Enrichment of high arsenic groundwater controlled by hydrogeochemical processes and sedimentary structure in Hetao basin

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SUMMARY: In this study we apply cumulative frequency distribution graphs to characterize the distribution of ionic ratios throughout the Hetao basin. All hydrogeochemical processes can basically be classified as recharge intensity of groundwater, evaporation concentration intensity and reductive degree that controlling the spatial distribution of arsenic (As). We found that the concentration of As is more than 10 μg/L when the $(HCO_3+CO_3)/SO_4$ ratio more than 4.1 (strong reductive area). As the evaporation concentration intensity increases, the median value of As rises from 10.74μg/L to 382.7μg/L in median reductive area, and rising from 89.11 μg/L to 461.45 μg/L rapidly in strong reductive area. As the river recharge intensity increases (with intensity index from 0 to 5), the median value of As drop from 40.2μg/L to 6.8μg/L in median reductive area, and drop markedly from 219.85 μg/L to 23.73μg/L in strong reductive area. The results provide new insight into the mechanism of As enrichment in groundwater.

1 INTRODUCTION

To quantitatively understand the mechanisms that control arsenic (As) mobilization in groundwater systems, it is essential to determine its hydrogeochemical processes in the aquifer system. Guo *et al.* (2012, 2015) indicate that hydrogeochemical process is the main factor in controlling groundwater As in the Hetao Basin, Inner Mongolia. Many Ionic ratios (Cl/Br, SO_4/Cl, Na/Cl and so on) have been jointly used to distinguishing hydrogeochemical processes, such as redox condition and evaporation concentration (Cartwright & Weaver, 2005, Cartwright *et al.*, 2006, Breit, 2015), identify redox condition, recharge and quantitatively evaluate groundwater systems in arid and semi-arid regions (Smedley & Kinniburgh, 2002, Breit & Guo, 2015), determine the impact of irrigation return flow on As mobilization in the groundwater system. There are some relations between the concentration of As and the hydrogeochemical processes, such as reductive degree, recharge intensity from ionic ratio and evaporation concentraon intensity. In this study, we apply cumulative frequency distribution graphs to characterize the distribution of ionic ratios throughout the Hetao basin, and thereby gaining the hydrogeochemical indicators that distinguish the suite of hydrogeochemical processes that govern groundwater composition. The result can be used to constrain the hydrogeochemical processes that control As mobilization and enrichment in groundwater.

2 METHODS/EXPERIMENTAL

2.1 *Field sampling*

447 samples (depths from 10 m to 40 m) were collected from the shallow aquifer which is composed of late Pleistocene and Holocene alluvial and lacustrine deposits. Of those, 80% wells are domestic water wells and the rest are the agricultural supply wells. The sampling campaign was undertaken during the period from June 10th to September 27th, 2010 (Fig.1) across the Hetao basin north to the foot of langshan, south to the Yellow River, west to the wulanbuhe desert and east to the Ulansuhai Nur.

2.2 *Ionic relationships*

The relationships between major ions (Na, Ca, Mg, K, Cl, HCO_3, CO_3 and SO_4) can provide information on the sources of groundwater and the processes that led to their composition. All units are expressed in milliequivalent per litre (meq/L), which converts concentrations to chemical "equivalents". This assists with understanding water-rock processes that may control groundwater composition. Because of the log-normal distribution of data, all axes are presented in logarithmic scale.

3 RESULTS AND DISCUSSION

3.1 *Spatial distribution of arsenic*

53.5% of shallow groundwater samples have As concentration exceeding 10 μg/L in Hetao basin. Among them, 134 samples contain more than 50 μg/L, accounting for 300% of all samples, and 56.1% in over-standard samples.

There are two As anomaly belt: first is located in the connected zone between the two main geomorphic units of northern Hetao basin along the Total Drainage Channel, namely the piedmont alluvial–proluvial plain and the Yellow River alluvial lacustrine plain. This region is the groundwater discharge area of Hetao basin with high pH, TDS, Cl, HCO_3^-, and low SO_4^{2-}. The second is distributed in the several large crevasse splay from Dengkou country to Urad Front Banner along the north bank of Yellow river. Comparing with the first high As belt, the As content of this region was on a low level with a range of 10~50 μg/L.

3.2 *Hydrogeochemical process by Ionic ratio*

Ionic ratio, including Na/Cl, $(HCO_3+CO_3)/Cl$, $Ca/(HCO_3+CO_3)$, Na/HCO_3, Cl/SO_4, $(HCO_3+CO_3)/SO_4$, were assessed using cumulative frequency distribution graphs to identify hydrogeochemical populations, and demarcation values established that can be used to characterize hydrogeochemical processes based on ionic relationships. In Hetao basin, the processes identified and constrained by this method include three main processes: reductive degree, recharge intensity and evaporation concentration intensity. Hydrogeochemical indicators were developed that define the critical values for differentiation of each process. Overlay analysis of the three main processes of As-contaminated groundwater can be used to constrain the hydrogeochemical processes that control As mobilization and enrichment in groundwater.

Table 1. Hydrogeochemical indicators for various chemical process controlling groundwater compositions in Hetao basin.

Ionic ratio	Hydrogeochemical indicator (meq/L ionic ratio)	Hydrogeochemical process
Na/Cl	0~1	Saline groundwater, Evaporative concentration of NaCl
	1~1.8	Background
	>1.8	Mineral hydrolysis or ion-exchange reaction
$(HCO_3+CO_3)/Cl$	0~1.3	Weak runoff area, evaporation concentration of salt
	>1.3	River recharge, fresher groundwater
$Ca/(HCO_3+CO_3)$	0~0.15	Strong reducing, evaporation concentration
	0.15~0.6	Intermediate process
	>0.6	Recharge by $Ca-HCO_3$ water (river recharge), fresher groundwater
Na/HCO_3	0.4~1	Irrigation of Yellow river
	1.1~3.8	Intermediate condition
	>3.8	Halite dissolution or deep fracture brine intrusion
Cl/HCO_4	0~1	Lateral flow recharge from Yinshan mountain or Yellow river, renew faster
	>3.3	High-salty, strong reduce, evaporation concentration
$(HCO3+CO3)/SO_4$	0~1.4	Weak reductive
	1.4~4.1	Intermediate condition
	>4.1	Strong reductive, discharge area with high TDS

3.3 *Hydrogeochemical control on As distribution*

The success of this assessment was variable for different ion-pairs, but mostly it was possible to assign hydrogeochemical indicators that distinguish the suite of hydrogeochemical processes that govern groundwater composition. The key indicators are defined in Table 1 and illustrate some commonality in between various tested ratio.

The factors of the high As groundwater in Hetao basin are very complex; it is not single hydrogeochemical process that explains the distribution characteristics. According to the previously mentioned, combine the evaporation concentration, reductive condition and the recharge intensity of groundwater.

4 CONCLUSIONS

We found that the concentration of As is more than 10 μg/L when the $(HCO_3+CO_3)/SO_4$ ratio more than 4.1 (strong reductive area). As the intensity of evaporative concentration increases, the median value of As increases from 10.74 μg/L to 382.7 μg/L in median reductive area, and rising from 89.11 μg/L to 461.45 μg/L rapidly in strong reductive area. As the river recharge intensity increases (with intensity index from 0 to 5), the median value of As drop from 40.2μg/L to 6.8μg/L in median reductive area, and drop markedly from 219.85μg/L to 23.73μg/L in strong reductive area. The results provide new insight into the mechanism of As enrichment in groundwater.

ACKNOWLEDGEMENTS

This study was supported by National Natural Science Foundation of China (No. 41402234) and the Geological Survey Projects Foundation of China (No. 1212010913010). We thank Dr. Huaming Guo for discussion and comment. We thank two anonymous reviewers for their comment and guest editor for greatly improving the manuscript.

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