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^{15}N Isotope Used for Study of Groundwater Nitrogen Pollution in Shijiazhuang City, China

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Abstract: Shijiazhuang City is the capital of Hebei province, China. Groundwater is the major water supply source for living and industry need of the city. Due to a rapid increase of population and development of industry and agriculture, a series of groundwater environmental problems are created. In the paper, the situation of groundwater pollution in Shijiazhuang city is reported. Based on the groundwater chemical data and ^{15}N measurement results both on groundwater and soils, the reason of groundwater nitrate pollution is studied.

Key words: Groundwater; Pollution; ^{15}N isotope; Shijiazhuang city
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1 Introduction

In China, especially in north part of China, the majority of the city's population relies on groundwater for drinking, agricultural or industrial requirements because of lack of surface water resources. Large amounts of groundwater resources are needed with the urbanization and improvement of public living conditions. Since the groundwater has been over—exploited with unplanned state, the water table was going down rapidly year after year. The regional water table drawdown led to partial dewatering of the major aquifer in the city. Many cities in north part of China are also facing the problem of groundwater pollution at present. According to the investigation data, the main pollutants include NO_3^-, hardness, SO_4^{2-}, Cl^-, heavy metals and so on.

2 General Situation of Shijiazhuang City

Shijiazhuang City, with area of 72 km^2, is the capital of Hebei province, China, and it is a center of provincial politics, economy and culture and a hub of communications in North China. The climate is semi-arid, so the temperature difference between summer and winter is very big and the normal mean annual temperature is 13℃, historical maximum 43.7℃ and minimum −26.5 ℃. The normal mean annual rainfall is 518.6mm, but about 70% rainfall concentrates in July to September. The evaporation is great and the normal mean annual potential evaporation ranges from 900mm to 1 200mm.

Groundwater is the major water supply source for living and industry need of the city, and it is intensively exploited from Quaternary aquifer due to a rapid increase of population and development of industry and agriculture. The water table has been dropping by 1 meter annually for many years. Meanwhile, a series of groundwater environmental problems are created. Continued lowering of the groundwater level and deterioration of the groundwater quality are grave consequences

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of the human activities. According to the groundwater monitoring data, the contents of groundwater chemical monitoring data, the contents of groundwater chemical components in Shijiazhuang City have increased year after year since 1959. Groundwater hardness and total dissolved solids (TDS) were also increasing in large scale. The typical pollutants in groundwater are Cl^-, NO_3^-, SO_4^{2-}, as well as some heavy metals such as Hg, Cr and so on. Nitrate appears to be one of the major pollutants reaching groundwater from human activities. So we take this pollutant as an example city for the study.

3 Hydrogeological Setting

Shijiazhuang city is located in upper of the alluvial fan. Groundwater mainly stores in the Quaternary sediments. On the basis of the lithologic property, deposit age, distribution of aquifers and hydrodynamic condition, the whole stratum can be divided into 4 aquifer groups (Ⅰ, Ⅱ, Ⅲ and Ⅳ), which belong to Q_4, Q_3, Q_2, Q_1 respectively.

In the study area, aquifer Ⅰ and Ⅱ develop very well. We called them the shallow aquifers. The groundwater in these aquifers is phreatic water. The lithology of aquifers is mainly coarse sand and gravel with total thickness of 34~70m. But aquifer Ⅰ has almost been dewatered. So that the aquifer Ⅱ is the main utilizable aquifer at present stage for urban water supply. The lithology of aquifer Ⅲ and Ⅳ is mainly fine sand. We usually called them the deep aquifers. In addition, between aquifer Ⅱ and aquifer Ⅲ, there is a continuous waterproof. So that the groundwater in aquifer Ⅲ and Ⅳ is confined water. That means the recharge condition is not so good for the deep aquifers. For this reason, deep aquifers are not the main exploitation layers for the city up to now.

4 Groundwater Nitrogen Pollution in Shijiazhuang City

Since 1978, the groundwater quality monitoring has been carried out continuously. In general, there are about 90 observation wells in the city. According to the monitoring data in different years, the statistics of mean NO_3^- content in groundwater has been done and the variation processes is shown in Figure 1.

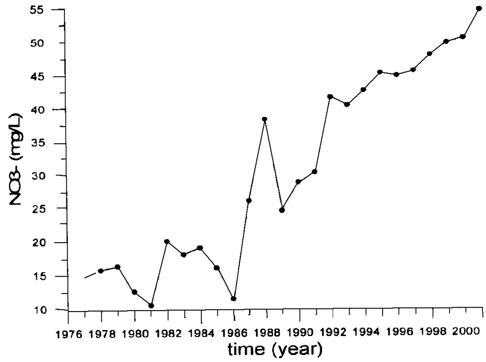

Fig.1 Variation processes of groundwater mean NO_3^- content in Shijiazhuang city

From Figure 1, it can be seen that before 1989 the variation processes of groundwater mean NO_3^- content went up in waves. After 1989, the variation processes shown obviously going up with the time increasing. In 2001, the mean NO_3^- content in groundwater was almost 4 times to that in 1978.

From the distribution of NO_3^- content in groundwater in the city in 2001. It can be seen the content of NO_3^- in groundwater is increased from north to south. In northern, eastern and western suburbs, the content of NO_3^- in groundwater is mostly less than 45mg/L, and in southern suburb the content of NO_3^- in groundwater is mostly more than 45mg/L, and the highest value of NO_3^- can reach 156.7mg/L.

In order to make the processes of NO_3^- pollution clearer, we did a frequency analysis about this. The result shows that the content of NO_3^- was mostly less than 20mg/L in 1980. Wells with NO_3^- content less than 10mg/L occupied 39.1% of the total wells, and the same for NO_3^- content from 10~20mg/L, and 21.8% for NO_3^- content from 20~40mg/L. There was no well with NO_3^- content exceeding the standard of drinking water (45mg/L). Up to 1985, the NO_3^- content of groundwater increased slightly in the whole area and was less than 20mg/L mostly. Wells with NO_3^- content less than 10mg/L occupied 23% of the total wells, and 50.8% for NO_3^- content from 10~20mg/L, and 13.1% for NO_3^- content between 20~30mg/L, and 10% for NO_3^- content more than 30mg/L. Up to 1990, the wells with NO_3^- content less than 20mg/ occupied only 23% of the total wells and most wells (51.9%) had NO_3^- content between 20 to 40mg/L. 13.4% of the total wells had the NO_3^- content exceeding the standard of drinking water (45mg/L). In 2001, wells with NO_3^- content less than 40 mg/L occupied only 14.7%, and 65.3 % of the total wells had the NO_3^- content exceeding the standard of drinking water (45mg/L). From this, it can be seen that the NO_3^- content of groundwater increased in a regional scale in the city.

5 The Composition of ^{15}N in Groundwater in Shijiazhuang City

28 groundwater samples were taken from different wells. In the sampling wells, some were used for city and village water supply and some for agriculture irrigation (Table 1). 2 samples of sewage collected for measurement of ^{15}N. The data of ^{15}N values and NO_3^- values are shown in Table 1.

Table 1 $\delta^{15}N$ and NO_3^- contents in groundwater (2002)

Sample No.	location	NO_3^- (mg/L)	$\delta^{15}N$ (‰)
1	Dongpingle	19.3	+3.654
2	Xibaizhuang	13.5	+2.265
3	Caocun	56.8	+7.136
4	Quyangqiao	47.9	+7.226
5	Angu	43.3	+6.416
10	Zilaishui	22.3	+7.430
12	Beiguan	147.6	+4.223
14	Shilipu	42.6	+5.677
15	Xizhaotong	20.7	+5.407
16	Takou	34.9	+3.965
17	Xiaomazhuang	42.7	+5.185
22	Chengjiaozhuang	95.6	+11.043
23	Erjianyu	77.7	+7.096
24	Pijiuchang	39.4	+4.826
26	Zhenzhichang	114.3	+7.546
30	Nangaoying	65.7	+8.017
31	Huaidi	71.2	+7.480
33	Dongliangxiang	99.7	+2.365
35	Huafeichang	42.1	+6.006
36	Nangaoji	44.9	+2.162
37	Gongjiazhuang	44.5	+6.200
41	Hengshan	60.7	+11.666
42	Shangzhuang	113.6	+5.380
43	Datan	79.3	+2.164
44	Yanchang	77.4	+11.430
45	Dieryinranchang	78.2	+8.904
46	Fangbei	99.1	+7.110
47	Liucun	14.9	+5.865

Through synthetic arrangement and analysis (Table 1), it can be found that the groundwater for the city water supply has the highest mean content of NO_3^- with value of 73.1 mg/L, and the groundwater for irrigation has the lowest mean content of NO_3^- with value of 53.9 mg/L. The groundwater for village water supply has a middle mean content of NO_3^- with value of 65.4 mg/L. That means the groundwater in urban area is more seriously polluted by nitrogen than that in village and farmland areas. In addition, the mean content of NO_3^- in sewage is very low with mean value of 0.5 mg/L, but the content of NH_4^+ is very high with mean content of 82.5mg/L. Considering the $\delta^{15}N$ values, it can be seen that the groundwater in the urban area with values ranging from +7.1 to +11.6 is familiar to the sewage with values ranging from +7.86 to +9.04. The groundwater in farmland area has the lowest $\delta^{15}N$ values between +2.16 and +4.83. The values of groundwater in village area are lower than that of sewage and higher than that of groundwater in farmland area.

6 The Composition of ^{15}N in Different Soil[1~3]

In order to recognize the nitrogen pollutant source in groundwater and to understand the reason of groundwater pollution, the samples in different soils for ^{15}N isotopic measurement were collected. The solution for measurement was extracted from the soil using deionized water as the extraction solution and the ratio of soil to deionized water is 1/10 in weight. Before the mixing was done, the soil was dried in air and then grinded into the powder with grain diameter less than 0.25mm, then putting the deionized water and grinded soil into the glass bottle, stirring them well and laying up for 24 hours, after that, filtering the mixture and getting the solution for NO_3^- and ^{15}N measurement.

In order to know the mechanism of the groundwater nitrate pollution in the study area, we had studied the variation law of $\delta^{15}N$ and NO_3^- with depth increasing in different soil profiles. Table 2 and Table 3 show the results. Profile 1 is located in the cotton field fertilized with manure. Profile 2 is in the wheat field fertilized with chemical fertilizer. Profile 3 was dug in the natural soil area, and Profile 4 was dug in cornfield irrigated with sewage. All profiles were dug to the depth of 4.5 m.

It can also be seen that the values of $\delta^{15}N$ are relatively lower for natural soil than that of other kinds of soils. For natural soil (Profile 3) the $\delta^{15}N$ value is from 1.6‰ to +2.5‰; For the mature soil (Profile 1) the $\delta^{15}N$ values are +11.2‰ to +13.5‰; For chemical fertilizer soil (Profile 2), the value is from +3.9‰ to +4.7‰. For sewage irrigation soil, the value is from +7.8‰ to +8.7‰. Besides, the content of NO_3^- is also lower for natural soil than that of mature soil, chemical fertilizer soil and sewage irrigation soil.

Table 2 The variations of $\delta^{15}N$ and NO_3^- with depth in Profile 1 and Profile 2

Profile 1 (cotton field fertilized with manure)				Profile 2 (wheat field fertilized with chemical fertilizer)			
Depth (m)	Lithology	NO_3^-	$\delta^{15}N$ (‰)	Depth (m)	Lithology	NO_3^-	$\delta^{15}N$ (‰)
0	soil	165.1	13.2	0	soil	197.4	4.4
0.5	soil	162.3	12.8	0.5	soil	185.2	4.5
1.0	clay	154.2	13.5	1.0	Clayey loam	197.3	4.7
1.5	clay	148.4	12.6	1.5	Clayey loam	197.1	4.5
2.0	Sub-sandy soil	132.1	11.2	2.0	Sub-sandy soil	165.9	4.0
2.5	Sub-sandy soil	100.5	11.3	2.5	Sub-sandy soil	161.2	3.9
3.0	Clayey loam	112.7	12.7	3.0	clay	173.1	4.4
3.5	Clayey loam	121.3	13.1	3.5	clay	182.4	4.2
4.0	Clayey loam	121.4	12.4	4.0	Sub-sandy soil	161.6	4.7
4.5	Clayey loam	105.2	11.8	4.5	Clayey loam	165.4	3.9

Table 3 The variations of $\delta^{15}N$ and NO_3^- with depth in Profile 3 and Profile 4

Profile 3 (natural soil)				Profile 4 (cornfield irrigated with sewage)			
Depth (m)	Lithology	NO_3^-	$\delta^{15}N$ (‰)	Depth (m)	Lithology	NO_3^-	$\delta^{15}N$ (‰)
0	soil	56.3	2.3	0	soil	74.5	8.7
0.5	soil	54.5	1.8	0.5	soil	72.3	8.5
1.0	Clayey loam	62.4	1.9	1.0	clay	74.5	8.6
1.5	Clayey loam	61.8	2.3	1.5	clay	72.6	8.4
2.0	Sub-sandy soil	58.9	2.1	2.0	Sub-sandy soil	68.3	7.9
2.5	Clayey loam	58.2	1.8	2.5	Clayey loam	71.5	7.8
3.0	silt	50.3	1.6	3.0	Sub-sandy soil	65.4	8.4
3.5	Clayey loam	52.9	2.5	3.5	Sub-sandy soil	69.7	8.1
4.0	clay	54.6	2.1	4.0	silt	64.5	8.6
4.5	clay	55.4	2.2	4.5	Sub-sandy soil	69.5	8.5

7 Determining the Sources of Nitrate in Groundwater in Shijiazhuang City

Comparing the $\delta^{15}N$ values both in groundwater and soil, it can be seen that groundwater for city water supply has the same value rang with that of manure and sewage irrigated soil. From this, it may be concluded that the nitrogen pollutant source of groundwater for city water supply (in higher population area) is mainly from excrement and sewage.

The groundwater for irrigation has the little higher value range of $\delta^{15}N$ than that of chemical fertilizer soil, which means the nitrogen pollutant source of groundwater in wells for irrigation (in lower population area) is mainly from chemical fertilizer nitrogen.

The groundwater for village water supply has $\delta^{15}N$ values little higher than that of chemical fertilizer soil and lower than that of manure and sewage irrigated soil. Which may indicate the nitrogen pollutants is mainly from excrement and partly from chemical fertilizer.

The natural soil nitrate with low $\delta^{15}N$ values is not the main cause of nitrate contamination of groundwater in the area.

8 Summary

The NO_3^- content of groundwater increased in a regional scale in Shijiazhuang city. The chemical and $\delta^{15}N$ isotope investigation of groundwater and soils carried out indicated that the nitrogen pollutant source of groundwater for city water supply (in higher population area) is mainly from excrement and sewage. The nitrogen pollutant source of groundwater in wells for irrigation (in lower population area) is mainly from chemical fertilizer nitrogen and the nitrogen pollutants is mainly from excrement and partly from chemical fertilizer. For the groundwater for village water supply, the natural soil nitrate is not the main cause of nitrate contamination of groundwater in the area.

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