Water Quality Analysis and Health Risk Assessment of Reservoir in Qilian Mountain

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Abstract: Qilian Mountain is an essential ecological security barricade in China, but the research on water quality investigation and health and safety evaluation of Qilian Mountain is currently blank. In this essay, the environment health of the water were assessed using the Nemero index technique and the health risk assessment method. The findings revealed that the reservoir's overall water quality in the national park was satisfactory, and the Nemerow index was between 2.142 and 3.548. Chromium (Cr), which accounted for more than 78% of the health risk value of chemical carcinogens, was the primary contributor to the carcinogenic risk. Ammonia nitrogen, fluorine, and mercury account for the majority of the health effects of non-carcinogenic substances, representing 60.01%~79.10% of the non-carcinogenic risk value. Chemical carcinogens were primarily responsible for the overall health risks. Afterward, on the basis of strict control of pollutant discharge standards, the government should focus on rehabilitating mines to ensure that heavy metal levels in the water were kept low. Research on the health hazards and quality of the water environment in Qilian Mountain National Park can help management and conservation of the water environment in this region.

1 INTRODUCTION

Due to their abundance, ease of bioaccumulation, persistence, and toxicity even at low concentrations, the heavy metals were considered serious environmental pollutants in aquatic environments. (Wang, et al. 2017, Zhao et al. 2020). Through the food chain, heavy metals can enter humans and cause health problems in some way, either directly or indirectly (Gaofeng et al. 2008). There are three primary means that people can be exposed to trace metals: directly intake, inhaling them through the mouth and nose, and absorbing them through exposed skin, and the main ways were through drinking water and the skin absorbing. (Giri et al. 2014). Chemical carcinogens account for 90% of cancers, according to previous studies, and drinking water was a major contributor (Giri et al. 2015, Smith et al. 1992). The high level concentration of heavy metal water pollution is strongly corresponded with the health risk posed by chemical carcinogens (Smith et al. 1992). Furthermore, a low dose and prolonged exposure to heavy metals can cause harm to the human body.

It should be pointed out that in the past, management and estimation of drinking water sources by individuals were often evaluated by comparing traditional water quality indicators. This comparison has some shortcomings and singleness, which minimizes or disregards the possibility of toxic and harmful causes having some effects on human health (Li et al. 2016a). At this stage, China's water quality estimation is mainly based on the surface water environment quality standard (China. Environment Protection Department, 2002). The method is simple and intuitive, and the evaluation conclusion is single. With the advancement of science and technology at home and abroad and the continuous progress of China's water environmental protection policies, it has been challenging to meet the current requirements for water environmental management with the current water quality standards (Ranran et al. 2016a). In 1980s, the National Academy of Sciences and the US Environmental Protection Agency (EPA) first introduced the health risk assessment model into their research (US. Emergency and Response, 1989). Some

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achievements have been made, and some evaluation guidelines and guidelines have been established, which makes the threat of water environmental safety to human health have a clear research direction. Based on the existing research, some scholars have studied the environmental health risks of surface water and drinking water from the perspectives of pharmacy and pathology (Lim et al. 2012, Robu et al. 2015).

In China's western region, Qilian Mountain serves as an essential ecological security barricade, which is located in the Yellow River Basin and Hexi Corridor. In addition, this region is a priority for China's conservation of biodiversity and a vital water source. Due to the important ecological safety position, for the water security of the Qilian Mountain National Park in China, heavy metal contamination in the surface water has been a significance issue.

Currently, research on water quality assessment methods focuses on the pros and cons, improving and applying the single-factor strategy, the Nemerow index strategy and the fuzzy all-inclusive strategy (Ranran et al. 2016b). Presently, in the estimation of the reservoir water environment in Qilian Mountain National Park, there is currently no research on combining water quality and health risk valuation. An all-inclusive awareness of reservoir water environment quality can be gained by combining water quality estimation with health risk valuation, understand the water environment status, and help strengthen the management and control of reservoir water risk, and formulate and implement corresponding pollutant control strategies. In addition, the environmental problem in Qilian Mountain National Park has always been a national key problem, and the closed mines have always been a major risk source due to historical reasons. Therefore, this study uses Nemerow index and EPA health risk evaluation strategy to estimate the water environment quality and water quality health risk of five reservoirs in Qilian Mountain, aiming at comprehensively understanding the current water quality situation in Qilian Mountain and providing reference for the restoration and management of Qilian Mountain.

2 MATERIAL AND METHODS

The water quality in the reservoir of Qilian Mountain National Park was evaluated using the Nemerow index, and the EPA health risk evaluation model was applied to study the health risk from drinking water.

2.1 Research Design

In this study, 99°30 '21 "E-102°40' 38" E, 37°30 '41 "N-39°9' 11" N in Qilian Mountain National Park were selected as the study areas, which are located in Zhangye and Wuwei cities of Gansu Province with a large population. It is a temperate continental climate with an annual average rainfall of 300~400mm and an altitude of 1640m~2470m. The typical reservoirs selected in this paper were D1 (Xiying Reservoir,102°40 '38 "E, 37°30' 41" N), D2 (Bailanghe Reservoir,99°30 '21 "E, 39°9" 11 "N), D3 (Longqu Reservoir,100°11 '44 "E, 56 38°33" N), D4 (Shuangshusi Reservoir,100°41 40 "E, 38°19 38" N), D5 (Dayekou Reservoir,100°44 "E, 38°31 25 "N), conducted water quality survey sampling from 10 to 15 August 2020. The study area is shown in Figure 1.

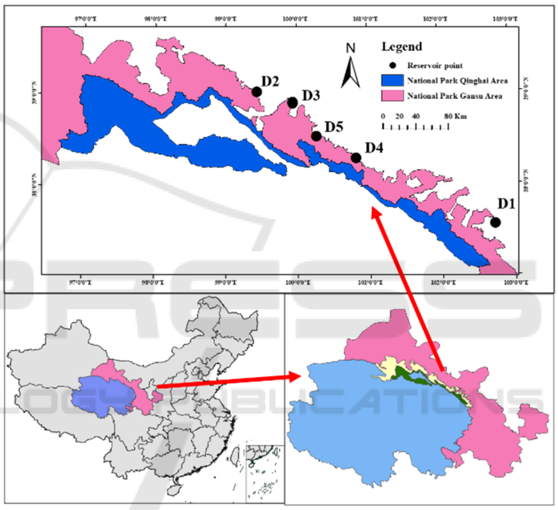

Figure 1: Map of sampling sites in the Qilian Mountain National Park. The insets show the Qilian Mountain National Park within the Gansu Province and Qinghai Province(lower left), and the position of the Gansu Province and Qinghai Province within China(lower right)

2.2 Physico-Chemical Analyses

In this paper, the conventional indexes stipulated in the surface water environmental quality standards were selected for testing. Considering that the fecal coliform was not included in the calculation of Nemero index method, the fecal coliform was excluded from the detection data. In addition, sulfides and anionic surfactants were not included in the detection index, mainly because the Qilian Mountain National Park was mainly dominated by mineral activities, animal husbandry and so on, and human domestic sewage discharge has little impact.

At the sampling point, ACH-HQ30D（America) was used to detect Water temperature (WT) and dissolved oxygen (DO) in the field. PHS-3C(LeiCi，Shanghai, China) acidity meter was used to detect pH. Chemical oxygen demand (COD), ammonia (NH_3-N), nitrate (NO_3-), total nitrogen (TN) and total phosphorus (TP) were measured in the laboratory, and measured by UV-visible spectrophotometer (UV-2800, UNICO,US). For the measurement of iron (Fe), copper (Cu), selenium (Se), manganese (Mn), mercury (Hg), arsenic (As), lead (Pb), cadmium (Cd), chromium (Cr), petroleum oil, volatile phenol, fluoride, cyanide, we send water samples to qualified companies for testing.

2.3 Correlation Analysis

Pearson correlation analysis was carried out in this study to test the relationship between the properties and occurrence of detected heavy metals and between heavy metals and other components. The correlation is deemed statistically significant if the significance level (P) is less than 0.05. SPSS (Version 22) was used for all statistical analyses.

2.4 Nemerow Index Method

Nemerow Index method is a weighted multi-factor environmental quality assessment method, which uses additional annotations and considers extreme values or significant maximum values. The surface water quality is determined according to the comprehensive assessment score *F* and the surface water quality classification (table 1)(Chen et al. 2012, Silva et al. 2019). The *F* is calculated according to formulas (1) and (2)：

Table 1: Surface water quality classification

Grade	Excellent	Preferable	Good
F	<0.80	0.80-2.50	2.50-4.25
	Worse	Worst	
F	4.25-7.20	>7.20	

$$F=\sqrt{\frac{F_{\max}^2+\bar{F}^2}{2}} \tag{1}$$

$$\bar{F}=\frac{1}{n}\sum_{i=1}^{n}F_i \tag{2}$$

In the formula, $\bar{F}$ is the average value of the score F of each individual component; F_i is the Single component score value of surface water (table2); F_{max} is the maximum value of the individual component averageF_i; n is the number of items.

Table 2: Single component scores of surface water

Water quality category	I	II	III	IV	V
F_i	0	1	3	6	10

2.5 Health Risk Assessment

Health risk estimation is to evaluate the risk of individual health being affected by harmful factors by estimating the probability of adverse effects of harmful factors on human health (Zhao et al. 2018). According to the classification of chemicals by the International Center for Cancer Research, chemicals in Class 1 (with sufficient evidence of human body cancer) and Class 2 Group A (with limited evidence of human body cancer but sufficient evidence of animal body cancer) are chemical carcinogens, while others are non-chemical carcinogens(US. Emergency and Response, 1989).

The health risk assessment models of chemical carcinogenic and non-carcinogenic metal elements are different.

2.5.1 Chemical Carcinogens Health Risk Assessment Model

$$R_{ig}^{c}=[1-\exp(-D_{ig}\times Q_{ig})]/L \tag{3}$$

$$D_{ig}=Q\times C_i/W \tag{4}$$

$$R^{c}=\sum\nolimits_{i=1}^{k}R_{ig}^{c} \tag{5}$$

Where $R^c{}_{ig}$ is the average annual personal carcinogenic risk (a^{-1}) of chemical carcinogen *i* through food route; D_{ig} is the daily average exposure dose of chemical carcinogen *i* per unit body weight (mg $(kg\cdot d)^{-1}$); Q_{ig} is the carcinogenic intensity coefficient (mg $(kg\cdot d)^{-1}$) of chemical carcinogen *i* through food route, their intensity coefficients are shown in table 3.; *L* is the average life span of human beings (a, take 70); *Q* is the average daily drinking water for adults ($L\cdot d^{-1}$, taking 2.2 $L\cdot d^{-1}$); C_i is the mass concentration of chemical carcinogen *i* ($mg\cdot L^{-1}$); *W* is the per capita weight (kg, calculated as 70 kg).

2.5.2 Non-Carcinogen Health Risk Assessment Model

$$R_{jg}^{n}=(D_{jg}\times10^{-6}/RfD_j)/L \tag{1}$$

$$D_{jg}=Q\times C_J/W \tag{7}$$

$$R^{n}=\sum\nolimits_{j=1}^{k}R_{jg}^{n} \tag{8}$$

Table 3: The values of Q_{ig} and RfD_j

Chemical carcinogen	Cr(VI)	Cd	As
Q_{ig}	41	6.1	15
Non-carcinogen	NO_3^-	NH_3-N	Volatile Phenol
RfD_j	1.6	9.7×10^{-1}	1.0×10^{-1}
Non-carcinogen	Fluoride	Cyanide	Hg
RfD_j	6.0×10^{-2}	3.7×10^{-2}	3×10^{-4}
Non-carcinogen	Pb	Cu	Zn
RfD_j	1.4×10^{-3}	5×10^{-3}	3×10^{-1}
Non-carcinogen	Fe	Mn	Se
RfD_j	3×10^{-1}	1.4×10^{-1}	5×10^{-3}

Where R^n_{jg} is the average annual personal carcinogenic risk of non-carcinogen j via the edible route (a^{-1}); RfD_j is the reference dose of the non-carcinogen j via the edible route (mg·(kg·d)$^{-1}$), and their reference measurement values are shown in table 3; C_j is the mass concentration of the chemical carcinogen j (mg·L^{-1}).

The overall health hazard risk R^t of water environment is:

$$R^t = R^c + R^n \tag{9}$$

At present, the public acceptable risk levels recommended by different institutions are different. Some European countries recommend $1\times10^{-6}a^{-1}$, the International Commission on Radiation Protection recommends $5\times10^{-5}a^{-1}$, and the US Environmental Protection Agency recommends $1\times10^{-4}a^{-1}$.

3 RESULTS AND DISCUSSION

Nemerow index method was used to evaluate the water quality of each reservoir, and USEPA health risk assessment model was used to evaluate the health risks of each reservoir. The results are as follows:

3.1 Water Quality Estimation

Figure 2 depicted the water quality evaluation scores of various reservoirs, which were used to conduct a comprehensive estimation of the water quality of five reservoirs in the Qilian Mountain Nature Reserve by the Nemerow index (F). The F values of Xiying reservoir, Bailanghe reservoir and Longqu reservoir are 2.837~3.548, and the corresponding evaluation results are good. The F values of Shuangshusi reservoir and Dayekou grottoes are 2.142 and 2.129, and the corresponding evaluation results were good.

Average concentrations of total phosphorus, mercury and cadmium in Xiying reservoir, Bailanghe reservoir and Longqu reservoir are 0.04, 0.00053 and 0.0011mg/L,0.03, 0.00037 and 0.0011mg/L,0.03, 0.00027 and 0.0011mg/L. The concentrations of total phosphorus, mercury and cadmium exceed the standard limits specified in the surface water environment quality standard, which leads to the reservoir evaluation performances being worse than other reservoirs. Therefore, the discharge of total phosphorus, mercury and cadmium pollutants in rivers and lakes should be strictly controlled.

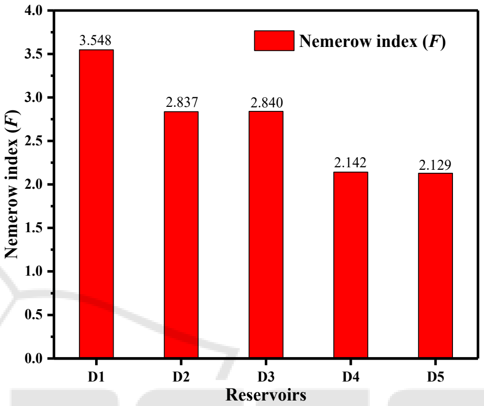

Figure 2: Comprehensive evaluation of the water quality of each reservoir

3.2 Correlation Analysis

Table 4: The correlation between reservoir elements and other components (1).

Item	Fe	Cu	Se	Mn
WT(2)	0.443	-0.615	-0.44	0.711
DO	-0.818	0.683	-0.499	-0.575
pH	0.291	-0.182	0.916*	-0.595
NH_3-N	0.158	0.545	0.258	0.242
NO_3^-	0.176	-0.961**	0.267	0
Item	Hg	As	petroleum oil	Pb
WT(2)	0.865	-0.678	-0.497	0.66
DO	-0.236	0.559	-0.387	-0.754
pH	-0.635	0.601	0.128	-0.409
NH_3-N	-0.497	-0.032	0.940*	0.279
NO_3^-	0.471	-0.382	-0.28	0.154

(1) ** shows that the correlation is significant when the confidence level (two-sided) is 0.01; * shows that the correlation is significant when the confidence level (two-sided) is 0.05, the same below.

Pearson correlation coefficient is used to express the strength of correlation among various factors. According to the correlation between elements and other components in Qilian Mountain National Park Reservoir (table 4), it can be seen that Cu and NO_3^- indicated a significant relationship, with a correlation coefficient of -0.961, showing a strong negative correlation. The concentration of Cu will decrease with the increase of NO_3^-. The positive correlation between pH and Se was extremely significant, with a correlation coefficient of 0.916. The concentration of Se will increase with pH. Petroleum oil is positively correlated with NH_3-N with a correlation coefficient of 0.940. Petroleum oil concentration increases with the increase of NH_3-N concentration. Except for this, there is no clear connection between the listed elements and their components. Elements such as Fe, Mn, Hg, As and Pb in Qilian Mountain Reservoir are not obviously affected by other components.

3.3 Health Risk Assessment

According to carcinogenicity of risk factors, health risks are divided into carcinogenic health risks and non-carcinogenic health risks.

3.3.1 Health Risks of Chemical Carcinogens

From the chemical carcinogenic health risk evaluation model, the health risk values of chemical carcinogens in reservoirs in Qilian Mountain National Park are calculated, and the results are shown in figure 3.

The mass concentration of metal Cr in each monitoring point is lower than the value of machine detection line, so the risk of chemical carcinogens is calculated with the value of machine detection line as its mass concentration. According to figure 3, the health risk value of chemical carcinogens in reservoirs in Qilian mountain national park is between 3.01×10^{-6} and 7.344×10^{-5} a^{-1}, which is lower than the public maximum acceptable risk value recommended by us environmental protection agency. The health risk of chemical carcinogens is mainly caused by Cr (VI), accounting for 78.17%-80.47% of the risk value, followed by Cd, accounting for 16.23%-18.63%. The health risk value of chemical carcinogens at each monitoring point is D3=D5>D2= D4>D1. Although the Cr, the main chemical carcinogenic health risk element, has reached the Class III water quality standard of surface water in five reservoirs, it still has a high carcinogenic risk, which is primarily attributable to the carcinogenic risk associated not only with the content of Cr but also with the carcinogenic intensity coefficient, the per-capita water consumption, the exposure frequency, the average body weight and the average life span of human beings.

However, due to a large number of mining activities in Qilian Mountain in early years (centralized remediation has been carried out in recent years, and all of them have been shut down for restoration and remediation), when rainfall causes natural disasters, chemical carcinogenic metals may enter the water body and enter the reservoir, so there is still a great risk of metal Cr. Once it is detected in the reservoir, its risk value will be 10 times higher than the current risk value. Because of paying attention to Cr element, it is necessary to do a good job in mine restoration and soil vegetation protection.

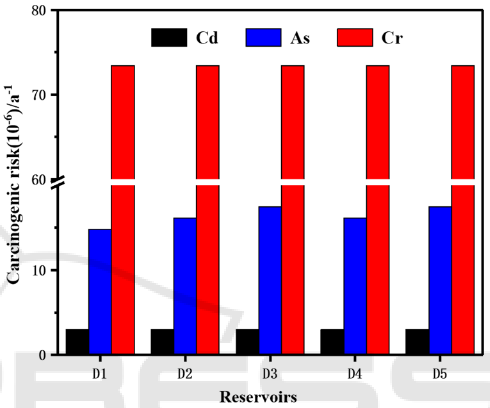

Figure 3: Health risks of chemical carcinogens in reservoirs in Qilian Mountain National Park

3.3.2 Health Risks of Non-Carcinogens

Table 5: Non-carcinogen health risk value of Qilian Mountain National Park Reservoir（$\times10^{-10}$）

Name	$R^n(NH_3$-N)	$R^n(NO_3^-)$	R^n(F)	R^n(Hg)
D1	2.722	0.370	7.483	7.932
D2	2.497	0.463	7.483	5.537
D3	2.133	0.417	7.483	4.041
D4	3.339	0.417	7.483	2.993
D5	3.339	0.185	7.483	1.946
Name	R^n(Pb)	R^n(Cu)	R^n(Zn)	R^n(Fe)
D1	0.609	1.167	0.012	0.958
D2	0.224	0.988	0.012	0.659
D3	0.224	1.347	0.012	0.943
D4	0.417	1.167	0.012	1.063
D5	0.224	5.478	0.012	0.763
Name	R^n(Mn)	R^n(Se)	R^n	
D1	1.379	1.257	23.890	
D2	0.048	1.706	19.618	
D3	0.077	2.065	18.742	
D4	0.673	2.604	20.168	
D5	0.212	1.706	21.348	

Many researchers believe that non-carcinogens include NH_3-N, NO_3^-, fluoride, volatile phenol, cyanide, mercury, lead, copper, zinc, iron, manganese, selenium, etc(Chai et al. 2021, Wu et al. 2021). According to the non-carcinogen health risk assessment model, the non-carcinogen health risk values of each reservoir monitoring point in Qilian Mountain National Park are calculated, among which volatile phenol and cyanide are lower than the instrument detection line values, so they are not listed in the table 5. The non-carcinogenic health risks caused by various pollutants are quite different. Among them, the health risks caused by ammonia nitrogen, fluoride, and mercury are relatively large. The health risks caused by these three pollutants account for 60.01%-79.10 of the non-carcinogenic risk values. the health risk value caused by other pollutants accounts for 20.90%-39.99% of the non-carcinogenic risk value. Among the three main health risk pollutants, fluoride has the highest risk value, followed by mercury and ammonia nitrogen. According to table 5, the non-carcinogenic health risks of the monitoring points of reservoirs in Qilian mountain range from 1.874×10^{-9} to 2.389×10^{-9} a^{-1}, and the order of non-carcinogenic health risks of the monitoring points of reservoirs is D1>D5>D4>D2>D3. The risk's value were less than the Royal Society's negligible risk level(10^{-7} a^{-1}) and the Netherlands Construction and Environment Agency's negligible risk level(10^{-8} a^{-1}), respectively. As a result, non-carcinogens pose no significant threat to human health through drinking water.

3.3.3 Total Health Risk

The total health risk of water environment is the sum of risks caused by chemical carcinogens and non-carcinogens, which reflects the potential risks of water environment to human health, animals and plants(Zhao et al. 2016, B et al. 2019), and long-term accumulation will lead to cancer, genotoxicity, etc. The overall health risk of each reservoir monitoring point in Qilian Mountain National Park is shown in figure 4.

As depicted in figure 4, each monitoring site in the Qilian Mountain National Park has a similar total health risk value, ranging from 9.136×10^{-5} to 9.402×10^{-5} a^{-1}, and the health risk value is mainly caused by the health risk of chemical carcinogens. As we all know, there used to be many mineral enterprises in Qilian Mountains, which were rich in mineral resources, resulting in serious illegal mining and serious environmental damage. Heavy metals have caused serious pollution to water bodies. In recent years, the state and local governments have taken many strict measures, shut down all mining activities in national parks, and carried out mine remediation and centralized restoration, with remarkable results.

The health risks of non-carcinogens ranged from 1.874×10^{-9} to 2.389×10^{-9} a^{-1}, and those of chemical carcinogens ranged from 3.01×10^{-6} to 7.344×10^{-5} a^{-1}. It can be seen that the health risks of non-carcinogens were significantly lower than those of carcinogens, which is similar to the research findings of many researchers (Rahman et al. 2020, A et al. 2020). Therefore, as a management department, we should be mindful of the health risks of chemical carcinogens and changes in the concentration of chemical carcinogens in water.

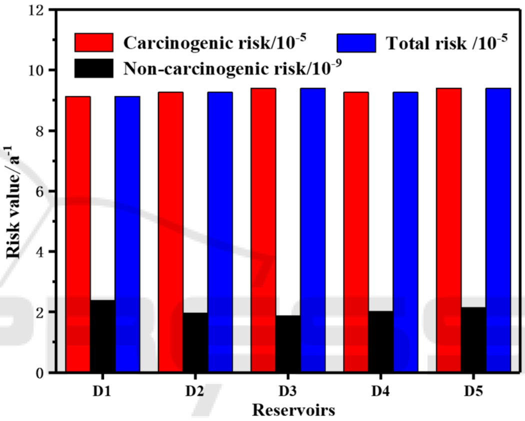

Figure 4: Total health risks of various reservoirs in Qilian Mountain National Park.

4 CONCLUSION

(1) The *F* value of each reservoir ranges from 2.142 to 3.548, and the overall water quality is stable at a good and better level. Because the Hg content of Xiying reservoir is the highest among the five reservoirs, the F value of Xiying reservoir is the highest, reaching 3.548, which should be paid attention to by relevant departments. Through correlation analysis, NO_3^-, pH and NH_3-N concentrations have a certain correlation with Cu, Se and Petroleum oil, and their changes affect each other.

(2) The health risks of chemical carcinogens in five typical reservoirs ranged from 3.01×10^{-6} to 7.344×10^{-5} a^{-1}, mainly produced by Cr (VI), accounting for more than 78% of the health risks of chemical carcinogens. The health risk value of chemical carcinogens in Longqu Reservoir is slightly

higher than other monitoring points. The non-carcinogen health risk of the five typical reservoirs is between 1.874×10^{-9}~$2.389\times10^{-9}\text{a}^{-1}$, mainly caused by ammonia nitrogen, fluoride, and mercury, It accounts for 60.01%~79.10% of the non-carcinogenic risk value.

(3) The total health risk values are little difference, ranging from 9.136×10^{-5} to $9.402\times10^{-5}\text{a}^{-1}$. The health risk values are mainly caused by the health risks of chemical carcinogens. From now on, we should pay attention to the restoration of mines on the basis of strict control of pollutant discharge standards to ensure that the heavy metal content in water remains low.

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