Full Length Research Paper

Evolution processes of groundwater quality in an urban area

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Groundwater quality evolution was investigated in an urban area of Beijing with multilayered geological formations. The majority of the samples collected during this investigation were found to contain high concentrations of nitrate, which is a serious water quality issue. In addition, this study attempted to explain the controlling processes responsible for the various facies. Overall, the distribution of soluble ions in the groundwater was stratified in the research area because of clay layers. Furthermore, the clay was found to control the concentration of cations and silica, as well as that of chloride ions in the groundwater. Taken together, these findings indicate that the clay layer is one of the most important factors involved in control of groundwater quality in the research area.

Key words: Groundwater, nitrate, clay, silica, cations, chloride.

INTRODUCTION

Investigation of the relationship between groundwater flow systems and groundwater quality is an important topic in groundwater research. Groundwater is one of the earth's most broadly distributed and important natural resources for municipal, agricultural, and industrial purposes, as well as environmental aspects. During analysis of groundwater systems, consideration must be given to the effects of groundwater withdrawals on water levels in nearby wells or wetlands, the flow of contaminants or salt water toward the wells, and the reduction of flow in nearby streams. In addition, variations in natural and human activities are reflected in the hydrochemical parameters of the groundwater. Indeed, differences in the concentrations of dissolved ions in groundwater are generally governed by lithology, groundwater flow, geochemical reactions, the solubility of salts, and human activities (Bhatt et al., 1996; Karanth, 1997). The quality of groundwater is dictated by its quantitative and qualitative composition of suspended solids and dissolved minerals or organic compounds (Jain et al., 2005).

Development of the equilibrium approach has had a revolutionary impact on chemical hydrogeology by introducing many chemical thermodynamic concepts, including the Nernst equation, which is related to the electromotive force, pH, temperature and dissolved species in groundwater (Krumbein and Garrels, 1952). The surface of clay minerals has a net negative charge that is primarily the result of substitution of lower valence cations for higher valence cations within the structure (Grim, 1968). The salt-exclusionary properties of clays arise when the compaction of clay slurry induces overlap of double layers of adjacent platelets. This overlap results in pore spaces between clay platelets, which have a negative electrical potential. Anions that attempt to migrate through such pores are repelled because the cations must remain with their anionic counterparts to retain electrical neutrality in the outer or "free" solution. However, water is freely admitted to the membrane structure. Some soil scientists have investigated the miscible displacement in porous materials with loam and clay. Laboratory (Dyer, 1965; Thomas and Swoboda, 1970; Smith, 1971) and field (Dyer, 1965) investigations have shown that, in some cases, the velocity of anions moving through soil may be faster than that of the water molecules present.

In this study, a comprehensive investigation of the

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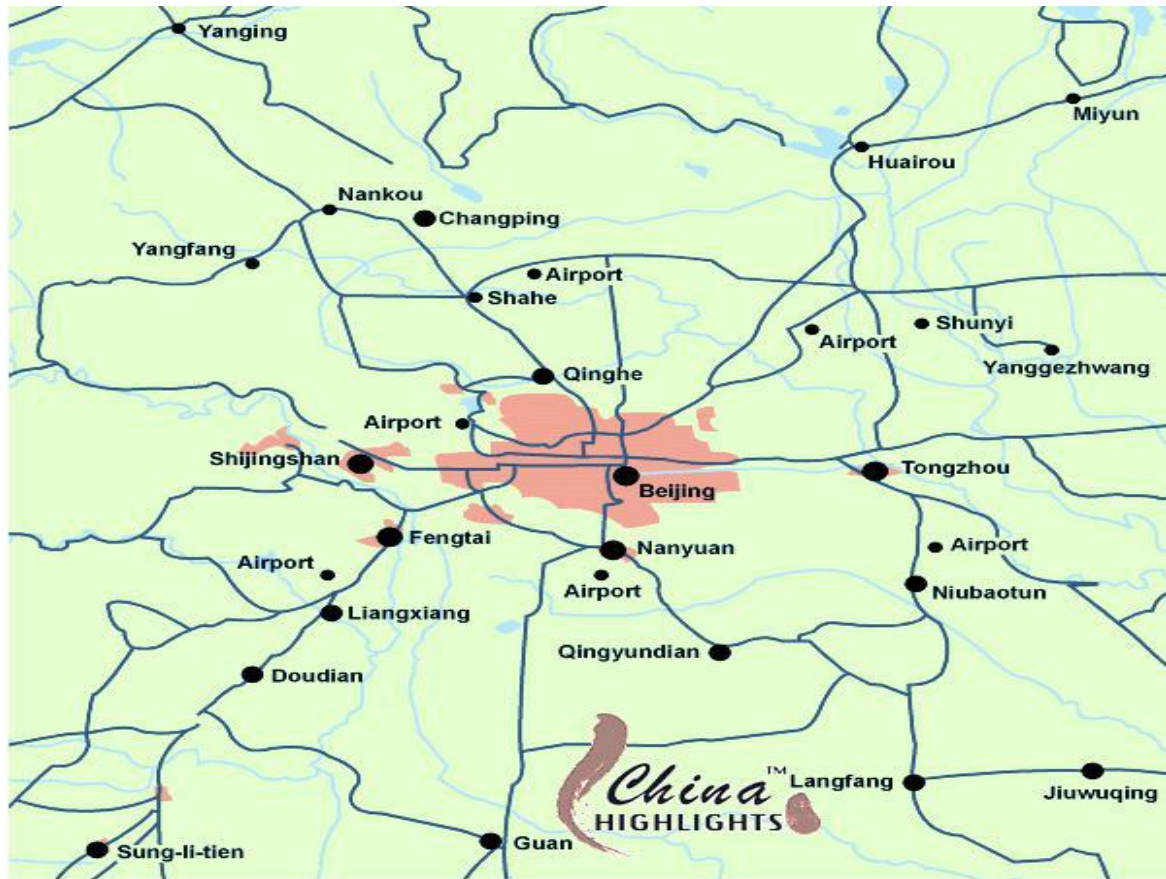
Figure 1. Site location map.

natural and artificial factors that influence groundwater quality was made to establish a clear relationship between groundwater flow systems and groundwater quality.

Study area

The study area is located between latitudes 39°57'42.48" to 39°54'30.53"N and longitudes 116°24'08.50 to 116°27'25.09"E, covering 1500 Hectares (Figure 1). The study area is situated in the Dongcheng 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, with a recorded high of 1,406 mm in 1959 and a low of 242 mm in 1869. Beijing has recorded 25 years of drought (based on below average rainfall (590 mm)) since the 1970s. Between 1999 and 2008, Beijing's average annual precipitation was 428 mm, or 28% below average.

Geological and hydrogeological aspects

The main aquifers in central Beijing are composed of alluvial gravel-sand sediments of the Quaternary period. The line from Haidian to Huangtugang 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,
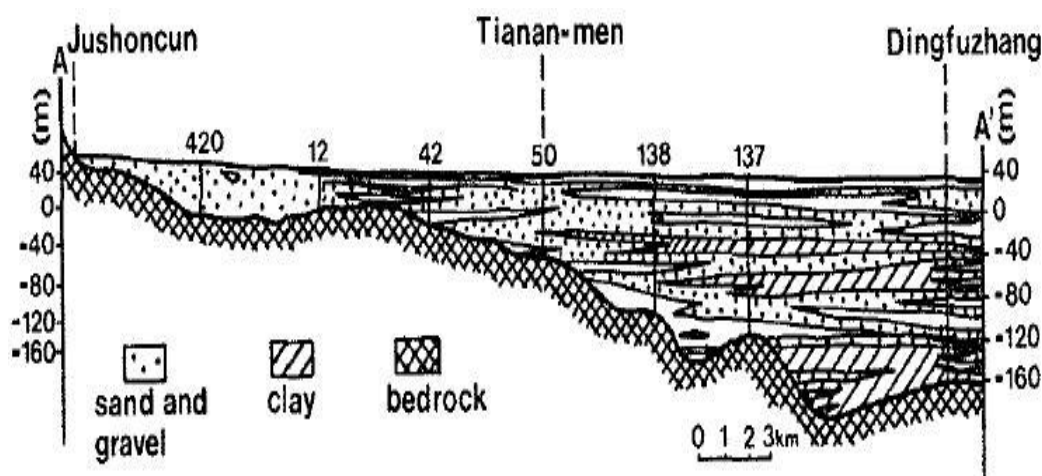
Figure 2. Geological sketch of quaternary aquifers in the study area.

and the four principal 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. A clay bed 3 to 15 m in thickness separates the first aquifer from the second aquifer. Considering the hydraulic conductivity of each layer, they can be divided into an upper aquifer and a lower aquifer along the clay layer.

MATERIALS AND METHODS

Sampling and analytical procedure

Samples were collected from borehole wells 80 to 132 m deep that were selected to provide a uniform distribution over most of the study area. Soil samples were also collected for mineralogical investigation. A global positioning system (GeoExplorer 3.0; Trimble GPS) was used to locate wells in the study area. Water samples were collected in May 2010. Physico-chemical parameters including temperature, pH, electrical conductivity and total dissolved solids were measured in the field, while the samples used for other analyses were transported to the laboratory for testing, where they were stored in the dark at 4°C until analysis. The major components (HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, Ca^{2+}, Mg^{2+}, NH_4^+, Na^+, K^+, Fe^{2+} and Mn^{2+}), were measured in the laboratory within 10 days of sampling. Analysis was conducted according to established methods as follows:

Alkalinity was determined by acid titration (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 hydrogeochemical results for the study area are presented in Table 1.

Soil phase analysis

Soil was collected from different depths in the Dongcheng District of Beijing. The soil samples were dry sieved and the <1 mm fraction was used for characterization and laboratory experiments (the > 1 mm fraction represented less than 1% of the total sample mass). The main components of the soil were determined by chemical and X-ray diffraction analyses. The cation exchange capacity of the soil was determined using the BaCl$_2$ Compulsive Exchange Method (Gillman et al., 1986). The total organic carbon was determined by titration. The results of all analyses are shown in Table 2.

Batch experiments

Batch tests were conducted at room temperature in 250 ml polycarbonate tubes. For all experiments, a solid/solution ratio of 10 g soil/100 ml distilled water was used. The soil was added to the tubes and weighed to the nearest 0.01 g. The required solutions (distilled water) were then added to each tube and brought into contact under mechanical agitation in rototubes for 2 h. Next, phase separation was conducted by temperature-controlled centrifugation at 14 000 *g* for 20 min. A known amount of supernatant was subsequently transferred to each tube and weighed, after which it was used for subsequent chemical analyses. To obtain mineral dissolution, the total concentrations of major cations released into the solution were determined (EPA, 2009).

Column experiments

Experiments were conducted over an average period of sixty days. Low-pressure linear chromatography was used to monitor the physiochemical parameters at the column output (conductivity, pH and optical density) as well as to recover the eluate fractions using a collector (Figure 3). Briefly, a chromatography column was filled with soil (clay-sand-clay) and then saturated with a packing solution prior to injecting solutes representative of the solute retention or desorption phenomenon targeted by the study. The pore volume of the columns was determined by a non-reactive tracer experiment.

   The methodology employed to interpret the results is based on the classical theory of multi-constituent chromatography (Tondeur, 1969; Helfferich and Klein, 1970), which is intended to characterize the physicochemical interactions occurring between a solid phase and solutes in the presence of a permanent, one-dimensional and only slightly-dispersive flow. The characterization is based on analysis of the chromatograms that result from a signal of the step or slot type with a known composition and imposed on a

Table 1. Statistical overview of hydrochemical characteristics of groundwater (May 2010).

Parameter	Unit	Min	Max	Mean
pH		6.56	7.15	6.9221
TDS	mg/l	323.78	1052.9	736.38
Ca	mg/l	59.97	126.48	91.754
Mg	mg/l	24.14	40.15	35.084
Na	mg/l	17.28	106.79	60.426
K	mg/l	1.46	4.09	3.1214
Fe(2)	mg/l	<0.02	<0.02	<0.02
Mn	mg/l	<0.005	<0.005	<0.005
Cl	mg/l	16.49	183.04	94.051
SO_4	mg/l	65.83	195.9	116.81
HCO_3	mg/l	131.15	268.4	208.05
NO_3	mg/l	112.67	164.3	142.82
SiO_2	mg/l	3.03	26.99	18.266

Table 2. Soil physical-chemical characteristics.

Well section (m)	Lithology	Mineral content (%)						Clay mineral amounts (%)	CEC (mg/L)	TOC (%)
		Quartz	Feldspar	Plagioclase	Calcite	Dolomite	Amphibole			
5.7–7.5	Clay	40.1	2.8	17.2	15.8	4.6	1.4	18.1	7.87	4.36 to 10.18
7.5–8	sand	40.0	10.4	14.5	6.0	5.2	0.6	23.3	3.70	
9.4-16.4	clay	30.3–46.2	4.5–24.5	13.2–28.4	15.4–16.2		1.4	7.3– 23.4	6.49–7.08	
16.4–18	sand	47.8	26.9	19.5	0.9		0.7	4.2	3.20	

porousmedium model with a uniform composition (Figure 3)

Experimental protocol

A glass column (Pharmacia LKB C16, diameter 5 cm and approximate length 50 cm) with polypropylene end pieces was equipped with 0.45 m hydrofoil Teflon membranes (HVLP, Millipore). Teflon capillaries with a diameter of 1.6 mm were used to connect the elements. The column was packed with dry soil and the soil bed length was measured and the amount of soil weighed (top clay, 160 g; sand, 300 g; bottom clay, 320 g). The chromatography column was filled with different soils to represent the vertical variation in the aquifer in the study area. The solutions (distilled water) were fed to a piston pump (Pharmacia P-500) connected to the top of the column at a flow rate of 10 ml/h, which gave a corresponding Darcy's velocity of 5.0 cm/h. The geometric characteristics of the column are listed in Table 3. The total concentrations of the ions were determined from fractions collected at the column output following acidification and filtration through a 0.45 m porosity membrane. The concentrations of the cations were determined using a Varian Liberty 200 ICP- OES and the anions were determined using a DX300 Dionex Ion Chromatograph (EPA, 2009). Alkalinity was determined by acid titration.

RESULTS

Groundwater quality

The distribution of groundwater quality in a three-dimensional space can be classified into two groups: Ca-Na-Mg-HCO_3-Cl-SO_4-NO_3 type and Ca-Mg-Na-HCO_3-Cl-NO_3 type. The chemical
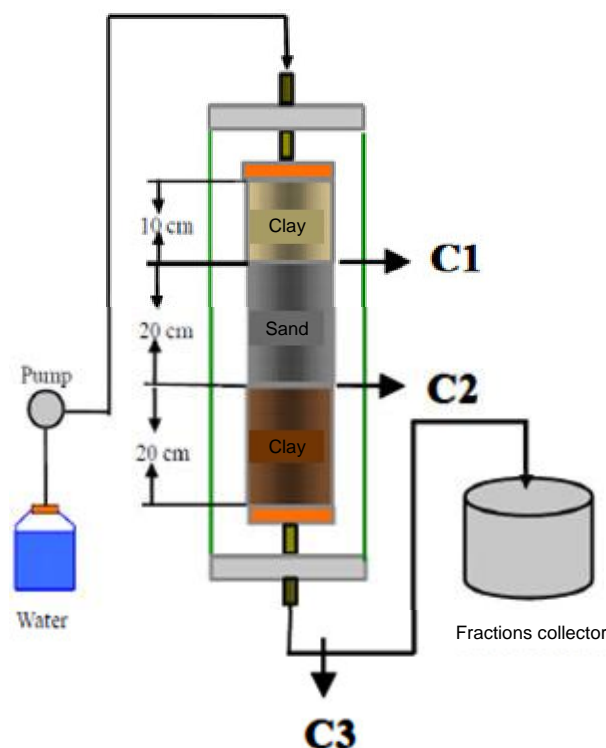
Figure 3. Set-up used for the column experiments.

Table 3. Column characteristics and transport model parameters.

Nature of Soil	Length (cm)	Diameter (cm)	Weight (g)	Geometric porosity ( )		Flow rate (Q) ml/h	Spiked solution volume (ml)
Top Clay	10		160	0.55			
Middle Sand	20	5	300	0.33		10.0	0.5
Bottom Clay	20		320	0.55			
Feed solution (mmol/l)	pH	K	Na	Ca	Mg	Cl	NO₃	SO₄
	7.1	0.01	0.09	0.10	0.10	0.03	0	0.04

composition of groundwater varied little from the recharge area to the discharge area within an aquifer when compared to the difference between aquifers. Groundwater also contained high concentrations of NO_3^-, which indicates a serious water quality issue. This NO_3^- originates from the soil surface and enters the groundwater via infiltration. However, due to the influence of land use, there was still a high level of horizontal variation in groundwater quality in the upper aquifer. Specifically, there were higher levels at the surface level due to atmospheric deposition and the use of various substances such as fuels, cleansing agents and salt for icy roads.

Most samples contained high concentrations of Na^+, while the concentration of K^+ was less than 4 mg/l in all samples. The concentrations of calcium (more than 90 mg/l) and magnesium (more than 35 mg/l) were higher in the lower aquifer than the upper aquifer.

The silica concentrations ranged from 3 to 27 mg/l, with the majority of samples containing less than 15 mg/l in the upper aquifer and more than 20 mg/l in the lower aquifer. There was a high concentration of chloride ions (>100 mg/l) in and above the clay layer. The concentration of chloride in the upper aquifer (generally more than 90 mg/l) was higher than in the lower aquifer (< 80 mg/l) due to the land use function and clay formation between the aquifers.

Batch studies

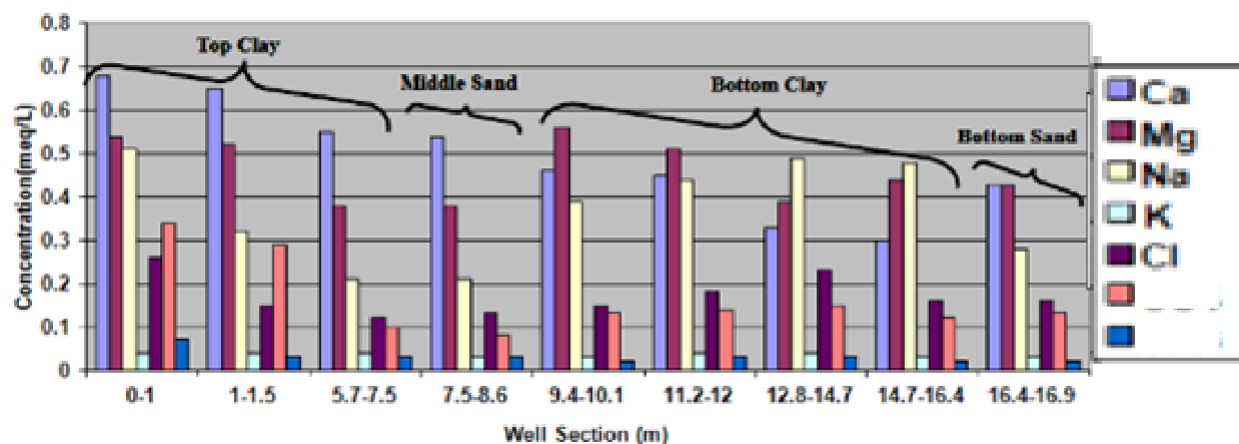In this study, a novel experiment was conducted to

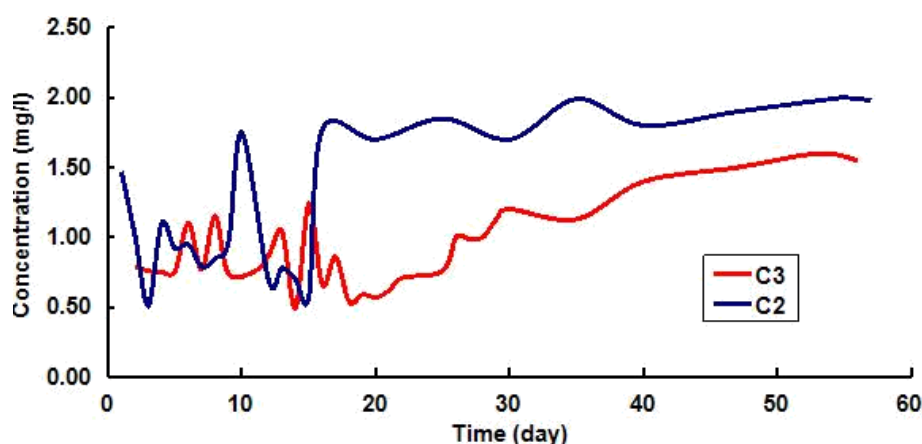**Figure 4.** Batch experiment results.
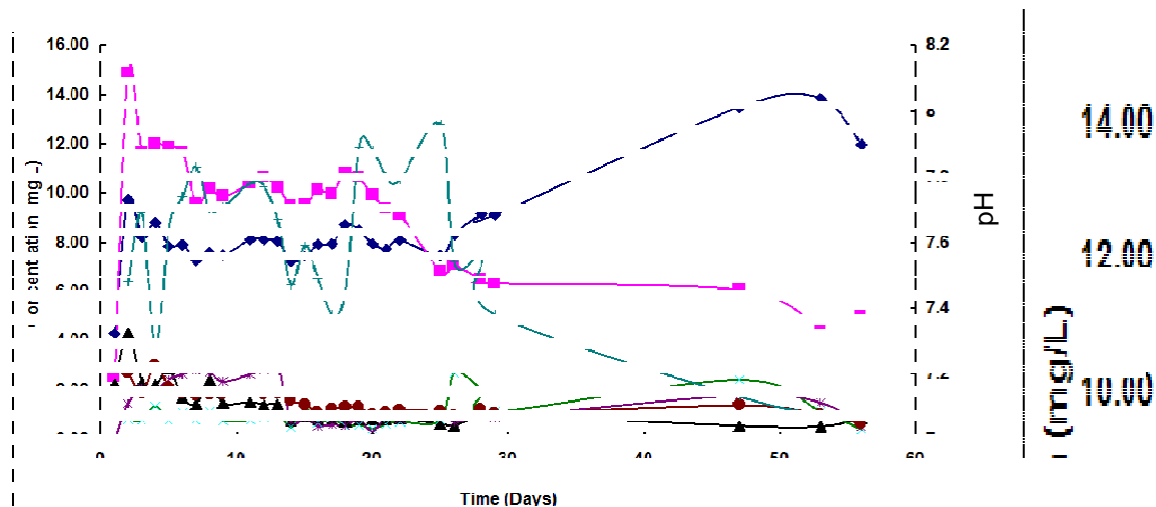

Figure 5. Variations in CI- concentrations.

determine the major ions desorption isotherm for the soil/water system. Direct batch experiments were conducted for this system and the resulting isotherms are shown in Figure 4. The concentration of potassium was lower than 0.04 meq/L in all samples. The concentrations of calcium (0.54 to 0.68 meq/L) and magnesium (0.38 to 0.54) were high in the top clay and middle sand layers. In the lower clay layer (9.4 to 12 m) the concentration of magnesium (0.51 to 0.56 meq/L) was higher than that of calcium (0.45 to 0.46 meq/L), but from 12 to 16.4 m, the concentration of sodium (0.48 to 0.49 meq/L) was relatively high. The dominant anions were HCO_3 (0.8 to 1.09 meq/L), Cl^- (0.12 to 0.26 meq/L) and SO_4 (0.08 to 0.34 meq/L).

Column experiment

Column experiments were also conducted to investigate the physical and chemical roles played by water quality evolution. The soils in the study area were used in this

experiment. The most interesting result was the variation in chloride ion concentration. The concentrations of chloride with time in the upper bottom clay (C2) and the lower bottom clay (C3) are shown in Figure 5. The concentration in the lower bottom clay increased gradually until it reached about 1.5 mg/L, after which it changed only slightly. However, the concentration in the upper bottom clay was always greater than 1.5 mg/L. These findings indicate that the chloride ion was only concentrated in the upper bottom layer of clay.

Anion exclusion in clay electrolyte systems with low hydraulic conductivity gives rise to salt filtration if the electrolyte solution is forced to flow across the clay. Under such conditions, cations in the pore will prevent both cations and anions in the external solution from passing through. Neutral molecules such as water can pass through so that, with time, the solution will become more concentrated on the inflow side and diluted on the outflow side. For example, chloride that is held back while water molecules pass through a clay layer might accumulate until a high concentration is reached. The

Figure 6. Variations in Ca, Mg, Na, SO4, NO3 and Cl concentrations in the water-soil interaction experiment.

selective behavior of such a layer also influences the residual concentration of cations. The more strongly retained ions in such a solution would attach to cation exchange sites more strongly. Calcium is commonly the preferentially held ion; thus, the following mechanism is suggested for the origin of calcium chloride observed in the research area: the hydraulic conductivity of the clay bed is very low and the mineral composition of the clay bed is different from that of the sand bed; therefore, the clay bed may provide more paths for groundwater flow, thus enabling the chloride to move through the clay bed more freely.

Figure 6 shows the experimental results of the water-soil interaction within the column experiment. During the first 25 days, the concentration of major ions in the solution varied greatly. After one month, the concentration of major ions in the water showed only a small variation. These findings indicate that the water-soil interaction approached an equilibrium state, while the Ca concentration continued increasing. In addition, the concentration of sodium decreased, whereas that of calcium and magnesium increased. These findings indicate that an ion-exchange reaction between monovalent ions and divalent ions occurred.

The beginning concentration of Mg was higher than the concentration of Ca. After 25 days, the concentration of Mg decreased, while the concentration of Ca continued increasing linearly. This likely led to the deceased pH. With continuing reaction between the groundwater and the aquifer matrix, it is possible that groundwater with a high degree of disequilibrium with respect to the matrix minerals may evolve from these waters to give waters that have achieved a chemical equilibrium with the appropriate silicates. When sodium passes through the clay formation with the groundwater, the sodium ion will replace the calcium ion or magnesium ion. This is why cation compositions change little within the upper and

lower aquifers, but greatly when groundwater flows from the upper aquifer to the lower aquifer. Because the ion exchange substances act as reservoirs, the upper and lower aquifers will dampen temporal fluctuations in the ionic composition of water passing through soil.

DISCUSSION AND CONCLUSION

As groundwater moves down across different layers or along the same aquifer, the chemical composition of groundwater in each layer depends on the chemical composition of water leaking vertically from the upper layer or recharging laterally from upstream, as well as the properties of the soil that the water flows through. The variation in the chemical composition of groundwater is especially high between the clay layer and the overlaying aquifer. It is known that some clays have low permeability, and that subsurface environments composed of these media form a groundwater system with many distinctive characteristics. Moreover, groundwater flow in these environments appears to influence the evolution of certain hydrological, geological and geochemical systems. The water in the aquifers in Central Beijing is heavily influenced by human activity. Indeed, all major ions can be found in this aquifer, and the variations in all major ions are largest in the study area. Investigation of the hydrochemical characteristics of this groundwater showed that the majority of samples contained a high level of nitrate ions. The high content of these chemical components, which has an adverse effect on drinking water quality, has resulted in the wells in this region no longer being used for human consumption.

As a result of environmental studies, water quality monitoring and other investigations, the calcite and dolomite contents of strata around Beijing are known to range from 8 to 15%, with the highest values being about

21%. Following environmental pollution, reactions occurred between sewage and the surrounding medium as the sewage infiltrated the ground. As a result of a series of physico-chemical and biochemical reactions, including dissolution, ion-exchange and reactions involving organic compounds, the Ca and Mg in the infiltrating solutions have increased. These solutions have infiltrated aquifers and increased the hardness of the groundwater, and this process has been accelerated by over pumping of groundwater.

Dramatic variations occur when the groundwater flows through the clay layer in the study area. For example, the concentration of silica increases to 25 mg/l because silica dissolves from the clay. In the clay bed formation, sodium in the groundwater is exchanged for calcium, which causes an increase in the calcium concentration of the groundwater up to 100 mg/l. The most interesting phenomenon is the increase in chloride concentration in this layer. The synthetic interactions of physical and chemical processes of clay formation in the research area may resist the movement of chloride ions, while permitting groundwater to flow freely. Accordingly, the velocity of the groundwater is different from that of chemicals, even chloride ions, when clays exist in the groundwater flow system. Therefore, chloride ions are not a suitable tracer in groundwater. After the groundwater flows through the clay layer formation, its quality is controlled only by the mineralogy of the aquifer. Sodium in the groundwater is continually exchanged by the calcium, which results in the concentration of chloride being less than 180 mg/l. Conversely, the concentration of HCO_3 increases up to 200 mg/l because of dissolution of the minerals in the clay formation.

Overall, the structure and mineral composition of clay were found to control the cations and silica concentrations in the groundwater, as well as the movement of chloride ions. Field observations and laboratory experiments revealed that chloride ions are concentrated where the clay formation exists. Therefore, the clay layer in the groundwater flow system is one of the most important factors controlling the variation in groundwater quality in the research area, and in turn the movement of chemicals in the groundwater system.

REFERENCES

AFNOR (1996). Water, test methods. Ed. Afnor, p. 624.

Bhatt KB, Salakani S (1996). Hydrogeochemistry of the upper Ganges River, India. J. Geol Soc. India, 48: 171-182

Dyer KL (1965). Unsaturated flow phenomena in panoche sandy clay loam as indicated by leaching of chloride and nitrate ions. Soil Sci. Soc. Am. Proc., 29: 121-126

EPA analytical method (2009). Federal Register. Tuesday, November 10, 2009 /Rules and Regulations, 74: 216.

Gillman GP, Sumpter EA (1986). Modification to the compulsive exchange method for measuring exchange characteristics of soils. Aust. J. Soil Res., 24: 61-66.

Grim RE (1968) Clay Mineralogy. McGraw-Hill, New York

Helfferich F, Klein G (1970). Multicomponent chromatography - Theory of interferences, Marcel Dekker, New York, Chromatogr. Sci. Series, p. 4.

Karanth KB (1997). Groundwater assessment, development and management. Tata McGraw-Hill Publishers, New Delhi.

Krumbein WC, Garrels RM (1952). Origin and classification of chemical sediments in terms of pH and oxidation reduction potentials. Geol., 60: 1-32.

Jain P, Sharma JD, Sohu D, Sharma P (2005). Chemical analysis of drinking water of villages of Sanganer Tehsil, Jaipur District. Int. J. Environ. Sci. Tech., 2(4): 373-379

Smith SJ (1971). Relative rate of chloride movement in leaching of surface soils. Soils Sci., 114: 259-263.

Thomas GW, Swoboda AR (1970). Anion exclusion effects on chloride movement in soils. Soil Sci., 110: 163-166.

Tondeur D (1969). Theory of ion exchange columns, Publications of the University of Nancy. Collection of theses of the Faculty of Physical Sciences, Nancy.