HYDROCHEMICAL VARIATIONS OF THE SPRINGS OF JINFO MOUNTAIN, CHONGQING, CHINA

HIDROKEMIJSKE SPREMEMBE IZVIROV NA GORI JINFO, CHONGQING, KITAJSKA

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Abstract

There are 18 springs within the Jinfo Mountain area of Chongqing, SW China (of which 10 epikarst springs are within the National Nature Reserve, and 4 epikarst springs and 4 non-epikarst springs are outside the National Nature Reserve). The hydrochemical characteristics of these springs were measured in 1977, 2004-2009, and 2011. The data show that the hydrochemistry type of springs in different areas, and for different years, is Ca-HCO3 and Ca-HCO3-SO4, whereas the concentrations of SO42– and NO3– are very sensitive to changes in human activities. All the springs with the highest SO42– and NO3– concentrations in the study area showed minimum concentrations in 1977 and an upward trend in concentrations from 2004 to 2008, followed by a period of lower concentrations. Springs with low SO42– and NO3– concentrations were distributed solely at the top of Jinfo Mountain in the National Nature Reserve. The hydrochemical variations observed in springs on Jinfo Mountain demonstrate that the implementation of environmental policy measures and industrial restructuring have successfully contributed to environmental protection of the springs.

Key words: Hydrochemical variations, SO42–, NO3–, human activities, Jinfo Mountain.

IZVLEČEK


Ključne besede: hidrokemijske spremembe, SO42–, NO3–, človekove dejavnosti, gora Jinfo.

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INTRODUCTION

Water is a key resource for human populations, required for drinking and irrigation (Hoek et al. 2001; Kirda 1997), but water scarcity and pollution have become an increasingly important problem in recent years, especially in karst areas. A large typical karst area is found in SW China, covering an area of about 620,000 km², and with a population of 100 million (Zhang et al. 2006; Peng et al. 2011). This karst area is a rich water resource that includes groundwater and epikarst springs. The epikarst zone is important to the storage and migration of the karst water resources, and is very sensitive to human activities because of the “soil upstairs and water downstairs” phenomenon in the karst area.

The hydrochemical features of epikarst springs are probably determined by (1) the interaction of water with soil and rock, (2) allogetic water mixed with epikarst water, and (3) human activities that affect the epikarst water (Zhu & Qian 2005). Many studies have proposed that studying the hydrochemistry of hydrological systems not only reflects the natural conditions, such as soil, vegetation, and lithology, but also provides important information on anthropogenic additions from agricultural activities, industrial sewage discharge and etc. (Stallard & Edmond 1981, 1983, 1987; Edmond et al. 1996; Gaillardet et al. 1999a, b; Grosbois et al. 2000; Barth et al. 2003; Lee et al. 2007; Raymond et al. 2008; Guo et al. 2010). Epikarst springs develop in the epikarst zone, an irregular karst zone occurring in surface carbonate rocks that consists of various individual and micro karst forms resulting from strong karstification processes. Precipitation and surface waters may readily drain into the complex network of subterranean karstic conduits, being retained within the aquifer for long periods before eventually re-emerging elsewhere as a spring. With rapid economic growth and population increase, land use has become one of the most important influences on the quality and viability of groundwater springs, especially in karst areas. Agricultural irrigation, industrial waste, and domestic waste have largely contributed to the contamination of springs. Concentrations of nitrate and sulphate have shown notable increases as a result of the application of large amounts of chemical fertilizers used in agriculture (Compton & Boone 2000; Jiang et al. 2008). Waste water and waste residues produced by the construction of factories and homes cause an increase of pollutants such as nitrogen and sulphate (Wakida & Lerner 2006). Several previous studies have examined the links between human activity and the hydrochemistry of springs in China (Jia & Yuan 2003; Zhang & Yuan 2004).

Jinfo Mountain (Mt. Jinfo) in Chongqing, SW China, is a typical subalpine karst area, and a key research area for karst water systems (Zhang et al. 2011; Gao et al. 2008), land utilization (Li et al. 2005; Zhang 2010), and biodiversity (Dai 2002; Liao et al. 2008). In this study, 14 epikarst springs and 4 non-epikarst springs at different altitudes on Mt. Jinfo were selected specifically for monitoring and a comparison of their hydrochemical variations for 1977, 2004–2009, and 2011. The aim of this study is to investigate the hydrochemical behaviours of springs in subtropical mountainous regions similar to Mt. Jinfo and to gain a general understanding of long-term geochemical variations of epikarst springs and their response to the application of environmental policies and industrial restructuring over these years.

STUDY AREA

Mt. Jinfo is located in the south of Chongqing, China, southeast of the Sichuan Basin (Fig. 1). It is part of Dalou Mountain Range, a typical karst landform formed with 108 peaks. Mt. Jinfo is approximately situated in the area 28°50’N–29°20’N, 107°00′E–107°15′E, and the highest elevation (above sea level) is 2251 m (Wang & Wang 1990). Mt. Jinfo was named as “the National Forest Garden of China” in 1991.

The vertical changes in climate and vegetation from the foot to the top of Mt. Jinfo are significant, including a temperature difference of c. 5–6 °C. The top of the mountain exhibits similar characteristics to temperate climates, with an annual mean rainfall of 1396 mm, and a rainy season from April to October. However, the lower part of the mountain has a subtropical humid monsoon climate, typical for SW China, with an annual average air temperature of 16.6 °C, annual rainfall of 1287 mm, and a rainy season from February to August (Zhang et al. 2011).

The geological structure of this area is a wide and gentle syncline, and includes fault structures along the NE–SW-oriented major tectonic line. The carbonate rock outcrop covers approximately two-thirds of the entire study area. The surface of Mt. Jinfo is underlain by...
Permian limestone ($P_{1}$) above 2000 m a.s.l., and large-scale karst formations are found in both the surface and subsurface. From 1000 to 1500 m a.s.l., the mountain is covered with Silurian shale and sandstone. Below 1000 m a.s.l. the mountain is composed of Cambrian limestone and Ordovician dolomite (Fig. 1, Tab. 1). The aquifer system in this region is controlled by the large-scale karst formations, and predominantly formed by karstic fissures and caves. Since the epikarst zone here is largely covered by vegetation, epikarst springs are ubiquitous on Mt. Jinfo. As a National Forest Garden, the land use pattern in the National Nature Reserve (NNR) on Mt. Jinfo...
consists only of forestland, while cultivated land, a small amount of industrial and mineral land, and grassland makes up the area outside this reserve.

In order to examine and compare the relationships between hydrochemical variations under different vertical climatic conditions and human activities for 1977, 2004–2009, and 2011, epikarst springs at different elevations were selected: springs 4–12 and 14 are within the NNR (Fig. 1), whereas springs 1–3 and 13 are located outside the NNR. Additionally, four non-epikarst springs (15–18) were included in the study. All 18 of the springs represent the most important sources of domestic water for local people. Springs 9–15 are at elevations of more than 1000 m (above sea level), with springs 10 and 11 representing the highest springs at the top of Mt. Jinfo (elevations of 2072 m and 2018 m respectively). Springs 1–6, 8, and 16–18 are at elevations of 630–838 m. Springs 1, 2, 10, and 11 are exposed in the Permian strata with surrounding limestone lithology. Springs 3, 6, 8, 9, 12, and 13 are exposed in Ordovician strata, again with surrounding limestone lithology. Springs 3, 6, 8, 9, 12, and 13 are exposed in Cambrian strata surrounded by dolomite lithology, and the non-epikarst springs (15–18) are exposed in Silurian strata with surrounding lithology of detrital stone. All springs have perennial streams and show different discharges: less than 1 L/s for springs 1–5, 9, 10, 13, 17, and 18; between 1 and 10 L/s for springs 6–8 and 14–16; and 10–15 L/s for springs 11 and 12 (Tab. 1).

### STUDY METHODS

**HYDROCHEMISTRY ANALYSIS**

The hydrochemical data of all springs for 1977 were gathered from the Nanjiang Hydrogeological & Engineering Geology Brigade, and continued monitoring of these springs was carried out by authors from 2004 to 2011. The measurement method in 1977 consisted of basic chemical analysis in the laboratory. These historical analyses may lack precision; however, large changes in data values were observed between 1977 and 2004, and so the level of precision is within acceptable limits. Temperature (T), pH, electrical conductivity (EC), and HCO$_3^-$ and Ca$^{2+}$ concentrations for these springs were tested in the field. T, pH, and EC were measured using Portable Water Quality Analyzers (produced by Hach Company, USA). The analysers’ accuracies are 0.1 °C for T, 0.01 for pH, and 1 μS/cm for EC. HCO$_3^-$ and Ca$^{2+}$ contents were measured by on-site alkalinity and calcium tests (Aqua-merck, Germany), with an accuracy of 0.1 mmol/L and 2 mg/L for HCO$_3^-$ and Ca$^{2+}$, respectively. AgNO$_3$ titration (0.1 mg/L) was applied to measure the Cl$^-$ content, and
RESULTS AND DISCUSSION

GENERAL WATER CHEMISTRY

DESCRIPTION

Epikarst springs on Mt. Jinfo generally displayed neutral pH (average pH from 2004 to 2009 was between 6.76 and 8.34), and temperatures ranging from 8.6 °C to 23.6 °C. The EC (average EC from 2004 to 2009) of the springs in the NNR was c. 168-564 μS/cm, and c. 239-584 μS/cm outside the NNR. The non-epikarst springs in the study area were similar to the epikarst springs in terms of pH, EC, and temperature (Tab. 1).

For all springs, HCO$_3^-$ was the dominant anion for the majority of samples (c. 31.97−380.93 mg/L), followed by SO$_4^{2-}$ (concentration 1.88−147.84 mg/L). Ca$^{2+}$ was the dominant cation for the majority of samples (c. 8.52−139.06 mg/L), followed by Mg$^{2+}$ (concentration 1.88−46.94 mg/L). SO$_4^{2-}$ and NO$_3^-$ (c. 0−75.36 mg/L) showed relatively large interannual variability, whereas those of Cl$^-$ (c. 0−14.82 mg/L), Na$^+$ (c. 0−26.62 mg/L), and K$^+$ (c. 0−6.08 mg/L) did not vary significantly. Major ion compositions are shown in the anion and cation ternary diagrams (Fig. 2). SO$_4^{2-}$ and HCO$_3^-$ together accounted for 80 % to 95 % of the total anions in the majority of samples. In general, Ca$^{2+}$ and Mg$^{2+}$ dominated the cation concentrations of the spring waters, accounting for more than 80 % of the total cation concentrations in the majority of epikarst springs (Fig. 2). Therefore, the hydrochemical water-type for these epikarst springs was Ca-HCO$_3^-$. The results also show that the four non-epikarst springs in this study had similar hydrochemical characteristics to the epikarst springs, which may indicate a common source of carbonate weathering for the major ions in all 18 springs.

Fig. 3 shows the cation triangular diagram for all springs for 1977, 2004−2009, and 2011. Major cation changes between years were not obvious for 1977 and 2004−2009. The triangular diagram for anions for 1977, 2004−2009, and 2011 (Fig. 4), shows that HCO$_3^-$ is the dominant anion for the majority of samples and, as for cations, no obvious changes are seen between these

KRIGING INTERPOLATION METHOD

The most common methods for spatial interpolation are Inverse Distance Weighting (IDW) and the Kriging method. Previous research has determined that the Kriging method is more accurate in its retention of original image features (Milillo & Gardella 2008), and in estimating radioactive contamination (Mabit & Bernard 2007) and soil mercury content (Hu et al. 2004). On the other hand, the IDW method is superior for estimating whole landfill methane flux (Spokas et al. 2003). Kriging interpolation has been widely used in spatial data analysis. The general equation of this method can be expressed (Matheron 1963; Li et al. 2000) as:

$$Z(x_0) = \sum_{i=1}^{n} \lambda_i Z(x_i)$$  \hspace{1cm} (1)

where $i = 1, 2, 3...n$, $Z(x_0)$ is the estimated variable value for the estimated point, $n$ is the number of measured points in a given range (here the springs on Mt. Jinfo), and $Z(x_i)$ is the value of the measured points. In this study the concentrations of SO$_4^{2-}$ and NO$_3^-$, $\lambda_i$ are the kriging weightings.

Suitable weightings of $\lambda_i$ are determined by two conditions. One is that $Z(x_0)$ and $Z(x_i)$ must have the same average value throughout the whole field, written as:

$$\sum_{i=1}^{n} \lambda_i = 1$$  \hspace{1cm} (2)

The other condition is that the kriging variance should take the smallest possible value, as estimated by:

$$\sigma^2 = \sum_{i=1}^{n} \lambda_i \gamma(x_i, x_0) + \mu - \gamma(x_0, x_0)$$  \hspace{1cm} (3)

where $\mu$ is the Lagrange multiplier and $\gamma(x_i, x_0)$ is the semivariogram, which can be estimated by the equation below:

$$\gamma(h) = \frac{1}{2n} \sum_{i=1}^{n} [Z(x_i) - Z(x_i + h)]^2$$  \hspace{1cm} (4)

where the vector $h$ is the distance between $x_i$ and $x_0$.
years. Also, significant changes are not seen between springs in or outside the NNR, or between epikarst and non-epikarst springs.

LITHOLOGY WEATHERING CONTROL ON WATER CHEMISTRY

Different geological formation periods and lithology is the major factor controlling the groundwater chemistry.

Fig. 2: Piper diagram of spring hydrochemistry at Mt. Jinfo.

Fig. 3: Cation diagrams for the springs for 1977, 2004–2009, and 2011.
HCO$_3^-$ concentrations were plotted against Ca$^{2+}$ concentrations for all Mt. Jinfo samples in different years (Fig. 5(a)). As expected, high linear correlation was obtained throughout the observation period (correlation coefficient $r = 0.651$), which strongly suggests that the main lithology of Mt. Jinfo is limestone. The projection point of the contrast ratio of Ca$^{2+}$ and HCO$_3^-$ (mmol/L) was near a best-fit curve, constrained to pass through (0, 0), gave a Ca$^{2+}$/HCO$_3^-$ ratio of 0.5 (Fig. 5(b)), which implies that the weathering in this area was mainly carbonate weathering. It may be that significant quantities of limestone from Permian and Ordovician strata mixed with the detrital stone, with the result that weathering in detrital stone areas in Silurian also takes the form of carbonate weathering. This could explain the similar hydrochemical features between springs 15–18 and the other epikarst springs.

Fig. 6 shows that there is little variation in Ca$^{2+}$ and HCO$_3^-$ concentrations of all springs for 1977, 2004–2009, and 2011. This is possibly because these two ion concentrations are controlled by carbonate dissolution, which is the main water/rock interaction in the karst aquifer. In Fig. 6, we can also observe that the concentrations of Ca$^{2+}$ in the NNR were lower than for springs outside the NNR, which may be due to the negative influence on carbonate dissolution of the high altitudes and lower
temperatures of the springs in the NNR (Tab. 1). Furthermore, the concentration of $\text{HCO}_3^-$ for springs outside the NNR did not show obvious variations, and may therefore be influenced by other ions.

EFFECT OF HUMAN ACTIVITIES ON EPIKARST SPRINGS

A spatial interpolation method set out in the “Study methods” section was applied to process $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ concentration data for the 18 springs for 1977, 2004−2009, and 2011, to indicate the concentration variation of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ in groundwater for the study area. The spatial interpolation method was used to indicate different grades by colour on a thematic map, and to illustrate the distribution of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ concentrations for 1977, 2004−2009, and 2011 on Mt. Jinfo (Fig. 7). Concentration of $\text{SO}_4^{2-}$ was lower than 40 mg/L in 1977 (Fig. 7(a)), and this value was used to reflect the natural low background levels of groundwater. According to the quality standard for ground water (GB/T 14848-93), $\text{SO}_4^{2-}$ concentration $<50$ mg/L in underground water is defined as water quality Class I. Obviously, all of the springs achieve water quality Class I in 1977 and the lowest $\text{SO}_4^{2-}$ concentration was found at the top of Mt. Jinfo; this is due to the dilution of the groundwater by the abundant precipitation. $\text{SO}_4^{2-}$ concentrations showed an upward trend from 2004 to 2008, then declined in 2009 and 2011. Most areas experienced increased $\text{SO}_4^{2-}$ concentrations, and only the area surrounding the peak of Mt. Jinfo maintained the low concentration observed in 1977. The highest concentration of $\text{SO}_4^{2-}$ (>150 mg/L) presented in the northwest and southeast of the study area, near Nanchuan city and Toudou town. Fig. 7(b) shows the interpolation map of the $\text{NO}_3^-$ concentrations in this study area and, as observed for sulphate, the lowest concentrations were seen in 1977 (<15 mg/L). In 2004, high $\text{NO}_3^-$ concentrations (>50 mg/L) were observed in the northwest of the study area, near Nanchuan city. This showed an upward trend from 2004 to 2007, then decreased in 2008 and 2009 (<30 mg/L) and returned to higher concentration in 2011 (>50 mg/L). The areas showing high $\text{NO}_3^-$ concentrations in the study area changed over time, whereas districts with low $\text{NO}_3^-$ concentrations in the springs were distributed in Mt. Jinfo NNR.

The highest concentration of $\text{NO}_3^-$ is distributed near Nanchuan city and Toudou town, as is the highest $\text{SO}_4^{2-}$ concentration. These areas of high concentration are located in the valley of Mt. Jinfo, where the terrain is relatively flat and major local settlements and farmland are located. Since the 1980s, rapid population growth and the large quantities of chemicals and fertilizers used in the industrial and agricultural sectors have resulted in large amounts of industrial waste, sewage, and fertilizer entering the groundwater system. Land use near Nanchuan city and Toudou town is predominantly cropland and construction land, but also includes many coal factories in the northeastern area and a large wine factory in Toudou town, which contribute to substantial increases in $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ concentrations in the area surrounding Mt. Jinfo. The concentrations of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ reduced
The hydrochemical features of 18 springs on Mt. Jinfo were measured for 1977, 2004−2009, and 2011. Results indicated that there were no obvious changes in the major ion concentrations, and the hydrochemical type of these springs remains Ca-HCO$_3$$_3$. Because of the different land utilization for different areas near Mt. Jinfo, the concentrations of SO$_4^{2−}$ and NO$_3^{−}$ in different springs was changed uncommonly in the past 35 years. Low concentrations remained unchanged at the top of Mt. Jinfo in the NNR, where the only land use is forest. In contrast, agricultural fertilization, industrial pollution, and sewage discharge have affected the concentrations of SO$_4^{2−}$ and NO$_3^{−}$ for the epikarst springs outside the NNR area, leading to an upward trend from 2004 to 2008, followed by a decrease in 2009 due to the implementation of environmental policies and industrial restructuring.

**CONCLUSIONS**

The hydrochemical features of 18 springs on Mt. Jinfo were measured for 1977, 2004–2009, and 2011. Results indicated that there were no obvious changes in the major ion concentrations, and the hydrochemical type of these springs remains Ca-HCO$_3$$_3$. Because of the different land utilization for different areas near Mt. Jinfo, the concentrations of SO$_4^{2−}$ and NO$_3^{−}$ in different springs was changed uncommonly in the past 35 years. Low concentrations remained unchanged at the top of Mt. Jinfo in the NNR, where the only land use is forest. In contrast, agricultural fertilization, industrial pollution, and sewage discharge have affected the concentrations of SO$_4^{2−}$ and NO$_3^{−}$ for the epikarst springs outside the NNR area, leading to an upward trend from 2004 to 2008, followed by a decrease in 2009 due to the implementation of environmental policies and industrial restructuring.
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