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Changes of hydrochemical composition and heavy metals concentration in shallow groundwater from karst hilly areas in Guiyang region, China

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Abstract: The quality changes of shallow groundwater from karst hilly areas in Guiyang region of China impacted by the urbanization were investigated. The results show that the major ions in shallow groundwater from the karst hilly areas are mainly composed of HCO_3^-, SO_4^{2-}, Ca^{2+} and Mg^{2+}, and the concentrations scopes of NO_3^-, Cl^-, K^+ and Na^+ of the groundwater in agricultural, residential and industrial areas are 4.5−9.6, 2.8−7.1, 3.9−6.3 and 2.5−4.9 times higher than those in the forest areas, respectively. The concentrations of As, Pb and Cd of shallow groundwater in the industrial areas are also significantly enhanced, followed by those in the residential areas and the agricultural areas. The concentrations of NO_3^-, SO_4^{2-}, As, Pb and Cd of the groundwater in the industrial areas and those of NO_3^-, SO_4^{2-}, As and Cd of shallow groundwater in the residential areas reach grade Ⅲ of the Groundwater Quality Standard of China (GB/T 14848—93), while the concentration of NO_3^- in the groundwater from the industrial areas exceeds grade Ⅴ. With the process of urbanization, NO_3^- is the key factor to influence the groundwater quality in karst hilly areas, followed by SO_4^{2-}, As, Pb and Cd.

Key words: karst hilly areas; shallow groundwater; urbanization; heavy metals; Guiyang

1 Introduction

Guizhou Province of China, covers a large typical karst area of more than 1×10^5 km^2, with a serious problem to constrain the sustainable development of this area due to the karst rocky desertification [1]. In karst hilly areas, dissolution lacunae, sink holes, underground conduits, and karst caves are common, which permit the rapid transport of groundwater and are susceptible to rapid introduction of contaminants since the conduit system receives localized inputs from surface streams [2−4]. So, the water environmental quality in karst areas is very fragile. Groundwater is a very important source for water supply in karst areas. In recent years, however, the use of groundwater for water supply in karst areas has been limited by the decrease in quantity or the deterioration in quality of aquifers.

Urban karst systems were typically considered more vulnerable to contamination and excessive storm discharge because of potential source areas, increasing sediment loading, and focusing of water from impervious surfaces [5]. The recovery of disturbed karst water environments was difficult in karst hilly areas and groundwater resource management became increasingly important for sustainable development in karst areas [2, 6−9]. Karst water chemistry was controlled by weathering of limestones and dolostones, and use of land [10−11]. The precipitation and human activities, however, also had a definite influence on the hydrogeochemistry of the waters [4, 12−13]. With the rapid increase of population in recent years, groundwater quality degraded greatly [14−15]. Therefore, studies of the geochemical properties and the processes of the shallow groundwater in karst areas are necessary in order to elucidate the karst environmental problems. The main objectives of this work were: (1) to study the hydrochemical composition of groundwater from wells or springs in karst hilly areas of Guiyang region in order to elucidate the major relationship among plant-rock-water systems and, (2) to identify the changes of groundwater quality in the process of urbanization, which provided a scientific basis for the protection and sustainable utilization of groundwater resources in karst areas.

2 Experimental

2.1 Background of sampling region

Guizhou Province, with carbonate rocks exposure covering more than 60% of the entire areas, is located in

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the center of the southeast Asian karst region where karstification is well developed and there are many diverse karst types [16]. In this work, the studied region is associated with the Guiyang City, the capital of Guizhou Province. The Guiyang region is located in the central areas of Guizhou Province. It covers an area from 25.19° to 27.24° N and from 107.95° to 108.22° E, with altitudes ranging from 950 to 1 240 m above the mean sea level, which has karst hills with a subtropical warm-moist climate, annual average temperature of 15.2 ℃ and annual precipitation from 1 100 to 1 200 mm. In this region, rainy season is from May to August with over 70% of the total rainfall, and dry season is focused on the period of autumn and winter.

Karst primeval forest in Guizhou Province is a subtropical evergreen broad-leaf forest, but it becomes secondary forest in most karst areas [17]. Dense forests are gradually reduced by irrational, intensive land use and urbanization, while vegetation coverage is continuously reduced, leading to the increase in the intensity of karst ecological environment degradation. With the rapid increase of population and live together in villages, most of karst hilly areas have a very high rate of land for agriculture and plant crops, such as corn, rice, rape, vegetables and tobacco.

In this work, 66 samples were collected in karst hilly areas of Guiyang region. Nine sampling spring points were selected from the karst secondary forest areas, where the forest coverage was 45%−70% and the vegetation coverage was 85%−95%. Compared with karst forest areas, there were higher population density in the villages and higher intensity agricultural activities in agricultural areas, where four sampling spring points were chosen. In central areas of Guiyang City with high density of population, five sampling spring points were selected as the studied residential areas. Industrialization was an important sign for urbanization. An industrial park of Guiyang City, which was an important industrial base of aluminum in China, was selected as the studied industrial areas with four sampling spring points. The sampling spring points were all erosion springs and water perennially flowed from dissolving gap. The sampling sites were along the land use succession from forest areas, agricultural areas and residential areas to industrial areas in the studied region. Groundwater samples were collected from the springs in the selected areas of the above description in April (rainless period), August (high water period) and December (median water period) of 2008, respectively.

2.2 Sampling and analysis

Each sample was collected with the three 500 mL polyethylene bottles, which were cleaned with acid and rinsed with deionized water prior to sampling. Reagent-quality HNO_3 was added in polyethylene bottle until pH of samples reached 1 for trace element analysis. Parameters including pH and electrical conductivity (EC) were measured and recorded at the sampling sites using portable EC meter and pH meter, which were calibrated before use. Then, water samples were filtered through 0.45 μm millipore filter paper in the laboratory and analyzed for cations (K^+, Na^+, Ca^{2+} and Mg^{2+}) and anions (HCO_3^-, Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}). All analytical methods were followed by the procedures described by the National Standard Methods of China. Especially, concentrations of K^+ and Na^+ were determined by flame spectrometry, concentrations of Ca^{2+} and Mg^{2+} were determined by atomic absorption spectroscopy, while the concentration of HCO_3^- was analyzed by electric potential titration method, the concentration of PO_4^{3-} was determined by the molybdenum blue of colorimetric method, the concentration of NO_3^- was analyzed by ultraviolet spectrophotometric method, the concentration of SO_4^{2-} was determined by EDTA indirect titration method, and the concentration of Cl^- was analyzed by nitrate silver titration method. Water samples for trace elements were treated by acid digestion and then aliquots were determined by inductively coupled plasma mass spectrometry (X2 ICP−MS, Thermo Electron Corporation, USA).

2.3 Statistical analysis

Statistical analysis was performed on the data using the SPSS software (version 13.0). The significance of data was based on multiple comparisons by SSR (Duncan's new multiple range method).

3 Results and discussion

3.1 Hydrochemistry characteristics of shallow groundwater in karst hilly areas

The chemical components of the shallow groundwater in karst hilly areas are listed in Table 1. The studied groundwater presents pH values ranging from 6.07 to 8.44, while EC varies widely from 47 to 1 186 μS/cm. The major ions in shallow groundwater from the karst hilly areas are composed of HCO_3^-, SO_4^{2-}, Ca^{2+} and Mg^{2+}, and the concentrations of HCO_3^-, SO_4^{2-}, Ca^{2+} and Mg^{2+} in the groundwater are 132.3−278.2, 30.0−334.0, 42.2−256.3 and 4.1−57.2 mg/L, respectively. The concentration of HCO_3^- is the highest among the anions while that of Ca^{2+} is the highest among the cations. The results indicate that the groundwater in the karst hilly areas is typical Ca-HCO_3 type water, and the characteristics of groundwater are similar to those of the surface water in this region [4, 12]. The studied groundwater hydrochemical characteristics are mainly

Table 1 pH, EC and concentrations of main ions of shallow groundwater

Area	pH	EC/(μS·cm^{-1})	$\rho(Ca^{2+})$/(mg·L^{-1})	$\rho(Mg^{2+})$/(mg·L^{-1})	$\rho(Na^{+})$/(mg·L^{-1})	$\rho(K^{+})$/(mg·L^{-1})
Forest area (*n*=27)	7.34±0.38	356.4±231.3	66.9±18.3^{b}	15.7±10.2^{b}	3.65±4.55^{c}	1.31±1.46^{b}
Agricultural area (*n*=15)	7.79±0.34	691.7±118.9	101.5±21.2$^{a, b}$	28.7±10.5$^{a, b}$	12.9±9.54$^{a, b}$	6.40±6.89$^{a, b}$
Residential area (*n*=12)	7.44±0.05	915.3±61.9	142.4±52.0^{a}	45.1±6.84^{a}	21.4±5.50^{a}	9.55±6.27^{a}
Industrial area (*n*=12)	7.49±0.10	848.3±160. 8	117.5±33.9$^{a, b}$	45.1±8.57^{a}	15.3±8.75$^{a, b}$	8.06±5.90$^{a, b}$

Area	$\rho(HCO_3^{-})$/(mg·L^{-1})	$\rho(SO_4^{2-})$/(mg·L^{-1})	$\rho(NO_3^{-})$/(mg·L^{-1})	$\rho(PO_4^{3-})$/(mg·L^{-1})	$\rho(Cl^{-})$/(mg·L^{-1})
Forest area (*n*=27)	214.5±47.8^{a}	61.1±13.3^{c}	4.04±5.08^{c}	0.011±0.008^{c}	4.35±6.13^{c}
Agricultural area (*n*=15)	218.5±4.67^{a}	129.6±25.0^{b}	22.2±17.2$^{a, b}$	0.039±0.074^{b}	16.6±9.43$^{b, c}$
Residential area (*n*=12)	173.3±38.7^{a}	192.9±38.1^{a}	26.4±4.14$^{a, b}$	0.093±0.083^{a}	35.2±6.00^{a}
Industrial area (*n*=12)	171.9±48.8^{a}	191.2±22.6^{a}	42.9±34.2^{a}	0.010±0.012^{c}	27.3±13.9$^{a, b}$

Note: Line with letters is mean± SD and different letters in the same column mean at significance $P<0.05$ level based on multiple comparisons by SSR.

influenced by the dissolution of limestone and dolomite chemistry weathering to obviously affect the chemical composition of groundwater in the karts hilly areas. The result shows that the chemical compositions of shallow groundwater from various areas are different due to the changes of land use ways.

The results based on multiple comparisons by SSR show that the concentrations of NO_3^{-}, Cl^{-}, K^{+} and Na^{+} are obviously enhanced in the groundwater with forest lands converted to agricultural lands, residential lands and industrial lands (Table 1). The concentration scopes of NO_3^{-}, Cl^{-}, K^{+} and Na^{+} of the groundwater in agricultural, residential and industrial areas are 4.5−9.6, 2.8−7.1, 3.9−6.3 and 2.5−4.9 times higher than those in the groundwater from the forest areas, respectively. The concentrations of SO_4^{2-}, PO_4^{3-}, Ca^{2+} and Mg^{2+} of the groundwater in agricultural, residential and industrial areas, however, are changed slightly. The chemical composition of the groundwater is significantly impacted by forest degradation, reclamation and cultivation, and urbanization. Therefore, chemical properties of shallow groundwater in the karst hilly areas are controlled both by natural geochemical processes and anthropogenic activities. The intensive anthropogenic promotes the intensity and the velocity of karst environmental degradation, including serious degradation of natural vegetations, intensive water and soil loss, and more pollutants putting into water bodies. So, it changes the interaction of surface/ground water, transport, transformation and provenances of contaminants to influence the hydrochemical environment of karst groundwater system.

3.2 Effect of agricultural activities on environmental quality of shallow groundwater

In studied region, most of deforestation lands are converted to farmland. The higher rate of land reclamation and agricultural activities change the chemical composition of the groundwater. The results show that the agricultural activities mainly contribute to the relatively high concentrations of NO_3^{-}, PO_4^{3-} and K^{+} in the groundwater (Table 1), and the average concentrations of NO_3^{-}, PO_4^{3-} and K^{+} of the groundwater in agricultural areas are 4.5, 2.5 and 3.9 times larger than those from the forest areas, respectively. Meantime, the concentrations of Ca^{2+} and Mg^{2+} in groundwater significantly increase.

The sources of NO_3^{-}, PO_4^{3-} and K^{+} of the groundwater are contributed to the application of fertilizers, including N fertilizer (mainly urea), P fertilizer (mainly calcium superphosphate), K fertilizer (mainly potassium sulfate), and organic fertilizer. In karst hilly areas of Guiyang region, agricultural soils are mainly upland fields cultivated with crops including corn, tobacco and generally apply the fertilizers of 12−15 g/m^2 N and 7.5−12 g/m^2 P_2O_5 in the soils with pH of 7.0−8.0 and soil depth of 30−80 cm in intensive agricultural regions, while additional 6−9 g/m^2 K_2O is applied in the soils planting tobacco. Irrational fertilizing causes discharges of N and P to surface waters or groundwater. In addition, the concentration of SO_4^{2-} of the groundwater in agricultural areas is obviously increased, and its average value is 1.1 times higher than that in the forest areas. The sources of SO_4^{2-} are mainly contributed to the application of fertilizers containing H_2SO_4. In karst agricultural areas, the concentrations of Hg, Cd, Cr, Pb and As of shallow groundwater are all increased (Table 2), and the concentrations of Cd and As of the groundwater are about 1.0 times higher than those of the groundwater in forest areas.

The concentration of NO_3^- of the groundwater in the agricultural areas during high water period is higher than that of the rainless period and median water period (Fig.1). The variations in chemical composition of groundwater under the condition of crop plantations demonstrate an active interaction or mass exchange between agricultural drainage and groundwater in karst environments. Therefore, compared with karst forest areas, the chemical composition of the groundwater in karst agricultural areas is typically characterized with the relatively high NO_3^- concentration (7.2−50.3 mg/L). According to the Groundwater Quality Standard of China (GB/T 14848—93), the average concentration of NO_3^- in the groundwater from the agricultural areas exceeds grade Ⅲ, while that of the groundwater from the forest areas is under grade Ⅱ.

3.3 Effect of industrial activities on environmental quality of shallow groundwater

Industrial wastewater and sewage discharge mainly influence the groundwater quality in the studied industrial areas. The results show that the concentrations of NO_3^-, SO_4^{2-}, Cl^- and Mg^{2+}, K^+, Na^+ of groundwater from this region are obviously enhanced. The average concentrations of NO_3^-, Cl^- and SO_4^{2-} of the groundwater are 1.9, 2.1 and 1.5 times as high as those in agricultural areas, respectively (Table 1). Especially, the concentration of NO_3^- (21.2−93.6 mg/L) is the highest among the four studied areas. So, nitrate is the most typical ion disturbed in the karst groundwater, which is significantly influenced by industrial activities. The concentration of SO_4^{2-} of shallow groundwater in the industrial areas is significantly higher than that in the forest and agricultural areas. The sources of SO_4^{2-} are mainly considered to result in burning coal for daily energy needs by industrial production process or local inhabitants [4, 12].

In industrial areas, the concentrations of heavy metals, such as Hg, Cd, Cr, Pb and As of shallow groundwater are also the highest among the four studied areas (Table 2). The results show that extensive industrial activities are contributed to Cd concentration

Table 2 Concentrations of As, Cd, Cr, Hg and Pb of shallow groundwater

Area	ρ(Hg)/(ng·L^{-1})	ρ(As)/(mg·L^{-1})	ρ(Cd)/(mg·L^{-1})	ρ(Cr)/(mg·L^{-1})	ρ(Pb)/(mg·L^{-1})
Forest area (n=27)	6.43±4.62	0.008±0.002	—	0.000 8±0.001	0.001 3±0.001
Agricultural area (n=15)	9.32±4.75	0.014±0.007	0.001±0.002	0.001 3±0.001	0.002 5±0.001
Residential area (n=12)	10.9±3.47	0.028±0.008	0.004±0.002	0.004 2±0.001	0.006 3±0.002
Industrial area (n=12)	14.4±1.56	0.033±0.004	0.0064±0.003	0.006 0±0.002	0.021 0±0.008

* Line is mean ±SD.

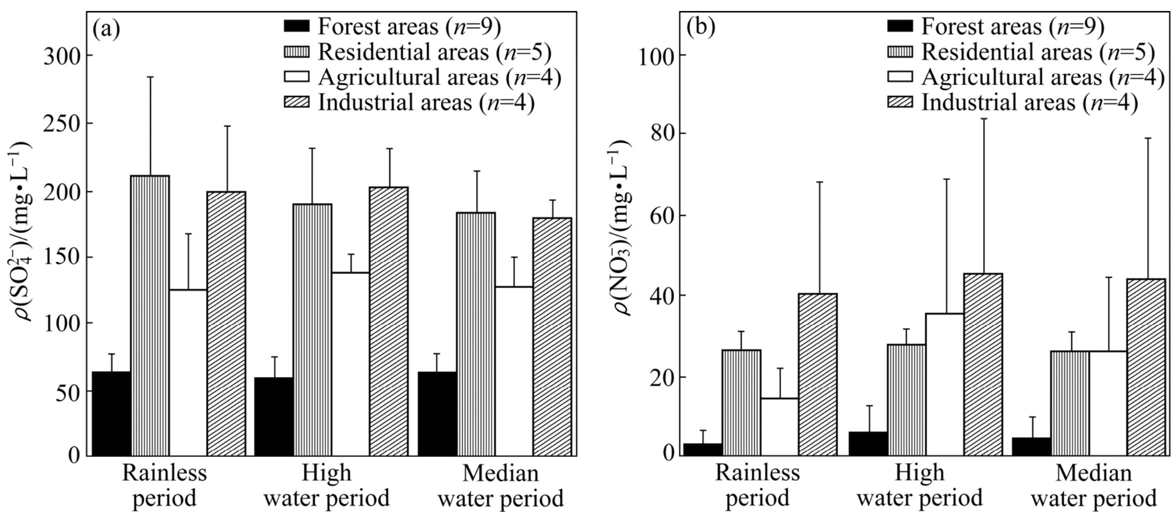

Fig.1 Concentrations of SO_4^{2-} (a) and NO_3^- (b) of shallow groundwater in Guiyang region

(0.004−0.008 mg/L), Pb concentration (0.015−0.026 mg/L) and As concentration (0.027−0.041 mg/L), and the average concentrations of Cd, Pb and As in the groundwater are 6.4, 8.4 and 2.4 times as high as those in the agricultural areas, respectively. The overall trends of heavy metal concentrations of shallow groundwater are basically the same during the rainless water period, high water period and median water period (Fig.2), and the

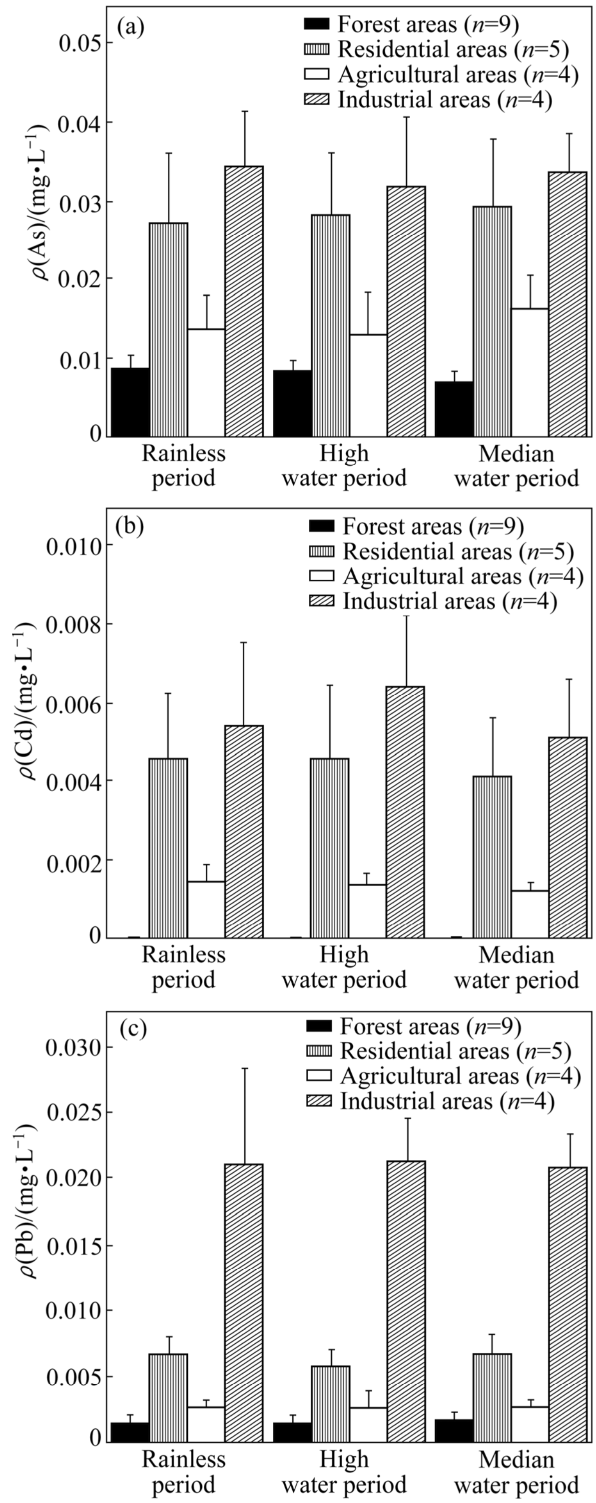

Fig.2 Concentrations of As (a), Cd (b) and Pb (c) of shallow groundwater in Guiyang region

concentrations of heavy metals of shallow groundwater in the industrial areas are significantly higher than those in the residential areas, followed by those from the agricultural areas and forest areas, respectively. According to the Groundwater Quality Standard of China, the concentrations of SO_4^{2-}, As, Pb and Cd of the groundwater in industrial areas reach grade Ⅲ. Especially, the concentration of NO_3^- of the groundwater exceeds grade Ⅴ.

3.4 Effect of residential activities on environmental quality of shallow groundwater

In the studied residential area with high density of population, a lot of sewage discharge into groundwater promoted the intensity and the velocity of water quality degradation. For the groundwater in residential areas, the concentrations of PO_4^{3-}, Cl^-, K^+, Na^+ and Ca^{2+} of groundwater are distinguishably higher than those of the groundwater in agricultural areas or industrial areas, while the concentration of $NO_3^-$of the groundwater is significantly higher than that in agricultural areas. Especially, the concentrations of PO_4^{3-} (up to 0.014−0.128 mg/L) and Ca^{2+} (up to 89.1−176.8 mg/L) are the highest among the four studied areas. The average concentration of SO_4^{2-} of the groundwater in the residential areas or industrial areas is 0.5 times higher than that in the agricultural areas. Similarly, in residential areas, the concentrations of Hg, Cd, Cr, Pb and As of shallow groundwater increase (Table 2), and those of Cd and As in the groundwater are 4.0 and 2.0 times as high as those of the groundwater in agricultural areas, respectively. According to the Groundwater Quality Standard of China, the concentration of NO_3^- of the groundwater in the residential areas exceeds grade Ⅲ, and the concentrations of SO_4^{2-}, As and Cd of the groundwater in the residential areas reach grade Ⅲ.

Urbanization causes a large of domestic sewage as a main source of N and P, and acid rain as a main source of SO_4^{2-} by the coal burning for daily energy. In karst areas, the major anthropogenic components on the surface and in groundwater are K^+, Na^+, Cl^-, SO_4^{2-} and NO_3^-, with NO_3^- being the main contributor to groundwater pollution [4]. In studied areas, the concentrations of NO_3^-, SO_4^{2-} and Cd, Pb, As in the groundwater from the industrial areas and residential areas are always high during the whole years, including rainless period, high water period and median water period (Figs.1−2). The concentrations of NO_3^-, SO_4^{2-}, Cd, Pb and As in the karst hilly areas are also greatly impacted by anthropogenic activities.

Nitrate would be obviously enhanced by geochemical and microbiological activity in the warm season and high water period, and infiltration of rainfall into the ground would accelerate oxidation of nitrogen materials into nitrate and increase nitrate leaching to groundwater [18−20]. So, N is the most typical ion significantly disturbed in the karst groundwater chemistry influenced by anthropogenic activities. The mean concentration of NO_3^- of the groundwater in the studied industrial areas or in the residential areas exceeds the Drinking Water Regulations of European Communities guide concentration of 25 mg/L [21]. Consequently, there is a potential risk of N transfer from surface water to shallow groundwater systems, which are difficult to self-remediate once being contaminated by nitrogen. In studied residential and industrial areas, there are intense human activities that lead to a lot of N putting into the water bodies with lower natural purification to distinguishably cause groundwater quality degradation. Therefore, NO_3^- is the key factor for the quality of the groundwater in karst hilly areas. Groundwater is the most sensitive and the largest body of freshwater in the karst areas and, in particular, also a main source of public drinking water supplies in many regions. It is suggested that the protection of groundwater in karst hilly regions highlights the importance of reducing sources of NO_3^- from surface water to groundwater. However, the concrete effects by the factors influencing groundwater quality and the time course of the groundwater environmental degradation in processing urbanization need further study by site-specific monitoring and data integration.

4 Conclusions

(1) The major ions of shallow groundwater in karst hilly areas are composed of HCO_3^-, SO_4^{2-}, Ca^{2+} and Mg^{2+}, and the chemical properties of shallow groundwater in the karst hilly areas are controlled by natural geochemical processes and anthropogenic activities. The concentrations of NO_3^-, Cl^-, K^+ and Na^+ are obviously enhanced in the groundwater with forest lands being converted to agricultural, residential and industrial lands.

(2) The concentrations of SO_4^{2-}, NO_3^-, Cl^-, Ca^{2+}, Mg^{2+}, K^+ and Na^+ of the shallow groundwater in residential or industrial areas are higher than those from the agricultural and forest areas. Heavy metals, such as Hg, Cd, Cr, Pb and As in shallow groundwater from residential or industrial areas are also significantly enhanced. In industrial areas, the concentrations of NO_3^-, As, Pb and Cd of the groundwater are the highest, while those of PO_4^{3-}, SO_4^{2-}, Cl^- and Na^+ of the groundwater are the highest in residential areas.

(3) In Guiyang region, the concentrations of NO_3^-, SO_4^{2-}, As, Pb and Cd of the groundwater in the industrial areas, and concentrations of NO_3^-, SO_4^{2-}, As and Cd of the groundwater in the residential areas, and concentration of NO_3^- of the groundwater in the agricultural areas reach grade Ⅲ of the Groundwater Quality Standard of China (GB/T 14848—93). Specifically, the concentration of NO_3^- of the groundwater in the industrial areas exceeds grade Ⅴ. With the process of urbanization, NO_3^- is the key factor for the groundwater quality in karst hilly areas, followed by SO_4^{2-}, As, Pb and Cd.

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