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The Analysis and Remediation Technology of the Pollution of the Groundwater Environment in Longkou Plain, China

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Abstract: In order to study the groundwater environment in the Longkou plain, 48 groups of water samples are collected, consisting of 7 groups of surface water samples and 41 groups of groundwater samples. The quality of groundwater in the Longkou Plain is poor, with class V water quality accounting for more than 90%, and no class I, II water quality, sporadic distribution of Class III and IV water quality. The influencing factors of water quality are mainly inorganic indicators such as nitrate, total hardness, chloride, salinity and sulfate, the detection rate of heavy metals is low. Nitrate is the main pollution index in this area, and the increase of nitrate content is closely related to the construction of underground reservoir. Based on the characteristics of groundwater pollution in the Longkou Plain, the *in-situ* chemical remediation of groundwater pollution is proposed.

Key words: Groundwater environment, quality assessment, pollution analysis, remediation technology.

1. Introduction

Longkou City is one of the open coastal cities of importance as well as one of the cities with serious contradiction of water supply and demand. In order to relieve crisis of water resources and enhance water supply ability, the government build an underground water reservoir in the lower reaches of the Huangshuihe River. However, in recent years, the environment of Longkou Plain has been contaminated more seriously for rapid industrialization and urbanization. Domestic garbage, industrial waste and excessive use of pesticides and fertilizers making the soil and groundwater polluted, do harm to the environment of farm producing and the safety of groundwater supply [1, 2]. The article studies the pollution situation of the groundwater environment in Longkou Plain by analyzing collected samples, and gives advice on remediation.

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2. The Rough Guide of Longkou City

Longkou City is located in the northwest of the Jiaodong Penisula, covering an area of 893 square kilometers with coastline 68.4 kilometers long. The territory is rich in mineral resources, abounding with gold, granite, limestone, lead, zinc, fluorite and quartz in the south mountain areas. The only large coastal coal base at low altitude of China is situated in Longkou, with lignite reserve reaching 2.6 billion tons and a production of more than 4 million tons.

It is simple in hydrographical condition in Longkou City, with two types of groundwater mainly—loose rock pore water and bedrock fissure water. The water-abundance of bedrock fissure water is worse, for the single well water yield is less than 100 m^3/d, partial section more than 100 m^3/d. In the water-rich zone, the water-abundance of loose rock pore water is better, the single well yield reaching 1,000-3,000 m^3/d in some places, which could make small sources of water locally. In other places, the water-abundance is not very well with the single well yield less than 1,000 m^3/d. The quaternary loose rock pore water,

water-bearing stratum dominated by fine sand and medium fine sand, is distributed along the piedmont and the coastal areas in Longkou, such as the river valley of the Huangshuihe River and the Yongwenhe River.

The Huangshuihe River, the largest in Longkou, with the total length of 53 km and the drainage area of 983 km^2, rises in the northern mountain area of Qixia City, runs through Zhaogezhuang Town in Qixia, Fengyidian Town, Shiliangji Town, Huangchengji Town in Longkou from north to south, passes through 206 National Highway to the northwest, and empties into the Bohai Sea. The Huangshuihe River has six tributaries, four of them (the Lanjiagou River, the Heishanhe River, the Laiyinhe River, the Jiangshuihe River) flowing into the river from the west land, and the other two (the Dahanjiagou River & the Huangchengji River) from the east, of which, the Jiangshuihe River and the Huangchengji River are larger. The mainstream and tributaries all rising in hills, 82% of the drainage area of the Huangshuihe River is hilly regions.

There are more than 1,000 industrial enterprises in the city with various industrial category, including mechanical manufacture, chemical industry, textile industry, garment processing, food industry, paper-making, metalworking, electroplating, plastic processing and etc., which makes the city more developed than other regions in China. We investigate 112 contamination sources in Longkou. The chemical plants, mines and food factories are main pollution sources, concentrated in the Middle-Lower Reaches of the Huangshuihe River and the hilly areas of the southern city.

3. The Current Situation of Water Pollution in Longkou

Forty-eight (48) groups of water samples are collected in Longkou, consisting of 7 groups of surface water samples and 41 groups of groundwater samples, most of them collected in the quaternary cover areas, mainly loose rock pore water.

3.1 The Present Situation of the Pollution of the Surface Water

In the 7 groups of surface water samples, 3 groups are water samples collected in the reservoir, 4 groups collected in the cross-section of river. The water in the reservoir is better than the class III water quality standard. Four (4) groups of water samples are collected from the Wangwu Reservior in the upper Huangshuihe, the Middle-Lower Reaches of the river and its tributary the Jiangshuihe River. The tests show that the water quality of the sample collected from the Wangwu Resevior is class II, and the other three samples belong to the national standards poor class V (Table 1).

The Wangwu Reservoir lies in the upper reaches of the Huangshuihe River. The ion contents of surface water samples become higher and the water quality gets worse as the river flows. The sulfate content rises from 180.61 mg/L in the middle reaches to 729.39 mg/L in the lower reaches by three times, 19 times as high as sample in the reservoir. The nitrate content increases by four times to 65.78 mg/L in the lower reaches, 14 times as in the reservoir.

3.2 The Present Situation of the Pollution of the Groundwater

3.2.1 Inorganic Substances in the Groundwater

The quality of shallow pore water in survey areas is poor according to the analysis of the samples of the groundwater. The inorganic influence factors mainly are nitrate, salinity, total hardness, chloride, sulfate, etc.. The detection rate of heavy metals is relatively low.

The tests reveal a high content of nitrate in shallow loose rock pore water (Fig. 1). According to the ground water quality standard, the nitrate content (calculated by nitrogen) of the class III water quality should not be higher than 20 mg/L. All the samples except for the samples collected in the south Lutou County are too poor to meet the quality standard in nitrate standard so that the water can not be drunk.

Table 1 The results of main indexes of surface water samples of the drainage of the Huangshuihe River. (unit: mg/L)

Sampling location	Petroleum	Chloride	Sulfate	Nitrate	Total hardness	Salinity
The Wangwu Resevior	0	24.65	35.7	4.4	116.96	245.18
The Huangshuihe River (middle reaches)	0	148.26	180.61	13.65	287.96	647.57
The Huangshuihe River (lower reaches)	7.37	202.45	729.39	65.78	584.88	1,585.78
The Jiangshuihe River	15.65	319.01	201.45	0.84	562.56	1,771.74

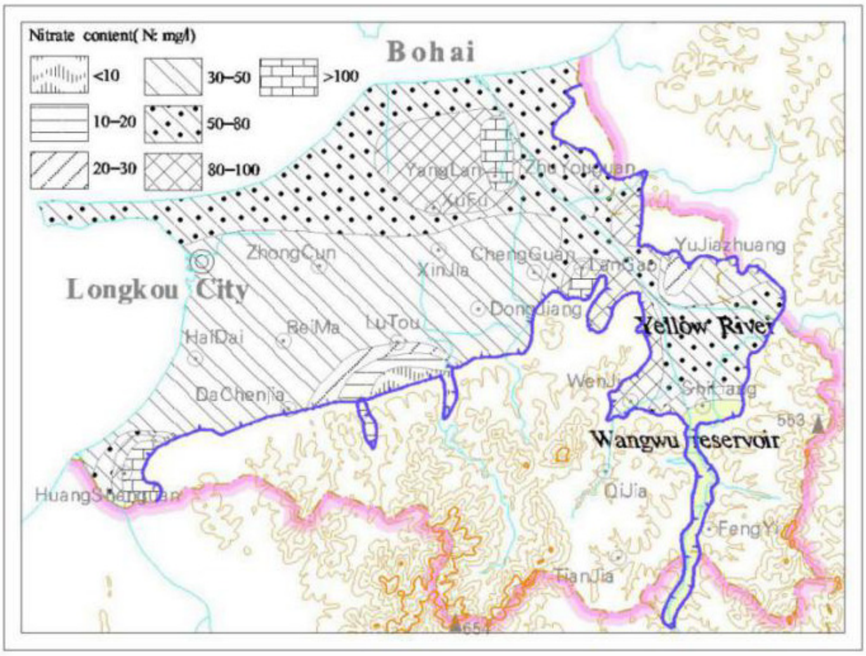

Fig. 1 The zone map of nitrate content of shallow pore water.

Especially in the drainage of the Huangshuihe River, the nitrate content (calculated by nitrogen) reaches to more than 50 mg/L with the highest up to 141 mg/L collected in Langao Village, Langao Town, 6 times higher than the class III water quality standard, which makes the nitrate content as one of the main factors for contamination in the groundwater in Longkou City.

The chloride content enhances gradually from piedmont to coastal areas (Fig. 2). Groundwater will be intruded by sea water as the chloride content of ground water is up to 250 mg/L, for which, the area intruded by sea water in Longkou City is as high as 180 square kilometers. However, the groundwater in most of the piedmont region meets the class III water quality standard.

The groundwater will be polluted for the increase of the sulfate content. The sulfate content in the collected samples is in a low level, except the sample collected near Yanglanzhen Town being more than 250 mg/L, worse than the class-III-water. Some other samples with a lower content (200-250 mg/L) are collected mainly in the groundwater reservoir area of the Huangshuihe River (Fig. 3).

All above, nitrate, total hardness, chlorite & total dissolved solids make the quality of the shallow loose rock pore water poor, with nitrate the major pollution. The increase of nitrate content is closely related to the construction of the groundwater reservoir.

3.2.2 Organic Substances in the Groundwater

The tests on the 41 groups of samples show that no organic substances are found in 15 groups, one kind of

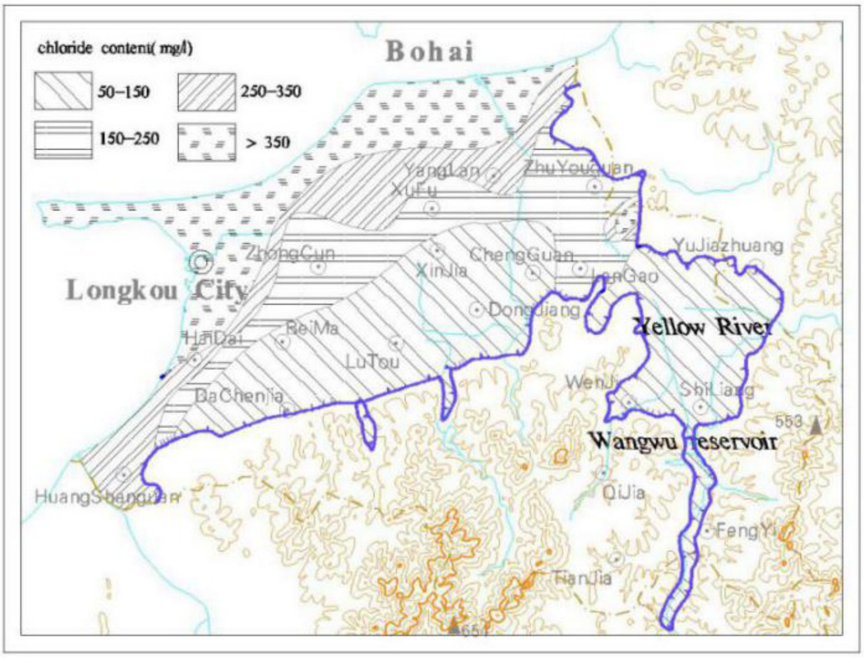

Fig. 2 The zone map of chloride content of shallow pore water.

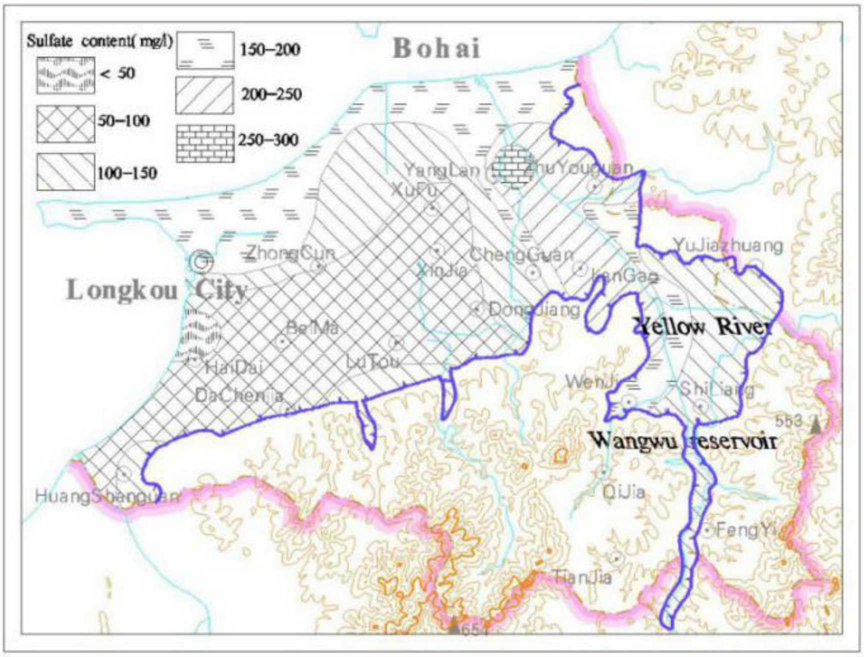

Fig. 3 The zone map of sulfate content of shallow pore water.

organic substance being detected in 10 groups, two in 7 groups, three or more in 9 groups, among which 6 organic indictors are detected in some samples up to the most. The organic indictors detected do not exceed the standard, with polycyclic aromatic hydrocarbons detected the most common organic substance (Fig. 4).

The detection of organic substances in groundwater is closely related to the distribution of pollution sources. The organic substances in groundwater are more easily detected in Chengguanzhen Town, Yanglanzhen Town,

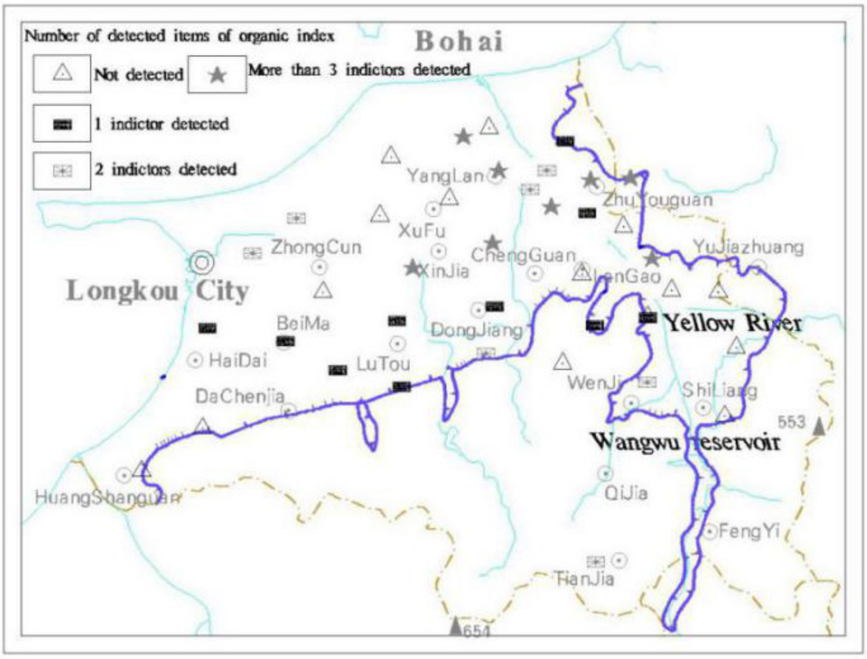

Fig. 4 The map of the items of organic substances tested out in groundwater samples.

Zhuyouguanzhen Town and Zhongcunzhen Town, the regions where the pollution sources concentrate. The water samples collected in Beimazhen Town and Lutouzhen Town, which are coal mining areas, are all detected one but not the same organic index. The depth of sampling well is similar to the mining depth, leading to the organic pollution of the groundwater [3].

3.2.3 Comprehensive Evaluation of the Groundwater Quality

According to Standard for Groundwater Quality (GB/T1448-2017), 48 types of chemical composition which influence human life greatly are tested, including 12 common chemical indexes, 5 inorganic toxicological indexes, 5 toxic heavy metal indexes, 21 volatile organic indexes and 5 semi-volatile organic indexes. The groundwater quality of all samples is assessed by single factor evaluation, and the water quality finally depends on the worst index or factor (Table 2 and Fig. 5).

The shallow groundwater quality is poor in Longkou City, and there is no water of class I & II. Water of class III & IV is sparse, while water of class V accounts for 90%. The inorganic substances influence the groundwater quality most. Thus, the shallow groundwater is contaminated by human activity seriously. Although measures have been taken to prevent the pollution since 2010, the water quality still remains at a poor level. Particularly, the water from the centralized water-supply resources around

Table 2 The assessment indexes of groundwater quality.

Index classification	Index containing
Common chemical indexes (12)	pH, Fe, Mn, Zn, Al, Cl^-, SO_4^{2-}, total hardness, TDS, oxygen demand, NH_4^+, Na.
Inorganic toxicological indexes (5)	Se, F^-, iodide, NO_3^-, NO_2^-.
Toxic heavy metal indexes (5)	As, Cd, Cr, Pb, Hg.
VOC indexes (21)	$CHCl_3$, CCl_4, CH_3CCl_3, C_2HCl_3, C_2Cl_4, CH_2Cl_2, CH_2ClCH_2Cl, $CH_2ClCHCl_2$, $CH_3CHClCH_2Cl$, $CHBr_3$, C_2H_3Cl, CH_2CCl_2, CHClCHCl, C_6H_5Cl, o-DCB, 1,4-dichlorobenzene, C_6H_6, C_7H_8, ethylbenzene, dimethylbenzene, styrene.
Toxic heavy metal indexes (5)	$C_6H_6Cl_6$, γ-BHC, DDT, HCB, BaP.

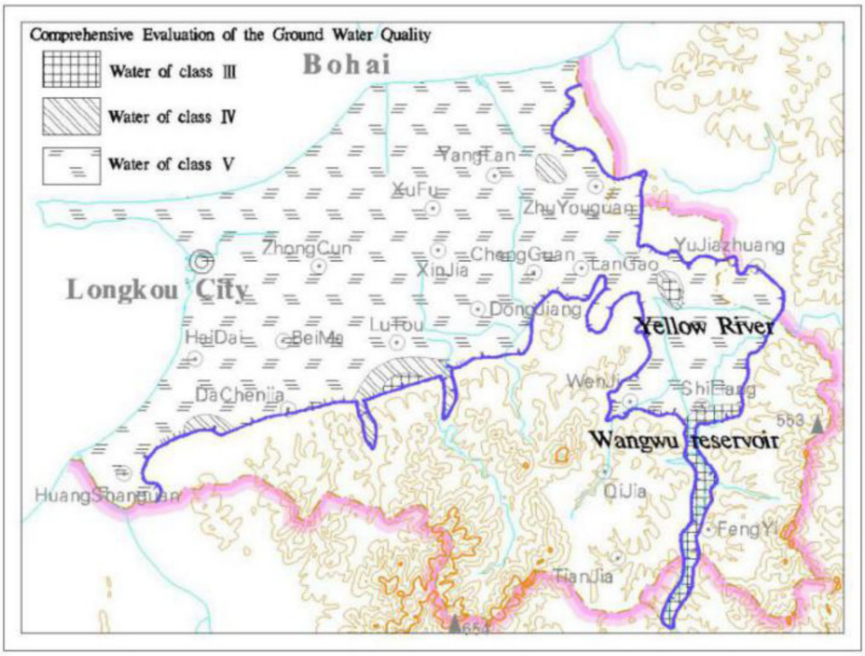

Fig. 5 The map of comprehensive assessment of shallow groundwater.

underground reservoir of Huangshuihe River is of class V, by which the water supply to citizens is threatened severely, so the shallow groundwater in Longkou is not fit for drinking now.

4. The Reasons for Ground Water Pollution

The ground water in Longkou Plain is polluted partly because of the dense population and relatively prosperous chemical enterprises, partly because of the construction of the underground water reservoir and no matching sewage treatment. What is more, along the Huangshuihe River are numerous factories and sewage ditches, some industrial and domestic sewage flowing into the Huangshuihe River. The industrial dust in the air seeps into the earth when raining, making the groundwater more contaminated [4, 5]. In addition, the aquifer in the study area is mainly composed of fine sand and medium coarse sand, so the vadose zone in the study area has poor antifouling performance and is easy to be polluted [6]. In no more than 6 years after the underground reservoir put into use, the deterioration of groundwater quality caused by seawater intrusion is controlled by the reservoir construction, but the contamination led by sewage discharge is getting more serious. The region where the indexes such as salinity, total hardness and chloride ion of groundwater have risen above the acceptable level took up 50% of the total reservoir area in the year 2010. As a result, the city began to take measures to promote sewage treating, prevented waste water discharging at will, and made the water quality under control. Some water quality indexes have been declining since 2013 with water quality becoming better.

5. The Suggestions to the Treatment of Groundwater Pollution

The remediation of tri-nitrogen contaminated groundwater is considered first to remediate the groundwater in Longkou. There are two main aspects of measures on tri-nitrogen pollution prevention [7, 8]. On the one hand, steps must be taken to control pollution resources strictly by stronger policies in order to avoid irrigation and apply fertilizer rationally, and on the other hand, excessive nitrate content in groundwater should be dealt with by advanced treatment technologies. By analyzing the strengths and weaknesses as well as the real condition, in-situ chemical remediation technology is suggested to cope with water pollution. *In-situ* chemical remediation is the technique that the pollutants in groundwater could be transformed into non-or-less toxic substances by putting oxidant or reducing agent into polluted water by oxidation or reduction. Reducing methods, which are more effective to remove chromate and nitrate in polluted groundwater, include catalytic reduction and active metal reduction by reducing agents. Catalyst is needed in both reducing methods for chemical reactions, with hydrogen, formic acid, methanol as reducing agents in catalytic reduction and metals such as iron, aluminum, zinc as reducing agents in active metal reduction. For example, nitrate can be reduced to nitrite, nitrogen and ammonia nitrogen by zero-valent iron colloid. Zero-valent iron can be injected through wells as well as along the route of pollutant flows, or directly into natural aquifers by injecting micron or even nano-sized zero-valent iron colloids.

6. Conclusions and Suggestions

The shallow groundwater quality is poor in Longkou City, for water of class V accounts for 90%, little of class III & IV, no class I & II. What make the water quality poor are inorganic factors, including nitrate, total hardness, chlorite and total dissolved solids, with nitrate the major pollution. The shallow groundwater is not for drinking. *In-situ* chemical remediation technology is considered to remediate the environment of ground water to guarantee the safety of water.

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