Heavy metal(loid)s in fruit-growing soils of tropical Hainan Island in China: Pollution, ecological-health risks, spatial assessment, and source analyses

Xiaofang Wu[1,2,3], Cailin Zhou[1,2,3], Yi Xie[1,2,3], Xiaogang Wang[1,2,3], Aini Deng[1,2,3*]

(1. *Analysis and Test Center, Chinese Academy of Tropical Agricultural Sciences, Haikou 571101, China*;
2. *Hainan Provincial Key Laboratory of Quality and Safety for Tropical Fruits and Vegetable Products, Haikou 571101, China*;
3. *Key Laboratory of Quality and Safety Control for Subtropical Fruit and Vegetable, Ministry of Agriculture and Rural Affairs, Haikou 571101, China*)

Abstract: Hainan Island is the most important tropical fruit production area in China. In this study, 372 soil samples and corresponding fruit and irrigation water samples were collected from Hainan orchards and analysed to determine the concentrations of six heavy metal(loid)s: Cd, Hg, As, Pb, Cr, and Cu. The pollution status, potential risks, possible sources, and spatial distribution patterns of soil heavy metal(loid)s were comprehensively investigated. The fruit and irrigation water samples had negligible amounts of heavy metal(loid)s, and the potential human health risk for fruit consumers was at a safe level. The heavy metal(loid) concentrations in most soil samples were lower than the national risk screening values. However, significant local accumulation of heavy metal(loid)s, especially Cd, Cr, and Cu, relative to their background values was observed. Moreover, the combined effects of the heavy metal(loid)s only led to a mild pollution level and low ecological risk throughout the study area. Noncarcinogenic risks were not observed among the local residents, and carcinogenic risks were within an acceptable range. The acidic soil in the study area increased the risk of soil Cd pollution, and organic matter affected the distribution of the tested metal(loid)s in the soil. Uncommon geogenic sources with high background values were the sources of Cr and Cu, anthropogenic activities primarily led to Cd, Pb, and As contamination, and a combination of anthropogenic and natural sources was responsible for Hg emissions. The research suggested that appropriate strategies must be implemented to track and reduce soil heavy metal contaminants in the northern and western region of the Hainan orchard area. The results can provide valuable information for policies on pollution prevention and management, the environment, and human health protection in the study region.

Keywords: heavy metal(loid)s, Hainan Island, orchard, pollution assessment, ecological-health risk assessments, spatial distribution, source analysis
DOI: 10.25165/j.ijabe.20231604.8011

Citation: Wu X F, Zhou C L, Xie Y, Wang X G, Deng A N. Heavy metal(loid)s in fruit-growing soils of tropical Hainan Island in China: Pollution, ecological-health risks, spatial assessment, and source analyses. Int J Agric & Biol Eng, 2023; 16(4): 231–244.

1 Introduction

Heavy metal(loid)s contamination in soil and corresponding crops is currently a major global issue, which pose significant threats to ecosystems, food safety, and human health due to their high toxicity, persistence behavior, bioaccumulation and biomagnification properties in the food chain[1,2]. As a basic medium for plant production and a pool of numerous nutrients and harmful pollutants, soil accumulates most of the released heavy metal(loid)s. Soil heavy metal(loid)s may emanate from natural sources (lithogenic components, parent materials, etc.) or anthropogenic sources (agriculture, urbanisation, and industrialisation), and various anthropogenic activities (e.g. over-fertilisation and pesticides, wastewater irrigation, traffic emissions, and industrial activities) are estimated to be the main sources of inputs of heavy metal(loid)s[3,4]. These metal(loid)s can enter the food chain and ultimately accumulate in consumers through specific routes, such as ingestion of soil, inhalation of dust, dermal contact with soil, and consumption of agricultural crops grown in contaminated soil, which has led to an increased frequency of chronic diseases[5]. The long-term presence of excessive heavy metal(loid)s in crop-cultivated soils creates accumulation problems in both the soil and the corresponding crop. The transfer of heavy metal(loid)s from soil to plants is the major pathway for human exposure to contaminants in soil[6]. Accordingly, heavy metal(loid)s in the soil environment as well as their effects on crops and potential risks have become the focus of research attention in recent years[1,2,7–10].

Moreover, assessing the pollution status using various pollution indices (i.e., pollution index (PI), geo-accumulation index (I_{geo}), enrichment factors (EF), Nemerow integrated pollution index (NIPI), and pollution load index (PLI)), ecological risk, health risk,

Received date: 2022-11-02 **Accepted date:** 2023-05-11
Biographies: Xiaofang Wu, MD, Research Assistant, research interest: quality and safety of agricultural products, Email: uog10212935@163.com; **Cailin Zhou**, BD, research interest: quality and safety of agricultural products, Email: 578306449@qq.com; **Yi Xie**, MD, Research Assistant, research interest: quality and safety of agricultural products, Email: 79925793@qq.com; **Xiaogang Wang**, MD, Research Assistant, research interest: quality and safety of agricultural products, Email: 251238854@qq.com.
***Corresponding author: Aini Deng**, MD, Associated Researcher, research interest: acidified soil improvement, and quality and safety of agricultural products. Chinese Academy of Tropical Agricultural Sciences, No.4, West Xueyuan Road, Haikou 571101, China, Tel: +86-18308980420, Email: xiaoyantoudan@163.com.

and source apportionment of heavy metal(loid)s provides a broad assessment of the heavy metal pollution in the environment[2–4]. Considering the specificity of each index, comparative assessments of various heavy metal pollution indices have been performed in recent years to comprehensively evaluate the pollution status of a given region[2–4,11,12].

Fruits are major agricultural products that play a vital role in the human diet because they are abundant sources of essential micronutrients[13]. In recent years, the area and production of orchards in China have ranked first in the world, accounting for 19.5% and 32.35% of the worldwide total, respectively[14]. Fruit production has become the pillar industry for fruit growers to increase their income and develop the agricultural economy in China; this shift has led to the irrational use of available agricultural resources, which has resulted in the degradation and heavy metal(loid) pollution of orchard soil, declines in fruit quality, decreases in yields, and threats to human health, thereby restricting the development of the fruit industry[14–16].

As the second largest island located off the coast of China, Hainan Island covers 42.5% of the total national tropical area[16]. Benefitting from abundant light and heat resources, Hainan is well-known as a "tropical base of agricultural production" and a 'natural greenhouse' for various of fruit trees that grow throughout the year. However, as the production base for high value-added fruits, the fruit planting area and production have increased rapidly in pursuit of high incomes, which has resulted in the incorporation of heavy metal(loid)s into the soil owing to the excessive use of pesticides and fertilisers. Over the past 30 years, the fruit planting area, the production, and the total N and P fertiliser consumptions have increased 3.6 times, 12.8 times, and 2.4 times, respectively, and the pesticide use intensity increased from 8.0 to 47.1 kg/hm^2, which represented the highest increase among the investigated factors[16]. As a 'national ecological civilisation pilot zone' and 'pilot zone for agriculture green development', Hainan should not only supply high-quality fruits but also provide high levels of ecological environment in terms of agricultural production.

Numerous studies on metal accumulation in agricultural soils or crops have been conducted in Hainan[17–26], it is a pity that lack of awareness with respect to agricultural activities and uncommon geogenic sources caused heavy metal pollution in the main crop production areas in Hainan, and this accumulation poses a risk to human health[23,25]. For example, several studies have reported the concentrations of Ni, Cr, and Cu in the cropland soils of Northern Hainan, where higher concentrations of heavy metal(loid)s are related to the mother rocks[22–25]. Studies have reported that As, Cd, Hg, and Pb in soils mainly originate from various anthropogenic sources[19,20] and groundwater in the industry-oriented western region is slightly contaminated with heavy metal(loid)s[27]. In agricultural ecosystems, heavy metal(loid) accumulation in crops depends on different parameters, such as soil quality, irrigation water quality, atmospheric deposition, and the nature of the crops[9]. Thus, the accumulation and risk of heavy metal(loid)s in soil-irrigated water-fruit systems in Hainan orchards must be assessed. However, a complete investigation of the heavy metal contamination of the soil, fruit, and irrigation water in these orchards has not been reported.

Hence, the aims of this study were to: (1) analyze heavy metal(loid) accumulation in soil, fruit, and irrigation water samples of Hainan orchards; (2) explore the relationship of metal-accumulation between fruits and soils; (3) investigate possible input sources of soil heavy metal(loid)s through multivariate and geostatistical analyses (correlation analysis, principal component analysis (PCA), and geographical information system); (4) comprehensively evaluate soil the pollution status and potential ecological threats as induced by concentrations of soil heavy metal(loid)s using various indices (i.e., pollution, Nemerow, Hakanson's ecological risk indices); and (5) estimate the noncarcinogenic and carcinogenic health risk of heavy metal(loid) contamination of soils and fruits on children and adults based on the health risk assessment model. This study aimed to perform a complete investigation of the contamination level and related ecological-health risks of heavy metal(loid)s in Hainan orchards, thereby providing valuable information for policies associated with pollution prevention and management, the environment, and human health protection in the study region.

2 Materials and methods

2.1 Study area

This study was conducted on tropical Hainan Island in southern China (108°36'-111°03'E, 18°10'-20°10'N). Hainan Island has the largest tropical land area in China at 3.442 million hm^2. It accounts for 42.5% of the total tropical and subtropical areas in China. Hainan Island is located at the northern edge of the tropics and has a tropical monsoon climate. The annual average temperature, precipitation and sunshine hours are 22°C-27°C, 923-2459 mm, and 1750-2650 h, respectively. Hainan Island is the most important tropical fruit producing area in China. Local tropical fruits include litchi, longan, banana, mango, wax apple, pitaya, cantaloupe, and jackfruit. Soils in the studied region are mainly classified as latosols according to the classification and codes for Chinese soil (GB/T 17296-2009), and they originated from parent materials basalt, granite, and sandstone. In this study, the relevant national standards can be downloaded in the website of food codex data (https://www.sdtdata.com).

2.2 Sampling and preparation

A total of 372 surface soil samples were collected from Hainan orchards following the relevant national standards (NY/T 1054-2021; NY/T 395-2012), as shown in Figure 1. Based on tropical fruit-growing area of Hainan Island, the sampling sites are densely distributed in southern, western, and northern Hainan, but sparse in the eastern and middle areas. The location and geographical coordinates of all samples were recorded using a Global Positioning System (GPS). As the orchard plots were of different sizes, three sampling areas were randomly selected from each orchard. Each soil sample was taken from the surface at a depth of 0-60 cm, mixed thoroughly, and packed in polyethylene bags for transport to the lab. Then, all soil samples were air dried at room temperature, sieved using 2, 0.25, and 0.149 mm sieves, and stored in sample bags until laboratory analysis according to the relevant national standard (NY/T 395-2012).

Simultaneously, fruit samples corresponding to the soil samples were collected from each orchard according to national standards (NY/T 896-2015). Mature fruit (3 kg) were collected from fruit trees. After transportation to the laboratory, the samples were washed with distilled water and air dried, and the edible parts of the fruits were homogenised. In irrigated agricultural systems, soils in Hainan orchards are usually irrigated with reservoir water or groundwater, while wastewater is not used for irrigation in the study area. Water samples were collected from the irrigation canals in each orchard in clean plastic bottles according to national standards (NY/T 396-2000). According to the site survey, local fruit-growing farmers also applied manures, inorganic fertilizers, herbicides, and pesticides in the growing period for plant-growth in orchard land.

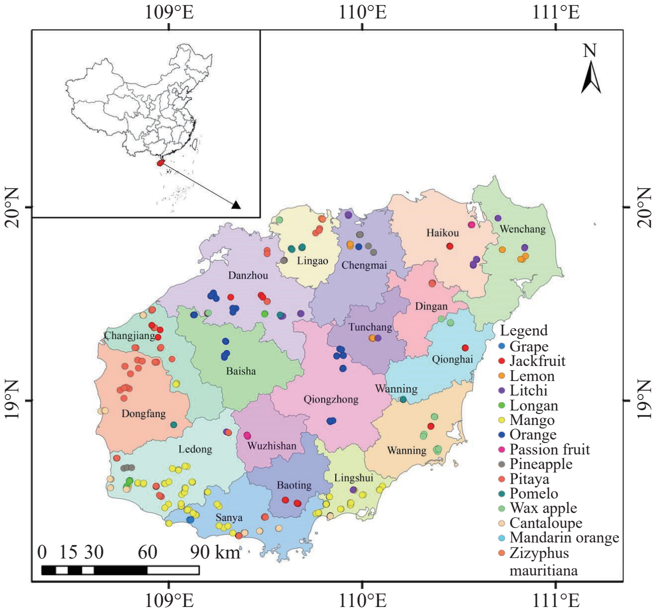

Figure 1 Distribution of sampling sites in Hainan orchards

2.3 Laboratory analysis

After sample collection, the organic matter (OM) concentration and pH in each soil sample and Cd, Hg, As, Pb, Cr, and Cu concentrations in the soil, fruit, and irrigation water samples were determined using the detection methods indicated by Chinese standards (see Table 4). Blind duplicates and standard reference materials were used to ensure quality control. Each sample was analysed three times.

2.4 Statistical analysis and spatial distribution

Data preprocessing and descriptive statistics (min, max, mean, etc.) were conducted using Microsoft Excel (Ver. 2021, Microsoft, USA). The types of potential pollution sources of these heavy metal(loid)s were explored using correlation analysis and PCA. The relationship between metal(loid)s was studied according to the similarity between paired metal data based on correlation matrices generated using R software (Ver. R-4.2.2, RStudio, USA). The degree of correlation is illustrated by the ellipse shape. A flatter ellipse indicates a stronger correlation. Positive correlations are denoted by blue, while negative correlations are indicated by red. The magnitude of the correlation coefficient is indicated by the color intensity. The orientation of the ellipse represents different correlation types: upper right-lower left represents a positive correlation, while upper left-lower right represents a negative correlation. Strong (*p<0.05) or significant (**p<0.01) correlations are marked by asterisks on the coefficients in the figure. In addition, Pearson correlation coefficients of heavy metal concentrations in the fruits and soils were calculated to understand the relationship between metal accumulation behaviour in fruits and soils using R software (Ver. R-4.2.2, RStudio, USA). SPSS Statistics (Ver. 26.0, IBM, USA) was used to perform a PCA on clustered metal(loid)s that behaved similarly to identify the potential sources of the heavy metal(loid)s, and it was also applied to perform a Kruskal-Wallis H-test to compare heavy metal concentrations among soils with different OM contents. Split-violin plots were generated using R software (Ver. R-4.2.2, RStudio, USA), violin diagram can reflect the distribution and probability density of the data, combining the advantages of box plot and kernel density diagram. The interior of the violin diagram is box diagram and the exterior is kernel density diagram. The larger the area of a certain area, the greater the probability of distribution near the values. Spatial distribution maps were generated to determine the position and spatial structural characteristics of the soil heavy metal(loid)s in the study area using ArcGIS (Ver. 10.5, ESRI, USA).

2.5 Pollution assessment and potential ecological risk assessment of soil heavy metal(loid)s

For the comprehensive pollution assessment of metal(loid)s in soils, pollution index (PI) and Nemerow integrated pollution index (NIPI) were employed and calculated based on the equations ($PI = C_i/C_{0i}$, $NIPI = \sqrt{[(P_{max})^2 + (P_{avg})^2]/2}$)[28], where C_i and C_{0i} refer to the concentration of metal (i) in soil samples(mg/kg) and its corresponding background value for the research region (mg/kg), P_{max} is the maximum PI value among all the metals' pollution indexes, and P_{avg} denotes the mean value of all PIs of the tested metals. Many researchers have chosen background concentrations of metal elements in the soils of certain provinces in China as reference[3,4,28]. Thus, the background values of Cd, Cr, As, Hg, Pb, and Cu in the surface soil of Hainan Province were chosen as reference values to calculate the PI values (Table 3)[29]. The potential ERI developed by Hakanson is a better evaluation method for estimating the ecological risk posed by toxic heavy metal(loid)s in soil[30]. The E_{ri} (the ecological risk index of metal i) and ERI (the sum of the E_{ri} calculated for each metal) can be calculated using $T_i \times PI_i$ and $\sum_{i=1}^{n} T_i \times PI_i$, respectively, where PI is the pollution index of metal i, T_i means the biological toxicity coefficient of metal i, which was regarded as Cr=2, Cu=Pb=5, Cd=30, As=10, and Hg=40[4,31]. The definitions, formulae, and classifications of two pollution indices and potential ERI are listed in in Table 1[4, 28, 31].

Table 1 Classification criterions for PI, NIPI, E_{ri}, and ERI

PI	Category	NIPI	Category	E_{ri}	Category	ERI	Category
PI ≤1	Unpolluted	NIPI≤0.7	No pollution	E_{ri}<40	Slight risk	ERI<150	Slight risk
1<PI≤ 2	Slightly polluted	0.7<NIPI≤1	Warning threshold	40≤E_{ri}<80	Medium risk	150≤ERI<300	Medium risk
2<PI ≤ 3	Mild polluted	1<NIPI≤2	Mild pollution	80≤E_{ri}<160	High risk	300≤ERI<600	High risk
3<PI ≤ 5	Moderate polluted	2<NIPI≤3	Moderate pollution	160≤E_{ri}<320	Very high risk	ERI≥600	Very high risk
PI > 5	High polluted	NIPI>3	Severe pollution	E_{ri}≥320	Extremely high risk		

2.6 Health risk assessment of heavy metal(loid)s in soil and fruit samples

According to the United States Environmental Protection Agency[32], the carcinogenic risk and noncarcinogenic risk of heavy metal(loid) in fruits and soils exposure to humans are used to assess human health risks. The average daily dose (ADD), the non-carcinogenic hazard quotient (HQ), the total non-carcinogenic hazard index (HI), the carcinogenic risk (CR), the total carcinogenic risk (TCR), can be determined according to the equations reported by Baltas et al.[33] and Chen et al.[28]. The average daily dose (ADD_{ing}, ADD_{inh}, ADD_{derm}) calculated for each element through three different exposure pathways such as ingestion, inhalation, and dermal contact can be determined using $\frac{C_{soil\ or\ fruit} \times IR_{ing} \times EF \times ED}{BW \times AT} \times 10^{-6}$, $\frac{C_{soil} \times InhR \times EF \times ED}{PEF \times BW \times AT}$, $\frac{C_{soil} \times SA \times SL \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6}$, where definitions and reference values of all parameters given in the above equations are listed in Table 2. The HQ, HI_{soil}, HI_{fruit}, CR, TCR_{soil}, and TCR_{fruit} can be calculated using $\frac{ADD_{ij}}{RfD_{ij}}$, $\sum HQ_{soil} = \sum \frac{ADD_{ij}}{RfD_{ij}}$, $\sum HQ_{fruit} = \sum \frac{ADD_i}{RfD_i}$, $ADD_{ij} \times SF_{ij}$.

Table 2 Exposure parameters of human health risk assessment

Indices	Unit	Definition	Adults	Children	References
C	mg/kg	Concentration of metal in the soils or fruits	–	–	This study
$IR_{ing\ (soil)}$	(mg/d)	Ingestion rate	100	200	[33, 35]
$IR_{ing\ (fruit)}$	(mg/d)	Ingestion rate	36	97	[36]
EF	(d/year)	Exposure frequency	350	350	[33, 37]
ED	(year)	Exposure duration	24	6	[33]
IR_{inh}	(m^3/d)	Inhalation rate	20	7.65	[33]
PEF	m^3/kg	Particle emission factor	1.36×10^9	1.36×10^9	[33]
SA	cm^2	Exposed area through dermal contact	1530	860	[33]
AF	mg/cm^2/d	Adherence factor of the skin	0.07	0.2	[33]
ABS	–	Dermal absorption factor	0.001	0.001	[33]
BW	kg	Average body weight	60	15	[35]
AT (Non-carcinogens)	d	Average exposure time	8760	2190	[33]
AT (Carcinogens)	d	Average exposure time	70 (lifetime) × 365	70 (lifetime) × 365	[33]

$\sum CR_{soil} = \sum ADD_{ij} \times SF_{ij}$, and $\sum CR_{fruit} = \sum ADD_i \times SF_i$, where *i* and *j* means different metal and different exposure pathway. RfD_{ij} (mg/kg·d) is regarded as reference exposure dose of heavy metal (i) through different exposure pathway(*j*). ADD_{ij} shows the average daily dose of heavy metal in soil (i) through different exposure pathway(*j*). SF_{ij} (mg/kg·d) means carcinogenic slop factor of metals(i) through different exposure pathway(j). The target hazard quotient (*HQ*) from fruits was also calculated in combination with average daily dose (ADD_{ing}) and the oral reference dose (*RfD*). According to USEPA report[34], *HQ* and *HI* values over 1 indicate there is a possibility of non-carcinogenic health effects of the exposed individual. In return, *HQ* and *HI* < 1 denote the absence of significant adverse health effects. The acceptable or tolerable range of the *CR* or *TCR* value is between 1×10^{-6} and 1×10^{-4}, *CR* or *TCR* value below 1×10^{-6} specifies no risk, while *CR* or *TCR* value over 1×10^{-4} indicates significantly carcinogenic risk to people. According to some studies in the literature, *RfD* for non–carcinogenic metals and *SF* for carcinogenic metals are listed in Table 3.

Table 3 The RfD for non-carcinogenic metals and SF for carcinogenic metals

Elements	Cd	Pb	Cu	Hg	As	Cr	References
$RfD_{ing\text{-}soil}$	1.0×10^{-3}	3.50×10^{-3}	4.0×10^{-2}	3.0×10^{-4}	3.0×10^{-4}	3.0×10^{-3}	[28, 38]
$RfD_{inh\text{-}soil}$	1.0×10^{-3}	3.52×10^{-3}	4.02×10^{-2}	8.57×10^{-5}	1.23×10^{-4}	2.86×10^{-5}	
$RfD_{derm\text{-}soil}$	1.0×10^{-5}	5.25×10^{-4}	1.20×10^{-2}	2.10×10^{-5}	1.23×10^{-4}	6.00×10^{-5}	
$Sf_{ing\text{-}soil}$	15	0.28	-	-	1.5	0.5	
$Sf_{inh\text{-}soil}$	6.3	0.28	-	-	15.1	42	
$Sf_{derm\text{-}soil}$	15	0.28	-	-	3.66	0.5	
$RfD_{ing\text{-}fruit}$	0.001	0.0035	0.04	0.004	0.0003	1.5	[39]
$Sf_{ing\text{-}fruit}$	6.1	0.0085			1.5		

3 Results and discussion

3.1 Soil properties and heavy metal(loid)s concentrations in soils

Descriptive statistics for the heavy metal(loid) concentrations and soil properties (pH and OM content) in the fruit-growing soils of the investigated area are presented in Table 4.

The soil pH ranged from 3.7-8.6, with an average of 5.5, and 90.6% of the soil samples had values below pH 7.0, indicating that most of the fruit-growing soils in Hainan Province were acidic. Compared to soil with high pH (>7), soil with a lower pH (<7) may show increased mobility of heavy metal(loid)s, which can increase the risk of heavy metal(loid)s pollution in the soil[40]. The OM values ranged from 0.522-64.2 g/kg, with a mean value of 13.2 g/kg. This value was below the national average OM content in agricultural soils (19.8 g/kg)[12], which was mainly attributed to unreasonable fertilisation in Hainan orchards. The coefficients of variation of soil pH and OM were 17.1% and 61.0%, respectively. These results indicate that fruit planting has more significant influence on soil OM than pH, which may be due to the different fertilisation patterns of the different orchards.

The contents of Cd, Hg, As, Pb, Cr, and Cu varied widely from 0.0045-0.42, 0.002 05–0.182, 0.0319-74.4, 0.62-104, 0.32-717, and 0.800-130 mg/kg, respectively, with corresponding average values of 0.047, 0.0357, 4.26, 26.1, 57.3 and 17.8 mg/kg. The average values of Hg, As, Pb, Cr, and Cu were lower than that of their national background values[29], whereas the average Cd content was greater than its background value. Furthermore, the maximum concentrations of Cr, Cu, Pb, As, Cd, and Hg were 717, 130, 104, 74.4, 0.42, and 0.182 mg/kg, respectively, which exceeded their background values. Moreover, Cd and Cr were 11.1- and 12.2-fold higher than their background values, respectively. When compared to the national environmental quality standard for agricultural soil at different pH values (GB 15618-2018), the overall exceedance percentages for Cr, As, Pb, Cd, Cu, and Hg were 10.2%, 1.88%, 1.08%, 0.269%, 0.0%, and 0.0%, respectively. The mean values of

Table 4 Statistical results of soil properties and heavy metal(loid)s concentrations in soils, irrigation water samples , and fruit samples

Soil properties/ HMs	Unit	Minimum value	Maximum value	Mean value	Standard Deviation (SD)	Coefficient of Variation	Background Value[a]	Exceedance rates (%)	Safety standards					Detection methods
Soil samples														
pH	-	3.7	8.6	5.5	0.934	0.171	-	-	≤5.5	5.5< pH≤ 6.5	6.5< pH≤ 7.5	>7.5		NY/T 1377-2007
Cd	mg/kg	0.0045	0.42	0.047	0.0549	1.18	0.037	0.269	0.3	0.3	0.3	0.6	GB 15618-2018	GB/T 17141-1997
Hg	mg/kg	0.00205	0.182	0.0357	0.0245	0.685	0.053	0	1.3	1.8	2.4	3.4		GB/T 22105. 1-2008
As	mg/kg	0.0319	74.4	4.26	7.94	1.86	10	1.88	40	40	30	25		GB/T 22105. 2-2008
Pb	mg/kg	0.62	104	26.1	16.6	0.639	40.1	1.08	70	90	120	170		GB/T 17141-1997
Cr	mg/kg	0.32	717	57.3	105	1.83	58.9	10.2	150	150	200	250		HJ 491-2019
Cu	mg/kg	0.8	130	17.8	22.1	1.24	20.4	0	150	150	200	200		HJ 491-2019
OM	g/kg	0.522	64.2	13.2	8.07	0.61	-	-	-	-	-	-		NY/T 1121.6-2006
Irrigation water samples														
Cd	mg/L	ND*(<0.00005)	0.00051	<0.000052	-	-	-	0	≤0.01				GB 5084-2021	HJ 700-2014
Hg	mg/L	ND*(<0.00004)	0.00062	<0.000041	-	-	-	0	≤0.001					HJ 694-2014
As	mg/L	ND*(<0.0003)	0.023	<0.00039	-	-	-	0	≤0.1					HJ 694-2014
Pb	mg/L	ND*(<0.00009)	0.018	<0.00029	-	-	-	0	≤0.2					HJ 700-2014
Cr	mg/L	ND*(<0.004)	0.028	<0.0045	-	-	-	0	≤0.1					GB/T 7467-1987
Cu	mg/L	ND*(<0.00008)	0.00022	<0.000081	-	-	-	0	≤1					HJ 700-2014
Fruit samples														
Cd	mg/kg	ND*(<0.001)	0.016	<0.0019	-	-	-	0	≤0.05				GB 2762-2017	GB 5009.15-2014
Hg	mg/kg	ND*(<0.003)	0.0043	<0.0030	-	-	-	0	≤0.01				GB 18406.2-2001	GB 5009.17-2021
As	mg/kg	ND*(<0.003)	ND*(<0.003)	ND*(<0.003)	-	-	-	0	≤0.5				GB 18406.2-2001	GB 5009.11-2014
Pb	mg/kg	ND*(<0.02)	0.06	<0.022	-	-	-	0	≤0.1				GB 2762-2017	GB 5009.12-2017
Cr	mg/kg	ND*(<0.05)	0.168	<0.0542	-	-	-	0	≤0.5				GB 18406.2-2001	GB 5009.268-2016
Cu	mg/kg	ND*(<0.05)	0.881	<0.0641	-	-	-	0	≤10				GB 15199-1994	GB 5009.268-2016

a Background values for soils in Hainan Province [29].
*ND-Not detected (its level is below the detection limit).

these elements decreased in the order of Cr>Pb>Cu>As>Cd>Hg, and they did not exceed the safety standard. Based on the above analysis, although heavy metal(loid) pollution is relatively safe, these metal(loid)s are locally enriched in the soils to different degrees. The coefficient of variation of the heavy metal(loid)s varied from 183% for Cr to 63.9% for Pb, implying a nonhomogeneous spatial distribution of soil metal(loid)s in the study area.

3.2 Heavy metal(loid) concentrations in irrigation water samples

The heavy metal(loid) concentrations (Cd, Hg, As, Pb, Cr, and Cu) in the irrigation water samples are listed in Table 4. The concentrations in all irrigation water samples from the Hainan orchards were far below the limit values set by the national standards of China and thus were at an acceptable level. Moreover, the metal(loid) concentrations in most samples were below the detection limit and in negligible amounts, suggesting that the irrigation water samples were not affected by heavy metal accumulation.

3.3 Heavy metal(loid)s concentrations in fruit samples

The contents of heavy metal(loid)s in fruits ranged from not detected (ND) (<0.001) to 0.016 mg/kg for Cd, ND (<0.003) to 0.0043 mg/kg for Hg, ND (<0.02) to 0.060 mg/kg for Pb, ND (<0.05) mg/kg to 0.168 mg/kg for Cr, and ND (<0.05) to 0.881 mg/kg for Cu, with average values of <0.0019, <0.0030, <0.022, <0.0542, and <0.0641 mg/kg, respectively (Table 4). All the fruit samples examined in this study had negligible As concentrations lower than the detection limit. The heavy metal(loid) contents in the fruits were much lower than the control values according to the national standards of China (Table 4), indicating that the accumulation capacity heavy metal(loid)s in fruits was relatively weak.

3.4 Interrelationship of metal-accumulation between fruits and soils

Soil properties and heavy metal(loid)s are the dominant factors affecting the accumulation of metal(loid)s in plants. The Pearson correlation coefficient analysis between the metal concentrations in fruits and soils and other soil properties was applied and are given in Figure 2. This correlation analysis did not consider the As concentrations in the fruit samples because the concentrations of As in all samples were below the detection limit at negligible amounts. The detection limits for Cd, Hg, Cr, and Cu were used in correlation analysis when the fruit samples contained heavy metal(loid) concentrations below the detection limits. The correlation matrix showed that the heavy metal(loid) concentration in fruits was positively and weakly related with that detected in the soil, with weak correlation coefficients of 0.30, 0.14, 0.30, and 0.40 for Cd, Hg, Cr, and Cu, respectively; however, only the coefficients for Cd (p<0.01), Cr (p<0.01), and Cu (p<0.01) were significant (Figure 2). Positive correlations were observed between Cr and Cu (p<0.01), and the accumulation behaviour of Cu in the fruits was likely very similar to that of Cr. However, significant correlations were not observed between the Pb levels in the fruit and soil samples in this study. The low concentrations of Hg and Pb in the orchard soil probably result in the insignificant correlation in Pb and Hg concentrations between the soil and fruit samples. Soil pH was weakly and negatively correlated with the Pb contents in fruits (r=−0.19, p<0.05). Furthermore, a significant and weak correlation was only observed between the fruit Cr content and soil OM content (r=0.20, p<0.05). Heavy metal accumulation in fruits may depend on multiple soil factors, which can affect the bioaccumulation rates of metal(loid)s in the fruits. In our study, the fact that fruits are not higher than the heavy metal standard limit indicates that the heavy metal(loid)s bioaccumulation rates from soils to fruits are relatively slow.

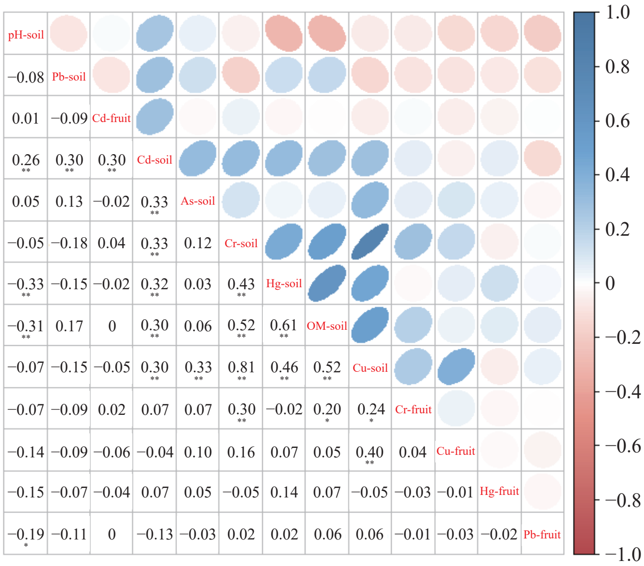

Figure 2 Pearson correlation analysis of heavy metal(loids) and soil properties (pH and OM)

3.5 Source analysis and pollution assessment of soil heavy metal(loid)s

3.5.1 Correlation between soil heavy metal(loid)s and soil properties

Pearson's correlation matrix was used to characterise the relationships between the tested elements and soil properties (pH and OM) (Figure 2). The correlation analysis showed that the Cr, Cu, Hg, and Cd concentrations were significantly correlated with each other (p<0.01); As was significantly correlated with Cu (r=0.33) and Cd (r=0.33); Pb was significantly correlated with Cd (r=0.30); and Cr was highly positively correlated with Cu (r=0.81) at a significance level of 0.01. If the correlation coefficients between heavy metal(loid)s are strong and positive, then these metal(loid)s probably have an interdependence and common source, or similar pathways in the environment. However, negative correlations existed between Cr and Pb (r=–0.18) and Pb and Cu (r=–0.15), indicating that Pb and Cr and Pb and Cu probably originated from different sources. No significant correlations were found between As and Hg, indicating that they likely have different sources.

Soil acidification is a serious environmental problem in the study area, where the mobility of heavy metal(loid)s is high. Cd was significantly positively correlated with pH, indicating that the content of Cd in soil is related to the soil pH. This is in accordance with previous reports showing that many areas of acidic soil in South China are contaminated by heavy metal(loid)s, among which Cd causes the most serious pollution[41,42]. Moreover, soil OM, which has a strong complexing capacity for metallic pollutants, was significantly and positively correlated with most of heavy metal(loid)s. Figure 3 illustrates the mean concentrations of heavy metal(loid)s in soils with different OM contents, based on Kruskal-Wallis H-test results. Noticeably, there are significant differences among the mean concentrations of heavy metal(loid)s in soils with different OM contents. The mean heavy metal(loid)s value with OM>15 g/kg was significantly higher than that with OM<15 g/kg. This is consistent with previous reports showing that OM plays an important role in controlling the sorption of heavy metal(loid)s by soil[43]. Different crop types, tillage methods, and fertilisation treatments may significantly affect the spatial distribution of heavy metal(loid)s in agricultural soils by changing the soil OM contents[44]. As discussed above, the spatial variability of heavy metal(loid)s at the sampling sites could be related to the activities that lead to variations of OM over time.

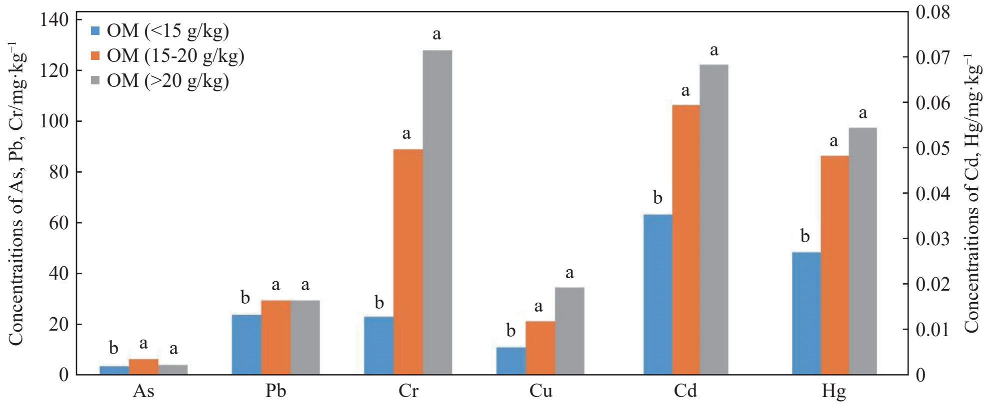

Figure 3 Mean heavy metal(loid)s concentrations in soils with different levels of OM contents. (a and b denote significantly different groups at 0.05 level)

3.5.2 PCA of soil samples

To explore the sources of the metal pollutants, PCA was employed to the entire soil metal dataset to reduce the initial dimensions of the dataset. Although it is difficult to distinguish the effects of natural or anthropogenic sources on soil, the association between heavy metal(loid)s and the PCA factor loadings matrix can reflect the hypothetical sources of metal pollutants. Varimax rotation with Kaiser normalisation was used to simplify the coefficient factors. The results obtained from varimax rotation are illustrated in Table 5, indicating that three principal components are significant with an Eigenvalue ≥1, and they explained 77.512% of the total variance (i.e., principal component 1: 39.788%, principal component 2: 22.230%, and principal component 3: 15.494%). The component plots of the three principal components in the rotated space and the factor contributions (%) estimated by PCA are shown in Figure 4.

Table 5 Principal component analysis of heavy metal(loid)s in soil

HMs	Component 1	Component 2	Component 3
Cd	0.303	**0.629**	0.254
Hg	**0.614**	**0.511**	–0.289
As	0.147	0.176	**0.916**
Pb	–0.235	**0.848**	0.084
Cr	**0.910**	–0.027	0.082
Cu	**0.885**	–0.014	0.294
Eigen value	2.387	1.334	1.000
% of variance	39.788	22.230	15.494
Cumulative %	39.788	62.018	77.512

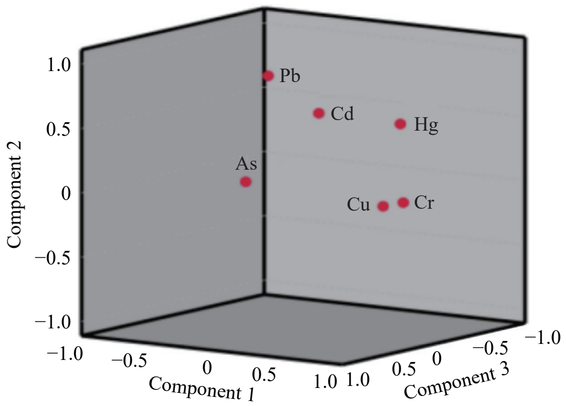

Figure 4 Loading plot of the principal components for six heavy metal(loid)s in the soils of the study sites using PCA analysis after varimax rotation

Component 1 explained 39.788% of the total variance in the metal data and had high loading values for Cr (0.910), Cu (0.885), and Hg (0.614). Cr, Cu, and Hg were mostly found in the same group because they have homologous characteristics and possibly originate from the same source. This was supported by the significantly strong linkage between Cr and Cu (r=0.81, p<0.01), as shown in the correlation analysis graph (Figure 2). The parent material and paedogenic processes are major factors affecting the amount and distribution of Cr[45]. The main areas with high Cr, Cu, and Hg concentrations were located in the northern part of Hainan (Figure 6). Similar results have been reported, where high concentrations of Cr and Cu in northern Hainan were attributed to parent materials in volcanic rock soil[23–25,46]. Hg was partitioned into two principal component axes (components 1 and 2), suggesting the existence of two main sources of Hg inputs in the investigated soils. Previous studies reported that Cr and Hg in the agricultural soil of Hainan Island were mainly affected by the soil background[19]. Thus, component 1 can be attributed to its natural origin.

Component 2 accounted for 22.230% of the variance in the soil data and had high loadings of Pb (0.848), Cd (0.629), and Hg (0.511), indicating some degree of homology of these elements, which is most probably anthropogenic activities. The average Cd content was greater than its background value, indicating that anthropogenic activities were the main sources of Cd. Cd is usually regarded as an elemental marker of agricultural production activity, and its accumulation usually results from the use of pesticides, fertilisers, and other agricultural inputs[19,20]. The sources of Pb commonly include vehicle exhaust, industrial fumes, pesticides, and phosphate fertilisers. As a famous tropical tourist area, a large amount of vehicle exhaust is emitted on Hainan Island every year; thus, the accumulation of Pb in the soil is likely affected by vehicle exhaust emissions. Furthermore, Wang et al.[47] and Liu et al.[48] reported that fertilisers are vital sources of Pb in agricultural soils in China. On Hainan Island, crop production is frequently accompanied by large amounts of chemical fertilisers and pesticides to obtain high replanting indices and economic benefits. The application of N, P, and K fertiliser on Hainan Island is up to 830,000 t, which is far higher than the national average dosage, and approximately 70% of the fertiliser is usually lost to the soil, water, and air with a low utilisation rate[19]. According to the site survey conducted among the orchard farmers, they applied manure, inorganic fertilizers, herbicides, and pesticides for plant-growth in the growing period. Excess application of agricultural fertilizers not only resulted in a decrease in soil pH, but also led to an increase in heavy metals. After a long history of intensive agro-fertilizer and pesticide application, most of the fruit-growing soils in Hainan province were acidic according to our results, thus leading to increased mobility of heavy metal(loid)s. Zhao et al.[48] found that the content of heavy metal(loid)s, including Pb and Cd, in the commercial fertiliser of Hainan Province exceeded the relevant standard level, thus leading to the accumulation of Pb and Cd in the soil. According to the above discussion, the high Pb content in the agricultural soils of Hainan orchards may be correlated with fertiliser application. Atmospheric deposition caused by anthropogenic activity is an important source of Hg in the soil. Similar results have been reported for traffic and atmospheric dust, which may serve as critical sources of Pb and Hg[49]. Water samples collected from the studied orchards contained negligible amounts of metal(loid)s, suggesting that the irrigation water did not affect the accumulation of heavy metal(loid)s in the soil. Therefore, component 2 accounts for a mix of anthropogenic sources, including agricultural production activities, traffic emissions, and atmospheric deposition.

Component 3 explained 15.494% of the total variance and had a high loading of As (0.916), and it showed a greater correlation with As than the other elements, which are mainly affected by regional factors, such as mining activities. Zhong[22] found that the extensive distribution of As in the arable land of Hainan Island is a result of local mining and exploration. Areas with high As concentrations are located in the southwestern part of Hainan Island near mining areas, such as Changjiang and Dongfang. The aforementioned claims were also confirmed by the GI maps of As in Figure 6, which indicate that Component 3 embodies the influence of mining activities.

3.5.3 Pollution assessment and spatial pattern of soil heavy metal(loid)s

The calculated PI values for all assessed heavy metal(loid)s are shown in Figure 5. The PI values for Cd, Hg, As, Pb, Cr, and Cu ranged from 0.122-11.4, 0.0387-3.43, 0.003 19–7.44, 0.0155-2.59, 0.005 43–12.2, and 0.0392-6.37, respectively. For all metal(loid)s except Cd, the average PI values were below 1. However, the maximum PI values of Cr, Cd, As, Cu, Hg, and Pb reached 12.2, 11.4, 7.44, 6.37, 3.43, and 2.59, respectively, exceeding 1 by 2-13 times. The number of sampling sites with PI values greater than 1 decreased in the following order: Cd>Cu>Cr>Hg>Pb>As. This finding indicated that the heavy metal(loid) contents in some sampling sites exceeded the background values.

To intuitively display the heavy metal(loid)s pollution level in Hainan orchards, the calculated PI values for all assessed heavy metal(loid)s were imported into ArcGIS to map the spatial distributions of pollution levels (Figure 6). The spatial pattern of different heavy metal(loid)s has proven to be a useful tool for assessing the origins of metal enrichment and pollution hotspots with high concentrations of heavy metal(loid)s. The spatial distribution maps of PI for the six metal(loid)s (Figure 6) demonstrate a significant local accumulation of heavy metal(loid)s, especially Cd, Cr, and Cu, over the entire study area.

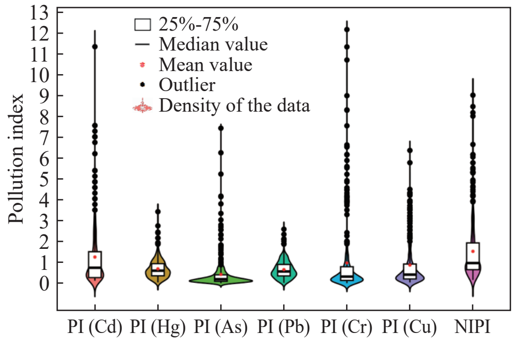

Figure 5 Split-violin plot of the pollution index (PI) for each individual heavy metal(loid) and Nemerow integrated pollution index (NIPI) in the soil samples (n=372)

As shown in Figure 6, the spatial distribution patterns of Cr and Cu showed a similar trend in that higher concentrations were mainly located in the northern of Hainan Province. For Cr and Cu, the percentages of slight-to-mild pollution cases are 11.0% and 15.6%, while the values of moderate-to-severe pollution ones are 10.2% and 7.8%, respectively. Numerous volcanoes north of Hainan Island represent the Quaternary volcanoes of China[50]. At least eight volcanic eruptions can be discerned in the Quaternary volcanic rocks distributed on northwestern Hainan Island. Intense volcanic activity has formed basalt and basalt-based soils, which reportedly contain high background levels of heavy metal(loid)s[23-25]. Soils in the northwestern area are mainly derived from pyroclastic and basic volcanic rocks. Furthermore, the spatial distributions of Cr and Cu showed a good correlation with the distribution of volcanic rock soils. The parent material of volcanic rocks with an uncommon geological background is likely the major factor affecting the levels and distributions of Cr and Cu in the soils of northwestern Hainan, which is consistent with the results of the PCA and correlation analysis.

Cd is usually considered an anthropogenic component of agricultural production. An examination of the spatial distribution of the Cd pollution level in soil samples showed that the percentages of slight and mild pollution cases are 17.5% and 9.4%, while the values of moderate and severe pollution ones are 5.9% and 3.5%, respectively. Most notably, the Hainan orchards have obvious Cd point source pollution characteristics, especially the central, western, and southern orchards, which are affected by different degrees of Cd pollution, probably due to human activities.

With respect to Pb, only a few soil samples exhibited slight and mild pollution levels with the percentages of 17.7% and 1.3%, respectively, and most cases were at the non-contaminated level. Anthropogenic Pb in agricultural soils may originate from traffic and industrial and agronomic practices. Sanya City was under slight and mild Pb contamination, which was largely due to a large amount of vehicle exhaust in this famous tropical tourist area. However, areas with Pb contamination were located in central and western parts, where were far from large cities and heavy traffic sites. Combined with the PCA analysis, the distribution analysis indicates that Pb may have primarily originated from traffic emissions and agricultural practices.

The entire study region exhibited no or slight pollution levels with respect to Hg. Higher Hg concentrations were observed in the northern and southern regions. Thus, one of the reasons for the high Hg content may be the high background value of volcanic rock soils in the northern area. Numerous oil wells, gas stations, and natural rubber industries are located in or around the northern parts of the study area, thereby increasing the atmospheric dry and wet deposition inputs[25]. Hg can accumulate in soil through atmospheric deposition. In the north latitude, Hg deposition of 15.8 μg/(m^2·a) is observed at 30°-70° and 19.8 μg/(m^2·a) is observed at 10°-30°, and the study area is within the high deposition range[46]. Thus, the second reason for the accumulation of Hg in the soil may be atmospheric deposition.

The spatial distribution of As exhibits distinct geographic features. Hotspots with moderate-to-severe As pollution, accounting for 2.1% of all hotspots, are mainly distributed in the western region of Hainan Island near the mining area. The mineral resources in Hainan Province are generally rich, their distribution is relatively concentrated, and their mineral types are relatively complete[51]. The central and western regions of Hainan Province, including Changjiang and Dongfang, are important areas for mining[52]. It was inferred that the high As contamination was mainly caused by mining activities in the study area. Although there was point-source pollution, the concentrations of As at most sample sites were lower than the background value. Previous studies have confirmed that the natural concentrations of heavy metal(loid)s in soils are relatively low and mainly originate from the soil parent material[53]. It can be explained that higher As levels were mainly affected by mining activities in the western part.

To comprehensively evaluate the integrated pollution status from all heavy metal(loid)s in the study area, the NIPI results were analysed as shown in Figure 5 and Figure 7. The average NIPI value of the study area was 1.54 (ranging from 0.157-9.02), and 48.4% of the sites exhibited mild-to-severe pollution levels. In Figure 7, the spatial distribution map of the NIPI reveals that 9.7% and 13.7% of soil sites in Hainan orchards were categorized as having medium and severe pollution levels, respectively, while the rest of the area exhibited either no pollution or mild pollution levels.

From a provincial and region perspective (Figure 8), Hainan orchards were divided into five regions. The first region was northern area with high geological background values, particularly Haikou City and Lingao Country, where the regional pollution pattern can be summarized as simultaneously moderate-to-heavy Cr and Cu pollution, while Cr pollution was worse. The western orchards suffering from mild pollution were located in industry-oriented region, including Changjiang Country and Dongfang City, where the mines are concentrated. The fruit-growing soils of the southern and central region were mainly slightly-to-moderate polluted by Cd. For the eastern region, only Qionghai City was under slight Cr and Cu contamination. As such, the whole Hainan orchards were recorded as mild pollution level (Figure 8), but the northern area needs more prevention and attention.

3.6 Potential ecological risks assessment of soil heavy metal(loid)s

According to the calculated E_{ri} values in Figures 7 and 9, the percentages of soil samples exceeding the low ecological risk category for As, Pb, Cu, and Cr were significantly lower than those for Hg and Cd. Owing to the high toxicity coefficients of Hg and Cd, 20.7% of Hg and 28.8% of Cd in the collected soil samples were exceeding the low ecological risk category. Cd and Hg were the main contributors to the ERI (47.7% and 34.9%, respectively), whereas the contributions of As, Cu, Pb, and Cr were significantly

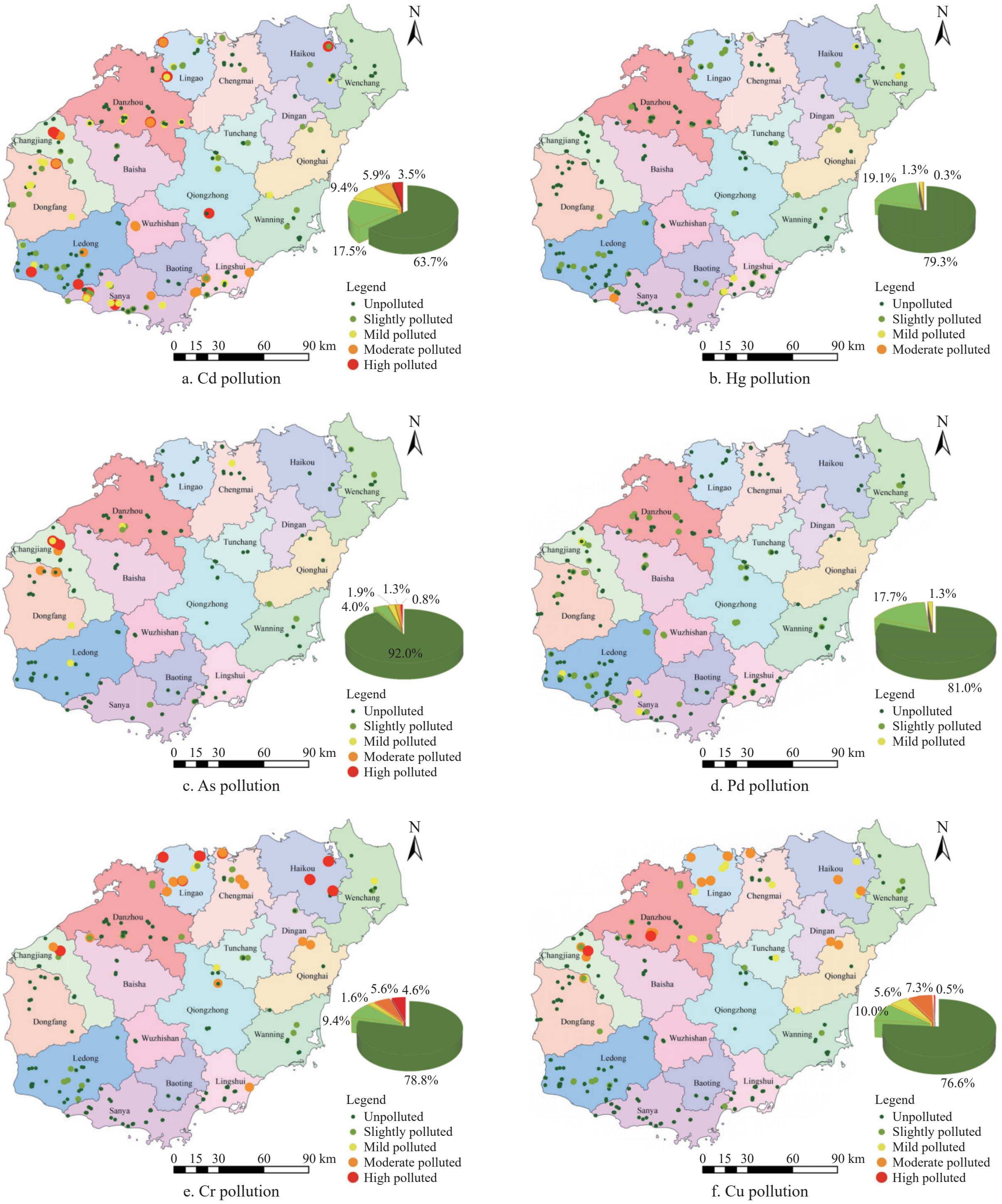

Figure 6 Spatial distributions of pollution index (PI) for heavy metal(loid)s Cd, Hg, As, Pb, Cr and Cu, with the dot size representing metal pollution level (PI)

lower, at 5.39%, 5.52%, 4.12%, and 2.47%, respectively. Only Cd and Hg were used to draw maps of the spatially interpolated E_{ri} values because the ecological risks of As, Hg, Cr, and Cu were excessively low. Figure 7 shows the spatial distribution differences in the ecological risk levels of Hg and Cd. The southern and western regions display medium-to-extremely high risk ecological risks owing to their high Cd content, whereas a few areas of Sanya City, Lingshui Country, Wenchang City, and Haikou City show a high ecological risk from Hg.

Regarding the combined potential ecological risks from all heavy metal(loid)s, the ERI values ranged from 10.9-358, with a spatial mean value of 79.1 (Figure 9). Only 10.4% of the collected soil samples exceeded the low-risk level, suggesting that the entire study area has a low ecological risk. The map of the spatially interpolated ERI in Figure 7 shows that moderate-to-high risk ecological risk mainly occurs in some orchards of southern, northern, central, and western Hainan orchards, whereas a low risk level is observed in the other areas.

3.7 Potential human health risk assessment in soils and fruits

3.7.1 Non-carcinogenic risk and carcinogenic risk of heavy metal(loid)s in soils

Table 6 presents the assessment results (i.e., ADD, HQ, and HI) of the noncarcinogenic risk for heavy metal(loid)s in soils exposure in children and adults. For both adults and children, the ADD_{total} of

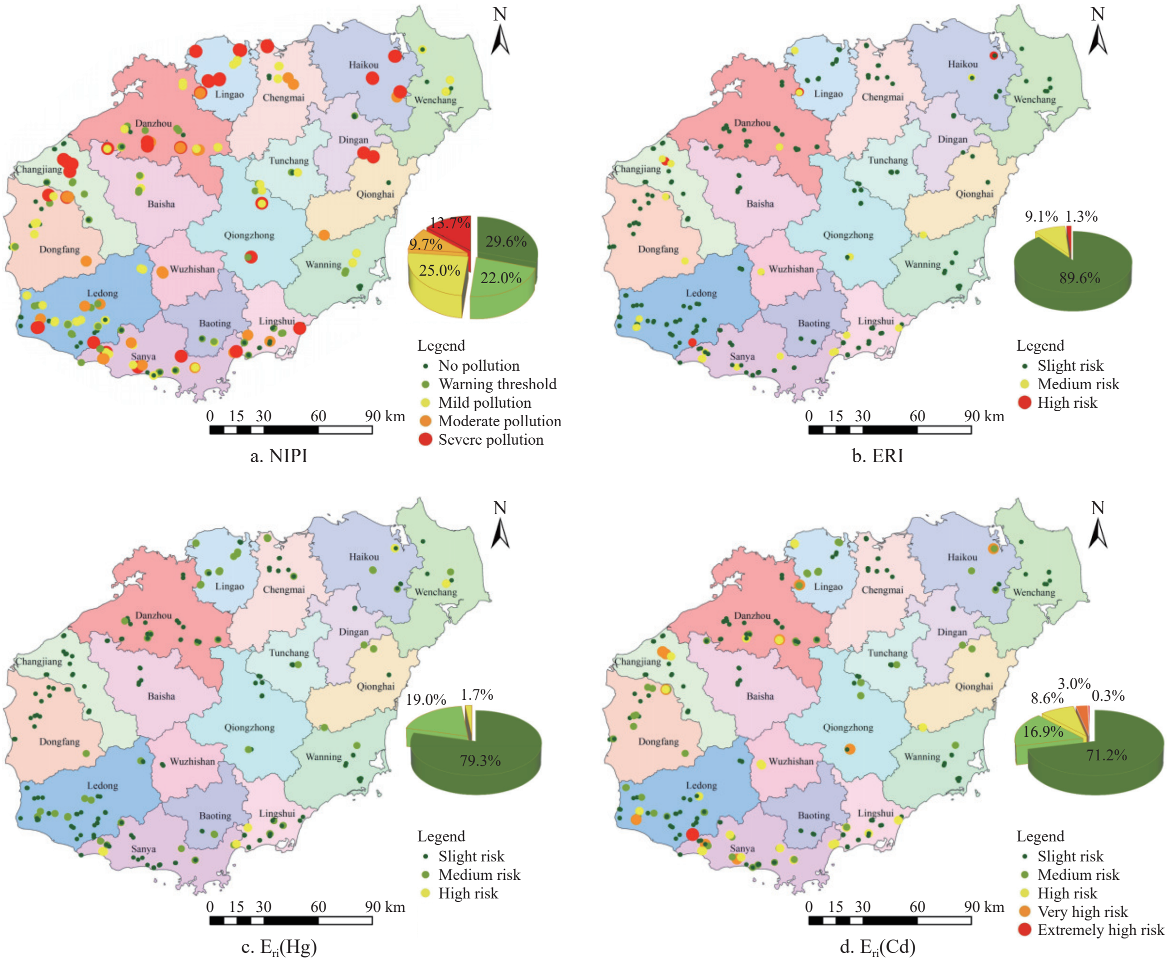

Figure 7 Spatial distributions of pollution ecological risk indices (Eri) for heavy metal Cd and Hg, integrated ecological risk index (ERI) and Nemerow integrated pollution index (NIPI) in Hainan province, with the dot size representing metal pollution level or risk level

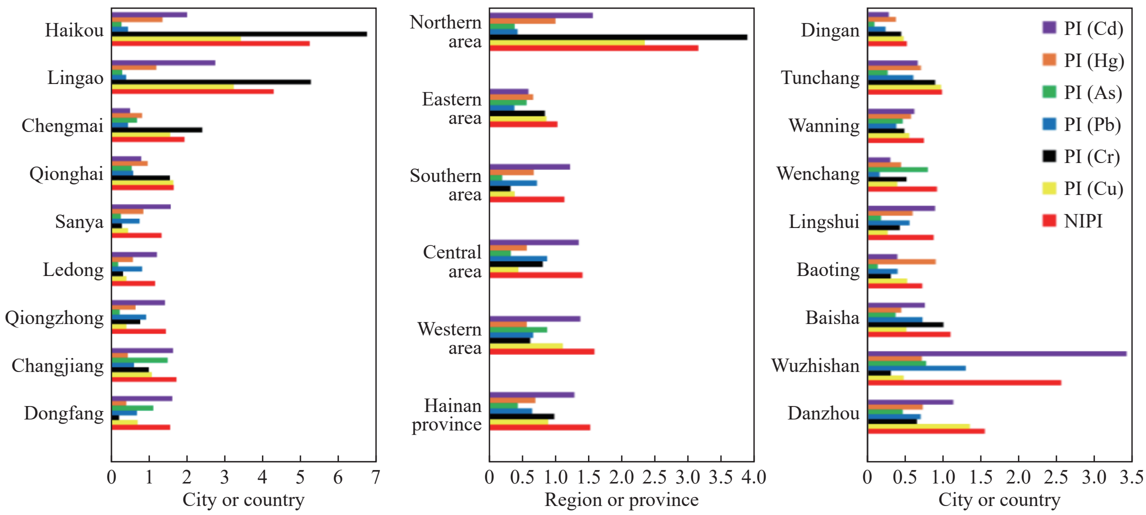

Figure 8 Average PI and NIPI at regional and provincial scales

heavy metal(loid)s in soils followed the order Cr>Pb>Cu>As>Cd>Hg, and the HQ values of heavy metal(loid)s decreased in the order Cr>As>Pb>Cu>Hg>Cd. When examining the noncarcinogenic risk of each heavy metal(loid), both the ADD_{total} and HQ values for children were over six times higher than those for adults, implying that children are much more vulnerable to toxic heavy metal(loid)s than adults. Similar to the data for children, the HQ values for the three exposure pathways in adults were ranked $HQ_{ing}>HQ_{dermal}>HQ_{inh}$, indicating that oral ingestion of toxic heavy metal(loid)s is the primary pathway of toxicity. The combined HI values of adults and children for all studied metal(loid)s were lower than the safety threshold of 1 (HI<1), suggesting that significant noncarcinogenic health risks posed by metal(loid)s in the investigated area were not likely to occur.

The carcinogenic risk results for toxic metal(loid)s (except for Hg and Cu) were determined through the three exposure pathways for both adults and children, as shown in Table 7. The carcinogenic ADD_{total} for Cr in the soils in the study region was the highest, followed by the corresponding values for Pb, Cu, As, Cd, and Hg. Among different exposure pathways, oral ingestion by children and

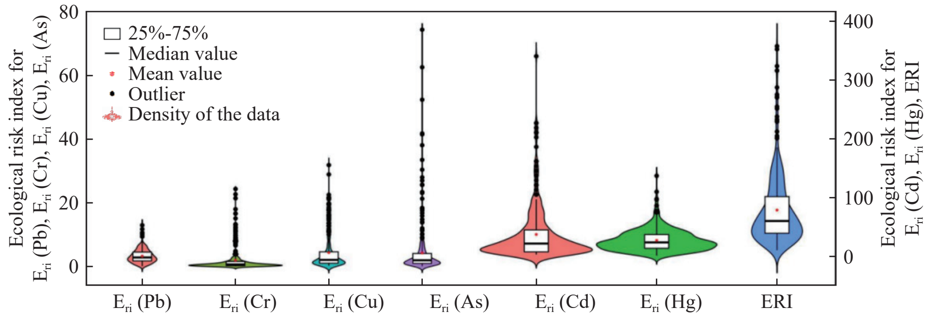

Figure 9 Split-violin plots of the potential ecological risk index (E_{ri}) for six heavy metal(loid)s, and the potential ecological risk index (ERI) (n=372)

adults was the primary route of carcinogenic ADD induced by the six metal(loid)s. Cr has a significant potential carcinogenic risk because its CR value is considerably higher than that of other metal(loid)s. Regardless of the daily intake and carcinogenic risk, the values for children were significantly higher than those for adults. Considering the total carcinogenic risks, the TCR values for adults and children were 2.38×10^{-5} and 4.73×10^{-5}, respectively. Overall, the results indicate that the potential carcinogenic health risks of soil heavy metal(loid)s for human in Hainan orchards are within an acceptable range (1×10^{-6}–1×10^{-4}). However, the risks posed by Hg and Cu could not be calculated because of a lack of parameter values in the CR assessment equations. In this case, the total carcinogenic risk of soil heavy metal(loid)s was lower than the actual risk.

Table 6 Non-carcinogenic risks to humans from soil heavy metal(loid)s

Group	Elements	ADD_{ing}	ADD_{inh}	ADD_{derm}	ADD_{total}	HQ_{ing}	HQ_{inh}	HQ_{derm}	HQ	HI
	Cd	5.95×10^{-7}	1.66×10^{-11}	5.12×10^{-10}	5.96×10^{-7}	5.95×10^{-4}	1.66×10^{-8}	5.12×10^{-5}	6.46×10^{-4}	
	Hg	4.67×10^{-7}	1.30×10^{-11}	4.02×10^{-10}	4.67×10^{-7}	1.56×10^{-3}	1.52×10^{-7}	1.91×10^{-5}	1.58×10^{-3}	
Children	As	5.45×10^{-5}	1.52×10^{-9}	4.69×10^{-8}	5.45×10^{-5}	1.82×10^{-1}	1.24×10^{-5}	3.81×10^{-4}	1.82×10^{-1}	0.543
	Pb	3.34×10^{-4}	9.34×10^{-9}	2.87×10^{-7}	3.35×10^{-4}	9.55×10^{-2}	2.65×10^{-6}	5.48×10^{-4}	9.61×10^{-2}	
	Cr	7.33×10^{-4}	2.05×10^{-8}	6.30×10^{-7}	7.33×10^{-4}	2.44×10^{-1}	7.64×10^{-4}	1.05×10^{-2}	2.56×10^{-1}	
	Cu	2.28×10^{-4}	6.36×10^{-9}	1.96×10^{-7}	2.28×10^{-4}	5.69×10^{-3}	1.58×10^{-6}	1.63×10^{-4}	5.71×10^{-3}	
Adults	Cd	7.44×10^{-8}	1.09×10^{-11}	7.97×10^{-11}	7.45×10^{-8}	7.44×10^{-5}	1.10×10^{-8}	7.97×10^{-6}	8.24×10^{-5}	0.0686
	Hg	5.84×10^{-8}	8.58×10^{-12}	6.25×10^{-11}	5.84×10^{-8}	1.95×10^{-4}	1.00×10^{-7}	2.98×10^{-6}	1.98×10^{-4}	
	As	6.81×10^{-6}	1.00×10^{-9}	7.29×10^{-9}	6.82×10^{-6}	2.27×10^{-2}	8.14×10^{-6}	5.93×10^{-5}	2.28×10^{-2}	
	Pb	4.18×10^{-5}	6.14×10^{-9}	4.48×10^{-8}	4.18×10^{-5}	1.19×10^{-2}	1.75×10^{-6}	8.52×10^{-5}	1.20×10^{-2}	
	Cr	9.16×10^{-5}	1.35×10^{-8}	9.81×10^{-8}	9.17×10^{-5}	3.05×10^{-2}	5.03×10^{-4}	1.63×10^{-3}	3.27×10^{-2}	
	Cu	2.85×10^{-5}	4.19×10^{-9}	3.05×10^{-8}	2.85×10^{-5}	7.12×10^{-4}	1.04×10^{-7}	2.54×10^{-6}	7.14×10^{-4}	

Table 7 Carcinogenic risks to humans from soil heavy metal(loid)s

Group	Elements	ADD_{ing}	ADD_{inh}	ADD_{derm}	ADD_{total}	CR_{ing}	CR_{inh}	CR_{derm}	CR	TCR
	Cd	5.10×10^{-8}	1.43×10^{-12}	4.39×10^{-11}	5.11×10^{-8}	7.65×10^{-7}	8.98×10^{-12}	6.58×10^{-10}	7.66×10^{-7}	
	Hg	4.00×10^{-8}	1.12×10^{-12}	3.44×10^{-11}	4.01×10^{-8}	–	–	–	–	
Children	As	4.67×10^{-6}	1.31×10^{-10}	4.02×10^{-9}	4.67×10^{-6}	7.01×10^{-6}	1.97×10^{-9}	1.47×10^{-8}	7.02×10^{-6}	4.73×10^{-5}
	Pb	2.87×10^{-5}	8.01×10^{-10}	2.46×10^{-8}	2.87×10^{-5}	8.02×10^{-6}	2.24×10^{-10}	6.90×10^{-8}	8.03×10^{-6}	
	Cr	6.28×10^{-5}	1.75×10^{-9}	5.40×10^{-8}	6.29×10^{-5}	3.14×10^{-5}	7.37×10^{-8}	2.70×10^{-8}	3.15×10^{-5}	
	Cu	1.95×10^{-5}	5.45×10^{-10}	1.68×10^{-8}	1.95×10^{-5}	–	–	–	–	
Adults	Cd	2.55×10^{-8}	3.75×10^{-12}	2.73×10^{-11}	2.55×10^{-8}	3.83×10^{-7}	2.36×10^{-11}	4.10×10^{-10}	3.83×10^{-7}	2.38×10^{-5}
	Hg	2.00×10^{-8}	2.94×10^{-12}	2.14×10^{-11}	2.00×10^{-8}	–	–	–	–	
	As	2.34×10^{-6}	3.43×10^{-10}	2.50×10^{-9}	2.34×10^{-6}	3.50×10^{-6}	5.19×10^{-9}	9.15×10^{-9}	3.52×10^{-6}	
	Pb	1.43×10^{-5}	2.11×10^{-9}	1.53×10^{-8}	1.43×10^{-5}	4.01×10^{-6}	5.90×10^{-10}	4.30×10^{-9}	4.02×10^{-6}	
	Cr	3.14×10^{-5}	4.62×10^{-9}	3.36×10^{-8}	3.14×10^{-5}	1.57×10^{-5}	1.94×10^{-7}	1.68×10^{-8}	1.59×10^{-5}	
	Cu	9.76×10^{-6}	1.44×10^{-9}	1.05×10^{-8}	9.77×10^{-6}	–	–	–	–	

3.7.2 Non-carcinogenic risk and carcinogenic risk of heavy metal(loid)s in fruits

Similar to soil, the noncarcinogenic risk posed by heavy metal(loid)s via fruits consumption was also evaluated by calculating HQ and HI in children and adults. The HQ and HI assessment results are presented in Table 8. The heavy metal(loid)s contents in fruits were significantly lower than that detected in soils. The detection limits for each heavy metal(loid) were used to calculate the target hazard quotient (HQ) when the fruit samples contained heavy metal(loid) concentrations below the detection limits. In the current study, the HQ and total HQ (HI) values in all metal(loid)s were far lower than 1, indicating that metal uptake via fruit consumption does not pose noncarcinogenic risks in Hainan orchards for adults and children.

The CR and TCR results are summarised in Table 8. The mean CR and TCR in adults and children were below the threshold value (1×10^{-6}), signifying that it can be considered safe at a low cancer risk. The present results also show that children may be more susceptible to heavy metal exposure via fruit consumption due to their lower body weight.

Table 8 Evaluated HQ, HI, CR and TCR of metal(loid)s in fruit samples

Group	Elements	HQ	HI	CR	TCR
Children	Cd	<1.15×10^{-5}	<1.26×10^{-4}	<6.01×10^{-9}	<8.50×10^{-9}
	Hg	<4.67×10^{-6}		-	
	As	<6.20×10^{-5}		<2.39×10^{-9}	
	Pb	<3.80×10^{-5}		<9.69×10^{-11}	
	Cr	<2.24×10^{-7}		-	
	Cu	<9.93×10^{-6}		-	
Adults	Cd	<1.06×10^{-6}	<1.17×10^{-5}	<2.23×10^{-9}	<3.15×10^{-9}
	Hg	<4.33×10^{-7}		-	
	As	<5.75×10^{-6}		<8.88×10^{-10}	
	Pb	<3.52×10^{-6}		<3.60×10^{-11}	
	Cr	<2.08×10^{-8}		-	
	Cu	<9.21×10^{-7}		-	

3.8 Recommendations

In present study, though the edible fruits were unlikely to be influenced by the contamination of these metal(loid)s in Hainan orchard soil, the transfer of heavy metal(loid)s from soil to fruits is the major pathway for human exposure to contaminants in soil, thus, special attention should be paid to Hainan orchards polluted by soil heavy metal(loid)s into achieve the lowest threat to agricultural production, environmental and human health. Furthermore, the high geochemical background northern part and industry-oriented western region should also be labeled as the priority control regions for soil heavy metal pollution.

The most effective approach to mitigating soil heavy metal pollution is the efficient control of pollution sources[28]. We recommend that essential remediation methods be used in some orchards polluted by soil heavy metal(loid)s, especially in areas with high geochemical backgrounds and industry-oriented western regions. The northern part of Hainan orchards with high heavy metal concentrations requires proper management. Industry-oriented regions should strictly enforce environmental regulations, especially in terms of the exhausts and wastewater discharge of industries, enterprises, and mining development in urban areas, which mainly results in the high pollution levels of heavy metal(loid)s in local ecosystems and local human health hazards. In fact, Hainan is not a highly developed industrial area but rather is primarily an agricultural area. Inappropriate measures have been taken to increase agricultural production, resulting in the accumulation of heavy metal(loid)s. The scientific and rational application of chemical pesticides and fertilisers is recommended for agricultural production. In future works, soil remediation study is required to focus on Hainan orchards with acid soil and high pollution levels combined with specific local conditions, and organic pollutants, soil physi-chemical, and biological indicators should be considered and supplemented to completely assess soil quality of Hainan orchards.

4 Conclusions

This present study provides the concentrations of six common heavy metal(loid)s (Cd, Hg, As, Pb, Cr, and Cu) in soil, fruit and irrigation water samples from the major producing area in Hainan orchards. In addition, pollution and risk assessments, spatial distribution analysis, and potential source analysis of the soil heavy metal(loid)s were completely detailed. Pollution was not detected in the investigated fruit and irrigation water samples, and the potential human health risk for fruit consumers was at a safe level. Although the mean concentrations of the studied soil heavy metal(loid)s did not exceed the corresponding national standards, the spatial distribution of soil metal(loid)s demonstrated a high degree of variation. Moreover, a significant accumulation of soil heavy metal(loid)s was observed based on the soil background level. The six heavy metal(loid)s (Cd, Hg, As, Pb, Cr, and Cu) showed mild-to-severe pollution levels (NIPI≤1) in 48.4% of the investigated soil samples and was at a safe level in the remaining samples. Overall, Cd, Cr, and Cu were the dominant metal pollutants in the soils of Hainan orchards. Additionally, the whole study area presented a low ecological risk, but some specific measures should be adopted to reduce the ecological risks posed by soil metal(loid)s in the northern, southern, and western areas because soil Cd and Hg may pose a potential threat to the local environment due to their high toxicity response coefficients. The health risks of the soil samples for residents were also within an acceptable range. It is estimated that the acidic soil properties in most of the study area increase the risk of Cd pollution in soils, and OM is a factor affecting most metal distributions in soils according to the correlation analysis. Further source apportionment showed that Cr and Cu were mainly attributed to uncommon geological conditions related to the high background values of volcanic rock-derived soil in the northern part of the Hainan Province, whereas soil contamination with Cd, Pb, and As was mainly related to human activities. It is worth noting that Hg originates from mixed sources that are partly related to agricultural activity and its natural origin. The results of this study indicate that the heavy metal concentrations in fruit products from these orchards are unlikely to be affected by the contamination of the orchard soil with these metal(loid)s. Therefore, this study provides scientific support for heavy metal risk management and the development of effective policies to reduce metal inputs and achieve sustainable environmental and economic development in Hainan Province.

Acknowledgements

This work was financially supported by Hainan Provincial Natural Science Foundation of China (Grant No. 322QN358, 421QN284, 320QN300). We would like to thank Editage (www.editage.cn) for English language editing.

[References]

[1] Gupta N, Yadav K K, Kumar V, Krishnan S, Kumar S, Nejad Z D, et al. Evaluating heavy metals contamination in soil and vegetables in the region of North India: Levels, transfer and potential human health risk analysis. Environ Toxicol Phar, 2021; 82: 103563.

[2] Prabagar S, Dharmadasa R M, Lintha A, Thuraisingam S, Prabagar J. Accumulation of heavy metals in grape fruit, leaves, soil and water: A study of influential factors and evaluating ecological risks in Jaffna, Sri Lanka. Environ Sustain Ind, 2021; 12(9): 100147.

[3] Doyi I, Essumang D, Gbeddy G, Dampare S, Kumassah E, Saka D. Spatial distribution, accumulation and human health risk assessment of heavy metals in soil and groundwater of the Tano Basin, Ghana. Ecotoxicol and Environ Safety, 2018; 165: 540–546.

[4] Fei X, Xiao R, Christakos G, Langousis A, Ren Z, Tian Y, et al. Comprehensive assessment and source apportionment of heavy metals in Shanghai agricultural soils with different fertility levels. Ecol Indic, 2019; 106: 105508.

[5] Ezez D, Belew M. Analysis of physicochemical attributes, contamination level of trace metals and assessment of health risk in mango fruits from Southern region Ethiopia. Toxicology Reports, 2023; 10: 124–132.

[6] Fang B, Zhu X. High content of five heavy metals in four fruits: evidence from a case study of Pujiang County, Zhejiang Province, China. Food Control, 2014; 39: 62–67.

[7] Yang L, Ren Q, Zheng K, Jiao Z, Ruan X, Wang Y. Migration of heavy

metals in the soil-grape system and potential health risk assessment. Sci Total Environ, 2022; 806: 150646.
[8] Xu M, Chen Q, Kong X, Han L, Zhang Q, Li Q, et al. Heavy metal contamination and risk assessment in winter jujube (Ziziphus jujuba Mill. cv. Dongzao). Food Chem Toxicol, 2023; 174: 113645.
[9] Kharazi K, Leili M, Khazaei M, Mohammad K, Mohammad Yusef A, Shokoohi. Human health risk assessment of heavy metals in agricultural soil and food crops in Hamadan, Iran. J Food Compos Anal, 2021; 100(1): 103890.
[10] Doabi S A, Karami M, Afyuni M, Yeganeh M. Pollution and health risk assessment of heavy metals in agricultural soil, atmospheric dust and major food crops in Kermanshah province, Iran. Ecotox Environ Safe, 2018; 163: 153–164.
[11] Tepanosyan G, Sahakyan L, Belyaeva O, Maghakyan N, Saghatelyan A. Human health risk assessment and riskiest heavy metal origin identification in urban soils of Yerevan, Armenia. Chemosphere, 2017; 184: 1230–1240.
[12] Xiao R, Guo D, Ali A, Mi S, Liu T, Ren C, Li R, et al. Accumulation, ecological-health risks assessment, and source apportionment of heavy metals in paddy soils: A case study in Hanzhong, Shaanxi, China. Environ Pollut, 2019; 248: 349–357.
[13] Govind M, Naresh K, Sayan S, Mradul K D, Mongjam M S, Tushar K J, et al. Heavy metal accumulation in fruits and vegetables and human health risk assessment: findings from Maharashtra, India. Environ Health Insig, 2022; 16(1): 1–10.
[14] Ren J, Li F, Yin C, Orchard grass safeguards sustainable development of fruit industry in China. J Clean Prod, 2023; 382: 135291.
[15] Fu X, Liu J, Huang W. Effects of natural grass on soil microbiology, nutrient and fruit quality of Nanfeng tangerine yard. Acta Horticulturae Sinica, 2015; 42: 1551–1558.
[16] Li T, Hong X, Liu S, Wu X, Fu S, Liang Y, et al. Cropland degradation and nutrient overload on Hainan Island: A review and synthesis. Environ Pollut, 2022; 313: 120100.
[17] Liu Y, Lin Y, Huang S. Tang Q, Zhang M, Fu J, et al. Distribution characteristics and assessment of soil heavy metals pollution in Hainan state farms. Chinese Journal of Tropical Agriculture, 2017; 37(7): 10–16. (in Chinese)
[18] Zhang Y, Kuang J, Xie Y, Wu X, Wang W. Characteristic analysis and evaluation of heavy metal contamination of agricultural products in Hainan province. Soil and Fertilizer Scienses in China, 2018(5): 169–176. (in Chinese)
[19] Li F, Li X, Yang F, Qi Z. Pollution evaluation and preliminary analysis of pollution sources of heavy metals in agricultural soil of Hainan Island. Natural Sciences Journal of Hainan University, 2013; 31(3): 211–217. (in Chinese)
[20] Liang J, Sun H, Ge C, Meng L. Distribution of heavy metal contents in soils of main crop production areas in Hainan and the health risk assessment. Chinese Journal of Tropical Crops, 2019; 40(11): 2285–2293. (in Chinese)
[21] Xie Y. Evaluation on environmental quality of soils in fruit producing areas of Hainan province. Chinese Journal of Tropical Agriculture, 2017; 37(11): 39–47. (in Chinese)
[22] Zhong P. Distribution of anthropogenic input of heavy metals in arable land soil of Hainan Islan. Hainan University, 2015. (in Chinese)
[23] Li J, Li X, Ge C, Yu H, Sun H, Chen M. Health risk assessment of heavy metal in soils in the north of Hainan Province with high background value. Chinese Journal of Tropical Crops, 2018; 39(1): 189–196. (in Chinese)
[24] Gao J, Gong J, Yang J, Wang Z, Fu Y, Tang S. Spatial distribution and ecological risk assessment of soil heavy metals in a typical volcanic area: Influence of parent materials. Heliyon, 2023; 9: e12993.
[25] Yang J, Sun Y, Wang Z, Gong J, Gao J, et al. Heavy metal pollution in agricultural soils of a typical volcanic area: Risk assessment and source appointment. Chemosphere, 2022; 304: 135340.
[26] Liu Y, Lin Y, Huang S, Ji J, Liu H, Chen Y. Concentration characteristics and geoaccumulation index assessment of soil heavy metals in tropical crops producing areas of Hainan Island. Guangdong Agricultural Sciences, 2017; 44(7): 59–64. (in Chinese)
[27] Shi H, Zeng M, Peng H, Huang C, Sun H, Hou Q, et al. Health risk assessment of heavy metals in groundwater of Hainan island using the Monte Carlosimulation coupled with the APCS/MLR model. Int J Environ Res Pub He, 2022; 19(13): 7827.
[28] Chen H, Teng Y, Lu S, Wang Y, Wang J. Contamination features and health risk of soil heavy metals in China. Sci Total Environ, 2015; 512: 143–153.
[29] China National Environmental Monitoring Center. The Soil Background Value in China, China Environmental Science Press, 1990, Beijing. (in Chinese)
[30] Hakanson L. An ecological risk index for aquatic pollution control. A sedimentological approach. Water Res, 1980; 14: 975–1001.
[31] Ke X, Gui S, Huang H, Zhang H, Wang C, Guo W. Ecological risk assessment and source identification for heavy metals in surface sediment from the Liaohe River protected area, China. Chemosphere, 2017; 175: 473–481.
[32] USEPA. Risk Assessment Guidance for Superfund, Volume 1: Human Health Evaluation Manual (Part A., Interim Final. US Environ Prot Agency, Off Emerg Remedial Response, 1989, Washington.
[33] Baltas H, Sirin M, Gökbayrak E, Ozcelik A E. A case study on pollution and a human health risk assessment of heavy metals in agricultural soils around Sinop province, Turkey. Chemosphere; 2020, 241: 125015.
[34] USEPA. Supplemental guidance for developing soil screening levels for superfund sites. Peer Rev. Draft. OSWER, 2001; 9355: 4–24.
[35] Wu J, Lu J, Li L, Min X, Luo Y. Pollution, ecological-health risks, and sources of heavy metals in soil of the northeastern Qinghai-Tibet Plateau. Chemosphere, 2018; 201: 234–242.
[36] Li J R. Heavy metal pollution assessment and health risk assessment of cultivated land based on soil-crop-human system. Zhejiang University, 2019. (in Chinese).
[37] UAEPA. Risk assessment guidance for superfund. Human Health Evaluation Manual (part A). EPA/540/1–89/002. vol. 1. Environmental Protection Agency, 1989; Washington,DC: 35–52.
[38] Yadav I C, Devi N L, Singh V K, Li J, Zhang G. Spatial distribution, source analysis, and health risk assessment of heavy metals contamination in house dust and surface soil from four major cities of Nepal. Chemosphere, 2019; 218: 1100–1113.
[39] AvaLeili K, Mohammad M, Mohammad A, Reza Y. Human health risk assessment of heavy metals in agricultural soil and food crops in Hamadan, Iran. J Food Compos Anal, 2021; 100(1): 103890.
[40] Ma X L, Zuo H, Tian M J, Zhang L Y, Meng J, Zhou X N, et al. Assessment of heavy metals contamination in sediments from three adjacent regions of the Yellow River using metal chemical fractions and multivariate analysis techniques. Chemosphere, 2016; 144: 264–272.
[41] Xu H J, Chen H, Wang X L, Zhang Y L, Wang J J, Li N, et al. Earthworms stimulate nitrogen transformation in an acidic soil under different Cd contamination. Ecotoxicol Environ Safety, 2018; 165: 564–572.
[42] Cui X, Cheng H, Liu X, Giubilato E, Critto A, Sun H, et al. Cadmium exposure and early renal effects in the children and adults living in a tungsten-molybdenum mining areas of South China. Environ Sci Pollut Res, 2018; 25(15): 15089–15101.
[43] Bhuiyan M A, Parvez L, Islam M A, Dampare S B, Suzuki S. Heavy metal pollution of coal mine-affected agricultural soils in the northern part of Bangladesh. J Haz Mat, 2010; 173(1): 384–392.
[44] Deng Y, Jiang L, Xu L, Hao X, Zhang S, Xu M, et al. Spatial distribution and risk assessment of heavy metals in contaminated paddy fields-A case study in Xiangtan City, southern China. Ecotoxicol Environ Safety, 2019; 171: 281–289.
[45] Sun C, Liu J, Wang Y, Sun L, Yu H. Multivariate and geostatistical analyses of the spatial distribution and sources of heavy metals in agricultural soil in Dehui, Northeast China. Chemosphere, 2013; 92: 517–523.
[46] Guo Y, Fu Y, He Y, Ma R, Zhang G. Evaluation and source analysis of the heavy metals and selenium in the farmland soils of volcanic area, north of Hainan Island. Journal of Safety and Environment, 2015; 15(1): 330–334. (in Chinese)doi: 1009-6094(2015) 01-0330-05.
[47] Wang Y, Duan X, Wang L. Spatial distribution and source analysis of heavy metals in soils influenced by industrial enterprise distribution: case study in Jiangsu Province. Sci Total Environ, 2020; 710: 134953.
[48] Liu H, Zhang Y, Yang J, Wang H, Li Y, Shi Y, et al. Quantitative source apportionment, risk assessment and distribution of heavy metals in agricultural soils from southern Shandong Peninsula of China. Sci Total Environ, 2021; 767: 144879.
[49] Zhao W, Pan Y, Lan T, Wu Z, Zhang L, Zhu Z, et al. Analysis of heavy metals and antibiotics content in Hainan commercial organic fertilizers. Environmental Chemistry, 2017; 36(2): 408–419. (in Chinese)doi: 10.7524/j.issn.0254-6108.2017.02.2016051803.
[50] Hainan Geological Survey, Geological Map of Hainan Province(1:

250000., Geological Publishing House, 2017. (in Chinese)

[51] Li P W. Remote sensing monitoring of mine development and recovery in Hainan Province. China University of Geosciences, 2020. (in Chinese)doi: 10.27493/d.cnki.gzdzy.2020.000664.

[52] Fu Y. Study on pollution and health risk assessment of heavy metal in typical mining areas of Hainan. Hainan University, 2019. (in Chinese)doi: 10.27073/d.cnki.ghadu.2019.000969.

[53] Wang G, Zhang S, Xiao L, Zhong Q, Li L, Xu G, et al. Heavy metals in soils from a typical industrial area in Sichuan, China: spatial distribution, source identification, and ecological risk assessment. Environ Sci Pollut Res, 2017; 24(20): 16618–16630.