Seasonal Hydrochemical Evolution of Shallow Groundwater in a Reservoir Area Under Hydrological Influences: A Case Study from a Section of the Middle Han River

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Abstract: This study mainly analyzes the effect of the hydrological states along the Hanjiang Reservoir on the chemical attributes of shallow groundwater.With the inverse model technology the main ion compositions of groundwater in both rainy season and dry season as well as the components related to oxidation - reduction are systematically examined by our system based on this analysis. The key geochemical processes controlling the chemical evolution of groundwater are identified and quantified.It is discovered that there is an obvious seasonal variation in the chemistry of shallow groundwater: during the rainy season, the groundwater changes from the calcium - bicarbonate type to the calcium - magnesium - bicarbonate type, and in the dry season it reverses, and this pattern is quite distinct.Further analysis shows that during the rainy season, the significantly increased precipitation and surface water recharge will have an obvious diluting effect on the groundwater system and also make the overall groundwater environment change into an oxidized state.Under these oxidizing conditions the iron is more prone to precipitate and get fixed in the form of trivalent iron oxides and a certain amount of exogenous organic matter enters the groundwater system. On the contrary during the dry season the groundwater recharge is greatly reduced and at the same time the residence time is prolonged slowly making the aquifer environment shift towards a reducing state.This environmental change not only leads to the reduction and dissolution of goethite as well as the precipitation of siderite but also strengthens the dissolution of carbonate minerals driven by the internal system reaction.Generally speaking the seasonal hydrological changes which have a seasonal nature mainly affect the chemical composition of the shallow groundwater by adjusting the recharge intensity and the redox conditions and then finally control the main evolutionary patterns of the water-rock interaction in the study area.

Keywords: Seasonal hydrology; Groundwater; Hydrogeochemistry; Inverse modeling

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1. Introduction

(1) Research background

In the mid-latitude monsoon region, a quite prominent climatic feature is the extremely uneven annual distribution of rainfall.Precipitation mainly concentrates in the rainy season, and the dry season is relatively arid. Such an obvious seasonal variation is directly reflected in the dynamic changes of the groundwater system.Actually, the process of rainfall itself and the resulting fluctuations in the groundwater level are the core driving factors of the regional

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seasonal hydrological process [1].Existing research has confirmed that when seasonal rainfall enters the groundwater system through recharge, it often brings about an obvious dilution effect, and then reduces the concentration levels of the main ions in the groundwater [2].Meanwhile the groundwater level rises and falls periodically which changes the intensity of the exchange between groundwater and surface water. After such a change in hydrodynamic conditions it further affects the chemical composition and evolution of groundwater as well [3].

In the river - reservoir compound hydrological system, especially in the high - water - level backwater area formed by the upstream reservoir [4], the shallow groundwater system often shows unique hydrological characteristics which are the strengthened recharge conditions and the relatively restricted groundwater circulation.Under such circumstances the chemical changes of groundwater are not simply because of simple rainfall dilution but often involve a series of more complex water - rock interaction processes for example the degradation of organic matter can continuously release electron donors and also promote the accumulation of carbon dioxide and the increased carbon dioxide may further drive the dissolution or precipitation of carbonate minerals.In other words within this relatively enclosed and rather active hydrological environment the seasonal variations of groundwater chemistry are mainly dominated by geochemical reaction processes to a great extent.It is worth noting that such a seasonal hydrochemical response dominated by reactions still hasn't been sufficiently recognized and discussed in the existing research. Under such a background this study directs its attention at the reservoir regions in the middle and upper reaches of the Han River in order to examine the hydrochemical response characteristics of the shallow phreatic aquifer system to seasonal rainfall. By contrasting the main ion compositions and redox properties of groundwater in the rainy season and the dry season this study further probes into the regulation mechanism of hydrological conditions on the groundwater chemical structure with a special focus on the roles played by carbonate equilibrium and relevant water-rock interaction processes.It is hoped that this research can enable us to more deeply figure out the seasonal hydrogeochemical response mechanism of the shallow groundwater within the river-reservoir composite system.

2. Study Area and Methods

(1) Geological and hydrological conditions

This research area is the region along the Han River in Hubei Province of China.The strata in this area are mainly composed of Quaternary alluvial and lacustrine sediments with the lithology mainly being silty clay silty soil and fine sand. These sediments that jointly form the shallow confined aquifer of the study area.Generally speaking the groundwater system in this region is deeply affected by seasonal hydrological conditions and has a strong hydraulic connectivity with the surrounding rivers.During the rainy season, because of the increased infiltration recharge from rainfall and the rise of river water levels, the groundwater level which shows obvious fluctuations with the change of seasons will usually rise significantly.Conversely, as the dry season progresses step by step, due to the decrease in rainfall and the reduction in supplies, the groundwater level gradually descends then.

(2) Sampling and analysis methods

During the rainy season (May) and the dry season (October), groundwater samples are collected from shallow monitoring wells that are arranged in different parts of the study area.Before formal sampling, approximately 15 - minute pumping and flushing are conducted for each well to expel stagnant water until in - situ parameters like pH value, electrical conductivity (EC), and oxidation - reduction potential (ORP) attain a steady state. Then all water samples pass through 0.A membrane with a thickness of 45 micrometers is employed to remove suspended particulate matters.For samples that contain redox - sensitive components and dissolved organic matter (DOM), after being collected in an argon - purged glove box, they are immediately filtered in order to minimize the oxidation interference that is caused by exposure to the air and to maintain their original chemical states.

When conducting sampling, portable instruments are used on-site to measure the pH value of groundwater, the

dissolved oxygen (DO), as well as the oxidation-reduction potential (Eh).Groundwater samples are collected and then the main dissolved components and the dissolved organic carbon (DOC) in them are analyzed. The measured parameters include divalent iron ions, trivalent iron ions, bicarbonate ions, chloride ions, sulfate ions, potassium ions, sodium ions, calcium ions and magnesium ions.All chemical analyses are implemented within the laboratory setting.

3. Results and Discussion

(1) Evolution of hydrochemical facies

From the perspective of hydrochemical facies classification based on the main ionic components, all the groundwater samples collected during the rainy season all belong to the calcium - bicarbonate type, which indicates that the hydrochemical characteristics are quite consistent.Conversely, in the dry season, the water chemical phases present a certain degree of differentiation, with one fourth of the samples turning into the calcium-magnesium bicarbonate type.

(2) Seasonal variation of major ions

The transition from the rainy season (May) to the dry season (October) shows the rather obvious seasonal changes in the concentrations of the main ions in the groundwater: the concentrations of potassium ions, sodium ions and calcium ions are all decreased to different extents, while the concentrations of magnesium ions and bicarbonate ions are obviously increased.The decrease in the concentrations of potassium ions, sodium ions, and calcium ions is mostly because of the dilution effect brought about by the large quantity of rainfall supplement during the rainy season. The continuous rainwater recharge effectively "dilutes" the ions in the existing groundwater, which is the main mechanism through which the rainy season has an impact on the ion concentrations.

During the dry season, there comes a complete change: the recharge of the groundwater is greatly reduced and the residence time of the groundwater in the aquifer is obviously prolonged.This kind of extending situation which will strengthen the interaction between water and the rocks especially greatly promote the dissolution process of the magnesium-containing carbonates and silicate minerals will finally lead to the increase of the concentrations of Mg^{2+} and HCO_{3-} in the groundwater.

(3) Evolution of redox environment

The redox conditions of the groundwater in the research area also show obvious seasonal variations.In the rainy season (May), the groundwater as a whole shows a situation from low-oxygen to micro-oxidation, and the oxidation-reduction potential fluctuates between -101 millivolts and 301 millivolts. It is worthy of being noted that although positive potential values are detected at some monitoring points, the iron dissolved in the groundwater mainly exists in the form of ferrous ions (Fe(II)), and the highest concentration reaches 5 (there may be a part missing in the original text here, temporarily translated according to the existing content).42 milligrams per liter.Meanwhile, the concentration range of dissolved organic carbon (DOC) is from 1.During this period the concentration is between 50 and 10.93 milligrams per liter which shows that there are abundant organic electron donors in the environment abundant enough to indeed sustain the reduction reaction.

When the dry season (October) arrives, the redox environment of the groundwater system experiences a remarkable transformation into a state that is highly reductive and deficient in oxygen.Negative oxidation - reduction potentials were recorded at all the monitoring sites. At this moment, this environmental change further intensifies the iron reduction process, leading to the concentration of dissolved ferrous ions in the groundwater to soar sharply, reaching a maximum of 27.0.06 milligrams per liter which is much higher than the level in the rainy season.In stark contrast, the concentration of dissolved organic carbon in groundwater in the dry season is usually lower than that in the rainy season.This phenomenon clearly indicates that the organic carbon has been consumed in great amounts by

the metabolic processes within the groundwater system.

(4) Hydrogeochemical inverse modeling

Based on the previous research findings [5], the riverbank sediments in this research area contain various iron - containing minerals like goethite, magnetite, siderite, and a large number of clay minerals that contain iron.The existence of these minerals which provides a solid material basis for the reduction and transformation of iron in groundwater is a key premise for our subsequent research.

Based on the previously analyzed seasonal variations of groundwater hydrochemical characteristics and oxidation - reduction conditions, calcite and dolomite, which are the main carbonate reaction stages, are specifically selected in the inverse modeling process.Meanwhile, iron oxide phases are intermingled in order to more scientifically quantify the processes in which water and rocks interact with each other[6].

Table 1: Inverse Modeling Results for the Rainy and Dry Seasons in the Study Area

Mineral Phase	Molar Transfer (mol)	Chemical Formula
Rainy Season (May)		
Organic Matter	-7.831×10^{-4}	$(CH_2O)(NH_3)_{0.03}$
Calcite	-1.026×10^{-3}	$CaCO_3$
Dolomite	9.143×10^{-5}	$CaMg(CO_3)_2$
Goethite	-9.271×10^{-3}	FeOOH
Magnetite	3.074×10^{-3}	Fe_3O_4
KX	4.906×10^{-7}	KX
NaX	-4.906×10^{-7}	NaX
Dry Season (October)		
Organic Matter	5.688×10^{-4}	$(CH_2O)(NH_3)_{0.03}$
Calcite	1.135×10^{-3}	$CaCO_3$
Dolomite	9.154×10^{-5}	$CaMg(CO_3)_2$
Goethite	2.285×10^{-3}	FeOOH
Siderite	-2.333×10^{-3}	$FeCO_3$
Gypsum	1.195×10^{-4}	$CaSO_4$
NaX	1.576×10^{-5}	NaX
CaX_2	-7.88×10^{-6}	CaX_2

Based on the hydrogeochemical simulation results during the rainy season (the specific data are in Table 1), several mineral phases and organic matters are involved in the regional water-rock interaction together.It is worth noting that the molar transfer rate of the organic matter is negative, with a value of -7.83×10^{-4} moles actually.This negative value stands for consumption or input, which directly verifies that exogenous organic matter enters the aquifer via rainfall or river recharge, thereby influencing the composition of dissolved organic carbon (DOC) in groundwater.This finding completely accords with the characteristics of the dissolved organic carbon concentrations that were observed during the rainy season as per the cited content.

The iron minerals that are prominently characterized by their reactive behaviors during water-rock interactions are mainly dominated by the processes of precipitation and fixation.Specifically speaking the precipitation of goethite is quite remarkable with a molar transfer amount of -9.27×10^{-3} moles and there is some situation of magnetite dissolution with a molar transfer amount of 3.0.007 moles.This phenomenon can rather easily be explained by the situation in which groundwater recharge increases during the rainy season - at this time the entire groundwater system is generally operating under relatively more oxidizing conditions.The dissolved ferrous ions are easily oxidized and then re - fixed into the oxides of trivalent iron. This is the key reason that the concentration of dissolved ferrous ions does not rise during the rainy season.

There are obvious differences in the reactions of carbonate minerals when calcite undergoes precipitation the molar transfer is - 1.There is 0.0003 moles whereas dolomite has slight dissolution and the mole transfer amount is 9.14×10^{-5}

moles.Essentially the water supplement's diluting action will trigger the dynamic adjustment of the carbonate system and finally the ion balance of calcium magnesium and bicarbonate in the groundwater is changed.In addition, the ion exchange process between sodium and potassium ions with a molar transfer rate at the level of 10^{-7} moles which has a negligible impact on the main ion composition of groundwater can be neglected in actual research.

On the contrary, during the dry season, there will be obvious changes in the water chemical processes.The molar transfer quantity of organic substances is 5.69×10^{-4} moles with a positive value signifying generation from the solid phase which indicates that the evolution of groundwater is mainly controlled by endogenous reactions.The reaction of iron minerals shows itself as reduced dissolution and re - precipitation.The dissolution of goethite (2.Two point nine multiplied by ten to the power of negative three moles, while siderite forms negative two point three three multiplied by ten to the power of negative three moles.This indicates that as the amount of supply decreases and the residence time increases, the groundwater becomes more reductive, thereby causing the dissolution of the trivalent iron oxides. The ferrous ions which have been released are then re - fixed into siderite.Meanwhile, in the arid season, the calcite (1.14×10^{-3} moles) and the gypsum (1.Also present is (20×10^{-4} mol), which shows that the sources of Ca^{2+}, HCO_3-, and SO_4^{2-} are increasingly dependent on water-rock interaction processes.

4. Conclusions

The main findings of this study are as follows:

(1) During the rainy season the groundwater is of a uniform calcium bicarbonate type and in the dry season it turns into a calcium magnesium bicarbonate type which indicates that as the recharge amount decreases the interaction between water and the rocks becomes more intense .

(2) In the rainy season the chemical property of water which is mainly dominated by the dilution effect brought about by recharge causes the concentrations of sodium potassium and calcium to be reduced.During the dry season, the relatively long time of stay will enhance the impact brought about by the dissolution of minerals, especially the impact of the dissolution of those minerals rich in magnesium.

(3) The oxidation - reduction environment that changes from a relatively oxidizing state in the rainy season (fixing iron into ferric oxide) to a very reducing state in the dry season drives the reductive dissolution of goethite and the precipitation of siderite in that way.

(4) In the rainy season, the dynamic change of organic matter is the input from the outside, and in the dry season, it turns into an internal endogenous reaction, thereby adjusting the redox conditions.

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