Original Research

Impact of Long-Term Irrigation with Sewage on Heavy Metals in Soils, Crops, and Groundwater – a Case Study in Beijing

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Abstract

The effect of sewage irrigation on the accumulation of heavy metals (HMs) in soil profiles, crops, and, groundwater was investigated by monitoring zones with wastewater for various lengths of time (20, 30, and 40 years) in the southeastern suburbs of Beijing. The non-sewage-irrigated region served as the control. Results show that long-term sewage irrigation increased the soil organic matter content. The zone irrigated for 40 years exhibited the greatest accumulations of Hg, Pb, and Cu in the topsoils (0-30 cm). The Cd, Cu, and Zn enrichment was evident in deeper soil layers (40-70 cm) near the sewage waterway. The transfer factors of the various examined HMs in the crop-soil system ranged from 0.002 to 0.491. The HMs of crop grains and kernels in sewage-irrigated zones did not exceed established limits. Long-term sewage irrigation does not constitute HM pollution in soil and shadow groundwater. However, the monitoring of Hg, Pb, and Cu concentrations should be emphasized in areas that engage in treated sewage irrigation to prevent these HMs from entering the food chain and posing health risks.

Keywords: sewage irrigation, treated sewage, heavy metals, soil, groundwater, risk

Introduction

Water shortages in arid and semi-arid regions promote the reuse of water resources, and the use of sewage for agricultural irrigation is the primary form of wastewater reuse [1-3]. Since the 1950s, a number of cities in northern China have used sewage for crop irrigation purposes [4-7]. Given that the awareness of the importance of environmental protection has increased in recent years, the use of treated sewage to irrigate farmland is likely to become more common [8-10]. Many nutrients, including nitrogen, phosphorus, and potassium, are rich in sewage, and they can effectively increase soil nutrient content and promote crop growth. Therefore, sewage irrigation also represents an important method of nutrient recycling and reuse [10-12].

However, sewage irrigation may pose certain environmental risks, most significantly the pollution of soil with heavy metals [13]. Heavy metal pollution is seriously problematic because it is persistent, difficult to detect, and remediate. Elements such as Cd, Cr, and Pb tend to accumulate over years of sewage irrigation [1]; as a result, significantly greater heavy metal contents have been found in the topsoil (0-20 cm) of farmland that has been irrigated with sewage for more than 10 years than in the topsoil from farmland that has been irrigated with clean water. It has been predicted that the soil contents of certain heavy metals would surpass standard limits after 5 to 60 years of sewage irrigation [14]. The sewage treatment process can signifi-

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cantly reduce the heavy metal content in it; however, significant heavy metal enrichment has been observed in the topsoil of farmland that was irrigated with treated sewage for 20 years [15]. These metals tend to be transferred downward with soil depths increasing as the irrigation duration increases [16]. It has been predicted that after 50 to 100 years of treated sewage irrigation, the soil content of certain heavy metals would reach the current thresholds for environmental concern [17]. Long-term sewage irrigation might also result in heavy metal enrichment in crops [13, 18, 19], which may pose certain health risks to humans through the food chain [20]. Several regions in the southeastern suburbs of Beijing began using sewage irrigation in the 1960s [13, 21, 22]. Studies have been carried out towards the sewage-irrigated topsoil in which certain heavy metals have accumulated. The possibility that the sewage effluent reclamation process could lead to heavy metal accumulation in soils and crops and the accompanying risks to groundwater safety and human health may limit the long-term and widespread use of sewage irrigation in agriculture [23]. Thus, the study of the heavy metal content in the topsoil and the overall soil profile in areas irrigated with sewage effluents for different durations is crucial for establishing the safety of sewage irrigation.

Our study focused on examining areas that had been subjected to long-term sewage irrigation for different lengths of time (40, 30, and 20 years). In particular, we investigated the following characteristics:

1) changes in soil organic matter (OM), soil pH, and the heavy metal content of groundwater
2) the heavy metal enrichment and transfer in soil profiles of 1 m depth
3) the transfer characteristics and enrichment patterns of heavy metals in soil-plant systems

Experimental Procedures

Study Area

As shown in Fig. 1(a), the study area was located in a southeast suburb of Beijing. The area of the entire irrigated district is 373 km^2. The district is characterized by a warm, temperate continental monsoon climate. The average annu-

a)

b)

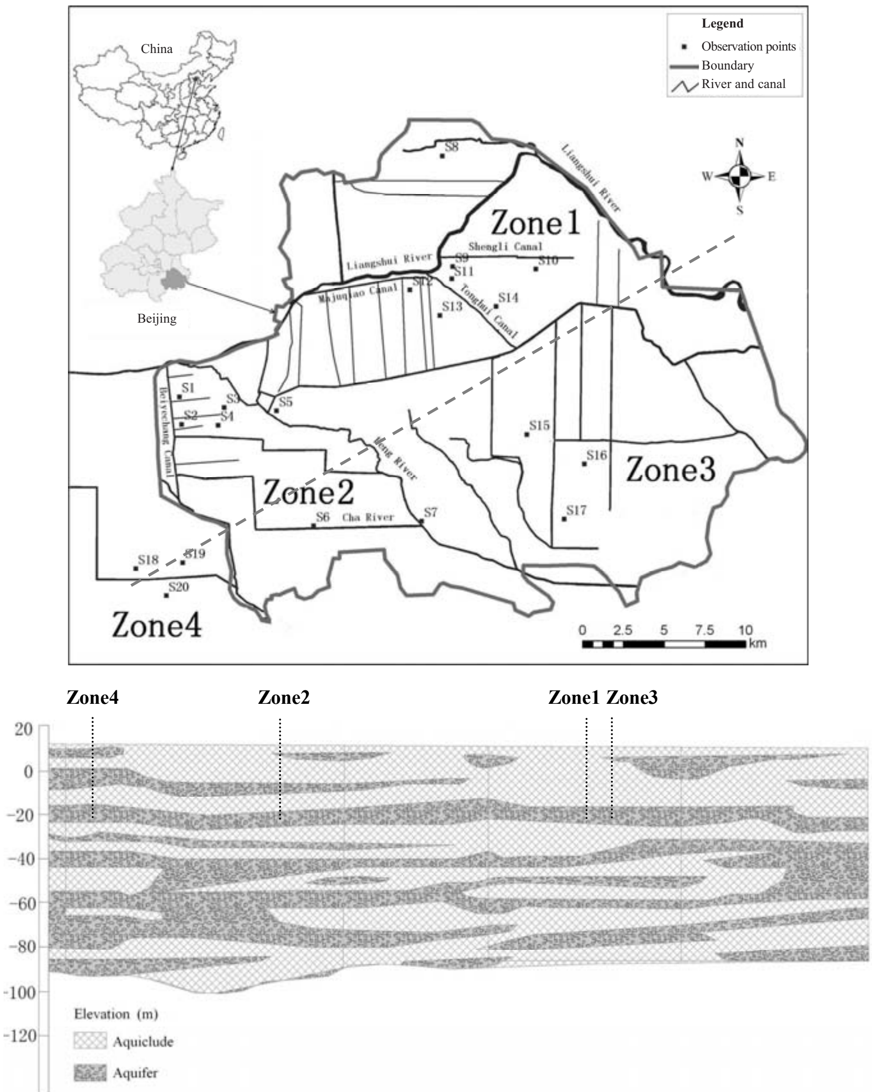

Fig. 1. A distribution map indicating the sampling site locations(a) and the hydro-geological condition in study area(b).

al rainfall in this region is 554.5 mm, with 70% of the rainfall concentrated between June and September.

Fig. 1(b) shows that the area is situated in the middle-lower parts of the alluvial fan of the Yongding River and has a flat topography. Overall, the terrain tilts slightly from northwest to southeast; the elevation ranges from 15-51 m with a gradient of between 0.03% and 1.6%. The Quaternary burial depth gradually increases from northwest to southeast with a maximum depth of 300 m. The top stratum of the alluvial fan is composed of relatively uniform sandy gravel with local clay interlayers. The aquifer in the middle-lower strata mainly comprises multiple layers of medium-fine sand structures, which present as sheet- or lens-shaped and are situated between the clay layers. A continuous aquitard is found at a depth of 80 m; its top is the shallow aquifer, and its bottom is the deep aquifer.

The surface soil in the study area is primarily composed of cinnamon soil and alluvial soil. The soil texture is silty clay loam, and the soil texture at a small scale in the northeast of the district is silty clay. The percentage range of sand, silt and clay in the studied soil is 1.5~15.0%, 65.1~74.0%, and 18.5~27.5%, respectively. The main crops planted in this region are summer maize and winter wheat.

Sewage effluents are transported to the study area for agricultural irrigation through various canals and rivers, including the major channels of the Tonghui, Beiyechang, and Majuqiao canals and the Feng River. A small portion of the effluents are deposited directly into the Liangshui River. There are certain similarities between the soil properties of the entire irrigated area and the water quality of the sewage effluents used for irrigation. As shown in Fig. 1, Zones 1, 2, and 3 were selected to represent regions with 40, 30, and 20 years of total sewage irrigation history, respectively. Zone 4 is the control region, which uses groundwater for irrigation. In recent years, treated sewage effluents have gradually become the main water source in the irrigated area. In particular, Zones 1, 2, and 3 have used treated sewage for 10, 5, and 0 years. The monitoring sites for soil and crop sampling in Zones 1, 2, and 3 are distributed along conveyance canals and rivers (S1-S17). There are three monitoring sites each in Zone 4, the control zone outside of the irrigated area (S18-S20). Thus, a total of 20 soil profile and crop monitoring sites were tested.

Sample Collection and Chemical Analysis

Soil and plant samples were collected from the 20 monitoring sites in the sewage-irrigated zones and the control zone in June 2010. During the sampling at each monitoring site, 0-100 cm cross-sections of soil were obtained from the 4 vertices of a 10×10 m square. Each cross-section was divided into layers of 10 cm in depth; at each monitoring site, a total of approximately 1 kg of soil was acquired for each layer from the four sampling points and mixed to produce each soil sample. Samples were collected from all 10 layers, for a total of 200 soil samples. The soil samples were stored in plastic bags, placed in a small refrigerated box, and transported to the indoor laboratory. Samples of winter wheat grains also were collected from each monitoring site. Summer maize kernel samples were collected from each monitoring site in September 2010. Treated sewage samples were acquired from the sewage treatment plants utilized in the district. Groundwater samples were obtained from agricultural irrigation wells in the monitored zones (Zone 1 through Zone 4). Non-metallic containers were used during sample acquisition, preservation, and processing to avoid sample contamination. Soil samples were air-dried indoors and then passed through a 100-mesh nylon sieve. The soil OM content was determined using the oil bath heating-K_2CrO_7 titration method. The pH values were determined by potentiometry using a water:soil ratio of 2.5:1 for each measurement. The total heavy metal contents of soil samples were obtained by HF-HNO_3-$HClO_4$ digestion. Treated sewage samples and groundwater samples were directly dispensed into separate tubes. The Hg contents were determined with cold vaporatomic fluorescence spectroscopy (CV-AFS), and the Cu, Pb, Zn, Cr, and Cd contents were determined by an inductively coupled plasma source mass spectrometer (ICP-MS). The chemical oxygen demand (COD_{Cr}) of each water sample was determined using dichromate, and the 5-day biochemical oxygen demand (BOD_5) of each water sample was determined using the dilution and seeding method.

Metal Transfer Factor

The soil-plant transfer factor for heavy metals was calculated by dividing C_{plant}, the concentration of a heavy metal in the edible portions of the plants based on dry weight, by C_{soil}, the total concentration of this heavy metal in samples of the corresponding cultivated soil (0-30 cm) [24].

The formula used for this calculation is shown in Equation (1):

$$TF = C_{plant}/C_{soil} \tag{1}$$

Pollution Load Index

The extent of pollution from each examined heavy metal in the soil was evaluated in terms of the pollution load index (*PLI*). The following equation (2) was used to calculate the PLIs of heavy metals in soil samples [21]:

$$PLI = C_{metal}(\text{Samples})/C_{reference} \tag{2}$$

In the above equation, C_{metal} represents the heavy metal content in the examined soil sample, and $C_{reference}$ represents the heavy metal content of a soil sample from the control zone.

Statistical Analysis

The experimental data were analyzed using SPSS v.13.0 (SPSS Inc., Chicago, IL, USA).

Table 1. Quality indicators for sewage water (SW), treated sewage (TS), and groundwater (GW) samples from the examined zones.

Parameters		pH	COD_{Cr} (mg/L)	BOD_5 (mg/L)	Cd (µg/L)	Cr (µg/L)	Hg (µg/L)	Pb (µg/L)	Cu (µg/L)	Zn (µg/L)
SW[a]	Rang	7.26-8.14	5.2-94.0	85.5-334.1	0.20-1.50	2-128	0.6-25	0.5-12.5	18-190	150-570
TS	Rang	6.7-7.5	20-46	nd-6.8	0.02-0.08	1.24-10.29	0.01-0.08	0.13-2.67	1.12-19.92	17.70-153.03
	Mean±S.D.	7.3±0.3	33±10	3.66±2.98	0.05±0.02	3.00±2.64	0.02±0.03	0.72±0.71	4.07±5.46	67.12±50.53
GW (Zone 1)	Rang	7.1-7.8	7.8-23.6	nd	0.02-0.05	2.03-2.59	0.008-0.023	0.32-0.40	0.14-1.04	2.10-7.20
	Mean±S.D.	7.5±0.1	13.4±6.2		0.03±0.01	2.32±0.18	0.016±0.005	0.37±0.03	0.44±0.29	3.25±1.77
GW (Zone 2)	Rang	7.4-7.7	5.2-17.3	nd	0.02-0.05	2.15-6.79	0.004-0.012	0.35-0.39	0.17-1.21	1.16-5.36
	Mean±S.D.	7.5±0.2	8.1±5.1		0.03±0.01	2.95±1.84	0.009±0.003	0.37±0.01	0.41±0.40	3.19±1.49
GW (Zone 3)	Rang	7.5-8.7	5.0-15.4	nd	0.02-0.08	1.81-2.30	0.012-0.023	0.28-0.37	0.23-0.25	2.71-5.86
	Mean±S.D.	7.8±0.5	11.8±3.7		0.04±0.04	2.00±0.26	0.017±0.005	0.33±0.05	0.24±0.01	3.90±1.71
GW (Zone 4)	Rang	7.5-7.7	6.5-18.2	nd	0.02-0.02	2.20-2.53	0.012-0.048	0.30-0.37	0.18-0.44	2.01-5.79
	Mean±S.D.	7.6±0.1	12.1±5.8		0.02±0.00	2.38±0.17	0.026±0.020	0.35±0.04	0.33±0.14	4.39±2.08

[a]Quality indicators for SW in a sewage-irrigated area were obtained from experimental data published by Dong et al. (1993) [25] and the SGPICSB (1980) [22]. The data in the table are expressed as the means±standard deviation.

Results

Table 1 shows the water quality indicators measured in the SW, TS, and GW samples. Historically, the SW used for irrigation has exhibited high COD_{Cr} (5.2-94.0 mg/L), BOD_5 (85.5-334.1 mg/L) and pH (7.26-8.14), along with the high concentrations of examined heavy metals. The mean pH value of the TS (7.3) was 0.13 to 0.46 lower than that of GW samples from the sewage-irrigated zones and the control zone. The mean COD_{Cr} (33 mg/L) of the TS was 2 to 4 times higher than that of the GW in the examined zones. There were no significant differences in COD_{Cr} levels among the GW samples from the examined zones (Zone 1 through Zone 4; $p<0.05$).The mean concentrations of Cd, Cr, Cu, Hg, Pb, and Zn in TS were 0.05, 3.00, 4.07, 0.02, 0.72, and 67.12 µg/L, respectively. The HMs in TS were 2 to 25 times higher than the corresponding concentrations in groundwater samples from sewage-irrigated zones. The HMs in GW from the sewage-irrigated zones did not significantly differ from those in the groundwater of Zone 4, the control zone ($p<0.05$).

Fig. 2 presents the pH and OM content levels of the 0-30 cm layers of soil from each examined zone. The mean pH values of the soil samples from Zones 1, 2, 3, and 4 were 8.10, 8.22, 8.17, and 8.27, respectively, whereas the mean OM contents of the soil samples from these zones were 18.6, 15.5, 13.1, and 14.2 g/kg, respectively. The mean pH values of the soils from Zones 1, 2, and 3 were 0.05 to 0.17 lower than the pH value of the soil from the control zone. The soil OM contents in Zone 1 and Zone 2 were 29.8% and 8.4% higher than the soil OM content of Zone 4, respectively.

Table 2 presents the descriptive statistics of the heavy metal concentrations of topsoils (0-30cm) and whole soil profiles (0-100 cm) from each examined zone and background values for the studied soils. The Cr concentrations in topsoils (0-30cm) and whole soil profiles (0-100cm) of Zone 1~Zone 4 were significantly higher ($p<0.05$) than its background value. The Cu concentrations in topsoils (0-30 cm) from the sewage-irrigated zones (Zone 1~Zone 3) and in whole soil profiles (0-100 cm) from Zone 2 were significantly higher ($p<0.05$) than its background value. The Hg concentrations in topsoils (0-30 cm) from Zone 1 were significantly higher ($p<0.05$) than its background value. The Zn concentrations in topsoils (0-30 cm) and whole soil profiles (0-100 cm) from Zone 2 were significantly higher

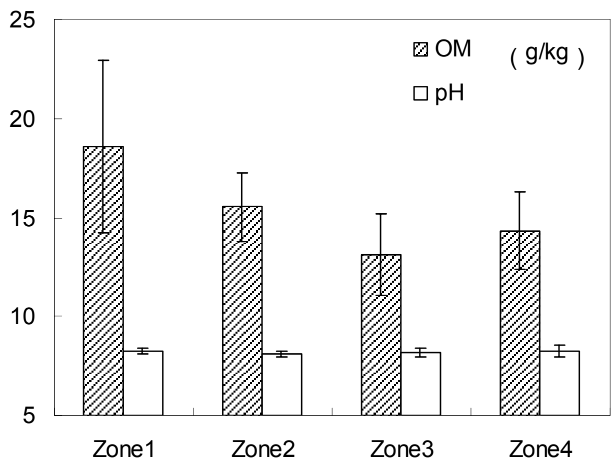

Fig. 2. The pH levels and OM contents of soil samples from the sewage-irrigated and control zones.

Table 2. Heavy metal concentration background values (mg/kg) in the studied soils.

Metals	Depth	Zone 1	Zone 2	Zone 3	Zone 4	Background values[a]	MPC[b]
		40 years	30 years	20 years	0 years		
		Mean±S.D				Mean±S.D.	
Cd	0-30 cm	0.152±0.008	0.151±0.020	0.148±0.013	0.151±0.019	0.145±0.112	0.60
	0-100 cm	0.121±0.015	0.139±0.024	0.122±0.005	0.107±0.010		
Cr	0-30 cm	70.51±5.60	68.95±4.48	64.82±4.17	65.92±5.04	31.10±9.29	250
	0-100 cm	69.24±5.51	72.29±6.65	67.67±1.81	64.27±5.98		
Cu	0-30 cm	26.76±1.77	23.82±1.26	22.97±2.19	21.80±1.90	19.70±6.33	100
	0-100 cm	24.01±4.01	25.56±4.03	23.13±1.82	19.88±1.68		
Hg	0-30 cm	0.136±0.070	0.095±0.022	0.069±0.025	0.058±0.011	0.069±0.051	1.00
	0-100 cm	0.076±0.036	0.067±0.026	0.052±0.017	0.064±0.052		
Pb	0-30 cm	26.49±3.34	23.51±1.22	23.52±1.16	21.98±0.95	25.10±5.08	350
	0-100 cm	22.99±2.80	23.08±2.56	21.74±0.70	20.27±1.52		
Zn	0-30 cm	72.42±4.69	73.06±13.68	65.88±5.43	71.14±10.45	59.06±19.29	300
	0-100 cm	64.58±8.12	70.93±11.02	63.40±3.07	61.69±1.99		

[a] Hg value from CNEMC (1990) [26], other heavy metal values from Chen et al. (2004) [27]
[b] Maximal permissible concentrations as defined by MEPC [28]

($p<0.05$) than its background value. Other heavy metal concentrations in topsoils (0-30 cm) and whole soil profiles (0-100 cm) from the sewage-irrigated zones had no significant difference compared with the background values. The soil heavy metal contents of topsoils (0-30 cm) and whole soil profiles (0-100 cm) in the sewage-irrigated zones were all lower than the second-level standards specified in the Environmental Quality Standard for Soils [28].

Fig. 3 shows the distributions of Pb, Hg, Cu, Cd, Cr, and Zn along the soil profile for each examined zone. The accumulation of Pb, Hg, and Cu in the 0-30 cm soil layers of Zones 1, 2, and 3 in the sewage-irrigated areas relative to Zone 4 (the control zone) exhibited a certain increased pattern. Compared with the control zone, the 0-30 cm samples from Zones 1, 2, and 3 exhibited 14.8%, 6.9%, and 6.9% greater Pb content; 131.6%, 81.6%, and 31.7% higher Hg content; and 22.72%, 9.24% and 5.35% higher Cu content, respectively(Table 2). The concentrations of Cd and Cr in each of the examined zones varied by ±7% from the corresponding concentrations in the control zone in the 0-30 cm soil layer. At 40-70 cm of soil depth, soil samples from Zone 2 exhibited 61.96%, 19.86%, 21.98%, 42.89%, and 26.75% higher Cd, Cr, Pb, Cu, and Zn contents, respectively, than soil samples from Zone 4.

Table 3 shows the calculated PLI values for each of these sewage-irrigated zones. In our study, the mean concentrations of each heavy metal in the 0-100 cm soil profile of Zone 4 was used as $C_{reference}$. C_{metal} represented the mean concentration of a given heavy metal in the 0-100 cm soil profile of each sewage-irrigated zone. The heavy metal PLI values for soils from all examined sewage-irrigated treatment zones generally ranged from 1 to 2.

Table 3. PLI values for different sewage-irrigated zones.

Metals	Zone 1 (40 years)	Zone 2 (30 years)	Zone 3 (20 years)
Cd	1.12	1.29	1.15
Cr	1.08	1.12	1.06
Cu	1.20	1.27	1.16
Hg	2.03	1.86	1.47
Pb	1.13	1.13	1.07
Zn	1.04	1.14	1.03

Table 4 shows the heavy metal contents of winter wheat grains and summer maize kernels from the examined zones. The mean concentrations of the heavy metals Cd, Cr, Cu, Hg, Pb, and Zn were 0.033, 0.212, 6.569, 0.002, 0.107, and 33.794 mg/kg, respectively, for winter wheat grains and 0.006, 0.136, 2.112, 0.002, 0.078, and 20.885 mg/kg, respectively, for summer maize kernels in the sewage-irrigated zones. The duration of sewage irrigation (40, 30, or 20 years) did not significantly impact the heavy metal content of winter wheat grains or summer maize kernels ($p<0.05$). Thus, for the examined heavy metals, the order of the total metal concentrations in winter wheat and summer maize in the irrigated regions was Zn>Cu>Hg>Cr>Pb>Cd. Table 5 shows the heavy metal transfer factors (TF) in the examined soil-plant systems. The order of TFs for the examined metals, from high to low, is $TF_{Zn}>TF_{Cu}>TF_{Cd}>TF_{Hg}>TF_{Pb}>TF_{Cr}$.

Discussion of Results

As shown in Table 1, the concentrations of the oxygen demands and all examined heavy metals were markedly higher in the SW than in TS and GW samples. In particular, the Cr (2-128 μg/L) and Hg (0.63-25 μg/L) levels measured in certain SW effluent samples were higher than the existing limits for sewage effluent reuse, which are 100 μg/L and 1 μg/L, respectively [29]. The Cu and Zn concentrations in TS were relatively high [30], but lower than the existing limits [29]. The heavy metal concentrations in the groundwater of all of the examined zones were markedly lower than standard limits [31]. The high percentage of clay and silt in the sewage-irrigated soils of the study area would facilitate the metals to cumulate in upper soil layers [13, 32]. As shown in Fig. 3 and Table 2, the HM contents exhibited a decreasing trend from upper to lower soil layers in the 0-100 cm soil profiles with 40 years irrigated history.

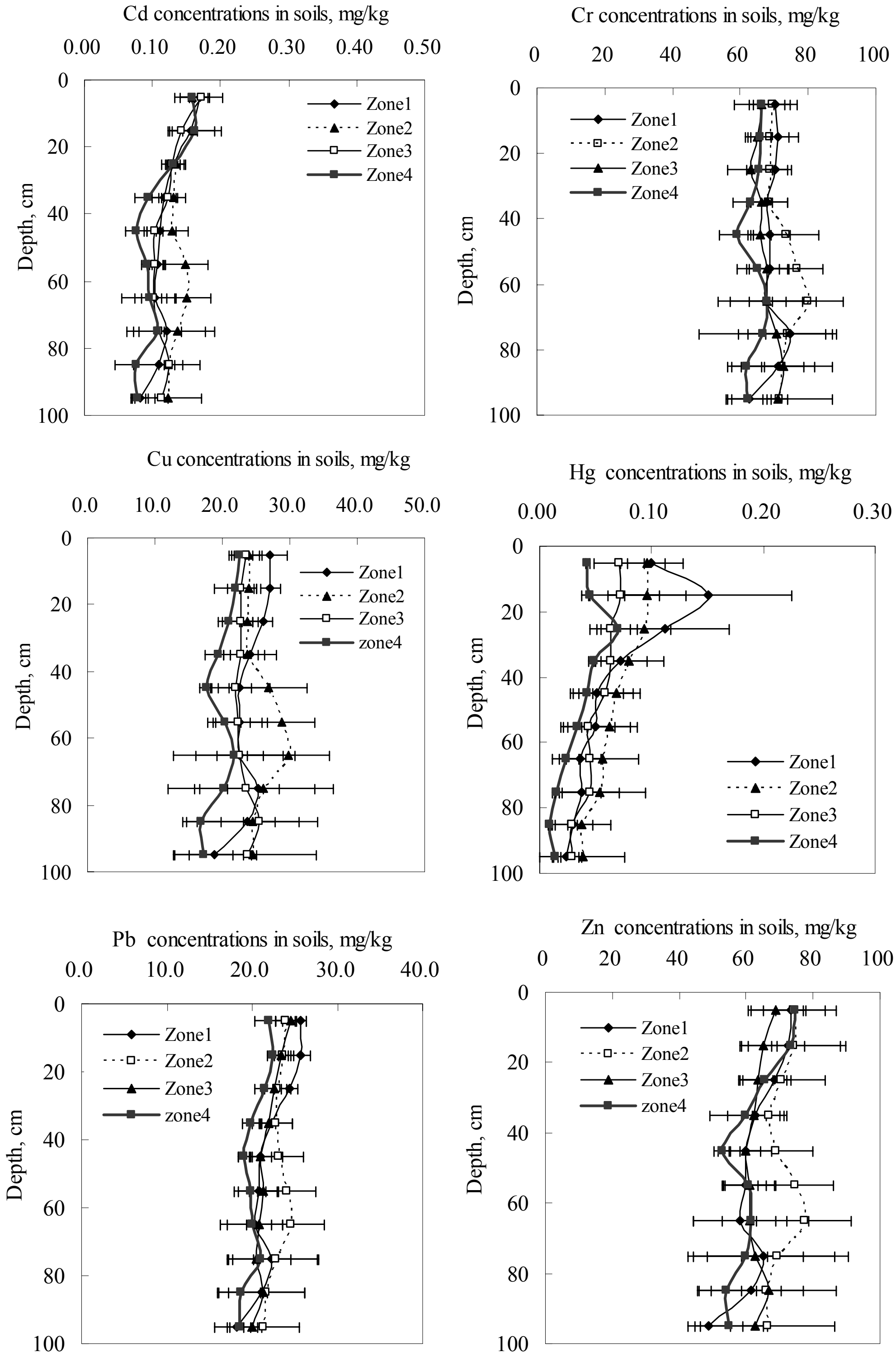

Fig. 3. Heavy metal concentrations in each 10-cm layer of the 0-100 cm soil profile for all examined zones.

Table 4. Mean concentrations of heavy metals in wheat and maize grains (dry weight) in the sewage-irrigated and control zones.

Metals	Species	Zone 1	Zone 2	Zone 3	Zone 4
Cd	Winter wheat	0.037±0.012	0.031±0.005	0.032±0.013	0.030±0.007
	Summer maize	0.007±0.002	0.006±0.001	0.007±0.002	0.005±0.001
Cr	Winter wheat	0.191±0.057	0.210±0.083	0.234±0.013	0.193±0.009
	Summer maize	0.139±0.027	0.135±0.023	0.135±0.068	0.111±0.015
Cu	Winter wheat	6.409±1.102	6.451±1.147	6.848±1.040	6.289±0.525
	Summer maize	2.225±0.138	2.137±0.213	1.974±0.283	2.317±0.418
Hg	Winter wheat	0.0016±0.0002	0.0016±0.0002	0.0015±0	0.0018±0.0003
	Summer maize	0.0015±0.0002	0.0017±0.0002	0.0015±0	0.0020±0.0003
Pb	Winter wheat	0.103±0.014	0.118±0.034	0.100±0.016	0.065±0.015
	Summer maize	0.091±0.026	0.088±0.017	0.056±0.014	0.048±0.039
Zn	Winter wheat	35.142±6.968	33.944±7.363	32.297±10.701	31.108±2.375
	Summer maize	20.385±2.305	21.183±2.075	21.088±3.896	16.254±1.695

Table data are expressed as the means±standard deviation

Table 5. TFs in the soil-plant systems of sewage-irrigated and control zones.

Metals	Species	Zone 1	Zone 2	Zone 3	Zone 4
Cd	Winter wheat	0.241	0.208	0.216	0.202
	Summer maize	0.043	0.037	0.048	0.032
Cr	Winter wheat	0.003	0.003	0.004	0.003
	Summer maize	0.002	0.002	0.002	0.002
Cu	Winter wheat	0.242	0.273	0.302	0.289
	Summer maize	0.083	0.090	0.087	0.108
Hg	Winter wheat	0.014	0.017	0.024	0.025
	Summer maize	0.016	0.018	0.024	0.029
Pb	Winter wheat	0.004	0.005	0.004	0.003
	Summer maize	0.003	0.004	0.002	0.002
Zn	Winter wheat	0.491	0.478	0.485	0.441
	Summer maize	0.281	0.295	0.324	0.230

In addition, the vadose zone and the shallow aquifer in the study area contain a large amount of clay and sand-clay interlayers, which has certain anti-pollution properties. Thus, the HMs would not easily transfer through the vadose zone into the shadow groundwater. Therefore, the long-term sewage irrigation would not constitute the accumulation of HMs in shadow groundwater [23].

The pH of the sewage effluent was lower than that of local groundwater. As a result, long-term sewage irrigation produced a decrease in soil pH [17, 30]. The high BOD in sewage effluents or treated sewage increases the OM content of soil irrigated with this water [23]. The zone subjected to sewage irrigation for 40 years exhibited the lowest pH and highest soil OM content. In addition, OM can provide important carriers that bind to certain heavy metals (including Cu, Ni, Zn, and Cr, among other elements) in the soil [33]. Thus, OM can affect the adsorption of heavy metals and other pollutants into the soil and reduce the risk of heavy metal leaching into deep soil layers or groundwater [11]. However, heavy metal accumulation in the topsoil can increase the transfer of these heavy metals to cultivated plants, thereby enriching the heavy metal concentrations of the associated crops; this effect poses certain risks to crop growth and human health [7].

As shown in Fig. 3, the soil from Zone 1 with 40 years of sewage irrigation history, which had the greatest topsoil

OM content among the examined zones, exhibited the highest levels of each of these heavy metals, with Pb, Hg, and Cu concentrations in the 0-30 cm soil layers reaching 26.49, 0.136, and 26.76 mg/kg, respectively. Pb, Hg, and Cu concentrations in the soils from Zone 1 were significantly higher ($p<0.05$) compared with that in the reference soils in Zone 4 (Table 2). The Pb and Hg contents of the 0-30 cm soil layers from this zone were higher than those reported for the 0-30 cm soil layers of Mexican regions that had undergone 41 years of sewage irrigation [1]. Compared with Zone 4 (the control zone), Zones 1, 2, and 3 exhibited 60.6%, 110.9%, and 67.6% greater Hg contents, respectively, in the 30-100 cm soil layer. Overall, the 0-100 cm soil profiles for each examined zone exhibited a trend of decreasing Hg contents at increasing depths (Table 2, Fig. 3).

As indicated in Table 1, the sewage effluents that had previously been utilized for sewage irrigation had high Hg concentrations (0.63-25 μg/L). Zone 1 is located near the city and the main Tonghui conveyance canal, and it was the first of the examined zones to use sewage irrigation (beginning in 1960). The resulting input of sewage effluents with high Hg levels produced obvious Hg enrichment in soils of 0-30 cm depth in 1979 [22]. Hg accumulation in the uppermost soil layers became more significant as the duration of sewage irrigation lengthened [34]. Zone 2 initiated sewage irrigation at a later date, and there was no significant soil impact from nearly 10 years of treated sewage application in this zone.

Studies of similar regions have indicated that sewage irrigation and soil parent material are the main causes of Pb accumulation in the surface layers of soil in sewage-irrigated areas [35]; in addition, the contribution of atmospheric dust to soil Pb accumulation was similar to that of sewage irrigation [36]. The SW used during the early stages of sewage irrigation in the examined regions exhibited high Cu (18-190 μg/L) and Zn (150-570 μg/L) contents. In addition, even the treated sewage used for irrigation at later time periods featured higher Cu and Zn contents than the groundwater. When sewage effluents with high concentrations of certain exogenous heavy metals (Cu, Zn, Cd, and Pb) enter the soil, Pb is the first metal to be adsorbed, followed by Cu. Among these metals, Cd and Zn are the most weakly adsorbed by soil, demonstrating the strongest transfer capabilities in soil, whereas Pb demonstrates the weakest transfer capability [37]. Therefore, long-term sewage irrigation is the main source of the increases in the Hg, Pb, and Cu contents of the 0-30 cm topsoil layers of the examined sewage-irrigated zones, particularly in Zone 1 (Table 2, Fig. 3).

The increases in Cd, Cu, and Zn at 40-70 cm soil depth of Zone 2 were greater than the increases in other zones. There was a marked enrichment of heavy metals at sampling sites along sewage-conveying waterways. For the 40-70 cm soil layers of the S5, S6, and S7 sampling sites along the Cha and Feng rivers in Zone 2, the soil Cd content reached 0.178, 0.177, and 0.149 mg/kg; the soil Cu content reached 32, 35, and 29 mg/kg; and the soil Zn content reached 86, 87, and 75 mg/kg, respectively. All of these concentrations were 29% to 103% higher than the corresponding mean concentrations of control samples. It indicated that the extent of heavy metal accumulation was higher in soils closer to sewage-conveying waterways [23, 34]. In addition, as sewage irrigation duration lengthens, heavy metals with stronger transfer capabilities tend to enrich deeper soil layers [16].

For each of the other examined heavy metals, the maximum PLI value (which ranged from 1.14 to 1.29) was found in Zone 2. The PLI_{Hg} for Zone 1 was 2.03; all of these calculated PLI were consistent with previous results found by Xu et al. in treated-sewage-irrigated areas with 3, 8, 20 years [16], which were lower than the mean calculated PLI values for similar areas [18, 21]. However, if long-term treated sewage irrigation is to continue in the study area, the soil Cu, Hg, and Pb contents should be monitored to avoid the risk of heavy metal pollution.

The heavy metal contents found in winter wheat grains were essentially consistent with previous results reported in studies in similar areas [38], whereas these found in summer maize in this study were significantly lower than those found by Khan et al. [18]. The Pb contents of winter wheat grains and summer maize kernels from Zones 1 and 2 were significantly higher than those in samples from Zone 4 ($p<0.05$). The Zn contents of summer maize kernels were significantly higher in samples from all sewage-irrigated zones than in samples from Zone 4 ($p<0.05$). With the exception of Pb and Zn, other heavy metals do not appear to become more concentrated in the grains and kernels of food crops with increases in the sewage-irrigated soil ($p<0.05$) [27, 39]. In addition, the observed accumulation of Pb in winter wheat in Zones 1 and 2 may be caused by the fall of atmospheric dust [21]. The observed contents of various heavy metals (Cd, Cr, Hg, and Cd) in crops from each sewage-treated zone were lower than the established standard limits [40].

Among the examined metals, Cd, Cu, and Zn exhibited the strongest transfer capabilities [18] and can therefore more readily be present at enriched levels in winter wheat and summer maize [41, 42]. The duration of sewage irrigation did not significantly impact the heavy metal TFs in soil-plant systems, suggesting that heavy metals in sewage-irrigated soil were not easily transferred into the plant chain and likely did not cause contamination risks [19]. However, soils in farmland near sewage waterways can accumulate heavy metals more readily; this phenomenon might lead to excessive heavy metal concentrations in crops, which would pose health risks [42].

Conclusions

Long-term sewage irrigation can increase the OM content of irrigated soils. The topsoils (0-30 cm) exhibited greater accumulations of the heavy metals (Pb, Hg, and Cu) in long-term sewage-irrigated zones. In addition, more obvious heavy metal accumulation in deeper soils was observed at areas that were close to sewage-conveying waterways than at other sites. The heavy metal contents of crop grains and kernels in sewage-irrigated zones did not exceed established limits. Zn, Cu, and Cd demonstrated stronger transfer capabilities in the soil-plant system and were therefore more likely to become enriched in plants, moreover, only Pb and Zn exhibited higher concentrations in crops in Zones 1 and 2 than in the control zone. Long-term sewage irrigation does not constitute a HMs pollution in soil accumulation or shadow groundwater. However, the monitoring of Hg, Pb, and Cu concentrations should be emphasized in areas that engage in treated sewage irrigation to prevent these HMs from entering the food chain and posing health risks.

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