Supplementary material

Hydrogeochemical characteristics and groundwater quality in a coastal urbanized area, south China: Impact of land use

Chunyan Liu[a,b], Qinxuan Hou[a,b,*], Yetao Chen[c], Guanxing Huang[a,*]

[a] Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences, Shijiazhuang, China

[b] Hebei Key Laboratory of Groundwater Remediation, Shijiazhuang, China

[c] Hebei Huanxue Environmental Protection Technology Company Limited, Shijiazhuang, China

*E-mail address: houqinxuan@163.com (Q. Hou); huangguanxing2004@126.com (G. Huang)

S3.1. Sampling and analysis

Groundwater samples were collected below the water table at a depth of 50 cm with a stainless-steel sampler after purging at least three well volumes. Two bottles were used to store groundwater. One used for the analysis of trace elements was acidified with nitric acid to pH < 2, whereas another one used for the analysis of other chemicals was not acidified. All samples were filtered (0.45-μm membrane) on-site and stored at 4 °C until the laboratory procedures could be performed (within two weeks after sampling). 3 parameters including pH, dissolved oxygen (DO), and redox potential (Eh) were measured on-site by a multi-parameters instrument (WTW Multi 340i/SET, Germany) which was calibrated before measure. The total dissolved solids (TDS) and HCO_3^- were measured using gravimetric and acid–base titration methods, respectively. NH_4^+ and other anions such as NO_3^-, SO_4^{2-}, Cl^-, NO_2^-, and I^- were measured using ion chromatography (Shimadzu LC-10ADvp, Japan). Metal(loid)s such as K^+, Na^+, Ca^{2+}, Mg^{2+}, Pb, As, Fe, and Mn were measured by inductively coupled plasma mass spectrometry (Agilent 7500ce ICP-MS, Tokyo, Japan). To ensure data quality, each sample was analyzed in triplicate, sample batches were regularly interspersed with standards and blanks, and all data were corrected for instrument drift. The relative errors of all parameters were less than ±6%.

S3.2. Fuzzy synthetic evaluation method (FSEM)

In this study, the fuzzy membership function was used to assess groundwater quality according to the groundwater quality standards of China (Table S1) (General administration of quality supervision inspection and quarantine of the people's republic of China (GAQSIQPRC), 2017). To reduce the complexity of the model, the linear membership functions are used as follows.

$$r_{ij} = \begin{cases} 0, (C_i \le S_{ij-1} \text{or } C_i \ge S_{ij-1}) \\ \frac{C_i - S_{ij-1}}{S_{ij} - S_{ij-1}}, (S_{ij-1} < C_i < S_{ij}) \\ \frac{S_{ij+1} - C_i}{S_{ij+1} - S_{ij}}, (S_{ij} < C_i < S_{ij+1}) \\ 1, (C_i = S_i) \end{cases} \quad \text{(S1)}$$

where r_{ij} indicates the fuzzy membership of indicator *i* to class *j*, every indicator is characterized by five classes (I, II, III, IV, V) according to the groundwater quality standards of China (GAQSIQPRC, 2017), C_i stands for analytical value of groundwater quality indicator i, S_{ij} stands for the allowable value of groundwater quality indicator. The fuzzy membership matrix R consists of groundwater quality indicators and classes.

The weight of groundwater quality indicator is expressed as

$$W_i = \frac{C_i}{S_i} \qquad \text{(S2)}$$

where W_i is the weight of groundwater quality indicator i, C_i is the analytical value of groundwater quality indicator i, S_i is the arithmetic mean of allowable values of each class. The normalized weight of each indicator is calculated by the formula

$$a_i = \frac{C_i}{S_i} / \sum_{i=1}^{m} \frac{C_i}{S_i} = W_i / \sum_{i=1}^{n} W_i \qquad \text{(S3)}$$

where a_i is the normalized weight of indicator i, W_i is the sum of weight to all groundwater quality indicators. The fuzzy A consists of weight of each groundwater quality indicator.

The water quality assessment by fuzzy membership is based on the matrix B,

$$B = A \times R \qquad \text{(S4)}$$

The fuzzy B is the matrix of membership to each groundwater quality class. Groundwater sample is classified to the class with the maximize membership.

Table S1 Groundwater quality standards for drinking and irrigation

Item	Class I	Class II	Class III	Class IV	Class V
TDS (mg/L)	≦300	≦500	≦1000	≦2000	>2000
Cl^- (mg/L)	≦50	≦150	≦250	≦350	>350
NO_3^- (mg/L)	≦8.9	≦22.1	≦88.6	≦132.9	>132.9
Na^+ (mg/L)	≦100	≦150	≦200	≦400	>400
SO_4^{2-} (mg/L)	≦50	≦150	≦250	≦350	>350
Fe (mg/L)	≦0.1	≦0.2	≦0.3	≦2	>2
Mn (mg/L)	≦0.05	≦0.05	≦0.1	≦1.5	>1.5
NH_4^+ (mg/L)	≦0.026	≦0.13	≦0.64	≦1.93	>1.93
NO_2^- (mg/L)	≦0.033	≦0.33	≦3.29	≦15.8	>15.8
Pb (μg/L)	≦5	≦5	≦10	≦100	>100
As (μg/L)	≦1	≦1	≦10	≦50	>50
I^- (μg/L)	≦40	≦40	≦80	≦500	>500
Suitability	Drinking, Irrigation	Drinking, Irrigation	Drinking, Irrigation	Irrigation	Not suitable

Data from (GAQSIQPRC, 2017).

Table S2 Kaiser-Meyer-Olkin and Bartlett's test for the suitability of principal components analysis (PCA) to groundwater chemical data in coastal alluvial aquifer.

Item		Coastal alluvial aquifer
Kaiser-Meyer-Olkin measure of sampling adequacy		0.535
Bartlett's test of sphericity	Approximate chi-square	2529
	Significance	0.000