Quality evaluation of groundwater in the North China Plain

FEI Yu-hong*, ZHANG Zhao-ji, LI Ya-song, GUO Chun-yan, TIAN Xia

Institute of Hydrogeology and Environmental Geology, CAGS, Shijiazhuang 050061, China.

Abstract: This paper presents a method combining single-indicator comprehensive evaluation and influence factor identification to measure groundwater quality. This method not only reflects groundwater quality classification with clear physical significance, but also divides the possibilities of man-made pollution in regional groundwater. The paper selects 6 063 representative groundwater wells in the North China Plain to evaluate 49 groundwater inorganic and organic index and comes to a conclusion: Controlled by geological environment and hydrogeological conditions, the groundwater quality in the North China Plain deteriorates from the bottom of maintain to coastal area, with Class I to III groundwater decreasing from 49% to 3.9% while Class V groundwater increasing from 21% to 86.9%; the quality of deep groundwater is better than that of shallow groundwater; the contribution rate of manganese, total hardness, total dissolved solids and iodide in shallow groundwater to over-III type water exceeds 50%; the contribution rate of nitrite in pollution index reaches 20%; while heavy metal and organic indexes have limited impact on regional groundwater quality. The North China Plain is an important economic area in China. Over decades, it has witnessed intense human activities, and water resource quantity demanded has been far greater than quantity supplied. Due to scarce surface water resource, groundwater becomes the pillar supporting regional economic development. This has led to increasing groundwater exploitation and development. According to statistics, the exploitation degree of shallow groundwater reaches 105% in the North China Plain and 118% in the Hebei Plain; the exploitation degree of deep groundwater reaches 143% in the North China Plain and 163% in the Hebei Plain. The serious over-exploitation of groundwater brings various geological environmental problems, with the worsening of groundwater quality being a typical one. Besides impact brought by human activities, the poor quality of natural water in the North China Plain is also an important factor. Therefore, to understand the current regional groundwater quality situation and to master influence factors and influence degree can provide reliable scientific protection for regional economic development.

Keywords: North China plain; Groundwater quality; Evaluation; Contribution rate

1 Fundamental philosophy

1.1 Concept

Definition of groundwater quality: According to the essential attribute of groundwater constituted of physical, chemical, biological and radioactive components of groundwater (State Administration for Quality Supervision and Inspection and Quarantine, 2007), groundwater quality describes the status of groundwater under the current situation and is confirmed by comparing given standards, namely groundwater quality evaluation, which is different from groundwater pollution evaluation for it compares not with a certain period in the past nor its changes.

There are two set of water quality standards being used in China: the first is the Quality Standards for Groundwater (GB/T14848-93) (State Administration for Quality Supervision and

*FEI Yu-hong (1960-), female, researcher, mainly engaging in hydrology and water environment. E-mail:yuhong_fei@163.com

Inspection and Quarantine, 1993) of which the evaluation index and thresholds in the Standards are not applicable anymore and are being updated; the other one is the Sanitary Standards for Drinking Water (GB5749-2006) (Standardization Administration of China, 2006), which mainly targets everyday drinking water and domestic water. The Standards was revised in 2006. As a compulsory national standard, the number of index increases from 35 to 106, especially the number of index of organic compounds, which increases by 50, and thresholds of water quality index are also set.

Water quality standards widely used in the international community with relatively big influence include the Guidelines for Drinking Water Quality (second edition) by the World Health Organization (WHO), the Council Directive on the Quality of Water Intended for Human Consumption (98/83) by the European Union (EC), and the Drinking Water Standards and Health Advisories (2006) by the United States Environmental Protection Agency (USEPA). WHO's standards include 159 pollution indexes, comprehensive, broad-based and in line with its position as a world water quality authority standard and important reference for each country; EC's standards have 48 indexes, including 20 non-obligatory indexes; USEPA's standards have 102 indexes, including 86 obligatory indexes, each controlled by Maximum Contaminant Level (MCL) and Maximum Contaminant Level Goal (MCLG). The latter is to protect human health and does not involve contaminant detection limit and control technology while the former is used for implementation.

1.2 Review of evaluation methods

Over the years, researchers at home and abroad have explored groundwater quality evaluation and presented various water quality evaluation methods, such as the synthetic index method, comprehensive evaluation of fuzzy mathematics and grey cluster comprehensive evaluation method (Štambuk-Giljanović, 1999; Helene *et al*. 2000; Reghunath *et al.* 2002; Shrestha and Kazama, 2007), GIS method (Shankar and Mohan, 2006; SÁnchez-martos *et al.*2002; Mogheir *et al*. 2003; Mogheir *et al*. 2006). Foreign scholars have recently started to mainly analyze toxicological index and introduced it into groundwater quality evaluation. Evaluation results are usually divided into three classifications: Good water quality (no organic contaminants have been detected and the content of inorganic components is no higher than background level and meets water consumption standards), ordinary water quality (organic contaminants have been detected, but concentration meets water consumption level; the content of inorganic components is higher than background level but meets water consumption standards) and poor water quality (organic contaminants have been detected, with concentration higher than water consumption standard limit; the content of inorganic components is higher than both background level and water consumption standard limit) (IIinois Environmental Protection Agency Bureau of Water, 2006).

China's Quality Standards for Groundwater (GB/T14848-93), based on China's groundwater quality status, human health reference value and groundwater quality protection target and referring to the maximum water quality requirements of domestic drinking water and water consumption in industry and agriculture, divides groundwater quality into five categories (Fig. 1). It recommends scoring method with attached notes (Nemerow Index method) and divides evaluation results based on certain scores into five categories: Excellent, good, ordinary, bad and poor. However, after years of application, people find that the Nemerow Index method identifies groundwater quality class based on the weight of maximum values, and thus fails to match with the definition of groundwater quality classifications; in addition, the results do not have explicit physical significance (GU Chao-jun *et al.* 2002; LI Ya-song *et al.* 2011). These deficiencies are shown as follows: ① maximum values of a single component are over considered, which leads to low probability of III class water occurrence; ② the five classes have no correspondence with the five classifications of groundwater quality, which leads to implicit physical significance of evaluation results and poor practicability; ③ chemical characters of groundwater quality index are different, with different harms on human health while the evaluation results cover up some facts that these characters are harmful to human health.

Table 1 Table of China's groundwater quality classification

Type	Function	Use
Class Ⅰ Class Ⅱ	Reflects low natural background values in chemical components of groundwater	Suitable for various uses
Class Ⅲ	Based on human health reference value	Applies in centralized domestic drinking water source and water consumption in industry and agriculture
Class Ⅳ	Based on requirements of water consumption in industry and agriculture	Besides water consumption in agriculture and some industries, also applies in domestic drinking water after treatment
Class Ⅴ	Not suitable for drinking	Water consumption for other purposes

1.3 Evaluation index

Quality Standards for Groundwater (GB/T14848-93) includes 39 indexes: Color, smell, turbidity, visible materials, pH value, total hardness, total dissolved solids, sulfate, chloride, iron, manganese, copper, zinc, molybdenum, cobalt, volatile phenols, anion synthetic detergent, permanganate index, nitrate, nitrite, ammonium-nitrogen, fluoride, iodide, cyanide, mercury, arsenic, selenium, cadmium, chromium, lead, beryllium, barium, nickel, dichlorodipheny-ltrichloroethane, hexachloro-cyclohexane, total coliforms, total bacterial count, gross α-radio-activity and total β-radioactivity. These indexes seldom involve organic contaminants. With the development of modern chemical industry, these standards cannot meet the requirements of objective evaluation of groundwater quality. In the revised Quality Standards for Groundwater by the China Geological Survey, besides the original indexes, 40 organic contaminant indexes detected in groundwater in the international community are added.

Evaluation index and thresholds are listed in Table 2.

1.4 Evaluation method in this paper

To match evaluation results with groundwater quality classifications with physical significance, this paper presents a method combining single-indicator comprehensive evaluation and influence factor identification, which reflects groundwater quality classifications with explicit physical significance and divides possibilities of man-made pollution in regional groundwater.

Table 2 Index and their thresholds in the “Quality Standards for Ground Water”

No.	Index	Groundwater quality threshold				
		Class I	Class Ⅱ	Class Ⅲ	Class Ⅳ	Class Ⅴ
	Conventional index & threshold					
1	pH value	6.5-8.5			5.5-6.5 8.5-9	<5.5 or>9
2	Iron/(mg/L)	≤0.1	≤0.2	≤0.3	≤2.0	>2.0
3	Manganese/(mg/L)	≤0.05	≤0.05	≤0.1	≤1.5	>1.5
4	Copper/(mg/L)	≤0.01	≤0.05	≤1.0	≤1.5	>1.5
5	Zinc/(mg/L)	≤0.05	≤0.5	≤1.0	≤5.0	>5.0
6	Aluminum/(mg/L)	≤0.005	≤0.05	≤0.2	≤0.5	>0.5
7	Sodium/(mg/L)	≤200	≤200	≤200	≤300	>300
8	Chloride/(mg/L)	≤50	≤150	≤250	≤350	>350
9	Sulfate/(mg/L)	≤50	≤150	≤250	≤350	>350
10	Total hardness (calculated with $CaCO_3$)/(mg/L)	≤150	≤300	≤450	≤650	>650
11	Total dissolved solids/(mg/L)	≤300	≤500	≤1 000	≤2 000	>2 000
12	Oxygen consumption (COD_{Mn} method, calculated with O_2) /(mg/L)	≤1.0	≤2.0	≤3.0	≤10	>10
13	Arsenic/(mg/L)	≤0.005	≤0.005	≤0.01	≤0.05	>0.05
14	Cadmium/(mg/L)	≤0.0001	≤0.001	≤0.005	≤0.01	>0.01
15	Chromium (hexavalent)/(mg/L)	≤0.005	≤0.01	≤0.05	≤0.1	>0.1
16	Lead/(mg/L)	≤0.005	≤0.005	≤0.01	≤0.1	>0.1
17	Mercury/(mg/ L)	≤0.00005	≤0.0005	≤0.001	≤0.001	>0.001
18	Selenium/(mg/L)	≤0.01	≤0.01	≤0.01	≤0.1	>0.1
19	Fluoride/(mg/L)	≤0.2	≤0.5	≤1.0	≤1.5	>1.5
20	Iodide/(mg/L)	≤0.004	≤0.004	≤0.04	≤0.08	>0.08
21	Nitrate (calculated with N)/(mg/L)	≤2.0	≤5.0	≤0	≤30	>30
22	Nitrite(calculated with N)/(mg/L)	≤0.001	≤0.01	≤0.02	≤0.1	>0.1
23	Ammonium-nitrogen/(mg/L)	≤0.05	≤0.05	≤0.5	≤1	>1
24	Trichloromethane/(mg/L)	≤0.0005	≤0.006	≤0.06	≤0.3	>0.3
25	Carbon tetrachloride/(mg/L)	≤0.0005	≤0.0005	≤0.002	≤0.02	>0.02

Table 2: Continued

No.	Index	Groundwater quality threshold				
		Class I	Class Ⅱ	Class Ⅲ	Class Ⅳ	Class Ⅴ
Unconventional index and thresholds/(μg/L)						
26	1,1,1-trichloroethane	≤400	≤400	≤2 000	≤4 000	>4 000
27	Trichloroethylene	≤0.5	≤7	≤70	≤210	>210
28	Tetrachloroethylene	≤0.5	≤4	≤40	≤300	>300
29	Dichloromethane	≤1	≤2	≤20	≤500	>500
30	1,2-dichloroethane	≤0.5	≤3	≤30	≤40	>40
31	1,1,2-trichloroethane	≤0.5	≤0.5	≤5	≤10	>10
32	1,2-dichloropropane	≤0.5	≤0.5	≤5	≤60	>60
33	Bromoform	≤1	≤10	≤100	≤800	>800
34	Chloroethylene	≤0.5	≤0.5	≤5	≤90	>90
35	1,1-dichloroethylene	≤0.5	≤3	≤30	≤1 500	>1 500
36	1,2- dichloroethylene	≤0.5	≤5	≤50	≤300	>300
37	Chlorobenzene	≤0.5	≤30	≤300	≤600	>600
38	Orthodichlorobenzene	≤0.5	≤100	≤1 000	≤2 700	>2 700
39	P-dichlorobenzene	≤0.5	≤30	≤300	≤3 000	>3 000
40	Benzene	≤0.5	≤1	≤10	≤100	>100
41	Methylbenzene	≤0.5	≤70	≤700	≤6 000	>6 000
42	Ethylbenzene	≤0.5	≤30	≤300	≤3 000	>3 000
43	Xylene	≤0.5	≤50	≤500	≤6 000	>6 000
44	Styrene	≤0.5	≤2	≤20	≤6 000	>6 000
45	hexachloro-cyclohexane (total amount)	≤0.01	≤0.5	≤5	≤10	>10
46	γ- hexachloro-cyclohexane (lindane)	≤0.01	≤0.2	≤2	≤9	>9
47	dichlorodiphenyltrichloroethane (total amount)	≤0.01	≤0.1	≤1	≤150	>150
48	Hexachlorobenzene	≤0.005	≤0.1	≤1	≤2	>2
49	Benzo a-pyrene	≤0.002	≤0.002	≤0.2	≤0.5	>0.5

Single-indicator comprehensive evaluation identifies groundwater quality according to the limit range where the indicator value locates; when different groundwater qualities have the same indicator limit, choose the better result. For example, when the standard values of ammonium-nitrogen Class I and Class II are both 0.02 mg/L, and if water quality analysis result is 0.02 mg/L, then the water quality should be identified as Class I instead of Class II Comprehensive evaluation identifies water quality result according to the highest class of the single-indicator evaluation result and indicates index with the highest class. For example, the content of chloride in certain groundwater is 400 mg/L, and the content of carbon tetrachloride is 350 μg/L, so these two indexes go to Class V; if the other indexes are lower than Class V, then the comprehensive classification of the groundwater quality goes to Class V.

Index of the groundwater quality evaluation can be divided into two categories: The first category is protogenetic chemical component due to exogenic geological process; the second category is groundwater pollution index due to human activities; “3-nitrogen” (nitrate, nitrite and ammonium-nitrogen), toxic heavy metal (cadmium, hexavalent chromium, lead and mercury) and organic index belong to “pollution index”.

Groundwater quality evaluated according to the mentioned method fails to reflect its toxicity and the source of chemical substances. For example, there are some sampling wells with Class V water quality: One with higher fluoride, one with higher iron and another one with carbon tetrachloride pollution. These wells have different impacts on human and have different pollution status; therefore it’s necessary to further identify influencing factors of groundwater quality. This paper mainly identifies major factors that impact groundwater quality through “single-indicator contribution ratio”.

“Single-indicator contribution ratio” is the ratio of the number of certain index with toxicity that is not lower than Class III groundwater to the total number of index that is not lower than Class III groundwater. The formula is as follows:

$$\text{Single index contribution ratio of super III class groundwater} = \frac{\text{the number of single} - \text{indicator of super III class groundwater}}{\text{the number of groundwater above III class}} \times 100\%$$

2 Groundwater qualities in the North China Plain

2.1 Hydrogeological conditions

The North China Plain is located in the east of the Tai-hang Mountains in east China, in the north of the Yellow River, in the south of the Yan Mountain and extends to the grand plains of the Bohai Sea, covering Beijing, Tianjin, all plain areas in Hebei Province, Shandong Province and plain in the north of the Yellow River in Henan Province, with an area of 139 200 km^2. The North China Plain can be divided into piedmont alluvial-proluvial inclined plain, alluvial lacustrine plain in the central part and alluvial marine plain in the coastal areas (Fig. 1) according to morphogenesis. Groundwater system of the North China Plain can be divided into the Luanhe River groundwater system, the Haihe River groundwater system and the ancient Yellow River groundwater system (ZHANG Zhao-ji and FEI Yu-hong, 2009). Groundwater constitutes the major source of water supply, accounting for 70% of the total water consumption (ZHANG Zhao-ji *et al*. 2009; ZHANG Guang-hui *et al.* 2010). In recent years, due to unreasonable discharge of industrial wastewater, a large amount of pesticide and fertilizer use and other human factors’ impact, groundwater quality in the North China Plain has changed greatly (WANG Lan-hua *et al*. 2014; LI Ya-song *et al*. 2014; FEI Yu-hong *et al*. 2007; ZHANG Guang-hui *et al*. 2009; TAN Ke-yan *et al*. 2011).

The loose pored groundwater burial condition in the North China Plain can be divided into piedmont alluvial-proluvial plan, alluvial plain in the central part and alluvial marine plain. Vertically, there are four aquifers: Aquifer I with the bottom buried 10-50 m, is the active cyclic alternating layer; although this layer has little exploitation and utilization significance, it’s important to the ecological environment; Aquifer II with the bottom buried 120-210 m, is a micro-confined and semi-confined groundwater; this layer has strong cyclic alternation capacity and is the major exploitation layer for agricultural water; Aquifer III with the bottom buried 250-310 m, is mainly exploited for drinking water and industrial water; Aquifer IV is partially exploited in the Binhai Plain. Usually Aquifer I and II are called shallow groundwater system while Aquifer III and IV are called deep groundwater system.

2.2 Evaluation data source

Evaluation data come from groundwater samples collected for the regional groundwater pollution investigation and evaluation in the North China Plain. The testing and sampling processes are strictly controlled as per industrial standards, especially the groundwater sample collection process, which is run strictly as per international standards and practices. These samples are sent to authority testing organization under low temperature preservation.

Three to four sampling sites are deployed in each area of 100 km^2 considering industrial distribution, agricultural planting structure and the distribution of fertilizer and pesticide use and groundwater pollution and local hydrogeological condition. Sampling periods lie in each autumn from 2006 to 2009. Organizations carrying out sample testing include: Groundwater and Mineral Water Testing Center of the Ministry of Land and Resources, the National Geological Experiment Testing Center and ALS Analysis (Shanghai) Ltd.

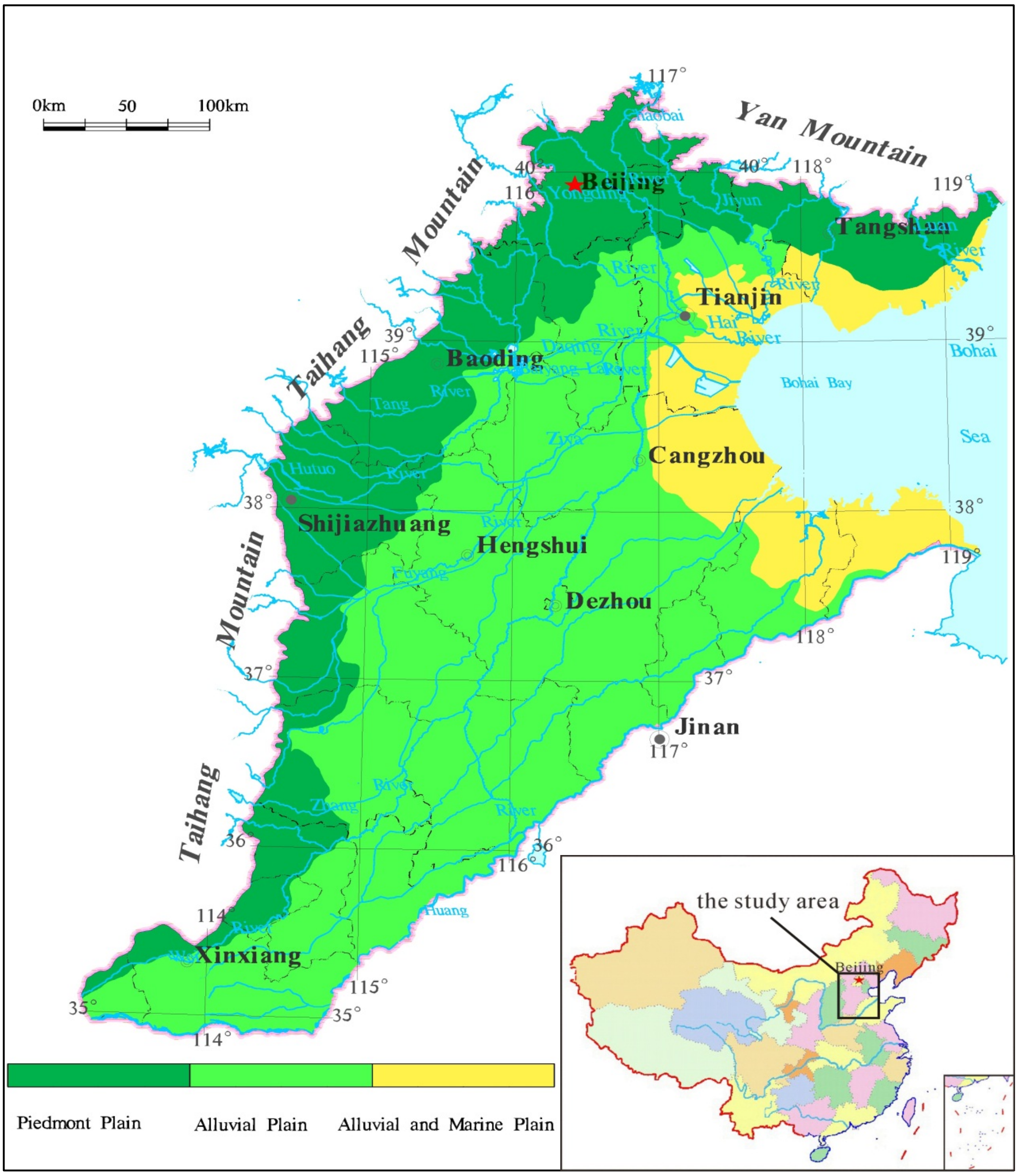

Fig.1 Geographical location of the North China Plain

2.3 Distribution characteristics of regional groundwater quality

Deep groundwater quality is better than that of shallow groundwater in the North China Plain (Fig. 2). Among 4 383 sampling sites of shallow groundwater, the number of sampling sites with Class I to III groundwater accounts for 22% of total sampling sites, the number of sampling sites with Class IV groundwater accounts for 21%, and the number of sampling sites with Class V groundwater, 57%; among 1 679 deep groundwater sampling sites, the number of sampling sites with I to III groundwater accounts for 26%, the number of sampling sites with IV groundwater accounts for 23% and the number of sampling sites with Class V groundwater 51%.

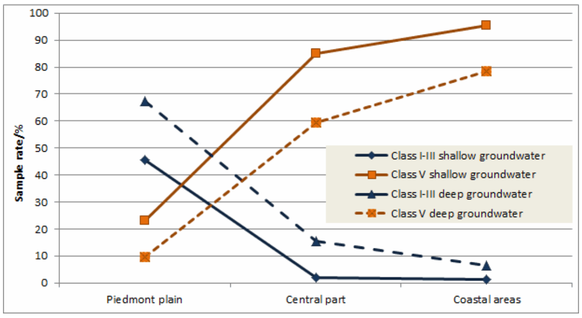

Fig. 2 Different characteristics of groundwater quality in the North China Plain

Groundwater quality worsens from the piedmont plain to the central part and coastal areas, with the proportion of Class I to III groundwater decreasing from 49% to 3.9% while that of Class V groundwater increasing from 21% to 86.9%.

2.4 Influence factor identification

2.4.1 Contribution rate of protogenetic component to regional groundwater quality

In the North China Plain, protogenetic components have the largest Class I to III water single-indicator contribution rate of shallow groundwater, including manganese, total hardness, total dissolved solids, iodide, sodium, sulfate, chloride, iron, fluoride and arsenic, with their contribution rate being 73%, 72%, 57%, 55%, 44%, 41%, 38%, 30%, 21% and 17% respectively. Class I to III water protogenetic component contribution rates of deep groundwater are fluoride 73%, iodide 53%, sodium 52%, total dissolved solids 24%, chloride 22%, pH value 21%, sulfate 16%, manganese 14%, arsenic 7%, total hardness 5% and iron 5% (Fig. 3).

2.4.2 Regional groundwater quality contribution rate of suspect pollution index

Of the shallow groundwater in the North China Plain, pollution indexes originated from human activities include: Nitrite, nitrate and ammonium-nitrogen, with their contribution rates being 20%, 9.5% and 6.4% respectively. The contribution rates of cadmium, hexavalent chromium, lead and mercury are 0.15%, 0.12%, 2.38% and 0.06% respectively. Benzene and carbon tetrachloride in organic pollution index have bigger contribution rates, both reaching 0.41%.

Of the deep groundwater, pollution index originated from human activities include: nitrite with a contribution rate of 5.4%, cadmium, hexavalent chromium, lead and mercury with their contribution rates of 0.16%, 0.49%, 1.7% and 0.24%; carbon tetrachloride of the organic index with a contribution rate of 0.32%.

3 Conclusions

(1) Quality evaluation indexes of regional groundwater are made up of protogenetic index and pollution index because of human activities;

influence factors should also be identified while evaluating groundwater quality. This paper presents a method combining single-indicator comprehensive evaluation and influence factors to measure groundwater quality. This method not only reflects groundwater quality classification with explicit physical significance, but also divides the possibilities of man-made pollution in regional groundwater.

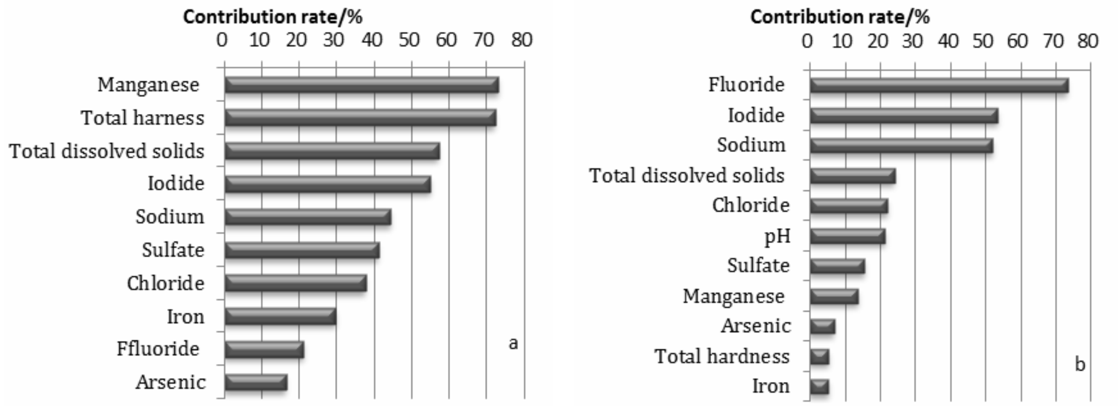

Fig. 3 Contribution rates of protogenetic components for ClassⅣ-Ⅴshallow groundwater (a) and Class Ⅳ-Ⅴdeep groundwater (b) in the North China plain

(2) Groundwater quality in the North China Plain: ①controlled by geological environment and hydrogeological conditions, the groundwater quality in the North China Plain deteriorates from Shanqian area to Binhai area, with Class I to Class III groundwater decreasing from 49% to 3.9% while Class V groundwater increasing from 21% to 86.9%; the quality of deep groundwater is better than that of shallow groundwater; ②the contribution rates of protogenetic components for Class I to III shallow groundwater of manganese, total hardness, total dissolved solids, iodide are 73%, 72%, 57% and 55% respectively; ③ contribution rates of pollution index originated from human activities: nitrite 20%, nitrate 9.5%, ammonium-nitrogen 6.4%, the contribution rate of cadmium, hexavalent chromium, lead and mercury are very low; the contribution rates of benzene and carbon tetrachloride in organic pollution index both reach 0.41%; ④of the deep groundwater, pollution indexes originated from human activities is mainly nitrite, with a contribution rate of 5.4%.

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