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Groundwater Quality Evolution Under Urbanization in Beijing Urban Area, Northern China

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Groundwater quality data from 1960 to 2008 were analyzed to determine hydrogeochemical evolution under urbanization in Beijing urban area in the North China Plain. The results demonstrated that urbanization had a significant impact on major groundwater chemistry composition of Ca^{2+}, Mg^{2+}, K^+, Na^+, HCO_3^-, Cl^-, NO_3^- and SO_4^{2-} in this aquifer. Cl^- and NO_3^- primarily originate from urban activities. The changes of concentrate of Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-} were partially attributed to carbonate and sulfate mineral dissolution, as well as to the anthropogenic inputs and these ions were under the control of responding mineral dissolution equilibrium. Urbanization processes led to the different hydrogeochemical facies which correspond to three stages in urbanization process, respectively. The saturation indices of calcite, aragonite, dolomite, gypsum, anhydrite and halite exhibited a wave-shaped increase from natural groundwater to urban groundwater. Mineral dissolution could occur when SI > 0 and mineral precipitation could occur when SI < 0. The critical SI value controlling the transition between dissolution and precipitation for these minerals was not applicable to all hydrogeochemical conditions.

Keywords: Urban groundwater, Temporal evolution, Hydrochemistry, Urbanization, Beijing.

INTRODUCTION

Rapid urbanization is occurring in many developing countries and this has brought a great stress not only on the water supply but also on the water quality. Many urban activities made water quality degradation, even deterioration. Ground water, which is a major water supply sources for urban in arid or semi-arid areas, is susceptible to the urban activities. The urban activities are often related to the presence of pollutant sources such as landfill, sewage, industrial effluents and septic tanks[1]. Thus, in the past several decades, urbanization has long been recognized as a threat to ground water quality[2-5].

In general, three methods have been widely used to evaluate urban ground water quality *i.e.*, traditional hydrogeochemical methods, isotope trace methods and statistical methods. The first method has usually been used to identify the water chemical characteristics and hydrogeochemical process. The isotope and other tracer, such as chlorine, nitrogen, oxygen, hydrogen, sulfur and strontium, are proved to be useful in the identification of specific source of the pollution[6-10]. The factor analysis is the most commonly used statistical method to indirectly analyze hydrogeochemical process and sources of pollution[11]. Despite of these different methods, a universally accepted conclusion is that nitrate (NO_3^-) and chlorine (Cl^-) are probably the most widespread contaminants in urban ground water and originate mainly from the leakage of sewage and septic tanks. There were some different conclusions as well. For example, the concentration of HCO_3^- and NO_3^- of urban ground water had the highest factor loading using the factor analysis[11]. As for the other major ions of Ca^{2+}, Mg^{2+}, Na^+, HCO_3^- and SO_4^{2-}, most of researches demonstrated that they were affected by both natural hydrogeochemical processes and human activities in urban ground water and the natural hydrogeochemical processes mainly include the dissolution of carbonate and halite and cation exchange. However, Jiang and Yan[12] illustrated that SO_4^{2-}, Na^+ and K^+ in the urban ground water were mainly from the sources related to human activities while Ca^{2+}, Mg^{2+} and HCO_3^- are primarily controlled by water-rock interactions. Choi *et al.*[13] showed that the concentrations of all the major ions examined increased with the degree of anthropogenic contamination in urban ground water. These diverse conclusions were apparently resulted from individual urban areas or aquifers. The other reason was likely related to different evolution stages of water chemistry. Most of researches were performed by the analysis of short-term water quality data and spatially compared urban ground water with natural ground water which occurred away from urban areas. The temporal hydrogeological evolution was ignored. Because the impact of urbanization on ground water quality is a long-term dynamic process and the chemical characteristics is different in each evolution stage, the instantaneous water quality data can not capture all the detailed information for water quality evolution. Therefore, it is necessary to analyze the influence of urbanization history on ground water using long-term data. Unfortunately, the analysis of long-term data is often unrealistic primarily due to the limited length of data sets.

In the present study, the ground water quality data from 1960-2008 were employed to study the hydrogeochemical evolution from natural ground water to contaminated ground water under urbanization in Bejing urban area, northern China. The evolution sequence of water chemistry, hydrochemical facies and saturation index were determined. The major hydrogeochemical processes were identified and urbanization impact on water quality was analyzed.

The study area, Beijing urban area, is in the Yongding river alluvial fan which is located in the northwest of the North China Plain (Fig. 1). The shape and deposit character of the alluvial fan is closely related to the historical change of the Yongding river. The Yongding river is the biggest tributary of the Hai river and it is across Beijing from north to south and flows into the Hai river after joining the Beiyun river in east of Beijing. The Yongding river underwent a great channel change in past 2000 years. It flowed eastward before A.D. 200 [14]. After that time the channel at the mountain pass changed direction by man-made embankment in order to prevent from flooding[15]. Since the engineered work, the paleochannel of the Yongding river was gradually pushed southeastward to the present location and an alluvial fan with an area of 1000 km^2 has been formed. Owing to the abundance of ground water resources, the alluvial fans become ideal sites for city water supplies. The whole ancient Beijing city was on the alluvial fans and till now one-fifth of the Beijing area (except for the mountain zone) still sits on it after the rapid urban expansion in the past several decades.

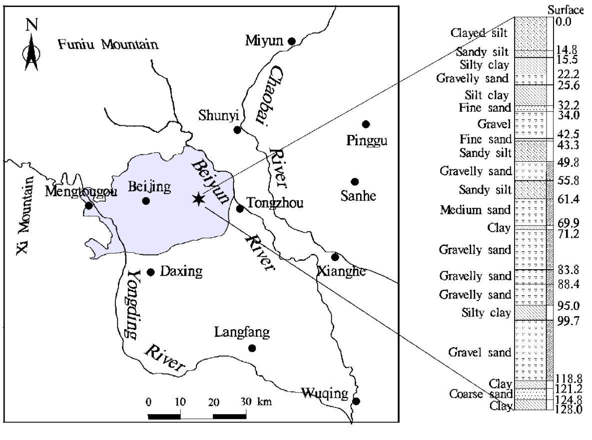

Fig. 1. Location map of the study area in the northwest of the North China Plain and the hydrogeological units in the sampling location

The study area belongs to a semi-arid climatic zone and has an annual mean temperature of 11.7 ºC. The mean annual precipitation was 610 mm from 1980-2005. The precipitation is dominated by the Asia summer monsoon between June and September and it accounts for about 85 % of annual precipitation. Annual mean potential evaporation was 1826 mm from 1980-2005.

Hydrogeological setting: The regional quaternary aquifers occur in the Yongding river alluvial fan. The thickness of the quaternary deposits varies considerably from 50-300 mm. The thin quaternary depot occurs in the piedmont alluvial area as an unconfined aquifer, which consist mainly of gravel and sand with high hydraulic conductivity values of 300-500 m/d. In the middle of the alluvial fan, the quaternary deposit with a thickness of 200-300 m consists of coarse sand, fine sand, clay and trace gravel, which is grouped into two or three aquifers with hydraulic conductivity values of 50-100 m/d. Ground water recharge is primarily from infiltration of precipitation occurring in the piedmont alluvial area and includes the leakage of the Yongding river. The ground water is mostly discharged by pumping for domestic and industrial uses. In the sediments of the alluvial fan, quartz and potassium feldspar are the dominant minerals and calcite is commonly present. Illite, kaolinite and montmorillonite may also be observed[16].

The study sites are located in a small-scale ground water catchment in the middle of the alluvial fan and between the East-2nd and East-3rd ring road of Beijing. It is about 7 km away from city center (There are six ring roads in Beijing now). Ground water was extracted from a confined aquifer for the domestic and industrial uses before 1980. Henceforth, most of wells in the catchment have been abandoned due to water quality degradation and only several wells remain in operation and are used for ground water quality monitoring. The Quaternary aquifer in the catchment has a thickness of 128 m and is interbedded with gravel, sand and clay. The depth to the ground water level decreased from 32 m in 1978 to 29 m in 2007. The depth for ground water extraction is at the depth of 50-118 m. The hydrogeological units of the aquifer are shown in Fig. 1.

Data setting: The ground water quality in the catchment was monitored twice each year in May and September from 1960-2008. The chemical analyses for major ions of the ground water were conducted in the laboratory of ground water supply using the standard methods. Total dissolved solid (TDS) were measured by sample evaporation techniques. HCO_3^- was measured by titration against stand HCl. Cl^- was estimated by titration against standard solution of $AgNO_3$. SO_4^{2-} was determined gravimetrically. Ca^{2+} and Mg^{2+} were analyzed by titration against standard EDTA solution. Na^+ and K^+ concentrations were measured by atomic absorption spectrophotometry. NO_3^- and SO_4^{2-} were analyzed colorimetrically using spectrophotometric technique. pH was measured at the well head using portable pH-meter.

All the records of the water chemistry from the monitoring wells are inconsecutive in 49 years. A relatively full record was collected but the record did not exist for 9 years: 1961, 1969, 1970, 1972, 1974-1976, 1997 and 2001.

EXPERIMENTAL

Ground water chemistry: The composition concentrations from 1960-2008 were shown in Table-1 and Fig. 2. In

TABLE-1
AVERAGE ANNUAL VALUE OF CHEMICAL COMPOSITIONS (MAJOR ELEMENTS) IN DIFFERENT STAGES. (CONCENTRATIONS ARE EXPRESSED IN mmol/L, TDS IN mg/L)

	TDS	pH	Ca^{2+}	Mg^{2+}	K^+	Na^+	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-
1960-1963	296	7.57	0.89	1.23	0.11	1.12	4.13	0.43	0.40	0.06
1963-1979	576	7.40	1.84	2.46	0.09	0.87	5.06	0.76	2.44	0.40
1980-2002	1101	7.25	2.96	3.69	0.15	1.49	7.01	1.52	4.19	0.67
2003-2008	1165	7.20	3.12	2.66	0.33	3.34	7.79	1.41	3.92	0.72

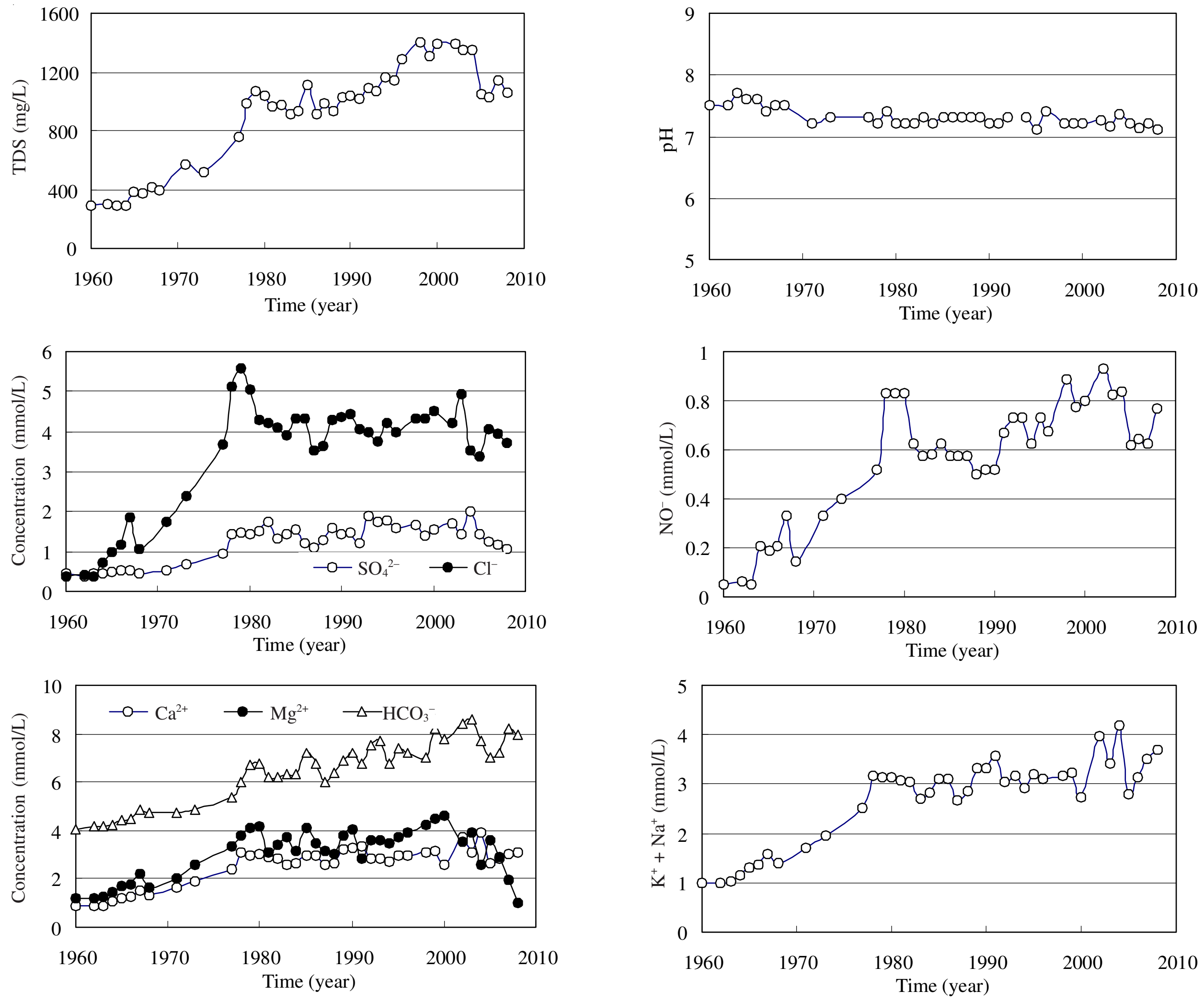

Fig. 2. Temporal evolution of major composition of groundwater from 1960 to 2008

the early 1960s, the composition concentration of ground water displayed an almost steady state. The low NO_3^- concentration indicates that ground water had not been seriously affected by intensive urban activities. Thus it was defined as a natural ground water. Since 1964, the composition concentrations of ground water tend to increase. In general, the TDS values of ground water show a systematic response to the water quality change. Therefore, according to the temporal variation of the TDS from 1964-2008, three evolution stages for natural ground water were identified.

The first stage was from 1964-1979. The TDS value displayed a significant increase with the average annual growth rate of 48.7 mg/L. The concentration of Cl^- increased the most rapidly from 0.74 mmol/L in 1964 to 5.57 mmol/L in 1979 and the concentrations of Ca^{2+}, Mg^{2+}, K^+, Na^+, HCO_3^-, SO_4^{2-} and NO_3^- also rapidly increased to 2.97, 4.09, 0.17, 1.77, 6.70, 1.47 and 0.83 mmol/L in 1979. pH values decreased to 7.30. The second stage was from 1980-2002. The TDS value characterized a slow increase with an average annual growth rate of 15.2 mg/L. The concentration of most of the ions displayed an irregularly fluctuation in most years in this stage except for an obvious decrease of Cl^- and NO_3^- in several years after 1980. The last stage was from 2003-2008. Although the TDS kept the higher annual average values than that in the second stage and had a slight increase from 2005-2008, it tended to decrease as a whole; Ca^{2+}, K^+, Na^+, HCO_3^- and NO_3^- had similar trend. The concentrations of Mg^{2+} and SO_4^{2-} displayed a significant decrease and were eventually down to 0.98 and 1.07 mmol/L in 2008, respectively.

In the three stages, the concentration variation of NO_3^- and Cl^- exhibited a similar trend, which is likely to imply that both these ions were originated from the same source. Many researches illustrated that the domestic sewage enriched the nitrate-nitrogen and chlorine concentrations[17]. Thus the change of NO_3^- and Cl^- was likely to be caused by domestic sewage leakage. In addition, in the first two stages, the concentration variation of Ca^{2+}, Mg^{2+} and HCO_3^- also showed a similar trend, which was more associated to the carbonate mineral dissolution and precipitation which can result in increase or decrease in the proportional to the molecules concentrations of Ca^{2+}, Mg^{2+} and HCO_3^- according to law of mass action.

Hydrochemical facies: The piper diagram (Fig. 3) was constructed using Aquchem Scientific Software using the water quality data from 1960-2008. Fig. 3 clearly shows three main ground water groups, namely:

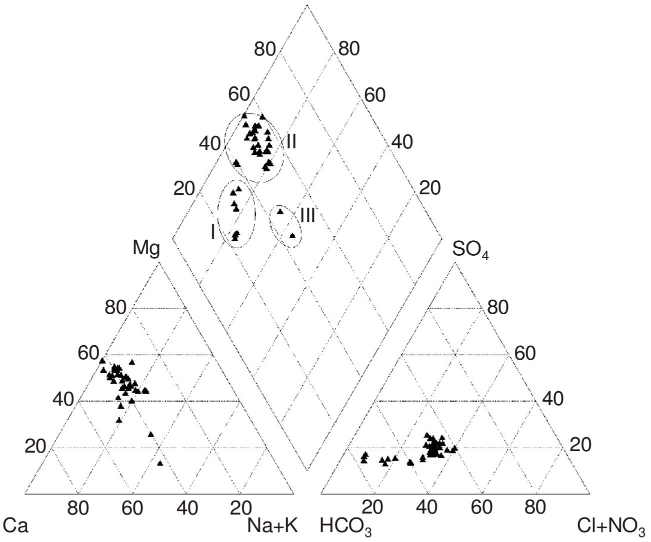

Fig. 3. Piper hydrogeochemical diagram in 1960-2008

Group I: Mg-Ca-HCO_3
Group II: Mg-Ca-HCO_3-Cl, Mg-Ca-HCO_3-Cl-SO_4, Ca-Mg-HCO_3-Cl-SO_4
Group III: Ca-Na-Mg-HCO_3-Cl, Ca-Na-HCO_3-Cl

Group I responds to the data from 1960-1968 (Table-2) and the unique facies, Mg-Ca-HCO_3, occurred. It is dominated with magnesium ranging from 1.21 to 2.22 mmol/L and bicarbonate ranging from 4.06 to 4.86 mmol/L. The average TDS value for the Mg-Ca-HCO_3 type is 343 mg/L. Unlike recharge areas in the most alluvial aquifer in which the dominant cation is calcium, magnesium is the dominant cation in the study area, which relates to high dolomite content in the aquifer. The low Na^+, Cl^- and SO_4^{2-} concentration and the low degree of water mineralization reflect the recharge water characteristics. Thus this facies can be interpreted as natural "background" type and the ground water hydrochemistry is controlled by water-rock interactions. Group I was approximately associated to the natural ground water in section of ground water chemistry above.

TABLE-2
HYDROGEOCHEMICAL FACIES FROM 1960 TO 2008

Year	Hydrogeochemical facies
1960-1968	Mg-Ca-HCO_3
1971-1980	Mg-Ca-HCO_3-Cl
1981-1985	Mg-Ca-HCO_3-Cl-SO_4
1986-1988	Mg-Ca-HCO_3-Cl
1989	Mg-Ca-HCO_3-Cl-SO_4
1990	Mg-Ca-HCO_3-Cl
1991	Mg-Ca-HCO_3-Cl-SO_4
1992	Mg-Ca-HCO_3-Cl
1993-1998	Mg-Ca-HCO_3-Cl-SO_4
1999-2000	Mg-Ca-HCO_3-Cl
2002	Ca-Mg-HCO_3-Cl-SO_4
2003	Mg-Ca-HCO_3-Cl
2004	Ca-Mg-HCO_3-Cl-SO_4
2005	Mg-Ca-HCO_3-Cl-SO_4
2006	Mg-Ca-HCO_3-Cl
2007	Ca-Na-Mg-HCO_3-Cl
2008	Ca-Na-HCO_3-Cl

Group II responds to the data from 1971-2006 and three facies occurred. The facies of Mg-Ca-HCO_3-Cl presented in 1971-1980 and alternated with the other two facies in succeeding years (Table-2). It characterizes the occurrence of chlorine appearance in dominant anions comparing with groupI. In general, the HCO_3-Cl type is considered to relate to seawater intrusion, dissolution of halogenous minerals and ground water evaporation in discharge zones. The dominant or sub-dominant cation is sodium in HCO_3-Cl type due to the cation exchange and/or dissolution of halite[18]. However, the dominant cation is magnesium in HCO_3-Cl type of the Group II, which is the most different chemistry compared to natural ground water. In addition, as mentioned above, the low Cl^- concentration in natural ground water suggests there were no natural chlorine sources in the aquifer of the study area; thus external sources of Cl^- existed in this period. The Mg-Ca-HCO_3-Cl-SO_4 type appeared for the first time in 1981 and alternated with Mg-Ca-HCO_3-Cl type for most of the following years. This HCO_3-Cl-SO_4 facies characterizes higher relative concentration of SO_4^{2-} than HCO_3-Cl type, which is primarily led by decreasing of concentration of Cl^-, not by the increasing of concentration of SO_4^{2-} (Fig. 2). The Ca-Mg-HCO_3-Cl-SO_4 type existed only in 2002 and 2004. The cations tend to be dominated with calcium replacing magnesium comparing the Mg-Ca-HCO_3-Cl-SO_4 type. Group II approximately responds to the first and second stage in the above analysis of ground water chemistry.

In group III, two facies of Ca-Na-Mg-HCO_3-Cl and Ca-Na-HCO_3-Cl occurred in 2007 and 2008, respectively. The dominant cation tends to be calcium and sodium tends to act as sub-dominant cation and the relative abundance of Mg^{2+} tends to decrease, which probably results from the cation exchange. Group III approximately responds to the third stage in the above analysis of ground water chemistry.

Thus, the main sequence for hydrogeochemical facies evolution may exist from natural ground water to urban ground water, namely, (Mg-Ca-HCO_3) → (Mg-Ca-HCO_3-Cl) → (Mg-Ca-HCO_3-Cl-SO_4) and the rapid change of facies occurred in a few years. These have a great difference from that in natural alluvial ground water. In natural ground water, hydrogeochemical facies in fixed location generally keep constant in hundreds of years due to steady geological, hydrological and meteorological conditions. Thus the rapid change of hydrogeochemical facies is an indication of urban ground water. In addition, the facies of Mg-Ca-HCO_3-Cl and Mg-Ca-HCO_3-Cl-SO_4 rarely occur in natural alluvial ground water. Although the HCO_3-Cl type usually occurs in natural ground water, the dominant cation is sodium. The facies of Mg-Ca-HCO_3-Cl and Mg-Ca-HCO_3-Cl-SO_4 are likely the unique ones occurring only in urban ground water.

Saturation index: The equilibrium of ground water with respect to one or more mineral phases and the potential for mineral precipitation or dissolution can be determined using the saturation index (SI), which is based on the relation between analytic activities (the ion activity product, IAP) and the thermodynamic calculation of the solubility product (K_{sp}). The saturation index of a mineral is determined using the following equation[19]

$$SI = \log_{10} \frac{IAP}{K_{sp}} \quad (1)$$

when SI > 0 the solution is theoretically oversaturated with respect to that the mineralization and precipitation may be expected. For SI = 0, the mineral and solution are in equilibrium and neither dissolution nor precipitation is predicted to occur. When SI < 0, the solution is theoretically undersaturated with respect to the minerals and if this condition is present in the system, dissolution might be possible.

In this study, saturated indices were obtained from the geochemical modeling program PHREEQC[20]. Fig. 4 shows the result of SI calculations for the ground water with respect to specific minerals, including calcite, aragonite, dolomite, gypsum, anhydrite and halite.

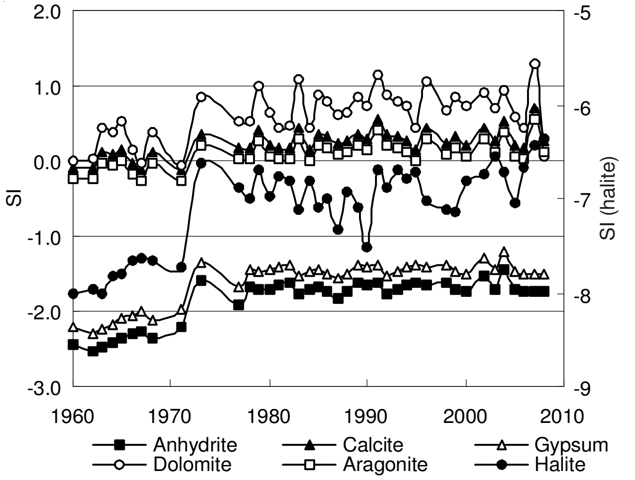

Fig. 4. Trend of saturation indices of calcite, aragonite, dolomite, gypsum, anhydrite and halite from 1960 to 2008

In Fig. 4, the SI values for six minerals showed wave-shaped increasing as a whole from 1960-2008. The magnitude sequence of SI for the six minerals in the same year is as follow: $SI_{dolomite} > SI_{calcite} > SI_{aragonite} > SI_{gypsum} > SI_{anhydrite} > SI_{halite}$. For dolomite and halite, the values of SI exhibit a great interannual variability, while they present a slight interannual fluctuation for calcite, aragonite, gypsum and anhydrite. The SI curves for calcite and aragonite in Fig. 4 show close shape and magnitudes for the whole period due to the similarity of chemical construction and constitution, as well as gypsum and anhydrite.

The SI values for dolomite have seven wave crests in Fig. 4 and show a repetition process with dissolution and precipitation for dolomite. The maximum SI value was 1.29 in 2007 and a great decrease occurred in 2008, which was ultimately down to 0.06 indicating a near equilibrium state (SI = 0) (Fig. 4). The SI curve shape for calcite and aragonite is identical to that for dolomite and wave crests and wave troughs have a same pattern for the three minerals for the whole period (Fig. 5). Thus the repetition process of dissolution and precipitation also occurred for calcite and aragonite. The maximum SI values for calcite and aragonite were 0.70 and 0.55 in 2007, respectively and they decreased to 0.25 and 0.10 in 2008, respectively, which indicate an undersaturated condition with respect to calcite and aragonite. The SI values for halite, gypsum and anhydrite were negative from 1960-2008, which indicate undersaturated conditions with respect to the three minerals. Thus dissolution process occurred and the SI values increase in most time. However, the obvious precipitation processes for gypsum and anhydrite occurred in 1973-1977 and 2004-2005 and for halite, there were several precipitations as well. The maximum SI values for halite, gypsum and anhydrite are -6.35, -1.19 and -1.43, respectively (Fig. 4). The dissolution and precipitation processes for the six minerals showed that although the dissolution process is theoretically expected to occur when SI < 0, it could occur when SI > 0 and although the precipitation process is theoretically expect to occur when SI > 0, it could occur when SI < 0. These phenomena illustrate that the critical SI value controlling the transition between dissolution and precipitation for minerals is not always applicable for all the time.

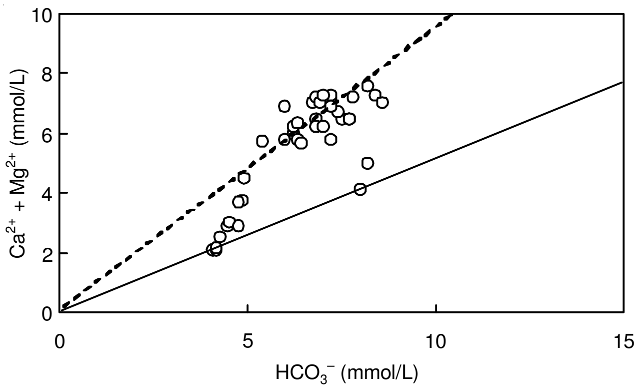

Fig. 5. Relation between Ca^{2+}+Mg^{2+} and HCO_3^- in 1960-2008. Dashed line denotes (Ca^{2+}+Mg^{2+})/HCO_3^- = 1 and solid line denotes (Ca^{2+} + Mg^{2+})/HCO_3^- = 0.5

In addition, the SI values for the six minerals were different from natural ground water to urban ground water. In the natural state in the early 1960s, the ground water was undersaturated with respect to the six minerals according to their negative SI values. The SI values characterize a steady change with slow hydrogeochemical process. In the anthropogenic state from 1970-2008 the SI values exhibited an inconstant occurrence, namely increase or decrease with a sharp fluctuation, which is related to the rapid change of ions concentration in the urban ground water.

RESULTS AND DISCUSSION

Urbanization influences: Beijing's urban area was bordered by the 2nd ring road before 1949. Since the late

1950s, areas between the 2nd and the 3rd ring road that were formerly farmland have partly become residential or commercial districts and had been completely urbanized in the early 1980s. The reform and open-door policy beginning in the early 1980s brought a rapid urbanization primarily driven by the industrial development, including township and village enterprises and economic and industrial development zone[21,22]. From 2000, Beijing started to implement a scheme to move out the industries located within the 4th ring road and tended to make these areas become residential or commercial areas.

The urbanization process responded well to the evolution stages for ground water quality mentioned above. It did not yet greatly affect the ground water quality at the beginning of urbanization before 1968 in the study area and the hydrochemical facies belonged to Mg-Ca-HCO_3 and represented the natural ground water. From 1969 to 1979, the urbanization process was characterized by the residential or commercial development, thus major ions greatly increased and the hydrochemical facies transformed into Mg-Ca-HCO_3-Cl. From 1980 to 2000, with industrial activities in urbanization, the higher relative concentration of SO_4^{2-} occurred and the facies of Mg-Ca-HCO_3-Cl-SO_4 or Ca-Mg-HCO_3-Cl-SO_4 appeared. After 2000, the industrial activities were reduced; therefore, the facies of HCO_3-Cl type became a dominant hydrochemical facies.

Nitrate in ground water is the most common composition in urbanization. Urban waste, domestic and industrial sewage and septic tanks contain higher concentration of NO_3^- and thus act as the NO_3^- sources of ground water. It is easy to discriminate the NO_3^- pollution in contaminated urban ground water and natural ground water due to the appearance of lower concentration in the latter. Thus, although NO_3^- is associated with the complex biochemical reaction which can change the concentration of NO_3^-, it still is the most sensitive indicator for evaluating the water quality of urban ground water[17]. In the present study, the evolution of NO_3^- in the ground water from 1960 to 2008 had a clear relation with the level of local urbanization process consequentially (Fig. 2). The remarkable increasing of NO_3^- concentration from 1964 to 1979 was a response to the initial urbanization. It is noted that the NO_3^- of ground water underwent the biochemical reaction, such as nitrification and denitrification, thus the data did not exactly reflect the loading of nitrogen.

Cl^- is a conservative ion suitable for indicating the urban ground water quality. However, it is generally associated with a higher concentration in natural ground water in arid or semi-arid areas which make it difficult to identify pollution in urban ground water. In this study, the evolution stage of Cl^- was similar to the NO_3^- as shown in Fig. 2. Thus, it was also attributed to the urbanization.

Actually, besides NO_3^- and Cl^-, the concentration of Ca^{2+}, Mg^{2+}, K^+, Na^+, HCO_3^- and SO_4^{2-} also had a significant increase in urban expansion period from 1964 to 1979, which demonstrates urbanization impact on major chemical composition above, not only on individual composition.

Mineral weathering: Rock weathering is often considered as a significant source to the composition of ground water. The carbonate and silicate are two kinds of minerals existing commonly in aquifers and in the vadose zone and they are the most important minerals for composition of natural water from the standpoint of reactivity[23]. Carbonate minerals such as calcite and dolomite largely influence the water chemistry because their dissolution rates are up to six orders of magnitude faster than those of aluminosilicate minerals[24]. Dissolution reactions of carbonate and dolomite can be described as[25]:

$$CaCO_3 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- + OH^- \qquad (2)$$

$$CaMg(CO)_3 + 2H_2O \rightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^- + 2OH^- \qquad (3)$$

According to the above dissolution reactions of carbonate and dolomite, if $Ca^{2+}$and Mg^{2+} originate only from dolomite dissolution, the molar ratio of Ca^{2+} to Mg^{2+} would be about 0.5:1 and if they originate only from calcite dissolution, their molar ratio is about 1:1. A scatter diagram of (Ca^{2+}+ Mg^{2+}) *versus* (HCO_3^-) and (Ca^{2+}+ Mg^{2+}) *versus* (HCO_3^-) is used to identify the carbonate and dolomite dissolution, respectively. The molar ratios of (Ca^{2+} + Mg^{2+}) to HCO_3^- between 1960 and 2008 in the study area are shown in Fig. 5 and the variation of molar ratios with time is shown in Fig. 6. In the early 1960s, the ratio of (Ca^{2+} + Mg^{2+}) to HCO_3^- was about 0.5:1, below 1:1. A deficiency of Ca^{2+} and Mg^{2+} relative to HCO_3^- existed and the excess negative charge of HCO_3^- must be balanced by K^+ and Na^+, which implies that the silicate dissolution also occurred besides carbonate dissolution. From 1964 to 1973, the ratio gradually increased to 1:1 and it was maintained until 2006. This ratio illustrates that silicate dissolution was inhibited and Ca^{2+}, Mg^{2+} and HCO_3^- were controlled by the equilibrium with carbonate dissolution. In 2007 and 2008, the ratio of (Ca^{2+} + Mg^{2+}) to (HCO_3^-) returned to about 0.5:1 and Ca^{2+} and Mg^{2+} depletion was the result of cation exchange which was different from that in the early 1960s. Thus carbonate dissolution was still preferential in these 2 years. Some of the results occurring above the expected 1:1 relation line in Fig. 6 indicate that the other equilibrium with Ca^{2+} and Mg^{2+} must exist. In addition, the molar ratio of Ca^{2+}-Mg^{2+} was *ca.* 0.7 and this ratio illustrates that dolomite dissolution prevail over calcite dissolution.

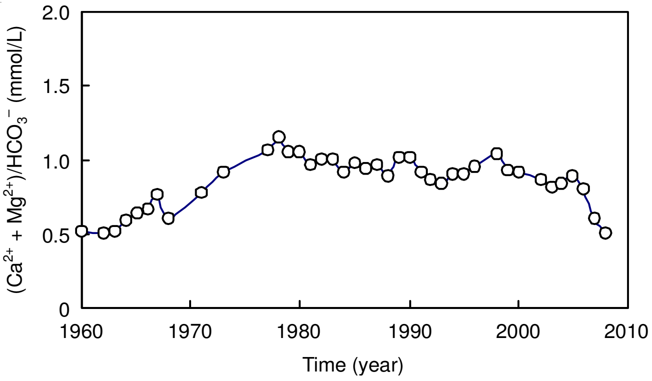

Fig. 6. Trend of the ratios of Ca^{2+}+Mg^{2+} to HCO_3^- from 1960 to 2008

Therefore, both equilibrium of silicate and carbonate dissolution occurred in natural ground water and the carbonate dissolution equilibrium occurred in the urban ground water and controlled the Ca^{2+}, Mg^{2+} and HCO_3^- concentrations. The mineral dissolution transformation from both silicate and carbonate dissolution to carbonate dissolution likely resulted from the decrease of pH (Fig. 2). pH plays a vital role in mineral dissolution and the solubility of most of minerals increases with decreasing of pH value. Especially carbonate is more susceptible to pH value than silicate[25]. In the study area, pH values decreased from 7.5 in 1964 to 7.2 in 1973 and this change accelerated carbonate dissolution and made the carbonate dissolution become a prevailing hydrogeochemical process.

In addition, gypsum is the common mineral in the aquifer of semi-arid areas. In the dissolution reactions of gypsum, the molar ratio of Ca^{2+} to SO_4^{2+} would be about 1:1[25]. Molar ratios of Ca^2 to SO_4^{2+} between 1960 and 2008 were about 2:1 in the study area. There was an apparent excess of Ca^{2+} with respect to gypsum dissolution equilibrium, which can probably be interpreted as excessive positive charge being balanced by HCO_3^-. However, a linear relation between Ca^{2+} and SO^{2+} occurs, which illustrates that Ca^{2+} and SO^{2+} are likely controlled under the gypsum dissolution equilibrium.

The discussion demonstrates that the Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2+} are in the equilibrium with responding mineral dissolution. However, it does not exactly illustrate that the Ca^{2+}, Mg^{2+} HCO_3^- and SO_4^{2+} originate from these mineral dissolution due to numerous anthropogenic input related these ions in urbanization activities. Obviously, these ions originating from either mineral dissolution or anthropogenic input are under the control of responding mineral dissolution equilibrium.

Cation exchange: Cation exchange is an important hydrogeochemical process, which directly affects the cations re-distribution, especially for (Ca^{2+} + Mg^{2+}) and Na^+. The exchangeable sodium in the clay tends to exchange for calcite and magnesium in water, which could result in an increase of Na^+ concentration and a decrease of Ca^{2+} and Mg^{2+}. The process can be described by the following equation[25]:

$$Ca^{2+}(\text{water}) + Mg^{2+}(\text{water}) + Na_2(\text{clay}) = Ca(\text{clay}) + Mg(\text{clay}) + 2Na^+(\text{water}) \qquad (4)$$

In order to identify the cation exchange in the study area, a diagram of Ca^{2+} + Mg^{2+}-HCO_3^--SO_4^{2-} *versus* Na^+-Cl^- was performed (Fig. 7) and the temporal ratios of these two parameters with time were also examined (Fig. 8). Na^+-Cl^- represents the amount of Na^+ gained or lost relative to that provided by chloride salt dissolution (mostly halite dissolution) and Ca^{2+}+Mg^{2+}-HCO_3^--SO_4^{2-} represents the amount of Ca^{2+} and Mg^{2+} gained or lost relative to that provided by gypsum, calcite and dolomite dissolution. In the case of absence of this process, all the data should be close to the origin and if this process has a significant controlling of the compositions, the relation between these two parameters should be linear with a slope of -1[26,27].

Fig. 7 shows that the relation between these two parameters is linear and most of data are close to the line. This linear relation is very clear in Fig. 8. The ratio of Ca^{2+}+Mg^{2+}-HCO_3^--SO_4^{2-} to Na^+-Cl^- was -1 in the early 1960s (natural ground water mentioned above), which indicates the occurrence of Ca (Mg) -Na exchange in the natural ground water. The ratios between these two parameters had a clear deviation from -1, down to -1.5 in 1964-1978 (the first stage) and they were expected to be disturbed by a remarkable increase of Cl^- in 1964-1968 which led to a smaller denominator value of Na^+-Cl^-. The ratio values were nearly close to -1 from 1979-2005 (the second stage) which were also disturbed by the higher concentration of Cl^-. In both 2007 and 2008 (the third stage), the ratios tended to arise to 0.8 due to a significant decrease of Mg^{2+} in 2007-2008 which resulted in a smaller numerator value of Ca^{2+}+ Mg^{2+}-HCO_3^--SO_4^{2-}. Therefore, the relation between these two parameters was affected by some ions related to human activities. However, they were nearly linear and the most of ratio values deviate just slightly from -1. This result illustrates that Ca(Mg)-Na exchange was the primary hydrogeochemical process in the study area and it had partial contribution to composition of Ca^{2+}, Mg^{2+} and Na^+. The results also demonstrates that it is a reliable method of examining cation exchange in urban ground water using the ratio of Ca^{2+} + Mg^{2+}-HCO_3^--SO_4^{2-} to Na^+-Cl^-.

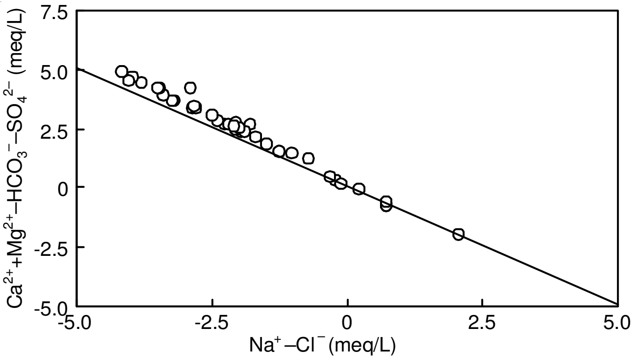

Fig. 7. Relation between Ca^{2+} + Mg^{2+}-HCO_3^--SO_4^{2-} and Na^+-Cl^- in 1960 to 2008

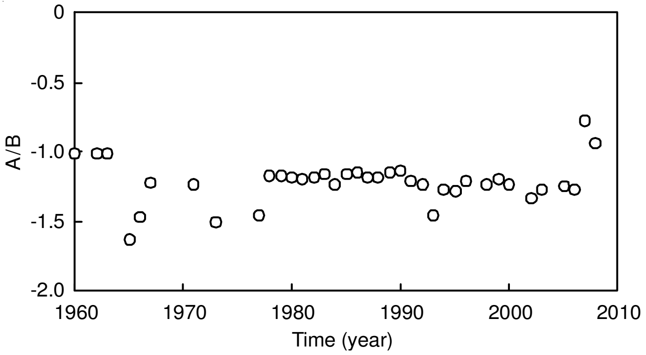

Fig. 8. Trend of the ratios of Ca^{2+} + Mg^{2+}-HCO_3^- - SO_4^{2-} to Na^+-Cl^- from 1960 to 2008. On the axis of ordinate, A denotes the values of Ca^{2+}+Mg^{2+}-HCO_3^--SO_4^{2-} and B denotes the values of Na^+-Cl^-

Furthermore, the Ca(Mg)-Na exchange can interpret a deficiency of Ca^{2+} and Mg^{2+} relative to HCO_3^- with respect to carbonate dissolution. As mentioned above, many ratio values of Ca^{2+} + Mg^{2+} to HCO_3^- were less than 1, which resulted from removing of Ca^{2+}+Mg^{2+} from the ground water due to Ca (or Mg)-Na exchange. Exceeding negative charges were balanced by Na^+ which migrated into the water from clay. The phenomena of the significant concentration increase of Na^+ in 2007-2008 can also be interpreted as the result of Ca (or Mg)-Na exchange.

Conclusion

In this study the ground water chemistry data for Beijing urban area in northwest of the North China Plain was analyzed to determine hydrogeochemical evolution with time under urbanization. Water quality data in 49 years from 1960 to 2008 were employed to demonstrate the impact of urbanization on ground water quality by hydrogeochemical methods. The following major conclusions can be drawn from the study. Urbanization had a significant impact on major ground water composition of Ca^{2+}, Mg^{2+}, K^+, Na^+, HCO_3^-, Cl^-, NO_3^- and SO_4^{2-}.Cl^- and NO_3^- primarily originate from urban activities. Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-} were partially attributed to carbonate and sulfate mineral dissolution as well as from anthropogenic input and these ions were under the control of responding mineral dissolution equilibrium no matter where they originated from. Urbanization processes responded to the different hydrogeochemical facies. The transformation of hydrogeochemical facies from natural groundwater to urban groundwater had an evolutional sequence: (Mg-Ca-HCO_3) → (Mg-Ca-HCO_3-Cl) → (Mg-Ca-HCO_3-Cl-SO_4), which were associated to three stages in urbanization process, respectively: the un-urbanization, residential and commercial process and industrial process. The change of facies occurred rapidly in a few years. The facies of Mg-Ca-HCO_3-Cl and Mg-Ca-HCO_3-Cl-SO_4 were the unique ones that occurred only in the urban groundwater. The saturation indices of calcite, aragonite, dolomite, gypsum, anhydrite and halite kept a wave-shaped increase from natural ground water to urban ground water. In urban ground water, mineral dissolution could occur when $SI > 0$ and mineral precipitation could occur when $SI < 0$. The critical SI value controlling the transition between dissolution and precipitation for these mineral was not always applicable to all hydrogeochemical conditions.

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