Asia Pacific Academy of Science Pte. Ltd.

Pollution Study 2023, 4(1), 2070.
https://doi.org/10.54517/ps.v4i1.2070

Article

The distribution characteristics of heavy metal contamination in the central segment of Xiaonan River, Shenyang

Yinglian Lan[1], Ying Ma[1], Jing Gao[1], Peng Zhou[1], Chuang Song[2], Yanlong Li[1,*]

[1] School of Energy and Environment, Shenyang University of Aeronautics and Astronautics, Shenyang 110000, Liaoning, China
[2] Tieling Ecological Environment Monitoring Center, Tieling 112000, Liaoning, China
*** Corresponding author:** Yanlong Li, liyanlong@sau.edu.cn

CITATION

Lan Y, Ma Y, Gao J, et al. The distribution characteristics of heavy metal contamination in the central segment of Xiaonan River, Shenyang. Pollution Study. 2023; 4(1): 2070. https://doi.org/10.54517/ps.v4i1.2070

ARTICLE INFO

Received: 8 January 2023
Accepted: 6 February 2023
Available online: 17 February 2023

Abstract: The middle segment of Xiaonan River, which feeds into the Puhe River, was chosen for research. Samples including its water, river bottom mud, river bank soil, and nearby vegetation were collected from six monitoring sites. These samples were analyzed by ICP-OES to determine heavy metal distribution. The results showed that main contamination of heavy metals in the Xiaonan River are Cd, Cr, Cu, Ni, Pb, and Zn. Notably, Cr and Zn are in high levels, and Cr surpassed the limit of third-grade standard, indicating severe contamination. By using the potential ecological risk index method, Cd showed a high coefficient, severely damaging the surface water and riparian soil. The migration patterns of Cr and Zn were different. Cr tended to accumulate more in riverbank soils, while Zn showed higher concentrations in river bottom mud. Plants of nearby vegetation showed minimal absorption and transfer capabilities for Cd, while Ni transferred most. By applying the ecological risk index, potential pollution sources were inferred to assess each metal's distribution, so to offer a basis from its origin, and to protect the ecological health of the Puhe River Basin.

Keywords: water body; sediment; heavy metals; pollution characteristics; Xiaonan River

1. Introduction

Puhe River began to receive part of the industrial wastewater and domestic sewage in Shenyang in 1960. The wastewater from the surrounding industries such as automobile, machinery, welding and coal factories, together with the underground sewage inflow of domestic water, has led to serious water pollution in Xiaonan River, a tributary of Pu River. As one of the main rivers in Shenyang, the ecological environment control of Puhe River is the focus of national ecological environment planning and construction. Therefore, it is particularly important to study the source of heavy metal pollution and put forward pollution control schemes. In this paper, the river water, river bottom mud, riparian soil and surrounding vegetation at 6 monitoring points are taken as the research objects to detect the content of heavy metals, study the correlation and variation coefficient of heavy metals, and analyze the risk of ecological hazard index, so as to provide theoretical support and scientific basis for the development of heavy metal pollution control project in Puhe River sediment and ecological environment construction.

2. Materials and methods

2.1. Study area

The study area is located in the Puhe River Basin, the branch of Hunhe River in Shenyang City, Liaoning Province. This area was once rich in coal, iron, manganese, oil, natural gas and auxiliary raw materials. It has a long history of mineral and oil exploitation. After years of development, it has gradually formed an industrial park dominated by copper processing and utilization, ferrous and non-ferrous metal manufacturing, and electronic components. The study area flows from the Qipanshan reservoir through the industrial zone of metal smelting, electroplating and mechanical equipment manufacturing from the southeast to the southwest. The study mainly focuses on the areas in the middle and upper reaches that do not pass through the ecological corridor and wetland greening.

2.2. Sample collection

Use polyethylene plastic bottles to collect river water samples, place the bottle mouth 10~30 cm below the central water surface of the river, let the water flow slowly, and strictly prevent impurities from entering; collect mud samples directly below the sampling point of water samples by using a column shaped mud sampler. Take 5~10 cm deep wet soil samples without impurities within 10 m^2 of the bank around the sampling point of water samples by using the five point distribution method [1], the same as the sampling method of riparian soil. The vegetation adopts the five point sampling method to collect various kinds of desliming plants. After collection, the samples are transported back to the laboratory in polyethylene plastic bags and sealed at 4 ℃.

2.3. Analysis method

The mud samples, soil samples and vegetation samples collected at 6 sampling points were simply dried, and the pilot scale 115 blast dryer was used to dry them at 105 ℃ for 48 h. Remove the residual roots of the plant after drying. Grind the three samples with wooden sticks, cool them to room temperature and grind them with an electric grinder. After grinding, screen them with a 100 mesh electric shaker. After screening, seal and pack them with polyethylene bags, and affix sample labels for digestion reaction.

Weigh 0.1 g of ground soil, mud and vegetation samples and filter the water sample with fixed volume into the digestion tank in the marked sequence. Before the digestion experiment, determine the proportion of mixed acid, and mix 2 mL of hydrochloric acid (superior pure GR), 5 mL of nitric acid (superior pure GR, 500 mL, Sinopharm) and 2 mL of hydrofluoric acid (superior pure GR, 500 mL, Sinopharm). Put the digestion tank filled with digestion solution into the microwave digestion instrument for digestion, cooling and acid removal, and then use the internal standard correction quantitative analysis method in the ICP-OES analysis method for determination. The national first-class reference materials gsr-1, gsr-5, gsr-8, gsr-21 and gsr-25 are used for quality control. The relative error (re) and standard deviation (RSD) of each element meet the specification requirements.

2.4. Potential ecological risk index

Potential ecological risk index is a potential hazard index method proposed by Swedish scientist Hakanson. It is a method to evaluate heavy metal pollution in sediments from the perspective of sedimentology. The potential ecological hazard index is expressed as follows:

$$RI = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} T_r^i \times \frac{C_s^i}{C_n^i}$$

where, *RI* represents the comprehensive ecological hazard index of various heavy metals; E_r^i indicates i the potential ecological hazard coefficient of the heavy metal T_r^i element; i indicates the toxicity response coefficient of the C_s^i heavy i metal; indicates the measured content C_n^i of heavy metal; indicates the reference value required for calculation, and the local soil background value is selected for comparison. According to the "element abundance principle" and "element release degree" proposed by Hakanson, the toxicity response coefficient of heavy metals is discussed, that is, the potential ecotoxicity of a heavy metal element is inversely proportional to its abundance or is directly proportional to its rarity. After data processing and standardization of the toxicity coefficient, the toxicity coefficients of metals Cr, Ni, Cu, Zn, Pb and Cd are set as 2, 5, 5, 1, 5 and 30 respectively, and the values are calculated by these T_r^i values [2,3].

See **Table 1** for the impact of potential ecological hazard coefficient and potential ecological hazard index on the degree of ecological hazard.

Table 1. Impact of potential ecological hazard coefficient and potential ecological hazard index on ecological hazard degree.

Ecological hazard	E_r^i	***RI***
Extremely strong	≤320	
Very strong	160~320	≤600
Strong	80~160	300~600
Secondary	40~80	150~300
Slight	<40	<150

3. Results and discussion

3.1. Heavy metal content analysis

See **Table 2** for the determination results of heavy metal content in water samples at 6 monitoring points. The average contents of heavy metals Cd, Cr, Cu, Ni, Pb and Zn are 0.83, 43.00, 6.17, 22.67, 15.33 and 48.00 respectively $\mu g/L^{-1}$; the average content of each element varies greatly, which is closely related to the factories in the upper reaches of the river.

Table 2. Contents of heavy metals in water samples of Xiaonan River.

Project	Heavy metal content in water sample/(μg·L^{-1})					
	Cd	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
First class standard limit of national surface water quality	1	10	10	20	10	50
National Grade III standard limit for surface water quality	5	50	1000	-	50	1000
Content range of heavy metals in water samples (n = 6)	0~3	38~51	4~15	20~28	9~17	15~115
Average value	0.83	43.00	6.17	22.67	15.33	48.00
Standard deviation	1.21	4.04	4.02	2.75	3.68	34.29
Exceeding class I standard limit/%	33.33	100	16.67	16.67	83.33	50
Level III standard limit exceeded/%	0	16.67	0	-	0	0

Among the 6 monitoring points, 6 kinds of heavy metals have detected points that exceed the national first-class standard limit for surface water quality. Among them, the number of detection points that Ni and Cu exceed the national first-class standard limit for surface water quality is 16.67%, and the standard deviation is less than 5. Therefore, the distribution of these two kinds of heavy metals in the measurement basin is relatively uniform and the pollution toxicity is small; the average content of Pb is low, but the number of detection points exceeds the limit value of the national first-class standard for surface water quality, accounting for 83.33% of the total detection points; although the content of Cd is the lowest, the toxicity coefficient is very high, reaching 30, so its pollution to water and surrounding vegetation is the most serious; according to the data, the content of Cr is relatively high. The number of detection points where Cr exceeds the limit value of the national level III standard for surface water quality accounts for 16.67% of the total number of detection points. The pollution sources of Cr are mainly manufacturing enterprises such as electroplating, dye, pharmaceutical, leather, etc. The waste residues and scraps existing in dye and electroplating are easy to enter the river and cause pollution [4]; the content of Zn is the largest, but the Toxicity Coefficient of Zn is small, only 1, so there are no detection points of Zn that exceed the limit value of the national level III standard for surface water quality.

See **Table 3** for the content statistics of heavy metals in the riverside soil, river bottom mud and vegetation along the Xiaonan River. The average contents of heavy metals Cd, Cr, Cu, Ni, Pb and Zn in riparian soil are 4, 87, 17, 27, 3 and 88 respectively μg/L; the heavy metal contents of CD, Cr, Cu, Ni, Pb and Zn in river bottom mud are 2, 81, 14, 27, 3 and 92 respectively μg/L; the heavy metal contents of CD, Cr, Cu, Ni, Pb and Zn in vegetation are 0, 67, 14, 33, 2 and 81 respectively μg/L. In the three research samples, the contents of Cr and Zn are all high, which is consistent with the distribution of Cr and Zn contents in water samples; heavy metals in the water settle and migrate to the river bottom mud and riparian soil under the action of gravity, while the vegetation enriches the heavy metals through adsorption and absorption. The content of heavy metals in sediments and plants increases with the increase of the content of heavy metals in the water [5]. From the coefficient of variation (CV) analysis, only PB has the largest coefficient of variation, which is more than 80% in the three measurement samples, indicating that Pb is unevenly distributed in the rivers in the measurement area, with great differences. According to the analysis of soil environmental background value in China, the contents of Cd, Cr and Ni in sediments are large, and there are monitoring points that exceed the soil environmental background value in China. Therefore, the sediments are seriously polluted by these three heavy metals. However, the Cd content in the vegetation is very small, so it can be seen that the Cd absorption capacity of the vegetation around the study area is very small. The Cd absorption of surrounding vegetation is concentrated in the root, the Cd content in other parts is low, and the Cd migration rate in plants is relatively low, which is basically consistent with the previous research results [6,7]. Like the water quality monitoring, the content of Cu and Pb is small. The number of detection points of Cu exceeding the background value of Chinese soil environment accounts for 16.67%. There are no detection points of Pb exceeding the background value of Chinese soil environment in river bottom mud, riparian soil and vegetation; the maximum content of Zn in water exceeds the background value of soil environment in China, accounting for 66.67%. Due to its minimum toxicity coefficient, the pollution hazard is relatively small.

Table 3. Contents of heavy metals in riverside soil, river bottom mud and plants of Xiaonan River.

Sample	Project	Cd	Cr	Cu	Ni	Pb	Zn
Riparian soil	Background value of soil environment in China/(mg·kg^{-1})	0.074	53.90	20.00	23.40	23.60	67.70
	Heavy metal content range/(mg·kg^{-1})	2~6	77~95	12~22	25~28	0~7	56~117
	Average/(mg·kg^{-1})	4	87	17	27	3	88
	Standard deviation/(mg·kg^{-1})	1.31	6.56	3.45	1.18	2.87	23.94
	CV/%	35.17	7.51	20.55	4.41	89.44	27.10
	Percentage exceeding background value/%	100	100	16.67	100	0	66.67
River bottom mud	Background value of soil environment in China/(mg·kg^{-1})	0.074	53.90	20.00	23.40	23.60	67.70
	Heavy metal content range/(mg·kg^{-1})	1~3	65~101	11~17	25~30	0~7	77~110
	Average/(mg·kg^{-1})	2	81	14	27	3	92
	Standard deviation/(mg·kg^{-1})	0.61	11.62	1.78	1.46	2.25	9.97
	CV/%	28.21	14.41	12.83	5.35	87.75	10.85
	Percentage exceeding background value/%	100	100	0	100	0	100
Vegetation	Background value of soil environment in China/(mg·kg^{-1})	0.074	53.90	20.00	23.40	23.60	67.70
	Heavy metal content range/(mg·kg^{-1}))	0	50~75	8~23	25~38	0~6	65~99
	Average/(mg·kg^{-1}))	0	67	14	33	2	81
	Standard deviation/(mg·kg^{-1}))	0.19	8.25	4.38	4.33	1.76	13.30
	CV/%	-	12.29	30.26	13.10	85.70	16.36
	Percentage exceeding background value/%	0	83.33	16.67	100	0	66.67

3.2. Analysis of potential ecological hazard index

The background value of Chinese soil environment is used as the reference, the solubility of heavy metals is based on the measured value, and the calculation results of ecological hazard coefficient and ecological hazard index are shown in **Table 4**. From the potential ecological hazard coefficient of a single heavy metal, cd pollution is a very strong ecological hazard, Ni is a strong ecological hazard in vegetation, cu is a medium ecological hazard, and Cr, Pb, Zn are all slight ecological hazards. The pollution order of the six heavy metals is Cd > Ni > Cu > Cr > Zn > Pb. According to the potential ecological hazard index of several heavy metals, those with *RI* ≥ 600 have overlying water, river bottom mud and riparian soil, which belong to extremely strong ecological hazards; vegetation with 300 ≤ *RI* <600 belongs to strong ecological hazard.

Table 4. Ecological hazard coefficient and ecological hazard index of each sample.

	Heavy metal	Overlying water	River bottom mud	Riparian soil	Vegetation
E_r^i	Cd	780	530	904	122
	Cr	4	18	19	39
	Cu	4	21	25	57
	Ni	11	35	34	110
	Pb	7	3	4	7
	Zn	2	8	8	19
RI		808	615	994	354

It can be seen that the ecological harm of heavy metal pollution in the study basin is extremely serious. The main sources of heavy metals in the river are nonferrous metal smelting, etc. According to the survey, the machinery manufacturing, auto parts and industrial parks in the upstream contain services such as hazardous waste treatment, solid waste treatment, recycling and wholesale of renewable materials, road transportation of dangerous goods, etc. The production and manufacturing process is very prone to pollution. If the treatment is not in place, it will affect the rivers, soil, vegetation, etc., and even the health of the surrounding residents.

3.3. Correlation analysis of heavy metals

Analyze the correlation of heavy metals between water samples and riparian soil, river bottom mud and vegetation, and obtain the migration characteristics of heavy metals. See **Table 5** for the correlation of heavy metal content between water sample and riparian soil.

Table 5. Correlation between heavy metal content of water sample and riparian soil.

	Water sample Zn	Water sample Cr	Water sample Ni	Riparian soil Zn	Riparian soil Cr	Riparian soil Ni
Water sample Zn	1					
Water sample Cr	0.254	1				
Water sample Ni	0.421	0.960	1			
Riparian soil Zn	−0.463	−0.489	−0.556	1		
Riparian soil Cr	−0.793	−0.479	−0.692	0.544	1	
Riparian soil Ni	0.133	−0.442	−0.420	0.575	0.273	1

See **Table 6** for the correlation of heavy metal content between water sample and river bottom mud.

See **Table 7** for the correlation between heavy metal contents in water samples and vegetation.

Table 6. Correlation between heavy metal contents in water samples and river bottom mud.

	Water sample Zn	Water sample Cr	Water sample Ni	River bottom mud Zn	River bottom mud Cr	River bottom mud Ni
Water sample Zn	1					
Water sample Cr	0.254	1				
Water sample Ni	0.421	0.960	1			
River bottom mud Zn	0.070	0.910	0.898	1		
River bottom mud Cr	−0.220	0.094	0.031	0.356	1	
River bottom mud Ni	−0.649	−0.217	−0.457	−0.176	0.366	1

Table 7. Correlation between heavy metal content in water samples and vegetation.

	Water sample Zn	Water sample Cr	Water sample Ni	Vegetation Zn	Vegetation Cr	Vegetation Ni
Water sample Zn	1					
Water sample Cr	0.254	1				
Water sample Ni	0.421	0.960	1			
Vegetation Zn	0.362	0.209	0.250	1		
Vegetation Cr	−0.112	0.313	0.445	0.256	1	
Vegetation Ni	0.134	0.494	0.656	0.132	0.928	1

It can be seen from **Tables 5** and **6** that the correlation between Zn in the water sample and Cr in the riparian soil is the highest, and the correlation between Cr in the water sample and Zn in the river bottom mud is the highest. According to the above analysis, the content of Cr and Zn in the water sample is large, and the correlation between the river bottom mud and riparian soil and the heavy metals in the water sample is different due to the different settlement and migration capacity of gravity. According to the correlation analysis between water samples and heavy metals in vegetation in **Table 7**, the correlation between Ni in water samples and Ni in vegetation is 0.656, which is more than 1.5 times that of other heavy metals. Therefore, it can be judged that most vegetation along the Xiaonan River has relatively strong ability to absorb and migrate Ni [8].

CR heavy metal elements mainly come from automobile manufacturing surface painting and oil and mineral energy exploitation. The waste flying debris and oil waste water produced by factory manufacturing are easy to be discharged into rivers with the movement of atmospheric precipitation [9] and form pollution; as a common element, Zn may enter the river with the waste water flowing through the container filter membrane, drainage pipe [10]. The morphological distribution of exogenous heavy metals in the water environment is different, and the characteristics of heavy metal distribution, sedimentation and migration over time are also different, while the migration of soluble heavy metals in different vegetation bodies is different, and the content of heavy metals in different sediments in the water is different [11−13], resulting in more Cr in the riparian soil and more Zn in the river bottom mud.

4. Conclusion

(1) From the analysis of metal content, the content of Cr and Zn is relatively large. Among them, Cr in the overlying water, river bottom mud, riparian soil and vegetation exceeds the background value of Chinese soil environment. In addition, Cr has the strongest toxicity coefficient, so it has the most serious pollution to the river.

(2) Using the potential ecological hazard index method, after comprehensively considering all heavy metal pollution in a certain environment, it is concluded that the ecological hazard coefficient of Cd is very strong, and the ecological hazard of overlying water and riparian soil is extremely serious.

(3) From the correlation analysis, Cr has a strong migration ability in soil, Zn has a strong gravitational settlement, and the vegetation has the weakest absorption ability of Cd, but the strongest absorption ability of Ni. It is analyzed that the upstream pollution source of the river is mainly affected by the material manufacturing, metal manufacturing and other painting material factories, so the pollution of the upstream river needs to be controlled.

Author contributions: Conceptualization, YL (Yinglian Lan) and YM; methodology, JG; software, PZ; validation, YL (Yinglian Lan), CS and YL (Yanlong Li); formal analysis, CS; investigation, JG; resources, YL (Yinglian Lan); data curation, YM; writing—original draft preparation, YM; writing—review and editing, PZ; visualization, CS; supervision, YL (Yanlong Li); project administration, YL (Yinglian Lan); funding acquisition, JG. All authors have read and agreed to the published version of the manuscript.

Funding: Shenyang University of Aeronautics and Astronautics student innovation and Entrepreneurship Project (x202010143347).

Conflict of interest: The authors declare no conflict of interest.

References

1. Li Y, Ji H, Wen Z, et al. Residue dynamics and safety risk assessment of three plant growth regulators in main fruits and vegetables in Beijing Tianjin Hebei region. Journal of food safety and quality inspection. 2017; 8(8): 3011-3017.
2. Li X, Bai Q, Pang J, et al. Grain size analysis and heavy metal pollution assessment of river surface sediments in Danjiang River Basin. Jiangxi Agricultural Journal. 2019; 31(4): 93-98.
3. Wang C, Pang X, Yang L, et al. Ecological hazard assessment of heavy metals in soil: taking a typical gold mine area as an example. Geochemistry. 2013; 42(6): 557-566.
4. Arnaudguilhem C, Larroque M, Sgarbura O, et al. Toward a comprehensive study for multielemental quantitative LA-ICP MS bioimaging in soft tissues. Talanta. 2021; 222: 121537. doi: 10.1016/j.talanta.2020.121537
5. Wang Y. Remediation of heavy metal pollution in soil was accelerated. Farmer Daily; 2014.
6. Yu Z. Response of soil bacterial community to heavy metal chromium pollution and its reduction mechanism in Lanzhou section of the Yellow River. Lanzhou: Lanzhou University; 2019.
7. Zhou X. Study on water pollution control technology of urban polluted river. Low carbon world. 2021; 11(2): 36-37.
8. Xia Z. Response analysis of diatom markers under heavy metal pollution in Le’an River. Nanchang: Nanchang Institute of engineering; 2019.

9. Guo Y. Research and design on solid-liquid separation of contaminated soil by pressure filtration. Shenyang: Shenyang University; 2018.
10. Cheng Y, Wang Y, Zhou Y, et al. Pollution status and sources of heavy metals and metalloids in groundwater system of Zhuhai City. Bulletin of mineral and rock geochemistry. 2019; 38(3): 595-603.
11. Zhao S, Wang J, Cai X, et al. A review on the speciation, biological impact analysis and remediation technology of soil lead pollutants. Modern chemical industry. 2020; 40(12): 8-12,18.
12. Feng Z. A soil remediation agent for heavy metal pollution and its preparation method. CN108192638B, 5 January 2021.
13. Wang X, Luo J, Zhang B, et al. Determination of acid soluble heavy metals and total heavy metals in Chinese patent medicines containing four heavy metals. Chinese herbal medicine. 2009; 32(4): 631-633.