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Assessment of Heavy Metal Pollution in Soil and Plants from Dunhua Sewage Irrigation Area

Jintao Liang [1], *Cuicui Chen* [1], *Xiuli Song* [1], *Yulan Han* [2], *Zhenhai Liang* [1,*]

[1] Taiyuan university of technology, No. 79 West Yingze Street, Taiyuan, Shanxi, 030024, China;
[2] Water Resources Bureau of Qingxu County, Qingxu, Taiyuan, Shanxi, 030400, China.
[*]E-mail: liangzhenhai@tyut.edu.cn

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To evaluate the heavy metal contamination of soil and plants in Dunhua sewage irrigation area (DIA), the area used wastewater for irrigation at least 20 years. 270 samples in different depth (0-120 cm) and 23 plant samples were collected at five different sites. Physical and chemical properties of the long-term sewage irrigation soil were analyzed, including soil texture, bulk density, pH, cation exchange capacity (CEC), organic matter; the heavy metal total concentrations were measured using AAS and AES. The average value of soil pH was 8.01, the soil was alkaline; the soil CEC changes from 59.35 mmol to 118.95 mmol, average value was 80.96 mmol; content of organic matter in surface soil maintained 1.27% to 2.18%; the bulk density of soil ranges from 0.94 to 1.57 g/cm^3; average concentrations of heavy metals in surface samples were: Cr, 28.249 mg/kg; Cd, 1.247 mg /kg; Pb, 37.468 mg/kg; heavy metal concentration in the three different crops of different portions was: root>stem>leaf>grain; the vertical distribution and migration the concentration of 0-20 cm soil was significantly higher than other soil layers, showing the characteristic of enrichment at surface, relatively stable in deep. Heavy metals pollution degree was Cd(2.069)>Cr(0.113)>Pb(0.107), pollution risk degree of different sample point's range was EC>MF>Xg>WD>XG. Irrigation by wastewater has increased the heavy metal concentrations in soil and plants of receiving area.

Keywords: Electrochemical Properties; Heavy Metals; Soil; Pollution Assessment; Plants; Dunhua sewage irrigation area

1. INTRODUCTION

With the rapid economic development, water shortage has become an important factor to limit people's lives and social development. In order to solve the problem of water shortage, from 20th century 50 years, China especially northern areas has begun to use wastewater for irrigation, it contains plant nutrients and organic matter, so this approach may be increased soil fertility, but wastewater composition is variable and contains high levels of toxic metals, therefore heavy metal contamination of agricultural soils has also become increasingly serious in sewage irrigation area[1]. Studies have shown that heavy metals are potentially toxic to crops, animals and humans when contaminated soils were used for crop production, because heavy metals are easily accumulated in vital organs to threaten crop growing and human health[2].

Heavy metal contamination of environment is a worldwide phenomenon that has attracted a great deal of attention[3]. Heavy metal contamination of soil resulting from wastewater irrigation is a cause of serious concern due to the potential health impacts of consuming contaminated produce[4]. In this study, with long history of Dunhua sewage irrigation area (hereafter abbreviated to DIA) was selected for the research, the wastewater originates from the industrial districts of Taiyuan, an assessment is made of wastewater irrigation on heavy metal contamination of DIA, and we hope to provide a reference for local eco-environmental management.

2. MATERIALS AND METHODS

2.1. Study area

DIA located in the Shanxi province of China, the area consists of five counties, where waste water was used to irrigate plants for at least 20 years. The irrigation area site extends from 112°9' to 112°38', lat. 37°27' to 37°47', north-south width is 35.8 kilometers, length of east to west is about 40.5 kilometers, and its boundaries encompass a total area of 609.13 square kilometers. According to the results of the second national soil survey, there are rich soil resources in irrigation area, the soils are classed to three major soil types, 18 soil genera, 114 species. Soil organic matter content of the study area is generally 1.00%-1.49%, with a maximum content 2.14%, the lowest content is 0.15%; total nitrogen content is about 0.05%-0.07%, the highest level is 0.179%, the lowest is 0.017%; available nitrogen content is between the 61-90 ppm, the highest level reached 108 ppm, the lowest concentration is 8 ppm; soil bulk density is 1.29 g/cm^3, porosity is 50.8%; pH value distributed around 8. Soil structure are mostly granular fragments and debris, color is generally brown-red, texture mostly are light soil, medium soil, deep soil, it with a higher degree of physical and chemical properties of production and is a kind ideal soil performance to develop agricultural.

2.2. Sampling

Soil sampling was carried out at 5 different locations in DIA, the location map of the Dunhua sampling sites was shown in Fig.1. The five sample points were Mengfeng town(MF), Xugou(XG), Wangda south (WD), Xigu (Xg), Echi(EC). The soils were sampled at six layers:0-20 cm, 20-40 cm, 40-60 cm, 60-80 cm, 80-100 cm and 100-120 cm, at the same time, three species crop were selected for study, which was corn, soybean and sunflower, which represented the major crop species growing in the area of study. At each sampling site, replicate samples (3) were random collected. Approximately, ≥1kg of soil and plants were collected from each layer at each point. In the laboratory, soil samples were air-dried for 7 days and then crushed, sieved to obtain<2 mm fraction; Crop samples were oven-dried to constant weights.

Figure 1. Map of the DIA with location of sampling sites of topsoils (solid points)

2.3. Analytical procedures

All chemicals ~~used~~ were analytical reagent grade; all solutions were prepared in deionized water. The main physic-chemical parameters determined for top soils from DIA include: pH values, cation exchange capacity and organic matter. Sample pretreatment and basic chemical analyses were conducted according to the routine analytical methods of agricultural chemistry in soil.

The pH values were determined using the classical method, about 4.0 g of the soils (<2 mm) were mixed with 10.0 mL deionized water in test tubes and measured using pH meter. The particle size distribution was tested by hydrometer, cation exchange capacity was measured according ammonium acetate exchange way, soil organic matter was determined by the Walkey-Black method; Soil samples were digested using aqua-regia (3:1 ratio of HCl to HNO_3), then using a hotplate as heating method. The extracts were analyzed by flame atomic absorption spectrometer (AA240FS Varian, Germany). Furthermore, all statistical analyses were obtained using SPSS13.0.

2.4 Evaluation Criteria and Methods

2.4.1. Evaluation Criteria

Soil quality evaluation criterion used the National Soil Environmental Quality Standard (GB15618-1995) of the Ⅱ-Standards (standard of agricultural land), as shown in table 1[5].

Table 1. Standard of soil environment qualification (mg/kg)

evaluation criteria		As	Hg	Cd	Pb	Cr	Cu	Ni	Zn
	pH<6.5	40	0.3	0.3	250	150	50	40	200
national Ⅱ-standard	6.5<pH<7.5	30	0.5	0.3	300	200	50	50	250
	pH>7.5	25	1.0	0.6	350	250	100	60	300

2.4.2. Evaluation methods

The current evaluation methods were mainly single index method and the composite index (Newmerow) method, the composite index method was divided into mean-based index and weighted index. Pollution index method was used in this study, quality of soil environment classification was measured using the composite index method, and single pollution index could be more directly reflects the pollution of the environment indicators, their calculation formula as follows:

$$Pi = Ci / Si$$

Where *Pi* was the pollution index; *Ci* and *Si* represent the heavy metal concentrations in the wastewater irrigated soil and evaluation criteria values, respectively[6].

Newmerow composite index method not only takes account all the individual evaluation factor which also highlights the importance of the most contaminated elements, concrete calculation formula as follows:

$$P_s = \sqrt{\frac{p_{ave}^2 + P_{\max}^2}{2}}$$

Where P_{ave} was the average pollution index; P_{max} was the maximum value of the pollution index.

Potential ecological risk assessment of soil has been proposed by Hankanson in 1980[7].

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$$RI = \sum_{i=1}^{n} E_r^i \,; \quad E_r^i = T_r^i \times C_f^i$$

$$C_f^i = \frac{C_{surface}^i}{C_n^i}$$

Where, *RI* was comprehensive potential ecological risk index, sampling points of soil heavy metals in; as a; *T* represents for a certain kind of metal toxicity response coefficient, *E*—potential ecological risks of individual factors; $C_{surface}$—the measured values concentration of heavy metals in soil surface; C_n—reference value concentration of soil; Cr, Cd and Pb coefficients of toxicity were 2, 30 and 40, respectively. Potential ecological risk index classification was listed in Table 2.

Table 2. Grades of potential ecological risks

E_r	Single-pollutent ecological risk	*RI*	Comprehensive-potential ecological risk
<40	slight	<90	slight
40-80	moderate	90-180	moderate
80-160	strong	180-360	Strong
160-320	very strong	360-720	very strong
320	highly strong	>720	highly strong

3.RESULTS AND DISCUSSION

3.1. Physicochemical parameters

Table 3 summarizes the physicochemical characteristics of soil samples. Soil texture classification was based on the fractions of separates present in the soil, the main constituents (clay, silt and clay) of DIA were given in Table3, irrigation area soil belong to loam texture class. Generally, pH values of soil divided into five degrees, strong acidic pH<5.0, acid pH 5.0-6.5, neutral pH 6.5-7.5, alkaline pH 7.5-8.5, strong alkaline pH>8.5, As can be seen from results the irrigation area of soils were alkaline and the pH value mainly ranges from 7.61 to 8.38, the overall average pH value was 8.01; cation exchange capacity(CEC) was used as a measure of fertility and nutrient retention capacity, the soil CEC changes from 59.35 mmol to 118.95 mmol, average value was 80.96 mmol; The electric field on interface of soil possesses some special important functions in soil systems, by the theoretical knowledge soil cation exchange capacity shows the same trend of change with soil pH values, because the charge amount on the surface of soil colloidal particle and cation exchange capacity decrease while the soil pH value reducing.

Soil organic matter (SOM) content not only determined the nutritional status, but also affected the migration of heavy metals, content of organic matter in surface soil maintained 1.27% -2.18%, the average content of the surface irrigated soil organic matter was 1.69%; the bulk density of soil ranges from 0.94 to 1.57 g/cm^3, the bulk density of soil depends greatly on the mineral make up of soil and degree of compaction, soil high in organics and some friable clay may have a bulk density well below 1 g/cm^3 ; soil moisture content ranged from 18.56% to 35.60% with an average value of 25.72%.

Table 3. Soil properties of the samples (0-20 cm)

	Clay (%)	Silt (%)	Sand (%)	pH	CEC (mmol/kg)	SOM (%)	Bulk density (g/cm^3)	Soil moisture (%)
Mean	8%	43%	49%	8.01	80.96	1.69	1.32	25.72
Minimum	5%	17%	30%	7.61	59.35	1.27	0.94	18.56
Maximum	11%	60%	78%	8.38	118.95	2.18	1.57	35.60

3.2.Heavy metal concentrations

3.2.1.Concentrations of Pb, Cr and Cd in topsoil

Table 4 shows distribution of Cr, Cd and Pb concentrations in the five different sample sites, in comparison with the Chinese soil Environmental Quality Standard (GB15618-1995), only Cd concentrations surveyed in these five areas was above the corresponding values of standard, it ranging from 0.90 to 1.76 mg/kg, average content reached 1.25 mg/kg, which was 2.11 times of the national standard value, and the coefficient of variation was small, this indicates that the pollution levels was consistent . As we all know, Cd was a non-essential elements of human health with a high biological toxicity, it mainly accumulated in the surface soil, which enter the body mainly through the digestive system[8], the local environmental protection departments should take steps to control the Cd pollution. Maximum Cr contents were observed in XG 30.79 mg/kg; the average Cr and Pb concentration were 28.25 mg/kg and 37.47 mg/kg, respectively.

Table 4. Cr, Cd and Pb contents of surface soil (mg/kg)

Sample points	MF	XG	WD	Xg	EC
Mean	28.71	30.79	28.69	28.76	24.29
Cr Maximum	46.48	49.21	51.58	59.07	54.49
Minimum	13.66	12.57	9.72	9.83	11.51
CV	0.40	0.37	0.43	0.52	0.46
Mean	1.23	1.42	1.26	1.22	1.11
Cd maximum	1.56	1.76	1.71	1.74	1.38
Minimum	1.04	1.20	0.97	0.93	0.90
CV	0.12	0.13	0.16	0.18	0.12
Mean	34.32	36.05	35.80	32.00	49.18
Pb maximum	44.86	51.58	46.89	51.57	110.82
Minimum	22.53	20.83	25.81	18.57	20.69
CV	0.20	0.31	0.21	0.28	0.63

3.2.2.Vertical distribution and migration of heavy metal

Heavy metal concentrations in different depth showed significant variations, this trend may be correlated with the soil properties that influence heavy metal availability in different depth. The concentration of 0-20 cm soil was significantly higher than other soil layers, showing the characteristic of enrichment at surface, relatively stable in deep soil layer, the fundamental reason was the long-term sewage irrigation; the relationship between heavy metals and the depth obey exponential distribution, the relationship formula was shown in Figure 2.

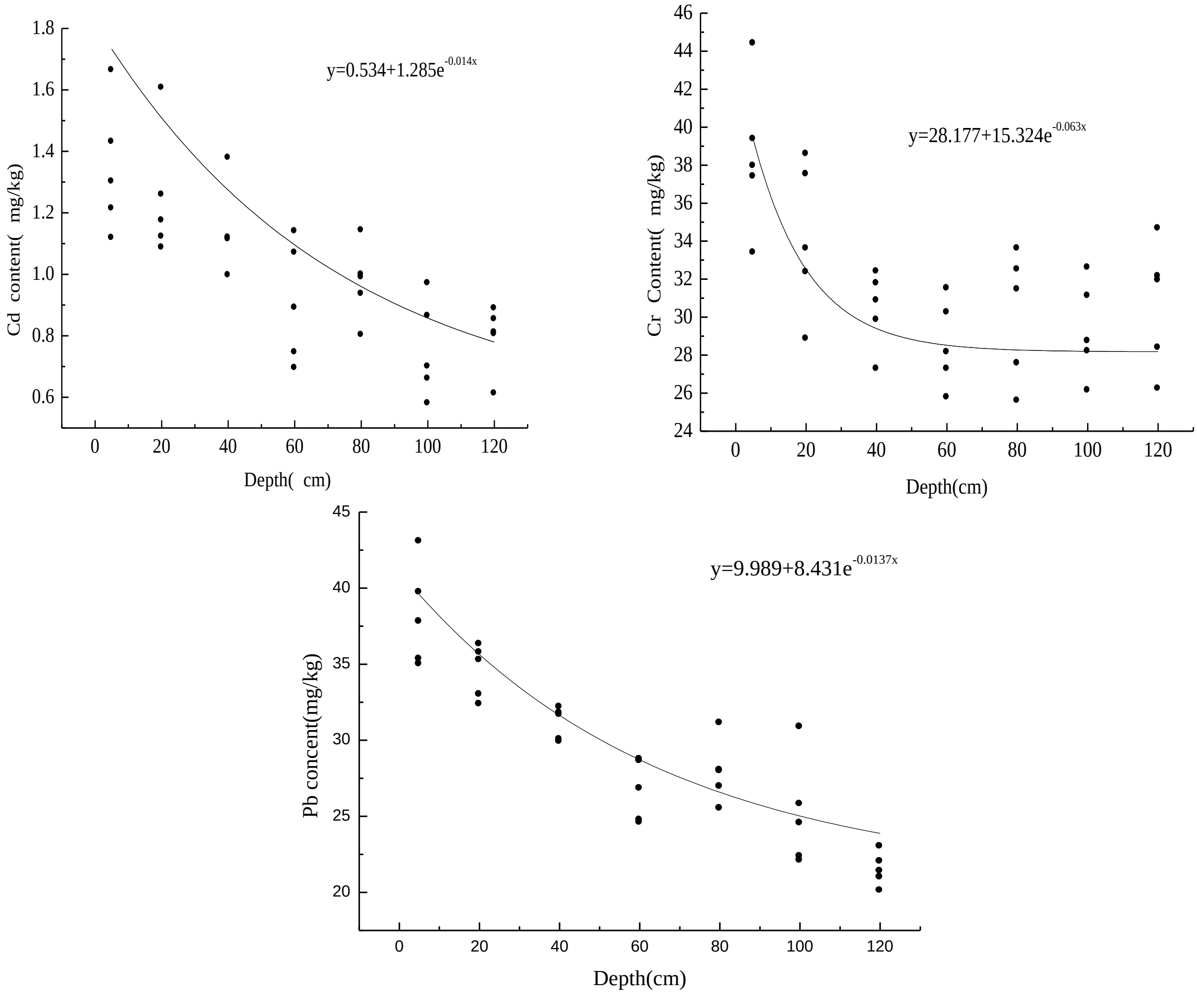

Figure 2. Distribution of heavy metal in profile soils

3.3. Heavy metal concentrations in plants

Mean contents of heavy metals in the dry matter of various plants grown on the soils of study were summarized in table 5, table 6 and table 7. In general, heavy metals in plants depended on the species and collection site, heavy metal concentration of the three kinds crop in different parts was: root>stem>leaf>grain[9].

Table 5. Content of Cd in organs of different plant (mean mg/kg)

plants	root	stem	leaf	seed
Corn	0.0552	0.0227	0.0127	0.0138
Soybean	0.433	0.224	0.396	0.0776
Sunflower	0.105	0.0341	0.0102	0.0112

Table 6. Cr Content of Cr in organs of different plant (mean mg/kg)

plants	root	stem	leaf	seed
Corn	2.446	1.983	2.077	0.361
Soybean	2.140	1.723	1.908	0.794
Sunflower	3.582	1.165	1.236	0.499

Table 7. Content of Pb in organs of different plant (mean mg/kg)

plants	root	stem	leaf	seed
Corn	0.974	0.851	0.209	0.138
Soybean	1.685	1.512	1.133	0.106
Sunflower	1.746	1.225	0.980	0.527

Cd concentration in plants was rather high and varied from 0.0102 to 0.433 mg/kg, Cd in soybean has the highest degree of enrichment, followed by sunflower, the lowest levels are found in corn, so soybean was a special crop suit for plant in the DIA; the degree of enrichment of heavy metals Cr in three kinds of crops was order in corn, sunflower and soybeans, respectively. Cr content in corn grains was 0.361 mg/kg far lower than the content in soybean 0.794 mg/kg; Pb was a heavy metal with a relatively large coefficients toxicity, but in the study of three crops, the concentration in a relatively low levels, mainly because of Pb compounds is not easy to migrate, high Pb values in plants were recorded for sunflower.

3.4. Assessment of soil heavy metal

3.4.1. Pollution index assessment

It was essential to estimate the pollution degree of soil, pollution index Ps of Cr, Cd, and Pb in soils together with median values are listed in table 8, the degree of pollution in five different points and between the heavy metals can be draw.

According to the average single pollution factors, the three kinds different heavy metals pollution degree was Cd(2.069)>Cr(0.113)>Pb(0.107), Cd was the most serious pollution heavy metal, it reached moderately pollution degree, Cr and Pb was slightly; Comprehensive pollution index presented the pollution degree of different sample point's range was XG(1.691)>WD(1.494)>MF(1.468)>Xg(1.445)>EC (1.317) , all of the pollution index≥1, heavy metal contamination of irrigation area was a mild level, indicated the crops have been affected[10].

Table 8. The result of pollution index assessment

Sample points	MF	XG	WD	Xg	EC	Mean
P_{Cr}	0.115	0.123	0.115	0.115	0.0972	0.113
P_{Cd}	2.057	2.370	2.049	2.025	1.845	2.069
P_{Pb}	0.0981	0.103	0.102	0.0914	0.141	0.107
Ps	1.468	1.691	1.494	1.445	1.317	1.483

3.4.2. Assessment of potential ecological risk

Hakanson ecological risk method was used to assessment the potential ecological risk of heavy metals, Er and RI of heavy metals were listed in table 9, the background concentration of soil in the area was used as comparison for assessment. The results showed that pollution of Cd was the main factor causing the risk of soil, the comprehensive risk index RI distributed in 362.701 to 453.491, which reached the strong degree of pollution. The total risk index was contributed by heavy metal Cd, account for above 97.59%, the other were lower, pollution risk degree of different sample point's range was EC>MF>Xg>WD>XG.

Due to the electrochemical character have different impact to heavy metals, the most serious potential ecological risks was Cd, the result was consistent with pollution index assessment, but the pollution degree of different sample points was great distinguish, it was because Hakanson ecological risk method stressed the toxicity coefficient of heavy metals, which also was the major different of two assessment methods[11].

3.5. Heavy metal transfer factors

Heavy metal concentration in the extracts of soils and plants were calculated on the basis of dry weight. The plant concentration factor (PCF) was calculated as follows:

$$PCF = \frac{Cplant}{Csoil}$$

Where C_{plant} and C_{soil} represents the heavy metal concentration in extracts of plants and soils on dry weight basis, respectively[12].

The PCF values were provided in Fig.3. Typically, the soil-to-plant transfer factor is one of the key component~~s~~ of human exposure to metals through the food chain. By compared the edible parts (seads), the calculate results indicate the transfer values in corns was Cr>Cd>Pb; in soybeans was Cd> Cr>Pb; in sunflowers was Cr=Cd>Pb, the diversity may be due to the differences in soil properties; enrichment factor of Pb was minimum, because activity of Pb was low, not easy to migrate. It also can through the theory of electrochemical properties to explain.Soil electrolyte plays an important role in the process of heavy metal transfer. The electrochemical properties of soil reflected through the temperature, pH and electrolyte concentration etc, thus influenced the migration transformation ability of heavy metal indirectly. By comparison with soil physicochemical parameters, the conclusion can be drawn: if the higher acidity of soil, the migration transformation ability more great, this is the main reason of heavy metals contents was below in alkalinity soil.

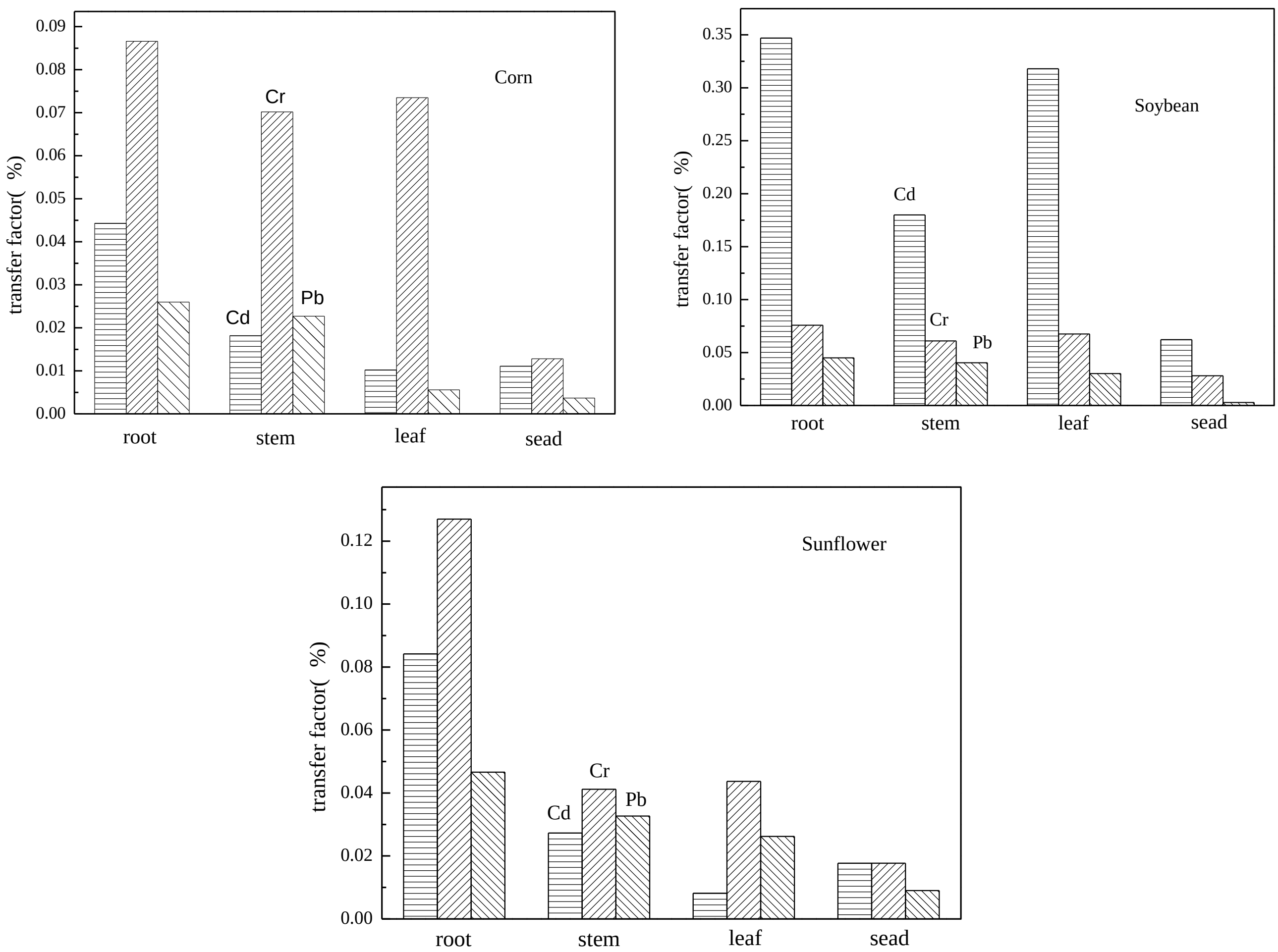

Figure 3. Heavy metal transfer factors (on dry weight basis) for different plants grown in wastewater irrigated soils

4. CONCLUSIONS

Table 9. The potential ecological risk factor of soils

Sample points	Cr	Cd	Pb	RI
		Er		
MF	1.225	402.680	6.600	410.505
XG	0.996	354.773	6.932	362.701
WD	1.245	375.464	6.884	383.593
Xg	1.226	390.000	6.154	397.38
EC	1.456	442.577	9.458	453.491

The study concludes that irrigation by wastewater has increased the heavy metal concentrations in soil and plants in receiving area. The irrigated soil was alkaline; the average cation exchange capacity was 80.96 cmol/kg, organic matter content of surface soil were 1.27%-2.18%; the long-term sewage irrigation led to serious contamination of Cd with average content up to 1.265 mg/kg, it was 2.11 times of the national standard value, pollution of Cd was the main factor causing the risk of soil. The soil environmental quality was the three grade, pollution degree of different sample sites was in the order: XG(1.691)>WD (1.494)>MF (1.468)> Xg(1.445)>EC(1.317); comprehensive risk index RI distributed in 362.701 to 453.491, which reached the strong degree of pollution. The total risk index was contributed by heavy metal Cd, account for above 97.59%, the other were lower. The range of different sample points pollution risk degree was EC>MF>Xg>WD>XG**.**

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