Survey on heavy metal concentrations and maturity indices of organic fertilizer in China

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Abstract: A nationwide survey of organic fertilizer was carried out in China, and 263 samples were collected to be analyzed for maturity indices (moisture content (MC), pH, electrical conductivity (EC), E4/E6, and germination index (GI)) and 7 heavy metals (Cu, Zn, Cd, Pb, Cr, As and Ni). The MC, pH, EC, E4/E6 and GI showed large variations among the organic fertilizer samples with ranges of 6.9%-66.68%, 4.40-9.19, 0.76-13.38 mS/cm, 1.07-9.40, and 10%-150%, respectively. The concentrations of 7 heavy metals (Cu, Zn, Cd, Pb, As, Cr, Ni) were also with large variations at 7.53-580.4, 0-2818, 0.02-149.3, 0 (not detected)-1321, 0.14-26.9, 3.70-1237, and 0 (not detected)-214.6 mg/kg dry weight. Compared with the limit values of the Chinese standard for organic fertilizers (NY525-2012), 9.51%, 73.4%, 3.19%, and 3.04% of the samples exceeded the limit values of Cd, Pb, As and Cr, respectively. No limits have been set for Cu, Zn and Ni in China, and 35.0%, 13.3% and 16.7% of the samples exceeded the Cu, Zn and Ni limits for composts in Germany, respectively. Monte Carlo simulations indicated that with the continuous application of organic fertilizer, Cu, Zn, Cd, Pb and Cr would accumulate to the risk control standard for soil contamination of agricultural land (GB15618-2018) within a relatively short period. It is urgent to establish suitable limits of heavy metals in organic fertilizer in China to control the risk of heavy metal pollution in agricultural land.

Keywords: heavy metal, organic fertilizer, risk assessment, maturity indices
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1 Introduction

Organic fertilizer application is a traditional practice to improve soil fertility and texture, and has significant effects on climate change mitigation[1,2]. In recent years, a variety of organic materials, such as livestock and poultry manures, biogas residues, mushroom residues, industrial by-products and other organic wastes, were used for organic fertilizer production[3]. According to the statistics, about 5.7 billion tons of organic resource stock was produced annually in China, of which about 3.8 billion tons were livestock and poultry manures[4]. Livestock and poultry manures are favored for increasing soil organic matter stock and supplying nutrients for crops because they have higher soil organic matter sequestration efficiency[5] and more available nutrients to crops[6,7].

Feed additives, such as heavy metals, were used to promote weight increase and improve productivity or control animal diseases for intensive cultivation of livestock and poultry in China[8-10]. In animal diets, about 90% of copper (Cu) is lost in the feces[11], and therefore, in many provinces and regions in China, manures are polluted by heavy metals, such as Cu, zinc (Zn), cadmium (Cd) and lead (Pb)[8,10,12]. The content of Cu in pig manure in some regions of the country has already been measured at 962.95 mg/kg[13], which is 9 times higher than the Germany rotten compost limit values; while the content of Pb has reached 87.40 mg/kg in some areas[14], which is close to the Germany rotten compost limit values. Li et al.[15] reported that the concentrations of Cd in pig manures were ranged from non-detectable to 129.76 mg/kg in Beijing and Fuxin. Wang et al.[16] found that the concentrations of Cu, Zn, and chromium (Cr) in livestock and poultry manures were 8.4-1726, 39.5-11379 and 1.0-1602 mg/kg respectively, while Cd, Pb, arsenic (As) and mercury (Hg) were less than 10 mg/kg in Jiangsu province. In addition, heavy metal concentrations varied greatly in different regions in China. For example, the mean Cu concentrations in pig, chicken and cattle manures from Jiangsu province were 399 mg/kg, 89 mg/kg and 46 mg/kg[17], which were close to those in England and Wales[18]. However, the concentrations of Cu in pig and chicken manures were 765 and 107 mg/kg in Guangdong province, which is a

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developed livestock husbandry region in China[19]. In the same area, heavy metal residues in livestock and poultry manures also showed diversity at farms of different scales.

With the livestock and poultry manures successively applied to agricultural land, heavy metals were excessively accumulated in soil, leading to adverse effects on soil quality[20-22]. Xiong et al.[23] found that the risk of soil Cu pollution would increase with continuous application of livestock and poultry manures in Fuxin city in Northeast China. For example, as pig manure was continuously applied to soil for 17 years, the soil Cd concentration was detected an 18-fold increase[24]. Long-term (>160 years) application of farmyard manures have increased soil Cu and Zn concentrations by approximately 60% in the Broadbalk classical experiment at Rothamsted, UK[25]. The accumulation of heavy metals in soil would affect agriculture product quality and soil fertility, and they may also migrate from agricultural soil to water resources through leaching or run-off[26,27]. Therefore, the residues in livestock and poultry manure and manure-based fertilizers should receive the scientific attention and it is imperative to monitor and minimize heavy metals inputs to agricultural soil[28].

Organic fertilizers were widely applied, especially to the cultivation of vegetables, crops and fruits in China. Many researches have reported the levels of heavy metals in livestock and poultry manure and manure-based fertilizers samples[10,13-17]. However, little information is available on the ranges of heavy metal concentrations and maturity indices in commercial organic fertilizer nationwide[28,29]. Considering the risk of heavy metal pollution to agricultural soil, this research was conducted: (1) to provide a profile of the concentrations of 7 heavy metals (Cu, Zn, Cd, Pb, As, Cr and Ni) in 263 organic fertilizer samples collected during 2017 in China; (2) to analyze the characterization of 5 maturity indices (moisture content (MC), pH, electrical conductivity (EC), E4/E6, and germination index (GI)) in surveyed organic fertilizer samples; and (3) to evaluate the potential risk of heavy metals from continuous application of organic fertilizers to agricultural soil.

2 Materials and methods

2.1 Sample collection

During 2017, 263 organic fertilizer samples were collected from 21 provinces in 7 regions of China, which consisted of 208 livestock and poultry manure based organic fertilizer samples and 55 other raw material based organic fertilizer samples, such as biogas residues, mushroom residues, sewage sludge and so on. The sampling information was listed in Table 1 in detail. The organic fertilizer is generally produced according to the following method: First, raw organic materials such as livestock and poultry manures and biogas residues are mixed with amendments and bulking agents such as sawdust or straw, and the C/N ratio of the mixture was adjusted to 20-25; Second, the mixture is high-temperature aerobically composted at 45℃-70℃ with an initial moisture content of 60%-65%; and lastly the compost was freeze-dried, milled and sieved, and/or applied directly as an organic fertilizer to the field[30,31].

Table 1 Location and raw materials of organic fertilizer samples

Region	Province	Raw material		Total
		Livestock and poultry manures	Others	
Beijing-Tianjin-Shanghai region	Beijing, Tianjin, Shanghai	26	1	27
Northeast China	Inner Mongolia	8	0	8
Eastern Coastal China	Fujian, Jiangsu, Zhejiang, Guangdong, Hainan	66	17	83
Central and Eastern China	Anhui, Jiangxi, Hubei, Hunan	18	2	20
North China Plain	Hebei, Shanxi, Shandong, Henan	53	5	58
Southwest China	Guangxi, Sichuan, Guizhou, Yunnan	33	30	63
Northwest China	Shaanxi, Gansu	4	0	4
	Total	208	55	263

In a single compost factory, 5 organic fertilizer samples from the most recently produced batches with storage time no more than one week, were collected and thoroughly mixed into a 2.5 kg sample. A 500 g (fresh weight) subsample was taken by using point-quarter sampling method, and transferred to a plastic container. The sample was further divided into two parts, one part was stored at 4℃; and another was dried at room temperature, milled pass through a 100 mesh sieve, and sealed in a labeled plastic container prior to analysis.

2.2 Sample analysis

Each dried sample (0.5 g) was analyzed for heavy metals (Cu, Zn, Cd, Pb, Cr, As and Ni) by HNO_3-$HClO_4$ digestion according to Hseu[32] and Wang et al.[16]. The concentrations of Cu, Zn, Pd and Cr were determined by inductively coupled plasma spectrophotometry (ICP, 7300, Agilent, USA), Cd was analyzed by inductively coupled plasma mass spectrometry (ICP-MS, 7500, Agilent, USA), and As was determined by hydrogen atomic fluorescence spectroscopy (HG-AFS, AF630, Beijing Ruili, China). Each composite sample was divided into 3 subsamples and each subsample was determined twice to avoid accidental error. The recorded results were the mean of 3 subsamples. The precision of analysis was checked using 2 soil standard samples (GBW07405 and GBW07408). The recovery of heavy metals was from 95% to 105% in GBW07405 and GBW07408. A 15% parallel replication of samples was also used as a quality control procedure.

MC was determined by drying 10 g fresh sample at 105℃ for more than 12 h until a constant weight. The pH, EC, E4/E6, and GI were measured by adding deionized water to the samples at a solid to water ratio of 1:10 (w/v). Then, pH and EC measured by pH/EC meter (Mettler S470). E4/E6 was the ratio of optical densities of humic acids and fulvic acids in the water extract at the wavelength of 465 and 665 nm respectively measured by an infrared spectrophotometer[33]. GI was determined and calculated using the method described by Guo et al.[34]. All index analyses were replicated for each sample.

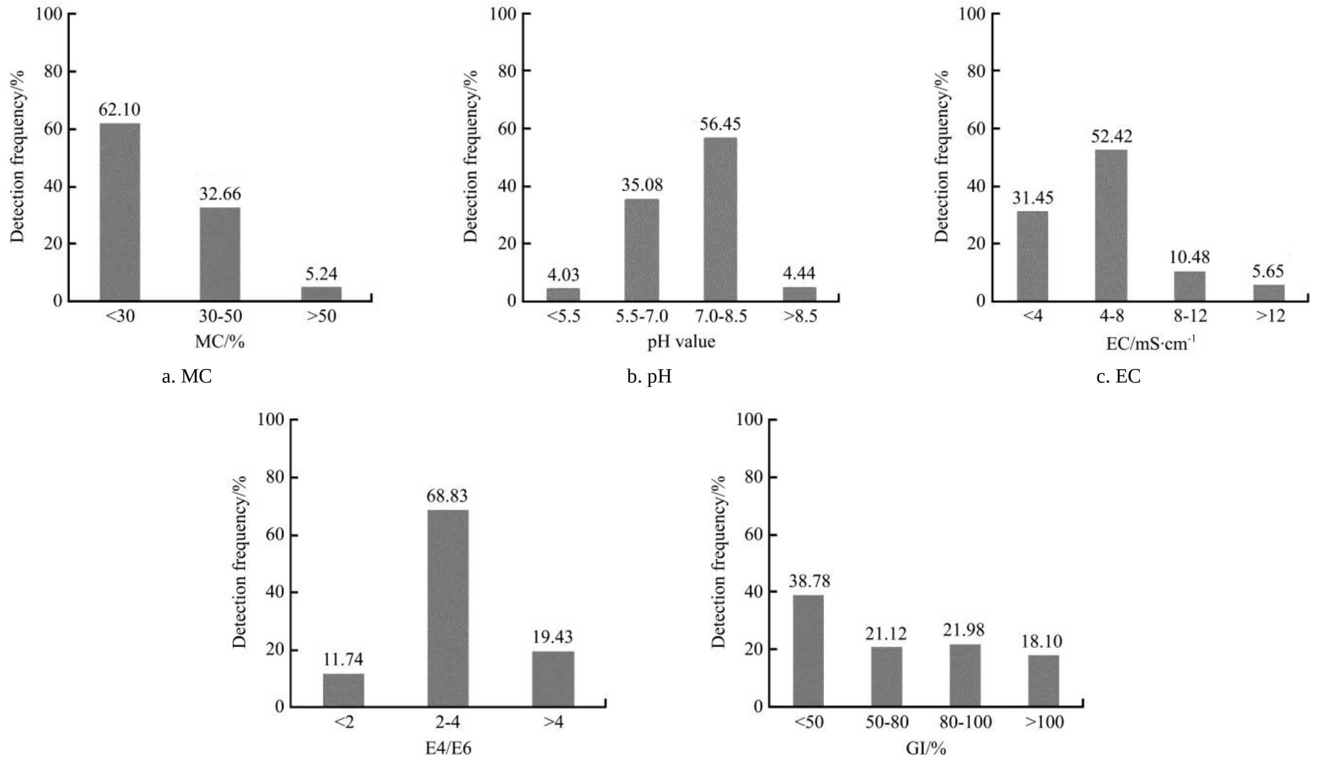
2.3 Statistical analysis

Statistical analyses on heavy metals were performed using the statistical software package SPSS (version 21, IBM, USA) and Microsoft Excel 2016 spreadsheets.

3 Results and discussion

3.1 Maturity indices

Organic fertilizer quality is a primary concern for applying to soil. According to previous studies, the pH, EC, GI, E4/E6 and some other stability and/or maturity indices were frequently used to assess the quality of organic fertilizer[35]. In this research, the MC, pH, EC, E4/E6 and GI presented large variations among the organic fertilizer samples as shown in Figure 1. Based on the Chinese national standard (NY 525-2012), the maximum permissible value for MC in organic fertilizer is 30%. The MC ranged from 6.9% to 66.68%, and only 62.10% of the samples in the survey met the guideline value for MC. The pH of the samples ranged in 4.4-9.2, and 91.53% samples ranged in pH 5.5-8.5 accounted for (Figure 1b), in accordance with the standard of organic fertilizer (NY 525-2012). And 4.44% of the samples exceeded the pH8.5, 4.03% of the samples was below the pH5.5, which was not suitable for adding to soils. The EC value reflects the salinity of organic fertilizer, and affects seed germination and plant growth[36]. EC values of organic fertilizer samples were from 0.76 to 13.38 mS/cm, and the samples lower than 4 mS/cm only accounted for 31.45% (Figure 1c), which was lower than the standard of farmland use[36]. The E4/E6 ratios of surveyed samples were ranged from 1.07 to 9.40, and the samples that below 2, only accounted for 11.74% (Figure 1d), and E4/E6 ratios of the organic fertilizers from 2 to 4 were reached to 68.83%. E4/E6 can reflect the degree of condensation of the aromatic nucleus of humus, indicating humification level of humic acid and organic fertilizer maturity. The smaller E4/E6 ratio the easier degradable organic matters were mineralized; and phenolic compounds were oxidized and bound to methoxyl groups and/or aliphatic side chains in humic substances[37]. GI is usually used to evaluate the phytotoxicity and maturity of organic fertilizers[35]. The GI values of the samples were from 10% to 150% that were widely different, and the GI values exceeded 80% only accounted for 40.08%, indicating the organic fertilizers reached maturity[38].



a. MC b. pH c. EC

d. E4/E6 e. GI

Figure 1 Detection frequency distributions of maturity indices in organic fertilizer samples

3.2 Heavy metal content

The concentrations of heavy metals in the 263 organic fertilizer samples were largely variable as showed in Table 2. The ranges of Cu, Zn, Cd, Pb, As, Cr, and Ni concentrations were 7.53-580.4, 0-2818, 0.02-149.3, 0 (not detected)-1321, 0.14-26.9, 3.70-1237 and 0 (not detected)-214.6 mg/kg, respectively. All data expressed non-normal distribution (Figure 2). Among the 7 heavy metals, the median concentrations values followed the order of Zn > Pb > Cu > Cr > Ni > As > Cd (Table 2 and Figure 2). Zn has the highest content in these fertilizer samples, with the median and mean contents of 142.6 mg/kg and 237.1 mg/kg, and Cd was the least, with the median and mean contents of 0.29 mg/kg and 3.95 mg/kg. The Cu mean concentration (105.2 mg/kg) of organic fertilizers is greater than Pb (101.5 mg/kg), while the Pb median concentration (86.62 mg/kg) of organic fertilizers is greater than Pb (73.00 mg/kg).

From this survey, it will be seen that Cu, Zn, Pb, Cd, Cr and Ni were present at high concentrations in some organic fertilizer samples in China. As reported in literatures, with heavy metals added to livestock and poultry feed for health and welfare reasons, high contents of heavy metals were detected in livestock and poultry manures[39]. For instance, the addition of Zn to feed could suppress bacteria in the gut and maximize feed utilization by the livestock and poultry, and Cu was applied to pig feed as a "cure-all" for scour, and farm animals excreted most of the Cu (72%-80%) and Zn (92%-96%) to manures[23,40]. Qian et al.[41] reported that the average concentration of Zn in pig manure based organic fertilizers from Zhejiang province was 1165 mg/kg. Yang et al.[28] reported that the range of Zn concentrations in 212 manure compost samples was 11.8-3692 mg/kg, and the mean concentration of Zn was 435 mg/kg in China. Compared to previously researches, the Zn concentrations in the organic fertilizers in this research were lower (Table 2). The average concentration of Cu was 351 mg/kg detected in pig manures in

England and Wales[18]. And similarly, in Austria, the mean Cu content was approximately 282 mg/kg in pig manures[42]. Cang et al.[17] and Wang et al.[16] found that the mean Cu concentration was 399 mg/kg and 300 mg/kg respectively in pig manures from the Jiangsu Province. Dong et al.[43] found a much higher mean Cu concentration of 1018 mg/kg in pig manures from the pig farms in Hangzhou, a large city in the Yangtze River Delta, China. As a result, large amount of Cu residues in manures resulted in the high levels of Cu in the organic fertilizers. For animals, Cd and Pb are not added to feed as they are non-essential nutrients[44], and Wang et al.[16] found that the Cd and Pb contents in manures were not statistically correlated with the feed levels. Cd in livestock and poultry manures may probably originate from supplements with high Cd[18]. Firdevs[45] reported that the high Cd and Pb in cattle manure were due to the high traffic and industrial pollution. Shen et al.[46] reported that many studies paid attention to Cu and Zn in livestock and poultry manures, while few considered Pb.

The maximum residue limits of heavy metals in organic fertilizers or composts that from Chinese and other national compost standards, were shown in Table 3. According with the Chinese national standards (NY 525-2012) for organic fertilizers, 9.51%, 73.4%, 3.19%, 3.04% of the surveyed samples exceeded the limit values for Cd (3 mg/kg), Pb (50 mg/kg), As (15 mg/kg) and Cr (150 mg/kg), respectively. By now, there were no guideline values of Cu, Zn and Ni in the Chinese national standards for organic fertilizers. Compared with the upper limit for composts in Germany of 100, 400, 150 and 50 mg/kg for Cu, Zn, Pb and Ni, the over limit ratios of these samples were 35.0%, 13.3%, 20.8% and 16.7%, respectively.

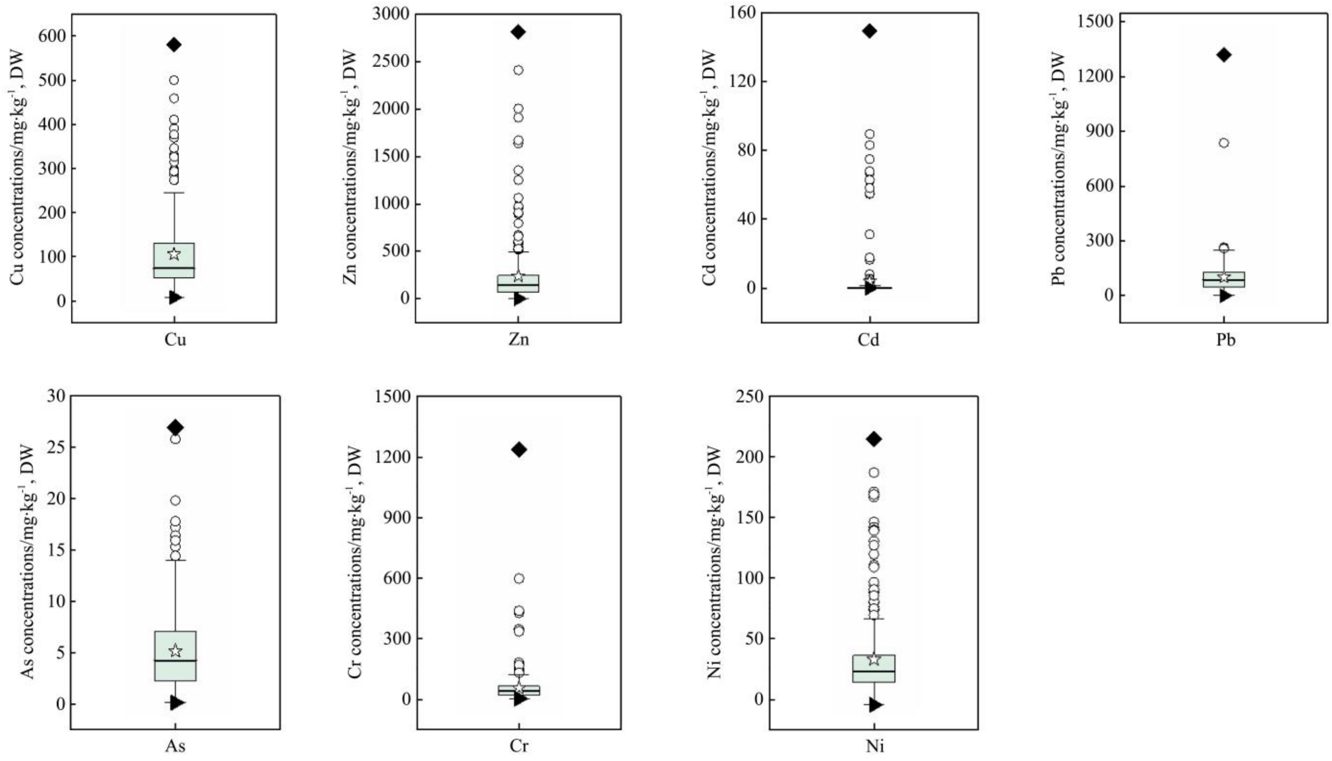
3.3 Changes of heavy metal concentrations in organic fertilizers

The heavy metals in organic fertilizer and composts reflected contents in livestock and poultry manures and environmental contamination[18,45]. The heavy metals in this research were compared with other studies[47,48,28] as shown in Table 4. In 2004 and 2014, Liu et al. and Huang et al. researched status of heavy metals in commercial organic fertilizers in China that made from livestock and poultry manures, biogas residues, mushroom residues, industrial by-products and other organic materials.162 and 180 samples were collected and analyzed, respectively. Also, 212 samples were collected from nationwide livestock and poultry manure-based composts in 2014, and heavy metals concentrations were analyzed[28].

Table 2 Heavy metal concentrations in organic fertilizer

	Cu	Zn	Cd	Pb	As	Cr	Ni
	mg ·kg^{-1}, DW						
Range	7.53-580.4	0-2818	0.02-149.3	N-1321	0.14-26.9	3.70-1237	N-214.6*
Mean	105.2	237.1	3.95	101.5	5.14	56.65	32.94
Median	73.00	142.6	0.29	86.62	4.25	39.45	22.86

Note: * N in range represented that the concentrations of organic fertilizer samples were lower than the limit of detection.



Note: The five-pointed star represents mean values, the band near the center of the box represents the median, and the top and bottom of the box express the upper (75th percentiles) and lower quartiles (25th percentiles), respectively. The vertical lines (whiskers) represent the 1.5 interquartile ranges of the upper and lower quartiles. The data outside the whiskers are outliers and plotted as parallelograms (the maximum values) or triangles (the minimum values).

Figure 2 Box plots of the concentrations of 7 heavy metals in organic fertilizer (n = 263).

Table 3 Heavy metal limits for composts/organic fertilizer in different countries and the comparison of heavy metals concentrations in organic fertilizers studied with these standards

	Cu	Zn	Cd	Pb	As	Cr	Ni
Limit value (mg/kg, DW)							
China[a]	–	–	3	50	15	150	–
Germany[b]	100	400	1.5	150	15	100	50
EU (Organic agriculture)[c]	70	200	0.7	45	–	70	25
EU (ECO Lable)[c]	100	300	1	100	10	100	50
Australia (Category A^+)[d]	70	200	0.7	45	–	70	25
Australia (Category A)[d]	150	500	1	120	–	70	60
Exceeding limit (%)							
China[a]	–	–	9.51	73.4	3.19	3.04	–
Germany[b]	35.0	13.3	14.1	20.8	3.19	8.37	16.7
EU (Organic agriculture)[c]	54.8	30.8	20.5	74.9	–	20.9	45.2
EU (ECO Lable)[c]	35.0	19.0	16.0	40.9	11.2	8.37	16.7
Australia (Category A^+)[d]	54.8	30.8	20.5	74.9	–	20.9	45.2
Australia (Category A)[d]	22.1	9.13	16.0	27.4	–	20.9	11.8

Note: –: Not stipulated in standard.
[a] Source: Standard of organic fertilizer (NY 525, Based on manure, plant/animal residues and/or by-products), Ministry of Agriculture of China, 2012.
[b] Source: German Bioabfallverordnung, Bundesgesetzblatt G 5702 Bonn 28. Sept. 1998 (revised March 1999) English Translation Available: Ordinance: Utilization of Bio-Wastes on Land used for Agricultural. (Compost quality standards & guidelines, 2000)
[c] Source: EU ECO Label, 64/2007 eco-label to growing media and 799/2006 eco-label to soil improvers; EU Regulation on organic agriculture, 889/2008, Compliance with limits required for compost from source separated bio-waste only, European Commission, SWD (2016)64/F1-EN, 2016.
[d] Source: Compost Ordinance: Class A^+ (organic farming); Class A (agriculture; hobby gardening), European Commission, SWD (2016)64/F1-EN, 2016.

Table 4 Comparison of heavy metal contents from different investigation researches

Research		Cu	Zn	Cd	Pb	As	Cr	Ni
		mg·kg^{-1}, DW						
This research (*n*=180)	Range	7.53-580.4	0-2818	0.02-149.3	N-1321	0.14-26.9	3.70-1237	N-214.6
	Mean	105.2	237.1	3.95	101.5	5.14	56.65	32.94
	Median	73.00	142.6	0.29	86.62	4.25	39.45	22.86
Huang et al.[48] (*n*=180)	Range	2.1-1187.9	10.9-1769.2	0.07-5.3	3.5-1265.3	0.00-23.3	3.4-4260.9	–
	Mean	122.2	260.6	1.2	34.3	5.6	165.2	–
	Median	81	165.2	1	22.3	5.2	16.4	–
Yang et al.[28] (*n*=212)	Range	3.55-916	11.8-3692	0.012-8.72	0.047-188.5	0.37-71.7	0.69-6603	0.68-72.7
	Mean	103	435	0.67	11.2	9.28	74.6	15.1
	Median	50.6	288	0.14	7.61	6.65	17.9	12.4
Liu et al.[47] (*n*=162)	Range	0-998.6	0-63647.5	0.2-256.0	0.7-1352.0	0-14.1	0.5-2386	3.6-84.4
	Mean	75.4	732.4	5.64	36.6	2.96	53.5	21
	Median	27.5	118.9	1.95	22.4	2.41	118.9	18.9

The increase in intensive livestock and poultry production and the changes in environmental contamination may have caused changes in the metal contents in manures and organic fertilizers. Compared with the Liu et al.[47], the mean and median concentrations of Cu and As were both higher in Huang et al.[48], Yang et al.[28] and this survey, which suggests that more Cu and As were added to the feeds. The Zn concentration in Huang et al.[48], and this survey were lower than Yang et al.[28], may be because the composts made from livestock and poultry manures have higher Zn in Yang et al.[28] Meanwhile, the concentration of Cd, Pb and Cr in Liu et al.[47], Huang et al.[48] and this survey were high than Yang et al.[28], and this may relate to the difference of raw materials and product processes. Cd, Pb and Cr were not added to feed, and the higher contents of these metals in manures were because of higher traffic and industrial pollution in China[45]. Cr was not an essential element and the trivalent form of Cr was ubiquitous in nature[44]. Cr concentrations were greatly increased in this study than in Liu et al.[47]. The Cr in livestock and poultry manures may have originated from abrasion of stainless steel or iron containers that contain about 18% Cr[42,44], or from feed additives with high Cr content[18].

3.4 Risk of heavy metal accumulation in soils applied organic fertilizers

Organic fertilizers, especially livestock and poultry manures based organic fertilizers are precious resources of soil organic matter and crop nutrients[49], and they are widely applied to farmlands in China. Therefore, long-time application of organic fertilizer may lead to the accumulation of heavy metals in agricultural land. To provide useful information about the risk of 7 heavy metals accumulation in agricultural land from organic fertilizers applied, the long-time effects on heavy metals contents in soils were predicted by Monte Carlo simulations[28]. Based on the median and maximum concentrations of 7 heavy metals in this research and the typical annual application rate in China (15 t/hm^2/yr), the median and minimum time to reach the risk control standard for soil contamination of agricultural land (GB15618-2018) of 7 heavy metals in Chinese soils with different soil pH were predicted (Table 5). The mean values for these heavy metals from a national soil survey were considered to be the ambient background values of Chinese agriculture soils. Outputs of heavy metals from the soil via crop uptake, erosion, leaching and so on are ignored in the calculations, as these are relatively litter compared with inputs[50].

Annual heavy metal input (AI) to soils are predicted as follows:

$$AI = C_F \times W_F \quad (1)$$

where, C_F repents the concentrations of heavy metal in organic fertilizers (mg/kg), and W_F repents the annual application rate of organic fertilizers (15 t/hm^2/yr) in China.

Increase from the background contents of 7 heavy metals to the risk control standard for soil contamination of agricultural land (GB15618-2018) in soils with different pH values, the time is predicted by the equation:

$$Time = \frac{(C_s - C_b) \times W_s}{C_F \times W_F} \quad (2)$$

where, C_s is limit values in the risk control standard for soil contamination of agricultural land (GB15618-2018); C_b is background concentration of heavy metal in soil (mg/kg), and W_s is weight of the plough layer (0-20 cm) soil per hectare (t/hm^2). For an average soil bulk density of 1.3 t/m^3, W_s is 2600 t/hm^2.

The annual inputs of 7 heavy metals from successive application of organic fertilizers, and time that heavy metals in different soils accumulated to the risk control standard for soil contamination of agricultural land (GB15618-2018) in China were predicted, and the results were shown in Table 5. The inputs of heavy metals to agricultural soils were ranged from 4.31 (Cd) to 2139 (Zn) g/hm^2/yr, predicted based on the median values in organic fertilizers and the manure regulation in China. With continuous application of organic fertilizer containing median heavy metal concentrations, the contents of heavy metals in different soils would be accumulated to the risk control standard for soil contamination of agricultural land (GB15618-2018), from their mean background levels, in 65.1-1237 years (e.g., in soils with pH >7, 184 years for Cu, 274 years for Zn, 303 years for Cd, 288 years for Pb, 563 years for As, 830 years for Cr and 1237 years for Ni). When organic fertilizers containing the maximum heavy metal concentrations were added to the soil with 5.5<pH≤6.5, it would be accumulated from the background contaminations in soil to the risk control standard for soil contamination of agricultural land (GB15618-2018) of Cu, Zn, Cd, Pb and Cr in 8.18, 7.74, 0.24, 8.4 and 12.5, respectively. Therefore, although the inputs from continuous application of organic fertilizers containing median concentrations of the 7 heavy metals exhibit only a low risk of soil heavy metal pollution, Cu, Zn, Cd, Pb and Cr at their maximum concentrations in the organic fertilizer would lead substantial risk to the environmental quality of soil.

The predicted results implied that it was very urgent to establish suitable limits of Cu and Zn in organic fertilizers in China. The limits of Cd (3 mg/kg) and Cr (150 mg/kg) in China standard for organic fertilizer (NY 525-2012) were relatively high compared to the Germany rotten compost and EU compost standard. Therefore, the heavy metal limiting values in organic fertilizers for agricultural soils in China should be adjusted. Many countries have set limits of heavy metals for organic fertilizers to be used in organic farming, agriculture soil, and lawns/gardens. For example, organic fertilizers used for EU organic farming must not exceed the following heavy metal limits (in mg/kg): Cd 0.7 and Cr 70[51]. It is important to establish appropriate organic fertilizer quality criteria, decrease the transfer of heavy metals from fertilizers and soils into agriculture products and reduce the environmental risks associated with heavy metals from organic fertilizers. In addition, given massive organic fertilizers made from complex raw materials were applied to agricultural soil in China, a suitable organic fertilizer application guide for cultivation of crops, vegetables or other plants should be established. A balance between the amount of heavy metals input to soils via fertilizer and the amount taken away through planting should be established to reduce the accumulation of heavy metals in soils to ensure the agricultural food safety[22,52].

Table 5 Predicted annual inputs of heavy metals and time to the risk control standard for soil contamination of agricultural land (GB15618-2018) from organic fertilizers applied continuously in China.

		Concentration (mg kg^{-1})	Input [a] (g hm^2 a)	Time with different soil pH [b]			
				pH≤5.5	5.5<pH≤6.5	6.5<pH≤7.5	pH>7.5
Cu	Maximum	580	8705	8.18	8.18	23.1	23.1
	Median	73.0	1095	65.1	65.1	184	184
Zn	Maximum	2818	42271	7.74	7.74	10.8	13.9
	Median	143	2139	153	153	214	274
Cd	Maximum	149	2240	0.24	0.24	0.24	0.58
	Median	0.29	4.31	122	122	122	303
Pb	Maximum	1321	19815	5.77	8.40	12.3	18.9
	Median	86.6	1299	88.0	128	188	288
As	Maximum	26.9	403.5	186	186	121	88.9
	Median	4.25	63.75	1175	1175	767	563
Cr	Maximum	1237	18550	12.5	12.5	19.5	26.5
	Median	39.5	592	391	391	611	830
Ni	Maximum	215	3219	26.7	34.8	59.0	132
	Median	22.9	343	251	327	554	1237

Note: [a] The maximum and median annual input of heavy metal concentrations due to the organic fertilizer applied (99% confidence interval).
[b] The maximum and median time that heavy metals accumulated to the risk control standard for soil contamination of agricultural land (GB15618-2018) in soil with different pH, from the background concentration.

4 Conclusions

Maturity indices (MC, pH, EC, E4/E6 and GI) and 7 heavy metals (Cu, Zn, Cd, Pb, Cr, As) were determined in 263 organic fertilizer samples in China. The MC, pH, EC, E4/E6 and GI presented large variation among the organic fertilizer samples with ranges of 6.9%-66.68%, 4.40-9.19, 0.76-13.38 mS/cm, 1.07-9.40, and 10%-150%, respectively. The concentrations of 7 heavy metals (Cu, Zn, Cd, Pb, As, Cr, and Ni) were with large variations of 7.53-580.4, 0-2818, 0.02-149.3, 0 (not detected)-1321, 0.14-26.9, 3.70-1237, and 0 (not detected)-214.6 mg/kg (dry weight), because of the differences of raw materials and product processes. There were 9.51%, 73.4%, 3.19%, 3.04% samples exceeded the limit values of Cd, Pb, As and Cr for organic fertilizer in China, and 35.0%, 13.3% and 16.7% of samples over the Cu, Zn and Ni limit for composts in Germany, respectively. The application of organic fertilizer would lead to low risk of soil heavy metal pollution at the median concentrations of the 7 heavy metals, however application of organic fertilizers of maximum Cu, Zn, Cd, Pb and Cr concentrations would accumulate these heavy metals to the risk control standard for soil contamination of agricultural land (GB15618-2018) within a relatively short period (0.24-12.5 years). It is urgent to establish suitable limits of Cu and Zn in organic fertilizer in China, and revise limiting values for other heavy metals (such as Cd, Pb and Cr), to make them more suitable for controlling the risk of heavy metal pollution in agriculture soils.

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