sustainability

MDPI

Article

Pollution and Health Risk Assessment of Carcinogenic Elements As, Cd, and Cr in Multiple Media—A Case of a Sustainable Farming Area in China

Kui Cai [1,2], Chang Li [3], Zefeng Song [4,*], Xin Gao [5] and Moxin Wu [6,*]

1 Institute of Geological Survey, Hebei GEO University, Shijiazhuang 050031, China; kcai@hgu.edu.cn
2 Department of Geological Science & Engineering, Kunsan National University, Jeonbuk 573-701, Korea
3 School of Business Administration, Wonkwang University, Jeonbuk 54538, Korea; changli1007@126.com
4 Institute of Resources and Environmental Engineering, Hebei GEO University, Shijiazhuang 050031, China
5 Business School, Hohai University, Nanjing 211100, China; gxtz1987@hhu.edu.cn
6 Department of Physiology, School of Medicine, Wonkwang University, Jeonbuk 54538, Korea
* Correspondence: zfsong@hgu.edu.cn (Z.S.); wumoxinsbsb@163.com (M.W.)

Received: 29 August 2019; Accepted: 17 September 2019; Published: 23 September 2019

Abstract: The high concentrations of trace elements in the environment, especially the carcinogenic elements Cr, Cd, and As, in populated areas can lead to an increased non-carcinogenic risk and carcinogenic risk in humans via the effective exposure pathways (inhalation and dermal contact). In this study, the concentrations of the trace elements Cd, Cr, and As in four media were comprehensively evaluated by collecting samples from atmospheric precipitates (A), wheat (W), soil (S), and groundwater (G) in the agricultural plain. This study not only considers the health risk level, but also focuses on the relationship between soil properties and the soil–wheat system. First, according to the results of the analysis, the concentration of carcinogenic elements in atmospheric precipitates was higher than that in other media. The sequence follows the order A > S > W > G. Moreover, the input flux of A was at a relatively higher level (determined via an input flux calculation) than other farming areas. Second, the pollution of Cr, Cd, and As in A and S were analyzed using the geoaccumulation method, and the level of Cd reached mild to moderate pollution. In addition, it was found that the bioaccumulation factors (*BAF*s) of Cd were much higher than those of As and Cr in the soil–wheat system. Furthermore, it was found that the negative relationship between *BAF*s and pH, CEC (cation exchange capacity), Corg (soil organic carbon), and clay was significant. Lastly, the hazard quotient (HQ) of the non-carcinogenic risk and carcinogenic risk (CR) of the three elements in multiple media were calculated using the health risk model. The HQ results showed that the total non-carcinogenic risk index (HI) of Cd, As, and Cr in the multiple-media did not exceed the risk limit (1.00), and there was no significant risk to the locally exposed population. However, the total carcinogenic risk index (TCR) indicated that the risk index of Cr, As and Cd in multiple media exceeded the safety index range ($\approx 10^{-6}$–10^{-4}), and the three elements posed a significant carcinogenic risk to local residents via the main pathways. In terms of individual elements, the risk of cancer was highest via the ingestion of the carcinogenic element Cd in G and W.

Keywords: multiple media; soil properties; bioaccumulation factors; carcinogenic risk; health risk model

1. Introduction

Due to the wide range and long duration of trace element pollution, it easily accumulates and becomes stable in the environment, and it is difficult for this pollution to decompose during biological material circulation and energy exchange. Therefore, trace elements experience multi-source,

concealed, long-distance transmission to a certain extent, and have severe pollution consequences [1,2]. In particular, pollution due to the carcinogenic elements Cr, Cd, and As in various media has received extensive attention. Relative to the ranking of the other elements (Pb, Zn, Ni, and Cu), arsenic and inorganic arsenic compounds (ranked no. 11), cadmium and cadmium compounds (ranked no. 25), and chromium (VI) compounds (ranked no. 28) are classified as class 1 carcinogens (amongst 116 species) by the World Health Organization (WHO) International Agency for Research on Cancer (IARC). Long-term exposure to these substances, mainly through drinking water, atmospheric exposure, and food, is higher in soils rich in these substances and can increase the risk of cancer. According to the "soil–crop–body" or "soil–water–body" food chain, the trace carcinogenic elements As, Cd, and Cr are easily accumulated in the body; are seriously harmful to human health; and can produce chronic cumulative effects in the human body through environmental media, such as soils, crops, groundwater, and atmospheric precipitates, and thus generate non-carcinogenic or carcinogenic risks [1–6]. When the human body ingests or inhales excessive trace elements, a series of lesions will be formed in various organs of the body. For example, when the human body is exposed to low doses of Cd for a long time, it may experience renal function damage, bone mineral density reduction, a calcium excretion increase, and reproductive toxicity [7]. Cadmium, which can be carcinogenic, can interfere with the secretion of human estrogen and accumulate in human tissues [1,7]. Arsenic is one of the most common and harmful substances causing human cancer in the current environment [8]. Chromium is an essential trace element in the human body, but if ingested in excess, it may cause kidney and liver damage, nausea, gastrointestinal tract stimulation, spasms, and even death [1,9].

According to the sources of trace elements pollution in various countries, pollution mainly includes industrial discharge [10,11], fertilization [12], mining and smelting [13,14], and sewage irrigation [12,15,16], resulting in intensified pollution. In China, in particular, rapid industrial growth is highly dependent on coal. In 2018, global coal consumption was the equivalent of 3.772 billion tons of oil. Despite the decline in coal consumption in recent years, China still accounts for 50.5% of global coal consumption. Coal-burning has contributed to environmental pollution and the greenhouse effect in northern China, including air pollution in Beijing, Tianjin, and other parts of northern China. Arsenic is also a particularly important element in coal burning. Coal-fired power plants have been identified as an As emission source [17]. It has been reported that plants can absorb harmful elements deposited on the leaves, resulting in the excessive carcinogenic content of crops [18,19]. In this case, carcinogenic element pollution is widespread in air, water, soil, and agricultural products.

It is common for people to use chemical fertilizer blindly and unreasonably. Due to the large number of harmful elements in chemical fertilizers, the harmful elements in soil increase day by day as the fertilizer enters the soil. This concentration is significantly higher than its natural background value, resulting in the destruction of farmland ecology and the deterioration of environmental quality. Fertilizers contain a variety of trace elements, such as As, Cd, and Cr, mainly from industrial sulfuric acid, phosphate ore, sludge, and household waste [10,20,21]. From 2012 to 2017, the total output of wheat, which is one of the main food crops in northern China, increased to 134 million tons. The amount of chemical fertilizers being used increased from 41.46 million tons in 2000 to 58.59 million tons in 2017 [22], which not only increased the grain output but also caused trace element pollution in the soil.

Groundwater resources are scarce in northern China, and in many places, irrigation with innocuous treated sewage is used to replenish agricultural water machines. The problem of carcinogenic element pollution in the soil in China's sewage irrigation areas is serious. According to the second national survey report of the Ministry of Agriculture on sewage irrigation areas, among the statistics on sewage irrigation areas, the agricultural land area affected by carcinogenic element pollution accounts for 64.8% of the total area of sewage irrigation areas [23]. Northern China is also one of the areas with serious trace element pollution. The Jidong plain is located in the Beijing and Tianjin–Tang qin economic zone and belongs to an important supply base of agricultural production in northern China, which is rich in wheat, corn, rice, and other food crops. It is a typical sewage irrigation area in northern China and has used industrial and urban sewage for sewage irrigation for more than 30 years. Although sewage

irrigation can solve the shortage of agricultural water, the trace elements that poisoned the sewage also enter the soil, causing a series of problems for the soil and water environment, ecological safety, and health safety. Meanwhile, industry has developed in the study area—including the production of coal, steel, building materials, chemicals, ceramics, cement, electric power, textiles, papermaking, and food—which has become an important pillar for the economy. The frequent mining activities cause extensive damage to the ecological environment. As an important aspect of agricultural production, safety evaluations of soil, water, and food are of great significance to sustainable development.

In addition, sampling is very important for the assessment of contamination, and the potential use of geostatistics can minimize the number of samples and obtain accurate results [24,25]. The prediction of soil and groundwater pollution distribution based on GIS technology takes into account the spatial variability prediction map obtained by calculating semivariance model parameters to predict the hot spot distribution and more accurately provide a basis for the next steps. The resulting maps are readily available to local authorities, policymakers, and decision-makers for use in soil pollution management and groundwater protection strategies.

Therefore, the main purposes of this study are three-fold: (1) To evaluate the pollution levels of Cr, Cd, and As in atmospheric precipitates, crops, soil, and groundwater. Further, it aimed to assess the relationship between soil properties pH, CEC (cation exchange capacity), Corg (soil organic carbon), and clay, and bioaccumlation factors. (2) To predict the distribution trend of trace elements in multiple media via the semivariance model parameters used. (3) To use the USEPA (US Environmental Protection Agency) health risk model to evaluate the health risks of the three trace elements—Cr, Cd, and As—in each medium to children and adults. This study provides a reference for the prevention and control of Cr, Cd, and As pollution in atmospheric precipitates, crops, soil, and groundwater. This study will not only assess the pollution and health risks for trace elements in multiple media, but also provide insight into the relationship between soil properties (pH, CEC, Corg, and clay) and bioaccumlation factors, with reference to other literature [26–28]. It will provide important value to the sustainable development of agricultural production and the maintenance of a good ecological environment in this research area.

2. Materials and Methods

2.1. Study Area

The research area is located to the east of Hebei province, bordering the Bohai Sea in the east and south, adjacent to Tianjin city in the west and the Yanshan mountain in the north, with a total area of 13,472 km^2. The administrative districts belong to Tangshan (TS) and Qinhuangdao (QHD), including Zunhua, Yutian, Qianxi, Qian'an, Luanxian, Luannan, Laoting, and Tanghai. The geographical coordinates are: 117°31′–119°19′ E, 38°55′–40°28′ N. The local area is a temperate monsoon area with a continental climate. The annual average temperature is 12.3 °C, the annual average precipitation is 650 mm, and the annual evaporation is 1800 mm. The local river system is well developed and can be divided into four river systems: the Luanhe river system, the Sha and Dou river system, the Jihe river system, and the eastern coastal system (Figure 1) [29]. According to the general survey of soil in Hebei province, there are three kinds of soil types in the area, including brown soil, moist soil, and saline soil (non-wheat growing areas) (Figure 2). Jidong plain is located in the Beijing–Tianjin–Tang–Qin Bohai economic zone and is an important agricultural production and supply base in northern China that is rich in wheat, corn, and other food crops and peanuts, as well as cotton and other cash crops. In addition, industrial and mining activities are also very commonplace.

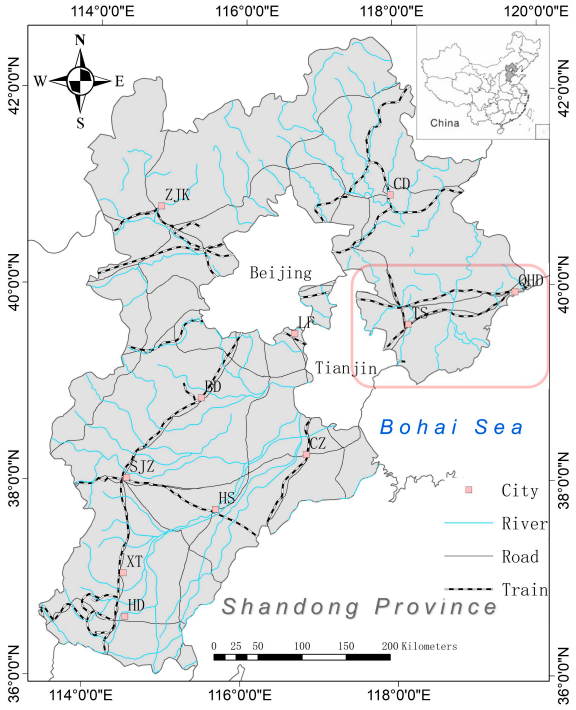


Figure 1. Map of the Jidong farming area (the red region represents the study area).

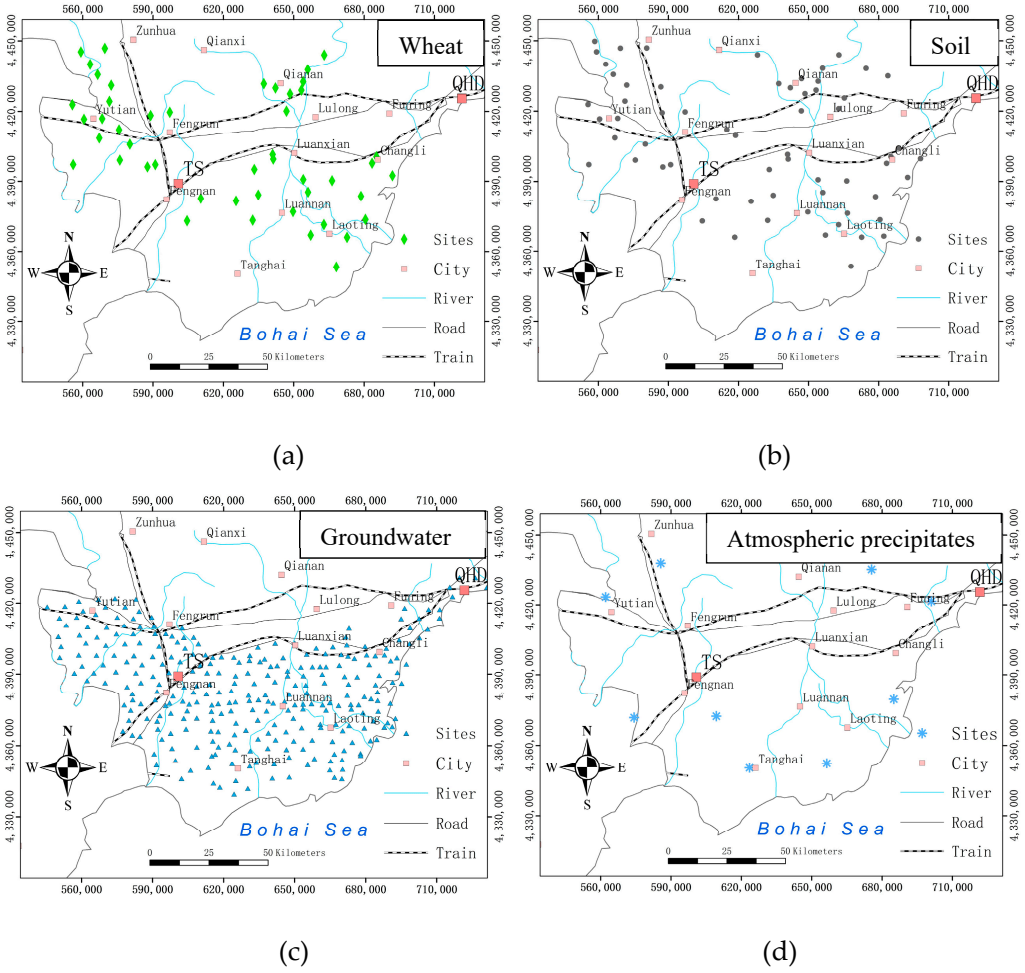


Figure 2. *Cont.*

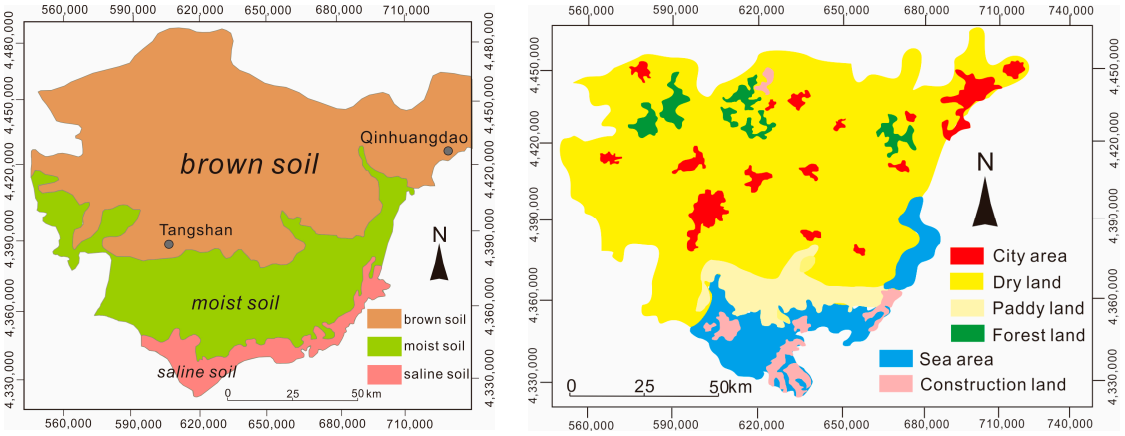


Figure 2. Sampling sites for wheat (**a**), soil (**b**), groundwater (**c**), and atmospheric precipitates (**d**), soil types map (**e**), and land use map (**f**) in the study area.

2.2. Sample Collection and Chemical Analysis

2.2.1. Sample Collection

- Soil and Wheat

Soil (S) and wheat (W) samples were collected during the wheat harvest. A total of 46 pair samples were carried out at random in the wheat planting region of the Jidong plain. The weight of each soil sample collected was 1 kg, the depth of the soil sample was 0–20 cm, and the weight of each fresh wheat sample was about 2 kg. Soil samples taken from fields were placed in a clean storage room and spread in a thin layer on the sample tray. The samples were placed indoors to keep them cool and avoid sunlight exposure. Meanwhile, the samples were strictly prevented from being polluted by other things. The dried S samples were then ground according to the chemical analysis requirements and put into a sample bottle for storage. Next, labels and other marks were made inside and outside the bottle. The W agricultural products were rinsed in a fresh state just after being collected to remove the adhesion soil and pollution caused by fertilization and pesticide spraying and then rinsed with distilled water 1–2 times and dried at room temperature. The samples were sent to the laboratory after passing through a 20-mesh sieve (<0.85 mm). After air-drying and mixing at room temperature, the S samples were reduced to 200 g. An agate pollution-free sample preparation machine was used to smash the samples to 100-mesh sieve (<0.15 mm), and the samples were bagged for later use.

- Atmospheric Precipitates

Twelve atmospheric (A) sampling points were uniformly arranged according to 10 points/10,000 km^2 covering the whole area. Each deposition-collecting cylinder was fixed on the open roof platform about 5–10 m away from the ground, and the sampling port was 1 m–1.5 m away from the platform to avoid the influence of dust on the platform. The dry and wet precipitation period of the receiving atmosphere was one year. The geometry sampler was made of antistatic plastic, and a cylindrical sedimentation tube with a height of about 30 cm, which was topped with a protective nylon mesh cap that prevented foreign matter, such as bird droppings, leaves, etc., from falling into the collecting sampler. Furthermore, in the freezing season, the addition in the cylinder of 60–80 mL 20% ethylene glycol ($C_2H_6O_2$) was considered to prevent freezing. After entering the sampler, the particles settled down to the bottom of the tube due to gravity. The sampler is described in more detail in References [30,31]. As the research area was located in the northern China plain with low rainfall, there was very little water in the barrel at the end of the sampling, making it difficult to collect suspension fluid. Consequently, the barrel was placed indoors to allow natural evaporation to dry the sediment. After weighing the records, the samples were sealed and numbered in the laboratory for testing.

- Groundwater

First, the groundwater (G) samples were prepared with a pH meter, water temperature meter, 1.5 L polyethylene plastic bottle, bottle frame, paper soft partition, measuring cup, wax, HNO_3, NaOH, and H_2SO_4. Chemical reagents were given a blank test and qualified before use. The polyethylene plastic bottle or glass bottle containing the water sample was soaked with 10% HNO_3 or HCl for three days before being washed with distilled water. A total of 295 groups of shallow groundwater samples were taken from wells or artificial digging holes (the samples were collected after the water table had balanced). An instantaneous sampling method was adopted for the G sample collection, and the groundwater body was disturbed as softly as possible during sampling. Before sampling, the well was flushed before the samples were collected. Moreover, the sample bottles were washed and plugged three to five times with the water to be taken, and then the sample bottle was sunk to a depth of 30 cm to collect and process the sample in parallel with the original sample. All samples were collected directly from the well head, and then the samples were sent to the laboratory for analysis, according to the relevant requirements. Sampling was in strict accordance with the relevant standards (HJ 493-2009) [32]. Groundwater As, Cr, and Cd samples were analyzed and measured in strict accordance with GB/T 5750.6-2006 standards [33].

2.2.2. Analytical Method

Soil pH was measured in a suspension of 1:2.5 soil:water using a pH meter. Corg was determined using the potassium dichromate volumetric method. The clay content in the soil sample was determined using a laser analyzer(Malvern Instruments Ltd., Melvin city, UK). The cation exchange capacity (CEC) was determined using the ammonium acetate method.

The content of Cd, Cr, and As in the soil samples was determined after digestion with a mixture of HF, HNO_3, and $HClO_4$ (2:1:1), as well as the use of inductively coupled plasma mass spectrometry (Agilent 7500 Series icp-ms, Agilent Technologies Company, Santa Clara, CA, USA) and atomic fluorescence spectrophotometry.

The contents of Cd, Cr, and As in the wheat grain were determined after being digested with a mixture of $HClO_4$ and HNO_3 (1:3), as well as the use of graphite furnace atomic absorption spectrophotometry (Agilent Technologies Inc., California, USA) and atomic fluorescence spectrophotometry (Beijing HaiGuang instrument co., LTD, Beijing, China). Regarding the analytical method of the trace elements Cr, Cd, and As, refer to the technical standard [34] for a more detailed description (such as digestion methods, standard solution preparation, etc.).

2.2.3. Quality Control

- Soil

By using the GBW07404 and GBW07406 soil standard substances to repeat the analyses, the ΔlgC (ΔlgC = |lgCi − lgCs|) between the measured value and the standard value was calculated, as well as the maximum value and the average value of 0.095 and 0.032, respectively. All ΔlgC were below the permissible limit in the specification for the "Multi-Target Area Geochemical Survey Specification (1:250,000)" [35] and met the requirement of a 100% accuracy qualification rate.

The logarithmic standard deviation (λ) was used for the calculated measurement of GBW07404, while the GBW07406 standard substance was calculated to measure the precision of the sample analysis. The logarithmic standard deviation maximum value was 0.125, and the average value was 0.049, which is less than the standard specification for Cai et al. [36]. The precision acceptance rate was 100%. The detection limits of the method were 0.5 μg/g for As, 0.03 μg/g for Cd, and 5 μg/g for Cr, which met the analysis requirements of the sample.

- Wheat

The use of national standard substances (GBW08503b (wheat flour) and GBW10011 (wheat)) was considered to calculate the relative error (RE) between the mean value of the analysis and the recommended value of the standard samples RE ≤ 30%. The qualification rate of each element in the standard sample was 100%.

A 100% repeat analysis of all submitted samples requires the relative deviation between the two measurements of the same sample RE to be ≤30%. The analysis accuracy (As—99.5%, Cd—99.5%, and Cr—99.9%) of the wheat samples complied with the Technical Requirements for the Analytical Analysis of Eco-geochemical Evaluation [34]. The detection limit of the method was 0.3 μg/g for As, 0.1 μg/g for Cd, and 0.5 μg/g for Cr, which met the analysis requirements of the sample.

- Atmospheric Precipitates

We used national standard soil substances (GBW07404, GBW07406) to calculate the logarithmic difference (ΔlgC) between the measured value and the standard value, in which the maximum value of ΔlgC was 0.092 and the average value was 0.036. All ΔlgC values were less than the allowable limits specified in the "Multi-Target Area Geochemical Survey Specification (1:250,000)" [35], and the pass rate of the primary standard material accuracy was 100%.

The logarithmic standard deviation (λ) was calculated between the measured and monitored values of the standard substance inserted in each batch of passwords, with a maximum λ value of 0.120 and an average value of 0.045, which were all less than the "Multi-Target Area Geochemical Survey Specification (1:250,000)." Requirements were established as the standard 100% qualification rate of standard materials. The reported rate of the element was 100%, which met the requirement of 90%. The detection limit of the method was 0.2 μg/g for As, 0.02 μg/g for Cd, and 3 μg/g for Cr, which met the analysis requirements of the sample [34].

- Groundwater

The samples were analyzed using national standard substances (GBW08603, GBW08608), and the relative error (RE = (Ci − Cs)/Cs) between the single measured value of a single sample and the recommended value of the standard substances was calculated, which required a RE% ≤ 1/$\sqrt{2}$ RD% (RD% as the relative double difference of the sample analysis, which is the difference between the two measurements divided by the mean value). The standard recovery rate was controlled between 95–105%. The detection limit of the method was 0.0004 mg/L for As, 0.05 mg/L for Cd, and 0.004 mg/L for Cr. The quality control was carried out in strict accordance with the DD2005-03 standard [34].

2.3. Input Flux Calculation

The input flux calculation method was based on the "Technical Standard of Geological Survey of China Geological Survey, Technical requirements for regional Eco-geochemical evaluation (DD2005-02)" [30]. Then, we calculated the amount of trace elements Cr, Cd, and As according to the amount of atmospheric precipitation for one year and the area of the collection instrument collecting the precipitation. The calculation formula is as follows:

$$f = \frac{C_X \times m}{\left(\frac{p}{2\pi}\right)^2 \times \pi \times 100} \quad (1)$$

where f is the deposition fluxes from Cr, Cd, and As for one year (g/hm^2·yr); C_X is the concentration of Cd, Cr, and As in the deposition (mg/kg); m is the total collected mass at each sampling site for one year (g/yr); p is the collector perimeter (29.5 cm), and π is 3.14 [36].

2.4. The Calculation of the Pollution Level

The soil geoaccumulation index method proposed by Muller [37] was used to quantitatively evaluate the soil trace metal(loid) pollution in the study area. This method was used to evaluate the degree of trace metal pollution in sediments and define the corresponding pollution level's classification standards (Table 1). This evaluation method can also be used to evaluate the pollution degree of trace metals in the soil. The basic principle model is as follows:

$$\text{Igeo} = \log_2 (C/1.5B) \quad (2)$$

where C is the measured concentration of trace elements, and B is the background value of the corresponding elements [37].

Table 1. The pollution index classification standard and trace elements for Cr, As, and Cd pollution degree classification.

Class	Igeo	Pollution Level	Mean Value (A and S)
0	≤0	Clean	Cr, As
1	0 < Igeo ≤ 1	Mild–moderate	Cd
2	1 < Igeo ≤ 2	Moderate	-
3	2 < Igeo ≤ 3	Moderate–intense	-
4	3 < Igeo ≤ 4	Intense	-
5	4 < Igeo ≤ 5	Intense–strong	-
6	5 < Igeo ≤ 10	Very strong	-

2.5. Bioaccumlation Factors

The bioaccumlation factors (*BAFs*) is a parameter that represents the influence of element content distribution in soil on the food chain and objectively reflects the ability of agricultural products to absorb or uptake trace elements from the soil's environment. This factor is one of the most common indicators of soil element behavior in modern environmental geochemistry research [38,39]. The bioaccumlation factors of this study were the element content in wheat grain compared to the corresponding content of soil. The calculation is expressed as:

$$BAFs = C_{wheat}/C_{soil} \quad (3)$$

where C_{wheat} is the trace element concentration of As, Cd, and Cr in the wheat grain; and C_{soil} is the corresponding element content of As, Cd, and Cr in the soil.

2.6. Health Risk Assessment Model

2.6.1. Health Risk Exposure Model and Parameters

This study used the United States Environmental Protection Agency (USEPA) to provide the HQ (health quotient) and CR (carcinogenic risk) index to quantitatively explain the non-carcinogenic and carcinogenic risk levels from the carcinogenic element content in each medium [40–42]. The main aspects included estimating the amount of pollutants entering the human body and assessing the relationship between the dose and the negative health effects. Specific steps included determining the exposure route, calculating the exposure dose, and calculating and evaluating the exposure risk. The International Center for Research on Cancer (IARC) classifies As, Cd, and Cr as category 1 substances, or "carcinogenic to humans." Therefore, these three carcinogenic elements were assessed for their chronic non-carcinogenic and carcinogenic health risks. According to the migration and transformation characteristics of carcinogenic elements in various media, the main exposure routes of pollutants into the human body are classified into the following three pathways: direct hand–mouth intake, skin contact, and respiratory system inhalation. The amount of pollutant exposure is expressed

as the amount of pollutant exposure per unit time and body weight. The calculation model of different exposure paths is shown in Equations (4)–(9). Referring to the USEPA soil health risk assessment method and related domestic and foreign studies, the values for the specific variables for the calculation of the average daily dose (ADD) of children and adults are shown in Table 2.

- Soil

According to the two major exposure risk pathways (oral and skin), the equation for the average daily dose of the soil is as follows:

$$ADD_{ingestion} = \frac{C_S \times IR_S \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (4)$$

$$ADD_{dermal} = \frac{C_S \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (5)$$

- Wheat

The health risk of carcinogenic elements in wheat mainly comes from oral ingestion, and average daily dose is calculated as follows:

$$ADD_{ingestion} = \frac{Cw \times IR_W \times EF \times ED}{BW \times AT} \quad (6)$$

- Atmosphere Deposition

Atmospheric precipitates mainly harm human health through inhalation. The formula for their average daily dose is as follows:

$$ADD_{inhale} = \frac{C_A \times IR_A \times EF \times ED}{PEF \times BW \times AT} \quad (7)$$

- Groundwater

Groundwater mainly enters the body through ingestion and skin contact, where it can harm human health. The average daily dose is calculated as follows:

$$ADD_{ingestion} = \frac{C_G \times IR_G \times EF \times ED}{BW \times AT} \quad (8)$$

$$ADD_{dermal} = \frac{C_G \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (9)$$

Table 2. The values and significance of the parameters for calculating health risk.

Parameters	Unit and Value	Significance	Reference
C_G	mg/L 95% UCL	Concentration in groundwater	[43,44]
C_S, C_W, C_A,	mg/kg 95% UCL	Exposure-point concentration (soil, wheat, atmospheric precipitates)	[43,44]
EF	365 d/yr	Exposure frequency	[44]
ED	adults 70 yr; children 6 yr	Exposure duration	[44]
AT	365 × ED day	Averaging time for (non)carcinogens	[44]
BW	adults: 70 kg and children: 18 kg	Bodyweight	[45]
SA	adults 5700 $cm^2 \cdot day^{-1}$, children and 2800 $cm^2 \cdot day^{-1}$	Exposed skin area	[45,46]

Table 2. *Cont.*

Parameters	Unit and Value	Significance	Reference
AF	adults 0.07 mg·cm^{-2}, children 0.02 mg·cm^{-2}	Adherence factor	[46]
ABS	0.001	Dermal absorption fraction	[46,47]
PEF	1.36×10^9 m^3·kg^{-1}	Particle emission factor	[46,47]
CF	10^{-6} kg·mg^{-1}	Units conversion factor	[47]
IR_A	adults 16.5 m^3·day^{-1}, children 5.6 m^3·day^{-1}	Respiratory frequency of atmospheric precipitates	[46]
IR_S	adults 100 mg·day^{-1}, children and 200 mg·day^{-1}	Ingestion rate of soil	[47]
IRw	adults 0.250 kg·day^{-1}, children 0.070 kg·day^{-1}	Ingestion rate of wheat	[22]
IR_G	adults 1.82 L person^{-1}·day^{-1}, children 1.06 L person^{-1}·day^{-1}	Ingestion rate of water	[45]
RFD-Cd	RFD ingestion: 1×10^{-3} mg·kg^{-1}·day^{-1}, RFD inhale: 1×10^{-5} mg·kg^{-1}·day^{-1}, RFD dermal: 1×10^{-5} mg·kg^{-1}·day^{-1}	Chronic reference	[47]
RFD-Cr	RFD ingestion: 3×10^{-3} mg·kg^{-1}·day^{-1}, RFD inhale: 2.86 × 10^{-5} mg·kg^{-1}·day^{-1}, RFD dermal: 6×10^{-5} mg·kg^{-1}·day^{-1}		[47]
RFD-As	RFD ingestion: 3×10^{-4} mg·kg^{-1}·day^{-1}, RFD inhale: 1.23×10^{-4} mg·kg^{-1}·day^{-1}, RFD dermal: 1.23×10^{-4} mg·kg^{-1}·day^{-1}		[47]
SF-Cd	SF ingestion: 15 kg·day·mg^{-1}, SF inhale: 6.3 kg·day·mg^{-1}.		[47]
SF-Cr	SF inhale: 4.2×10^1 kg·day·mg^{-1}	Slope factor	
SF-As	SF ingestion: 1.5 kg·day·mg^{-1} SF inhale: 1.51×10^1 kg·day·mg^{-1} SF dermal: 3.66 kg·day·mg^{-1}		[45,47]

IRw (ingestion rate of wheat) was calculated based on the consumption per person from the Statistics Yearbook 2018 [22]. Note: By combining C (exposure point concentration; mg/kg or mg/L) with the values of the above exposure factors, the estimated value of "reasonable maximum exposure" [43] can be attained; that is, the upper limit of the mean value with a 95% confidence interval. Since the concentration of the three carcinogenic elements in each medium sample has an approximately lognormal distribution, the 95% confidence limit is calculated as shown in Equation (8) [48]. The calculation of the exposure point concentration of the logarithmic transformation data is as follows:

$$C_{95\%UCL} = \exp\left\{\overline{X} + 0.5 \times S^2 + \frac{S \times h}{\sqrt{n-1}}\right\} \quad (10)$$

where $\overline{X}$ is the arithmetic mean value after the log is transformed, S is the standard deviation of the data after being log-transformed, h is the h statistic [49,50], and n is the sample number of each medium.

2.6.2. Health Risk Characterization

In the health risk assessment, non-carcinogenic pollutants were estimated by using the non-carcinogenic risk index method:

$$HQi = ADDij/RFDij \quad (11)$$

HQ (hazard quotient) is a non-carcinogenic risk quotient that represents the non-carcinogenic risk of single pollutants in each exposure pathway. RFD refers to the reference dose, indicating the maximum amount of pollutants that will not cause adverse reactions in the human body per unit of

time and body weight. When HQ < 1, the risk is considered small or negligible; when HQ > 1, there is a non-carcinogenic risk. The formula of the total non-carcinogenic risk in each medium is as follows:

$$HI = \Sigma HQij = \Sigma ADDij/RFDij \quad (12)$$

where HQi is the non-carcinogenic health risk index of a single element, and HI is the total non-carcinogenic risk index. When the HI or HQi is greater than 1.0, there is an obvious carcinogenic risk.

Considering the role of exposure in carcinogenic health risk, when calculating the carcinogenic health risk of multiple media, the carcinogenic exposure amount of Cd, Cr, or As is multiplied by its slope factor, as shown in Equation (12):

$$TCRi = \Sigma CR = \Sigma ADDij \times SFij \quad (13)$$

where (T)CR is the (total) carcinogenic risk index in one or more media, and SF is the carcinogenic slope factor corresponding to the carcinogenic elements. When the CR or TCR value is lower than approximately 10^{-6}–10^{-4}, there is basically no cancer risk [40–42].

2.7. Statistical Treatment

The health risk (non-carcinogenic risk) index in the study area was calculated via Excel 2016 (Microsoft Corporation, Redmond, Washington, USA). The statistics (minimum, maximum, mean, and standard deviations) were produced using SPSS 24.0 (IBM, Armonk, NY, USA); the semivariance model (Table 3) and predicted map of the Cr, Cd, and As trace elements in A, W, S, and G was carried out using Surfer 13.0 (Golden Software, LLC., Golden, CO, USA). The correlation matrix between the bioaccumulation factors (Figure 3) and soil properties (pH, Corg, CEC, and clay) was produced using OriginPro 2018 (One Roundhouse Plaza Originlab Corporation, Northampton, MA, USA).

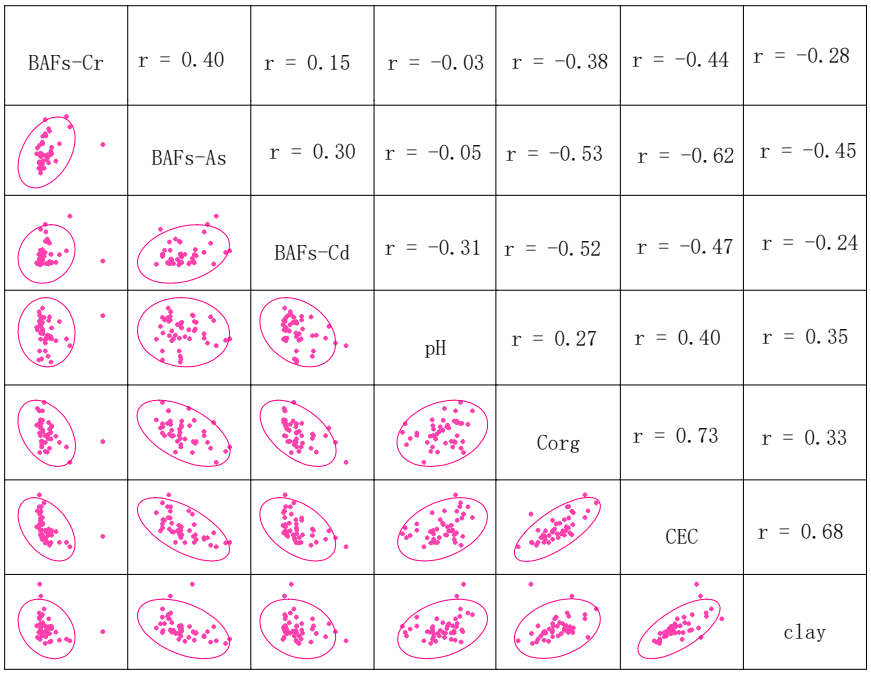


Figure 3. The correlation matrix between the trace elements and soil properties (pH, CEC, Corg, and clay) at a 95% confidence interval.

Table 3. The semivariogram model of the trace elements of Cr, Cd, and As in the soil, wheat, and groundwater in the study area.

Medium	Elements	Nugget (C_0)	Sill ($C_0 + C$)	Range (m)	$C/(C_0 + C)$	R^2	Model
S	Cd	0.019078	0.019078	174890	0.0001	0.648	linear
	Cr	0.011	0.992	880055	0.989	0.766	Gaussian
	As	0.02	0.66	885077	0.970	0.544	Gaussian
W	Cd	0.0001	0.0402	8140	0.998	0.577	Gaussian
	Cr	0.00902	0.02794	26500	0.677	0.426	Gaussian
	As	0.000006	0.000107	6200	0.940	0.205	Spherical
G	Cd	0.0122	0.0447	633000	0.727	0.931	Exponential
	Cr	0.0272	0.0703	25200	0.613	0.870	Exponential
	As	0.1953	0.4056	50400	0.518	0.901	Exponential

Note: S, W, and G represent soil, wheat, and groundwater, respectively.

3. Results and Discussion

3.1. Pollution Level and Distribution

3.1.1. Atmospheric Precipitates

According to the statistical analysis (Table 4), the average value of As was 9.51 mg/kg in the atmospheric precipitates in the Jidong plain, while the average value of Cd was 2.048 mg/kg, and the average value of Cr was 68.51 mg/kg. The average value of As was slightly higher than the local background value of the soil elements (6.73 mg/kg), and Cr was slightly higher than the local background value of the soil elements (66 mg/kg). The average value of Cd was significantly higher (22.76 times higher) than the local background value (0.08 mg/kg). The soil background value was used as the As background content classified by the geoaccumulation index. The mean Igeo of the As (−0.05) and Cr (−0.16) pollution degree indexes were both less than 1, and there was no pollution. The Cd pollution index was 1.14, which indicates a mild to moderate pollution level.

Table 4. Descriptive statistics of the Cr, Cd, and As trace elements in A, S, W, and G in the study area (unit: mg/kg).

Medium	Statistics	Cr	Cd	As
A	Min	57.50	0.70	5.28
	Max	89.00	5.1800	14.54
	Mean	68.510	2.048	9.51
	Standard deviation	10.658	1.489	3.0871
S	Min	21.3000	0.050	2.80
	Max	172.2000	0.31	16.60
	Mean	63.4625	0.1492	7.0558
	Standard deviation	26.3238	0.0513	2.9678
	Local background	66	0.08	6.73
	Risk limit	250	0.6	25
W	Min	0.0140	0.0230	0.0020
	Max	0.1400	0.1800	0.0500
	Mean	0.0359	0.0554	0.0208
	Standard deviation	0.0180	0.0313	0.0104
	Food limit	1	0.1	0.5
G	Min	0.0008	0.0004	0.0004
	Max	0.0240	0.0021	0.1100
	Mean	0.0015	0.0005	0.0063
	Standard deviation	0.0018	0.0003	0.0128
	Risk limit	0.1	0.01	0.05

Note: A, S, W, and G represent atmospheric precipitates, soil, wheat, and groundwater, respectively.

The mean concentration of Cr in the atmospheric precipitates was lower than that in the domestic cities of Lanzhou (80.69 mg/kg) [51], Harbin (87.1 mg/kg) [52], and Nanjing (135.7 mg/kg) [53]. It was much lower than the national average of atmospheric precipitates (Cd (4.68 mg/kg), Cr (174.18 mg/kg), and As (28.98 mg/kg) [54].

According to the atmospheric precipitate flux Equation (1), the mean values of the three trace elements were As (16.8 g/hm^2·yr), Cd (2.83 g/hm^2·yr), and Cr (118.38 g/hm^2·yr). Compared with other cities or agricultural areas, these values were higher than for Cd (0.7 g/hm^2·yr) and Cr (64.3 g/hm^2·yr) in the Pearl River Delta of China [55] and close to the mean flux values of Cd (2.36 g/hm^2·yr) and Cr (118.55 g/hm^2·yr) in the plain area of Beijing, which was less than As (29 g/hm^2·yr) [56]. These values were lower than the mean values of Cd (5.27 g/hm^2·yr) and Cr (144.0 g/hm^2·yr); higher than As (7.61 g/hm^2·yr) in the western Chongqing agricultural area [57]; and higher than Cd (1.46 g/hm^2·yr), Cr (72.89 g/hm^2·yr), and As(10.93 g/hm^2·yr) in the farming area, Ganan County, Heilongjiang Province [58]. Compared with values from other nations, the mean value of Cd was higher than Cd in the urban area of Varanasi in India (1.21 g/hm^2·yr) [59] and Northern France's Agrosystem (0.47 g/hm^2·yr) [60].

3.1.2. Soil

The mean value of pH, CEC (cation exchange capacity), clay, and Corg (organic carbon) in the study area were 7.38 (dimensionless), 11.72 × 10^{-6} (dimensionless), 92.46 g/kg, and 0.98%. Meanwhile, the range of the pH, CEC, clay, and Corg in the study area were 6.2–8.3, (2.7–27.4) × 10^{-6}, 16.2–270.6 g/kg, and 0.16–1.77%, respectively.

The statistical results of the contents of Cr, Cd, and As in the soil are shown in Table 4. The contents of the carcinogenic elements in the soil were as follows: Cr (21.3–172.2 mg/kg), Cd (0.05–0.31 mg/kg), and As (2.8–16.6 mg/kg) (Figure 4). The average value of Cr (63.46 mg/kg) was lower than the local soil background value, while the average values of Cd (0.15 mg/kg) and As (7.06 mg/kg) were higher than the local soil background value, exceeding the average by 1.86 times and 1.05 times, respectively. However, the maximum content of trace elements was at the safety limit of the agricultural soil [61]. In terms of the local geoaccumulation pollution index, Cd presented mild pollution, while Cr and As did not reach a pollution state. However, there were individual samples that evidenced contamination levels for all three trace elements. In total, 11 samples of As, six samples of Cr, and 42 samples of Cd accounted for 17.19%, 9.38%, and 65.63% of the soil samples, respectively.

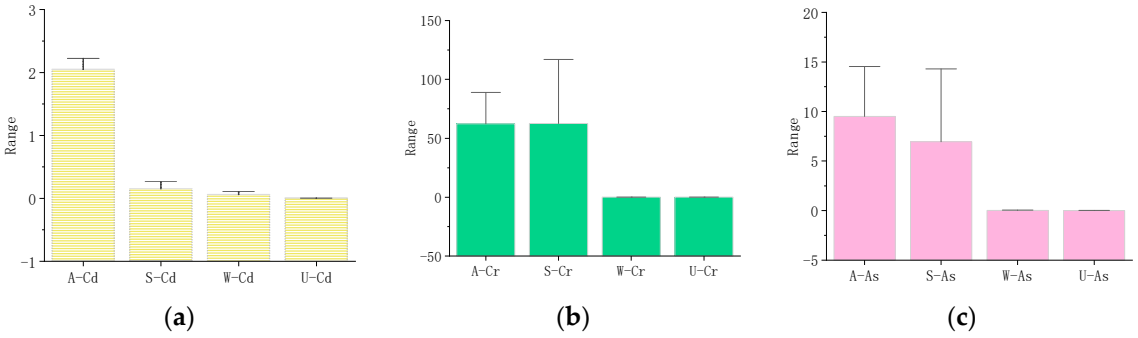
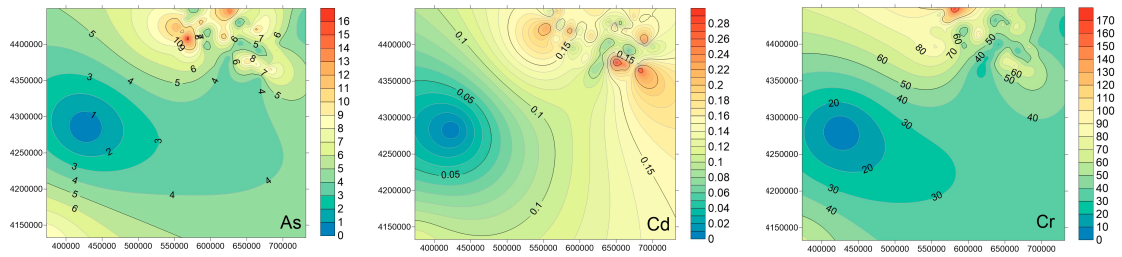


Figure 4. The error bars of the trace elements Cd, Cr, and As in the study area (A, atmospheric precipitates; S, soil; W, wheat; G, groundwater): (**a**) the contents levels with error bars for Cd, (**b**) the content levels with error bars for Cr, and (**c**) the content levels with error bars for As.

The content of this soil sample was lower than that of As (11.29 mg/kg) and Cr (77.59 mg/kg), and higher than that of Cd (0.113 mg/kg) in the Yangtze River delta plain [62]. The average value of Cr (63.46 mg/kg) was higher than that of Cr (52.2 mg/kg) in the cultivated land of Pakistan, and the average value of Cd (0.15 mg/kg) was lower than that of Cd (1.11 mg/kg) in the cultivated land of Pakistan [1].

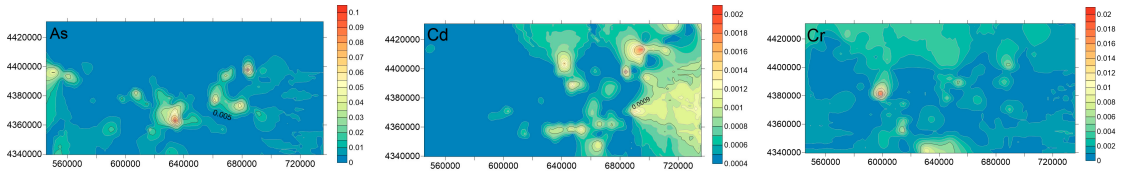
According to the contour distribution map (Figures 5–7), the high-value area of Cd was mainly concentrated around Tanghai county, forming a large area with a Cd anomaly. The terrain of this

abnormal area is high in the north and low in the south. The local river channels are interlaced, and the river systems are developed. Due to the numerous depressions in the south and the poor flow of the river, Cd is transported mechanically, especially those related to clay minerals. The Cd easily adheres to the clay mineral migration, forming a high content area. In addition, local sewage irrigation has a history of more than 20 years, and the application of fertilizers, pesticides, and local atmospheric subsidence may also contribute to the accumulation of Cd [63]. The Cd enrichment degree, and its causes in the coastal areas of eastern Hebei, show that there was a high concentration of Cd in the shallow soil of eastern Hebei that originated from human activities [64]. The overall enrichment degree of Cr in the surface soil of the Jidong plain was not high, but it was higher in some areas (mainly concentrated in Zunhua, near Qian'an, and the southern region of Tangshan). The mining of mineral resources in Zunhua, Qian'an, and other places may be the main reason for this high Cr content, while the high Cr content in the farmland area in the south was mainly caused by local human activities (such as the application of pesticides and fertilizers, sewage irrigation, etc.).The overall enrichment degree of As on the surface of the Jidong plain was not high. However, there was some enrichment in certain areas, mainly distributed in Yutian and the southern area of Tangshan. The high concentration in Yutian may be mainly caused by the development of local mineral resources and industrial pollution, while the high content in the farmland areas in the south of Tangshan may be caused by the unreasonable application of local phosphate fertilizers.



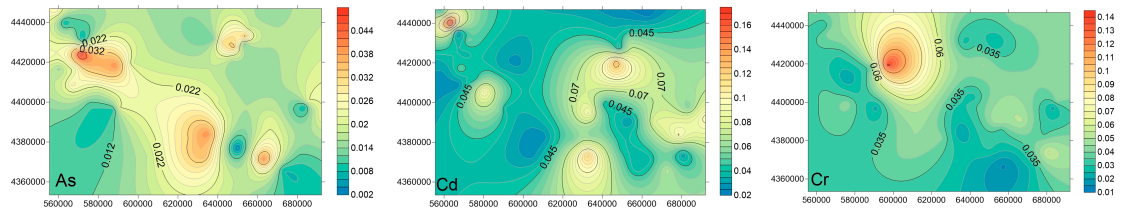
(**a**) (**b**) (**c**)

Figure 5. The predicted map of Cr, Cd, and As in S in the Jidong plain area: (**a**) the predicted map of As in the study area, (**b**) the predicted map of Cd in the study area, and (**c**) the predicted map of Cr in the study area.



(**a**) (**b**) (**c**)

Figure 6. The predicted map of Cr, Cd, and As in G in the Jidong plain area: (**a**) the predicted map of As in the study area, (**b**) the predicted map of Cd in the study area, and (**c**) the predicted map of Cr in the study area.



(**a**) (**b**) (**c**)

Figure 7. The predicted map of Cr, Cd, and As in W in the Jidong plain area: (**a**) the predicted map of As in the study area, (**b**) the predicted map of Cd in the study area, and (**c**) the predicted map of Cr in the study area.

3.1.3. Wheat

Trace elements in soil can be absorbed into plants through the roots of crops and accumulated in different organs and tissues of crops. If a large number of trace elements accumulate in the edible parts of crops, the transfer of trace elements through the food chain will have a serious impact on the human body. The carcinogenic element content in the wheat collected from cultivated soil in the study area is shown in the table. According to the maximum levels of contaminants in foods (GB2762-2012) [65], all the trace elements were at a safe level: 0.1 mg/kg for Cd; 1 mg/kg for Cr; and 0.5 mg/kg for As. The sample concentration range of the trace elements was 0.014–0.14 mg/kg for Cr; 0.023–0.18 mg/kg for Cd; and 0.002–0.05 mg/kg for As (Figure 4). For the average value, the Cd (0.055 mg/kg), Cr (0.036 mg/kg), and As (0.021 mg/kg) in wheat did not exceed the food limit. However, four samples (0.1 mg/kg, 0.12 mg/kg, 0.13 mg/kg, 0.18 mg/kg) of Cd exceeded the food limit. The intake of wheat with excessive Cd content poses a potential risk to human health, which deserves further attention.

The content of wheat in local areas was lower than that in domestic and foreign areas. As and Cr were lower than As (0.16 mg/kg) and Cr (0.12 mg/kg) in Zhengzhou in the south–north China plain [3]. Cd was higher than Cd (0.018 mg/kg) in Zhengzhou in the south–north China plain. Cd was higher than the value of the foreign Pakistani (Swabi) area (0.025 mg/kg) and much lower than As (0.184 mg/kg) and Cr (0.138 mg/kg) [66].

The bioaccumlation factors of Cr, As, and Cd from wheat to soil (calculated using Equation (3)) were: 0.069%, 0.364%, and 45.927%, respectively. This result indicates that the bioaccumulation factors of Cd (close to 50%) were far higher than those of Cr and As. Building the relationship between the trace elements and soil properties (pH, CEC, Corg, and clay) in this study (Figure 3) showed the negative correlation of soil properties and the bioaccumulation factors of Cr, As, and Cd. The correlation coefficient of soil properties and the bioaccumulation factors for Cr, As, and Cd (at $p < 0.01$) were −0.03, −0.05, and −0.31 for pH; −0.38, −0.53, and −0.52 for Corg; −0.44, −0.62, and −0.47 for CEC; and −0.28, −0.45, and −0.24 for clay, respectively.

Furthermore, the statistics of Cr, As, and Cd in the wheat–soil system with brown soil and moist soil are summarized Table 5, which was based on soil types in the Jidong plain (Figure 2). The results indicate no significant differences in the bioaccumulation factors of the brown soil and moist soil of the research regions (Table 5). Therefore, the influence of soil type was not the main factor for bioaccumulation. In addition, the physiological characteristics of wheat were also important factors affecting the bioaccumulation factors [67–69]. The high-level bioaccumulation factors of Cd need to also be considered as an important next step in further studies.

Table 5. The statistical parameters and property differences between soil types in the study area (unit: mg/kg).

Soil Types/Sample Numbers	Elements	Minimum	Maximum	Mean Value	BAFs (%)
Brown soil/28	As_{soil}	2.8	16.6	7.11	0.35
	As_{wheat}	0.007	0.05	0.02	
	Cd_{soil}	0.067	0.23	0.14	44.79
	Cd_{wheat}	0.023	0.18	0.056	
	Cr_{soil}	26.0	112.1	64.75	0.07
	Cr_{wheat}	0.022	0.14	0.037	
Moist soil/18	As_{soil}	2.8	10.5	6.03	0.39
	As_{wheat}	0.002	0.041	0.02	
	Cd_{soil}	0.05	0.31	0.15	47.85
	Cd_{wheat}	0.027	0.12	0.055	
	Cr_{soil}	25.0	92.6	55.39	0.07
	Cr_{wheat}	0.014	0.057	0.035	

3.1.4. Groundwater

According to China's groundwater quality and human health risks, and considering drinking water, industry, agriculture, and other water quality requirements [70,71], we take category 4 as the most critical value of health risk assessment (Cr ≤ 0.1 mg/L, Cd ≤ 0.01 mg/L, As ≤ 0.05 mg/L). It can be seen that the mean value of Cr (0.0015 mg/L), Cd (0.0005 mg/L) in the groundwater in the Jidong plain were all less than the health risk value. Moreover, the Cr value reached the level 1 standard, the Cd value reached the level 2 standard, and the groundwater was suitable for various purposes [70,71]. The average value of As (0.0063 mg/L) was less than the level 4 health risk value, which was suitable for agriculture and some industrial water, and could also be used as domestic drinking water after proper treatment. According to the WHO (provisional) guidelines for drinking water (Cd, 0.003 mg/L; Cr 0.05 mg/L and As, 0.01 mg/L) [7], these averages are safe. However, six values of the As samples (0.052 mg/L, 0.0525 mg/L, 0.0611 mg/L, 0.066 mg/L, 0.1007 mg/L, 0.11 m g/L) exceeded the health risk values. The reasons for this increased health risk were as follows: (1) This risk was related to As in the soil, as the area east of Hebei province has a long history of industry. (2) Rural coal ash, firewood ash, and other household wastes were dumped in significant quantities by the river. All these substances contain a certain amount of As. (3) In industrial production, the heat treatment of raw materials, fuel combustion, waste incineration, and other processes were released into water sources. (4) Agricultural land was the main land use mode of water sources. (5) The higher concentrations of As, Cd, and Cr in groundwater may be related to land use. As such, city lands have higer concentrations than other land types (Figure 2). It was also found in the survey that industrial gas emissions and straw burning are common in agriculture.

3.2. Health Assessment

3.2.1. Noncarcinogenic Risk Assessment

According to Equations (11) and (12), the HQ (health quotient) and HI (total health quotient index) values of Cr, Cd, and As in the three pathways in the four media were calculated and are summarized in Table 6. The non-carcinogenic health risks of Cr, Cd, and As caused by the three exposure pathways in the exposed population were evaluated using the target risk coefficient method. The HQ and HI values for both adults and children were less than 1. These results show that the Cr, Cd, and As in wheat had no obvious health risks to the locally exposed population through the three pathways. For children, the risk index HI was 0.55, which was higher than the risk index of adults (0.40), indicating that Cr, Cd, and As posed a greater non-carcinogenic health risk to local children than to adults via the three pathways. This result may be related to the physical qualities of children and the different daily intakes of adults and children. In terms of individual elements, the multi-pathway Cr (through the three pathways) posed a higher risk to adults and children than Cd and As. Through the above study, it was found that although Cd mildly to moderately contaminated the soil, and some samples of Cd in wheat exceeded the standard, Cd did not significantly pose a non-carcinogenic risk. The risk posed by As to the human body was in the highest order of magnitude (10^{-1}), and therefore posed the greatest risk. Three kinds of trace elements did not constitute significant health risks, but there is usually a variety of trace elements that compound pollution in a natural environment. Therefore, evaluating the three kinds of trace elements based only on population health risks has some limitations and cannot be fully reflected in a variety of cases where the compounded pollution has exposed people to health risks. In addition, the study area in this paper is in the eastern Hebei province. The diet structure of other populations may be different, so the study has a possible deviation relative to other areas.

Table 6. The noncarcinogenic health risk calculation of the trace elements Cr, Cd, and As in A, S, W, and G in the Jidong plain area.

Medium	Health Index	Cr	Cd	As	
A-inhale	ADD-a	2.75×10^{-7}	3.76×10^{-10}	4.20×10^{-8}	
	ADD-c	4.66×10^{-7}	6.38×10^{-10}	7.11×10^{-8}	
	HQ-a	9.61×10^{-3}	3.76×10^{-5}	3.41×10^{-4}	
	HQ-c	1.63×10^{-2}	6.38×10^{-5}	5.78×10^{-4}	
S-ingestion	ADD-a	6.49×10^{-5}	5.09×10^{-7}	7.22×10^{-6}	
	ADD-c	1.05×10^{-4}	8.27×10^{-7}	1.17×10^{-5}	
	HQ-a	2.16×10^{-2}	5.09×10^{-4}	2.41×10^{-2}	
	HQ-c	3.52×10^{-2}	8.27×10^{-4}	3.91×10^{-2}	
S-dermal	ADD-a	3.56×10^{-7}	8.37×10^{-10}	3.96×10^{-8}	
	ADD-c	1.94×10^{-7}	4.57×10^{-10}	2.16×10^{-8}	
	HQ-a	5.94×10^{-3}	8.37×10^{-5}	3.21×10^{-4}	
	HQ-c	3.24×10^{-3}	4.57×10^{-5}	1.76×10^{-4}	
W-ingestion	ADD-a	7.04×10^{-5}	1.74×10^{-4}	6.50×10^{-5}	
	ADD-c	1.40×10^{-4}	2.16×10^{-4}	8.11×10^{-5}	
	HQ-a	2.35×10^{-2}	6.50×10^{-2}	2.17×10^{-1}	
	HQ-c	4.67×10^{-2}	8.11×10^{-2}	2.70×10^{-1}	
G-ingestion	ADD-a	4.42×10^{-8}	1.53×10^{-5}	1.86×10^{-7}	
	ADD-c	4.71×10^{-8}	2.80×10^{-5}	3.06×10^{-7}	
	HQ-a	1.47×10^{-5}	1.53×10^{-2}	6.19×10^{-4}	
	HQ-c	1.57×10^{-5}	3.05×10^{-2}	1.02×10^{-3}	
G-dermal	ADD-a	2.91×10^{-7}	1.00×10^{-10}	1.22×10^{-6}	
	ADD-c	4.89×10^{-7}	1.69×10^{-10}	2.05×10^{-6}	
	HQ-a	4.85×10^{-3}	1.00×10^{-5}	9.93×10^{-3}	
	HQ-c	8.15×10^{-3}	1.69×10^{-5}	1.67×10^{-2}	
Total	HI-a	6.55×10^{-2}	8.10×10^{-2}	2.52×10^{-1}	0.40
	HI-c	1.10×10^{-1}	1.12×10^{-1}	3.28×10^{-1}	0.55

Note: A, S, W, and G represent atmospheric precipitates, soil, wheat, and groundwater, respectively. The abbreviation a represents adults and c represents children, respectively. ADD—average daily dose; HQ—health quotient.

3.2.2. Carcinogenic Risk Assessment

Through Equation (13) and the parameter calculation, the average value of the carcinogenic risks of Cr, As, and Cd in multiple media in the Jidong plain was determined (Table 7) as follows: TCR-Adult: Cr (1.15×10^{-5}), Cd (2.84×10^{-3}), and As (1.14×10^{-4}); TCR-Child: Cr (1.96×10^{-5}); Cd (3.68×10^{-3}); and As (1.48×10^{-4}). The Cr, Cd and As carcinogenic risk index exceeded the safe index range of 10^{-6} to 10^{-4}; therefore, the three elements can be considered to have a carcinogenic risk. For single elements, wheat (adult—2.60×10^{-3}; children—3.24×10^{-3}) and groundwater (adult—2.29×10^{-4}; children—4.19×10^{-4}) had the highest carcinogenic risk index, since the Cd intake exceeded the safe values needed to avoid the danger of carcinogenic risk on human health. The order of the risk of carcinogens was Cd > As > Cr.

This study used the carcinogenic element pollutants in an exposed groundwater pathway as the evaluation method for human health risk without considering other toxic materials (such as persistent organic pollutants (POPs)); therefore, the real total health risk of the carcinogenic elements in the environment far exceed the risk value in the study. In addition, the risk of groundwater exposure was closely related to factors such as people's consumption habits and types of occupations, which need more complex exposure evaluation methods to obtain their pollutant exposure doses. The average life expectancy of the population was taken to be the average human life expectancy of 70 years rather than the population's average life expectancy in the local area, which also created uncertainty. The health risk assessment of groundwater pollutants in the preliminary study also needs to be further improved in future work. In conclusion, the study area's groundwater carcinogens cause particular harm to

people's health through drinking water, which should not be ignored, and ought to arouse the attention of environmental protection departments.

Table 7. The carcinogenic risk calculation of the carcinogenic elements, Cr, Cd, and As by inhalation, ingestion, and dermal pathways in A, S, W, and G in the Jidong plain area.

Medium	Health Index	Cr	Cd	As	
A-inhale	CR-a	1.15×10^{-5}	2.37×10^{-9}	6.33×10^{-7}	
A-inhale	CR-c	1.96×10^{-5}	4.02×10^{-9}	1.07×10^{-6}	
S-ingestion	CR-a	-	7.63×10^{-6}	1.08×10^{-5}	
S-ingestion	CR-c	-	1.24×10^{-5}	1.76×10^{-5}	
S-dermal	CR-a	-	-	1.45×10^{-7}	
S-dermal	CR-c	-	-	7.91×10^{-8}	
W-ingestion	CR-a	-	2.60×10^{-3}	9.76×10^{-5}	
W-ingestion	CR-c	-	3.24×10^{-3}	1.22×10^{-4}	
G-ingestion	CR-a	-	2.29×10^{-4}	2.78×10^{-7}	
G-ingestion	CR-c	-	4.19×10^{-4}	4.59×10^{-7}	
G-dermal	CR-a	-	-	4.47×10^{-6}	
G-dermal	CR-c	-	-	7.51×10^{-6}	
Total	TCR-a	1.15×10^{-5}	2.84×10^{-3}	1.14×10^{-4}	2.97×10^{-3}
	TCR-c	1.96×10^{-5}	3.68×10^{-3}	1.48×10^{-4}	3.84×10^{-3}

Note: A, S, W, and G represent atmospheric precipitates, soil, wheat, and groundwater, respectively. Abbreviation a represents adults and c represents children. CR—carcinogenic risk; TCR—total carcinogenic risk.

4. Conclusions

In this study, the trace elements of Cr, Cd, and As in atmospheric precipitates, wheat, soil, and groundwater were comprehensively evaluated. First, the concentration of the trace elements in each medium was compared with the corresponding safety values; four samples of Cd in W and six samples of As exceeded the safety limit. We suggest that local departments and governments pay greater attention to these issues. The concentration of trace elements was highest in the atmospheric precipitates, and the mean values of the input flux of the three trace elements were As (16.8 g/hm^2·yr), Cd (2.83 g/hm^2·yr), and Cr (118.38 g/hm^2·yr), higher than values for other cities or agricultural areas. Second, Cd pollution levels in the soil and atmospheric precipitates were at mild–moderate levels and also need special attention. The mean value for the *BAF*s of Cd in the soil–wheat was highest (45.927%) and had a significant negative correlation with pH, CEC, Corg, and clay; these factors were insignificant with regard to other soil types. Lastly, we calculated the HI index of Cr, Cd, and As through three major pathways in multiple media. The children's HI risk index was 0.55, which was higher than the adult's risk index (0.40), showing that Cr, Cd, and As, through three pathways, presented greater health risks to children than to adults but did not exceed the safety limits (1.00). It is important to note that the TCR index of Cr, Cd and As exceeded the range of the safety index (10^{-6}–10^{-4}). Thus, the three elements pose a significant carcinogenic risk to the local human body. Most importantly, the highest CR index of Cd was found in wheat and groundwater.

There are some limitations to the scope of our study. (1) After investigation, the main sources of drinking water for local residents, including groundwater and water from the water supply company, and the trace elements in two drinking water sources, should be separately evaluated. (2) In the health risks assessment, respiratory contact with trace elements in the soil and skin contact with trace elements in the atmosphere were not calculated. (3) Wheat intake was calculated through total consumption according to the statistical yearbook and was not investigated through questionnaires, so there may be some deviation. Nevertheless, the results of this study provide a valuable reference for the local environmental department to accurately determine the harm to and from the environment.

Author Contributions: Conceptualization, K.C. and Z.S.; methodology, K.C.; software, C.L., M.W., and X.G.; formal analysis, K.C.; investigation, K.C. and Z.S.; data curation, K.C.; writing—original draft preparation, K.C. and Z.S.; writing—review and editing, Z.S. and M.W.; project administration, K.C and C.L.

Funding: This study was financially supported by the Science and Technology Research Project of Institutions of Higher Learning of Hebei Province (No. QN2018131) and the Social Science Development Research Project of Hebei Province (No.201803020211).

Acknowledgments: The authors would like to express their appreciations to the anonymous reviewers and the editors.

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

References

1. Huma-Khan, N.; Nafees, M.; Bashir, A. Study of heavy metals in soil and wheat crop and their transfer to food chain. *Sarhad J. Agric.* **2016**, *32*, 70–79. [CrossRef]
2. Yaseen, I.A.A.B.; Al-Naeem, T.A. Assessment of Groundwater Pollution with Heavy Metals at the Al-Akaider Landfill Area, North Jordan. *Res. J. Environ. Earth Sci.* **2018**, *10*, 16–23. [CrossRef]
3. Liu, W.X.; Liu, J.W.; Wu, M.Z.; Li, Y.; Zhao, Y.; Li, S.R. Accumulation and Translocation of Toxic Heavy Metals in Winter Wheat (Triticum aestivum L.) Growing in Agricultural Soil of Zhengzhou, China. *Bull. Environ. Contam. Toxicol.* **2009**, *82*, 343–347. [CrossRef] [PubMed]
4. Afzal, M.; Shabir, G.; Iqbal, S.; Mustafa, T.; Khan, Q.M.; Khalid, Z.M. Assessment of Heavy Metal Contamination in Soil and Groundwater at Leather Industrial Area of Kasur, Pakistan. *CLEAN Soil Air Water* **2013**, *42*, 1133–1139. [CrossRef]
5. Yang, K.; Yu, Z.; Luo, Y.; Yang, Y.; Zhao, L.; Zhou, X. Spatial and temporal variations in the relationship between lake water surface temperatures and water quality—A case study of Dianchi Lake. *Sci Total Environ.* **2018**, *624*, 859–871. [CrossRef]
6. Mondal, D.; Ganguli, B.; Sen Roy, S.; Halder, B.; Banerjee, N.; Banerjee, M.; Samanta, M.; Giri, A.K.; Polya, D.A. Diarrhoeal Health Risks Attributable to Water-Borne-Pathogens in Arsenic-Mitigated Drinking Water in West Bengal are Largely Independent of the Microbiological Quality of the Supplied Water. *Water* **2014**, *6*, 1100–1117. [CrossRef]
7. World Health Organization (WHO). *Cadmium in Drinking-Water. Background Document for Preparation of WHO Guidelines for Drinking-Water Quality*; World Health Organization: Geneva, Switzerland, 2003.
8. World Health Organization (WHO). *Arsenic in Drinking-Water. Background Document for Preparation of WHO Guidelines for Drinking-Water Quality*; World Health Organization: Geneva, Switzerland, 2003.
9. World Health Organization (WHO). *Chromium in Drinking-Water. Background Document for Preparation of WHO Guidelines for Drinking-Water Quality*; World Health Organization: Geneva, Switzerland, 2003.
10. Maqbool, A.; Xiao, X.; Wang, H.; Bian, Z.; Akram, M.W. Bioassessment of Heavy Metals in Wheat Crop from Soil and Dust in a Coal Mining Area. *Pollution* **2019**, *5*, 323–337.
11. Osma, E.; Serin, M.; Leblebici, Z.; Aksoy, A. Assessment of Heavy Metal Accumulations (Cd, Cr, Cu, Ni, Pb, and Zn) in Vegetables and Soils. *Pol. J. Environ. Stud.* **2013**, *22*, 1449–1455.
12. Wang, Q.R.; Dong, Y.; Cui, Y.; Liu, X. Instances of Soil and Crop Heavy Metal Contamination in China. *Soil Sediment. Contam. An. Int. J.* **2001**, *10*, 497–510.
13. Nnabo Paulinus, N. Assessment of Heavy Metal Contamination of Water Sources from Enyigba Pb-Zn District, South Eastern Nigeria. *Int. J. Sci. Technol. Res.* **2015**, *4*, 186–196.
14. Okegye, J.I.; Gajere, J.N. Assessment of Heavy Metal Contamination in Surface and Ground Water Resources around Udege Mbeki Mining District, North-Central Nigeria. *J. Geol. Geophys.* **2015**, *4*, 1–7. [CrossRef]
15. Hassan, N.U.; Mahmood, Q.; Waseem, A.; Irshad, M.; Faridullah; Pervez, A. Assessment of Heavy Metals in Wheat Plants Irrigated with Contaminated Wastewater. *Pol. J. Environ. Stud.* **2013**, *22*, 115–123.
16. Sharma, R.K.; Agrawal, M.; Marshall, F.M. Metals contamination in vegetables grown in wastewater irrigated areas of Varanasi, India. *B Environ. Contam. Toxicol.* **2006**, *77*, 312–318. [CrossRef] [PubMed]
17. Zhao, C.; Luo, K. Household consumption of coal and related sulfur, arsenic, fluorine and mercury emissions in China. *Energy Policy* **2018**, *112*, 221–232. [CrossRef]

18. Agrawal, M. *Enhancing Food Chain Integrity: Quality Assurance Mechanism for Air Pollution Impacts on Food and Vegetable System*; Final Technical Report (R7530); Department for International Development: London, UK, 2003.
19. Pandey, J.; Pandey, U. Atmospheric Deposition and Heavy Metal Contamination in an Organic Farming System in a Seasonally Dry Tropical Region of India. *J. Sustain. Agric.* **2009**, *33*, 361–378. [CrossRef]
20. Bose, S.; Bhattacharyya, A.K. Heavy metal accumulation in wheat plant grown in soil amended with industrial sludge. *Chemosphere* **2008**, *70*, 1264–1272. [CrossRef]
21. Abtahi, M.; Fakhri, Y.; Oliveri Conti, G.; Keramati, H.; Zandsalimi, Y.; Bahmani, Z.; Ghasemi, S.M. Heavy metals (As, Cr, Pb, Cd and Ni) concentrations in rice (Oryza sativa) from Iran and associated risk assessment: A systematic review. *Toxin Rev.* **2017**, *36*, 331–341. [CrossRef]
22. National Bureau of Statistics of China. *China Statistical Yearbook 2018*; China Statistical Press: Beijing, China, 2018.
23. Zhang, X.M.; Zhang, X.Y.; Zhong, T.Y.; Jiang, H. Spatial distribution and Accumulation of Heavy Metal in Arable Land Soil of China. *Environ. Sci.* **2014**, *35*, 693–699.
24. Bartzas, G.; Tinivella, F.; Medini, L.; Zaharaki, D.; Komnitsas, K. Assessment of groundwater contamination risk in an agricultural area in north Italy. *Inf. Process. Agric.* **2015**, *2*, 109–129. [CrossRef]
25. Nobre, R.C.M.; Rotunno Filho, O.C.; Mansur, W.J.; Nobre, M.M.M.; Cosenza, C.A.N. Groundwater vulnerability and risk mapping using GIS, modeling and a fuzzy logic tool. *J. Contam. Hydrol.* **2007**, *94*, 277–292. [CrossRef]
26. Liu, X.M.; Song, Q.J.; Tang, Y.; Li, W.L.; Xu, J.M.; Wu, J.J.; Wang, F.; Brookes, P.C. Human health risk assessment of heavy metals in soil-vegetable system: A multi-medium analysis. *Sci. Total Environ.* **2013**, *463*, 530–540. [CrossRef]
27. Komnitsas, K.; Modis, K. Geostatistical risk assessment at waste disposal sites in the presence of hot spots. *J. Hazard. Mater.* **2009**, *164*, 1185–1190. [CrossRef]
28. Yang, X.; He, Z.L. Heavy metal pollution and health risk assessment of agricultural soils in a typical peri-urban area in southeast China. *J. Environ. Manag.* **2018**, *207*, 159–168.
29. Luan, W.L.; Wen, X.Y.; Ma, Z.S.; Cui, X.T.; Song, Z.F.; Du, J. Geochemical Characteristics of Heavy Metal Elements in Soils of Eastern Hebei Plain. *Geoscience* **2008**, *22*, 939–946.
30. Technical Standard of Geological Survey of China Geological Survey. *Technical Requirements for Regional Eco-Geochemical Evaluation (DD2005-02)*; Standard Press of China: Beijing, China, 2005.
31. Waza, A.; Schneiders, K.; May, J.; Rodríguez, S.; Epple, B.; Kandler, K. Field comparison of dry deposition samplers for collection of atmospheric mineral dust: Results from single-particle characterization. *Atmos. Meas. Tech. Discuss.* **2019**. [CrossRef]
32. National Environmental Protection Standards of the People's China. *Water Quality Sampling—Technical Regulation of the Preservation and Handling of Samples (HJ 493—2009)*; Environmental Protection Department: Beijing, China, 2009.
33. Ministry of Health of the People's Republic of China and National standardization administration of China. *Standard Examination Methods for Drinking Water-Metal Parameters GB/T 5750.6–2006*; The State Standard of the People's China: Beijing, China, 2006.
34. Technical Standard of Geological Survey of China Geological Survey. *Technical Requirements for Eco-Geochemical Evaluation of Sample Analysis (DD2005-03)*; Standard Press of China: Beijing, China, 2005.
35. Technical Standard of Geological Survey of China Geological Survey. *Multi-target Area Geochemical Survey Specification (1:250,000) (DD2005-01)*; Standard Press of China: Beijing, China, 2005.
36. Cai, K.; Yu, Y.Y.; Zhang, M.J.; Kim, K.J. Concentration, Source, and Total Health Risks of Cadmium in Multiple Media in Densely Populated Areas, China. *Int. J. Environ. Res. Public Health* **2019**, *16*, 2269. [CrossRef]
37. Müller, G. Index of geoaccumulation in sedimentsof the Rhine river. *Geojournal* **1969**, *2*, 108.
38. Retamal-Salgado, J.; Hirzel, J.; Walter, I.; Matus, I. Bioabsorption and Bioaccumulation of Cadmium in the Straw and Grain of Maize (*Zea mays* L.) in Growing Soils Contaminated with Cadmium in Different Environment. *Int. J. Environ. Res. Public Health* **2017**, *14*, 1399. [CrossRef]
39. Hu, B.; Jia, X.; Hu, J.; Xu, D.; Xia, F.; Li, Y. Assessment of Heavy Metal Pollution and Health Risks in the Soil-Plant-Human System in the Yangtze River Delta, China. *Int. J. Environ. Res. Public Health* **2017**, *14*, 1042. [CrossRef]

40. United States Environmental Protection Agency (USEPA). *National Primary Drinking Water Regulations: Radionuclides, Proposed Rule. 40CFR*; United States Environmental Protection Agency: Washington, DC, USA, 1991.
41. United States Environmental Protection Agency (USEPA). *Guidelines for Carcinogen Risk Assessment*; USEPA/630/P-03/001F; Risk Assessment Forum: Washington DC, USA, 2005.
42. United States Environmental Protection Agency (USEPA). *Exposure Factors Handbook—Update, External Review Draft*; EPA/600/R-09/052A; U.S. Environmental Protection Agency: Washington, DC, USA, 2009.
43. United States Environmental Protection Agency (USEPA). *Risk Assessment Guidance for Superfund Volume 1 Human Health Evaluation Manual (Part A)*; Office of Emergency and Remedial Response, U.S. Environmental Protection Agency: Washington, DC, USA, 1989.
44. United States Environmental Protection Agency (USEPA). *Exposure Factors Handbook Edition (Final Report)*; U.S. Environmental Protection Agency: Washington, DC, USA, 2011.
45. Chen, L.; Zhou, S.; Shi, Y.; Wang, C.; Li, B.; Li, Y.; Wu, S. Heavy metals in food crops, soil, and water in the Lihe River Watershed of the Taihu Region and their potential health risks when ingested. *Sci. Total Environ.* **2018**, *615*, 141–149. [CrossRef]
46. Wang, Z.S.; Duan, X.L.; Liu, P.; Nie, J.; Huang, N.; Zhang, J.L. Human Exposure Factors of Chinese People in Environmental Health Risk Assessment. *Res Environ Sci.* **2009**, *22*, 11641170.
47. Antoniadis, V.; Shaheen, S.M.; Levizou, E.; Shahid, M.; Niazi, N.K.; Vithanage, M.; Yong, S.O.; Bolan, N.; Rinklebe, J. A critical prospective analysis of the potential toxicity of trace element regulation limits in soils worldwide: Are they protective concerning health risk assessment?—A review. *Environ. Int.* **2019**, *127*, 819–847. [CrossRef]
48. United States Environmental Protection Agency (USEPA). Guidance on Use of Modeled Results to Demonstrate Attainment of the Ozone NAAQS, EPA-454/B-95-007. 1996. Available online: http://www.epa.gov/ttn/scram/(filename:\T1\textquotedblleftO3TEST\T1\textquotedblright) (accessed on 16 August 2019).
49. Gilbert, R.O. *Statistical Methods for Environmental Pollution Monitoring*; Van Nostrand Reinhold: New York, NY, USA, 1987; pp. 177–185.
50. Fang, F.; Wang, H.; Lin, Y. Spatial distribution, bioavailability, and health risk assessment of soil Hg in Wuhu urban area, China. *Environ. Monit. Assess.* **2010**, *179*, 255–265. [CrossRef]
51. Yang, L.P.; Chen, F.H.; Zhang, C.J. Chemical characteristics of atmospheric dust in Lanzhou. *J. Lanzhou Univ. (Nat. Sci.)* **2002**, *38*, 115–120.
52. Tang, J.; Han, W.Z.; Li, N.; Li, Z.Y.; Bian, J.M.; Li, H.Y. Multivariate Analysis of Heavy metal Element Concentration in Atmospheric Deposition in Harbin City, Northeast China. *Spectrosc. Spectr. Anal.* **2011**, *31*, 3087–3090.
53. Li, S.Q.; Yang, J.L.; Ruan, X.L.; Zhang, G.L. Atmospheric deposition of heavy metals and their impacts on soil environment in typical urban areas of Nanjing. *China Environ. Sci.* **2014**, *34*, 22–29.
54. Wang, M.M.; Yuan, M.Y.; Su, D.C. Characteristics and spatial-temporal variation of heavy metals in atmospheric dry and wet deposition of China. *China Environ. Sci.* **2017**, *37*, 4085–4096.
55. Wong, C.S.C.; Li, X.D.; Zhang, G.; Qi, S.H.; Peng, X.Z. Atmospheric deposition of heavy metals in the Pearl River Delta, China. *Atmos. Environ.* **2003**, *37*, 767–776. [CrossRef]
56. Cong, Y.; Chen, Y.L.; Yang, Z.F.; Hou, Q.Y.; Wang, H.C. Dry and wet atmospher ic deposition fluxes of elements in the Plain area of Beijing Municipality, China. *Geol. Bull. China* **2008**, *27*, 257–264.
57. Bao, L.R.; Yang, L.C.; Dong, J.X.; Zhou, J. Atmospheric deposition characteristic and its influence on the earth surface in western Chongqing agricultural area. *Environ. Pollut. Control* **2016**, *38*, 41–46.
58. Deng, C.Z.; Sun, G.Y.; Yang, W.; Li, Y.P.; Zhang, L.D.; Ding, J.S.; Fu, A.Z. Analysis of the deposition flux and source of heavy metal elements in atmospheric dust fall in Ganan County, Heilongjiang Province. *Earth Environ.* **2012**, *40*, 342–348.
59. Sharma, R.K.; Agrawal, M.; Marshall, F.M. Atmospheric deposition of heavy metals (Cu, Zn, Cd and Pb) in Varanasi City, India. *Environ. Monit. Assess.* **2007**, *142*, 269–278. [CrossRef]
60. Sam, A.; Philippe, C.; Isabelle, L.; Daniel, T. Heavy Metal Determination in Atmospheric Deposition and Other Fluxes in Northern France Agrosystems. *Water Air Soil Pollut. Springer Verlag* **2004**, *157*, 295–313.
61. Chinese Environmental Protection Administration (CEPA). *Soil Environmental Quality Risk Control Standard for Soil Contamination of Agricultural Land (GB15618-2018)*; Standards Press of China: Beijing, China, 2018.

62. Yu, M.D.; Zhang, H.; He, X.S.; Zhang, Y.; Ma, L.N.; Tan, W.B.; Gao, R.T. Pollution characteristics and ecological risk assessment of heavy metals in typical agricultural soils. *Chin. J. Environ. Eng.* **2016**, *10*, 1501–1506.
63. Song, Z.F.; Luan, W.L.; Cui, X.T.; Li, S.M.; Wang, W.; Li, W. An analysis of the sources of heavy metals in soils of eastern Hebei plain. *Geol. China* **2010**, *37*, 1531–1537.
64. Zhang, X.Z.; Wang, S.M.; Li, J.H. The study on cadmium enrichment and causing analysis in coastal areas of Jidong. *Earth Environ.* **2007**, *35*, 321–326.
65. Ministry of Health of China (MHC). *Maximum Levels of Contaminants in Foods (GB2762-2012)*; Standard Press of China: Beijing, China, 2012.
66. Al-Othman, Z.A.; Ali, R.; Al-Othman, A.M.; Ali, J.; Habila, M.A. Assessment of toxic metals in wheat crops grown on selected soils, irrigated by different water sources. *Arab. J. Chem.* **2016**, *9*, 1555–1562. [CrossRef]
67. Cai, K.; Song, Z. Bioconcentration, Potential Health Risks, and a Receptor Prediction Model of Metal(loid)s in a Particular Agro-Ecological Area. *Appl. Sci* **2019**, *9*, 1902. [CrossRef]
68. Grant, C.A.; Bailey, L.D.; McLaughlin, M.J.; Singh, B.R. management factors which influence cadmium concentrations in crops. In *Cadmium in Soils and Plants*; MeLaughlin, M.J., Singh, B.R., Eds.; Springer: Dordrecht, The Netherlands, 1999; pp. 151–198.
69. Huang, M.L.; Zhou, S.L.; Sun, B.; Zhao, Q.G. Heavy metals in wheat grain: Assessment of potential health risk for inhabitants in Kunshan, China. *Sci. Total Environ.* **2008**, *405*, 54–61. [CrossRef]
70. The State General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China; National Standardization Administration of China. *Standard for Groundwater Quality GB/T 14848–2017*; The State Standard of the People's China: Beijing, China, 2017.
71. Ministry of Health of the People's Republic of China; National Standardization Administration of China. *Standards for Drinking Water Quality GB/T 5749–2006*; The State Standard of the People's China: Beijing, China, 2006.