ORIGINAL ARTICLE

Vulnerability of groundwater in Quaternary aquifers to organic contaminants: a case study in Wuhan City, China

Yanxin Wang · Broder J. Merkel · Yilian Li · Hui Ye · Surong Fu · Dana Ihm

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Abstract More than 30 organic contaminants were detected in shallow groundwaters at Wuhan, the largest city in central China. Seriously contaminated groundwaters were from densely populated, industrial and commercial areas. Abnormal concentrations were found in groundwater from Hankou, downtown Wuhan: trimethylbenzene up to 29 µg/L, tetramethylbenzene up to 866 µg/L, and trichloroethene up to 9.5 µg/L. Benzene, Toluene, Ethylene and Xylene (BTEX) contamination of groundwater is serious and widespread at Wuhan, ranging between 0.14 and $25.0 \mu g/L$. Considering the hydrogeological conditions of most Chinese cities, DRAMIC, a modified version of the widely used DRASTIC model, was proposed by the authors for assessing vulnerability of groundwater to contamination. The factors D, R, A and I in DRAMIC model are the same as in DRASTIC. The factor topography is ignored. The factor soil media is substituted by a new factor aquifer thickness (M) and the factor hydraulic conductivity of the aquifer by a new factor *impact of contaminant* (C). The equation for determining the DRAMIC Index is: DRAMIC = $5D_{R} + 3R_{R} + 4A_{R} + 2M_{R} + 5I_{R} + 1C_{R}$. The calculated DRAMIC Index can be used to identify areas that are

Y. Wang (⊠) · Y. Li · H. Ye · S. Fu School of Environmental Studies and MOE Biogeology and Environmental Geology Laboratory, China University of Geosciences, 430074 Wuhan, China e-mail: yx.wang@cug.edu.cn

B. J. Merkel · D. Ihm Institute of Hydrogeology, Technical University Bergakademie Freiberg, 09599 Freiberg, Germany more likely to be susceptible to groundwater contamination relative to each other. The higher the DRAMIC Index is, the greater the groundwater pollution potential. Applying DRAMIC, a GIS-based vulnerability map for Wuhan city was prepared. Interestingly, places such as downtown Hankou, where enhanced concentrations of BTEX have been detected, correspond quite well with those with higher DRAMIC ratings.

Keywords Urban groundwater · Vulnerability assessment · Organic contamination ·

Geographic information system · China

Introduction

The concept of vulnerability of groundwater to contamination was introduced in the 1960s in France by Margat (1968). He used the term "vulnerability" to mean the degree of protection that the natural environment provides against the ingress of pollutants to groundwater. Since then, several definitions of vulnerability have been proposed. Groundwater vulnerability to contamination can be defined as the propensity or likelihood for contaminants to reach some specific position in the groundwater system after their introduction at some point above the top of the uppermost aquifer (Rao and Alley 1993). Vulnerability of groundwater is a specific feature of the groundwater system; however, it cannot be measured in the field. Generally speaking, the level of groundwater contamination is determined by the natural attenuation processes occurring within the zone between the pollution source and the aquifer. Various natural physical processes and chemical reactions that occur in the soil, unsaturated

zone and saturated zone can cause contaminants to change their physical states and their chemical forms, leading to attenuation of contaminants. Chemical reactions may work individually or in combination with other processes to result in a varying degree of attenuation. These reactions rely on the specific soil and aquifer characteristics and particular geochemical properties of each contaminant. Therefore, groundwater vulnerability is a function of geology, hydrogeology, and physico-chemical properties of the contaminants, which may vary from place to place.

The concept of groundwater vulnerability includes two particular notions: intrinsic vulnerability and specific vulnerability. Intrinsic vulnerability refers to the vulnerability of groundwater to contaminants generated by human activities taking into account the inherent geological, hydrological and hydrogeological characteristics of an area but being independent of the nature of the contaminants. Specific vulnerability is used to define the vulnerability of groundwater to particular contaminants or a group of contaminants taking into account the contaminant properties and their relationship with the various components of intrinsic vulnerability (Doerfliger et al. 1999; Gogu and Dassargues 2000). Groundwater vulnerability assessment methods can be grouped into three categories: (1) overlay and index methods; (2) methods employing process-based simulation models, and (3) statistical methods (National Research Council 1993). In general, overlay and index methods and statistical methods have been used for assessments at map scales smaller than 1:50,000 (i.e., a large study area), while methods based on simulation models are at larger map scales (i.e., a small study area) (Rao and Alley 1993). Overlay and index methods and statistical methods are used to assess intrinsic vulnerability, while methods employing process-based simulation models are used to assess specific vulnerability. Models of index methods include GOD (Foster 1987), DRASTIC (Aller et al. 1985), AVI rating system (Van Stempvoort and Evert 1993), SEEPAGE, SINTACS, ISIS (Gogu and Dassargues 2000), EPIK (Doerfliger et al. 1999), and DIVERSITY (Ray and Odell 1993).

In recent years, GIS methods have been widely used in groundwater vulnerability mapping (Loague et al. 1996; Evans and Myers 1999; Hrkal 2001; Rupert 2001; Lake et al. 2003). The major advantage of GIS-based mapping is the best combination of data layers and rapid change in the data parameters used in vulnerability classification.

Results of monitoring indicate that groundwater beneath most Chinese cities have been contaminated in different degrees. However, there are few data about the types, contents and spatial-temporal distribution of organic contaminants in these waters. On the other hand, groundwater vulnerability assessment has not been done systematically for most regions of China. Applying or developing GIS-based vulnerability assessment models is urgently needed for groundwater protection in China.

Wuhan lies at the river mouth where the Yangtze River is joined by its main tributary, the Hanjiang River. It has a population of eight million and an area of 8,467.11 km². With abundant water resources, Wuhan depends heavily on exploiting and utilizing of surface waters but has taken less care in protecting them. Untreated municipal wastewater with many kinds of pollutants and some industrial wastewaters drain directly into the surface water. This is the main reason for the degradation of surface water quality at Wuhan. Wastewater discharge amounted to 2.2×10^6 m³/day in 1999. According to monitoring results reported by Wuhan Environmental Protection Bureau (Wuhan EPB 2001), 56% of the rivers and 89% of the lakes have been polluted. The principal pollutants are COD, BOD, nitrate and total phosphorus. As surface waters have been seriously polluted, it has been argued whether groundwater should be exploited on a larger scale at Wuhan.

The objectives of this case study are: (1) to investigate organic contamination levels of shallow groundwaters at Wuhan, and (2) to assess groundwater vulnerability at Wuhan.

DRAMIC: a modified model of DRASTIC

DRASTIC method introduced by the US Environmental Protection Agency (EPA) is probably the most widely used tool for vulnerability mapping, although it is typically a poor predictor of groundwater contamination (Rupert 2001). DRASTIC is an acronym for seven factors: depth to water (D), net recharge (R), aquifer media (A), soil media (S), topography (T), impact of the vadose zone (I), hydraulic conductivity of the aquifer (C). A numerical ranking system to assess ground water pollution potential contains weights, ranges and ratings, allowing the user to determine a numerical value for any hydrogeologic setting by using an additive model (Aller et al. 1985):

 $D_R D_W + R_R R_W + A_R A_W + S_R S_W + T_R T_W + I_R I_W + C_R C_W = \text{DRASTIC index},$

where R is rating and W is weight. Once a DRASTIC index has been computed, it is possible to identify areas that are more likely to be susceptible to groundwater contamination relative to one another. The higher the DRASTIC index is, the greater the groundwater potential. Agricultural DRASTIC was specifically designed to address the important processes offsetting the fate and transport of herbicides and pesticides in the soil.

There are some limitations when DRASTIC is applied in urban areas. First, the factor *hydraulic conductivity* is closely related to (or even the most important feature of) the factor *aquifer media*. Second, the topography of most cities is relatively flat. Therefore, the factor *topography* can be ignored at urban areas in most cases. Third, the ground surface of most of densely populated cities is covered by structures and concrete, and it is difficult to obtain comparable values of the factor *soil media* for most cities. To improve the predictability and applicability of the DRASTIC model, the authors proposed a new model: DRAMIC. The factors and assigned weights of DRAMIC are listed in Table 1, together with those of DRASTIC for comparison.

From Table 1, it can be seen that the factors D, R, A and I in DRAMIC model are the same as in DRAS-TIC. The factor topography is ignored. The factor *soil media* is substituted by a new factor *aquifer thickness* and the factor *hydraulic conductivity of the aquifer* by a new factor *impact of contaminant*. The equation for determining the DRAMIC Index is:

$$DRAMIC = 5D_R + 3R_R + 4A_R + 2M_R + 5I_R + 1C_R$$

 Table 1
 Assigned weights for DRASTIC and DRAMIC indices

DRASTIC			DRAMIC	
Factor	Weight		Factor	Weight
	Normal	Pesticide		
D, depth to water	5	5	D, depth to water	5
R, net recharge	4	4	R, net recharge	3
A, aquifer media	3	3	A, aquifer media	4
S, soil media	2	5	M, aquifer thickness	2
T, topography	1	3		
<i>I</i> , impact of vadose zone	5	4	<i>I</i> , impact of vadose zone	5
C, hydraulic conductivity of the aquifer	3	2	<i>C</i> , impact of contaminant characteristics	1

where R is rating. Once a DRAMIC Index has been calculated, it can be used to identify areas, which are more likely to be susceptible to groundwater contamination relative to one another.

The higher the DRAMIC Index is, the greater the groundwater pollution potential. The hydrogeological significance, ranges and ratings for the factors D, R, A, and I are the same as in DRASTIC. The ranges and ratings for the two new factors aquifer thickness and contaminant characteristics are listed in Table 2. The water quantity in an aquifer controls its ability to dilute contaminants and, therefore, affects the pollution potential. Generally speaking, for the same region, the greater the aquifer's thickness is, the lower the vulnerability. As an intrinsic vulnerability assessment model, DRASTIC did not take into account the effect of contaminant properties. However, the fate and transport of different contaminants are often different in the underground media. The type of contaminants, the distance to the main aquifer, and the amount and pathway of contaminants all affect the pollution potential, while the physico-chemical properties of contaminants determine their stability or reactivity underground. Two major factors were considered in the DRAMIC model: the contaminant's stability and ease of infiltration into aquifer. Groundwater is usually less vulnerable to unstable contaminants that cannot easily infiltrate into the aquifer.

Organic contamination of groundwater at Wuhan

In April 2000, 32 groundwater samples were collected from the Quaternary aquifers at Wuhan. Temperature,

 Table 2 Ranges and ratings for aquifer thickness and contaminant characteristics

Aquifer thickness		Contaminant characteristics		
Range (m)	Typical rating	Characteristics	Rating	
0–6	9	Stable, easy to infiltrate into aquifer	9	
6-15	7	Stable, relatively easy to infiltrate	7	
15–25	5	Stable, uneasy to infiltrate	5	
25–32	4	Relatively stable, easy to infiltrate	5	
32–40	3	Relatively stable, relatively easy 4 to infiltrate		
40–50	2	Relatively stable, uneasy to 3 infiltrate		
>50	1	Unstable, easy to infiltrate	3	
		Unstable, relatively easy to infiltrate	2	
		Unstable, uneasy to infiltrate	1	

pH, conductivity and alkalinity were in situ tested. The water samples were taken in plastic bottles rinsed with the sampled water several times before sampling (usually 5 times). Samples were filtered and preserved with an acid (1:1 HNO₃) for analysis of heavy metals. One part of each sample was used for analysis using gas chromatography. The sampling was done with an on site spray and trap system (Bruker Daltonik GmbH) consisting of water tube WS100 and drying unit. With a sprayed sample volume of 100, 2 ml the released organic substances were absorbed in the Tenax tube during a Spray and Trap cycle of 3.5 min. This cycle is divided in a 5-s check of the program, 10-s fill-in of the spray cock, 90-s spraying and blowing-off of the sample, 90-s blowing-off of the spray cock and 15-s emptying of the spray cock. It is possible to get a better enrichment of the organic matter by repeating the spray and trap cycle. Before sampling the Tenax tubes were heated two or three times until free of organic contamination and were wrapped in tin foil. After sampling the Tenax tubes were wrapped again in tin foil and put in a metal box.

Cations and anions were detected by using the ion chromatography (Dionex-120 model). Metals and some main components were analyzed with inductively coupled plasma-mass spectrometry (ICP-MS) (Jarrell-Ash POEM3). Atom adsorption spectrometry was used to detect arsenic, whereas As(III) and As(V) were analyzed separately and thus the total arsenic. At the Institute of Hydrogeology of Technical University of Freiberg, organic substances were analyzed with gas chromatography-mass spectrometry (GC-MS using the EM 640 from Bruker Daltonik GmbH, Bremen).

More than 30 organic contaminants were investigated. The ranges and average concentration of some organics are listed in Table 3. Most of the contaminants were found in densely populated downtown areas at Wuhan. For instance, although trichloroethene, trimethylbenzene and tetramethylbenzene (including

Table 3 Ranges and average concentrations of some organic contaminants in Quaternary groundwater samples at Wuhan (in $\mu g/L$)

Contaminant	Range	Average concentration	
Benzene	0.21-13.0	3.92	
Ethylbenzene	0.14-19.0	9.0	
Toluene	7.6-17.0	13.08	
<i>m</i> -Xylene	0.29-25.0	15.75	
o-Xylene	0.16-20.0	12.0	
Benzoethylene	0.33-25.0	17.53	
Benzaldehyde	3.3-421.0	91.98	
Naphthalene	1.6–165.0	61.2	

1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5trimethylbenzene, 1,2,3,5-tetramethylbenzene, 1,2,3,4tetramethylbenzene and 1,2,4,5-tetramethylbenzene) were detected, abnormal concentrations were only found in groundwater from Hankou, downtown Wuhan: trimethylbenzene up to 29 μ g/L, tetramethylbenzene up to 866 μ g/L, trichloroethene up to 9.5 μ g/L. Benzene, Toluene, Ethylene and Xylene (BTEX) contamination of groundwater is serious and widespread at Wuhan.

Result of vulnerability assessment at Wuhan

In the plain areas at Wuhan, the aquifers can be divided into Quaternary unconfined aquifers and confined of unconsolidated sediments and confined aquifers of fractured clastic rocks. The Quaternary aquifers of unconsolidated sediments are in the first and second terraces of the Yangtze River and cover an area of 2,394 km². The aquifers consist of Holocene and upper Pleistocene alluvial and deluvial sands and gravel. Sources of recharge are mainly from the leakage of precipitation, surface water, and irrigation water through the unconfined aquifers, upward leakage of underlying aquifers and lateral movement of neighboring aquifers. Seepage by rivers is also a potential source.

The DRAMIC model was applied at Wuhan to assess vulnerability of shallow groundwaters to organic contamination. The aquifers under consideration are confined Quaternary aquifers that have been exploited in some places for water supply. Six GIS-based maps of the DRAMIC Index were prepared.

Depth to water (D): as the target aquifers are confined aquifers, the factor D refers to the distance between ground surface and the top of the aquifer. The burial depth of most groundwater ranges between 10 and 30 m at Wuhan.

Net recharge (R): the annual average net recharge of the aquifers at Wuhan is between 80 and 280 mm.

Aquifer media (A): the aquifer material at Wuhan is mostly sand, gravel, fine sand and silt.

Aquifer thickness (M): the aquifer thickness at Wuhan ranges between 6 and 50 m.

Impact of vadose zone (I): the aquifers under consideration are confined aquifers at Wuhan. So the ratings are 1.

Impact of contaminant characteristics (C): considering the serious problems of BTEX contamination at Wuhan, vulnerability to BTEX is assessed. Most of BTEX compounds are biodegradable, especially **Fig. 1** Map of vulnerability of groundwater in Quaternary aquifers to contamination at Wuhan



when the concentrations of iron, manganese and bicarbonate are high in the groundwater, as observed at Wuhan. Therefore, BTEX for the Quaternary aquifers at Wuhan are considered as relatively stable. The ratings for the factor *contaminant characteristics* are five, four and three at different places, depending on the thickness and content of organics and clays of vadose zone.

The six maps of factor rating were then overlaid to obtain the groundwater vulnerability map at Wuhan (Fig. 1). The pollution potential for different areas is shown on the map. It is quite interesting that places such as downtown Hankou where enhanced concentrations of BTEX have been detected correspond quite well with those with higher DRAMIC ratings.

Conclusions

More than 30 organic contaminants were investigated in the study. Most of the contaminants were found in densely populated downtown areas at Wuhan. Benzene, Toluene, Ethylene and Xylene (BTEX) contamination of shallow groundwater is serious and widespread at Wuhan.

A new groundwater vulnerability assessment model, DRAMIC, a revised version of the widely used model DRASTIC is proposed in this study. Comparing the result of groundwater vulnerability assessment at Wuhan using DRAMIC with that of this organic contamination investigation, the spatial correlation is quite good. In other words, places such as downtown Hankou, where enhanced concentrations of BTEX have been detected correspond quite well with those with higher DRAMIC ratings. Therefore, DRAMIC might be useful tool for groundwater pollution potential assessment in urban areas. Comparative studies are still needed to verify its applicability in other cities. Although the results of groundwater vulnerability assessment only reflect the tendency of pollution, they are very important for city planning and environmental management. For areas with high scores of vulnerability assessment, special attention must be paid to avoid pollution and risk assessment is needed in land use and industrial development.

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