



ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14808



Variations of Hydrogeochemical Characteristics of Shallow Groundwater Caused by Agricultural Activities

Jianhua $Wu^{1,2,*}$, Peiyue $Li^{1,2}$ and $Hui Qian^{1,2}$

¹School of Environmental Science and Engineering, Chang'an University, No. 126 Yanta Road, Xi'an 710054, P.R. China ²Key Laboratory of Subsurface Hydrology and Ecology in Arid Areas, Ministry of Education, No. 126 Yanta Road, Xi'an 710054, P.R. China

*Corresponding author: Fax: +86 29 82339952; Tel: +86 29 82339327; E-mail: wjh2005xy@126.com

(Received: 10 November 2012;

Accepted: 29 June 2013)

AJC-13724

To investigate the variations of hydrogeochemical parameters of shallow groundwater forced by agricultural irrigation in Nanshantaizi area, 56 water samples were collected in two different periods. The major physio-chemical parameters of samples of the two periods were analyzed and compared spatiotemporally and the groundwater chemistry evolution was also discussed. The study shows that most major ions in 2012 have higher concentrations than those in 2010 and shallow groundwater quality in the study area has deteriorated. All major ions show a sharp increase during the infiltration process of irrigation water because of the dissolution of salts contained in soil media. Along groundwater flow path, two parameter variation patterns can be observed because of different reactions or processes dominated in different sections. Groundwater quality deterioration calls for a change in current irrigation pattern.

Key Words: Groundwater pollution, Hydrogeochemical evolution, Agricultural activity, Water quality.

INTRODUCTION

Groundwater is an important resource for domestic, agricultural, industrial and ecological uses in many parts of the world, especially in arid and semi-arid areas where available surface water is limited^{1,2}. However, due to rapid expansion of urbanization and population, groundwater is heavily abstracted and influenced by human activities³, causing many ecological and environmental problems, such as soil salinization, groundwater quality deterioration, land subsidence and land desertification. Agricultural activities, especially when they are not managed scientifically, can impose significant influences on shallow groundwater dynamics and groundwater quality, resulting in the variations of hydrogeochemical characteristics.

During the past several decades, groundwater environments in many areas have undergone vast changes because of human activities and global climate change. Loáiciga⁴ made a general review on the relationship of climate change with hydrological and aquifer processes. Gas'kova *et al.*⁵ carried out a research on the variation of geochemical compositions of natural water near a storage site of low-activity liquid radioactive wastes. Guardiola-Albert and Jackson⁶ investigated the climate change impacts on natural recharge and groundwater-wetland dynamics. These studies have proved that anthropogenic and natural interferences can both influence the hydrodynamics and hydrogeochemistry of groundwater

systems. Therefore, more and more scientists have carried out various investigations on groundwater chemistry evolution and groundwater vulnerability⁷⁻¹².

Nanshantaizi is a traditional agricultural area located to the south of the Yellow river in Ningxia, Northwest China. Recent years, a land consolidation project has been implemented in this area. This project will not only change the land cover, but will also change the groundwater flow filed, resulting in the change of physiochemical parameters of groundwater. Therefore, the present study aims at investigating the spatiotemporal variations of major indices forced by agricultural activities.

EXPERIMENTAL

The study area, located between longitude $105^{\circ}09'05''$ to $105^{\circ}29'55''E$ and latitude $37^{\circ}22'22''$ to $37^{\circ}30'06''N$, includes two major parts. In the north where the Yellow river alluvial plain is located, many villages are distributed and in the south is the Nanshantaizi area which was formed by alluvial and pluvial deposits. The Yellow river, providing large amounts of irrigation water for Ningxia, runs through the study area along the northern boundary. From April to August and from October to November each year, a large amount of water ($ca. 6.5 \times 10^7 \text{ m}^3/\text{a}$) is diverted through pipe lines to the Nanshantaizi area for the purpose of irrigation. The large amount of water infiltrates into aquifer and then flows towards

7442 Wu et al. Asian J. Chem.

north where the Yellow river alluvial plain is situated, causing the significant rise of groundwater level in the alluvial plain and producing many related environmental problems as a result.

A total of 56 water samples were collected during August 2010 and during July to August 2012. Among these samples, 54 were collected from shallow hand pumping wells and boreholes (27 for each period) and the other two were collected from the Yellow river (one for each period). Samples were collected with white plastic bottles. Before sampling, the wells were continuously pumped for 0.5 h to minimize the influence of static water in the well. All bottles were washes three times thoroughly with the water to be sampled. All these samples were analyzed in laboratory for physiochemical indices such as major ions (Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, HCO₃⁻, SO₄²⁻ and NH₄⁺), total hardness (TH), total dissolved solids (TDS) and pH, *etc*. Sample collection, handling and storage followed standard procedures recommended by the Chinese Ministry of Water Resources to ensure data quality and consistency.

RESULTS AND DISCUSSION

General statistics of alluvial plain water: Statistical analysis was first used to investigate the variation in groundwater chemistry between different periods. In Table-1, 27 groundwater samples were collected from the Yellow river alluvial plain in 2010 and another 24 were collected in the same area in 2012. Compared the results of two different periods, it is easy to conclude that groundwater chemistry has undergone vast variations and groundwater quality in the alluvial plain has deteriorated. Most indices except pH in 2012 have higher mean values than those in 2010, which is probably caused by mineral dissolution or external human interferences such as fertilizer utilization and domestic sewage disposal. On the other hand, the mean pH value in 2012 is lower than that in 2010 and this is probably because the pH value of irrigation water in 2012 (pH = 7.69) is lower than that in 2010 (pH = 8.09).

Variation of hydrochemical types: A Piper diagram¹³ on which all collected samples were plotted was used to show the variation of hydrochemical types of waters. It can be seen from the Fig. 1 that groundwater in the alluvial plain has undergone a transition from mostly HCO₃·Cl-Ca·Mg·Na type in 2010 to Cl·SO₄-Ca·Mg·Na and HCO₃·Cl·SO₄-Na Ca·Mg·types

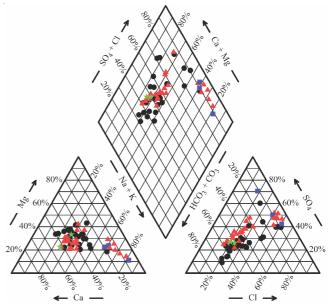


Fig. 1. Piper plots of collected samples. ● and ▲ represent samples collected in alluvial plain in 2010 and 2012, respectively, ■ denotes samples collected in Nanshantaizi area and ★ represents the Yellow river water samples

in 2012. This transition has indicated the vast addition of Na⁺, Cl⁻ and SO₄²⁻ in groundwater. The Yellow river water used for irrigation in Nanshantaizi is of HCO₃-Ca·Na type, which is fresh water with good quality. However, after it infiltrates into aquifer and mixes with existing groundwater, the hydrochemical type of groundwater has transformed into SO₄·Cl-Na type. This means the irrigation has brought Na⁺, Cl⁻ and SO₄²⁻ preserved in soils into aquifers, causing the deterioration of groundwater quality. Intensive phreatic water evaporation may also lead to the increase of ion concentrations, since in the alluvial plain depth to water table is usually less than 3 m. Besides, the concentrations of major ions may also be influenced by natural water-rock interaction. The large amount of irrigation water that infiltrates into aquifers may change the hydrodynamics of the aquifers and more minerals can dissolve into groundwater. These dissolution reactions include:

$$NaCl \rightarrow Na^{+} + Cl^{-}$$

$$CaCO_{3} + H^{+} \rightarrow Ca^{2+} + HCO_{3}^{-}$$

$$CaSO_{4} \rightarrow Ca^{2+} + SO_{4}^{2-}$$

TABLE-1										
STATISTICAL ANALYSIS OF GROUNDWATER SAMPLES COLLECTED FROM THE YELLOW RIVER ALLUVIAL PLAIN										
			July to August, 2012							
Index	Sample size	Min	Max	Mean	Standard deviation	Sample size	Min	Max	Mean	Standard deviation
K ⁺	27	3.00	8.00	5.22	1.37	24	2.20	18.25	6.24	3.48
Na ⁺	27	57.00	480.00	146.26	110.52	24	76.80	1693.60	339.23	405.83
Ca ²⁺	27	76.80	224.64	129.07	43.63	24	94.16	223.94	148.72	33.32
Mg^{2+}	27	32.59	164.12	66.86	32.34	24	38.07	202.70	86.02	47.12
Cl-	27	72.49	676.59	207.50	157.34	24	72.10	1035.00	319.43	317.69
SO_4^{2-}	27	52.31	916.85	267.92	231.07	24	123.50	1546.32	528.92	441.97
HCO ₃ -	27	213.69	609.65	398.05	101.57	24	186.95	576.32	400.92	112.11
NO ₃ -N	27	0.00	16.95	3.69	3.93	22	1.03	19.74	7.94	4.99
TDS	27	539.75	2248.98	1042.48	510.64	24	678.85	3977.17	1683.28	1141.41
pН	27	8.01	8.15	8.07	0.03	24	7.20	7.84	7.51	0.19
TH	27	363.10	1108.69	587.80	207.57	24	456.79	1225.90	714.74	216.03

Groundwater chemistry evolution: The above discussion has shown that irrigation activity in Nanshantaizi has great influence on groundwater chemistry evolution. However, the deterioration of groundwater quality in the alluvial plain is a result of many influencing factors. To reveal the spatial evolution of groundwater chemistry, a cross section along the flow path was chosen. Along the cross section, three groundwater samples are located, *i.e.*, NT1, NT2-1 and NT3. Besides, the Yellow river water sample collected in 2012 (W3-2) is also analyzed as it is regarded as the irrigation source water. The chemical analysis results of the 4 samples are listed in Table-2.

It can be seen from Table-2 that all the major ions show a sharp increase in concentration compared to those of the Yellow river water. This can be explained as follows. Soils in the area contain enough soluble salts such as NaCl, Na₂CO₃, NaHCO₃ and Na₂SO₄. When large volumes of Yellow river water infiltrates into aquifer through the unsaturated zone, the soluble salts will dissolve and enter the aquifer along with infiltrated irrigation water, causing the observed sharp increase of these ions. This is a simple process that can be understood easily. After the irrigation water which contains large quantities of dissolved salts enters the aquifer system, it becomes a part of groundwater and then flows along the flow path from south to north. Obviously, two different variation patterns can be observed from Table-2. First, the concentrations of Na⁺, SO₄²⁻, HCO₃⁻ and TDS continue to increase from NT1 to NT2-1 and then to NT3. This can be explained by water-rock interactions happened during groundwater flow. Aquifer media contains minerals that can dissolve into groundwater under certain conditions. Another pattern is represented by K⁺, Ca²⁺, Mg²⁺ and Cl⁻. The concentrations of these ions first decrease from NT1 to NT2-1 and then increase from NT2-1 to NT3. The decrease in concentrations can be explained by ion exchange. For example, the decrease of Ca²⁺ and Mg²⁺ from NT1 to NT2-1 can be explained by ion exchange expressed as follows:

$$2\text{NaX} + \text{Ca}^{2+} \rightarrow \text{CaX}_2 + 2\text{Na}^+$$
$$2\text{NaX} + \text{Mg}^{2+} \rightarrow \text{MgX}_2 + 2\text{Na}^+$$

With the continuously dissolution of minerals and the addition of irrigation induced salts, the concentrations of major ions will become bigger, resulting in the continuous increase of TDS. A figure has been produced to explain the reactions and processes involved in groundwater chemistry evolution (Fig. 2). As shown in Fig. 2, the Yellow river water is first diverted to the Nanshantazi and then it infiltrates into aquifer through unsaturated zone, during which many soluble salts dissolve and enter the aquifer along with the irrigation water. After entering the aquifer, groundwater flows downwards and mineral dissolution and ion exchange together influence the water chemistry by increasing the concentrations

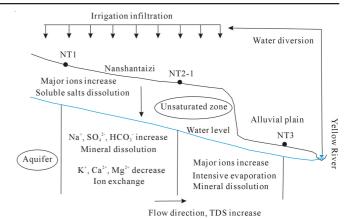


Fig. 2. Groundwater chemistry evolution along groundwater flow path

of Na⁺, SO₄²⁻ and HCO₃⁻ and decreasing the concentrations of K⁺, Ca²⁺, Mg²⁺ and Cl⁻. From NT2-1 to NT3, intensive evaporation as a result of elevated water level caused by irrigation becomes the most influencing process which increases the concentrations of all major ions. In the entire flow path, TDS shows an increase trend, indicating the deterioration of water quality. Different reactions predominated in different sections of the flow path. In fact, these reactions and processes are significantly influenced by irrigation which is a driving force making the hydrodynamic and hydrogeochemical fields changed.

Conclusion

Human activities and natural evolution processes can have significant influences on groundwater chemistry. In the present study, the hydrogeochemical evolution forced by irrigation in a Yellow river alluvial plain was investigated. The following conclusions can be summarized.

Temporally, shallow groundwater quality in the study area shows a deterioration trend. Most major ions in 2012 have higher concentrations than those in 2010. This is because the irrigation pattern has changed regional hydrodynamics and made more soluble salts dissolved in groundwater.

Spatially, all major ions show a sharp increase during the irrigation water infiltration process because of the dissolution of salts contained in unsaturation zone media. Along groundwater flow path, the variations of major physiochemical parameters show two different patterns, because different reactions or processes dominated in different sections of the flow path.

Agricultural irrigation has imposed great influences on groundwater quality and groundwater chemistry evolution by changing regional hydrodynamic field and by bringing large amounts of soluble salts from soil media into aquifer. The fact that groundwater quality has deteriorated calls for a change in current irrigation pattern.

TABLE-2											
MAJOR PARAMETERS OF 4 CONCERNED SAMPLES (UNIT: mg/L)											
Sample No.	Water type	K ⁺	Na ⁺	Ca ²⁺	Mg^{2+}	Cl-	SO ₄ ²⁻	HCO ₃ -	TDS		
W3-2	Yellow river water	1.77	34.15	63.97	16.77	39.83	72.46	190.23	324.06		
NT1	Groundwater	7.50	457.60	103.72	95.08	436.99	739.95	192.95	1969.10		
NT2-1	Groundwater	3.00	643.10	48.21	45.92	210.82	1104.00	221.05	2227.84		
NT3	Groundwater	18.25	750.80	156.70	202.70	894.93	1288.00	325.96	3538.14		

7444 Wu et al. Asian J. Chem.

ACKNOWLEDGEMENTS

This research was supported by the Doctoral Postgraduate Technical Project of Chang'an University (CHD2011ZY022 and CHD2011ZY025), the special Fund for Basic Scientific Research of Central Colleges, Chang'an University (CHD2011ZY020 and CHD2012TD003) and the National Natural Science Foundation of China (41172212).

REFERENCES

- 1. P.Y. Li, H. Qian, J.H. Wu and J. Ding, Water Sci. Eng., 3, 282 (2010).
- P.Y. Li, J.H. Wu and H. Qian, Environ. Earth Sci., Online first; DOI: 10.1007/s12665-012-2049-5 (2012).
- 3. P.Y. Li, H. Qian and J.H. Wu, E-J. Chem., 8, 1164 (2011).

- 4. H.A. Loáiciga, Ann. Assoc. Am. Geographers, 93, 30 (2003).
- O.L. Gas'kovaa, A.E. Boguslavskiia and T.G. Sirotenkob, Water Resour., 38, 597 (2011).
- 6. C. Guardiola-Albert and C.R. Jackson, Wetlands, 31, 907 (2011).
- 7. H. Qian and P.Y. Li, Asian J. Chem., 23, 2927 (2011).
- 8. P.Y. Li, H. Qian and J.H. Wu, E-J. Chem., 8, 565 (2011).
- H. Qian, P.Y. Li, K.W.F. Howard, C. Yang and X.D. Zhang, *Environ. Monit. Assess.*, **184**, 3613 (2012).
 - 0. H. Qian, X.D. Zhang and P.Y. Li, Asian J. Chem., 24, 668 (2012).
- 11. H. Qian and P.Y. Li, Asian J. Chem., 24, 2257 (2012).
- 12. C. Sadashivaiah, C.R. Ramakrishnaiah and G. Ranganna, *Int. J. Environ. Res. Public Health*, **5**, 158 (2008).
- A.M. Piper, A Graphic Procedure in the Geochemical Interpretation of Water Analysis. United States Geological Survey, Washington D.C. (1953).