# scientific reports



### **OPEN**

# Heavy metals concentrations in commercial organic fertilizers and the potential risk of fertilization into soils

Kunjie Su<sup>1,4</sup>, Qingliang Zhang<sup>2,4</sup>, Anjing Chen<sup>2</sup>, Xiaoqin Wang<sup>2</sup>, Lingling Zhan<sup>3</sup>, Qiang Rao<sup>2</sup>, Jinxia Wang<sup>3</sup> & Hongjun Yang<sup>1</sup>

Inductively coupled plasma mass spectrometry (ICP-MS) was used to detect heavy metals in 74 typical and representative commercial organic fertilizers (COFs) collected in major COF production areas in China. The potential risk of fertilization into soils was evaluated. The concentrations of heavy metals (mg kg<sup>-1</sup>) in these COFs were 1.55–36.95 (As), 0.04–2.32 (Hg), 1.43–78.05 (Pb), 0.15–7.49 (Cd), 11.03–212.90 (Cr), 7.74-555.11 (Cu), 21.46-2705.68 (Zn), and 5.62-244.47 (Ni), respectively. Based on China's Organic Fertilizer Standard (2021), COFs with excessive heavy metals accounted for 45.95% (As), 1.35% (Hg), 2.70% (Pb), 8.11% (Cd), and 6.76% (Cr). According to the European Union standard (2019), the rate of COFs with excessive heavy metals was 32.43% for Cu, 75.68% for Zn, and 85.14% for Ni. Estimated by applying 3854 kg hectare<sup>-1</sup> (dry bass) of fertilizer per hectare per year, to guarantee the safe use of organic fertilizer, the risk monitoring of Cd in soil should be emphasized. China should formulate appropriate standards for the limits of Cu, Zn, and Ni in organic fertilizer as soon as possible and should pay great attention to heavy metal pollution of soils.

Keywords Commercial organic fertilizer, Heavy metals, Potential risk, Pollution

In crop cultivation, organic fertilizers can increase soil fertility, provide plant nutrients, and improve crop quality<sup>1-4</sup>. Traditionally, animal manure and plant residues are directly used as organic fertilizers in agriculture<sup>5</sup>. In recent decades, however, a large quantity of waste from animal farms, food processing industries, edible mushroom factories, city plant residues, etc. has been processed into commercial organic fertilizers (COF) in China<sup>6-8</sup>. More and more COFs appear in markets and are added to soils in crop cultivation. For example, the market size of COFs has increased 17 times since 2014 and the economic output arrives at \$150 billion in China in 2022<sup>9</sup>. With the diversity of raw materials used for COF production, COFs may greatly vary in the heavy metals content<sup>10,11</sup>. Wei et al. (2019) found lower heavy metal concentrations in COFs from plant residues than animal manure<sup>12</sup>. Even if animal manure is used as raw material, COFs produced may also vary in both concentration and type of heavy metals<sup>13</sup>. Pig manure COFs often contain much higher Cu and Zn compared to those produced from cattle and sheep mamure<sup>14</sup>.

Fertilizers are one of the important contributors to heavy metals in soils. The long-term use of COFs with higher heavy metals in crop cultivation may produce a risk of accumulating heavy metals in soils and crops, adversely influencing food security<sup>15–17</sup>. A ten-year experiment (2002–2011) showed that Cd accumulated in the soil was increased by 13.6 times after applying the COF from cattle manure<sup>18</sup>. Based on the long-term field experiments severally conducted in Northeast and South China, the application of COFs produced from animal manure for 17 years increased Cd by 18 folds and Cd concentration reached 1.1 mg kg<sup>-1</sup> soil after applying pig manure COF<sup>19</sup>. This concentration in the soil can make Cd in rice grains high enough to be harmful to human bone tissues if consumed for a long time. Li et al. (2021) and Pan et al. (2013) reported a significant increase in Cd, Cr, Cu, Zn, and As in the soil following consecutive use of chicken and pig manure COFs<sup>15,20</sup>. Another long-term field experiment (> 160 years) in the UK found that the application of farmyard manure increased Cu and Zn by approximately 60%, which could further contribute to excessive levels in crop grains and humans<sup>21</sup>.

<sup>1</sup>College of Resources and Environment, Southwest University, Chongqing 400715, China. <sup>2</sup>Luzhou Laojiao Co. Ltd, Luzhou 646000, Sichuan, China. <sup>3</sup>College of Resources and Safety, Chongqing Vocational Institute of Engineering, Chongqing 402260, China. <sup>4</sup>Kunjie Su and Qingliang Zhang contributed equally to this work. <sup>™</sup>email: jinxiawang@cqvie.edu.cn; meilirensheng@swu.edu.cn

It is worth pointing out that "China's Organic Fertilizer Standard (NY/T 525–2021)" do not specify a lower limit for Cu, Zn, and Ni in organic fertilizers. Thus, less attention has been paid to these three heavy metals in COFs in China. In addition, few studies have been performed to understand heavy metals in COFs and to evaluate the risk of applying COFs for the accumulation of heavy metals in soils. In the present experiment, therefore, 74 typical and representative COFs made from different raw materials were collected in major cropgrowing areas in China. Then we analyzed heavy metals (including As, Hg, Pb, Cd, Cr, Cu, Zn, and Ni) using inductively coupled plasma mass spectrometry (ICP-MS). Based on the nationwide collection and the analysis of heavy metals, we evaluate the potential risk of applying these COFs in the accumulation of heavy metals in soils.

#### Materials and methods Samples collection

Seventy-four samples of typical and representative COFs were collected from COF factories (production capacity  $\geq 30,000$  tons) in major COF production areas in 23 provinces/autonomous regions in China from August to December 2023 (Fig. 1). The raw materials for producing these COFs included pig manure (9 samples), chicken manure (8 samples), cattle manure (4 samples), sheep manure (10 samples), mixed animal manure (10 samples), and plant source (33 samples).

#### Analysis of heavy metals concentration in COFs

The collected samples (2.5 kg per sample) were oven-dried at 105 °C, ground to pass through a 0.15 mm sieve, and  $\mathrm{HNO_3}$ - $\mathrm{HCIO_4}$  digested. Heavy metals in the digest solutions, including As, Hg, Pb, Cd, Cr, Cu, Zn, and Ni, were determined by inductively coupled plasma mass spectrometry (ICP-MS: NexION1000G, PerkinElmer, USA)<sup>22</sup>. Three parallel samples were measured for each sample, and the arithmetic mean of the parallel samples was taken as the result. The standard samples used for testing were GBW07428, obtained from the Institute of Geophysical and Geochemical Exploration of China, the blank control was also set up.

#### Evaluation criteria and data analysis of heavy metals in COFs

All data obtained were subjected to comparison with a lower limit for heavy metals (i.e. As  $\leq$ 15 mg kg<sup>[-1</sup>, Hg  $\leq$ 2 mg kg<sup>[-1</sup>, Pb  $\leq$ 50 mg kg<sup>[-1</sup>, Cd  $\leq$ 3 mg kg<sup>[-1</sup>, Cr  $\leq$ 150 mg kg<sup>[-1</sup>, Cu  $\leq$ 70 mg kg<sup>[-1</sup>, Zn  $\leq$ 200 mg kg<sup>[-1</sup>, Ni  $\leq$ 25 mg kg<sup>[-1</sup>) in "China's National Organic Fertilizer standard" (NY/T525-2021) and European Union's standard (EU 2019/1009).

The over-standard rate of heavy metals in COFs was calculated by the number of COFs with excessive heavy metals divided by the total number of COFs and was expressed as a percentage.

To evaluate the risk of heavy metal accumulation in soils, the rate of heavy metal accumulation in soils (R) and the longest time for applying COFs containing heavy metals ( $T_{max}$ : expressed as maximum years) were calculated by (1), (2), and (3)<sup>23,24</sup>:

$$R = M \times C/W \tag{1}$$

In the Eq. (1), M = annual amounts of COFs applied (kg hectare<sup>[-1</sup>), application of dry organic fertilizer 3854 kg hm<sup>[-2</sup>, C = heavy metal concentration in COFs (mg kg<sup>[-1</sup>), W = the mass of soil per hectare (kg hm<sup>[-2</sup>).

$$W = A \times h \times p/1000 \tag{2}$$

In the Eq. (2), A = the area of soil per hectare,  $10^4 \times 10,000$  cm<sup>2</sup>. h = the thickness of the plow layer (0–20 cm), p = soil capacity, 1.3 g cm<sup>[-3]</sup>, 1000 = conversion factor of g into kg.

$$T_{\text{max}} = (C_{sv} - C_{bv})/R \tag{3}$$

In the Eq. (3),  $C_{sv}$  = safe value of heavy metals in soils, the  $C_{sv}$  for a given heavy metal is obtained from "China's soil pollution risk control standard for agricultural land" (GB 15618 – 2018)<sup>25</sup>, and  $C_{bv}$  = background value of heavy metals in the soil<sup>24</sup>.

#### Data statistical analysis

The relevant data was collected by Excel 2010, and the statistical analysis of data was using SPSS19.0. The figures were completed using Origin 8.0.

#### Results

#### General characteristics of heavy metals in COFs

The ranges of As, Hg, Pb, Cd, and Cr concentrations (mg kg<sup>[-1</sup>) in the 74 COFs samples were 1.55–36.95 (As), 0.04-2.32 (Hg), 1.43-78.05 (Pb), 0.15-7.49 (Cd), and 11.03-212.90 (Cr) (Fig. 2a-e). As in 34 COFs, Hg in 1 COF, Pb in 2 COFs, Cd in 6 COF, and Cr in 5 COFs exceeded the lowest limits specified in "China's National Organic Fertilizer standard" (NY/T 525–2021). The over-standard rates of heavy metals in COFs were 45.95% (As), 1.35% (Hg), 2.70% (Pb), 8.11% (Cd), and 6.76% (Cr). Cu concentrations in COFs (mg kg<sup>[-1</sup>) ranged from 7.74 to 555.11, Zn from 21.46 to 2705.68, and Ni from 5.62 to 244.47 (Fig. 2f-h). According to the European Union standard for organic fertilizer (EU 2019/1009)<sup>26</sup>, the over-standard rates of Cu, Zn, and Ni were 32.43%, 75.68%, and 85.14%, respectively.

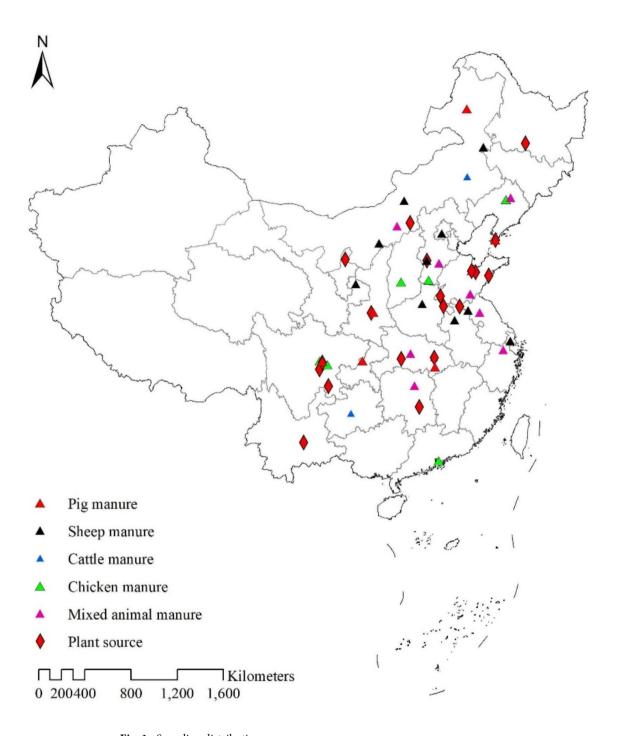


Fig. 1. Sampling distribution map.

#### Analysis of heavy metal concentrations in COFs produced from different raw materials

The heavy metal concentrations of COFs made from different raw materials are shown in Fig. 3; Table 1. Chicken manure organic fertilizer had the highest As concentration, pig manure organic fertilizer had the lowest As concentration and the rate of exceedance of the As concentration of organic fertilizers from different sources was greater than 0%. The Hg concentration of organic fertilizers from different sources was below 2 mg kg<sup>[-1</sup>, with only organic fertilizers of plant origin exceeding the standard for Hg. Sheep manure organic fertilizer and mixed manure organic fertilizer had higher Pb concentrations, plant source organic fertilizer had the lowest Pb concentration, and only mixed manure organic fertilizer and plant source organic fertilizer exceeded the Pb standard. Plant-source organic fertilizer had the highest Cd concentration, chicken manure organic fertilizer had the lowest Cd concentration, and with only cattle manure and plant-source organic fertilizers had Cd exceedances. The Cr concentration of plant-sourced organic fertilizer was the highest, pig manure organic

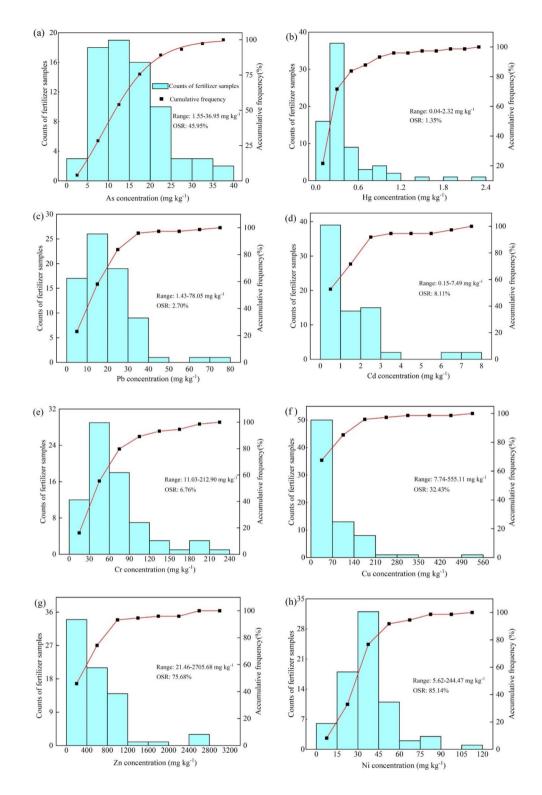
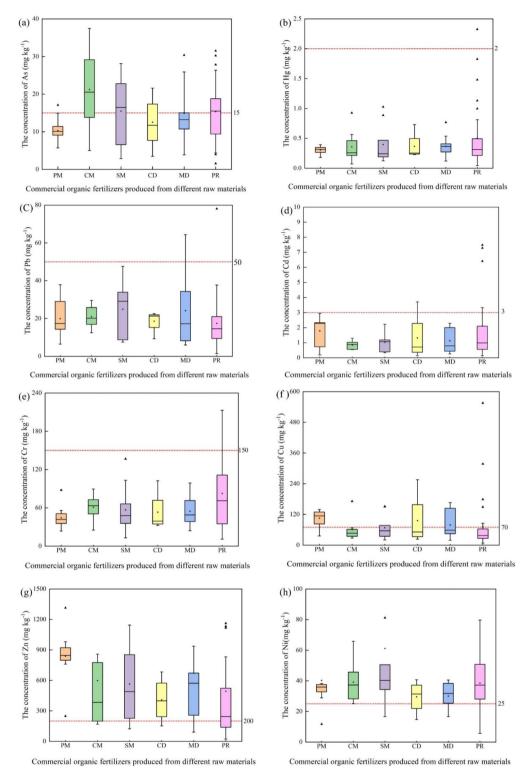


Fig. 2. Frequency distribution and accumulative frequency of heavy metal concentrations in commercial organic fertilizers. (a) As concentration, (b) Hg concentration, (c) Pb concentration, (d) Cd concentration, (e) Cr concentration, (f) Cu concentration, (g) Zn concentration, (h) Ni concentration. Range: the range of heavy metal concentration, OSR: the over-standard rate of heavy metals in COFs.



**Fig. 3.** Heavy metal concentrations of commercial organic fertilizers are produced from different raw materials. PM: pig manure, CM: chicken manure, SM: sheep manure, CD: cattle manure, MD: mixed manure, and PR: plant sources. The black dots in the box indicate the mean, the band near the center of the box indicates the median, the top and bottom of the box indicate the upper (75%) and lower quartiles (25%), the vertical line (whiskers) indicates the 1.5 quartile spacing between the upper and lower quartiles, the data outside the whiskers are the outliers, and the red line represents concentrations of Cu, Zn, and Ni based on the European Union standard.

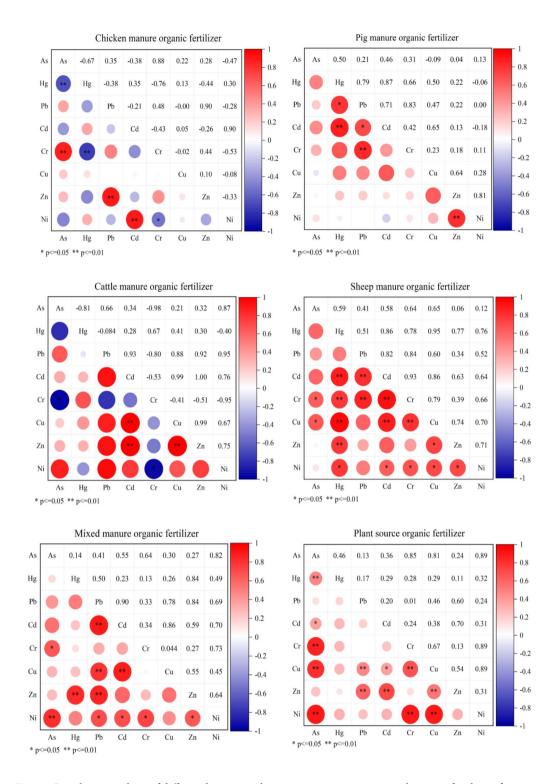
	Project	Pig manure COFs (n=9)	Chicken manure COFs (n=8)	Sheep manure COFs (n=10)	Cattle manure COFs (n = 4)	Mixed manure COFs (n=10)	Plant source COFs (n = 33)	
	Range (mg kg <sup>-1</sup> )	6.03-25.72	5.79-36.95	3.06-26.38	6.72-20.02	6.04-30.36	1.55-31.50	
As	Average (mg kg <sup>-1</sup> )	10.31 ± 3.07	$21.23 \pm 10.81$	15.50 ± 8.42	12.54 ± 6.04	14.89 ± 7.34	15.36 ± 7.33	
	Coefficient of variation (%)	28.05	47.63	88.75	41.68	46.79	130.34	
	Over standard rate (%)	20	75	44.44	25	30	51.52	
	Range (mg kg <sup>-1</sup> )	0.18-1.03	0.07-0.93	0.13-0.89	0.23-0.73	0.12-0.77	0.04-2.32	
Hg	Average (mg kg <sup>-1</sup> )	$0.30 \pm 0.07$	0.36 ± 0.27	$0.40 \pm 0.31$	0.37 ± 0.24	0.37 ± 0.19	$0.50 \pm 0.52$	
	Coefficient of variation (%)	21.11	70.52	74.73	57.38	48.51	100.62	
	Over standard rate (%)	0	0	0	0	0	3.03	
Pb	Range (mg kg <sup>-1</sup> )	6.42-47.61	12.47-29.55	7.44-36.40	9.23-22.57	5.96-64.36	1.43-78.05	
	Average (mg kg <sup>-1</sup> )	19.87 ± 10.38	20.96 ± 5.81	24.89 ± 14.07	18.59 ± 6.27	24.13 ± 18.52	17.38 ± 14.01	
	Coefficient of variation (%)	49.27	25.94	53.61	29.21	72.81	79.37	
	Over standard rate (%)	0	0	0	0	10	3.03	
Cd	Range (mg kg <sup>-1</sup> )	0.19-2.94	0.54-1.30	0.33-1.92	0.15-3.71	0.25-2.29	0.15-7.49	
	Average (mg kg <sup>-1</sup> )	1.79 ± 0.98	$0.85 \pm 0.28$	1.04 ± 0.64	1.32 ± 1.62	1.13 ± 0.81	2.12 ± 3.15	
	Coefficient of variation (%)	51.8	30.71	58.72	106.14	68.13	146.64	
	Over standard rate (%)	0	0	0	25	0	15.15	
	Range (mg kg <sup>-1</sup> )	23.73-136.67	25.17-89.55	12.87-103.21	32.40-102.39	24.11-98.90	11.03-212.90	
Cr	Average (mg kg <sup>-1</sup> )	44.53 ± 19.31	60.99 ± 19.48	56.85 ± 37.76	53.25 ± 32.96	54.72 ± 24.56	82.61 ± 57.48	
Ci	Coefficient of variation (%)	40.88	29.88	63	53.6	42.59	68.52	
	Over standard rate (%)	0	0	0	0	0	15.15	
	Range (mg kg <sup>-1</sup> )	35.88-150.36	27.70-171.35	20.44-151.36	23.84-255.84	19.39-166.42	7.74-555.11	
C.,	Average (mg kg <sup>-1</sup> )	104.97 ± 33.23	60.60 ± 46.64	67.97 ± 46.88	95.75 ± 107.78	78.74 ± 53.16	$72.70 \pm 105.13$	
Cu	Coefficient of variation (%)	29.85	72	65.44	97.49	64.05	142.39	
	Over standard rate (%)	90	12.5	11.11	25	30	12.12	
	Range (mg kg <sup>-1</sup> )	248.791313.33	169.41-1897.49	123.99-982.62	151.83-683.56	91.08-2484.54	21.46-2705.68	
Zn	Average (mg kg <sup>-1</sup> )	839.03 ± 276.03	598.20 ± 584.82	65.23 ± 348.50	$408.13 \pm 223.50$	672.96 ± 687.08	493.77 ± 629.24	
	Coefficient of variation (%)	31.02	91.45	58.49	47.43	96.86	125.49	
	Over standard rate (%)	90	100	77.78	75	90	63.64	
	Range (mg kg <sup>-1</sup> )	11.70-244.47	25.11-65.83	16.65-81.18	14.73-40.70	16.63-40.52	5.62-79.72	
Ni	Average (mg kg <sup>-1</sup> )	40.30 ± 26.83	39.17 ± 13.55	61.18±66.63	29.56 ± 10.97	30.06 ± 8.67	38.45 ± 17.99	
	Coefficient of variation (%)	62.77	32.35	103.32	32.13	27.36	46.07	
	Over standard rate (%)	90	100	88.89	75	80	81.82	

**Table 1**. Heavy metal concentrations in commercial organic fertilizers.

fertilizer was the lowest, with only cattle manure organic fertilizer and plant sourced organic fertilizer had Cr exceeding the standard. Plant-source organic fertilizer had the highest concentration of Cu and Zn, chicken manure organic fertilizer showed the lowest concentration of Cu, sheep manure organic fertilizer showed the highest concentration of Ni, cattle manure organic fertilizer showed the lowest concentrations of Zn and Ni, and the over-standard rate of heavy metals in COFs made from different sources were all > 0%.

#### Correlation analysis of heavy metals in different types of COFs

There was a correlation between the heavy metal concentrations of COFs from different sources (Fig. 4). There was a significant correlation between As and Hg, Cr, and also between Hg and Pb in the heavy metal concentrations of COF made from chicken manure. In the heavy metal concentrations of commercial organic fertilizer made from pig manure, Hg was significantly correlated with Pb and Cd, Pb was significantly correlated with Cd and Cr, and Zn was significantly correlated with Ni. The Cd was significantly positively correlated with Ni and As in cattle manure organic fertilizer. In the heavy metal concentrations of commercial manure organic fertilizer made from sheep, several heavy metals were significantly correlated. In the heavy metal concentrations of commercial organic fertilizer made from mixed animal manure, As and Cr were significantly correlated with Ni, Hg, and Zn were significantly correlated with Ni and Zn was significantly correlated with Ni. In the heavy metal concentrations of commercial organic fertilizer made from plant materials, As was significantly correlated with Hg, Cd, Cr, Cu, and Ni, Pb was significantly correlated with Cu and Zn, Cd was significantly correlated with Cu and Zn, Cd was significantly correlated with Cu and Ni, and Cu was significantly correlated with Zn and Ni.



**Fig. 4.** Correlation analysis of different heavy metal concentrations in commercial organic fertilizers from different sources.

## Accumulation rate and cumulative risk of heavy metals in soils fertilized with different types of COFs

The rate of soil heavy metal accumulation varied according to the application of different types of COFs (Table 2). The application of chicken manure fertilizer will result in the highest accumulation rates of As in the soil; the application of pig manure organic fertilizer will result in the highest accumulation rates of Pb, Cu, Zn, and Ni; the application of pig manure source COFs and plant source COFs resulted in the highest accumulation rates of

Samples	As	Hg	Pb	Cd	Cr	Cu	Zn	Ni
Chicken manure source COFs $(n=8)$	0.036	0.001	0.035	0.001	0.102	0.102	1.002	0.066
Pig manure source COFs $(n=10)$	0.02	0.001	0.038	0.003	0.09	0.183	1.457	0.102
Sheep manure source COFs $(n=9)$	0.024	0.001	0.037	0.002	0.08	0.099	0.839	0.068
Cattle manure source COFs $(n=4)$	0.021	0.001	0.031	0.002	0.089	0.16	0.684	0.05
Mixed manner source $COFs(n=10)$	0.025	0.001	0.04	0.002	0.092	0.132	1.128	0.05
Plant source COFs(n=33)	0.026	0.001	0.029	0.003	0.138	0.122	0.827	0.064

**Table 2**. The accumulation rate of heavy metals in the soil after application of different types of commercial organic fertilizers /  $mg \cdot (kg \cdot a)^{-1}$ .

Samples		Hg	Pb	Cd	Cr	Cu	Zn	Ni
Chicken manure source COFs (n = 8)		3781	2503	42	1348	706	166	1094
Pig manure source COFs $(n=10)$	972	3601	2317	20	1530	391	114	706
Sheep manure source COFs $(n=9)$		4137	2345	40	1714	728	199	1050
Cattle manure source COFs $(n=4)$	918	3695	2822	27	1544	447	244	1450
Mixed manner source COFs $(n=10)$	774	3675	2174	32	1503	543	148	1426
Plant source COFs(n=33)	750	2688	3018	20	995	589	201	1114

**Table 3**. Maximum years of application of different types of commercial organic fertilizers.

Cd in the soil. The application of plant manure source COFs will result in the highest accumulation rates of Cr in the soil. The application of organic fertilizers from different sources resulted in the same soil Hg accumulation.

The current background values of each heavy metal element in the soil were used as the soil heavy metal basal concentration<sup>24</sup>. The longest years of continuous application with the same organic fertilizer were determined and the results are shown in Table 3. The risk of soil Cd exceedance is the greatest with continuous application to COFs with different raw materials, and the maximum application period is less than 50 years, among which the lowest period of soil Cd exceedance was 20 years for plant source COFs and pig manure source COFs. Continuous application of plant source COFs and pig manure source COFs for 20 years may result in Cd concentrations in soil exceeding the risk limit values. Similarly, the application of chicken manure source COFs for 42 years, sheep manure source COFs for 40 years, cattle manure source COFs for 27 years, and mixed manner source COFs for 32 years may result in soil Cd concentration above acceptable risk values.

#### Discussion

#### Analysis of heavy metal concentration in COFs

In recent years, the heavy metal content of organic fertilizers in China has been of great concern, and exceedance of the standard still exists. According to the China Organic Fertilizer Standard, Yang et al. (2017) found that 13.70%, 4.20%, 2.40% and 1.40% of the samples exceeded the standard limits for four heavy metals in COFs<sup>22</sup>, after a 3-year tracking study of the heavy metal concentration of organic fertilizers in China, Yi et al. (2018) found that the heavy metal As had the highest frequency of exceeding the standard and Hg had the lowest<sup>27</sup>. The study revealed that the exceedance rates of As, Hg, Pb, Cd, and Cr in organic fertilizers were 45.95%, 1.35%, 2.70%, 8.11%, and 6.76%, respectively. According to the European Union's standard (EU 2019/1009), China's COFs with high exceedance rates of Cu, Zn and Ni, the maximum concentration of Cu reached 555.11 mg kg<sup>[-1</sup>, while Zn reached 2705.68 mg kg<sup>[-1</sup> and Ni reached 244.47 mg kg<sup>[-1</sup>. At present, China does not limit these three elements, the European Union's organic standard limit value is the most stringent, and according to the U.S. organic fertilizer standard (AAPFCO Product Label Guide 2019), these three heavy metals exceeded the rate greatly reduced, which can be seen in different countries and regions, there are large differences in standards. These three elements should be followed up in future research and should be considered in the future development of heavy metal limits for organic fertilizers in China.

#### Organic fertilizer sources influence heavy metal concentrations in COFs

China's commercial organic fertilizers are mainly produced by plant residues, organic waste, and animal manure as the main raw materials. Due to the variety of raw materials for organic fertilizers, the heavy metal concentration varies greatly in organic fertilizers produced from different raw materials. This study showed that there were exceedances of As in different types of organic fertilizer samples, among, which in organic fertilizers of animal origin, there were exceedances of Cd in organic fertilizers of cattle manure and exceedances of Pb in organic fertilizers of mixed manure. Due to the complexity of the sources of these common heavy metal elements in organic fertilizers, it is necessary to ensure the quality and safety of organic fertilizer products by first understanding the possible sources of the heavy metal elements in them. As a feed additive inhibits pathogenic microorganisms, promotes animal growth, and improves the appearance and color of livestock products, this indicates a problem with arsenic addition to some of the feeds from different livestock<sup>22,27</sup>. A study has shown that Cd, Pb, and Hg in organic fertilizers mainly originate from organic fertilizer raw materials or production

and processing additives or the production environment<sup>28</sup>, but in this study, the concentrations of these three heavy metals were low, probably because of livestock and poultry manure farming in China, and the organic fertilizer production process is becoming increasingly standardized. The Cr concentration in this study was low and only existed in the organic fertilizer of seaweeds of plant origin, which may be caused by the enrichment of Cr by seaweeds and needs to be further investigated.

Cu and Zn are the essential trace elements for crops. Crops do not require high amounts of Cu and Zn, but they are essential for crop growth and development, and excessive amounts of Cu and Zn can damage the crops, or even cause excessive levels in crop products, posing a threat to human health. Some studies have shown that Cu and Zn are essential nutrients for livestock growth and are often added to feed to promote growth and development. In this study, the exceedance rate of Cu and Zn in pig manure organic fertilizer was greater than that in organic fertilizer from other raw materials, probably because more Cu and Zn were added to pig feeds than to other feeds. Ni is often used as a feed additive in chicken rearing and is contained in the feed itself, which is the main cause of Ni contamination in organic fertilizers<sup>29</sup>. Hence the monitoring of heavy metals in different types of organic fertilizers should be increased.

#### Risk of heavy metal contamination of soil due to large-scale and long-term application of commercial organic fertilizers

The long-term application of organic fertilizers containing heavy metals can lead to the accumulation of heavy metals in farmland soil, which will ultimately contaminate agricultural products<sup>30–33</sup>. The safe application period for organic fertilizers varies depending on the type of fertilizer and the accumulation rates of various heavy metals in the soil. In this study, different types of COFs contained Cd, Pb, Cr, Hg, and As with low overall concentrations, and Cu, Zn, and Ni with generally high concentrations. The risk of safe use of As, Hg, Pb, Cr, and Ni was determined to be relatively low based on the annual application of 3854 kg hm<sup>[-2]</sup> (dry weight) of fertilizers. In contrast, the risk of safe use of Cd, Cu, and Zn was identified as relatively high. It is therefore imperative to ensure the safe promotion and use of organic fertilizers, with particular attention paid to the monitoring of Cd in soil. Furthermore, the formulation of limited standards for Cu, Zn, and Ni in organic fertilizers should be prioritized, with the aim of reducing the pollution of heavy metals in organic fertilizers.

#### Conclusion

- (1) In this study, the exceedance rates of As, Hg, Pb, Cd, and Cr in organic fertilizers ranged from 1.35 to 45.95%. As exhibited the highest exceedance rate (45.95%), while Hg demonstrated the lowest (1.35%). By the European Union standard, the over-standard rate of Cu was 32.43%, 75.68% for Zn, and 85.14% for Ni.
- (2) According to the Chinese Organic Fertilizer Standard, the As concentrations of organic fertilizers made from different raw materials have exceeded the national standard. The heavy metals concentrations of organic fertilizers made from different sources had exceeded the standard of Cu, Zn, and Ni.
- (3) The application of organic fertilizer from different raw materials has the greatest risk of exceeding Cd in soil, and the maximum application period is below 50 years. Specifically, plant-based and pig manure-based fertilizers have the shortest safe application periods, with Cd levels exceeding safety thresholds after 20 years. It is crucial to prioritize monitoring of Cd levels in soil, and we should also pay increased attention to monitoring levels of Cu and Zn.

#### Data availability

The datasets used and/or analyzed during the current study are available from the corresponding authors on reasonable request.

Received: 7 June 2024; Accepted: 11 November 2024 Published online: 07 January 2025

#### References

- 1. Xu, J. et al. Quantification and identification of microplastics in organic fertilizers: the implication for the manufacture and safe application. Water Air Soil Pollut. 235, 169 (2024).
- 2. Yang, Y. et al. Effect on soil properties and crop yields to long-term application of super absorbent polymer and manure. Front. Environ. Sci. 10, 859434 (2022).
- 3. Xu, Y. et al. What role does organic fertilizer actually play in the fate of antibiotic resistance and pathogenic bacteria in planting soil. J. Environ. Manage. 317, 115382 (2022).
- 4. Hellen, L. et al. Hydrothermal carbonisation of manure-derived digestates: Chemical properties and heavy metals distribution in end-products. Chem. Eng. J., 154110 (2024).
- 5. Wu, J., Lu, Z. & Hu, D. Scientifically understanding the role of organic fertilizer in agricultural production. Crops. 5, 1-6 (2017).
- 6. Zhao, H. et al. Microplastic pollution in organic farming development cannot be ignored in China: perspective of commercial organic fertilizer. J. Hazard. Mater. 460, 132478 (2023)
- 7. Li, Q., Wagan, S. A. & Wang, Y. An analysis on determinants of farmers' willingness for resource utilization of livestock manure. Waste Manage. 120, 708-715 (2021).
- 8. He, H., Peng, M., Lu, W., Hou, Z. & Li, J. Commercial organic fertilizer substitution increases wheat yield by improving soil quality. Sci. Total Environ. 851, 158132 (2022).
- 9. Du, W., Tang, B. & Wang, H. The status of organic fertilizer industry and organic fertilizer resources in China. Soil. Fertilizer Sci. China. 3, 210-219 (2020). 10. Huang, S., Jiwei, T. & Li, C. Status of heavy metals, nutrients, and total salts in commercial organic fertilizers and organic wastes in
- China. J. Plant. Nutr. Fertilizers. 23, 162-173 (2017).
- 11. Wang, J. et al. Speciation analysis method of heavy metals in organic fertilizers: a review. Sustainability. 14, 16789 (2022).
- 12. Wei, Y. et al. Characteristic of heavy metal contents in agricultural wastes and agricultural risk assessment. Trans. Chin. Soc. Agricultural Eng. 35, 212-220 (2019).

- 13. Shen, Y., Ma, W., Deng, X., Chen, S. & Lu, R. Spatio-temporal characteristics of ingredients contents of organic fertilizers in Zhejiang. Acta Agriculturae Zhejiangensis. 31, 2073-2083 (2019)
- 14. Wang, F. et al. Analysis of heavy metal contents and source tracing in organic fertilizer from livestock manure in North China. Trans. Chin. Soc. Agricultural Eng. 29, 202-208 (2013).
- 15. Pan, X. et al. Heavy metal contents in pig manure and pig feeds from intensive pig farms in Shandong province. Agricultural Environ. Sci. 1, 160-165 (2013).
- 16. Qaswar, M. et al. Soil nutrients and heavy metal availability under long-term combined application of swine manure and synthetic fertilizers in acidic paddy soil. J. Soils Sediments. 20, 2093-2106 (2020).
- 17. Hussain, B. et al. A field evidence of cd, zn and Cu accumulation in soil and rice grains after long-term (27 years) application of swine and green manures in a paddy soil. Sustainability. 13, 2404 (2021).
- 18. Zhao, Y., Yan, Z., Qin, J. & Xiao, Z. Effects of long-term cattle manure application on soil properties and soil heavy metals in corn seed production in Northwest China. Environ. Sci. Pollut. Res. 21, 7586-7595 (2014).
- 19. Wu, L. et al. Cadmium bioavailability in surface soils receiving long-term applications of inorganic fertilizers and pig manure. Geoderma, 173, 224-230 (2012).
- 20. Li, K., Xie, S., Sun, T. & Sun, Y. Effects of organic fertilizers from chicken manure on soil heavy metals and microbial community structure in facility vegetable soil. Acta Ecol. Sin. 41, 4827-4839 (2021).
- 21. Fan, M. et al. Evidence of decreasing mineral density in wheat grain over the last 160 years. J. Trace Elem. Med Biol. 22, 315-324 (2008).
- 22. Yang, X. et al. Heavy metal concentrations and arsenic speciation in animal manure composts in China. Waste Manage. 64, 333-339 (2017)
- 23. Mu, H. et al. Heavy metal contents in animal manure in China and the related soil accumulation risks. Environ. Sci. 41, 986-996 (2020).
- 24. Huang, Y. et al. Current status of agricultural soil pollution by heavy metals in China: a meta-analysis. Sci. Total Environ. 651,
- Soil environmental quality Risk control standard for soil contamination of agricultural land GB 15618 2018, Preprint at (2018). https://www.mee.gov.cn/ywgz/fgbz/bz/bzwb/trhj/201807/t20180703\_446029.shtml
- 26. Li, J., Li, G. & Wang, B. Comparative study on relevant standards of organic fertilizer in China and foreign countries. Soil. Fertilizer Sci. China. 04, 230-237 (2023).
- 27. Yi, X. et al. Status of heavy metal in organic fertilizers in main tea growing regions of China. Environ. Sci. 43, 4613-4621 (2022).
- 28. Qian, X. et al. Heavy metals accumulation in soil after 4 years of continuous land application of swine manure: a field-scale monitoring and modeling estimation. Chemosphere. 210, 1029-1034 (2018).
- 29. Ye, X. et al. Variations of heavy metal contents and the risk management of commercial organic fertilizers in Zhejiang Province. J. Plant. Nutr. Fertilizers. 26, 954-965 (2020).
- 30. Wang, M. et al. Heavy metals in fertilizers and effect of the fertilization on heavy metal accumulation in soils and crops. J. Plant. Nutr. Fertilizers. 20, 466-480 (2014).
- 31. Zaccone, C., Di Caterina, R., Rotunno, T. & Quinto, M. Soil-farming system-food-health: Effect of conventional and organic fertilizers on heavy metal (cd, cr, Cu, Ni, Pb, Zn) content in Semolina samples. Soil Tillage. Res. 107, 97-105 (2010)
- 32. Ru, S. et al. Effects of continuous application of organic fertilizer on the accumulation and migration of heavy metals in soil-crop systems. Ecol. Environ. 28, 2070 (2019).
- 33. Átafar, Z. et al. Effect of fertilizer application on soil heavy metal concentration. Environ. Monit. Assess. 160, 83-89 (2010).

#### Acknowledgements

This work was supported by the National Key Research and Development Program of China (2018YFC19011003) and Sichuan and Chongqing Science and Technology Co-operation Projects of Beibei district, Chongqing (2024cykjhz-31).

#### **Author contributions**

K.S. and Q.Z., Experiment, Software, Writing-Original draft preparation; A. C. and X. W., Experiment, Data curation, Writing-Original draft preparation; L.Z. and Q.R., Methodology, Investigation, Data curation; J.W. and H.Y., Data collection, Editing, Software analysis, Experimental operation.

#### **Declarations**

#### Competing interests

The authors declare no competing interests.

#### Additional information

**Correspondence** and requests for materials should be addressed to J.W. or H.Y.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License, which permits any non-commercial use, sharing, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if you modified the licensed material. You do not have permission under this licence to share adapted material derived from this article or parts of it. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommo ns.org/licenses/by-nc-nd/4.0/.

© The Author(s) 2024