and loadings for the surface soils are shown in Fig. 7, and Table 5 lists the eigenvalues, principal components, percentages of variance, and cumulative percentages. The first two principal components of the surface soils were 58.16%. As shown in Fig. 7, Cr, Cu, Ni, Zn, Cd, Pb, and Hg were grouped along the Principal Component 1 (PC1) axis, demonstrating 39.43% of the total variance, whereas As, Cd, Hg, and Pb were concentrated along the Principal Component 2 (PC2) axis, indicating 18.73% of the total variance.

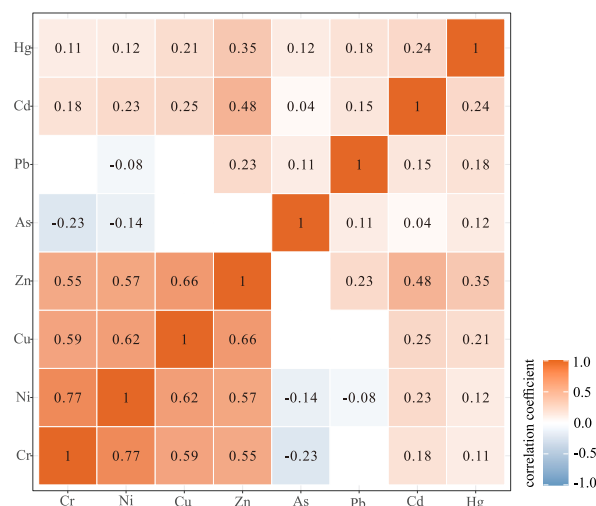


Fig. 6. Correlation matrix among heavy metals (Hiding when $p > 0.05$).

3.6. Source identification of heavy metals

The Ni, Cr, Cu, and Zn concentrations are generally high in dark minerals, such as pyroxene and amphibole, which are primarily associated with dark minerals in the parent rocks [42]. Combined with the vertical distribution characteristics of these four elements, relationship with Sc, and Pearson correlation, the significant effect of the parent rocks on the Cr, Cu, Ni, and Zn concentrations in surface soils indicates that the major source of these four heavy metal elements is the geological background. Thus, PC1 and PC2 represent the geological and external (anthropogenic activities) influences, respectively. Although parent rocks substantially contribute to the Cd, Pb, and Hg concentrations in surface soils, the external input also has similar influence on the As, Cd, Hg, and Pb concentrations in surface soils.

The area with high As concentrations in the surface soil of the study area is located in the Shishan–Cangxi region, and the favorable areas for breeding and pasturing livestock, such as tidal flats, are relatively concentrated. One reason for the accumulation of As could be that As-containing feed is used in animal husbandry, eventually rendering As to enter the soil through the metabolic products of animals [43]. In addition, excessive phosphate fertilizers could be an important contributor [44].

Automobile emissions are typically considered a source of Pb pollution [45]. However, owing to the relatively closed environment of Hainan Island and popularity of electric vehicles on the island, the Pb concentrations in the surface soils of the study area are not high.

The only heavy metal element that can occur in the atmosphere as vapor is Hg, which has a high vapor pressure and long residence time and can easily migrate to the surface along cracks from deep underground [46]. Approximately 60–80% of global Hg originates from anthropogenic emissions [47]. Coal burning, oil production, and waste incineration from industrial activities increase Hg emissions and reach the soil surface via atmospheric deposition [48, 49, 50]. The study area is not a highly developed industrial area but primarily agricultural area; thus, Hg concentrations may be related to local burned wastes.

Studies have revealed that Cd can generally be used as a marker for agricultural activities such as pesticides and fertilizers [51, 52]. The accumulation of Cd in the surface soils may be closely related to the locally developed crop industry.

Based on this, it can be inferred that the accumulation of As, Cd, Hg, and Pb in surface soils is primarily controlled by anthropogenic activities. The accumulation of Cd, Hg, and Pb is partly influenced by geological background because it shows PC1 factor loading scores. The accumulation of Cr, Cu, Ni, and Zn in surface soils is primarily controlled by geological background. However, it is the limitation that only potential sources of pollution are given, and the exact sources need further work, such as measuring isotope ratios.

3.7. Evaluation of geo-accumulation index

Igeo was applied to further analyze heavy metal accumulation levels based on the selected geochemical background concentrations. Consequently, the mean Igeo values of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn were 0.85, 1.53, 2.48, 2.46, 1.49, 3.44, −0.87, and 0.90 kg^{-1} , respectively (Table 6).

The Igeo of As, Cd, Hg, and Zn in surface soils mostly fell into the light–moderate pollution class. The Igeo of Cr, Cu, and Ni in surface soils mostly fell into the moderate–heavy and heavy pollution classes. The Igeo of Ni was particularly high, with more than 50% of the study area being heavily polluted by Ni. The Igeo results indicate that Shishan and Yunlong are almost free from Pb pollution.

The Igeo values of As, Cd, and Hg were mapped to determine the distribution of soils affected by exogenous pollution as shown in Fig. 8A, Fig. 8B and C, respectively (As Pb pollution was not evident, Pb was not mapped). The regional distribution between Shishan and Cangxi–Bochang was sporadic (closer to the Haikou urban area) and relatively concentrated in the southwest of Yunlong. The areas where the Hg Igeo in the surface soil reached moderate–heavy or was relatively high were primarily concentrated between Shishan and Yongxing and in the southwest of Yunnan. Notably, Shishan and Yongxing were the most affluent and most affected by anthropogenic activities in the study area. The area with a Cd Igeo reaching moderate–heavy or above was concentrated between Shishan and Yongxing. However, this area overlapped with the Qh^1 's exposed area, where Cd concentrations in soils with Qh^1 's as the

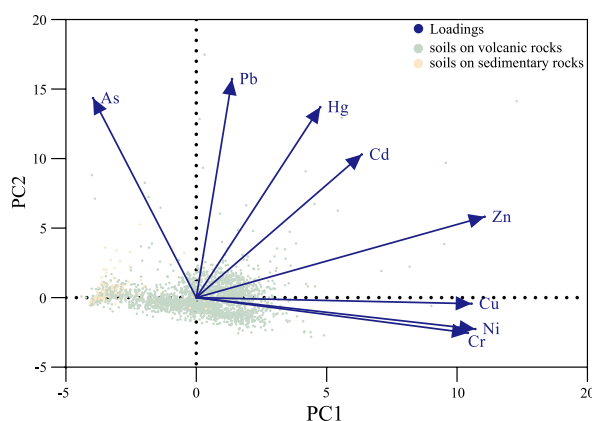


Fig. 7. PCA biplot of Heavy metals in soils.

Table 5

Variance explained by each principal component and component loadings for Principal Component 1 (PC1) and Principal Component 2 (PC2) .

Elements	PC1	PC2
As	-0.09	0.57
Cd	0.49	0.41
Cr	0.81	-0.37
Cu	0.82	-0.06
Hg	0.37	0.55
Ni	0.83	-0.33
Pb	0.11	0.63
Zn	0.86	0.23
Eigenvalue	3.154	1.499
Proportion of variance	39.43%	18.73%
Cumulative proportion of variance	39.43%	58.16%

Table 6

Land extent of different concentrations of heavy metals in soil based on the I_{geo} .

Heavy metals I_{geo}	Mean	Extent (km ²)						
		Free	Light	Moderate	Moderate-heavy	Heavy	Heavy-extremely	Extremely
As	1.08	24.87	56.98	162.56	16.94	0.79	0.92	0.00
Cd	1.21	29.60	105.70	47.41	68.59	11.22	0.47	0.06
Cr	3.34	0.13	3.39	16.92	31.64	189.37	21.60	0.00
Cu	2.76	0.40	8.26	33.47	95.65	123.63	0.97	0.67
Hg	0.90	47.53	103.78	70.54	35.11	4.03	1.53	0.53
Ni	4.25	0.07	1.34	10.17	17.34	44.02	147.98	42.13
Pb	-0.75	239.11	22.86	0.74	0.03	0.25	0.06	0.00
Zn	1.24	25.23	40.81	164.20	32.43	0.37	0.00	0.00

parent material were high, implying that the high Cd concentration in soils is highly influenced by the geological background.

3.8. Evaluation of potential ecological risk

The statistical results for the ecological risk indices in the study area are presented in Table 7. Although the mean I_{geo} was ranked $Pb < Hg < As < Cd < Zn < Cu < Cr < Ni$, the mean ecological risk values ranged from the highest to the lowest as follows: $Ni (170.29) > Hg (145.39) > Cd (142.89) > Cu (57.61) > As (36.57) > Cr (33.52) > Pb (4.86) > Zn (4.01)$, owing to the different toxicity response factors. More than 20% of the land had an extremely high potential ecological risk for Cd and Hg, and more than 40% had a high potential ecological risk for Ni. Most land had light to moderate potential ecological risk for As, Cu, and Cr, and Pb and Zn had a light ecological risk. The RI of the study areas had a mean of 595.15 and showed an overall high to significantly high ecological risk. The RI distribution map is shown in Fig. 9.

Approximately 88% of land areas had high or low ecological risk. The accumulation of Cd, Hg, and Ni in surface soils requires further attention. Thus, when making land use plans, the government should pay attention to the influence of Ni from geological sources and strictly control human Cd and Hg pollution.

4. Conclusions

Compared with the BCHS, the concentrations of heavy metals in the surface soils in the study area were several times higher, except that of Pb. Parent materials were the primary source of Cr, Cu, Ni, and Zn in surface soils, whereas anthropogenic activities greatly influenced As, Cd, Hg, and Pb.

The effects of land use types on soil heavy metal accumulation varied with parent materials.

The I_{geo} of As, Cd, Hg, and Zn in surface soils mostly fell into the light-moderate pollution category. In contrast, the I_{geo} of Cr, Cu, and Ni in surface soils mostly fell into the moderate-heavy and heavy pollution categories. Based on the I_{geo} results, Pb pollution was not evident.

The RI of the study area showed high to significantly high ecological risk. Therefore, soils with heavy metals (Cr, Cu, Ni, and Zn), primarily originating from parent materials, require proper management, and the As, Hg, and Cd pollution from anthropogenic activities should be controlled to avoid further accumulation.

Author contribution statement

Shixin Tang: Conceived and designed the experiments.

Jianweng Gao: Analyzed and interpreted the data; Wrote the paper.

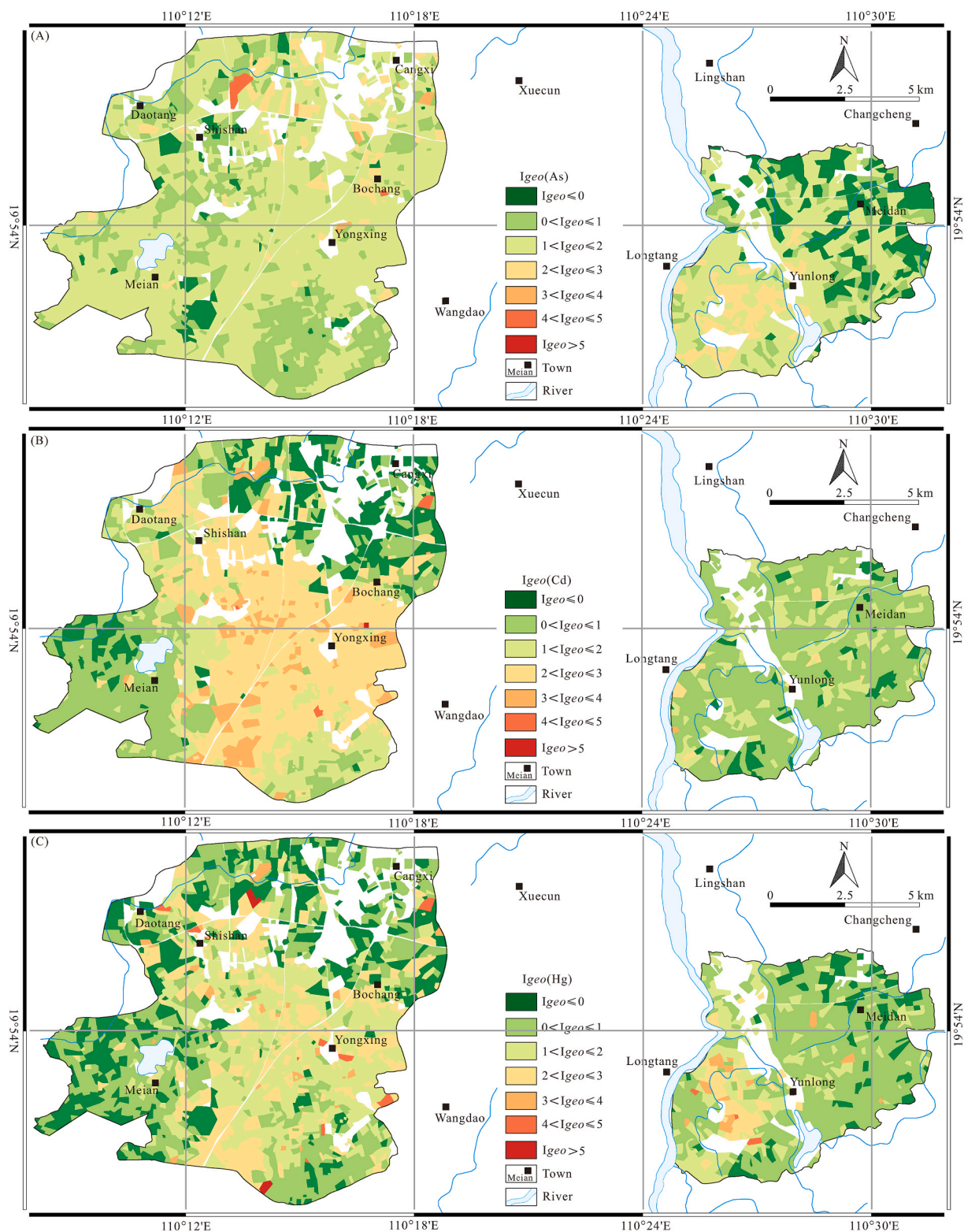


Fig. 8. Distribution maps with I_{geo} of As, Cd and Hg.

Table 7
Potential ecological risk coefficient for each heavy metal in soils.

	Heavy metals	Range and mean value			Extent of heavy metal classes with E_r & RI (km ²)				
		Min	Max	Mean	Light	Moderate	High	Significantly high	Extremely high
E_r	As	0.44	346.40	36.57	163.46	95.44	3.09	0.82	0.24
	Cd	9.12	6893.99	142.89	21.02	98.07	59.01	60.41	24.54
	Cr	0.73	82.09	33.52	191.22	71.79	0.04	0.00	0.00
	Cu	3.30	521.50	57.61	69.38	154.61	38.27	0.40	0.39
	Hg	12.68	2815.69	145.39	10.78	86.77	83.48	67.33	14.70
	Ni	6.06	506.70	170.29	16.43	24.29	79.54	135.03	7.76
	Pb	1.10	125.99	4.86	262.75	0.16	0.14	0.00	0.00
RI	Zn	0.44	22.75	4.01	263.05	0.00	0.00	0.00	0.00
		84.40	7367.49	595.15	2.54	28.56	126.12	101.61	4.22

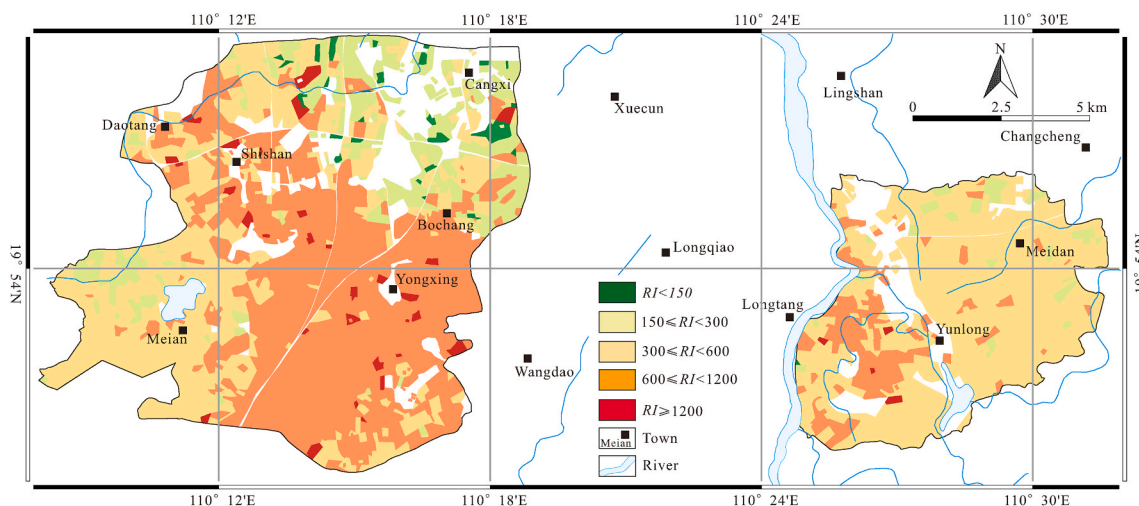


Fig. 9. Distribution maps with RI .

Jingjing Gong and Jianzhou Yang: Performed the experiments.
Zhenliang Wang, Yangang Fu and Shengming Ma: Contributed reagents, materials, analysis tools or data.

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Data availability statement

The authors do not have permission to share data.

Declaration of interest’s statement

The authors declare no competing interests.

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