Health Assessment of Trace Metal Concentrations in Organic Fertilizer in Northern China

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Received: 23 December 2018; Accepted: 17 March 2019; Published: 21 March 2019

Abstract: The application of organic fertilizer could be accompanied by potential hazards to soil and humans caused by trace metals. A wide survey of organic fertilizers was carried out in northern China. A total of 117 organic fertilizer samples were collected to analyze the concentrations of seven trace metals. Simulation models were used to estimate the trace metal accumulation risk in soil and non-carcinogenic and carcinogenic risks to the human body. The concentrations of trace metals varied widely (Cr: 2.74–151.15; Ni: 2.94–49.35; Cu: 0.76–378.32; Zn: 0.50–1748.01; As: 1.54–23.96; Cd: 2.74–151.15; and Pb: 1.60–151.09 mg·kg⁻¹). Chinese organic fertilizer standard limits were exceeded by 0.85% for Cr, 5.98% for As, 1.71% for Cd, and 4.27% for Pb. Monte Carlo simulations showed that repeated application of organic fertilizer likely significantly increased the concentrations of Zn, Cd, and As in soil compared with the soil background levels according to the Soil Environmental Quality Standards of China. As and Cr pose high risks to human health, especially as carcinogenic risk factors with a skin exposure pathway. Reducing the content of Cr, Cu, Zn, As, and Cd in organic fertilizer would be of great significance for minimizing the damage caused by trace metals.

Keywords: organic fertilizer; trace metal; soil accumulation risk; human exposure; human health risk

1. Introduction

The consumption of fertilizers in China is widespread. According to the China Statistical Yearbook (1953–2017), the annual use of chemical fertilizers in cultivated land increased from 78,000 tons in 1952 to 59.841 million tons in 2016, thus improving food production [1]. However, at the same time, increased fertilizer use has given rise to problems such as greenhouse gas emissions and compaction and acidification of soil [2–4]. To this end, in recent years the Ministry of Agriculture and Rural Affairs of the People’s Republic of China has issued a series of action plans, such as the “Action Plan for Zero Growth of Fertilizer Consumption until 2020” in 2015 (Nong Nong Fa [2015] NO.2) and the “Replacing Chemical Fertilizer with Organic Fertilizer (Fruits, Vegetables, and Tea) Action Plan” in 2017 (Nong Nong Fa [2017] NO.2), to improve organic fertilizer use, reduce unreasonable investment, ensure sufficient supply of grains and other major agricultural products, and promote the sustainable development of agriculture. The use of organic fertilizers is not only a means to effectively reuse agricultural waste resources, but also an agricultural waste management method...
Organic fertilizers are also a critical link in the virtuous cycle of livestock–soil–plant systems [5–7]. Agricultural waste, including livestock manure and crop straw, can stabilize nutrients through aerobic fermentation, thus becoming safer and more stable fertilizers (organic fertilizers) [8].

Organic fertilizers are a beneficial source of plant nutrients and organic matter. Farmers often use it in plant production to increase productivity. However, organic fertilizers can also be a potential source of environmental pollution. There is increasing evidence that organic fertilizers can have high concentrations of trace metals such as Cr, Ni, Cu, Zn, As, Cd, and Pb. If organic fertilizers are applied to an agricultural area, some trace metals could be accumulated in agricultural lands, some of which could be transferred to the human body [9,10]. Therefore, investigating the trace metal contents of organic fertilizers is important for preventing the contamination of soil, water, and livestock [11,12]. Some researchers have conducted large-scale research on trace metal and nutrient contents in Chinese organic fertilizers [13,14]. The trace metal contents of these fertilizers exceeded the standard values. For example, the concentrations of Cr, As, Cd, and Pb in 212 samples of Chinese organic fertilizers containing livestock manure exceeded the standard value by 4.2%, 13.7%, 2.4%, and 1.4%, respectively [13]. The presence of trace metals in organic fertilizers has also become an important reason for limiting the use of these fertilizers. It is important to understand the status and extent of soil contamination of trace metals from organic fertilizers to develop sustainable management strategies for agricultural soils. It has been reported that atmospheric deposition and livestock manure were the predominant sources of trace metals entering agricultural soils in China [15], with atmospheric deposition responsible for 43–85% of the total As, Cr, Hg, Ni, and Pb inputs, and livestock manure accounting for approximately 55%, 69%, and 51% of the total Cd, Cu, and Zn inputs, respectively [16]. According to Ding et al., compost and atmospheric deposition were sources of pollution into agricultural land, with compost contributing 12.82–89.06% of trace metals (Zn: 36.03%; Ni: 51.50%; Cu: 42.52%; Zn: 73.94%; As: 12.82%; Cd: 89.06%; and Pb: 64.22%) [17]. It can be seen that organic fertilizer was the major source contributing trace metals to the environment, with manure and compost being the two kinds of organic fertilizer [17,18], even though other activities (such as atmospheric deposition or mining) could also cause soil accumulation [19]. Analysis of the trace metal content of organic fertilizers and estimation of the time (in years) required for trace metal concentration in soil to exceed limit values are beneficial for monitoring the soil environmental quality, ensuring the safety of agricultural products, and protecting the ecosystem.

Trace metals can also cause harm to human health, and occupational exposure increases the risk of this. According to the list of carcinogens published by the World Health Organization’s International Agency for Research on Cancer on 27 October 2017, As, Cd, Cr(VI), and Ni compounds are a class of carcinogens. Inorganic Pb is a Class 2A carcinogen, and Ni, Pb, and Cr(III) are Class 2B carcinogens (http://samr.cfda.gov.cn/WS01/CL1991/215896.html). Occupational exposure increases the risk to human health, and long-term exposure to trace metals increases the risk of non-carcinogenic and carcinogenic cells [20]. There are three main ways in which the human body can be exposed to trace metals in the soil: (1) oral absorption; (2) absorption by dermal contact (skin exposure); and (3) inhalation of floating soil particles (respiratory exposure) [21–23]. Studying the carcinogenic and non-carcinogenic risks to human health through these three exposure pathways can not only reveal high-risk exposure pathways and trace metal species, but they can also help farmers to avoid risks in their agricultural businesses [24].

In summary, this study used chemical testing and simulation prediction methods to achieve the following objectives: (1) determination of concentrations and above-standard levels of seven trace metals (Cr, Ni, Cu, Zn, As, Cd, and Pb) in organic fertilizers produced in different regions of northern China; (2) estimation of potential risks of organic fertilizer application to the accumulation of trace metals in the soil; and (3) simulation of potential human health risks following exposure to organic fertilizer containing trace metals.
2. Materials and Methods

2.1. Sample Collection and Processing

2.1.1. Sample Collection and Pre-Treatment

Samples were obtained from organic fertilizer factories in eight provinces in northern China from June to August 2017 (Figure 1). These factories collected manure (Table 1) from local livestock farms and produced organic fertilizers by commercial operation. Each organic fertilizer sample consisted of three subsamples. The subsamples were collected from five points from a single composted pile, mixed thoroughly into a 2–3 kg sample, and transported to the laboratory. Samples were dried at 70 °C for 48 h, and ground to pass through a 100-mesh (0.15 mm) sieve prior to analysis. The remaining samples were stored at < −80 °C until analysis.

Table 1. Proportion of manure used for making organic fertilizers in the research area.

| Manure  | North China (n = 48) | Northwest China (n = 55) | Northeast China (n = 14) |
|---------|----------------------|--------------------------|--------------------------|
|         | n     | Proportion (%) | n     | Proportion (%) | n     | Proportion (%) |
| Cattle  | 2     | 4.17         | 18    | 32.73          | 5     | 35.72          |
| Sheep   | 15    | 31.25        | 12    | 21.82          | 1     | 7.14           |
| Poultry | 12    | 25.00        | 3     | 5.45           | 4     | 28.57          |
| Pig     | 0     | 0.00         | 6     | 10.91          | 0     | 0.00           |
| Rabbit  | 2     | 4.17         | 0     | 0.00           | 0     | 0.00           |
| Mixed   | 17    | 35.41        | 16    | 29.09          | 4     | 28.57          |

Note: n denotes the number of sampled organic fertilizers.

Figure 1. Sketch map of research areas and sampling points in northern China. (a) Sketch map of research areas; the blue and yellow areas denote northern China, with the blue indicating the research area of this article. (b) Sampling points in northern China (n = 79), including Northwest China, North China, and Northeast China. (c) Sampling points in Northwest China (n = 32), including Shaanxi, Ningxia, Gansu, and Qinghai Provinces. (d) Sampling points in North China (n = 37), including Inner Mongolia and Shaanxi Provinces. (e) Sampling points in Northeast China (n = 10), including Heilongjiang and Jilin Provinces. Note: n denotes the number of sampled organic fertilizer enterprises.
2.1.2. Sample Preparation and Analysis for the Total Concentration of Trace Metals

All glassware and plastic containers were immersed in 5% (v/v) nitric acid solution for 24 h and then rinsed with ultrapure water and reserved for use. The dried samples were analyzed for trace metal contents in accordance with Wang et al. and Hseu [25, 26]. In brief, samples were digested in HNO$_3$–HClO$_4$ (80/20, v/v) and concentrations of Cr, Ni, Cu, Zn, As, Cd, and Pb were analyzed by inductively-coupled plasma mass spectrometry (7900 ICP-MS, Agilent Technologies, Santa Clara, CA, USA). Method blanks, duplicate samples, and soil standard samples (GBW07456, Geophysical and Geochemical Exploration Institute of the Chinese Academy of Geological Sciences) were added in the analytical process of each batch sample for quality assurance and control.

2.2. Risk of Trace Metal Accumulation in Soil from the Applications of Fertilizer

To provide meaningful information about the risk of trace metal accumulation in farmland soil caused by the application of organic fertilizers, Monte Carlo simulations were used to estimate the long-term effects of applications on seven trace metal concentrations in soil [13, 17].

2.2.1. Accumulation of Trace Metals in Soil

The accumulation of trace metals in the soil is the total value of soil background and the amount of trace metals in organic fertilizer.

\[
Q_i = Q_{p,i} + Q_{0,i}
\]

where \(i\) refers to the seven trace metals, Cr, Ni, Cu, Zn, As, Cd, and Pb; \(Q_i\) is the cumulative amount of contaminant in the soil, in mg·kg$^{-1}$; \(Q_{p,i}\) is the input amount of contaminant \(i\), in mg·kg$^{-1}$; and \(Q_{0,i}\) is the initial content of contaminant \(i\) in the soil, in mg·kg$^{-1}$, which is the average of the study area (Table 1).

2.2.2. Amount of Trace Metals in Soil from Organic Fertilizer

The accumulation of trace metals in the soil was assessed by the input fluxes of organic fertilizer:

\[
Q_{p,i} = \frac{IR_f \times a_i}{\rho_b \times V}
\]

where \(Q_{p,i}\) is the input of contaminant \(i\), in mg·kg$^{-1}$; \(IR_f\) is the amount of organic fertilizer applied to the soil, in t·hm$^{-2}$·year$^{-1}$ (Table 1), which is the average of the study area; \(a_i\) is the median content of contaminant in the organic fertilizer, in mg·kg$^{-1}$; \(\rho_b\) is the soil bulk density, in g·cm$^{-3}$ (Table 2); and \(V\) is the volume of soil per hectare of the plow layer (20 cm), 2 × 10$^3$ m$^3$·hm$^{-2}$.

### Table 2. Soil trace metal background value and organic fertilizer application rate.

| Parameter                           | Unit          | North China | Northwest China | Northeast China | References |
|-------------------------------------|---------------|-------------|-----------------|-----------------|------------|
| Initial content of Cr in soil \(Q_{0,Cr}\) | mg·kg$^{-1}$ | 51.60       | 65.70           | 52.65           | [27]       |
| Initial content of Ni in soil \(Q_{0,Ni}\) | mg·kg$^{-1}$ | 25.75       | 32.55           | 22.10           | [27]       |
| Initial content of Cu in soil \(Q_{0,Cu}\) | mg·kg$^{-1}$ | 20.50       | 22.45           | 18.55           | [27]       |
| Initial content of Zn in soil \(Q_{0,Zn}\) | mg·kg$^{-1}$ | 67.30       | 69.25           | 75.55           | [27]       |
| Initial content of As in soil \(Q_{0,As}\) | mg·kg$^{-1}$ | 8.65        | 12.33           | 7.65            | [27]       |
| Initial content of Cd in soil \(Q_{0,Cd}\) | mg·kg$^{-1}$ | 0.091       | 0.115           | 0.093           | [27]       |
| Initial content of Pb in soil \(Q_{0,Pb}\) | mg·kg$^{-1}$ | 17.65       | 20.43           | 26.50           | [27]       |
| Soil bulk density (\(\rho_b\)) | g·cm$^{-3}$  | 1.35        | 1.38            | 1.41            | [26]       |
| Organic fertilizer application rate (\(IR_f\)) | t·hm$^{-2}$·year$^{-1}$ | 33.92 | 80.30           | 115.89          | [29–32]   |

\(Q_{0,Cr}, Q_{0,Ni}, Q_{0,Cu}, Q_{0,Zn}, Q_{0,As}, Q_{0,Cd}, Q_{0,Pb}\) refer to the initial content of Cr, Ni, Cu, Zn, As, Cd, Pb in the soil, respectively; \(\rho_b\) is the bulk density of soil; \(IR_f\) is the amount of organic fertilizer applied to the soil.
2.2.3. Time Scale (in Years) Needed to Double the Trace Metal Concentrations in Soil from Its Background Levels

Analysis of the trace metal content of organic fertilizers and estimation of the time (in years) required for trace metal concentration in soil to exceed limit values can be calculated using the following equation:

\[ T_i = \frac{C_{s,i} - Q_{0,i}}{Q_{p,i}} \]

where \( T_i \) is the time scale (in years) needed to double the trace metal concentrations in soil from its background levels according to the Soil Environmental Quality Standard of China (GB15618-2018); \( C_{s,i} \) is the limit value of dry land in contaminant \( i \) at \( \text{pH} > 7.5 \), according to the Soil Environmental Quality Agricultural Soil Risk Control Standards (GB15618-2018); and \( Q_{0,i} \) of Cr, Ni, Cu, Zn, As, Cd, and Pb are 250, 190, 100, 300, 25, 0.6, and 170 mg·kg\(^{-1} \), respectively.

2.3. Human Body Exposure Model for Trace Metals

2.3.1. Oral Exposure

The concentration of trace metals entering the body through food can be calculated as follows:

\[ Q_{f,i} = \frac{Q_i \times IR_p \times EF_a \times ED_a \times \beta_i \times 10^{-6}}{BW \times LT} \]

where \( Q_{f,i} \) is the concentration of the contaminant \( i \) entering the human body through the mouth, in mg·kg\(^{-1} \)·day\(^{-1} \); \( IR_p \) is the adult intake, 100 mg·day\(^{-1} \) [33]; \( EF_a \) is the exposure frequency, 250 day·year\(^{-1} \) [33]; \( ED_a \) is the length of exposure, 25 years [33]; \( \beta_i \) is the absorption coefficient of contaminant in the stomach, where the gastrointestinal absorption coefficients for Cr, Ni, Cu, Zn, As, Cd, and Pb are 2.5 × 10\(^{-2} \), 1.6 × 10\(^{-2} \), 1.00, 1.00, 1.00, 5.00 × 10\(^{-2} \), and 1.00, respectively [10]; \( BW \) is the average weight of adults, 56.8 kg [33]; and \( LT \) is the human exposure time, 26,280 days [33].

2.3.2. Skin Exposure

The concentration of trace metals entering the body through the skin can be calculated as follows:

\[ Q_{s,i} = \frac{Q_i \times EW \times SA \times \mu \times EF_a \times ED_a \times \eta \times \gamma_i \times 10^{-6}}{BW \times LT} \]

where \( Q_{s,i} \) is the concentration of contaminant \( i \) entering the body through the skin, in mg·kg\(^{-1} \)·day\(^{-1} \); \( EW \) is the skin contact frequency, 1 day\(^{-1} \) [33]; \( SA \) is the skin surface area, 1.614 m\(^2 \); \( \mu \) is the proportion of skin exposure, 18% [33]; \( \eta \) is the adhesion factor of skin to soil, 0.2 mg·cm\(^{-2} \) [33]; and \( \gamma_i \) is the absorption coefficient of contaminant \( i \) in the skin, 1.00 × 10\(^{-3} \), 1.6 × 10\(^{-2} \), 1.00 × 10\(^{-3} \), 6.00 × 10\(^{-4} \), 1.00 × 10\(^{-3} \), 1.00 × 10\(^{-3} \), and 2.08 × 10\(^{-5} \) for Cr, Ni, Cu, Zn, As, Cd, and Pb, respectively [10].

2.3.3. Respiratory Exposure

The concentration of trace metals entering the body through breathing can be calculated as follows:

\[ Q_{b,i} = \frac{Q_i \times \omega \times IR_b \times ED_a \times \theta_i \times (fsp_{od} \times EFOD_a +fsp_{id} \times EFDI_a) \times 10^{-6}}{BW \times LT} \]

where \( Q_{b,i} \) is the concentration of contaminant entering the body through breathing, in mg·kg\(^{-1} \)·day\(^{-1} \); \( \omega \) is the concentration of suspended particulates in the air, 0.15 mg·m\(^{-3} \) [33]; \( IR_b \) is the breathing rate, 14.5 m\(^3\)·day\(^{-1} \) [33]; and \( \theta_i \) is the absorption coefficient of contaminant \( i \) in the lungs, 0.016, 0.3, 0.2, 0.01, and 0.15 for Ni, Cu, Zn, Cd, and Pb, respectively [10]. The absorption coefficients of Cr and As in the lungs has not been reported in the literature and is assumed to be 1.00; \( fsp_{od} \) is the fraction of soil suspended particles outdoors, 0.8 [33]; \( EFOD_a \) refers to the outdoor exposure frequency of adults, 87.5 day·year\(^{-1} \) [33]; \( fsp_{id} \) is the fraction of soil suspended particles outdoors, 0.5 [33]; and \( EFDI_a \) is the outdoor exposure frequency of adults, 262.5 day·year\(^{-1} \) [33].
2.4. Human Health Risk Assessment

The seven trace metals in the study, Cr, Ni, Cu, Zn, As, Cd, and Pb, all exhibit non-carcinogenic risks, among which Cr, Ni, As, and Cd also exhibit carcinogenic risk.

2.4.1. Potential Non-Carcinogenic Risk

Based on exposure assessment, the non-carcinogenic risk of trace metal contaminants in all exposure routes was calculated using a dose–response assessment and risk characterization. It can be calculated using following equations:

\[ HQ_i = \sum_{j=1}^{3} \frac{Q_{ij}}{RfD_{ij}} \] \hspace{1cm} (7)

\[ HI = \sum_{i=1}^{7} HQ_i \] \hspace{1cm} (8)

where \( HQ_i \) represents the potential non-carcinogenic risk index for contaminant \( i \); \( CDI_{ij} \) is the daily average exposure of contaminant \( i \) through route \( j \), in mg·kg\(^{-1}\)·day\(^{-1}\); \( j \) refers to the three exposure pathways of the human body, oral exposure (abbreviated as \( f \)), skin exposure (abbreviated as \( s \)) and respiratory exposure (abbreviated as \( b \)); \( RfD_{ij} \) is the reference dose of non-carcinogenic contaminant \( i \) through exposure route \( j \), in mg·kg\(^{-1}\)·day\(^{-1}\) (Table 3); and \( HI \) is the total non-carcinogenic risk index through all exposure routes in the list. Trace metals are expected to have adverse effects on humans when the value of \( HI \) is more than 1.0 [9].

Table 3. Reference dose and slope coefficient of contaminants through different exposure routes (IRIS, US EPA).

| Contaminants | SF (kg·day·mg\(^{-1}\)) | RfD\(_f\) (mg·kg\(^{-1}\)·day\(^{-1}\)) | RfD\(_s\) (mg·kg\(^{-1}\)·day\(^{-1}\)) | RfD\(_b\) (mg·kg\(^{-1}\)·day\(^{-1}\)) |
|--------------|--------------------------|-------------------------------|-------------------------------|-------------------------------|
| Cr           | 4.20 × 10\(^1\)         | 3.00 × 10\(^{-3}\)          | 2.9 × 10\(^{-5}\)           | 6.00 × 10\(^{-5}\)          |
| Ni           | 8.40 × 10\(^{-1}\)      | 2.00 × 10\(^{-2}\)         | 2.00 × 10\(^{-2}\)         | 5.40 × 10\(^{-3}\)         |
| Cu           | 4.00 × 10\(^{-2}\)      | 4.00 × 10\(^{-2}\)         | 1.20 × 10\(^{-2}\)         |                              |
| Zn           | 3.00 × 10\(^{-1}\)      | 3.00 × 10\(^{-1}\)         | 6.00 × 10\(^{-2}\)         |                              |
| As           | 1.51 × 10\(^1\)        | 3.00 × 10\(^{-4}\)        | 3.00 × 10\(^{-4}\)        | 1.20 × 10\(^{-3}\)        |
| Cd           | 6.30                    | 1.00 × 10\(^{-3}\)        | 1.00 × 10\(^{-3}\)        | 1.00 × 10\(^{-5}\)        |
| Pb           | 3.50 × 10\(^{-3}\)      | 3.50 × 10\(^{-3}\)        | 5.20 × 10\(^{-4}\)        |                              |

SF is the carcinogenic risk slope coefficient. RfD\(_f\), RfD\(_s\), RfD\(_b\) are the non-carcinogenic reference doses through the exposure routes of food, skin, and breathing, respectively.

2.4.2. Potential Carcinogenic Risk

Based on the exposure assessment results from all exposure routes, the carcinogenic risk from soil pollution can be calculated as follows:

\[ CR_i = \sum_{j=1}^{3} Q_{ij} \times SF_{ij} \] \hspace{1cm} (9)

\[ TCR = \sum_{i=1}^{4} CR_i \] \hspace{1cm} (10)

where \( CR_i \) is the potential carcinogenic risk index of carcinogenic contaminant \( i \); \( SF_{ij} \) is the carcinogenic risk slope coefficient of carcinogenic contaminant \( i \) through exposure route \( j \), in kg·day·mg\(^{-1}\) (Table 3); and \( TCR \) is the total carcinogenic risk of contaminants through all exposure routes. The carcinogenic risk is negative when \( CR_i \) or \( TCR \leq 10^{-6} \); the maximum acceptable risk value is when \( CR_i \) or \( TCR \) is 10\(^{-4}\).
2.5. Statistical Analysis

The normality of variances was checked by the Shapiro–Wilk test. Significant differences ($p < 0.05$) between organic fertilizers for different trace metals were assessed by ANOVA, and correlation analysis (Spearman’s $r$) was performed between the concentrations of trace metals in organic fertilizers. Monte Carlo simulations were carried out to predict the time scale (in years) during which the trace metal content of farmland soil increase from background level to the maximum permissible limit as a result of using organic fertilizer. The simulations were performed with Crystal Ball 11.1 software (Oracle Corporation, Redwood City, CA, USA). All figures were performed with the Microsoft Visio 2003 (Microsoft Corporation, Redmond, WA, USA), ArcGIS10.2 (Esri, Redlands, CA, USA), and Origin 2017 (OriginLab, Northampton, MA, US) software. All data were expressed on a dry weight (DW) basis.

3. Results and Discussion

3.1. Characteristics of Trace Metal Concentration in Organic Fertilizers

The measured concentration of trace elements in the organic fertilizer was widely variable according to both the element analyzed and the region (Table 4, Figure 2). Among the 48 samples collected in North China, the trace metal contents varied significantly (Cr: 6.53–151.15; Ni: 3.54–16.9; Cu: 0.76–378.32; Zn: 0.50–1595.42; Cd: 0.04–5.25; and Pb: 5.08–151.09 mg kg$^{-1}$), with variability coefficients of 50.38–138.36%. Among the 55 samples taken from Northwest China, the trace metal contents also varied significantly (Cr: 2.74–36.34; Ni: 2.94–35.11; Cu: 4.55–355.52; Zn: 4.11–1748.01; As: 1.55–21.00; Cd: 0.03–1.73; and Pb: 1.60–55.98 mg kg$^{-1}$), with variability coefficients of 53.17–170.92%. Among the 14 samples from Northeast China, the trace metal contents were Cr: 6.43–63.46; Ni: 4.33–19.09; Cu: 4.69–155.68; Zn: 16.09–493.15; As: 2.93–17.19; Cd: 0.05–1.00; and Pb: 4.43–29.34 mg kg$^{-1}$, with variability coefficients of 41.39–117.19%.

Table 4. Trace metal concentrations in organic fertilizer in northern China (mg kg$^{-1}$).

| Region      | Cr     | Ni     | Cu     | Zn     | As     | Cd     | Pb     |
|-------------|--------|--------|--------|--------|--------|--------|--------|
| North China | Range  | 6.53–151.15 | 3.54–49.35 | 0.76–378.32 | 0.50–1595.42 | 1.54–23.96 | 0.04–5.25 | 5.08–151.09 |
| Mean        | 24.14  | 17.01  | 75.19  | 581.91 | 7.76   | 0.79   | 0.02   |
| Median      | 17.02  | 16.90  | 44.85  | 478.11 | 6.96   | 0.38   | 15.46  |
| SD          | 22.55  | 8.57   | 83.83  | 429.65 | 4.89   | 1.09   | 27.27  |
| C.V. (%)    | 93.43  | 50.38  | 111.50 | 73.83  | 63.02  | 138.36 | 111.46 |
| P$_{S-K}$   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   |
| Northwest China | Range | 2.74–36.34 | 2.94–35.11 | 4.55–355.52 | 4.11–1748.01 | 1.55–21.00 | 0.03–1.73 | 1.60–55.98 |
| Mean        | 12.26  | 12.21  | 34.20  | 174.08 | 5.30   | 0.35   | 13.05  |
| Median      | 10.75  | 10.98  | 19.84  | 86.71  | 4.92   | 0.31   | 11.36  |
| SD          | 6.75   | 6.49   | 49.72  | 297.55 | 3.04   | 0.29   | 9.23   |
| C.V. (%)    | 55.03  | 53.17  | 145.39 | 170.92 | 57.35  | 82.75  | 70.70  |
| P$_{S-K}$   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   |
| Northeast China | Range | 6.43–63.46 | 4.33–19.09 | 4.69–155.68 | 16.09–493.15 | 2.93–17.19 | 0.05–1.00 | 4.43–29.34 |
| Mean        | 23.75  | 11.09  | 46.53  | 124.53 | 8.93   | 0.26   | 10.99  |
| Median      | 17.47  | 11.23  | 23.02  | 60.86  | 9.08   | 0.17   | 9.73   |
| SD          | 17.89  | 4.59   | 46.83  | 145.93 | 4.56   | 0.26   | 6.49   |
| C.V. (%)    | 75.35  | 41.39  | 100.64 | 117.19 | 50.40  | 100.42 | 59.09  |
| P$_{S-K}$   | 0.023  | 0.713  | 0.010  | 0.001  | 0.524  | 0.001  | 0.007  |
| Northern China | Range | 2.74–151.15 | 2.94–49.35 | 0.76–378.32 | 0.50–1748.01 | 1.54–23.96 | 0.05–5.25 | 1.60–151.09 |
| Mean        | 18.51  | 14.05  | 52.49  | 335.47 | 6.74   | 0.52   | 17.49  |
| Median      | 13.03  | 12.05  | 31.67  | 144.14 | 5.96   | 0.31   | 12.41  |
| SD          | 17.27  | 7.62   | 67.97  | 401.56 | 4.27   | 0.76   | 19.50  |
| C.V. (%)    | 93.28  | 54.23  | 129.50 | 119.70 | 63.37  | 146.32 | 111.50 |
| P$_{S-K}$   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   |

SD: standard deviation, C.V.: Coefficient of Variance, P$_{S-K}$: p-value of Shapiro–Wilk test.

It can be seen that the median contents of most trace metals in organic fertilizer in Northwest China were lower than those in other regions, due to the fact that its main raw material was cattle and...
sheep manure (Table 1). According to the research of Liu et al., the content of trace metals in manures followed the trend of pig manure > poultry manure > cattle manure > sheep manure [14] (Table 5). The Ni, Cu, Zn, Cd, and Pb contents of organic fertilizer in North China were the highest, and the Cr and As contents in Northeast China were the highest of the research areas, which was related to their raw materials (Table 1).

Figure 2. Trace metal concentrations of organic fertilizers in North China ($n = 48$), Northwest China ($n = 55$), and Northeast China ($n = 14$). Squares represent mean values, the band near the middle of each box represents the median, and the bottom and top of the boxes represent the lower quartile (LQ; 25th percentiles) and upper quartile (UQ; 75th percentiles), respectively. The vertical lines (whiskers) represent the 1.5 inter-quartile ranges (IQRs) of the lower and upper quartiles. Data outside the whiskers are outliers and are plotted as dots.
Table 5. Trace metal concentrations in compost in published articles (based on median/mean value) (mg·kg\(^{-1}\)).

| Region          | Type of Organic Fertilizer                  | n   | Cr     | Ni      | Cu      | Zn      | As     | Cd     | Pb     | References |
|-----------------|--------------------------------------------|-----|--------|---------|---------|---------|--------|--------|--------|------------|
| Austria         | Compost                                   | NA  | 38.3   | 25.7    | 100     | 267     | 7.0    | 0.43   | 43.4   | [34]       |
|                 | Organic fertilizer: poultry dung          | NA  | 10.7   | 8.5     | 66      | 314     | NA     | 0.43   | 5.4    |            |
|                 | Organic fertilizer: pig dung              | NA  | 7.8    | 8.9     | 62      | 399     | NA     | 0.33   | 5.0    |            |
|                 |                                            |     |        |         |         |         |        |        |        |            |
| UK \(^a\)       | Straw-based farmyard dairy cattle manure   | 6   | 5.32   | 3.7     | 37.5    | 153     | 1.63   | 0.38   | 3.61   | [35]       |
|                 | Straw-based farmyard beef cattle manure   | 12  | 1.41   | 2.0     | 16.4    | 81      | 0.79   | 0.13   | 1.95   | [35]       |
|                 | Straw-based farmyard pig manure           | 17  | 1.98   | 7.5     | 374     | 431     | 0.86   | 0.37   | 2.94   |            |
| Canada \(^a\)   | Peat/manure compost                        | 11  | 3.53 ± 0.51 | 3.8 ± 1.6 | 16.9 ± 7.3 | 142 ± 61 | NA     | 0.26 ± 0.15 | 4.8 ± 2.2 | [36]       |
|                 | Straw/manure compost                      | 14  | 4.5 ± 1.1 | 5.4 ± 1.8 | 25.1 ± 7.2 | 159 ± 35 | NA     | 0.21 ± 0.05 | 1.7 ± 1.7 |            |
| Switzerland     | Compost                                   | 81  | 20     | 16      | 52      | 147     | NA     | 0.11   | 38     | [12]       |
| China           | Animal manure composites                  | 212 | 17.90  | 12.40   | 50.60   | 288.0   | 6.65   | 0.14   | 7.61   | [13]       |
| China           | Commercial organic fertilizer             | 162 | 53.5   | 21      | 75.4    | 732.4   | 2.96   | 5.64   | 36.6   | [14]       |
| China           | Commercial organic fertilizers            | 126 | 165.2 ± 583.2 | NA  | 122.2 ± 166.8 | 260.6 ± 272.1 | 5.6 ± 4.0 | 1.2 ± 0.97 | 34.3 ± 112 | [37]       |
| North China     | Livestock manure organic fertilizer       | 42  | 45.42  | 16.5    | 69.22   | 274.58  | 3.21   | 0.21   | 87.4   | [38]       |
| Jiangsu Province, China | Composite pig manure            | 80  | 8.0    | NA      | 113.7   | 427.2   | 0.9    | 0.37   | 3.8    | [25]       |
|                 | Composite dairy manure                   | 35  | 9.9    | NA      | 45.5    | 186.3   | 1.0    | 0.32   | 8.4    | [25]       |
|                 | Composite poultry manure                 | 65  | 9.8    | NA      | 56.7    | 391.2   | 1.5    | 0.42   | 4.5    |            |
| Zhejiang Province, China | Manure-based fertilizers       | 219 | 21.2   | NA      | 160     | 465     | 7.9    | 0.6    | 8.1    | [39]       |

\(^a\) mean value; NA, not available in the article.
The trace metal contents of organic fertilizer in Northern China (0.03–1748.01 mg kg\(^{-1}\)) were lower than those in China (0.012–3692 mg kg\(^{-1}\)) and Southern China (Zhejiang Province: 0.1–5712 mg kg\(^{-1}\); Jiangsu Province: N–11,378.9 mg kg\(^{-1}\)). This might be due to the fact that the raw material used in Northern China was cattle, poultry, and sheep manure instead of pig manure. The concentration of trace metals in organic fertilizers in China is significantly higher than that reported in Switzerland (0–1021 mg kg\(^{-1}\)), Australia (<0.02–1439 mg kg\(^{-1}\)), and the UK (<0.10–780 mg kg\(^{-1}\)). While China is working to reduce the concentration of trace metals in organic fertilizer, according to Ding et al., the mean value of trace metal content tended to decrease with time in commercial composts from 2002–2013 [17].

3.2. Limit Standards and Exceeding Standards for Trace Metals in Organic Fertilizers

Trace metals have always been the focus in organic fertilizer standards. Establishing and implementing limit standards for trace metals in organic fertilizers could prevent agricultural pollution. Compliance with these standards ensures that fertilizers are safe for use; however, there is no guarantee that they will meet the specific need of end use [40]. Table 5 lists the maximum acceptable concentrations of Cr, Ni, Cu, Zn, As, Cd, and Pb in organic fertilizers in 24 regions of 20 countries. Some regions (Canada, Germany, Hong Kong, Taiwan, etc.) are set for different uses [41]. Different trace metals have higher threshold limits in agriculture/organic agriculture and lower thresholds for nonagricultural use. These standards have been established over many years of research, and different backgrounds and applications have led to large differences in standards among various countries. As seen in Table 6, the maximum acceptable concentrations of trace metals in the United States are significantly higher than those in other countries. Among these, the requirements in Mauritius and New Zealand are stringent. At present, organic fertilizer standards are not fixed, and some countries including China are exploring this field. At the end of 2017, Zhaocong Shang released the “fertilizer classification” on the official website of the Ministry of Industry and Information Technology of the People’s Republic of China [42]. The standard is a draft of the requirements, and divides all commercial fertilizers into farmland and ecological grades and sets different limits for trace metals. However, Cu and Zn are still not regulated by Chinese standards. In this survey, based on the limits of Cr, As, Cd, and Pb in the Chinese organic fertilizer standards and the regulations of Cu, Zn, and Ni in the German organic fertilizer standard class I (Table 6), the above-standard levels for Cu and Zn were the highest, followed by As and Pb; the rates for Cr, Ni, and Cd were the lowest. Although Cu and Zn are essential nutrients for agricultural soils, the introduction of excessive concentrations into the food chain may pose a threat to human health [43]. Therefore, monitoring and setting Cu and Zn limits for organic fertilizers is of great significance to prevent the accumulation of trace metals in soils, especially when the raw materials in organic fertilizers are livestock manure and sewage sludge [44,45].

Of all 117 samples, the Chinese Organic Fertilizer Standard limits were exceeded by 0.85% for Cr, 5.98% for As, 1.71% for Cd, and 4.27% for Pb. In Germany, the maximum acceptable concentrations were exceeded by 1.71% for Ni, 17.09% for Cu, and 35.04% for Zn. Excessive trace metals in organic fertilizers were not consistent in different regions. All trace metals in North China exceeded the standard. The standard limits for Cr, Ni, Cu, Zn, As, Cd, and Pb were exceeded by 2.08%, 2.08%, 29.17%, 8.33%, 8.33%, 4.17%, and 8.33%, respectively. In Northwest China, Cr and Cd did not exceed the limit. The contents of Ni, Cu, Zn, As, and Pb exceeded the standard by 1.82%, 7.27%, 10.91%, 1.82%, and 1.82%, respectively. In Northeast China, only Cu, Zn, and As exceeded the limit, by 14.29%, 14.29%, and 14.29%, respectively. Source control is the most effective way to prevent organic fertilizers from polluting the ecological environment. Trace metals in inorganic fertilizers mainly control the trace metal content in feed additives [46].
Table 6. Maximum trace metal concentration acceptable for compost in different countries (mg kg\(^{-1}\)).

| Region                      | Cr  | Ni  | Cu   | Zn  | As  | Cd  | Pb  | Standard File                  |
|-----------------------------|-----|-----|------|-----|-----|-----|-----|-------------------------------|
| Africa                      |     |     |      |     |     |     |     |                               |
| Mauritius                   | 50  | 50  | -    | 300 | 10  | 3   | 100 | MS 164 (2010)                 |
| America                     |     |     |      |     |     |     |     |                               |
| United States               | 1200| 420 | 1500 | 2800| 41  | 39  | 300 | USCC-2001                     |
| United States, Washington   | -   | 210 | 750  | 1400| 20  | 10  | 150 | WSDA, 2009                    |
| Canada A                    | 210 | 62  | 400  | 700 | 13  | 3   | 150 | CCME-2005                     |
| Canada B                    | 1060| 180 | 757  | 1850| 75  | 20  | 500 | CAN/BNQ/CCME/AAFC             |
| Europe                      |     |     |      |     |     |     |     |                               |
| EU organic agriculture      | 70  | 25  | 70   | 200 | -   | 0.7 | 45  | Biowaste Directory           |
| EU ecological standards     | 100 | 50  | 100  | 300 | 10  | 1   | 100 | Biowaste Directory           |
| EU soil amendment           | 100 | 50  | 100  | 300 | -   | 1   | 100 | Biowaste Directory           |
| United Kingdom              | 100 | 50  | 200  | 400 | -   | 1.5 | 200 | BSI-PAS 100-2011             |
| France                      | 120 | 60  | 300  | 600 | -   | 3   | 180 | NF U44-051                   |
| Netherlands                 | 50  | 20  | 90   | 290 | -   | 1   | 100 | Amended National Fertilizer Act from 2008 |
| Italy                       | -   | 50  | 150  | 500 | -   | 1.5 | 140 | Law on Fertilizer L 748/84   |
| Belgium                     | 100 | 50  | 150  | 400 | 20  | 2   | 150 | Royal Decree                 |
| Denmark                     | -   | 30  | 1000 | 4000| 25  | 0.8 | -   | Statutory Oder Nr.1650       |
| Spain A                     | 70  | 25  | 70   | 200 | -   | 0.7 | 45  | Spain RD 506-2013            |
| Spain B                     | 250 | 90  | 300  | 500 | -   | 2   | 150 | Spain RD 506-2013            |
| Spain C                     | 300 | 100 | 400  | 1000| -   | 3   | 200 | Spain RD 506-2013            |
| Germany I                   | 70  | 35  | 70   | 300 | -   | 1   | 100 | Biowaste Ordinance           |
| Germany II                  | 100 | 50  | 100  | 400 | -   | 1.5 | 150 |                               |
| Switzerland                 | 100 | 30  | 100  | 400 | -   | 1   | 120 | Swiss Federal Council-2013   |
| Oceania                     |     |     |      |     |     |     |     |                               |
| New Zealand compost         | 50  | 10  | 25   | 75  | 5   | 0.7 | 65  | SDU-1991                     |
| New Zealand clean compost   | 50  | 20  | 60   | 200 | 15  | 1   | 100 | SDU-1991                     |
| Aureli A                    | 70  | 25  | 70   | 200 | -   | 0.7 | 45  | SWD 64/F1-EN,2016            |
| Aureli A                    | 70  | 60  | 150  | 500 | -   | 1   | 120 | SWD 64/F1-EN,2016            |
| Australia                   | 400 | 60  | 200  | 250 | 20  | 3   | 200 | Compost Ordinance/AS 4454-2012 |
| Region                      | Cr  | Ni  | Cu  | Zn  | As  | Cd  | Pb  | Standard File                                      |
|-----------------------------|-----|-----|-----|-----|-----|-----|-----|---------------------------------------------------|
| Malaysia                    | 200 | 150 | -   | -   | -   | 5   | 300 | MS 1517-2012                                      |
| India                       | 50  | 50  | -   | 1000| 10  | 3   | 150 | World Bank, 1997                                  |
| Indonesia                   | 50  | 50  | -   | 300 | 10  | 3   | 100 | Ministry of Environment and Forests                |
| Japan                       | 500 | 300 | -   | -   | 50  | 5   | 100 | Fertilizer Management Act                          |
| Korea                       | 300 | 50  | 500 | 900 | 5   | 5   | 150 | Fertilizer Management Act                          |
| Hong Kong organic agriculture| 100 | 50  | 300 | 600 | 10  | 1   | 100 | Hong Kong ORC, 2005                                |
| Hong Kong general agricultural use | 210 | 62  | 700 | 1300| 13  | 3   | 150 | Hong Kong ORC, 2005                                |
| Hong Kong nonagricultural use | 1200 | 420 | 1500| 2800| 41  | 19  | 300 | Hong Kong ORC, 2005                                |
| Taiwan livestock and poultry composting | 150 | 25  | 100 | 500 | 25  | 2   | 150 | Fertilizer Management Act                          |
| Taiwan general compost      | 150 | 25  | 100 | 250 | 25  | 2   | 150 | Fertilizer Management Act                          |
| Taiwan miscellaneous compost | 150 | 25  | 100 | 250 | 25  | 2   | 150 | Fertilizer Management Act                          |
| Mainland China              | 300 | -   | -   | -   | 30  | 3   | 100 | NY525-2012                                       |
3.3. Correlation Analysis of Trace Metal Concentrations in Organic Fertilizer

All the data in this paper showed a skewed distribution (Table 4, Figure 2). Spearman correlation analysis was performed on seven trace metals. It can be seen from the correlation matrix (Figure 3) that there is only a low negative correlation ($p < 0.01$) between Cr and Zn in North China, so the negative correlation between trace metals in organic fertilizer was negligible, while the trace metal concentrations were positively correlated.

There were differences in the correlations between different trace metals in different regions. Cr and Pb were highly correlated in research area. Except for Northeast China, Cu and Zn, and Cr and Ni, were closely correlated. The correlation between Cd and Pb was high, except in Northwest China. Moderate correlations were observed between Cr and Pb, Cu and Cd (North China), Ni and As, As and Pb, Ni and Cd, Cr and As, Ni and Pb (Northwest China), and Cr and Cd (Northeast China).

![Figure 3](image-url)

**Figure 3.** Spearman correlation analysis of trace metal concentrations in organic fertilizer. (a) organic fertilizers in North China ($n = 48$); (b) organic fertilizers in Northwest China ($n = 55$); (c) organic fertilizers in Northeast China ($n = 14$); and (d) organic fertilizers in northern China ($n = 117$). Degree of significance: * $p < 0.05$; ** $p < 0.01$.

A significant positive correlation between trace metals suggests a shared source. The relationship between Cu and Zn, Cr and Pb, Cr and Ni, and Cd and Pb was relatively close among the seven trace metals (Figure 3), and the content of these elements in organic fertilizer was high (Table 4, Figure 2). Source control is the most effective way to prevent organic fertilizers from polluting the ecological environment.
environment, and there is a significant positive correlation between the content of trace metals in organic manure and livestock manure corresponding to raw materials. The raw materials for the production of organic fertilizers in this paper were mainly livestock manure, while the trace metals in livestock manure were mainly from animal feed. The trace metals in organic fertilizers may be mostly derived from animal feeds high in Zn, Cu, Cr, and Pb [46]. Since Zn, Cu, Cr, and Pb were the four most abundant elements in the feeds, they represented a certain degree of environmental risk. It is important to limit their content. China’s current Feed Hygiene Standard (GB 13078-2017) does not regulate the highest levels of Zn and Cu, which may pose potential risks to the environment, even though these elements can improve the feed nutrients and pharmaceutical ingredients of livestock and poultry [43].

3.4. Accumulation Risk of Trace Metals in Soil from Organic Fertilizer

The long-term application of organic fertilizer containing trace metals can cause soil pollution. In order to estimate the time scale (in years) during which the trace metal content of farmland soil would increase from background level to the maximum permissible limit as a result of using organic fertilizer according to Soil Environmental Quality Standard of China (GB15618-2018), the data of annual application rate in the research area (Table 2) and the median concentrations of seven trace metals in the organic fertilizers were used (Table 5) [47].

According to Equations (2) and (3), the times needed to double the trace metal concentrations in soil from their background levels in North China, Northwest China, and Northeast China were 39, 46, and 46 years, respectively (Table 7). The simulation result was slightly overestimated, as the calculations did not consider the outputs of trace metals from the soil via leaching, runoff, and crop uptake, since these outputs were typically small compared with inputs [15,17,48]. Moreover, atmospheric deposition, which has a greater impact on trace metal accumulation in soil, was not counted. Nevertheless, this research shows the importance of setting the proper application amount and monitoring key trace metals in different regions. In North China, the average annual application rate could be higher, under the control of the content of Zn in organic fertilizer. In Northwest and Northeast China, the application should be reduced, as the time needed to double the trace metal concentrations in soil from their background levels was found to be short for Cd, As, and Zn (Table 7). Generally speaking, applying organic fertilizer, rather than chemical fertilizer, in agriculture is much better for soil quality and food safety. However, trace metal concentrations are usually high, and the soil fertility in Northern China has been decreasing annually [49,50]. In addition to monitoring the trace metal concentration and setting the proper application amount of organic fertilizer, other measures for fertility, such as no-tillage and fallow, can be explored.

In the process of simulating the accumulation of trace metals in the soil after the application of organic fertilizer, it was found that for the entire northern region of China, Zn, Cd, and As showed the highest risks, and Zn and Cd required the most attention as they were found to have the greatest impact on trace metal accumulation in soil during the 16 years of research of Wang et al. [47]. The highest-risk trace metals in different regions were different. In North China, Northwest China, and Northeast China, Zn, As, and Cd were the most important trace metals accumulated in trace metals. There was evidence that Zn, Cd, As, and Cu came from animal feed [51,52], since Zn and Cu were essential elements in commercial feeds to suppress bacteria and maximize feed utilization [25,53]. As it is used for disease control [51], concentrations of Cd were high in phosphorus-containing minerals used as animal feed ingredients, even though Cd is a nonessential element for animals [34,54]. Controlling the contents of Cu, Zn, As, and Cd in animal feed is the most effective way to reduce the risk of organic fertilizers causing the accumulation of trace metals in soil. In the current Feed Hygiene Standards, Organic Fertilizer Standards, and Bio-Organic Fertilizer Standards of China, there is no limit for the content of Zn, which poses risks to the environment. During the standard revision process, a limit value for Zn could be included by referring to values in other countries or regions (Table 6). Additionally, the limit for Cd in agricultural land in the Soil Environmental Quality Control and Control Standards for
Soil Pollution Risk of Agricultural Land (Trial) (GB15618-2018), which is 0.6 mg·kg\(^{-1}\), differs largely from that in the China Organic Fertilizer Standard (NY525-2012), which is 3 mg·kg\(^{-1}\). Therefore, this could be adjusted appropriately during standard revision. The content of Cr, Ni, and Pb were higher in the soil environmental quality standard than those found in the background value of trace metals in northern China, and the limit could be appropriately lowered.

### Table 7. Input of trace metals and time needed to double the trace metal concentrations of soil from its background levels in the research area.

| Area      | Cr  | Ni  | Cu  | Zn  | As  | Cd  | Pb  |
|-----------|-----|-----|-----|-----|-----|-----|-----|
| North China  |     |     |     |     |     |     |     |
| Amount of application (mg·kg\(^{-1}\)) | 0.21 | 0.21 | 0.56 | 6.01 | 0.087 | 0.0048 | 0.19 |
| Time (year) | 928  | 774 | 141 | 39  | 187 | 107 | 784 |
| Northwest China | | | | | | | |
| Amount of application (mg·kg\(^{-1}\)) | 0.37 | 0.37 | 0.68 | 2.95 | 0.17 | 0.011 | 0.39 |
| Time (year) | 504  | 421 | 115 | 78  | 76  | 46  | 387 |
| Northeast China |     |     |     |     |     |     |     |
| Amount of application (mg·kg\(^{-1}\)) | 0.72 | 0.46 | 0.95 | 2.50 | 0.37 | 0.0070 | 0.40 |
| Time (year) | 275  | 364 | 86  | 90  | 46  | 73  | 359 |
| Northern China |     |     |     |     |     |     |     |
| Amount of application (mg·kg\(^{-1}\)) | 0.39 | 0.36 | 0.96 | 4.36 | 0.18 | 0.0094 | 0.38 |
| Time (year) | 484  | 443 | 82  | 53  | 82  | 53  | 396 |

### 3.5. Risks of Trace Metals to Human Health through Soil

According to Equations (1) and (4)–(8), the non-carcinogenic risk of organic fertilizers was low, while the risk of Cr exposure on the skin was the highest (Table 8). Combined with Table 9, keeping the trace metal input constant and simulating the safe use of non-carcinogenic risk in the study area, HI = 1.00 is regarded as the maximum acceptable risk. Under the current fertilization level, North China, Northwest China, and Northeast China will experience adverse effects on human health after 403, 233, and 129 years, respectively, which are much longer than the time during which trace metal content of farmland soil will increase from background level to the maximum permissible limit. This might be due to the fact that the study only considered the effects of soil on human health but not the risk of human health in the food chain. More research on other exposure pathways in the study area is needed in the future [55–57].

The carcinogenic risks for As and Cr were high for both oral and dermal absorption routes, while they were low or moderate for the inhalation of suspended particles (Figure 4). For all three exposure routes, As posed a higher risk to the human body than Cr (Table 7). Controlling the content of these two trace metals in organic fertilizer, especially As, can help prevent and control carcinogenic risks caused by the application of organic fertilizers in the soil. The results showed that arsenic in organic fertilizers was mainly As(V) (arsenate), followed by DMA (dimethylarsenite); organic arsenic in livestock manure was converted to inorganic arsenic during composting [58,59]. In addition to the prevention and control of As, the prevention of the conversion of organic arsenic into inorganic arsenic is an important research direction. Unfortunately, the risk assessments of As might be overestimated, with those conducted by the US-EPA having used faulty data in the dose–response estimation for cancer risk. There is an intense policy debate about the risk from As exposure, and final decisions may not be reached for years because of lawsuits that have been filed to challenge the change in cancer slope factor [60].

In general, human health (non-carcinogenic and carcinogenic) in northern China is considered to be at high risk (Figure 4, Table 10). Of the three exposure routes, skin exposure posed the highest risk; all trace metal elements produced a risk index that was at least half an order of magnitude higher than that for other exposure routes. Residents and agricultural workers in vegetable fields should minimize the chance of skin contact with the soil in production and life to reduce the risk to human health. Among the seven trace metals, the risks to human health from Cr and As were higher than those from other trace metals.
Table 8. Non-carcinogenic risk indices in the study area.

| Exposure Route     | Cr    | Ni    | Cu    | Zn    | As    | Cd    | Pb    |
|--------------------|-------|-------|-------|-------|-------|-------|-------|
|                    | 1.81  | 8.70  | 2.21  | 1.04  | 1.22  | 2.01  | 2.14  |
| North China        | 10^{-4}| 10^{-6}| 10^{-4}| 10^{-4}| 10^{-2}| 10^{-6}| 10^{-3}|
| Oral exposure      | 1.09  | 5.05  | 1.28  | 5.95  | 7.09  | 1.17  | 1.24  |
| Skin exposure      | 10^{-1}| 10^{-5}| 10^{-3}| 10^{-4}| 10^{-2}| 10^{-5}| 10^{-2}|
| Respiratory exposure| 1.58  | 5.64  | 1.29  | 8.96  | 5.34  | 3.51  | 2.52  |
| All ways of exposure| 1.09  | 5.98  | 1.51  | 7.06  | 8.31  | 1.72  | 1.48  |
| Comprehensive      | 0.24  |       |       |       |       |       |       |
|                    | 2.31  | 1.10  | 2.42  | 1.01  | 1.74  | 2.63  | 2.50  |
| Northwest China    | 10^{-4}| 10^{-5}| 10^{-4}| 10^{-4}| 10^{-2}| 10^{-6}| 10^{-3}|
| Oral exposure      | 1.39  | 6.41  | 1.41  | 5.86  | 1.01  | 1.53  | 1.45  |
| Skin exposure      | 10^{-1}| 10^{-5}| 10^{-3}| 10^{-4}| 10^{-1}| 10^{-5} | 10^{-2}|
| Respiratory exposure| 2.02  | 7.15  | 1.41  | 8.82  | 7.63  | 4.60  | 2.93  |
| All ways of exposure| 1.39  | 7.58  | 1.67  | 6.95  | 1.19  | 2.25  | 1.73  |
| Comprehensive      | 0.28  |       |       |       |       |       |       |
|                    | 1.86  | 7.56  | 2.04  | 1.09  | 1.12  | 2.09  | 3.22  |
| Northeast China    | 10^{-4}| 10^{-6}| 10^{-4}| 10^{-4}| 10^{-2}| 10^{-6}| 10^{-3}|
| Oral exposure      | 1.12  | 4.39  | 1.19  | 6.33  | 6.51  | 1.22  | 1.87  |
| Skin exposure      | 10^{-1}| 10^{-5}| 10^{-3}| 10^{-4}| 10^{-2}| 10^{-5} | 10^{-2}|
| Respiratory exposure| 1.63  | 4.90  | 1.19  | 9.54  | 4.90  | 3.67  | 3.79  |
| All ways of exposure| 1.12  | 5.20  | 1.40  | 7.51  | 7.63  | 1.79  | 2.23  |
| Comprehensive      | 0.21  |       |       |       |       |       |       |
|                    | 2.07  | 9.58  | 2.30  | 1.04  | 1.45  | 2.35  | 2.59  |
| Northern China     | 10^{-4}| 10^{-6}| 10^{-4}| 10^{-4}| 10^{-2}| 10^{-6}| 10^{-3}|
| Oral exposure      | 1.24  | 5.57  | 1.34  | 6.06  | 8.45  | 1.37  | 1.50  |
| Skin exposure      | 10^{-1}| 10^{-5}| 10^{-3}| 10^{-4}| 10^{-2}| 10^{-5} | 10^{-2}|
| Respiratory exposure| 1.81  | 6.21  | 1.34  | 9.13  | 6.37  | 4.12  | 3.05  |
| All ways of exposure| 1.25  | 6.59  | 1.58  | 7.19  | 9.91  | 2.01  | 1.79  |
| Comprehensive      | 0.24  |       |       |       |       |       |       |
### Table 9. Carcinogenic risk indices and risk rating in the study area.

| Exposure Route          | Cr        | Ni        | As        | Cd        |
|-------------------------|-----------|-----------|-----------|-----------|
| North China             |           |           |           |           |
| Oral exposure           | $2.28 \times 10^{-5}$ | $1.46 \times 10^{-7}$ | $5.52 \times 10^{-5}$ | $1.26 \times 10^{-8}$ |
| Skin exposure           | $1.33 \times 10^{-4}$ | $8.49 \times 10^{-7}$ | $3.21 \times 10^{-4}$ | $7.34 \times 10^{-8}$ |
| Respiratory exposure    | $3.99 \times 10^{-7}$ | $2.56 \times 10^{-9}$ | $9.67 \times 10^{-7}$ | $2.21 \times 10^{-10}$ |
| All ways of exposure    | $1.56 \times 10^{-4}$ | $9.98 \times 10^{-7}$ | $3.77 \times 10^{-4}$ | $8.62 \times 10^{-8}$ |
| Comprehensive           | $5.34 \times 10^{-4}$ |                   |                   |           |
| Northwest China         |           |           |           |           |
| Oral exposure           | $2.90 \times 10^{-5}$ | $1.85 \times 10^{-7}$ | $7.90 \times 10^{-4}$ | $1.66 \times 10^{-8}$ |
| Skin exposure           | $1.69 \times 10^{-4}$ | $1.08 \times 10^{-6}$ | $4.59 \times 10^{-4}$ | $9.62 \times 10^{-8}$ |
| Respiratory exposure    | $5.09 \times 10^{-7}$ | $3.24 \times 10^{-9}$ | $1.38 \times 10^{-6}$ | $2.90 \times 10^{-10}$ |
| All ways of exposure    | $1.98 \times 10^{-4}$ | $1.27 \times 10^{-6}$ | $5.40 \times 10^{-4}$ | $1.13 \times 10^{-7}$ |
| Comprehensive           | $7.39 \times 10^{-4}$ |                   |                   |           |
| Northeast China         |           |           |           |           |
| Oral exposure           | $2.35 \times 10^{-5}$ | $1.27 \times 10^{-7}$ | $5.07 \times 10^{-5}$ | $1.32 \times 10^{-8}$ |
| Skin exposure           | $1.36 \times 10^{-4}$ | $7.38 \times 10^{-7}$ | $2.95 \times 10^{-4}$ | $7.66 \times 10^{-8}$ |
| Respiratory exposure    | $4.11 \times 10^{-7}$ | $2.22 \times 10^{-9}$ | $8.88 \times 10^{-7}$ | $2.31 \times 10^{-10}$ |
| All ways of exposure    | $1.60 \times 10^{-4}$ | $8.67 \times 10^{-7}$ | $3.46 \times 10^{-4}$ | $9.00 \times 10^{-8}$ |
| Comprehensive           | $5.08 \times 10^{-4}$ |                   |                   |           |
| Northern China          |           |           |           |           |
| Oral exposure           | $2.61 \times 10^{-5}$ | $1.61 \times 10^{-7}$ | $6.59 \times 10^{-5}$ | $1.48 \times 10^{-8}$ |
| Skin exposure           | $1.51 \times 10^{-4}$ | $9.35 \times 10^{-7}$ | $3.83 \times 10^{-4}$ | $8.61 \times 10^{-8}$ |
| Respiratory exposure    | $4.56 \times 10^{-7}$ | $2.82 \times 10^{-9}$ | $1.15 \times 10^{-6}$ | $2.60 \times 10^{-10}$ |
| All ways of exposure    | $1.78 \times 10^{-4}$ | $1.10 \times 10^{-6}$ | $4.50 \times 10^{-4}$ | $1.01 \times 10^{-7}$ |
| Comprehensive           | $6.29 \times 10^{-4}$ |                   |                   |           |

### Table 10. Potential human health risk grade.

| Potential Human Health Risk Grade | Potential Non-carcinogenic Risk |
|----------------------------------|---------------------------------|
| Low risk                         | Low risk                        |
| Moderate risk                    | Low risk                        |
| High risk                        | Low risk                        |
| Extreme risk                     | Low risk                        |
| Low risk (≤ 0.25]                | Low risk (0.25–0.50]            |
| Moderate risk (0.25–0.50]        | Moderate risk (0.50–0.75]        |
| High risk (0.50–0.75]            | Extreme risk (0.75–1.00]         |
| Low risk (≥ 10^{-5}]             | Low risk                        |
| Moderate risk (10^{-5}–10^{-4}]  | Moderate risk                   |
| High risk (10^{-4})              | High risk                       |
| Extreme risk (≥ 10^{-4})         | Extreme risk                    |

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**Notes:**
- The table represents carcinogenic risk indices and risk rating for four regions of China: North China, Northwest China, Northeast China, and Northern China. Each region is evaluated for different exposure routes: oral, skin, respiratory, and all ways of exposure. Comprehensive ratings are also provided at the end for each region.
- The risk indices are presented in the format $10^{-n}$, indicating the magnitude of the risk.
- The risk ratings for potential human health risk are categorized into low, moderate, high, and extreme, with corresponding non-carcinogenic risk levels.
- The table includes potential cancer risk with similar risk grading as the potential human health risk.
Figure 4. Risk level hotspot map of trace metals through oral, skin, and respiratory exposure pathways in North China, Northwest China, Northeast China, and northern China. (a) Carcinogenic risk level hotspot map of Cr, Ni, As, and Cd. (b) Human health risk level hotspot map of Cr, Ni, Cu, Zn, As, Cd, and Pb. Color description: orange-red represents extreme risk, purple-red represents high risk, purple-blue represents moderate risk, and gray represents low risk.
4. Conclusions

Reducing trace metal inputs in agricultural soils is an important strategy to protect farmland and ensure food safety. Estimation of the impact of the application of organic fertilizer on soil and human health is urgently needed to develop sound management practices and policies, which require information on the trace metals present in organic fertilizer. In this study, research was conducted in northern China to determine the metal contents in organic fertilizer.

A total of 117 organic fertilizer samples were collected, and concentrations of Cr (2.74–151.15 mg·kg⁻¹), Ni (2.94–49.35 mg·kg⁻¹), Cu (0.76–378.32 mg·kg⁻¹), Zn (0.50–1748.01 mg·kg⁻¹), As (1.54–23.96 mg·kg⁻¹), Cd (2.74–151.15 mg·kg⁻¹), and Pb (1.60–151.09 mg·kg⁻¹) were measured. The contents of trace metals varied significantly, with variability coefficients of 54.23–146.32%. High correlations were observed between Cu and Zn, Cr and Pb, Cr and Ni, Cr and Cd, Ni and Pb, Cr and As, and Cu and Cd, which might have similar sources or cause co-pollution in the environment. Compared with the trace metal limit standards for organic fertilizers in 24 regions of the world, these trace metals exceeded the limits, showing different values. The Chinese organic fertilizer standards were exceeded for Cr (by 0.85%), As (by 5.98%), Cd (by 1.71%), and Pb (by 4.27%). The maximum acceptable concentrations of the German standard were exceeded by 1.71% for Ni, 17.09% for Cu, and 35.04% for Zn.

Monte Carlo simulations showed that after 39, 46, 46, and 53 years, the concentrations of Zn, Cd, and As will exceed the limits of the Soil Environmental Quality Standards of China in North China, Northwest China, Northeast China, and northern China, respectively. As and Cr pose high risks to human health, especially as carcinogenic risk factors with a skin exposure pathway. The simulation result was slightly overestimated; in future research, the outputs of organic fertilizer in the soil (leaching, runoff, and crop uptake) and the dose–response relationship of non-carcinogenic and carcinogenic risk factors should also be considered. It is important to control and monitor the additions of Cr, Zn, As, and Cd in organic fertilizer.

Author Contributions: Q.G. contributed to writing—original draft. Q.G. and R.S. contributed to data curation. Q.G. and C.S. contributed to formal analysis. Q.G. and Y.G. contributed to investigation. Q.G. and X.Z. contributed to methodology. X.Z. and P.C. contributed to funding acquisition and project administration. X.Z. and R.S. contributed to supervision. X.Z. and S.-A.Z. contributed to writing—review and editing. All authors have read and approved the final manuscript.

Funding: This work was supported by the National Key Research and Development program of China [Nos. 2016YFD0800606, 2016YFD0201200, 2016YFD0201201, and2017YFD0800210].

Conflicts of Interest: The authors declare no conflict of interest.

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