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Water Rock Interaction [WRI 14]**Factors controlling spatial variation of iodine species in groundwater of the Datong basin, northern China**Junxia Li^a, Yanxin Wang^{a*}, Wei Guo^a, Xianjun Xie^a, Liping Zhang^a*School of Environmental Studies & State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, 430074 Wuhan, China***Abstract**

To better understand the distribution of iodine speciation composition and the controlling factors in groundwater from the Datong basin, hydrochemical studies were conducted. Total iodine concentrations in groundwater ranges from 6.2 to 1380 µg/L, with the mean value of 243 µg/L. Speciation of iodine in groundwater is mainly controlled by redox potential. Under reducing conditions, iodide is the dominant dissolved species, while in sub-oxic and oxic conditions, iodate is the major species, with a lower proportion of iodide. The evident existence of organic iodine in several groundwater samples may be related to anthropogenic activities.

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Keywords: iodine; speciation; distribution; groundwater; Datong basin**1. Introduction**

Iodine in aquatic systems on earth can be grouped into three species: iodide, iodate and organo-iodine. The speciation of iodine is affected by water chemical properties, such as pH, redox status and organic carbon content. Although several studies have reported the iodine species composition in estuaries, rivers, rain and even groundwater, iodine-affected groundwater in some inland areas such as the Datong basin are poorly documented [1-2]. Moreover, iodine mobility, environmental transport and biological uptake in aquifer systems vary greatly with iodine speciation. For example, soils rich in iron oxide have high affinities for iodate [3]. Therefore, the aims of this study are: 1) delineate the composition and distribution

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of iodine species in groundwater of the Datong basin; and 2) understand the factors affecting its speciation to address the behavior of iodine in Datong basin groundwater.

2. Material and Methods

A total of 83 groundwater samples were collected in August 2012 (Fig. 1). Concentrations of total iodine were determined by ICP-MS (PE ELAN DRC-e). Samples were analyzed for iodide and iodate within a week after sampling using HPIC-ICP-MS (AS14 analytical column, ICS-1500, Dionex, USA; PerkinElmer ELAN DRC-e, USA) with the method detection limits for iodate and iodide of 0.035 $\mu\text{g/L}$ and 0.025 $\mu\text{g/L}$, respectively. Dissolved organic iodine in groundwater is calculated by the difference between total iodine and total inorganic iodine [4].

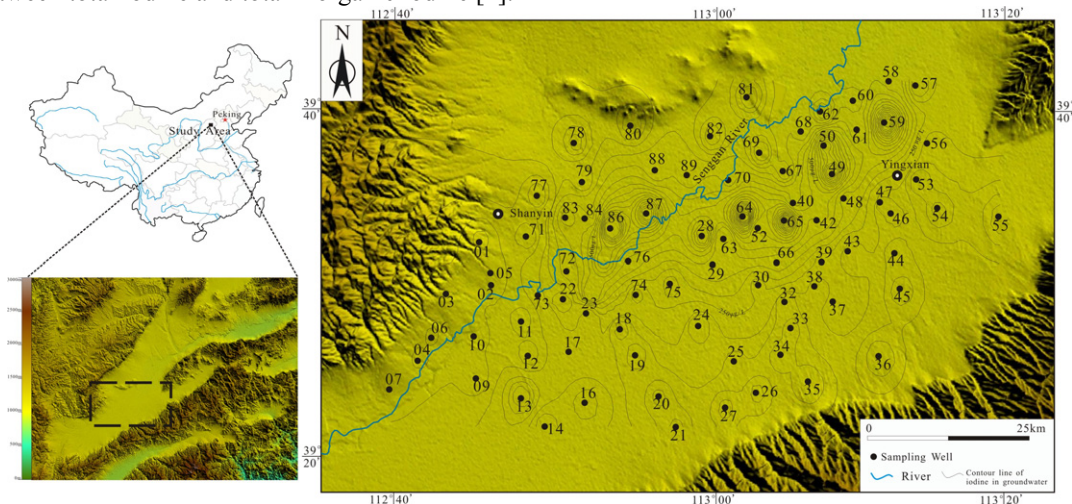


Fig. 1. Location of the Datong basin and sampling sites.

3. Results and discussion

3.1. Spatial variation of iodine concentration

Total iodine concentration in groundwater ranged from 6.2 to 1380 $\mu\text{g/L}$, with the mean value of 243 $\mu\text{g/L}$. 46% of groundwater samples contain iodine concentrations higher than 150 $\mu\text{g/L}$, the recommended concentration in drinking water by the Chinese government. The horizontal distribution of iodine in the groundwater is shown in Fig. 1. High iodine groundwaters are mainly localized in the center of basin, especially in the narrow belt along the Senggan River. Fig. 2a, shows that high iodine groundwater is present at all sampling depths, but the samples with iodine concentrations higher than 600 $\mu\text{g/L}$ are usually at depths of 10-20 m and 70-100 m.

Composition of iodine species in groundwater is variable. 57% of samples have ratios of iodate to total iodine greater than 60%, while iodide is the major species in 22% of samples (Fig. 2b). The remaining samples contain iodate, iodide and organic iodine together. Organic iodine was calculated in 73% of samples with ratios ranging from 0 to 44% (median: 6.7%). 9 of 83 samples were found to contain organic iodine higher than 100 $\mu\text{g/L}$. The complex composition of iodine species in groundwater indicates that iodine speciation may be controlled by several factors.

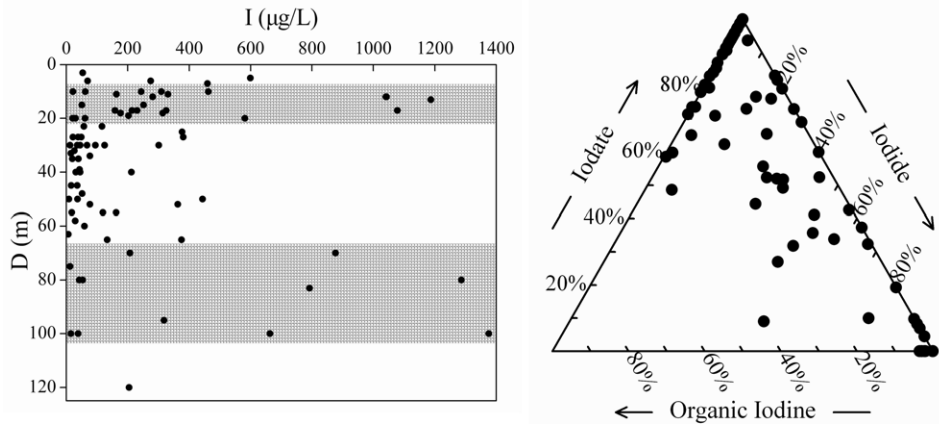


Fig. 2. (a) Variation of iodine concentration in groundwater with the depth; (b) Ternary diagram of iodine species in groundwater.

3.2. Factors controlling the mobilization and speciation of iodine

All groundwater pH is near-neutral to weakly alkaline (6.90-9.73, mean: 7.90). Several studies have documented the importance of pH conditions on controlling the kinetics of iodine transfer in aquifer systems [5]. The correlation of iodine with pH is shown in Fig. 3a. High iodine groundwaters have pH values in the range from 7.75 to 8.60, indicating that high pH conditions favor iodine enrichment in groundwater. As pH values increase, the positive charge in the surface of metal oxide minerals decreases, which favors the iodine mobilization from sediments into groundwater. Moreover, organic iodine absorbed by organic matter can be transformed into inorganic iodine by abundant OH^- in alkaline solution [6]. Redox potentials range from -170 to 224 mV with the median value of 125 mV, suggesting that the aquifer changes from sub-oxic to reducing conditions. High iodine groundwaters are characterized by moderate Eh, implying that the generation of high iodine groundwater is associated with sub-oxic environment in the aquifers (Fig. 3b).

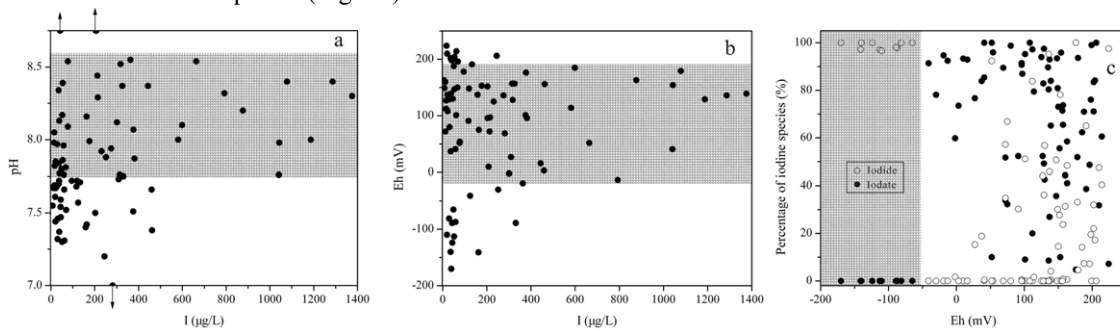


Fig. 3. Variation of iodine concentration with pH and Eh and iodine species with Eh in groundwater samples

Under environment conditions, the speciation of inorganic iodine is generally controlled by pH and Eh. In the Datong basin, the groundwater pH has a narrow range. Thus, inorganic iodine speciation is more controlled by redox potential. Iodide is the dominant iodine species under reducing condition (Fig. 3c). With the increasing Eh, iodine species composition becomes more complex and iodate is the major iodine species. Sub-oxic environments provide favorable conditions for iodate existence in the groundwater. On

the other hand, relatively high pH conditions enhance the proportion of groundwater iodate generally, and nearly all groundwater samples of the Datong basin are alkaline as discussed above. Thus, it is reasonable to expect significant contributions of iodate in groundwater. Notably, under sub-oxic conditions, iodide is also the dominant species in several samples, possibly due to the greater mobility of iodide. Compared with iodate, iodide is more easily released into groundwater due to the lower affinity for minerals [3]. Moreover, clay minerals such as kaolinite, illite, etc. in sediments exhibit an appreciable capability for iodate reduction [1]. The highest calculated organic iodine concentration in the Datong basin was 360 µg/L with the median value of 4.5 µg/L. However, the samples with higher organic iodine concentration are mainly collected in public wells near poultry farms. The surrounding environment is strongly polluted by excretion of poultry. On the other hand, our previous studies show that sediments in the Datong basin contain higher organic matter, which may be also related to the existence of organic iodine. Therefore, more detailed work is needed to quantitatively understand the dominant factors controlling the iodine species in aquifer systems.

4. Conclusion

From the hydrochemical properties of groundwater and distribution of iodine species in the Datong basin, the following characteristics and controlling factors can be inferred.

- (1) High iodine groundwater is mainly distributed in the center of basin, especially in the narrow belt along the Senggan River.
- (2) Speciation composition of iodine in groundwater is more controlled by redox potential. Under reducing conditions, iodide is the dominant species. With increasing Eh, speciation distribution becomes more complex.
- (3) Higher concentrations of organic iodine may be related to anthropogenic activities. More detailed work is needed to further quantitatively understand the processes that make organic iodine.

Acknowledgements

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