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Research Article

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Risk evaluation of heavy metals in soil in the sewage irrigation area A case study of shijiazhuang

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ABSTRACT

In this dissertation, we take the typical sewage irrigation area as research objects and the area irrigated by underground water as control area, gathering the soil samples in different area and then we may have some comparison with the heavy metals content of As, Pb, Cd, Hg and Cr. Single factor Index and integrated pollution index of Nemero was used to evaluate the contamination of soil heavy metals, Potential ecological risk index of Hakanson was used to evaluate the potential ecological risk of soil heavy metals in the sewage irrigation area.

Key words: heavy metals risk evaluation soil sewage irrigation area

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INTRODUCTION

Heavy metals refer to those metals whose relative density is equal to or more than 5 ,such as Au、Ag、 Pb, Cd, Hg and Cr. As's chemical properties and environmental effect is similar to heavy metals, so it is often classified with heavy metals [1].

Heavy metals pollution of the soil is due to the human activity, when the harmful element in the soil exceeds the background value; Excessive deposition of the harmful element makes the contamination [2].

Sewage irrigation refers to the use of irrigation water quality standards, urban sewage and industrial wastewater irrigated farmland in order to make full use of the sewage fertilizer efficiency. Sewage irrigation will affect the savings of the heavy metal content in the soil, resulting in the pollution.

While in many parts of China, the waste water is used for irrigation without being treated to meet the national hygienic standard. As a result, the heavy mental concentration in soil is over standard and the groundwater is polluted though infiltration [3-4].

Soil heavy metals pollution impact on crops [5], thereby affecting the health of the human body through the food chain, the harm caused by heavy metals in the human body is multifaceted, multi-level [6].

This study is carried on in Shijiazhuang, which has a long history of sewage irrigation. The project takes soil samples in sewage irrigation region in Shijiazhuang and the soil samples in groundwater irrigation region for the control so that we can confirm the heavy mental pollution status and carry on the following risk evaluation.

1 General situation of the region

The rivers in Shijiazhuang are divided into two water systems, Daqing river System and Ziya river System. The rivers in central south parts like Hutuo River, Xiao River, Jin River, Huai River, Zhu River are parts of Ziya River system. Especially, the Xiao River, which is originated in southern suburbs of Luquan, 48 kilometers long, is the main river channel for floods.

The sewage irrigation of Shijiazhuang dates back to a long time ago[7].Parts of Shijiazhuang suburbs began to take groundwater instead of sewage irrigation since 1981. Dongming Canal and Xiao river are arranged for pollution discharge and agriculture irrigation. Most of the pollutants in the water come from the domestic and industrial sewage of Shijiazhuang city, Luancheng County, Zhao County .Especially the wastewater of the Douyu industrial region in Luancheng, the medical bases of counties wastewater and the wastewater from Shijiazhuang oil refinery. Half of The total sewage is industrial waste water.

EXPERIMENTAL SECTION

2.1**Experimental Instruments**

Atomic absorption spectrum (PerkinElmer, Analyst800);
Inductance coupling plasma atom emission spectrometer (PerkinElmer, OPTiMA2000DV)
Atomic fluorescence spectrometer (Beijing Ruili analysis Instrument Company)
PH meter (Shanghai fine scientific instruments company)
BD120 fridge (Qingdao Haier Company)
Electronic analytical balance (Shanghai fine scientific instruments company, FA1104N)
Super pure water machine (MILLOPORE, Milli-Q Element)
Controlled temperature electric heating plate (Lab Tech Company, EG20A)

2.2 **Main reagent and Material**

Nitric acid, hydrochloric acid, high chlorine acid, hydrofluoric acid(Tianjin Fengchuan chemical reagent company, guarantee reagent.)
Cr, Cd, Pb, Hg, As standard solution(National Institute of Metrology,1000μg/L)
Soil standard metal (GBW-07427)(Beijing Longtian Taoyue company, North China plain soil)
Thiourea(Shanghai Darui fine chemicals company, guarantee reagent)
KOH(Beijng Yili fine chemicals company, guarantee reagent)
PBH(Beijng Yili fine chemicals company, guarantee reagent)

2.3 Soil measuring methods

There are a lot of method to detect the heavy metals in soil, such as Determination on heavy metals in soil by flame atomic absorption spectrometry using graphite digestion device [8], in this study, methods taken in this dissertation are as follows: Pb and Cd are detected by method of graphite Furnace Atomic Absorption (GB/T17141-1997);Cr is detected by method of inductor coupling plasma activation atomic emission spectrum(ICP-AES)[9].As and Hg are detected by method of atomic Fluorescence Spectrophotometer(AFS). (GB/T22105.1-2008).

3 The evaluation methodology and standard for the heavy metals pollution in soil

3.1 **The evaluation standard**

Considering the Region difference, we chose the local soil background value which matches the real condition better. The evaluation of the heavy mental potential ecological risk will take the local soil background value as the only evaluation standard. Evaluation standards are as follows:

The background soil value of Shijiazhuang(mg/L)
As=13.6；Pb=21.5；Hg=0.036；Cr=68.3；Cd=0.094

3.2 Evaluation methods

The evaluation methods for the heavy metals pollution in the soil are single factor index method and Nemero comprehensive index method (multiple factors comprehensive index methods) [10-11].

The single index method formula is as following.
$P_i = C_i/S_i$
Where Pi is the single factor index of i pollution, Ci is the measured concentration of the heavy element i(mg/L), Si is the evaluation standard or the background of the pollutants.

$P_i \leq 1$ means the soil is clear；$P_i > 1$ means the soil has been polluted；The bigger the Pi is, the worse the soil becomes.

As the base of multiple factors index, single factor index method is often used to evaluate whether a kind of heavy metals element becomes the pollution or not. Though the multiple functions of the all kinds of heavy metals is the direct reason of the soil pollution, it cannot comprehensively reflect the degree of the soil contamination. In order to confirm each pollutant's comprehensive harm to the soil, the Nemero method is widely adopted in our country at present. The formula is as following.

$$P=\sqrt{\frac{avr(Pi)^2+\max(Pi)^2}{2}}$$

Where P is the Nemero index, avr(Pi) is the average value of all pollutant index , max(Pi) is the maximum of all the heavy mental elements index.

The formula above contains the max single pollution distribution index which is the maximum of all the heavy mental pollutants, namely in certain conditions the degree of the most harmful heavy mental element of all the elements can produce to the soil. The standards of soil contamination by Nemero are as follow. $P\le0.7$，safe and clear；$0.7<P\le1$，less clear and alert；$1<P\le2$，light contamination；$2<P\le3$，middle contamination；$P>3$，heavy contamination。

3.3 **The evaluation method of the heavy mental potential ecological risk in soil**

The potential ecological contamination effect in the sewage irrigation region soil is evaluated by Hakanson potential ecological harmful index method. It takes the Shijiazhuang soil background value for control so that we can analysis the potential ecological risk of the heavy mental in soil. The formula is as follows [12].

$$C_f^i=C_s^i/C_n^i$$

$$E_r^i=T_r^i\times C_f^i$$

$$RI=\sum_{i=1}^{n}E_r^i$$

Where RI is the heavy mental comprehensive potential ecological harm index, E_r^i is the single heavy mental potential ecology harm coefficient, T_r^i is the toxicity reaction coefficient of one certain element on the sampling point(Cr=2,Pb=5,As=10,Cd=30,Hg=40;according to Hakanson)[13-14], C_f^i is the gathering coefficient of the heavy mental, C_s^i is the measured value of the heavy mental, C_n^i is the reference value.

4 **The risk assessment of heavy metals in the soil**

4.1 Single factor index method

4.1.1 Evaluation of single factor index in sewage irrigation area and the control area

As can be seen from Table 1, compared with the background values of Shijiazhuang,the five heavy metals in sewage irrigation list in order of single factor evaluation index: Cd> Hg> Pb> Cr> As, numerical order is 6.0526、4.2283、2.2683、1.3224、0.9370, the control group rank in order of the single factor evaluation index: Cd> Hg> Pb> Cr> As, numerical order is 5.4191, 3.6871, 1.5568, 0.9397, 0.6752. In sewage irrigation, All the heavy metals' single factor index are more than 1 except As, that means the soil is not contaminated by As elements, the remaining four elements of single factor index are more than 1, that means the soil is in a state of Cd, Cr, Hg and Pb pollution.

The single factor index of Cr and As in Control area is less than 1, that means the soil is not contaminated by Cr and As , the rest of the three elements of single factor index are more than 1, that means the soil in Control area is polluted by Cd, Hg and Pb. Single factor index shows that regardless of the sewage irrigation or control area the biggest single factor index is Cd , five single-factor index of heavy metals in sewage irrigation are more than in the control area.

4.1.2 Single factor index evaluation of sludge

As can be seen from Table 2, compared with the background values of Shijiazhuang, The evaluation index of As in the sludge is less than 1, the sludge is not contaminated by As. The evaluation index of Pb, Hg, Cr and Cd were more than 1, According to the order of Single factor index : Pb> Hg> Cd> Cr, numerical order is 25.0568、16.1969、4.3933、2.9780. Sludge is polluted by four heavy metals of Pb, Hg, Cd, Cr.

4.1.3 Single factor index evaluation different sampling sites

As can be seen from Table 2, compared with the Shijiazhuang background value, the single pollution index of Hg and Pb at all sampling sites are more than 1, sampling sites' soil has been polluted by them. There three sampling sites which are polluted by Hg most seriously, they are number 5, 19, 21,the numbers are 10.5050、9.4523、6.3738; The three sampling sites that Pb pollution is the most serious are number 15, 6, 3, the numbers are 14.0987、3.6914、3.0156;

According to the evaluation of single factor index, the soil is contaminated by Cr except sampling site 1, 21, 22, The three sampling sites that polluted heaviest by Cr are the number 2, 16, 3, numerical order is 2.4662、1.6139、1.6048; All the Single factor indexes of Cd are more than 1 except sampling site 4, most of the soil is polluted by Cd. The three sampling sites that polluted heaviest by Cd are number 20, 7, 9, numerical order is 9.7156、9.5950、9.3960; the single pollution index of As in the sampling sites 2, 6, 10, 11, 12, 14, 18 is more than 1，these sampling sites soil are polluted by As; The rest sampling sites evaluation index are less than 1, the rest soil is not contaminated by As. The three sampling sites that polluted heaviest by As are number 2, 10, 11, numerical order is 1.0763、1.0515、1.0298. Sampling sites of number 21, 22 belong to the sampling of the control area, but the single factor index of Hg, Cd, Pb is still more than 1.

4.2 evaluation of integrated pollution index (Nemero)

4.2.1 Evaluation of integrated Pollution Index (Nemero) in sewage irrigation area and the control area

Compared with the background values of Shijiazhuang, the integrated Pollution Index (Nemero) of sewage irrigation is 4.7653,the control area is 4.2070, the two areas are in a state of severe pollution;

Table 1 Pollution index of soil contaminated by heavy metal

Evaluate standard	Sewage irrigation					Control area				
	Cd	Hg	Pb	Cr	As	Cd	Hg	Pb	Cr	As
background	6.0526	4.2283	2.2683	1.3224	0.9373	5.4191	3.6871	1.5568	0.9397	0.6752

table 2 Heavy metal pollution index at 23 different sites

Sampling area	Sampling sites	Pb（Pi）	Cd（Pi）	Hg（Pi）	Cr（Pi）	As（Pi）	Nemero（P）
Sewage irrigation	1	1.7762	4.5684	7.4324	0.8840	0.8558	5.6952
	2	2.8637	6.5223	2.3082	2.4662	1.0763	5.0905
	3	3.0156	3.5807	4.5610	1.6048	0.9546	3.7635
	4	2.0086	0.6440	4.6676	1.1588	0.8963	3.5568
	5	2.2052	1.7281	10.5050	1.1681	0.9744	7.7893
	6	3.6914	6.4810	5.4914	1.3371	1.0032	5.2425
	7	1.1805	9.5950	4.7189	1.2798	0.6873	7.2200
	8	2.3361	6.0063	5.3607	1.4222	0.8769	4.8124
	9	1.8159	9.3960	3.5052	1.1923	0.9295	7.0578
	10	1.4534	7.8405	3.4233	1.2802	1.0515	5.9385
	11	2.2611	5.4991	3.9861	1.1112	1.0298	4.3563
	12	1.5576	3.8817	3.6979	1.3287	1.0155	3.1891
	13	1.4957	6.2022	3.0974	1.2099	0.7113	4.7400
	14	2.4077	2.2375	5.5279	1.1296	1.0148	4.2794
	15	14.0987	4.4184	3.4288	1.3225	0.9575	10.5412
	16	1.3956	7.1252	4.1835	1.6139	0.9197	5.4798
	17	1.5457	3.1542	3.2435	1.1673	0.9825	2.7014
	18	2.4885	3.6053	4.4762	1.0847	1.0249	3.6378
	19	1.1182	5.9143	9.4523	1.1546	0.8863	7.1790
	20	1.9534	9.7156	4.0178	1.5623	0.7541	7.3266
Control area	21	1.3423	5.6716	6.3738	0.9730	0.6680	4.9828
	22	1.8031	5.1319	3.1160	0.9026	0.6844	3.9846
Sediment area	Sludge	25.0568	4.3933	16.1969	2.9780	0.0874	19.0098

4.2.2 integrated Pollution Index (Nemero) of different sampling points

As can be seen from Table 2, compared with the background values of Shijiazhuang, the 17th sampling site is moderately polluted and all the rest of integrated Pollution Index (Nemero) at the sampling site is more than 3, they have been heavily polluted. The higher of integrated Pollution Index (Nemero) at the three sampling sites are 15, 5, 20 ,numerical order is 10.5412、7.7893、7.3266.

4.2.3 integrated Pollution Index (Nemero) in Sludge

As can be seen from Table2, compared with the background values of Shijiazhuang, integrated Pollution Index (Nemero) in Sludge is 19.0098, much more bigger than 3, the Sludge is polluted by heavy metals seriously.

5 **potential risk evaluation of heavy metals in soil**

5.1 **single factor index of heavy metals in soil**

As can be get from the Tables, five kinds of heavy metals potential ecological hazard risk index in sewage irrigation area and control area sampling sites arranged in descending order: Hg> Cd> Pb> As> Cr, in both sewage irrigation area and control area, Hg, Cd reache deadly ecological damage, Cr, As and Pb doesn't reach the lower limit of ecological hazards. The main elements of the potential ecological hazards of soil heavy metals are Hg and Cd. According to the potential ecological risk, the most serious of the three sampling sites of Hg are No. 5,19,1; they are all in sewage irrigation, values E_r^i of Hg are 420.1747、378.0761、297.2779, sampling sites of number 5, 19 achieve to a strong ecological hazards，the 1st sampling site is in strong ecological hazards; Most serious of the three sampling sites in sewage irrigation are no20,7,9， values E_r^i of Cd are 290.4501、288.8327、282.8622,serious ecological hazards will happen in these sampling sites; According to the potential ecological risk, all the sampling site of Pb does not reach the limit of a minor ecological harm except sampling site 15,no 15 achieve a moderate degree of ecological risk, For As and Cr, potential ecological risk of each sampling site did not reach the upper limit of the standard minor ecological harm.

5.2 **Potential ecological risk heavy metals in soil**

As can be get from the Tables, comprehensive risk potential value (RI) of heavy metals in soil in the sewage irrigation area and control area are 384.4351 and 367.3024, the state of potential ecological harm is bad; the RI values of the control area is slightly lower than the sewage irrigation RI value. The potential ecological risk index of Sampling site 5 in sewage irrigation is highest, the potential ecological risk index is 495.0999,each soil sampling points mainly due to differences in ecological risk of heavy metals, may be related to the distribution of samples, this needs further study. View from the contribution of various heavy metals on ecological risk,

The Potential ecological risk of Cd in sewage irrigation area is 43.51% of the total risk,Hg is 50.90% of the total risk; The Potential ecological risk of Cd in control area is 43.42% of the total risk,Hg is 41.02% of the total risk. We can get that Cd and Hg have the largest contribution to the total risk of the potential ecological risk in both sewage irrigation area and control area.

CONCLUSION

4.1Wastewater irrigation led to the deterioration of soil quality, and Cr and As content in the soil increased more obvious.

4.2 In sewage irrigation soil, Hg, Cd, Pb, and Cr content is far more than the local background values in the state of severe pollution. Cd content of individual sampling sites exceeded the national standard, and is no longer suitable for crop cultivation.

4.3 In sewage irrigation soil , the potential ecological risk of heavy metals is more serious, Hg and Cd make more contribute to the heavy metals of soil.

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