Accumulation Characteristics and Health significance of As, Cd and Cr Elements in Different Plants

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Abstract

To evaluate the impacts of vegetable and soil variables on phytoaccumulation of arsenic (As), cadmium (Cd) and chromium (Cr) and identify their interactions and predictors, 33 paired soil-vegetable samples were collected from the production areas of celery (Oenanthe javanica), green onion (Allium), pak choy (Brassica rapa subsp. chinensis), rape (Brassica campestris L.) and spinach (Spinacia olearacea) in the Wuqing District of Tianjin, China. The concentrations (mean ± sd in mg kg^{-1}) of As, Cd, and Cr were 12.9 ± 2.4, 0.21 ± 0.19, 68.2 ± 11.2 in soils, respectively, higher than their soil backgrounds, and 0.19 ± 0.13, 0.17 ± 0.11, and 1.33 ± 0.94 in shoots (leaves & stems) of all vegetables, respectively. Only Pak Choy's Cd was significantly higher than its soil concentration and threshold. All vegetables, except green onion, with the lowest concentration of As, Cd, and Cr have been heavily contaminated with Cr. For all vegetables except spinach, Cd concentration in shoots can be well predicted with 0.1M HCl extracted soil Cd (clCd) ($R^2 > 0.75$) with soil clNi; and shoot Cr concentration with shoot Fe (stFe) for celery, pok choy, rape, and spinach ($R^2 > 0.90$).Generally, the concentration of As, Cd, and Cr in shoots depends not only on the availability of their specific forms in soil and soil pH but also on the interactions with other elements (especially Fe) in shoots, despite their variations with vegetable species. Both Cd and Cr have a high accumulation potential, which can be better predicted with either 0.1M HCl extractable soil Cd or Fe concentration in shoots. So, how a trace element interacts with other ingredients and its specific form in the soil should be seen as essential factors in how it gets into the shoots.

1. Introduction

Trace element accumulation and potential contamination in agricultural soils and vegetation are becoming a global ecological and environmental concern and a food security issue. For example, cadmium (Cd) is not required but ubiquitous in plants and is the most toxic trace element of all other trace elements in the environment, even at a low soil concentration (Stohs et al., 2001; Thomas et al., 2009). It is just the high transferability of Cd from soil to plants (Liu et al., 2007) and its high phyto-availability (Norton et al., 2015; Yang et al., 2016) that makes it necessary for foods and vegetables produced from Cd potentially-contaminated soils to be routinely monitored and evaluated. On the other hand, the element As is usually a tiny fraction of its total content in the soil available for a plant's uptake, and its concentration in plants varies with its form, plant species, and environmental conditions. Generally, the total content of As and Cd in soil cannot be used as a viable indicator of phyto-availability for evaluating their potential risk of dietary toxicity (Wang et al., 2004). Chromium (Cr) is frequently present in a variety of environmental media as trivalent (Cr^{3+}) or hexavalent (Cr^{6+}) species (Bagchi et al., 2001); Cr^{3+} is an essential human nutrient, but Cr^{6+} is carcinogenic (Costa and Klein, 2006; Thompson et al., 2012). A high level of Cr exposure during pregnancy has been related to a higher risk of low birth weight (Xia et al., 2016).

Vegetables are an essential component of the human diet, and their portion consumed in the total diet has elevated over time because of their high nutritional value. Meanwhile, vegetables are also critical pathways through which trace elements enter the food chain and directly affect human health (Rehman et al., 208; Rafiq et al., 2014). Many leafy vegetables, compared to cereal crops, have been known to be capable of accumulating higher concentrations of trace elements in their edible parts (Yang et al., 2010). The plant uptake factor (PUF), defined as the ratio of a trace element concentration in edible plant tissues to that of the paired-soil (Zhang et al., 2011; Yang et al., 2016), is commonly used to estimate the potential transfer of an element from soil to plant, despite the fact that there is considerable uncertainty when it is related to a wide range of environmental variables (Swartjes et al., 2013; Augustsson et al., 2015). For example, the edible parts of vegetables can accumulate a high concentration of Cd even when grown in soils with a low concentration of Cd (Chen et al., 2010; Rafiq et al., 2014), so that the consumption of vegetables contributes up to 80% of the total Cd intake by humans in many countries (Swartjes et al., 2013; Yang et al., 2016). There are a lot of things that can change the way trace elements behave in soil and how they build up in plants, which affects how they are taken in and how much they build up in plants. These factors include vegetable species, quality of irrigated water (Haroon et al., 2019), fertilizer application (Nabulo et al., 2012; Zhao et al., 2015), and soil pH, SOM, and soil texture. (Xiao et al., 2018). An increasing portion of vegetables consumed in the total diet has raised a big concern about the accumulation of trace elements and potential risks to human health. Most popular vegetables such as spinach (*Spinacia olearacea*), pak choy (*Brassica Chinensis* L.), celery (*Oenanthe javanica*), green onion (*Allium*), and rape (*Brassica campestris L.*) are all widely grown and consumed in China. Both accumulation and distribution of these trace elements vary with growing environments and vegetable cultivars and tissues (Liang et al., 2013). Although many critical environmental factors have been recognized to have significant impacts on the intake of common trace elements by popular vegetable species, few studies have been conducted to reveal their interactions with other elements in vegetable tissues (shoots and roots) and their specific forms in soils. This study aims to understand how the accumulations of As, Cd, and Cr vary with vegetable species and then to reveal predictors. A densely vegetated area in Tianjin, China, was chosen as a case study to find out how these three trace elements interact with other things within and between shoots (stems and leaves), roots, and soil.

2. Materials And Methods

2.1. Study area

The Wuqing District of Tianjin covers a total land area of 1,574 km2, of which the cultivated land area accounts for 58%. The study area is at 116°46'117°19' E and 39°07'9°42' N. It is in a climate zone that is semi-arid and semi-continental with monsoons. The annual precipitation varies between 500 and 600 mm, of which about 80% occurs in July and August. The river generally has no natural runoff except for a small amount of sewage in the dry season. Since about 1982, most of the sewage from the Beijing Sewage River, the North Canal, and the Yongding River has been used to irrigate this area; in particular, sewage irrigation has become more prominent after the year 2000 due to the lack of water resources (Yu et al., 2000). Before being grown with vegetables, the area was mainly cultivated with wheat and corn. The soil types consist mainly of fluvo-aquic soils and tidal soils (Jiang, 1990). The location of this study area and soil distribution can be seen from Fig. 1.

2.2. Sampling and processing of soils and vegetables

The methods and procedures for sampling and sample treatments were followed according to the criteria required by the PRC Ministry of Ecology and Environment (2018) and the PRC Environmental Protection and Administration (2006a and 2006b). According to the spatial distribution of each vegetable species and their topographical characteristics and soil types, representative fields in the grid were selected as sampling points. For a large field with complicated topography, about ten mixed samples were collected in the "S-shaped" route, and the coordinates were positioned at the most representative points using a portable high-precision global positioning instrument. To create a mixed sample, samples were taken from five points in a small field with a single landform at the same time. At the central point, the coordinates were written down. Vegetable residues and the top (about 1 cm) of surface soil were removed prior to sampling, and the sample (about 1.0 kg total) was collected from the topsoil layer (120 cm deep) using a stainless steel drill. Simultaneously, samples of vegetable roots and shoots (including stems and leaves) were collected from the same exact location as the soil sample. (Fig. 1 illustrates the distribution of samples associated with each vegetable species in the study area.) Soil samples were air-dried at a temperature of 25°C. Following the removal of plants, roots, stones, and other debris, each soil sample was passed through a 2 mm sieve to determine general soil properties. To determine trace element concentrations, about 100g were ground and passed through a sieve with a 0.15 mm diameter. Finally, the shoots and roots were brought to the lab and immediately dried at 120°C for two hours before being sealed in a moisture-proof bag.

2.3. Chemical analyses of samples

The pH of the soil was measured with a pH meter using a $CaCl_2$-to-soil ratio of 2.5:1 (v/w) and 0.01M $CaCl_2$. The potassium dichromate oxidation-external heating method is used to measure soil organic matter (SOM). Using a soil densitometer, the fraction of soil particles 0.002mm in diameter was identified as clay in this study.

The total amount of each trace element in soil and vegetables: Approximately 0.200g of soil sample was treated with 8 ml of aqua regia-perchloric acid microwave digestion (Milestone ETHOS UP); the residue was dissolved with 3% HNO3 and a 25-ml solution was prepared for analysis: Cr concentrations were measured utilizing flame atomic absorption spectrometry (Analytik Jena novAA 350), Cd concentrations utilizing a graphite furnace atomic absorption spectrometer (Analytik Jena ZEEnit 650P), and As concentrations utilizing an atomic fluorescence spectrometer (Beijing Jitian, AFS-933). Plant and manure samples were treated identically.

2.4 Analysis of various forms of each trace element in soil

We weighed 0.300g of soil, added 30ml of 0.1M HCl, shook for 48 hours at room temperature, centrifuged, and filtered a 0.22m filter membrane in order to measure target element concentrations with ICP-MS. The phenanthroline method was used to measure the amount of divalent iron (Fe^{2+}), and the hydroxylamine hydrochloride reduction method and a microplate reader (Biotek) were used to measure the amount of total iron (Fe).

Exchangeable soil As (exAs) and adsorptive soil As (adAs) are measured by adding 1.00g of soil to 30 ml of 0.05 M (NH_4) $2SO_4$ solution, shaking it for two hours at room temperature, repeating the extraction twice, and storing the filtered solution. 1.00g of soil should be dissolved in 25 ml of 0.05 M $NH_4H_2PO_4$ and allowed to sit at room temperature for 12 hours before filtering through a 0.22 m filter membrane and using ICP-MS to determine the exAs and adAs.

3. Results And Discussion

3.1 Descriptive statistics of As, Cd and Cr in soils and vegetables

There are many different types of trace elements in soil, but only a small portion of the total amount or some particular forms are available to plants. In other words, their total content in soil cannot serve as a reliable gauge of their bioavailability or a sufficient factor for assessing their potential dietary toxicity (Wang et al., 2004). As a result, in addition to As, Cd, and Cr's total contents in soils and their various forms, they were extracted and quantified as shown in Table 1. The soils had pH values ranging from 6.60 to 8.13.SOM ,and with SOM of 18.35.8 and CEC of 12.62.6, indicating a moderate level of soil fertility.

Table 1
Descriptive statistics of basic soil properties and the contents of As, Cr, and Cd in topsoil, manure, shoots and roots of vegetables in the study area

Source	Element	N	Unit	Min	Max	Mean	SD	CV(%)	% of soil content	Bacround	Threshold
Soil (0-20cm)	**PH**	33		6.60	8.13	7.55	.34	4			
	SOM	33	g kg^{-1}	7.17	28.98	18.33	5.83	32			
	CEC	33	cmo1 kg^{-1}	7.68	18.79	12.63	2.57	20			
	Clay	31	g kg^{-1}	146	384	241	60	25			
	EC	33	mS cm^{-1}	.170	1.83	.58	.44	75			
	sAs	33	ppm	9.69	20.61	12.94	2.41	19	100.00	8.4†	20‡
	sCd	33	ppm	.06	1.22	.22	.19	91	100.00	8.4†	0.4‡
	sCr	33	ppm	48	96	68	11	16	100.00	8.4†	250‡
	exAs	33	ppm	.07	.37	.19	.08	100	1.40		
	oxAs	33	ppm	.70	2.13	1.21	.27	23	9.40		
	clAs	33	ppm	.03	1.06	.38	.25	67	2.90		
	clCd	33	ppm	.06	.56	.22	.15	59	99.40		
	clCr	33	ppm	.00	2.81	.33	.52	158	0.50		
	clCu	33	ppm	.28	18.34	6.28	3.72	14			
	clNi	33	ppm	.01	3.26	.97	.90	1			
	clZn	33	ppm	2.24	54.89	18.79	11.70	137			
	clFe	33	ppm	45.48	54.89	54.01	3.00	9			
Roots	**rtAs**	33	ppm	.12	1.68	.53	.35	66	4.10		
	rtCd	33	ppm	.06	.56	.25	.15	59	116.30		
	rtCr	33	ppm	.08	13.18	1.91	2.21	116	2.80		
Shoots (stems & leaves)	**stAs**	33	ppm	.02	.48	.19	.13	65	1.50		0.5§
	stCd	33	ppm	.04	.40	.17	.11	67	76.60		0.5§
	stCr	33	ppm	.18	3.63	1.33	.94	71	1.90		0.5§

†,Song et al., 2016; ‡PRC EPA, 2006a; §,PRC NHFPC, 2017.

SD, standard deviation; SOM, soil organic matter; CEC, cation-exchage capacity; EC, electrical conductivity;

Clay, < 0.002mm soil particles; sAs, sCd and sCr refer to total soil As, Cd and Cr contents, respectively;

exAs, exchangeable soil As; oxAs, Ammonium oxalate extracted soil As; clFe, 0.5M HCL extracted soil iron;

clAs, clCd, clCr, clCu, clNi, and clZn refer to 0.1M HCL extracted soil As, Cd, Cr, Cu, Ni, and Zn, respectively.

3.1.1. Concentrations of As, Cr and Cd and their various forms in soils

The average concentrations of As, Cd, and Cr in topsoil were 12.94 ± 2.41, 0.21 ± 0.19, and 0.68 ± 0.11 ppm, respectively, as shown in Table 1. The fact that they are all above background levels (Song et al., 2016) but below the pollution threshold (PRC EPA, 2006a) suggests that some additional doses of these trace elements have been added to the soil, even though they are not high enough to qualify it as contaminated soil. And soil Cd (sCd) showed the highest spatial variation (CV = 91%).

Adsorptive As (adAs), exchangeable As (exAs), and ammonium oxalate extracted As (oxAs), in that order, made up 4.8%, 2.9%, 1.4%, and 9.4% of the total As content. The amounts of As (clAs), Cd (clCd), and Cr (clCr) that were extracted by 0.1M HCl were 0.380.25, 0.220.15, and 0.330.52, respectively. The amount of clAs, however, was only 2.9% of the soil's total As content (sAs). The clCr comprised only about 0.5% of the soil's total Cr content (sCr), while the clCd was almost the soil's total C (99.4 percent). Figure 2 (A1, A2, and A3) shows how clAs, clCd, and clCr are spread out in space, with clCr having the most spatial variation (CV = 158%). According to Fan and Zhang (2002) and Liao et al. (2019), their regional variations are more likely to be the result of changes in land use (from crops to vegetables), fertilizer, and historical wastewater irrigation than their geochemical basis. Liao et al. (2019) say that there is a significant positive correlation between Cd, soil organic carbon, the age of tillage, and long-term solid fertilization (chemical fertilizers and animal manure). These elements (Cu and Zn) contribute to the soil's accumulating Cd. However, it has been shown that soil As and Cr is more strongly linked to soil Fe and Al (hydro)oxide than to human activities (Liu et al., 2011; Liao et al., 2019).

3.1.2 As, Cd, and Cr concentrations in roots (i.e., rtAs, rtCd, and rtCr)

All vegetables had mean rtAs, rtCd, and rtCr concentrations of 0.53 ± 0.35, 0.25 ± 0.15, and 1.91 ± 2.21ppm, respectively. These values corresponded to 4.1, 116, and 2.8% of the total soil content of the vegetables, respectively. It is important to note that Cd content in roots was 16% greater than in soil, indicating that it is more mobile and has a larger accumulation potential than As and Cr. These trace elements' high CV values vary significantly depending on their habitat and the kind of plant they are in.

3.1.3 As, Cd, and Cr concentrations in shoots (i.e., stAs, stCd, and stCr)

Celery and pak choy both had markedly higher levels of As, and pak choy had the highest concentration of Cd, which was not only 25% higher than the threshold but also 17% higher than its soil concentration (PRC NHFPC, 2017). This finding supports the notion that Cd is highly mobile and accumulable in edible parts of vegetables regardless of its concentration in soils (Chen et al., 2010; Rafiq et al., 2014). The concentrations of stAs, stCd, and stCr in green onions were historically the lowest; their stCr concentration (0.39 ± 0.15ppm) was roughly 25% that of other vegetables and 0.6% that of their soil (sCr). Unexpectedly, the stCr content was 164% higher than the pak choy criterion, 224% higher than the celery criterion, 144% higher than the rape criterion, and 116% higher than the spinach criterion. This indicates that these plants' edible parts were seriously contaminated with Cr.

The phyto-availability of trace elements was discussed by Zhang et al. (2011) using FUF as a predictor of As and Cd concentrations in vegetable shoots. According to Fig. 3, the PUF of As and Cr for all vegetables was incredibly low. However, all roots and shoots had Cd values greater than 1.0, with the exception of celery and green onions, which is again consistent with the results of earlier research as shown in Fig. 3.(Zhang et al.,2011; Yang et al., 2016). In order to determine whether these vegetables are contaminated with As and Cr, PUF appears to be insufficient. According to Wang et al. (2004), total soil As (sAs) is neither a good predictor of phyto-availability nor a good way to gauge the risk of As toxicity in food.

3.2 Differences in As, Cd and Cr concentrations and their correlations among shoots, roots and soils

On average, As, Cd, and Cr concentrations in shoots were significantly lower than in roots, and their Cr concentrations were noticeably higher than those in soils (Table 1).

According to Table 2's Pearson correlation coefficients, As accumulation in shoots (stAs) might be boosted by stFe and stCr (in shoots) and rtAs, rtFe, and rtCr (in roots). The stCd might be positively connected with the Cd in roots (rtCd), SOM, clCd, clCr, clNi, and clCu in soils, but negatively correlated with soil pH, rtCu, adAs, clZn, and 0.5M HCl extracted soil iron (clFe) in soils, which is consistent with the conclusion reached by Rafig et al. (2014). stCr was substantially connected to stFe and stNi; similarly, rtCr was positively correlated to rtFe and rtNi; however, neither stCr nor rtCr has a strong correlation with soil factors.

Table 2
Pearson correlation coefficients of As, Cd and Cr in shoots and roots of vegetables and soils in the study area

Source	Element	Shoots (ppm)			Roots (ppm)		
		stAs	stCd	stCr	rtAs	rtCd	rtCr
Shoots(33)	stAs	1.000	− .015	**.480**	**.710**	− .053	**.536**
	stCd	− .015	1.000	**.291**	− .002	**.858**	− .005
	stCr	**.480**	**.291**	1.000	.212	.214	**.301**
	stCu	− .147	− .119	.207	− .155	− .041	− .113
	stNi	**.510**	.119	**.771**	.285	.114	.170
	stZn	.095	− .006	**.352**	− .180	− .157	− .153
	stFe	.533	.317	.971	.276	.260	.345
Root(33)	rtAs	.710	− .002	.212	1.000	.161	.699
	rtCd	− .053	.858	.214	.161	1.000	.171
	rtCr	.536	− .005	.301	.699	.171	1.000
	rtCu	− .022	− .353	− .139	.192	− .065	.344
	rtNi	.495	− .019	.327	.709	.211	.878
	rtZn	.232	− .062	**.329**	.080	− .072	.008
	rtFe	**.546**	.051	**.350**	**.730**	.234	**.950**
Soil(33)	PH	− .124	**− .517**	− .105	− .090	**− .400**	− .181
	CEC	**.336**	.129	.110	.265	.105	**.310**
	EC	− .041	.020	.202	− .086	− .046	− .092
	SOM	.071	0288	.028	.081	.181	.165
	Clay	.282	.036	.267	.299	.096	.210
	sAs	− .085	− .179	− .119	− .220	− .228	− .100
	sCd	.130	.034	**.345**	.179	− .053	.088
	sCr	− .055	− .098	.154	.037	− .103	.208
	sCu	**.321**	− .107	.239	.126	− .146	.216
	sNi	− .049	− .012	.096	− .033	− .041	.134
	sZn	.191	− .120	− .003	− .083	− .229	− .007
	exAs	**.454**	− .220	.130	**.335**	− .161	**.323**
	clAs	.155	.030	− .031	− .012	− .002	.245
	clCd	− .052	.859	.213	.161	**1.000**	.171
	clCr	.027	**.413**	.130	− .037	**.304**	.079
	clCu	.202	**.298**	.016	.179	**.305**	.255
	clNi	.115	**.551**	.010	.088	**.512**	.076
	clZn	.195	**− .354**	.008	− .009	**− .449**	− .146
	clFe	− .053	**− .333**	− .043	− .022	**− .320**	**− .390**
SOM, soil organic matter							
SOM, soil organic matter; CEC, cation-exchage capacity; EC, electrical conductivity;							
Clay, < 0.002mm soil particles; sAs, sCd and sCr refer to total soil As, Cd and Cr contents, respectively;							
clAs, clCd, clCr, clCu, clNi, and clZn refer to 0.1M HCL extracted soil As, Cd, Cr, Cu, Ni, and Zn, respectively.							
clFe, 0.5M HCL extracted soil iron; exAs, exchangeable soil As;							
All values in bold refer to statistically significant at p < 0.05 level.							

3.3 Interactions of As, Cd and Cr among shoots, roots and soils

As shown in Tables 1 and 4, the concentrations of these three elements were generally higher in roots than in shoots and soils. However, Bakhshayesh et al. (2014) reported that Cd concentrations in spinach shoots were significantly higher than in roots. Table 3 shows that, in addition to the synergy between stAs and stCr and the mutual exclusion between stCd and rtCu, these elements have close relationships with both shoots and roots, and that stCr depends a lot on stFe alone. RtAs is closely related to rtFe and stAs between roots and soils, whereas rtCd and rtCr are dependent on clCd and rtFe, respectively. rtAs is closely related to rtFe and stAs between roots and soils, whereas rtCd and rtCr are dependent on clCd and rtFe, respectively. Due to their relationships with shoots and soils, stAs and exAs could be accurately predicted with stFe and stCr, stFe with stCr, and soil clCd. Even though Cd tends to accumulate in shoots in a soil with a lower pH when soil pH > 7.0, which seems to contradict the results obtained from vegetables grown in acidic soils in southern China (Wu et al., 2018), these results indicate that soil pH and vegetable type must be considered when determining the soil Cd threshold. When shoots, roots, and soil were looked at as one continuous system, it was found that stAs was not only closely related to rtAs and stFe but also interacted negatively with rtCd; Cd accumulation in shoots (stCd) could be mostly increased by soil clCd and SOM but likely slowed down by Cu in roots (rtCu); and stCr was almost entirely related to stFe.

Table 3

General regressions of contents of As, Cd, and Cr with relevant elements among shoots, roots and soils

Variable	Regression equation†	Adjusted R^2	F test Sugbuf.	Partual Signif. ‡	N
Shoots-Roots	$stAs = 0.018 + 0.693rtAs + 0.263stCr$	0.558	< 0.001	< 0.05	33
	$stCd = 0.066 + 0.850rtCd - 0.281rtCu$	0.807	< 0.001	< 0.05	33
	$stCr = 0.291 + 0.977stFe$	0.954	< 0.001	< 0.05	33
Roots-Soils	$rtAs = 0.173 + 0.788rtFe + 0.443stAs$	0.649	< 0.001	< 0.001	33
	$rtCd = 1.000clCd$	1.000	< 0.001	< 0.001	33
	$rtCr = 0.500 + 0.950rtFe$	0.900	< 0.001	< 0.01	33
Shoots-soils	$stAs = 0.015 + 0.464stFe + 0.366exAs$	0.375	< 0.001	< 0.05	33
	$stCd = 0.536 + 0.776clCd - 0.207opH$	0.758	< 0.001	< 0.01	33
	$stCr = 0.152 + 0.940stFe + 0.145sCd$	0.960	< 0.001	< 0.01	33
Shoots-Roots-Soils	$stAs = 0.068 + 0.635rtAs + 0.427stFe - 0.266rtCd$	0.661	< 0.001	< 0.05	33
	$\mathrm{stCd} = 0.023 + 0.809\mathrm{clCd} - 0.312\mathrm{rtCu} + 0.163\mathrm{SOM}$	0.836	< 0.001	< 0.05	33
	$stCr = 0.268 + 0.971stFe$	0.940	< 0.001	< 0.001	33

†,Including only variables whose partial significance is at p < 0.05; ‡ All variables are tested at the signification level.

SOM, soil organic matter

clCd, clCr, clCu refer to 0.1M HCL extracted soil Cd, Cr and Cu, respectively; exAs, exchangeable soil As;

sCd, total soil Cd concentration; dtZn, 0.005M DTPA extracted soil Zn; clFe,0.5M HCL extracted soil iron;

CEC, PH, and SOM refer to soil pH, soil cation exchangeable capacity, and soil organic matter, respectively.

Table 4
Contents of As, Cd, Cr, and Fe in shoots and roots in association with soil variables for each vegetable species

Source	Element	Unit	Celery (n = 7)			Green onion (n = 5)			Pak choy (n = 4)			Rape (n = 4)			Spinach (n = 5)		
			Mean	SD	%†	Mean	SD	%†	Mean	SD	%†	Mean	SD	%†	Mean	SD	%†
Shoots	stAs	ppm	.24	.13	2.1	.11	.07	.9	.23	.12	1.4	.14	.11	1.2	.17	.06	1.4
	stCd		.16	.11	54	.15	.13	53	.25	.15	73	.19	.14	77	.17	.07	54
	stCr		1.62	.80	2.4	.39	.15	.6	1.52	.94	2.1	1.27	.76	1.9	1.59	.58	2.4
	stFe		655	414	1195	99	41	180	584	489	1116	461	339	896	519	215	972
Roots	rtAs		.84	.48	7.3	.40	.20	3	.32	.16	2	.40	.28	3	.44	.25	4
	rtCd		.28	.21	93	.24	.18	88	.31	.15	89	.22	.15	90	.30	.09	95
	rtCr		3.37	4.41	4.9	1.13	.97	2	1.42	.67	2	1.39	1.10	2	2.02	1.03	3
	rtFe		1870	2261	3410	386	275	702	358	199	684	538	521	1046	507	267	950
Soils (0 – 20cm)	pH		7.54	.19		7.44	.38		7.29	.51		7.48	.35		7.54	.39	
	SOM	g kg-1	16.3	7.2		20.4	6.0		22.7	3.4		18.6	6.3		16.5	8.1	
	CEC	cmol kg-1	12.4	2.9		11.9	1.9		14.0	3.2		12.5	2.2		12.2	3.4	
	EC	mS cm-1	.99	.61		.41	.32		.55	.26		.62	.42		.45	.42	
	sAs	ppm	11.6	1.1	100	13.3	2.3	100	16.1	4.4	100	12.1	2.5	100	12.2	1.2	100
	sCd		.30	.05	100	.28	.08	100	.35	.08	100	.25	.05	100	.31	.05	100
	sCr		68	13	100	69	9	100	72	18	100	66	14	100	67	9	100
	exAs		.22	.07	1.9	.18	.05	1.4	.16	.05	1.0	.19	.01	1.5	.13	.08	1.1
	clAs		.38	.29	3.3	.47	.18	3.6	.53	.41	3.3	.47	.30	3.9	.30	.14	2.5
	clCd		.28	.21	93	.24	.18	88	.31	.15	89	.22	.15	90	.30	.10	95
	dtCd		.12	.09	41	.15	.04	53	.11	.06	33	.12	.07	51	.10	.05	33
	clCr		.24	.22	.4	.33	.34	.5	.36	.43	.5	.43	.27	.6	.69	1.19	1.0
	clCu		1.42	2.13		2.07	2.18		2.01	2.58		1.77	1.61		1.12	1.97	
	clNi		.89	.74		1.13	.99		1.39	1.38		1.12	.88		1.21	1.13	
	clZn		18.2	8.5		17.2	8.2		14.8	5.5		20.6	6.6		13.7	11.5	
	clFe		54.8	3.3	100	55.0	1.5	100	52.4	2.9	100	51.4	4.6	100	53.4	2.1	

†, Percentage of the sAs, sCd, sCr, and clFe concentrations in soils, respectively; ‡, PRC NHFPC, 2017; §, PRC EPA, 2006a.

SD, standard deviation; SOM, soil orgaic matter; CEC, cation-exchage capacity; EC, electrical conductivity;

sAs, sCd and sCr refer to total soil As, Cd and Cr contents, respectively; aexAs, exchangeable soil As; clAs, clCd, clCr, clCu, clNi and clZn

refer to 0.1M HCL extracted soilAs, Cd, Cr, Cu, Ni, and Zn, respectively; clFe, 0.5M HCl extracted soil iron.

The stCd clearly depends on the clCd in soil, which is consistent with the results of controlled experiments by Bakhshayesh et al. (2014), and the stCr can be significantly predicted by the stFe, which accounts for more than 75% of the variance. Even though only about 40% of the variance can be explained, the variables affecting stAs do evolve over time to become more complex and unpredictable. Despite the interactions between these variables, our research (Hough et al., 2004; Tian et al., 2018) indicates that the soil pH, CEC, SOM, or clay are not always in control of the amount of As, Cd, and Cr in these vegetables. This is true unless the soil has very minor trace element contamination.

3.4 Predictors of As, Cd, and Cr in shoots of individual vegetables

Table 4 shows that soil As, Cd, and Cr concentrations were below their respective criteria, indicating that these soils had not yet been poisoned. For example, the concentrations of the metals As, Cd, and Cr in plant shoots and roots are greatly affected by their mobility and interactions with other factors. With the exception of pak choy, whose Cd was just above the threshold, the stAs and stCd of all vegetables were below their respective criteria. Their stCr concentrations, on the other hand, were far above the threshold. While rtAs and rtCd were higher in roots than in shoots, and rtCd exceeded the threshold in all vegetables, the root condition is equivalent to that of shoots. There were far more Fe concentrations in shoots and roots than in the soils of all vegetable species studied.

Figure 2 shows that the concentration of each trace element in shoots is not always proportional to the concentration in soil, particularly for Cd (B3 vs. A3 in Fig. 2). In other words, phyto-availability determines the concentration of stAs, stCr, or stCd, which varies between vegetable species. As shown in Table 5, with the exception of spinach, whose stCd is primarily dependent on soil clNi, the stCd of the other four vegetable shoots is primarily dependent on soil clCd, as experimentally demonstrated by Bakhshayesh et al. (2014). With the exception of green onions, all vegetables' stCr concentrations can be predicted by their stFe concentrations. Despite the fact that the relationship between stAs and other plant parts and factors appears to be becoming more complex and diverse across plant species, highly synergistic interactions between stAs and stFe for spinach, stZn and stFe for green onion, and lFe and stCr for celery have been observed. At a significance level of p 0.05, none of the variables in Table 4 predicted the stAs for pak choy and rape.

Table 5
Predictors for As, Cd, and Cr contents in shoots (stems & leaves) of vegetables between shoots and soils.

Vegetable	Standardized regression of shoots with soils†	Adjusted R^2	F test Signif.	Partial Signif.‡	Size of samples
Green onion	stAs = -0.030 + 0.954stZn + 0.326stFe	0.998	< 0.001	< 0.01	5
	stCd = -0.020 + 0.994clCd	0.984	< 0.001	< 0.01	5
	stCr = N/A				
Pak choy	stAs = N/A				
	stCd = -0.057 + 1.000clCd	0.999	< 0.001	< 0.01	4
	stCr = 0.404 + 0.996stFe	0.988	< 0.01	< 0.05	4
Rape	stAs = N/A				
	stCd = -0.17 + 0.996clCd	0.988	< 0.01	< 0.01	4
	stCr = 0.248 + 0.993stFe	0.980	< 0.01	< 0.01	4
	stCr = 0.466 + 0.912stFe − 0.141stAs	1.000	< 0.01	0.05	4
Spinach	stAs = 0.031 + 0.902stFe	0.751	< 0.05	< 0.05	5
	stCd = 0.096 + 0.930clNi	0.820	< 0.05	< 0.05	5
	stCr = 0.205 + 0.985stFe	0.960	< 0.01	< 0.01	5
	stCr = 0.257 + 0.900stFe + 0.192clCr	1.000	< 0.01	< 0.05	5
Celery	stAs = 1.505−0.643clFe + 0.575stCr	0.947	< 0.001	< 0.01	7
	stCd = -0.176 + 1.227clCd + 0.400stZn	0.984	< 0.001	< 0.01	7
	stCr = 0.396 + 0.963stFe	0.913	< 0.001	< 0.01	7

†: Including only variables whose partial significance is at p < 0.05 level;

‡: Refering to the least significant level of one of all variables.

clCd, clCr, clCu, and clNi refer to 0.1M HCl extracteed soil Cd, Cr, Cu, and Ni, respectively;

clFe, 0.5M HCl extracted soil iron.

Despite apparent geographical heterogeneity in these correlations, Yi et al. (2020) showed that plant trace element concentrations are positively correlated with soil Cd concentrations. $Ca(NO_3)$2 extracted soil Cd, for example, could explain more than 76% of the variation in Cd content in spinach leaves and onion bulbs. Except for spinach, whose stCd may be challenging to predict with soil clCd when soil clNi is added as a predictor, our results generally show a significant positive association between stCd and soil clCd. According to research by Rafig et al. (2014), pak choy Cd phyto-availability was significantly impacted by soil pH, SOM, total Zn, and Cd levels. According to Cavanagh et al. (2019), soil Cd and pH can be used to predict the Cd content of onion shoots. Inferring that raising pH and soil carbon (or SOM) may help reduce Cd uptake in onions and spinach. Soil Cd and exchangeable magnesium or total carbon can be used to predict Cd content in bunching spinach. However, their function might be constrained if the information in Tables 3 and 5 reveals potential synergy or exclusion interactions between components of the same tissue. In the meantime, soil clCd may be a better indicator of element Cd's bioavailability and toxicity than total soil Cd level, which is consistent with Tracy and Sheila (2006) prior suggestion.

4. Conclusions

According to the results of 33 paired vegetable-soil samples, only pak choy's Cd was significantly greater than its soil content and threshold; all vegetable species, except green onion, were heavily polluted with Cr; and the concentration of As, Cd, and Cr in a vegetable is determined not only by the availability of their specific forms in soil and soil properties, but also by their interactions with other elements.

The phyto-availability and toxicity of Cd and Cr can be better indicated by the 0.1M HCl extractable soil Cd and shoot Fe, respectively. Compared to other studies of the same kind, our results show that regional differences (especially in soil pH) can be significant in predicting how much these trace elements build up in common vegetable species. This finding should be considered when figuring out how dangerous Cd might be in soils used for farming.

Declarations

Author Contributions: Conceptualization, methodology, L.W.;. and H.Y formal analysis, H.Y.; datacuration, R.Z.; writing—original draft preparation, L.W.; writing—review and editing, T,Z. and H.Y.; discussed the results, Y.H. and Y.S.; project administration, L.W.; funding acquisition, L.W. and Z.Z. All authors have read and agreed to the published version of the manuscript.

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Figures

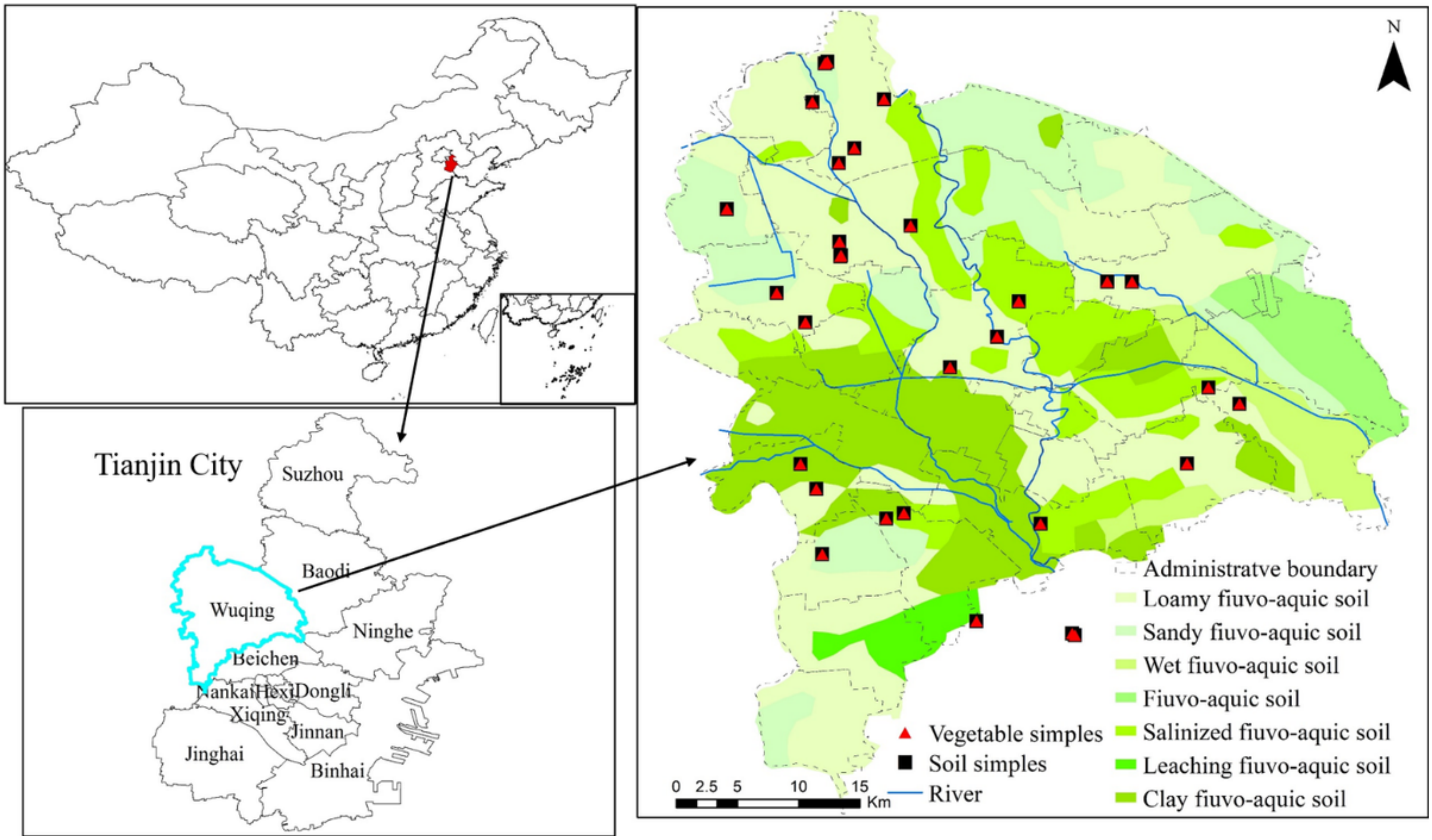

Figure 1

The location of this study area and sample points in association with major vegetable species.

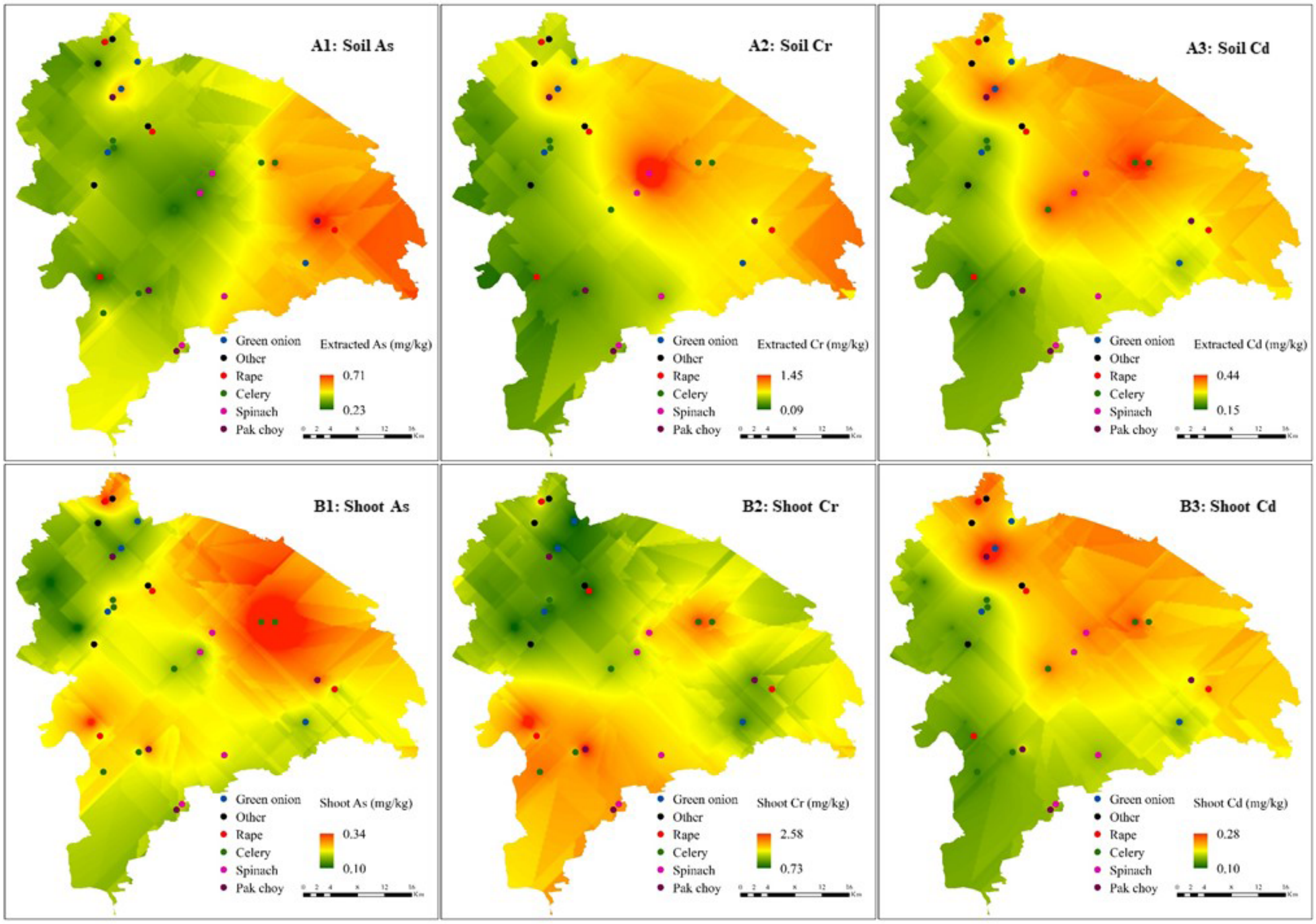

Figure 2

Spatial variations of 1N HCl extracted soil As, Cd, and Cr and As, Cd, and Cr concentration in shoots.

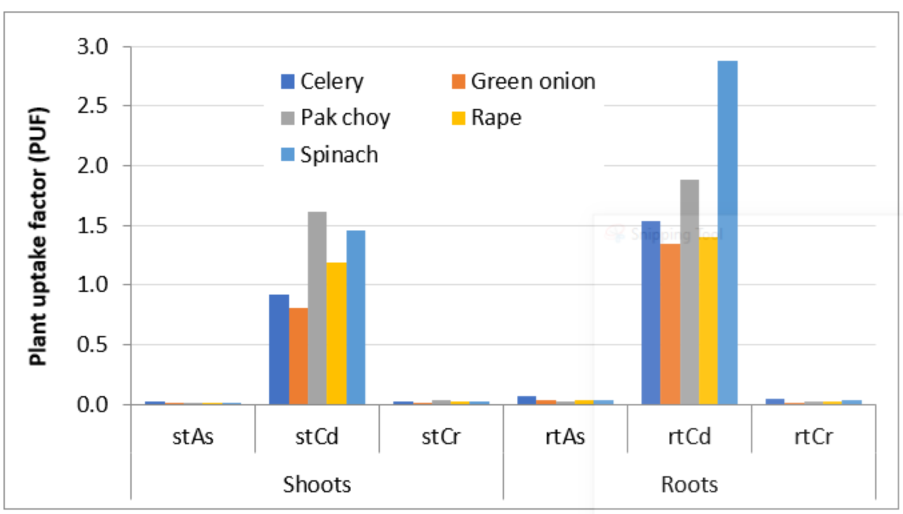

Figure 3

Plant uptake factor (PUF) of As, Cd, and Cr in association with common vegetables in the stud area (stAs, stCd, and stCr refer to their concentrations in shoots (leaves & stems). rtAs, rtCd, and rtCr refer to their concentrations in roots. PUF refers to the ratio of a trace element concentration in edible plant tissues relative to that of the paired-soil (Zhang et al., 2011; Yang et al., 2016)).

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