Bioconcentration, Potential Health Risks, and a Receptor Prediction Model of Metal(loids) in a Particular Agro-Ecological Area

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Abstract: To investigate the bioconcentration and potential health risks of metal(loids) in a particular agro-ecological area, 230 pairs of soil and corresponding crop grain samples were collected from typical corn and wheat plants. The geo-accumulation index (Igeo), bioconcentration factors (BCF), health risk assessment (the target hazard quotient), and Receptor Prediction Model (PCs-SMLR) analysis were adopted to study the spatial distribution, assess the health risks, and predict the relationship between metal(loids) and soil properties. It was found that the mean concentrations of Cu, Zn, Pb, Hg, and Cd in the study area's agricultural soils exceeded the background soil concentrations, especially for Cd (0.2 mg/kg). Meanwhile, the corresponding Cd concentration in wheat samples was higher than the food quality limit. The results of the Igeo showed that the samples with a value higher than 0 for Cd and Hg accounted for 47.83% and 33.48%, respectively. The results of BCF of Cu, Zn, Cd, and As were higher in wheat than in corn, except for Ni. The target hazard quotient (TTHQ) of health risk of wheat, corn, and soil were higher for children (2.48) than adults (1.78), showing a potential health risk for individuals who mostly consume wheat. In addition, the PCs-SMLR analysis of the BCF prediction model for Cu, Zn, As, and soil properties showed differences in terms of the influences from wheat and corn. These results provide valuable information that not only can help local residents improve the staple food structure, but also can get provide a reference metal(loids) concentration level for agricultural soils in the study area and restore a sustainable agro-ecological environment.

Keywords: Hebei plain; metal(loids); accumulation; health risks; PCs-SMLR

1. Introduction

Soils are one of the main sources of metal(loids) in crops. Soil metal(loids) can easily move through soils, have a long residual time, can be difficult to detect, and have high toxicities. They can be absorbed by crops and then enter the food chain. Alternatively, metal(loids) can enter water bodies or the atmosphere and threaten human health and animal reproduction [1–9]. Therefore, the treatment of soils contaminated with metal(loids) is a significant, yet challenging, research topic around the world.

Metal(loids) in contaminated soils are considered to be among the greatest risks to food safety and human health in China. According to the National Soil Pollution Investigation Bulletin, the environmental quality of cultivated soils in China is worrying. A survey found that 16.1% of soil samples were polluted and that 82.8% of the pollutants were inorganic toxins [10]. These pollutant levels are above the standard rates and are primarily Cd, Hg, As, Cu, Pb, Cr, Zn, and Ni. Crops (such as wheat and corn) absorb excessive metal(loids), such as Cd, Hg, and As, from the...
soil [6–8,11–13]. These metal(loid)s are easily absorbed and accumulated by crops in edible tissues, depending not only on the species, but also on the soil properties. Moreover, a high enough level of bioconcentration can lead to harmful effects on human health [11–16].

Dietary habits are thought to be the main pathway by which metal(loid)s accumulate in the body. Wheat and corn are the main crops in the world, especially in northern China, where wheat and corn are staple foods. The annual consumption of wheat and corn is very large. The per capita annual consumption of grain is 120 kg, of which wheat consumption is 80 kg. Wheat consumption is much higher in northern than in southern China. Metal(loid)s that have accumulated in the body over a long period can lead to chronic diseases and cancer, with As, Cr, and Cd being considered as carcinogens [17–24].

Many studies have reported that basic soil characteristics, including pH, organic matter, cation exchange capacity (CeC), and soil clay content, affect the absorption of metal(loid)s by wheat and corn crops. However, most of these studies were conducted within carefully controlled environments using potted plants or field plots, and focused on relevant variables in specific fields [20,25–30]. A smaller number of studies have been conducted on a regional scale examining spatial variability and the relationships of metal(loid)s with soil and crops. Because wheat and corn crops are affected by the external environment throughout the growing season, the relationships between soil properties and metal(loid)s are more complex. On a relatively large scale, the information from previous studies cannot adequately explain the complex relationship between soil and wheat or corn crops.

Geostatistical analysis that includes multiple variables is an effective method to clarify these complex relationships [31–33]. Geostatistical methods have been widely used to study the spatial relationships between soil and plants. General ordinary kriging (OK) prediction of geochemical maps can provide a visualization of geological information and directly identify problem areas. Principal component analysis (PCA) has been widely used in environmental ecology. PCA has the advantages of reducing the loss of original data, simplifying the data structure, and avoiding subjective randomness. Meanwhile, a principal component scores multi-regression (PC_S-SMLR) analysis solves the problem of collinearity of independent variables and ensures the accuracy of the results. Thus, it provides a theoretical basis for the treatment of metal(loid) pollution in local agriculture.

In this study, the concentrations of metal(loid)s in crops and surface soil were measured at the same point on the Hebei plain. Basic soil properties were also measured. The main research objectives for the current study were: (1) To investigate metal(loid)s concentration, distribution, and contamination levels; (2) To compare the bioconcentration factors (BCF) differences of metal(loid)s from soils to wheat and corn; (3) To evaluate the health risks to adults and children from metal(loid)s in wheat and corn; (4) To determine the bioconcentration relationship between wheat and corn crops, and soil properties by using PC_S-SMLR.

2. Materials and Methods

2.1. Study Area

The Hebei plain is an important part of the North China Plain (Figure 1). It borders Henan and Shandong in the south, Beijing and Tianjin in the north, the Taihang Mountains in the west, and the Bohai Sea in the east. It includes the cities of Langfang (LF), Baoding (BD), Hengshui (HS), Changzhou (CZ), Shijiazhuang (SJZ), and Xingtai (XT). The population is about 50 million people. The total area of Hebei plain is approximately 62,000 km². It was mainly formed by alluvial deposits from the Yellow River and the Haihe River. The terrain is low-lying and the elevation ranges from approximately 3 m to 100 m along the coast of the Bohai Sea. The plain area has a warm, temperate monsoon climate with obvious seasonal changes that include cold, dry winters. The average annual temperature is 12 °C, with an annual average rainfall of 350–770 mm. The study area has ample sunshine, which makes this a good region for agriculture. Soils are predominately fluvo-aquic, cinnamon, and coastal saline.
The main crops are corn, with an annual yield of 17.54 Mt, and wheat, which has an annual yield of 14.33 Mt.

Figure 1. The sampling site map of soils and crops in the study area. (The city names Langfang, Baoding, Shijiazhuang, Cangzhou, Hengshui, Xingtai, and Handan have the abbreviations LF, BD, SJZ, CZ, HS, XT, and HD.).

2.2. Sample Collection and Analysis

In the primary wheat- and corn-growing areas of Hebei plain, 230 soil surface layer and agricultural samples were collected. The sample points were located using GPS. The soil sample points were selected by the diagonal method (the distance from the ground edge was greater than 1 m). Wheat grain samples of 500 g were collected at each point using a 1 m × 1 m sample square. Within the crop sample points, the cultivated soil layer was collected between a depth of 0 to 20 cm. When the soil surface was being collected, weeds, grassroots, gravel, bricks, fertilizer clumps, and other debris were removed. To ensure that representative samples were taken from each sample site, during sampling one point was taken as a fixed point, and three to five sub-samples were collected 20 m around it. Sampling was conducted until at least 1.0 kg of material had been collected. Cultivated soil and wheat samples were collected at the same time, whereas corn samples were collected separately. The wheat and corn samples were dried and sent to a laboratory for analysis. Soil samples used for chemical analyses were first air-dried and passed through a 20-mesh nylon screen to remove roots, residue, and stones.

The total concentrations of Cu, Zn, Cr, Cd, Ni, Pb, As, and Hg in soils were extracted by an acid digestion mixture (HNO$_3$ + HF + HClO$_4$). Ni, Cu, Zn, Cr, Cd, and Pb levels were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, 7500a, Agilent Technologies, Calif, USA). As and Hg levels were determined by atomic fluorescence spectrometry (AFS) [34].

Soil pH was measured using a pH meter (1:2.5 soil:water mixture). Total organic carbon (TOC) was analyzed using the potassium dichromate oxidation and REDOX volumetric method [35–37]. Next, the clay samples were determined using the hydrometer method [38]. CeC was determined with the ammonium acetate method and N was determined using the acid–base titration volumetric
method. The content of Fe, P, K, Mn, Ca, Mg, and other soil properties was determined using the powder tablet XRF method [39].

National level soil reference materials (GBW07402 and GBW07406) were used to check the data for accuracy and precision. Random soil samples were selected and checked for quality control. Abnormal points were identified in relation to the quality checks. Quality analyses were also made for replicated samples, where analyses were repeated to assess whether sampling or analysis errors had any significant influence on regional geochemical changes.

The wheat and corn samples were cleaned, dried, and broken up before being passed through a 2-mm sieve. The samples were then homogenized before being analyzed. Crop grain samples were digested by a mixture of HNO_3 and HClO_4 (4:1, v:v). The metal(loid) concentrations in the samples were determined as described by [33]. Quality control was implemented in accordance with GBW08502 (rice flour), GBW08503b (wheat flour), GBW10010 (rice), GBW10011 (wheat), and GBW10013 (soybeans), which were also used for accuracy control. The relative error (RE) was less than 30%. The precision of the analyses for the crop metal(loid)s were As (98.5%), Cd (99.5%), Hg (99.6%), Pb (99.9%), Cr (99.9%), Ni (100%), Cu (100%), and Zn (100%).

2.3. Statistical Analysis

Basic statistical analyses (e.g., minimum, maximum, standard deviation, and box plots) were conducted using SPSS 24. When needed, the raw data were either log-transformed or cox-box-transformed to fit a normal distribution and improve the prediction accuracy. A distribution map of soil metal(loid)s was drawn using the ArcGis10.5 kriging method [37,40]. A stepwise linear multiple regression (PCS-SMLR) analysis was conducted using SPSS 24 to evaluate the relationship between BCF and soil properties.

2.4. Index of Geo-Accumulation (Igeo)

The evaluation method can be used to evaluate the contamination levels of metal(loid)s in soils [41,42]. The Igeo was computed using the following equation:

\[ I_{geo} = \log_2 \left( \frac{C_n}{K \times B_n} \right), \tag{1} \]

where \( C_n \) is the concentration of metal (n) in the sample and \( B_n \) is the geochemical background concentration of the metal (n) with reference to the Chinese soil element background value from 1990. A background matrix correction factor of 1.5 was used to account for the lithogenic effects [43]. Igeo is classified into seven levels: Unpolluted (Igeo ≤ 0), unpolluted to moderately polluted (0 < Igeo ≤ 1), moderately polluted (1 < Igeo ≤ 2), moderately to strongly polluted (2 < Igeo ≤ 3), strongly polluted (3 < Igeo ≤ 4), strongly to extremely polluted (4 < Igeo ≤ 5), and extremely polluted (Igeo > 5).

2.5. Health Risk Quotient (HQ) Method

The main methods used to assess health risk included the health quotient (HQ), health risk index (HRI), and lifetime cancer risk index (ILTR). These risk assessment methods can only be used to evaluate the health risk of a single metal(loid). In this study, a target hazard quotient (THQ) was used to evaluate the health risks of multiple paths, such as soil, wheat, and corn. The THQ method is a USEPA human health risk assessment method for external substances intake [44,45]. When the THQ value is less than 1, there is no significant health risk in the exposed population. However, a THQ value over 1 indicates a health risk. The HQ for a single metal(loid) is calculated as follows:

\[ HQ = \frac{EF \times ED \times IR \times C}{RfD \times BW \times AT}, \tag{2} \]
where EF is the exposure frequency with a value of 365 d/a; ED is the exposure range with a value of 70 a; IR is the intake rate (kg person/d); C represents the concentration of the soil and crop (mg/kg), and RfD is a reference control (Cd, Cu, Ni, Pb, Zn, As, and Hg are 0.001, 0.04, 0.02, 0.004, 1.5, 0.03, 0.0003, and 0.0003 mg/kg/d, respectively) [44–47], BW is the average body weight (61.6 kg for adults and 18.7 kg for children 0–6 years old) [48], and AT is the average exposure time for non-carcinogenic effects (ED × 365 d⁻¹·y⁻¹).

The THQ formula is calculated as follows:

\[ \text{THQ} = \sum_{i=0}^{n} \text{THQ}_i = \text{THQ}_{\text{Cu}} + \text{THQ}_{\text{Zn}} + \text{THQ}_{\text{Pb}} + \text{THQ}_{\text{Cd}} + \text{THQ}_{\text{Cr}} + \text{THQ}_{\text{As}} + \text{THQ}_{\text{Ni}} + \text{THQ}_{\text{Hg}} \]  

(3)

The total target hazard quotient (TTHQ) is calculated via three pathways. Typically, potential exposure routes for humans to metal(loid)s include the consumption of food and soil. TTHQ is equal to the sum of THQ for each exposure route, as described below:

\[ \text{TTHQ} = \sum_{i=0}^{n} \text{TTHQ}_i = \text{THQ}_{\text{corn}} + \text{THQ}_{\text{wheat}} + \text{THQ}_{\text{soil}} \]  

(4)

where THQcorn, THQwheat, and THQsoil represent THQ for a specific metal(loid) encountered during the consumption of corn and wheat by humans, and the oral ingestion of soil by humans.

2.6. Prediction Methods

To model the ability of crops to absorb and accumulate metal(loid) elements from soils, a bioconcentration factor (BCF) was defined as \( \frac{C_{\text{crops}}}{C_{\text{soil}}} \), where \( C_{\text{crops}} \) represents the content of metal(loid) elements in crops (mg/kg) and \( C_{\text{soil}} \) represents the content of metal(loid) elements in the soil (mg/kg) surrounding roots. BCF is calculated as:

\[ \text{BCF} = \frac{C_{\text{crops}}}{C_{\text{soil}}} \]  

(5)

A principal component analysis (PCA) was used to analyze datasets and compress data dimensions. By analyzing the relationships between multiple variables, fewer representative factors were needed to illustrate the main trends from the variables. The mathematical model of PCA is as follows:

\[ F_1 = a_{11}x_1 + a_{21}x_2 + \ldots + a_{p1}x_p \]
\[ F_2 = a_{12}x_1 + a_{22}x_2 + \ldots + a_{p2}x_p \]
\[ \ldots \ldots \ldots \ldots \]
\[ F_n = a_{1n}x_1 + a_{2n}x_2 + \ldots + a_{pn}x_p, \]

where \( F_1, F_2, \ldots, F_n \) is the largest variance of all linear combinations of \( x_1, x_2, \ldots, x_p \) (where the coefficients satisfy the above equations), respectively.

Data processing occurred after the data were standardized. A covariance matrix was calculated from the standardized data, where all eigenvalues in the characteristic equation were calculated; the number of principal components was determined according to the cumulative proportion of the eigenvalues, and the load value and principal component score of the principal components were calculated. Additionally, the BCF and absolute principal component score (PCS) of each component obtained from standardized data were used for a stepwise multiple linear regression (SMLR) analysis to calculate the relationship between BCF and each component:

\[ \log Y_{\text{BCF}} = a + bX_{\text{PCS}_n}. \]  

(6)
3. Results and Discussion

3.1. Characterization and Distribution of Metal(loid)s in Soil

In general, the soil was strongly alkaline (the average pH was 8.30), and the pH of the soil ranged from 7.43 to 9.05. The median total organic matter (TOC) content was 1.04% and ranged from 0.31% to 2.67%. The soils had moderate cation exchange capacities (CeC) (mean 11.07 cmol/kg) that ranged between 3.76 and 24.20 cmol/kg. Clay content ranged from 16.0 to 265.2 g/kg, with a mean value of 98.1 g/kg (Figure 2).

The concentrations of eight metal(loid)s in the soil are given, along with the permissible amounts according to the Chinese standards, in Table 1. The standard values for the different metal(loid)s are the most recent ones published by the Environmental Protection Administration of the PRC to assist with protecting the soil environment and agricultural production [49].

|          | mg/kg | Mean   | Coefficient of Variable (CV), % | Food Threshold [50] | Local Background Values [51] | Soil Environmental Quality [49] |
|----------|-------|--------|---------------------------------|---------------------|-------------------------------|-------------------------------|
| Cu corn  | 1.40  | 26.75  |                                 |                     |                               |                               |
| Cu wheat | 4.63  | 21.21  |                                 |                     |                               |                               |
| Cu soil  | 25.72 | 58.50  |                                 | 21.8, 100           |                               |                               |
| Pb\textsuperscript{2} corn | 0.05  | 71.83  |                                 |                     |                               |                               |
| Pb\textsuperscript{3} wheat | 0.06  | 59.07  | 0.20                            |                     |                               |                               |
| Pb soil  | 24.76 | 39.25  |                                 | 21.5, 170           |                               |                               |
| Zn corn  | 21.46 | 17.43  |                                 |                     |                               |                               |
| Zn wheat | 32.07 | 23.08  |                                 |                     |                               |                               |
| Zn soil  | 78.47 | 74.47  | 71.9, 300                       |                     |                               |                               |
| Cr corn  | 0.03  | 68.64  | 1.00                            |                     |                               |                               |
| Cr wheat | 0.03  | 35.26  |                                 |                     |                               |                               |
| Cr soil  | 67.74 | 10.84  |                                 | 68.3, 250           |                               |                               |
| Ni corn  | 0.22  | 29.52  |                                 |                     |                               |                               |
| Ni wheat | 0.10  | 48.04  | 1.00                            |                     |                               |                               |
| Ni soil  | 28.84 | 17.20  |                                 | 30.8, 190           |                               |                               |
| Cd corn  | 0.0043| 79.70  |                                 |                     |                               |                               |
| Cd\textsuperscript{2} wheat | 0.03  | 50.71  | 0.10                            |                     |                               |                               |
| Cd soil  | 0.20  | 191.69 |                                 | 0.09, 0.6           |                               |                               |
| As corn  | 0.01  | 68.35  |                                 |                     |                               |                               |
| As wheat | 0.03  | 76.41  | 0.50                            |                     |                               |                               |
| As soil  | 9.89  | 30.73  | 12.8, 25                        |                     |                               |                               |
| Hg\textsuperscript{2} corn | 0.0040| 92.39  | 0.02                            |                     |                               |                               |
| Hg\textsuperscript{1} wheat | 0.0022| 82.54  |                                 |                     |                               |                               |
| Hg soil  | 0.06  | 62.78  |                                 | 0.04, 3.4           |                               |                               |

* Pb\textsuperscript{2} corn, Cd\textsuperscript{3} wheat, Hg\textsuperscript{2} corn, and Hg\textsuperscript{1} wheat represent crops that exceed the guidelines for soil food quality (GB2762-2012) [50].

The results of agricultural soil Cu, Pb, Zn, Cr, Ni, Cd, As, and Hg contents averaged 25.72, 24.76, 78.47, 67.74, 28.84, 0.20, 9.89, and 0.06 mg/kg, respectively. Most of these values are below the soil environmental quality risk control standard for soil contamination of agricultural land (GB15618-2018) (based on different pH) safety limits [51]. However, Cu and As each had one sample that exceeded the safety limit value. Compared with the background values, most metal(loid)s exceeded the local background values. The mean value of Cd was more than double the local background value [51] and had a coefficient of variation of 1.9, indicating that it was greatly affected by exogenous factors. Only Ni and As had values below the background values.
The Igeo values of the agricultural soil from the study area decreased in the following order: Cd > Hg > Cu > Pb > Zn > Ni > Cr > As. These values ranged from −0.293 to 1.438 (average 0.008) for Cd, −0.499 to 0.777 (average: −0.048) for Hg, −0.372 to 0.845 (average: −0.127) for Cu, −0.318 to 0.585 (average: −0.134) for Pb, −0.402 to 0.911 (average: −0.165) for Zn, −0.439 to −0.029 (average: −0.211) for Ni, −0.336 to −0.072 (average: −0.182) for Cr, and −0.891 to 0.187 (average: −0.309) for As (Figure 2). However, Igeo values were higher than 0 in the Cd 47.83%, Hg 33.48%, Cu 4.35%, Pb 3.04%, Zn 2.17%, and As 0.87% samples, and the sample numbers of Cd and Hg far exceed the other six metal(loids).

The box plots in Figure 2 indicate that the study area soils are contaminated (Igeo > 0) by Cd, Hg, and especially Cd, which probably originated from anthropogenic sources. Moreover, the distribution shows a large high-value area of Cd and Hg (Figure 3). The high Cd values are mainly concentrated in the BD, SJZ, and CZ areas (Figure 1). Liu et al. (2011) showed that the metal(loids) in this area primarily originated from a chemical fiber factory that had industrial wastewater rich in Cd, which polluted the soil [52]. The high Hg values are mainly concentrated in the BD, SJZ, XT, and HD areas (Figure 1). China’s use of phosphate fertilizer ranks first in the world, accounting for about 25% of the world’s phosphate fertilizer consumption. The application of phosphate fertilizer is a main source of Hg and As in farmlands within the study area [53]. Additionally, emissions from coal burning also increased soil Hg levels in the study area [54]. Cu, Pb, and Zn distribution patterns point to source pollution. Figure 3 shows that areas with high Zn, Cu, and Pb levels are mainly concentrated southeast of Baoding city and in the southern part of Shijiazhuang City. Researchers have confirmed that the metal(loids) pollution was due to toxic substances (e.g., dust, sewage) from lead–zinc ore smelters, paper mills, and chemical plants. The metal(loids) entered and polluted farmland soils via atmospheric deposition and sewage [42,55]. However, Ni and Cr levels were not large enough to be considered soil contaminants in the study area and were likely from natural origins.
3.3. BCF of Metal(loid)s in Corn and Wheat

Figure 3. The distribution of metal(loid)s and soil properties.

3.2. Concentrations of Metal(loid)s in Corn and Wheat

Among the crops, there are differences in the concentrations of metal(loid)s between corn and wheat. The average corn crop values for Cu, Pb, Zn, Cr, Ni, Cd, As, and Hg are 1.4, 0.05, 21.46, 0.03,
0.22, 0.0043, 0.01, and 0.004 mg/kg, respectively. The average wheat crop values for Cu, Pb, Zn, Cr, Ni, Cd, As, and Hg are 4.63, 0.06, 32.07, 0.03, 0.10, 0.03, 0.03, and 0.0022 mg/kg, respectively. Cu and Zn are essential to plant micronutrients [56–58] and are the most abundant metals in wheat and corn [59]. Based on 230 wheat grain samples, Zn concentrations ranged from 17.4 to 63.4 mg/kg and Cu ranged from 2.38 to 8.82 mg/kg. Using 230 corn grain samples, the concentration of Zn ranged from 10.9 to 34.84 mg/kg and Cu ranged from 0.06 to 2.36 mg/kg.

Our results showed that the mean content of Cu, Zn, and Cd in wheat was significantly higher than in corn. Within the wheat and corn crops, Pb, Cd, As, and Hg had variation coefficients that exceeded 50%. When compared with the food safety limits (GB2762-2012), the Cd, Hg, and Pb concentrations in wheat, and Hg and Pb in corn, exceeded the standard samples (Table 1). Industrial production (smelters, chemical plants, paper mills) in the study area is the likely source of excessive metal(loid) levels [60,61].

3.3. BCF of Metal(loid)s in Corn and Wheat

The bioconcentration factor (BCF) is the ratio of the concentration of metal(loid)s in crops and soil (Equation (6)) and is a crucial index to measure the degree of absorption of metal(loid)s by plants. BCF values are shown in Figure 4. Through statistical analysis of the BCF, the enrichment ability of agricultural products to metal(loid)s in soils and agricultural products was evaluated. Higher BCF values indicate a stronger migration ability of metal(loid) elements into plants. BCF is a common parameter often used in the study of environmental contamination [62,63].

Zn had the highest average BCF for wheat and corn, with values of 0.446 and 0.297, respectively, which explains the high Zn concentration in these plant samples. Huang et al. (2008) also found that the BCF of Zn was highest in wheat [48]. Wang et al. (2013) reported that the BCF of Zn had a higher accumulation in grain than Cu [64]. The study also showed that the BCF of Cu in wheat and corn is lower than that of Zn, at about 0.195 and 0.059, respectively. The BCF of wheat is higher than that of corn in the study area and is similar to values found by Huang et al. (2008) and Wang et al. (2013) [48,64]. Nan and Cheng (2001) reported that corn’s ability to move Zn [65], which is the most bioavailable metal in contaminated soils, from roots to other parts of the plant was greater than for Cu.

The BCF of wheat Cd is greater than corn Cd, yet similar to BCF of Zn, resulting in three wheat samples that exceeded the national food standard. Huang et al. (2008) showed that the BCF of Cd was higher than for the other metal(loid)s tested [47], which would harm human health. In comparison, the BCF of As (0.003 for wheat and 0.0015 for corn) was lower than the other metal(loid)s in this study and also significantly lower than the values reported by Liu et al. (2005). Huang et al. (2008) also found that the crop BCF of As was significantly lower than the values for Cd, Zn, Cu, and Pb [47,66].

The corn BCF values for Cu, Zn, and Cd were higher than the BCF value for Hg (0.080 and 0.045, respectively), both of which are higher than the BCF values reported by Huang et al. (2008) for wheat (0.0176). Importantly, the Hg concentrations of three grain samples exceeded the Chinese standard limits of 0.02 mg/kg. Previous studies have shown that Hg pollution is caused by emissions from coal-burning and large applications of phosphate fertilizers containing Hg, which increases soil and crop Hg levels.

The BCF values for Ni and Cr were lower than for Pb, and also lower than the BCF values reported for carrots [47,67,68]. These results agreed with the findings of Gigliotti et al. (1996), who found that Cr, Ni, and Pb are less mobile in corn and wheat plants [69]. However, the Pb concentrations of five grain samples exceeded the Chinese tolerance limits of 0.2 mg/kg. Variations of Pb concentrations in corn and wheat grains were considerably higher than those in soil.

In general, the order of average metal(loid) BCF values in corn was Zn (0.297) > Hg (0.08) > Cu (0.059) > Cd (0.026) > Ni (0.008) > Pb (0.002) > As (0.0015) > Cr (0.0004). For wheat, this order was Zn (0.446) > Cd (0.195) = Cu (0.195) > Hg (0.045) > As (0.003) > Pb (0.002) > Cr (0.0004) > Ni (0.00004). The crop BCF values for Zn were greater than for the other metal(loid)s. Additionally, the BCF values for Cd and Cu were also larger than the values for Ni, Pb, As, and Cr.
The large BCF values for Zn, Cd, and Cu indicate that the three metal(loid)s have strong migration abilities in crops. The strong enrichment capacity of Zn and Cu indicates that the ability of Zn and Cu to migrate from the soil to the edible parts of the crops is significantly higher than for other elements, especially in wheat, which is consistent with the results found by Li et al. (2018) [70]. The BCF value for Cd in wheat was 0.195, which is higher than for corn (0.026). Grant et al. (1999) showed that the
absorption of Cd in corn was much lower than that in wheat [71]. Yang et al. (2011a) found that Cd had little enrichment capacity in corn seeds and was more easily absorbed by crops in a reduction environment [23]. Additionally, long-term fertilization gradually reduced the effectiveness of Cr and Ni, with the unstable form (exchangeable state and carbonate binding state) being transformed into a more stable form (Fe–Mn oxide binding and organic binding fractionation), resulting in reduced Cr migrating into crops [70]. Comparing the BCF values for each element shows that the metal(loid)s content in corn is small. First of all, this is due to the biomass of the non-seed parts of corn plants grown in dryland soil being large. Because the biological dilution effect is strong, metal(loid)s in crops are generally distributed as follows: Roots > stem leaves > seeds. Plant absorption of metal(loid) content is approximately 20% to 40% of the total crop uptake, with corn seeds’ uptake being the lowest [23,72]. Secondly, this is due to variation in species, e.g. cabbage was determined to have a higher bioconcentration than garlic and Leping radish for metal(loid)s [12], Yang et al. (2018) also reported a higher and more sensitive bioconcentration of wheat than corn [8], which indicated that strains of each type accumulate very differently for metal(loid)s.

In a word, the BCF value of metal(loid)s showed that some differences between wheat and corn in the study area depend not only on the soil properties, but also on the biological characteristics of a species and variation between species.

3.4. Health Risks

To assess the total risk of metal(loid)s in wheat, corn and soil to human health, the TTHQ approach was developed based on the EPA’s Guidelines for Health Risk Assessment of Chemical Mixtures [46]. The hazard index is equal to the sum of the hazard quotients, as described in Equation (2–4). A significant variable in calculating health risks is the IR, which measures (kg/individual/d) the daily contact rate to an exposure medium (for soil this is 64 mg/d for adults and 104 mg/d for children) [44,45,47].

According to the 2018 statistical yearbook of Hebei province, for wheat IR the annual adult consumption in Hebei province is 81.74 kg/individual, which is 223.93 g/individual/d. For children, the consumption is 74.57 g/individual/d, which is approximately one-third that of adults. The statistical yearbook of Hebei province did not give statistics on corn consumption. The IR of corn in this study used consumption rates reported by Yang et al. (2011a) [23], which for adults were 150 g/individual/d and for children was 100 g/individual/d.

When the HQ exceeds 1, there may be concern about potential health effects (Table 2). It is important to recognize that, although no single metal exposure exceeds 1, the total risk of all metal(loid)s being consumed from crops and soil is significant for children and adults (Figure 5). The soil THQ for adults and children (0.015 and 0.024, respectively) indicates that people are unlikely to be endangered by metal(loid)s through soil consumption. However, the corn THQ for adults and children (0.47 and 1.04, respectively) indicates that corn is a likely source of exposure for children, which could result in adverse health effects. The wheat THQ for adults and children (1.29 and 1.42, respectively), as well as the TTHQ (2.48 and 1.78, respectively), will lead to health risks for both adults and children.
Table 2. Health Risk Quotient (HQ) and target hazard quotient (THQ) statistics of three paths (soil, corn, wheat).

| Metal(loid) | Soil Adult | Soil Child | Corn Adult | Corn Child | Wheat Adult | Wheat Child |
|------------|------------|------------|------------|------------|-------------|-------------|
| Cu         | 6.68 x 10^{-4} | 1.09 x 10^{-3} | 8.50 x 10^{-2} | 0.19       | 0.42        | 0.46        |
| Pb         | 6.43 x 10^{-3} | 1.04 x 10^{-2} | 2.99 x 10^{-2} | 6.76 x 10^{-2} | 5.60 x 10^{-2} | 6.15 x 10^{-2} |
| Zn         | 2.72 x 10^{-4} | 4.42 x 10^{-4} | 0.17       | 0.38       | 0.39        | 0.43        |
| Cd         | 3.43 x 10^{-3} | 5.56 x 10^{-3} | 1.05 x 10^{-2} | 2.34 x 10^{-2} | 3.90 x 10^{-2} | 4.28 x 10^{-2} |
| Cr         | 2.0 x 10^{-5} | 3.25 x 10^{-5} | 4.35 x 10^{-5} | 9.54 x 10^{-5} | 7.93 x 10^{-5} | 8.69 x 10^{-5} |
| Ni         | 3.52 x 10^{-3} | 5.72 x 10^{-3} | 2.69 x 10^{-2} | 5.88 x 10^{-2} | 1.86 x 10^{-2} | 2.04 x 10^{-2} |
| As         | 7.04 x 10^{-3} | 1.14 x 10^{-3} | 0.11       | 0.25       | 0.34        | 0.37        |
| Hg         | 2.07 x 10^{-4} | 3.37 x 10^{-4} | 3.22 x 10^{-2} | 7.03 x 10^{-2} | 2.6 x 10^{-2}  | 2.85 x 10^{-2} |
| THQ        | 1.52 x 10^{-2} | 2.48 x 10^{-2} | 0.47       | 1.04       | 1.29        | 1.42        |

TTHQadult 1.78
TTHQchild 2.48

Figure 5. Comparison of the distribution of HQ and THQ under the three paths.

The HQ of As, Cu, and Zn in crops is higher than that of the other metal(loid)s. In particular, the HQ of As, Cu, and Zn in wheat all exceed 0.3, with 2% of the As samples in wheat having HQ values greater than 1. Additionally, the contribution of Zn, Cu, and As in crops to total risk was the largest for different receptor populations, with the three values contributing more than 17%. A valuable finding is that the contribution to risk in wheat exceeded 25% (30.05%, 32.63%, and 26.49%), and the contribution to overall health risk in wheat was more than 80% (Figure 6). The HQ values for Hg (corn 6.79%, and wheat 2.02%), Ni (corn 5.68%, and wheat 1.44%), Cd (corn 2.25%, and wheat 3.02%), Pb (corn 6.46%, and wheat 4.34%), and Cr (corn 0.009%, and wheat 0.006%) in crops contributed to TTHQ values that were less than 10%.
When the HQ exceeds 1, there may be concern about potential health effects (Table 2). It is important to recognize that, although no single metal exposure exceeds 1, the total risk of all metals and metal(loid)s being consumed from crops and soil is significant for children and adults (Figure 5). The TTHQ values for children were greater than the TTHQ values for adults (Figure 7). Long-term consumption of large amounts of food contaminated with metal(loid)s poses a significant risk to human health (especially for children). The health risk of metal(loid)s in wheat is higher than that of corn. This suggests that a reduction in the intake of staple foods containing wheat will reduce the BCF of Cu, Zn, and As in crops, and reduce the health risks.

![Figure 6. Contribution of metal(loid)s in three mediums (soil, wheat, and corn) to the total health risk for adults and children.](image)

Overall, the results show that the TTHQ values for children were greater than the TTHQ values for adults (Figure 7). Long-term consumption of large amounts of food contaminated with metal(loid)s poses a significant risk to human health (especially for children). The health risk of metal(loid)s in wheat is higher than that of corn. This suggests that a reduction in the intake of staple foods containing wheat will reduce the BCF of Cu, Zn, and As in crops, and reduce the health risks.

![Figure 7. The distribution map of TTHQ for adults and children in the study area.](image)

3.5. Receptor Prediction Model

Thurston et al. (1985) first proposed that, after the normalization of original data, the absolute real score of a factor could be obtained using factor analysis [73], and then combined with a multivariate linear regression model to calculate a common factor contribution rate on water targets. PC$_S$-SMLR can quantitatively depict the main factor’s contribution to the receptor of each index, such as the air and water pollution source analysis used in studies [54,74]. This methodology has rarely been used in the soil environment. Because it only focuses on linear regression to determine the relationships between multiple influencing factors on metal(loid)s in crops [33], it cannot eliminate the collinearity between elements, leading to inaccurate prediction results. PC$_S$-SMLR is a method that eliminates the collinearity of soil factors [37], reduces the complexity of factors, and provides more accurate results.

The results of a Kaiser–Meyer–Olkin (KMO) test (0.804) and Bartlett’s sphericity test ($P < 0.001$) indicated that the dataset was acceptable for use in a PCA. The variance of PC2-PC14 from 7.58%...
to 3.59%, except for PC1 (21.67%), and 14 components out of 16 were extracted with the component loadings rotated with maximum variance. The total cumulative contribution rate was 98.98%. Fe₂O₃, Mn, clay, and CeC possessed the most significant loadings in PC1 (principal component 1), where P and N were significant loadings in PC2. Similarly, significant loadings were found for available Fe in PC3, and available Mn in PC4. Additionally, B, CaO, pH, Mo, TOC, MgO, K, F, clay, and N had relatively higher loadings in PC5 to PC14 (load value > 0.6; Table S1, Figure 8), respectively. The scores obtained from PCA were then used as independent variables in the SMLR analysis to determine the most significant PCs for soil properties and BCF.

![Figure 8.](image)

**Table 3.** The prediction and analysis results of BCF of Cu, Zn, and As in wheat and corn, plus soil properties by PCs-SMLR.

| Crop     | Prediction Models by PC₅-SMLR for Cu, Zn, and As | R     | P     |
|----------|-----------------------------------------------|-------|-------|
| Wheat    | \( \text{Cu}_{\text{BCF}} = 1.268\)*** - 0.034PC₅₁ *** - 0.022PC₅₉ *** + 0.015PC₅₅ * \ | 0.76  | <000  |
|          | \( \text{Zn}_{\text{BCF}} = 1.627\)*** - 0.027PC₅₁ *** - 0.016PC₅₁₄ *** \ | 0.62  | <000  |
|          | \( \text{As}_{\text{BCF}} = -0.611\)*** - 0.085PC₅₅ *** - 0.066PC₅₁₁ *** + 0.045PC₅₁₄ ** \ | 0.56  | <000  |
| Corn     | \( \text{Cu}_{\text{BCF}} = 0.736\)*** - 0.06PC₅₁ *** + 0.055PC₅₁₃ ** - 0.031PC₅₁₀ ** \ | 0.64  | <000  |
|          | \( \text{Zn}_{\text{BCF}} = 1.457\)*** - 0.063PC₅₁₀ *** + 0.033PC₅₆ *** \ | 0.66  | <000  |
|          | \( \text{As}_{\text{BCF}} = -0.955\)*** - 0.172PC₅₇ *** - 0.087PC₅₄ *** \ | 0.58  | <000  |

*Correlation is significant at the \( P < 0.05 \) level; **Correlation is significant at the \( P < 0.01 \) level; ***Correlation is significant at the \( P < 0.001 \) level.

The predictive model R of BCF values for corn Cu is 0.64 \( (P < 0.000) \), where corn Cu is related to the components PC₅₁, PC₅₁₀, and PC₅₁₃. The predictive model R of BCF values for corn Zn is 0.66 \( (P < 0.000) \), where corn Zn is related to the components PC₅₁₀ and PC₅₆. The predictive model R of BCF values for corn As is 0.58 \( (P < 0.000) \), where corn As is related to the components PC₅₇ and PC₅₄.
According to the results of the PC₅-SMLR (Table 3) and the correlation (Table 4), we know that PC₅₁ (Fe₂O₃, Mn, CeC, and clay) and PC₅₉ (TOC) have an impact on the BCF values for Cu in wheat; PC₅₁ (Fe₂O₃, Mn, CeC, and clay) and PC₅₁₄ (N) have a negative impact on the BCF values for Zn in wheat; PC₅₅(B),PC₅₁₁ (K₂O), and PC₅₁₄ (N) have a negative impact on the BCF values for As in wheat. PC₅₁ prevented the migration of Cu and Zn from soil to wheat. Wang et al. (2013) showed that Fe had significant influences on Cu and Zn accumulation in wheat [64]. PC₅₁₄ was considered a component of a nitrogenous fertilizer group, where the application of the fertilizer should promote the BCF of wheat Zn. Zhang et al. (2018) also reported that nitrogenous fertilizers have a positive influence on BCF and should be controlled to an appropriate level [9]. However, as there are differences between other heavy metals and As in the soil, it is important to explain that N competes with As in the soil solid phase of the study area. On the other hand, BCF values for corn As increased with a decrease in pH (Tables 3 and 4). The prediction model also indicated that the Asₜₐₜₜ of corn and PCs₇ (pH) have a negative relationship. The pH is high in the study area, where there is a higher solubility of As(V). The dissolved As(V) easily leaches out and then migrates to the crops [75], leading to As accumulating in crop grains.

Table 4. The relationship between BCF of crop and soil properties.

| Parameters | Corn | Wheat |
|------------|------|-------|
|            | Cuₜₐₜₜ | Znₜₐₜₜ | Asₜₐₜₜ | Cuₜₐₜₜ | Znₜₐₜₜ | Asₜₐₜₜ |
| PH         | 0.39  | −0.104 | −0.443 ** | 0.234 ** | 0.097 | −0.117 |
| CaO        | −0.027 | −0.071 | −0.225 ** | 0.077 | 0.019 | −0.085 |
| MgO        | −0.437 ** | −0.501 ** | −0.281 ** | −0.260 ** | −0.309 ** | −0.221 ** |
| Fe₂O₃      | −0.515 ** | −0.524 ** | −0.130 * | −0.630 ** | −0.505 ** | −0.362 ** |
| K₂O        | −0.235 ** | −0.174 ** | 0.136 * | −0.406 ** | −0.297 ** | −0.081 |
| Mn         | −0.465 ** | −0.523 ** | −0.220 ** | −0.555 ** | −0.476 ** | −0.445 ** |
| P          | −0.122 | −0.046 | 0.148 * | −0.155 * | −0.123 | 0.218 ** |
| N          | −0.250 ** | −0.217 ** | 0.144 * | −0.383 ** | −0.310 ** | 0.152 * |
| F          | −0.380 ** | −0.418 ** | −0.323 ** | −0.352 ** | −0.310 ** | −0.276 ** |
| Mo         | −0.066 | −0.042 | −0.023 | 0.042 | −0.023 | −0.016 |
| B          | −0.010 | −0.112 | −0.354 ** | −0.036 | −0.077 | −0.330 ** |
| TOC        | −0.331 ** | −0.284 ** | 0.063 | −0.512 ** | −0.381 ** | −0.064 |
| CeC        | −0.492 ** | −0.468 ** | −0.225 ** | −0.576 ** | −0.465 ** | −0.392 ** |
| clay       | −0.305 ** | −0.347 ** | −0.073 | −0.378 ** | −0.336 ** | −0.264 ** |
| available Mn | −0.235 ** | −0.158 * | 0.055 | −0.408 ** | −0.236 ** | −0.144 * |
| available Fe | −0.098 | −0.129 | 0.191 ** | −0.298 ** | −0.220 ** | 0.092 |

** Correlation is significant at the p < 0.01 level. * Correlation is significant at the p < 0.05 level.

In addition, a significant negative correlation was found for wheat and corn metal(loid) BCF values and CeC and clay content (Table 4, Tables S2 and S3). This may be because CeC and clay absorb the metal(loid) ions and prevent the metal(loid)s’ migration from soil to crops, thereby decreasing the BCF. Liu et al. (2007) and Zhang et al. (2017) also found that CeC and clay fixed metal(loid)s in soils, making it difficult for the metal(loid)s to migrate to crops [76,77]. However, the correlation results showed that the BCF values for corn Cu and Zn were negatively affected by CeC, TOC, and clay. The BCF value for As was also negatively affected by CeC and clay (Table 4).

Overall, the BCF is very complicated and is related to the type of crops [70] plus the soil physical and chemical properties [78–80]. Zang et al. (2017) also reported that the concentration of metal(loid)s in crops was related to other metal(loid)s [33], and some of them played a role in promoting the enrichment of other metals. Ruiz-Huerta et al. (2017) and Mohamed et al. (2013) also reported that water-soluble and exchangeable levels of metal(loid)s contributed to the BCF [16,36]. Additionally, correlation and prediction models show that the influences of physical and chemical properties on BCF in corn and wheat are different, which may be related to the variation in species. Moreover, the effects of the mobility of metal(loid)s from soil to crop grains are still worthy of further study.
4. Conclusions

In this study, data on metal(loid)s in agricultural soil of Hebei plain of north China were collected as part of a comprehensive approach to evaluating the soil–crop system. According to the distribution and pollution assessment, the average concentrations of Cu, Pb, Zn, Cd, and Hg in soils from the study area were high when compared with the soil background concentration for Hebei province. Cd had especially high concentrations in soil. The Igeo values for soil Cd were higher than 0, which is equivalent to having unpolled to moderately polluted levels. Furthermore, the corresponding crop samples had higher metal(loid) concentrations than the soil food quality limit, indicating an anthropogenic input source. For the BCF, values of metal(loid)s in wheat were significantly higher than in corn, and the Cu, Zn, and Cd concentrations of the two crops were significantly different, with differences in BCF more closely related to variation in species. Based on the results of the health risk assessments, the health risk order is wheat > corn > soil. The risk levels were higher for Cu, Zn, and As than for the other metal(loid)s studied in the system, which showed that a potential health risk existed, especially for children, who are at a greater risk than adults. Adverse health effects are predicted for children and adults who consume wheat and corn, or ingest soil. We suggest taking measurements of the metal(loid)s in staple foods (such as wheat flour). The prediction model of Cu, Zn, and As in wheat and corn showed the different factors influencing metal(loid) BCF values for wheat and corn. The results will provide information crucial for knowing the concentrations of metal(loid)s in wheat and corn. For sustainable agro-ecology development in the study area, special attention should be paid to Cd, Cu, Zn, and As.

Supplementary Materials: The following are available online at http://www.mdpi.com/2076-3417/9/9/1902/s1, Table S1: The results of a Principal Component Analysis for PCs-SMLR; Table S2: The relationship between BCF of wheat and soil properties; Table S3: The relationship between BCF of corn and soil properties.

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