Original Research

Ecological and Health Risk Assessment of Potentially Toxic Elements in Soils from Black Soil Region, Northeast China

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Abstract

In order to understand the pollution status of potentially toxic elements (Hg, Cd, Cr, Ni, Pb, Zn, As, and Cu) in the surface farmland soil of black soil in Northeast China and its impact on human health, Hailun City, a representative area of black soil in Northeast China, was selected as the study area. The pollution degree, ecological risk, and health risk of soil and potentially toxic elements in this area were evaluated by the index of geoaccumulation method (Igeo), the potential ecological hazard index method (RI), and the health risk assessment model (HRA). The results showed that the average contents of eight potentially toxic elements in the soil in this area were higher than the soil background value in Hailun City, showing different degrees of accumulation. There are Cd and Hg pollution and ecological risks in the soil of Hailun City. Cd has slight, medium, strong, and extremely strong ecological risks, and the risk index ranges from 19.32 to 751.64; Hg takes second place. Children are more vulnerable to the health threat of potentially toxic elements, and oral intake is the main source of soil exposure risk. The potentially toxic elements As and Cr are more likely to cause human health risks.

Keywords: black soil, potentially toxic elements, ecological risk, health risk, Hailun City, Northeast China

Introduction

Black soil in cold climates is rich in organic matter and loose, making it ideal for farming. There are three black soil plains in the northern hemisphere of the world:

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the Mississippi Plain in North America, the Ukrainian Plain in Europe, and the Northeast Plain in Asia. Especially the black soil in Northeast China, commonly known as "granary". The main crops are soybeans, corn, and rice. The black soil is called "giant panda in cultivated land" (giant panda is China's national treasure). With the high input of chemical fertilizers and fungicides, the lag of regulations and standards, the low efficiency of monitoring and management, and the *2 Sun Q., et al.*

weak awareness of people's environmental protection, potentially toxic elements (PTEs) are released into the soil [1-3]. The problem of Potentially toxic elements in soils has attracted extensive attention from scholars and policymakers at home and abroad [4-6]. Recently, the ecological and health problems of soil Potentially toxic elements pollution have become prominent.

Awake et al. (2021) [7] assessed the health risks of potentially harmful elements in vegetables grown on untreated and treated wastewater irrigated soil in Albaminqi, Ethiopia. Studies have shown that the values of Pb and Cd in waste water irrigated vegetables are greater than unity, which may lead to non-carcinogenic diseases in adults and children under short-term/lifelong exposure. Soghra et al. (2021) [8] investigated a large number of nutrients, potentially harmful elements, and polycyclic aromatic hydrocarbons (PAHs) in agricultural soils and vegetables in Ahvaz metropolis. The calculated potentially harmful element enrichment factors, pollution factors, and ecological risks show that agricultural soils are moderately polluted by Cd and P. Ali et al. (2021); Kianpoor et al. (2021) [9] conducted Potentially toxic elements pollution and health risk assessment on the soil of Khamees-Mushait municipal solid waste dump in Saudi Arabia. The pollution of Co, Ni, Pb, Cu, Cr, Mn, and Zn is serious in different zones of the study area. Tao et al. (2021) [10] studied the geological load and health risk of Potentially toxic elements absorbed by tea from soil. Under an acidic environment for the growth of tea, weathering pedogenic processes were shown to be the primary source for releasing Potentially toxic elements into the soil. More than 75% of soil Cd, Hg, Pb, and Zn exceeded background levels. In spite of this, the amount of Potentially toxic elements in tea samples was below the limits set by China, the WHO, and the EU.

The above studies were conducted in other countries and regions. Although they have a certain guiding role for this study, targeted research is still needed to truly grasp the ecological and health risks of Potentially toxic elements in farmland soil in the black soil region of Northeast China.

Song et al. (2018) [11] took Hailun as an example to research the spatial distribution pattern and influencing factors of Potentially toxic elements in a typical cold black soil area. Liu et al. (2020) [12] conducted a geochemical evaluation of land quality in Changfa Town, Hailun City, and put forward development suggestions. Chen et al. (2015) [13] studied the characteristics of Potentially toxic element contents in farmland soil in Hailun City. Chen et al. (2012) [14] conducted a pollution assessment of Potentially toxic elements in farmland soil in Hailun City. These studies have mainly focused on the geochemical characteristics and spatial distribution patterns of Potentially toxic elements without assessing their ecological and health risks. From the perspective of environmental protection and human health, this work is particularly important.

Fig. 1. Sample point distribution.

Materials and Methods

Study Area, Sampling, and Analysis

Helen City is located in the central part of Heilongjiang Province, China (46°58′-47 °52′E, 126°14′- 127°45′N), covering an area of 4551km, with a distance of 150 km from northeast to southwest and 78 km from north to south. Hailun City is located in the middle of Heilongjiang Province, with an area of 4667 km2 . It is in the center of the black soil region of northeast China. It belongs to the northern temperate zone with a continental monsoon climate. Winter is cold with a northwest wind, but summer is hot with heavy rainfall. The annual average temperature and precipitation are about 1.5º and 550 mm. The terrain of the area is gently undulating. Soil is formed from the quaternary loess-like parent material. The main soil types in the area are black soil and meadow soil. The main crops are soybeans, maize, and rice. In the last three decades, the consumption of chemical fertilizers was 106275, 122950, and 15680 tons in 2007, 2010, and 2017. The increasing use of chemical fertilizers could affect soil quality.

298 surface soil samples were collected in the black soil farming area of Hailun City, and the sample distribution is shown in (Fig. 1).

The sample test is carried out by the Harbin Natural Resources Comprehensive Survey Center in accordance with the relevant technical requirements (CGS, 2005). The accuracy and precision of elemental analysis meet the requirements of the National Geochemistry Survey of Land Quality Project (NGSLQP) (CGS, 2014). The analysis methods and detection limits are shown in the table (Table 1.).

Evaluation Method

The geoaccumulation index method (*Igeo*) proposed by German scientists is used to evaluate the pollution level of soil for Potentially toxic elements [15]. The background value of soil Potentially toxic elements in soil is calculated from the data of the National Geochemistry Survey of Land Quality Project (NGSLQP). The classification of Potentially toxic elements in pollution is shown in Table 2. [16, 17].

Index of geoaccumulation I_{geo}	Level	Pollution degree
$I_{\rm geo}{<}0$	0	Pollution-free
$0 \leq I_{geo} < 1$	1	Light pollution
$1 \leq I_{geo} < 2$	$\overline{2}$	Medium pollution
$2 \leq I_{geo} < 3$	3	Medium to heavy pollution
$3 \leq I_{geo} < 4$	4	Heavy pollution
$4 \leq I_{geo} < 5$	5	Heavy to extremely heavy pollution
	6	Extremely heavy pollution

Table 2. *I geo* index level and pollution degree.

The ecological risk of soil Potentially toxic elements in the study area is evaluated by the Hakanson potential ecological hazard index method [18]. The ecological hazard classification of single Potentially Toxic Elements Potential Ecological Hazard Index E_r^i and total potential for the Potentially Toxic Elements Ecological Hazard Index *RI* is shown in Table 3. [19-21].

The human health risk of soil Potentially toxic elements is evaluated by the health risk assessment model published by the US EPA [22-24]. The exposure parameters are shown in Table 4. [25-28] Exposure pathway reference measures and carcinogenic slope factors are shown in Table 5. [29-31].

Results and Discussion

Distribution Characteristics of Potentially Toxic Elements in Soil

The contents of Potentially toxic elements in the soil of the study area (Table 6.) are higher than those in the soil of Hailun City, indicating that Potentially toxic elements accumulate in the soil to a certain extent. The range of Cd content is $0.05 \sim 1.83$ mg/kg, and the average value is 0.13 mg/kg, which is 1.86 times of the background value; The average value of Cr is 63.93 mg/kg, which is 1.51 times of the background value; and Zn, Hg, Ni, Pb, Cu, and As are about $1.10 \sim 1.33$ times of

Table 1. Analysis method and detection limit (mg·kg-1).

Index	Determination method	Detection limit	Index	Determination method	Detection limit
Сr			Cu		
Pb	X ray fluorescence spectrometry		Ni	Plasma emission spectrometry	
Zn			Mn		10
As	Atomic fluorescence	0.2	Cd	Plasma mass spectrometry	0.02
Hg	spectrometry	0.0005	pH	PH meter electrode method	0.1

Note: pH is dimensionless.

Table 3. Single and overall potential ecological hazard assessment indicators.

Ecological hazards	Slight	Medium	Strong	Very strong	Extremely strong
Potential ecological hazard index of single potentially harmful elements E_{i}^{i}	$<$ 40	$40 - 80$	$80 - 160$	$160 - 320$	>320
Total potential ecological hazard index RI	< 150	$150 - 300$	$300 - 600$	$600 - 1200$	>1200

Table 4. Exposure assessment parameter reference value.

Symbol	Parameter	Unit	Adult reference value	Child reference value
ED	Exposure years	a	25	6
BW	Average weight	kg	56.8	15.9
EF	Exposure frequency	$d \cdot a^{-1}$	350	350
AT	Average exposure time	d	carcinogenic26280, noncarcinogenic9125	carcinogenic26280, noncarcinogenic2190
IngR	Daily soil intake	$mg \cdot d^{-1}$	100	200
InhR	Daily air respiration	$m^3 \cdot d^{-1}$	14.5	7.5
SA	Exposed skin surface area	cm^2	2415	1295
SL.	Skin adhesion coefficient	$mg (cm2·d)-1$	0.2	0.2
PEF	Surface dust emission factor	m^3 ·kg ⁻¹	1.36×10^{9}	1.36×10^{9}
ABS	Skin absorption factor		0.001	0.001

Table 5. Potentially toxic elements reference measurements and carcinogenic slope. factor.

the background value. On the whole, Cd accumulation in soil is the most obvious effect, followed by Cr, and the order is Cd >Cr> Hg>Cu> Zn>Pb>Ni>As. Based on the coefficient o variation (CV), the value ranges of 0.07-0.77. Hg and Cd, reaching 0.77 and 0.76, are significantly more variable than other elements. The CV of other elements is between 0.07~0.16. In soil, the larger the coefficient of variation, the less even the distribution of elements is.

The pH value of soil ranged from 4.55 to 7.96 in the study area. The distribution characteristics of different Potentially toxic elements are shown in Fig. 2. Cd, As, Cu, Pb, Cr, Ni, Hg, and Zn did not exceed the screening value of the soil pollution risk of agricultural land [32].

Analysis of Potentially Toxic Element Pollution Degree

Taking Helen's soil background value as the evaluation standard, the geoaccumulation index of soil Potentially toxic elements pollution degree in the study area is evaluated (Table 7.). The average value of the Potentially Toxic Elements Pollution Index from high to low is Cd>Cr>Cu>Zn>Hg>Pb>Ni>As. Cd and Cr are at the light pollution level, and Cu, Zn, Hg, Pb, Ni, and As are at the pollution-free level. However, from the perspective of individual pollution points, soil Cd pollution is the most serious, one point reaches heavy to extremely heavy pollution, there are 4 medium pollution

Potentially toxic elements		As	C _d	Cr	Cu	Hg	Ni	Pb	Zn
Minimum value		6.27	0.05	48.16	8.62	0.02	12.48	16.58	32.81
Maximum value		15.7	1.83	73.3	33.06	0.51	35.65	40.29	103.74
Average value		10.06	0.13	63.93	23.18	0.04	28.01	25.2	67.52
Coefficient of variation		0.16	0.76	0.06	0.09	0.77	0.09	0.07	0.09
Hailun soil background value		9.14	0.07	42.46	17.78	0.03	23.65	20.23	52.05
	$pH \leq 5.5$	30	0.3	150	50	0.5	60	70	200
Risk screening value of agricultural soil pollution	$5.5 - 6.5$	30	0.3	150	50	0.5	70	90	200
	$6.5 - 7.5$	25	0.3	200	100	0.6	100	120	250
	pH > 7.5	20	0.6	250	100		190	170	300

Table 6. Statistic values of Potentially toxic elements content in the surface soil of Hailun City.

points and 238 light pollution points, accounting for 79.87%; Hg has 1 heavy pollution, 1 medium to heavy pollution point, 5 medium pollution points, and 52 light pollution points, accounting for 17.45%. There are 172 light pollution points in Cr, accounting for 57.72%. There are different amounts of light pollution in Cu, Zn, Pb, Ni, and As.

Potential Ecological Risk Assessment

The risk degree of potential ecological hazards in the soil is evaluated by taking the soil background value of Hailun City as the reference (Table 8). In terms of the ecological risks posed by individual Potentially toxic elements, the risk index of Cd ranges from 19.32 to 751.64, with slight, medium, strong, and extremely strong ecological risks, accounting for 41.28%, 54.7%, 3.69%, and 0.33%, respectively. Risk index of Hg ranges from 21.68 to 655.48, with slight to extremely strong ecological risks, accounting for 20.47%, 72.82%, 5.7%, 0.67%, and 0.33%, respectively. Cr, Ni, Pb, As, Cu, and Zn is a slight ecological risk with the index less than 40. Therefore, Hg and Cd are the primary Potentially toxic elements, and other elements are at a slight level. Hg is the element with the most serious ecological risk.

Fig. 2. Box plot of Potentially toxic element concentration.

Potentially	Index		Number of samples at all levels								
harmful mean elements		Pollution- free	Light pollution	Medium pollution	Medium to heavy pollution	Heavy pollution	Heavy to extremely heavy pollution	Extremely heavy pollution			
Pb	-0.27	296	2	θ	0	θ	θ				
Zn	-0.22	286	12	Ω	0	Ω	Ω	Ω			
Cr	0.00	126	172	Ω	θ	θ	Ω	θ			
C _d	0.21	55	238	$\overline{4}$	Ω	Ω		Ω			
Ni	-0.35	297		Ω	Ω	θ	Ω				
As	-0.46	292	6	Ω	θ	Ω	Ω	Ω			
Hg	-0.26	239	52	5			Ω	Ω			
Cu	-0.21	290	8	θ	θ	θ	Ω	Ω			

Table 7. Classification of Potentially toxic elements in soil based on I_{nc}.

Table 8. Potential ecological risk coefficient of Potentially toxic elements in soil.

Hazard index			Number of samples at all levels							
		Distribution range	Slight	Medium	Strong	Very strong	Extremely strong			
	C _d $19.32 - 751.64$		123	163	11	Ω				
	Hg	$21.68 - 655.48$	61	217	17	2				
	Cr	$2.27 - 3.45$	298	$\overline{0}$	θ	θ	θ			
Ei	As	$6.85 \sim 17.18$	298	$\overline{0}$	Ω	Ω	θ			
	Ni	$2.64 - 7.54$	298	$\mathbf{0}$	θ	θ	θ			
	Pb	$4.10 - 9.96$	298	$\mathbf{0}$	θ	θ	θ			
	Zn	$0.63 - 1.99$	298	θ	θ	θ	θ			
Cu		$2.42 - 9.30$	298	$\mathbf{0}$	θ	θ	$\overline{0}$			
	RI	$61.08 - 445.75$	231	65	θ	\overline{c}	$\overline{0}$			

The range of the *RI* of Potentially toxic elements in Hailun is 61.08~445.75, with slight, medium, and very strong ecological risks accounting for 77.51%, 21.81%, and 0.67% respectively. The spatial pattern of *RI* (Fig. 3.) shows that Aimin township has the highest ecological risk, and the soil has a strong ecological risk. The investigation found that the animal husbandry in the region is mainly raising pigs, cattle, and sheep, and the soil is polluted by Hg and Cd Potentially toxic elements. There is a medium risk in the east of Qianjin town. In other areas, pigs, cattle, and sheep are not mainly raised. The ecological risk is low and shows a slight intensity.

Human Health Risk Assessment

Potentially Toxic Element Exposure Assessment

The results (Table 9. and Table 10.) show that the average daily exposure to non-carcinogenic elements is as follows: $ADD_{\text{ing}} > ADD_{\text{dem}} > ADD_{\text{inh}}$, in which, oral intake is the main factor. Compared to adults, children's average daily exposure to oral intake, skin contact, and respiratory inhalation is higher. The order of average daily intake of Potentially toxic elements is Zn>Cr>Ni> Pb>Cu>As>Cd>Hg. The average daily exposure to carcinogenic elements is as follows: $ADD_{\text{ing}} > ADD_{\text{derm}}$ $>ADD_{\text{inb}}$, in which oral intake is the main factor as well. The order of average daily intake of Potentially toxic elements is: Cr>Ni>As>Cd.

Health Risk Assessment

Eight Potentially toxic elements were assessed as non-carcinogenic indexes and four as carcinogenic indexes in the study area. Results are listed in the following tables (Tables 11. and 12.).

Non-carcinogenic health risk assessment has the following rules: $HQ_{ing} > HQ_{derm} > HQ_{inh}$. Oral intake is the main factor in non-carcinogenic health risks. The non-carcinogenic health risks of Potentially toxic elements are as follows: Cd<Hg<Zn<Cu<Ni<Pb<Cr<As, with the average value of HQ for adults being 0.118 and for children being 0.795; the maximum HQ value

Fig. 3. *RI* spatial distribution map.

for adults is 0.171 and for children is 1.16. According to this study, single Potentially toxic elements have no noncarcinogenic risk to adult health, whereas there is a large noncarcinogenic risk to children, so prevention should be stressed. (Fig. 4, Fig. 5(a)).

The health risk assessment of carcinogenesis has the following rules: $CR_{\text{ing}} > CR_{\text{derm}} > CR_{\text{inh}}$. The risk is linked to the exposure route. The carcinogenic risk of different Potentially toxic elements is as follows: As>Cd>Cr>Ni. As is the highest carcinogenic risk element. The average value of the CR for adults is 9.54E-06, and the

maximum value is 2.06E-05. The average value of the CR for children is 2.56E-05, and the maximum value is 5.57E-05. The CR of all Potentially toxic elements is between 10-6 and 10-4. The carcinogenic risk caused by Potentially toxic elements in Hailun soil is within the acceptable range, but the carcinogenic risk index exceeds the value of 10-6 proposed by the US. EPA. In terms of hazard degree, children have a higher risk of carcinogenesis than adults (Fig. 5(b)). Prevention should be strengthened.

Table 9. Average daily exposure to Potentially toxic elements in soil; non-carcinogenic risk assessment.

Potentially			Adult		Children				
harmful elements	$ADD_{\rm ing}$	ADD_{inh}	$ADD_{\rm{dem}}$	ADD	$ADD_{\rm ing}$	ADD_{inh}	$ADD_{\rm{derm}}$	ADD	
Pb	4.25E-05	4.54E-09	2.06E-07	4.28E-05	3.04E-04	8.38E-09	3.94E-07	3.04E-04	
Zn	1.14E-04	1.22E-08	5.51E-07	1.15E-04	8.14E-04	2.25E-08	1.05E-06	8.15E-04	
Cr	1.08E-04	1.15E-08	5.21E-07	1.08E-04	7.71E-04	2.13E-08	9.99E-07	7.72E-04	
C _d	2.27E-07	$2.42E-11$	1.10E-09	2.28E-07	1.62E-06	4.47E-11	2.10E-09	$1.62E-06$	
Ni	4.73E-05	5.04E-09	2.28E-07	4.75E-05	3.38E-04	9.32E-09	4.38E-07	3.38E-04	
As	1.70E-05	1.81E-09	8.20E-08	1.71E-05	1.21E-04	3.35E-09	1.57E-07	1.22E-04	
Hg	7.19E-08	7.67E-12	3.47E-10	$7.23E-08$	5.14E-07	$1.42E-11$	$6.65E-10$	5.14E-07	
Cu	3.91E-05	4.17E-09	1.89E-07	3.93E-05	2.80E-04	7.71E-09	3.62E-07	2.80E-04	
<i>ADD</i>	3.68E-04	3.93E-08	1.78E-06	3.70E-04	$2.63E-03$	7.25E-08	$3.41E-06$	$2.63E-03$	

Potentially			Adult		Children			
harmful elements	ADD_{ing}	ADD_{inh}	ADD_{dem}	<i>ADD</i>	ADD_{ing}	ADD_{inh}	ADD_{term}	ADD
Cr	3.75E-05	4.00E-09	1.81E-07	3.77E-05	0.000102	5.77E-09	2.64E-07	0.000102
C _d	7.88E-08	8.40E-12	3.80E-10	7.92E-08	$2.14E-07$	1.21E-11	5.55E-10	$2.14E-07$
Ni	1.64E-05	1.75E-09	7.93E-08	1.65E-05	4.46E-05	2.53E-09	1.16E-07	4.47E-05
As	5.90E-06	$6.29E-10$	2.85E-08	5.93E-06	1.60E-05	9.08E-10	4.16E-08	1.61E-05
<i>ADD</i>	5.99E-05	6.38E-09	2.89E-07	$6.02E - 05$	$1.63E-04$	$9.21E-09$	4.22E-07	1.63E-04

Table 10. Average daily exposure to Potentially toxic elements in soil; carcinogenic risk assessment.

Table 11. Non-carcinogenic health risk index of Potentially toxic elements in the soil in Hailun.

Potentially harmful elements				Adult		Children				
		HQ	$H{\cal Q}_{\text{ing}}$	$H{\cal Q}_{inh}$	$H{\cal Q}_{\mathit{derm}}$	HQ	$H{\cal Q}_{\text{ing}}$	HQ_{inh}	HQ_{derm}	
Pb	Max	2.01E-02	1.94E-02	2.07E-06	6.20E-04	1.40E-01	1.39E-01	3.83E-06	1.19E-03	
	AVG	1.25E-02	1.22E-02	1.30E-06	3.88E-04	8.76E-02	8.69E-02	2.39E-06	7.43E-04	
	Max	5.87E-04	5.84E-04	$0.00E + 00$	2.82E-06	4.18E-03	4.17E-03	$0.00E + 00$	5.40E-06	
Zn	AVG	3.82E-04	3.80E-04		1.84E-06	2.72E-03	2.71E-03		3.52E-06	
	Max	4.97E-02	4.12E-02	5.17E-04	7.97E-03	3.11E-01	2.95E-01	9.56E-04	1.53E-02	
Cr	AVG	4.34E-02	3.60E-02	4.51E-04	6.95E-03	2.71E-01	2.57E-01	8.34E-04	1.33E-02	
Cd	Max	3.72E-03	3.09E-03	3.29E-05	5.97E-04	2.33E-02	2.21E-02	6.08E-05	1.14E-03	
	AVG	2.73E-04	2.27E-04	2.42E-06	4.38E-05	1.71E-03	1.62E-03	4.47E-06	8.40E-05	
	Max	3.65E-03	3.01E-03	2.79E-04	3.63E-04	2.27E-02	2.15E-02	5.15E-04	6.96E-04	
Ni	AVG	2.87E-03	2.36E-03	2.19E-04	2.86E-04	1.78E-02	1.69E-02	4.05E-04	5.47E-04	
	Max	8.90E-02	8.84E-02	1.88E-04	4.27E-04	6.33E-01	6.31E-01	3.48E-04	8.18E-04	
As	AVG	5.70E-02	5.66E-02	1.21E-04	2.73E-04	4.05E-01	4.05E-01	2.23E-04	5.24E-04	
	Max	3.06E-03	2.86E-03	3.05E-07	1.97E-04	2.08E-02	2.04E-02	5.63E-07	3.78E-04	
Hg	AVG	2.56E-04	2.40E-04	2.56E-08	1.65E-05	1.74E-03	1.71E-03	4.72E-08	3.17E-05	
	Max	1.40E-03	1.40E-03	$0.00E + 00$	6.74E-06	9.98E-03	9.97E-03	$0.00E + 00$	1.29E-05	
Cu	AVG	9.83E-04	9.78E-04		4.72E-06	7.00E-03	6.99E-03		9.05E-06	
	Max	1.71E-01	1.60E-01	1.02E-03	1.02E-02	$1.16E + 00$	$1.14E + 00$	1.88E-03	1.95E-02	
HQ	AVG	1.18E-01	1.09E-01	7.95E-04	7.96E-03	7.95E-01	7.78E-01	1.47E-03	1.53E-02	

Note: Max-maximum value, AVG-average value.

Discussion

The background values of heavy metal elements As, Cd, Cr, Cu, Hg, Ni, and Zn in the soil of Helen City are 9.14 mg/kg, 0.07 mg/kg, 42.46 mg/kg, 17.78 mg/kg, 0.03 mg/kg, 23.65 mg/kg, 20.23 mg/kg, and 52.05 mg/kg, respectively. The content of Potentially toxic elements in the soil of Hailun city is higher than the background value of Hailun city (Table 6.). The accumulation effect of Cd in the soil is the most obvious, followed by Cr, in the order of Cd>Cr>Hg>Cu>Zn>Pb>Ni>As, reaching 1.10-1.86 times of the soil background value, respectively, indicating that Potentially toxic elements accumulate in the soil to a certain extent. In 2008, the content of Cd in the soil of Hailun city was significantly lower than the background value; Cr, Zn, and Hg were higher than the background value and the values of other elements were similar to the background value [14]. It shows that compared with ten years ago, the pollution of soil with Potentially toxic elements has an aggravating trend, especially as the content of Cd increases the most, followed by the increase of Cu, Pb, Ni, and As, and there is basically no change in Cr, Zn, and Hg. The survey found that agricultural activities, aquaculture, sewage irrigation, automobile exhaust emission, and traffic dust are the main factors

Note: Max-maximum value, AVG-average value.

Fig. 4. Contribution of 8 Potentially toxic elements in the soil to *HQ* for adults and children.

Fig. 5. Comparison of non-carcinogenic and carcinogenic Potentially toxic elements in adults and children.

causing soil Potentially toxic element pollution [33, 34]. The pollution of Cd mainly comes from the use of pesticides, fertilizers, and plastic films. Years of use of pesticides containing Cd, Pb, Hg, As, etc., unreasonable use of fertilizers, and extensive use of plastic greenhouses and films lead to the accumulation of heavy metals in the soil. This phenomenon has been found for the first time in this region. It needs to be paid great attention to whether there is a significant increase in Cd in soil due to the large use of pesticides and chemical fertilizers in agricultural production in other parts of China and around the world.

The study finds that the content of Potentially toxic elements in the soil of Hailun City (Table 6.) is higher than the background value, indicating that most Potentially toxic elements accumulate in the soil.

Compared with ten years ago [14], soil Potentially toxic elements pollution has an aggravating trend, especially the content of Cd changes the most. In 2008, the content of Cd in Hailun city was significantly lower than the background value, while at present, the content of Cd is significantly higher than the background value. The variation coefficient ranges from 0.07 to 0.77. Both Hg and Cd are considerably higher than other Potentially toxic elements, but the variation rule is the same as it was ten years ago. At the same time, the survey found that farming activities, aquaculture, sewage irrigation, traffic dust, and automobile exhaust emissions are the main factors causing soil Potentially toxic elements pollution.

The potential ecological risk assessment shows that the distribution range of the total RI of Potentially toxic elements in the study area is 61.08~445.75, with slight, medium, and strong ecological risks accounting for 77.52%, 21.8%, and 0.67%, respectively. The impact factors are Cd and Hg. Cd has slight, medium, strong, and extremely strong ecological risks, while Hg has slight, medium, strong, very strong, and extremely strong ecological risks. Other Potentially toxic elements have slight ecological risks. Mirzaei et al. (2020) [35] found that Cd has the greatest ecological risk in Chaharmahal and Bakhtiari provinces of Iran,.Nihal et al. (2021) [36] found Zn and Mn have low ecological risk in Ramsar area, Assam state, India. As to our study, the ecological risk level of Hailun City is very strong, which needs more attention. In addition, it is necessary to strengthen the early warning mechanism for other areas with slight, medium, and strong ecological risks, where the risks should be identified as soon as possible. Furthermore, we need effective measures to control soil pollution [37].

Potentially toxic elements in the farmland soil of Hailun City have no carcinogenic or non-carcinogenic hazards to adults. The average value of the CR for adults and children is 9.54E-06 and 2.56E-05, respectively, and the maximum value is 2.06E-05 and 5.57E-05, respectively. Both of them are between 10-6 and 10-4. As a result, the carcinogenic risk of Potentially toxic elements is generally acceptable and does not cause significant harm to the health of the local population. However, they all exceed the soil treatment benchmark value of 10⁻⁶ proposed by the US EPA, and prevention should be strengthened. The average value of the HQ of Potentially toxic elements for children is 0.795, with a maximum value of 1.16, indicating that Potentially toxic elements in soil in this area have a great non-carcinogenic health risk for children, so prevention should be strengthened. In the human health risk assessment of Potentially toxic element pollution in urban soil in southern India, Adimalla et al. (2020) [38] believe that Potentially toxic elements have a carcinogenic risk and a non carcinogenic risk to humans. The Potentially toxic elements with non carcinogenic risk come from Cr and Pb, and the carcinogenic risk comes from Cr control. Zhang et al. (2021) [39] Assessed the health risk of

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Potentially toxic elements in the soil of the Shihe River Basin in China and found that chromium from natural sources has a carcinogenic risk value for children, while the carcinogenic risk for adults and non carcinogenic risk for adults and children are at an acceptable level. Shen et al. (2021) [40] evaluated the health risk of Potentially toxic elements in the soil of the Yellow River irrigation area in China and considered that 0.64% and 9.32% of the total area of the Yellow River irrigation area constitute high HQ areas for children and adults, respectively. In particular, the regions of 0.68% and 1.12% were identified as high HQ regions of As and Cr, and the critical probability was 0.9. The research of domestic and foreign scholars shows that the health risks of Potentially toxic elements are different in different countries and regions, especially in areas with high risks. We should strengthen the prevention of the health risks of Potentially toxic elements [41, 42].

Conclusions

The Potentially toxic elements As, Cd, Cr, Cu, Hg, Ni, Zn, and Pb in Hailun soil were higher than the background value. Cd was the most prominent element, with an average content of 0.13 mg/kg, which was 1.86 times of the background value, and the quantity increased significantly. The average content of Cr is 63.93 mg/kg, which is 1.51 times of the background value. The CV of Cd is also high, at 0.76. It is seriously affected by the centralized development of animal husbandry, showing the current situation of uneven pollution. There are Cd and Hg pollution and ecological risks in the soil. The Cd ecological risk index is 19.32~751.64, with a slight, medium, strong, and extremely strong level of ecological risks. Hg takes second place, and the risk index is 21.68~655.48, with a slight to extremely strong level of ecological risk; Cr, Ni, Pb, Zn, As, and Cu are generally in a pollution-free state with no obvious harm. The soil Potentially toxic elements pollution, ecological risk, and health risk in Hailun City are generally low, and most of them are in the state of no pollution and no obvious harm, so they can be used safely. However, the excessive phenomenon of Hg, Cd, As, Cr, and other individual elements in individual indicators should be given more attention, and prevention strategies should be strengthened. Children are more vulnerable to the health threat of Potentially toxic elements, and oral intake is the main route of exposure risk from soil. Human health risks are more likely to be caused by As and Cr.

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Availability of Data and Material

The sample test was conducted by Harbin natural resources comprehensive investigation center in accordance with the relevant technical requirements (CGS, 2005). The data is accurate and reliable.

Author Contributions

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Conflicts of Interest

There is no conflict of interest in the article.

References

1. XIONG S.J., PENG Y.Q., CHEN K., LU S.Y., JIANG W.Q., LI X.D., WANG F., CEN K.F. Phase distribution, migration and relationship of polychlorinated dibenzo-pdioxins and dibenzofurans and heavy metals in a largescale hazardous waste incinerator. Journal of Cleaner Production, **341**, 0959, **2022**.

- 2. LI Z., JIANG Y., ZU Y., MEI X., QIN L., LI B. Effects of Lime Application on Activities of Related Enzymes and Protein Expression of Saponin Metabolism of Panax notoginseng under Cadmium Stress. Polish Journal of Environmental Studies, **29** (6), 4199, **2020**.
- 3. SUN Q.F., SUN Z., XING W., HAO G., LI X., DU J., LI C., TIAN H., LI X. Ecological health risk assessment of heavy metals in farmland soil of Changchun New Area. Polish Journal of Environmental Studies, **30** (6), 5775, **2021**.
- 4. ALI I.H., SIDDEEG S.M., IDRIS A.M., BRIMA E.I., ARSHAD M. Contamination and human health risk assessment of heavy metals in soil of a municipal solid waste dumpsite in Khamees-Mushait, Saudi Arabia. Toxin Reviews, **40** (1), 102, **2019**.
- 5. KIANPOOR K.Y., HUANG B., HU W., MA C., GAO H., THOMPSON M.L., BRUUN HANSEN H.C. Environmental soil quality and vegetable safety under current greenhouse vegetable production management in China. Agriculture, Ecosystems & Environment, **307**, 0167, **2021**.
- 6. KORÇA B., DEMAKU S. Evaluating the Presence of Heavy Metals in the Vicinity of an Industrial Complex. Polish Journal of Environmental Studies, **29** (5), 3643, **2020**.
- 7. AWOKE G., ASAMIN Y., SHETIE G., ABEBE W., LIU W.Z., FIDELIS O.A., AIJIE W. Evaluating the Health Risks of Heavy Metals from Vegetables Grown on Soil Irrigated with Untreated and Treated Wastewater in Arba Minch, Ethiopia. The Science of the Total Environment, **761** (0), 0048, **2021**.
- 8. SOGHRA B., FARID M., BEHNAM. Evaluation, Source Apportionment and Health Risk Assessment of Heavy Metal and Polycyclic Aromatic Hydrocarbons in Soil and Vegetable of Ahvaz Metropolis. Human and Ecological Risk Assessment: An International Journal, **27** (1), 71, **2021.**
- 9. BARTKOWIAK, A., PIATEK, M. Analysis of Heavy Metal Content in Soil Fertilised with Fresh and Granulated Digestate. Polish Journal of Environmental Studies, **29** (5), 3517, **2020**.
- 10. TAO C., SONG Y., CHEN Z., ZHAO, W., JI, J., SHEN, N., AYOKO, G., FROST, R. Geological Load and Health Risk of Heavy Metals Uptake by Tea from Soil: What Are the Significant Influencing Factors?. CATENA, **204**, 0341, **2021**.
- 11. SONG H.F., WU K.N., LI T., SHI W.Y., LI H.R. The Spatial Distrihulion anil IiifluerKtirig Factors of Heavy Metals in the Cold Black Soil Region: A Case of Hailun County. Chinese Journal of Soil Science, **49** (6), 1480, **2018**.
- 12. LIU G.D., YANG Z., DAI H.M., ZHANG Y.H., XIAO H.Y., CHEN J. Geochemical evaluation of land quality and development suggestion of land in Hailun City, Heilongjiang Province. Geology and resources, **29** (6), 533, **2020**.
- 13. CHEN Y.D., ZHOU J.M., XING L., FENG Y.F., HANG X.S., WANG H.T. Characteristics of Heavy Metals and Phosphorus in Farmland of Hailun City, Heilongjiang Province. Soils, **47** (5), 965, **2015**.
- 14. CHEN Y.D., WANG H.Y., ZHOU J.M., ZHAO Y.C. Heavy Metals Distribution Characteristics and Pollution Assessment in Farmland Soils of Hailun City, Heilongjiang Province. Soils, **44** (4), 613, **2012**.
- 15. MÜLLER G. Schwermetalle in den Sedimenten des Rheins-Veränderungen seit 1971. Umschau in Wissenschaft und Technik, **79**, 778, **1979**.
- 16. SUN Q.F., ZHENG J.L., SUN Z.A., WANG J.H., LIU Z.J., XING W.G., HAO G.J., LIU T., SUN Z.L., TIAN H. Study and risk assessment of heavy metals and risk element pollution in shallow soil in Shanxi Province, China. Polish Journal of Environmental Studies, **31** (4), 1, **2022**.
- 17. WANG Z., LIU S.Q., CHEN X.M., LIN C.Y. Estimates of the exposed dermal surface area of Chinese in view of human health risk assessment. Journal of Safety and Environment, **15** (4), 152, **2008**.
- 18. Ministry of Environmental Protection of the People's Republic of China. Technical guidelines for risk assessment of contaminated: HJ 25.3– 2014. Beijing: China Environmental Science Press, **2014**.
- 19. USEPA. Exposure factors handbook. Washington: National Center for Environmental Assessment, **2011**.
- 20. USEPA. Regional screening level (RSL) for Chemical contaminants at superfund sites. Washington, DC: U.S. Environmental Protection Agency, **2013**.
- 21. USEPA. Highlights of the child specific exposure factors handbook (Final Report). Washington, DC: U.S. Environmental Protection Agency, **2009.**
- 22. LIU QING, WANG JING, SHI YANXI, ZHANG YANYU, WANG QINGHUA. Health risk assessment on heavy metals in soil based on GIS – a case study in Cixi city of Zhejiang Province. Chinese Journal of Soil Science, **39** (3), 634, **2008**.
- 23. WU H.J., FANG F.M., WU J.Y., YAO Y.R., WU M.H. Bioaccessibility and health risk of heavy metals at topsoil in primary schools in a coal mining city. Chinese Journal of Soil Science, **48** (5), 1247, **2017**.
- 24. SUN Q.F., SUN Z., WANG J., XING W., HAO G., LIU Z., LIU T., SUN Z., LI X., TIAN,H., ZHU W. Heavy metal pollution and risk assessment of farmland soil in Ecotourism resort. Arabian Journal of Geosciences, **15** (6), 491, **2022**.
- 25. AWOKE G., ASAMIN Y., SHETIE G., ABEBE W., LIU W.Z., FIDELIS O.A., AIJIE W. Evaluating the Health Risks of Heavy Metals from Vegetables Grown on Soil Irrigated with Untreated and Treated Wastewater in Arba Minch, Ethiopia. The Science of the total environment, **761** (0), 0048, **2021**.
- 26. SONG H.F., WU K.N., LI, T., SHI W.Y., LI H.R. The Spatial Distrihulion anil IiifluerKtirig Factors of Heavy Metals in the Cold Black Soil Region: A Case of Hailun County. Chinese Journal of Soil Science, **49** (6), 1480, **2018**.
- 27. LIU J., WANG Y.N., LIU X.M., XU J.M. Occurrence and health risks of heavy metals in plastic-shed soils and vegetables across China. Agric., Ecosyst. Environ, **321**, 0167, **2021**.
- 28. DALIA A.E., SALY F.G., GEHAN A.I. Efficacy of two seaweeds dry mass in bioremediation of heavy metal polluted soil and growth of radish (*Raphanus sativus* L.) plant*.* Environmental Science and Pollution Research, **28** (10), 12831, **2021**.
- 29. FASSLER E., ROBINSON B.H., STAUFFER W., GUPTA S.K., PAPRITZ A., SCHULIN R. Phytomanagement of metal-contaminated agricultural land using sunflower, maize and tobacco. Agriculture, Ecosystems & Environment, **136** (1), 49, **2010**.
- 30. FENG K.H., FAN J., LIK U.S., LUO Q.S., CAO X.D., XU X.Y. Human health risk assessment of heavy metals in soil

from a smelting plant based on bioaccessibility. China Environmental Science, **41** (1), 442, **2021**.

- 31. DEEP S., PRASOON K.S. In situ phytoremediation of heavy metal – contaminated soil and groundwater: a green inventive approach*.* Environmental Science and Pollution Research, **28** (4), 4104, **2021**.
- 32. JIA J., BAI J.H., XIAO R., TIAN S.M., WANG D.W., WANG W., ZHANG G.L., CUI H., ZHAO Q.Q. Fractionation, source, and ecological risk assessment of heavy metals in cropland soils across a 100-year reclamation chronosequence in an estuary, South China. Science of The Total Environment, **807** (2), 151725, **2022.**
- 33. LIU Y.L., LIU S.L., ZHAO W., XIA C.B., WU M., WANG Q., WANG Z.M., JIANG Y., ANDREW V.Z., TIAN X.L. Assessment of heavy metals should be performed before the development of the selenium-rich soil: A case study in China. Environmental Research, **210**, 112990, **2022**.
- 34. RENU D., TALLAPRAGADA S., VINOD K. G. Spatial distribution of heavy metals in rice grains, rice husk, and arable soil, their bioaccumulation and associated health risks in Haryana, India, Toxin Reviews, **40** (4), 859, **2021**.
- 35. MIRZAI M., MAROFI S., SOLGI E., ABBASI M., KRIMI R., RIYAHY B., HAMID R. Ecological and health risks of soil and grape heavy metals in long-term fertilized vineyards (Chaharmahal and Bakhtiari province of Iran). Environmental Geochemistry and Health, **42** (1), 27, **2020**.
- 36. NIHAL G., SUDIP M., ANKIT S., RICHA A., LATHA R., ELDON R.R., MAHAVEER P.S. Speciation, contamination, ecological and human health risks assessment of heavy metals in soils dumped with municipal solid wastes. Chemosphere, **262** (0), 128013, **2021**.
- 37. SUN Q.F., YANG K., SUN Z.A., WANG J.H., XING W.G., HAO G.J. Study on Risk Model of Heavy Metals and Risk Element Pollution in Surface Farmland Soil in Cold Black Soil Region of China – Qianjin Town as an Example. Polish Journal of the Environmental Studies, **32** (4), 3309, **2023**.
- 38. ADIMALLA N., CHEN J., QIAN H. Spatial characteristics of heavy metal contamination and potential human health risk assessment of urban soils: A case study from an urban region of South India. Ecotoxicology and Environmental Safet, **194**, 110406, **2020**.
- 39. ZHANG Y., GUI H., HUANG Y., YU H., LI J., WANG M. Characteristics of Soil Heavy Metal Contents and its Source Analysis in Affected Areas of Luning Coal Mine in Huaibei Coalfield. Polish Journal of Environmental Studies, **30** (2), 1465, **2021**.
- 40. SHEN W.B., HUA Y., ZHANG J., ZHAO F., BIAN P.Y., LIU Y.X. Spatial distribution and human health risk assessment of soil heavy metals based on sequential Gaussian simulation and positive matrix factorization model: A case study in irrigation area of the Yellow River. Ecotoxicology and Environmental Safety, **225**, 112752, **2021**.
- 41. OLATUNDEA K.A., SOSANYA P.A., BADAA B.S., OJEKUNLEA Z.O., ABDUSSALAAMA S.A. Distribution and ecological risk assessment of heavy metals in soils around a major cement factory, Ibese, Nigeria*.* Scientific African, **9**, 2468, **2020**.
- 42. HEIMANN L., ROELCKE M., HOU Y., OSTERMANN A., MA W., NIEDER R. Nutrients and pollutants in agricultural soils in the peri-urban region of Beijing: Status and recommendations. Agriculture, Ecosystems & Environment, **209** (0), 74, **2015**.