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Full Length Research Paper

Hydrochemical investigation of groundwater contamination in an urban area of Beijing aquifer: Impact of irrigation with industrial waste water

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Groundwater quality in Beijing, China was evaluated by measuring the quantities of major and minor elements, temperature, pH, total dissolved solids (TDS), and electrical conductivity (EC). Most samples contained high concentrations of NO_3^- (5.13 to 164.0 mg/L), which is a serious water quality issue. This NO_3^- originates from the soil surface and enters the groundwater by infiltration. Factor analysis modeling demonstrated that NO_3^-, Cl^-, SO_4^{2-}, Ca^{2+}, and Mg^{2+} in the system are produced by anthropogenic sources, but a portion of the (Ca^{2+}, Mg^{2+}) comes from ion exchange and mineral dissolution. The strong correlation observed between NO_3^- and Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-} suggests that they have the same origin. The parameters in Factors 1–3 reflected the importance of the acid-rain recharge of the aquifers in the area, anthropogenic impact and salinity, respectively. Hierarchical cluster analysis was used to group the wells into homogeneous zones for future monitoring of groundwater quality. Multivariate statistical techniques were used to identify key parameters that described the groundwater quality, characterize spatial variability of groundwater quality data and allow future groundwater quality control studies to be performed using a reduced number of measurements on a small number of sampling points, respectively.

Key words: Groundwater, hydrochemica, multivariate statistical, nitrate, contamination.

INTRODUCTION

Groundwater is an important source of drinking water for many people around the world, and contamination from natural sources or human activities is a serious problem. The resource in several places becomes contaminated from natural source or numerous human activities. During the last two decades, demands for groundwater from urban, industrial development and extensive agricultural activities in the Beijing basin, northeastern China, particularly in the Intra-urban, Su-urban and Peri-urban plains regions have resulted in increased withdrawals from the Quaternary shallow aquifer (Mande et al., 2011). As an example of water supply related problem generalized water level decline and the deterioration of groundwater quality. Indeed, in recent times, soils have become increasingly polluted by waste water and agricultural chemicals. In shallow groundwaters this pollution can easily be transported.

The major economic role of the shallow aquifer has raised concerns relating to the effects on groundwater resource as (i) the recharge rate of shallow aquifer is not known with precision and (ii) the detrimental effect on the environment in relation with the groundwater contamination and salinization, which put a strain on the existing

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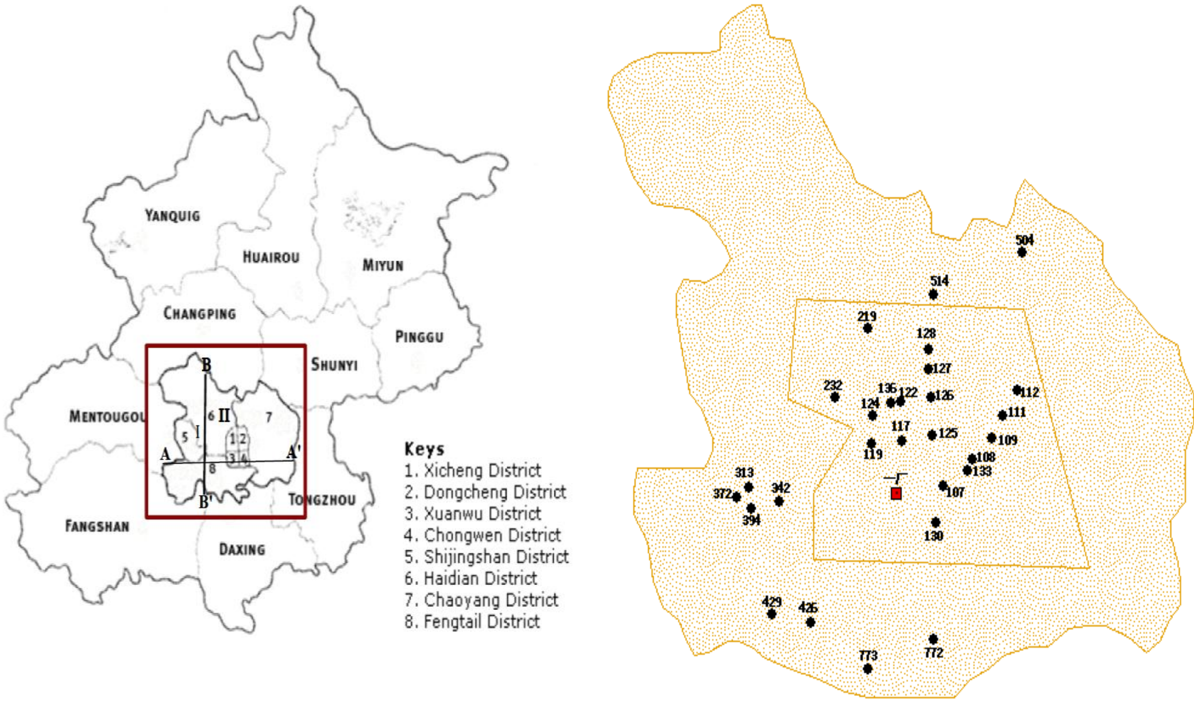

Figure 1. Plan of Beijing City and suburban area showing the distribution of observation wells geology and hydrogeology.

fresh water that supports the regional development. Subsequently there is a requirement for agreed and consistent examination and assessment activities to recognize the source of the pollution and evaluate its current amount and future expansion. It is within this framework that is undertaken the present study, which aims to provide reliable information about the hydrochemical characteristics of groundwater and the main groundwater mineralization processes. It also investigates the impact of regional agricultural and industrial activities on groundwater quality.

Physiochemical data from groundwater can be analyzed using statistical methods such as factor analysis and the hierarchical cluster analysis. Both these techniques can be used to characterize and plan monitoring of the groundwater quality (Zeng and Rasmussen, 2005). Factor analysis can be used to determine the structure in the relationships between water quality parameters and identify the most important factors contributing to this structure. Hierarchical cluster analysis is used to reduce the data by grouping them into clusters with similar properties.

Study area

The study area is located between latitudes 39°49'51.52" to 40°00'38.01"N and longitudes 116°14'45.70.50 to 116°31'14.19"E, covering 130 Km^2 (Figure 1). The study area is situated in the urban core of Beijing (Xicheng, Dongcheng, Xuanwu and Chongwen Districts), Chaoyang District, Haidian District and Fengtai District of central Beijing. The study area is subject to a monsoon influenced humid continental climate characterized by hot, humid summers due to the East Asian monsoon, and generally cold, windy, dry winters that reflect the influence of the vast Siberian anticyclone. The average temperature in the region is about 11.7°C, with the highest temperature recorded being 42°C (July and August) and the lowest recorded temperature being - 27°C (January). Most of the area is a flat plain, with surface elevations ranging from 45 to 50 m a.s.l. Beijing’s rainfall varies geographically, seasonally and annually. Overall, 85% of the annual precipitation falls between July and September. Rainfall also varies between the sub-watersheds within the municipality, particularly between mountainous areas and the low-lying plain. The average annual precipitation in Beijing is 590 mm.

The main aquifers in central Beijing are composed of alluvial gravel-sand sediments of the quaternary period. The line BB' (Figure 1) from Haidian to Fengtai divides this region into two parts, the unconfined aquifer consisting of a single gravel stratum in the west and the confined aquifer consisting of multiple gravel and sand strata in the east (Figure 2).

The aquifer lying between the fan shaped zone at the foot of the mountains and the plain changes gradually from a single pebble bed to multiple beds of pebble-sand and clay. The thickness of the aquifer ranges from 50 to more than 200 m from west to east, and the four principal

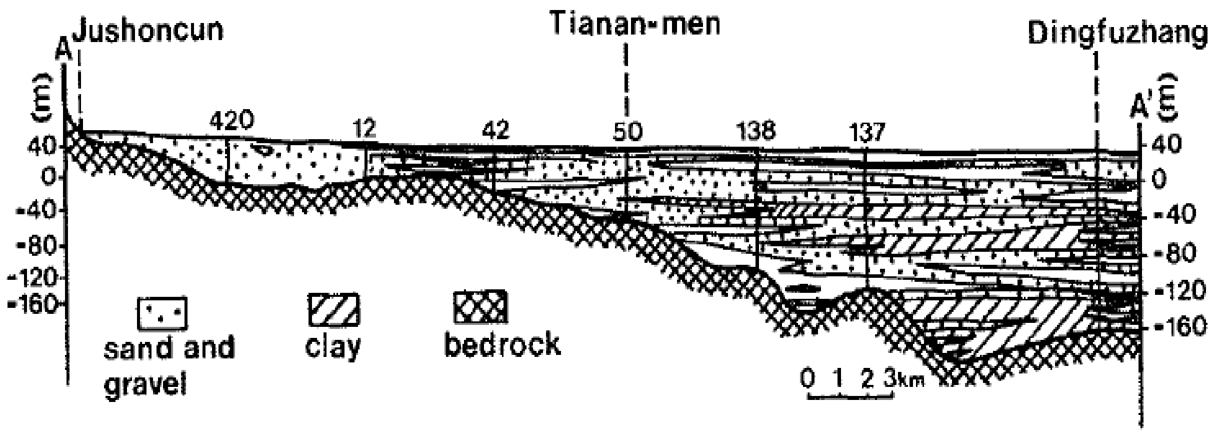

Figure 2. Geological sketch showing quaternary aquifers in the Beijing area (A-A' geological section: See Figure 1) (Mande et al., 2011).

Table 1. Eigenvalues and variance of the factors.

Factor	Eigenvalues		Total variance	
	Total	Cumulative	% of variance	Cumulative (%)
1	6.839	6.839	35.997	35.997
2	0.806	7.645	28.989	64.986
3	0.485	8.13	25.353	90.339

aquifers lie at depths of 45, 50 to 60 m, 60 to 70 and 80 m. The uppermost aquifer is the unconfined aquifer. This aquifer has the longest history of extraction and heavy pollution due to human activities and its discharge is no longer very great.

MATERIALS AND METHODS

Samples were collected from borehole wells, which were selected to provide a uniform distribution over most of the drinking water supply area. The geographic coordinates of the wells were obtained using a GPS and used to create a distribution map using ArcGis 9.2 software. Water samples were collected from May, 2010. Physicochemical parameters, including temperature, pH, electrical conductivity (EC) and total dissolved solid (TDS), were conducted in the field. Other samples were transported to the Laboratory for testing. Major components (HCO_3^-, Cl^-, $S0_4^{2-}$, NO_3^-, Ca^{2+}, Mg^{2+}, Na^+ and K^+), iron and manganese were measured in laboratory within 15 days of sampling. Samples were stored in the dark in a cold room at 4°C. Analysis was carried out according to established methods as follows: volumetric analysis for HCO_3^- (AFNOR, 1996); cations were analyzed using a Varian Liberty 200 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) and anions were analyzed using a DX300 Dionex Ion Chromatograph (EPA 2009).

The results were analyzed using a Schoeller diagram created using AquaChem 5.1, which is a software package developed specifically for graphical and numerical analysis and modeling of water quality data (Waterloo Hydrogeologic Inc., 2009). All the data were statistically analyzed by factor analysis and hierarchical cluster analysis. Before analysis, the data were normalized to a distribution with a mean of zero and standard deviation of one. Factor extraction was performed using principal component analysis. Three factors with eigenvalues above one were retained following the Kaiser criterion (Kaiser, 1958). They represented 90.33% of the total variance. Varimax rotation was applied to these factors. Table 1 gives the eigenvalues of the three factors and the percentage of variance that they explain.

RESULTS AND DISCUSSION

Hydrogeochemical analysis

The hydrogeochemical results for the study area are presented in Tables 2 and 3.

pH and temperature

The temperature of the groundwater varied by 5°C among the sample sites, and the minimum and maximum temperatures were 12°C (chaoyang) and 17°C (urban core), respectively. Approximately 35.71% of the wells were slightly basic (pH>7.0) and 64.28% were slightly acidic (pH<7.0). 57.13% of the wells were nearly neutral (pH 6.5 to 7.5). The acidity of the water in the study area is mainly related to CO_2 in the soil surface layers, which is produced by biological activity or infiltration of precipitation.

EC

The EC results for the wells ranged from 224 to 1782

Table 2. Results for groundwater obtained in the (May 2010) in Beijing, China. All units are in mg/L, except for electrical conductivity (EC, μS/cm).

Well no	pH	EC	NO_3^-	HCO_3^-	SO_4^{2-}	Cl^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	Mn^{2+}	Fe^{2+}
109	6.8	1602	164.3	234.85	131.76	124.68	91.26	3.65	91.69	39.19	<0.005	<0.02
122	6.91	1570	131.74	250.1	167.7	125.29	98.98	3.62	94.40	40.15	<0.005	<0.02
128	6.95	1430	152.82	240.95	92.53	99.99	59.00	3.31	104.19	39.01	<0.005	<0.02
219	7.00	642	112.67	207.4	109.87	110.17	50.20	3.02	103.94	37.97	<0.005	<0.02
232	6.78	688	152.6	268.4	132.03	102.34	88.08	3.89	89.18	38.69	<0.005	<0.02
313	6.95	1060	75.84	198.25	139.35	140.53	69.30	3.77	98.85	36.50	<0.005	<0.02
342	7.13	620	53.67	207.4	91.38	67.13	47.55	2.82	97.18	33.75	<0.005	<0.02
372	7.15	530	7.96	140.3	68.47	17.52	17.90	1.52	61.33	24.56	<0.005	<0.02
394	7.15	424	7.23	131.15	65.83	16.49	17.28	1.46	59.97	24.14	<0.005	<0.02
426	6.56	1472	110.53	244	127.71	86.05	68.79	3.80	89.12	36.22	<0.005	<0.02
429	6.62	1434	108.64	237.9	123.11	85.98	67.50	3.65	105.92	35.15	<0.005	<0.02
504	7.14	872	5.13	146.4	109.14	59.66	30.64	2.31	72.01	32.03	<0.005	<0.02
514	7.12	668	96.46	146.4	80.58	97.85	32.70	2.79	90.30	35.92	<0.005	<0.02
773	6.65	1782	104.32	259.25	127.71	86.05	106.79	4.09	126.48	37.89	<0.005	<0.02

Table 3. Wells with critical levels of nitrate.

Location	Urban core	Haidian district	Fengtai district	Chaoyang district
NO_3^- (mg/L)	164.3	75.84	110.53	96.46

μS.cm^{-1}. The World Health Organization (WHO) standard for EC for drinking water is between 500 and 1500 μs.cm^{-1} (Rodier, 1996). However, only 7% of the wells had EC<500 μS.cm^{-1}, and an additional 43% could be classed as moderately mineralized (EC=500–1000 μS.cm^{-1}) and 25% as highly mineralized (EC=1000–1500 μS.cm^{-1}). Many of the wells (25%) could be classed as excessively mineralized (EC>1500 μS.cm^{-1}). The EC values vary in a wide range from 224 to 1782 μS.cm^{-1} that lends support to the interference of numerous natural and anthropogenic processes.

Correlation coefficients (*r*) between EC and each of the ions were calculated using data from all the wells as follows (ion, *r*): Na^+, 0.787; SO_4^{2-}, 0.758; K^+, 0.738; HCO_3^-, 0.708; Cl^-, 0.686; Ca^{2+}, 0.632; Mg^{2+}, 0.631; and NO_3^-, 0.607. These correlation coefficients show that the EC is strongly influenced by Na^+, HCO_3^-, K^+, Cl-, and SO_4^{2-}, and to a lesser extent by Ca^{2+}, Mg^{2+} and NO_3^-.

Major and minor elements

The most abundant cation in the groundwater was Ca^{2+}, which was at levels ranging from 59.97 to 126.48 mg/L. This was followed by Mg^{2+} (24.14 to 40.15 mg/L), Na^+ (17.28 to 106.79 mg/L), and K^+ (1.46 to 4.09 mg/L). At levels of < 0.02 mg/L (Fe^{2+}) and <0.005 mg/L (Mn^{2+}), Fe^{2+} and Mn^{2+} were well below the WHO standards of 0.3 mg/L (Fe^{2+}) and 0.05 mg/L (Mn^{2+}) for drinking water (WHO, 2006). The dominant anion in the groundwater was HCO_3^- (60.06 to 2682.94 mg/L). This was followed by Cl^- (16.49 to 183.04 mg/L). It may also originate from human waste, particularly urine and some cleaning products. The groundwater concentration ranges for SO_4^{2-}, and NO_3^- were 65.83 to 195.9 mg/L and 5.13 to 164.0 mg/L, respectively. The NO_3^- concentrations at some locations (79% of the wells) exceeded the 50 mg/L limit specified by the WHO drinking water standard (Table 3).

The high nitrate levels are a concern because they could be involved in transformation of hemoglobin to methemoglobin. Nitrate can be reduced to nitrite, which can oxidize the hemoglobin iron from the ferrous to ferric state. This forms methemoglobin, which is unable to bind oxygen to carry to tissues. Depending on the proportion of methemoglobin, this can lead to various symptoms including mild cyanosis, reduced level of consciousness, and death (Walton, 1951; WHO, 1996; U.S. EPA, 1997; Winton et al., 1971; NRC, 1981; Kross et al., 1992). Because of these serious consequences, water with high nitrate levels must be treated before human consumption.

The chemical compositions of groundwater samples obtained in May, 2010 are summarized in Table 2. Groundwater in the central part and southern part of the study area was characterized by elevated NO_3^- and SO_4^{2-} concentrations, whereas groundwater in the western part had lower NO_3^- and SO_4^{2-} concentrations (Table 2, Figure 1). The groundwater was characterized by elevated concentrations of NO_3^-, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-} at both sampling dates, especially in the central part and southern part of the study area. NO_3^- and cation concentrations

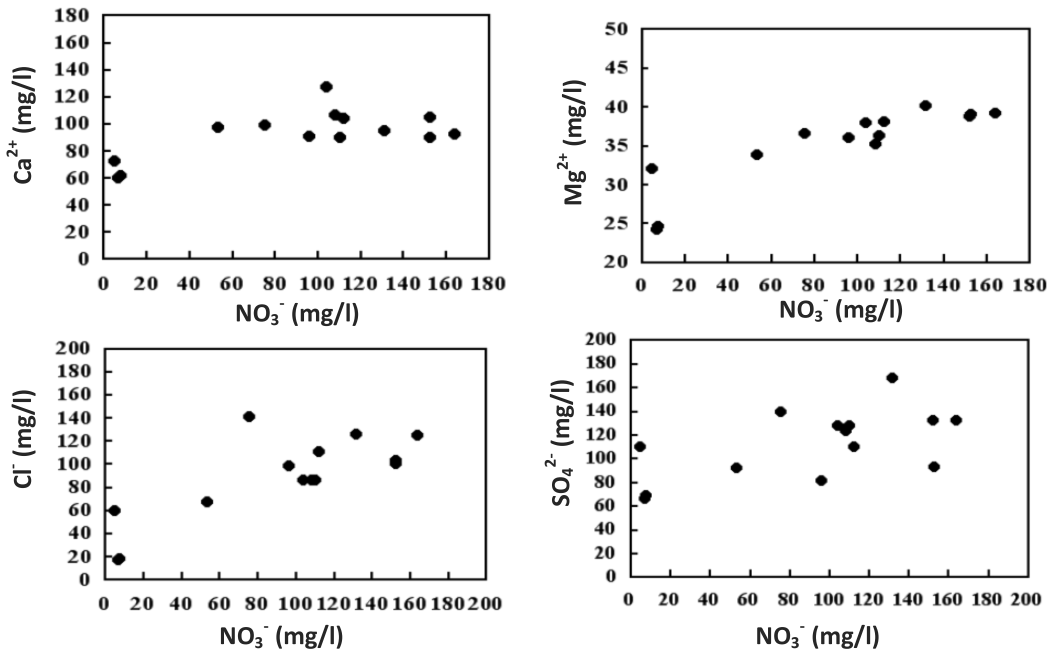

Figure 3. Cation (Ca^{2+} and Mg^{2+}) and anion (SO_4^{2-} and Cl^-) versus NO_3^- concentrations in groundwater.

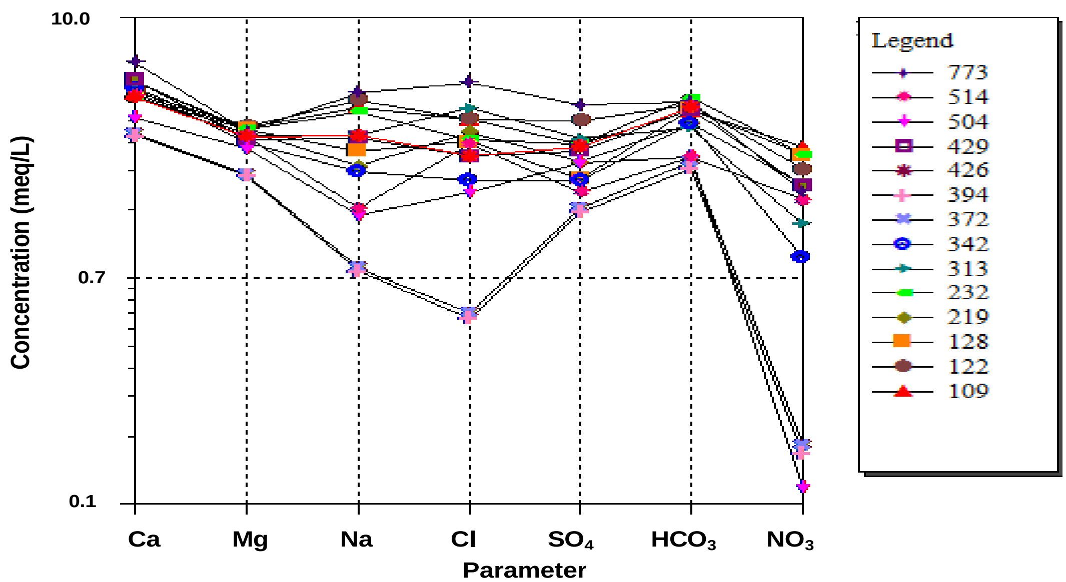

Figure 4. Schoeller diagram of groundwater wells in the study area.

(Ca^{2+} and Mg^{2+}) showed strong correlations indicating that they originated from the same sources (Figure 3). Species such as Ca^{2+}, NO_3^-, and Mg^{2+} may be derived from chemical fertilizers and manure (NH_4NO_3, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, (Ca, Mg)CO_3, and KCl). The plots of anions (Cl^- and SO_4^{2-}) and NO_3^- also show strong correlations (Figure 3).

Water types

A Schoeller diagrams (Figure 4) was used to compare the different wells and highlight the dominant anions and cations in each well. This showed the groundwater in the study area was characterized by abundant Ca^{2+}, Na^+, Mg^{2+}, HCO_3^-, Cl^-, SO_4^{2-}, and NO_3^-. The Schoeller diagram

Table 4. Factor loadings.

Variable	Factor		
	F_1	F_2	F_3
Na^+	0.841	0.352	0.355
SO_4^{2-}	0.815	0.498	0.005
K^+	0.678	0.498	0.502
HCO_3^-	0.797	0.283	0.458
Cl^-	0.363	0.882	0.248
Mg^{2+}	0.483	0.755	0.394
NO_3^-	0.431	0.619	0.506
EC	0.141	0.197	0.905
Ca^{2+}	0.451	0.374	0.634

Table 5. Saturation Index modeling.

Parameter	Max	Min	AM	Standard deviation
Alkalinity	0.0040015	0.0023001	0.0033846	0.00094219
Ionic strength	0.02097	0.0080722	0.01422	0.0064699
si_Albite	-3.5157	-6.9542	-4.7767	1.8936
si_Anhydrite	-1.7271	-2.054	-1.8475	0.17965
si_Aragonite	-0.6705	-0.9369	-0.78853	0.13577
si_Barite	0.8699	0.4577	0.6638	0.29147
si_Calcite	-0.5201	-0.7856	-0.6373	0.13545
si_Chalcedony	0.3045	-0.6379	-0.0188	0.53633
si_Dolomite	-1.2133	-1.7528	-1.451	0.2754
si_Fluorite	-2.3207	-2.8162	-2.5685	0.35037
si_Goethite	5.837	3.9838	4.811	0.94247
si_Gypsum	-1.478	-1.8068	-1.5985	0.18111
si_Halite	-6.5338	-8.0574	-7.1305	0.81372
si_Hematite	13.639	9.9278	11.582	1.8881
si_Pyrite	-85.239	-95.44	-89.822	5.1786
si_Quartz	0.7692	-0.1799	0.44253	0.53926
si_Siderite	-2.1624	-2.5602	-2.3714	0.19967
si_Talc	-4.5893	-6.2822	-5.6172	0.90289
si_Witherite	-3.6394	-3.8299	-3.7347	0.1347

also illustrated the impact of well location on water quality, and samples from different wells clearly had different dominant chemical species. The diagrams illustrate that most of these wells contained high levels of nitrate. The peaks in a Schoeller diagram indicate the water type. In this case, the ground water samples mainly contained Ca^{2+}, Na+ and $HCO_3^−$, $Cl^−$ (Ca–Na-HCO_3–Cl type) or Ca^{2+}, Mg^{2+} and $HCO_3^−$, $Cl^−$ (Ca – Mg-HCO_3–Cl type).

Factor analysis

The factor loadings of the variables (Table 4) reflect their correlation with the extracted factors. The first factor (F1) contained HCO_3^-, SO_4^{2-}, K^+ and Na^+ and explained 35.99% of the total variance. Factor 1 is strongly determined by the $HCO_3^−$ concentration, which could originate from the presence of dissolved CO_2. This factor reflects the dissolution of minerals (Table 5) and increases the concentrations of major ions in the groundwater. The second factor (F2) contained the variables Mg^{2+}, $Cl^−$ and $NO_3^−$, and explained 28.98% of the total variance. $NO_3^−$ is naturally present in groundwater at very low concentrations, and its source is human activities such as domestic or industrial waste or agricultural. Consequently, F2 also reflects the anthropogenic impact of domestic sewage, industrial waste, uncontrolled landfill waste, fertilizers, and manure on the study area. The use of various substances, e.g., fuels, cleansing agents and salt for icy roads, in urban areas and may also explain the presence of those elements in the waters. Indeed, the

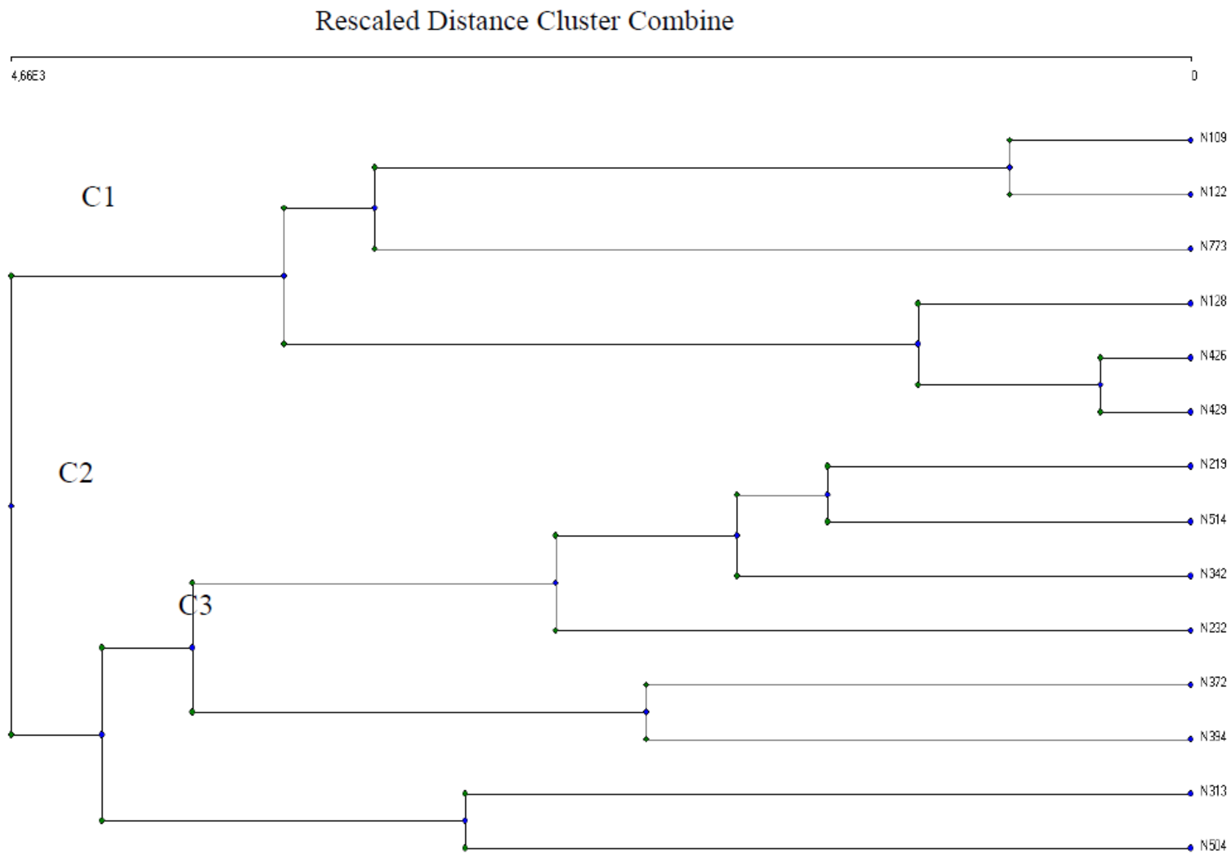

Figure 5. Hierarchical cluster analysis dendrogram obtained using Ward's method.

positive relationship between NO_3 and SO_4 (Figure 3) suggests that both N and S are used in the study area in the form of $(NH_4)_2SO_4$-fertilisers. Moreover, some groundwater samples show a well-defined relationship between NO_3 and cation (Ca^{2+} and Mg^{2+}) (Figure 3), highlighting that both elements are mostly originated from the excessive use of $Ca(NO_3)_2$-fertilizers. Therefore, the nitrate contamination is a result of the local hydrogeological setup coupled with the traditionally applied flood irrigation and the complete lack of environmental awareness regarding the over-fertilization and the utilization of recycled waste water. The third factor (F3) explained 25.35% of the total variance and contained EC and Ca^{2+}. The variables contained in F3 reflect the dependence of the EC on Ca^{2+} concentrations in the water samples.

Together these three factors accounted for 90.33% of the variability of groundwater quality. Their parameters include HCO_3^-, SO_4^{2-}, K^+ and Na^+ (F1), Mg^{2+}, Cl^- and NO_3^-(F2), and EC and Ca^{2+} (F3). However, measurement of only three parameters (HCO_3^-, NO_3^-, and EC) is sufficient for regular monitoring of the quality of well water. The other parameters can be determined by simple linear regression, because of their correlation to these three parameters (Table 5).

Hierarchical cluster analysis

The groundwater wells were grouped into three clusters (C1, C2 and C3) with similar parameters using hierarchical cluster analysis (Figure 5). C1 included wells 109, 122, 773, 128, 426 and 429. C2 included wells 219, 514,342, 232, 372 and 394 and C3 contained well 313 and 504. It is clear from Table 2 that all wells within each group have very similar pH, TDS, EC, and major and minor element content. Clustering of the wells reduces the number of sampling sites that would be required in any future studies. For example, when conducting a new field campaign to reconfigure the water supply network, and when testing the reliability of any proposed network by mapping the evolution of the chemistry of groundwater.

Conclusion

The present examination offers new, constructive, data for assessing the groundwater quality in Beijing aquifer, one of the most important water reservoirs in the city. The results of this investigation lend support to the presence of both natural and anthropogenic processes that contribute to the groundwaters salinisation and may result in concentrations locally exceeding recommended limits. Elevated concentrations of NO_3 are ascribed to anthropogenic processes such as: (i) the return flow of irrigated water enhanced by the flood irrigation practices, over-fertilization and pesticides leached downward; (ii) the intensive irrigation by the treated waste water; and (iii) the rejection of industrial nontreated waste waters in the drainage network. Furthermore, with increased water-rock interaction, the Beijing shallow groundwaters naturally become more mineralized. The source of nitrate in a contaminated aquifer is critical for managing surface operations to prevent future contamination, and for evaluating exposure of human populations to nitrate. Stable isotope compositions of nitrogen and oxygen in nitrate dissolved in the groundwater could be used to determine its origin. The variability in the water quality depended on the following three factors: alkalinity (HCO_3^-), the impact of human activities (domestic or industrial discharge), and salinity. Hierarchical cluster analysis grouped the wells into three clusters. This knowledge could allow future groundwater quality control studies to be performed using a reduced number of measurements on a small number of sampling points.

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