Effects of water-sediment interaction and irrigation practices on iodine enrichment in shallow groundwater

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Abstract: High iodine concentrations in groundwater have caused serious health problems to the local residents in the Datong basin, northern China. To determine the impact of water-sediment interaction and irrigation practices on iodine mobilization in aquifers, isotope (²H, ¹⁸O and ⁸⁷Sr/⁸⁶Sr) and hydrogeochemical studies were conducted. The results show that groundwater iodine concentrations vary from 14.4 to 2180 µg/L, and high iodine groundwater (> 150 µg/L) mainly occurs in the central area of the Datong basin. Sediment iodine content is between <0.01 and 1.81 mg/kg, and the co-occurrence of high iodine and high DOC/TOC concentrations of groundwater and sediment samples

in the deeper aquifer indicates that the sediment enriched in iodine and organic matter acts as the main source of groundwater iodine. The $^{87}\text{Sr}/^{86}\text{Sr}$ values and groundwater chemistry suggest that aluminosilicate hydrolysis is the dominant process controlling hydrochemical evolution along groundwater flowpath, and the degradation of TOC/iodine-rich sediment mediated by microbes potentially triggers the iodine release from the sediment into groundwater in the discharge area. The vertical stratification of groundwater ^{18}O and ^2H isotope reflects the occurrence of a vertical mixing process driven by periodic surface irrigation. The vertical mixing could change the redox potential of shallow groundwater from sub-reducing to oxidizing condition, thereby affecting the iodine mobilization in shallow groundwater. It is postulated that the extra introduction of organic matter and $\text{O}_2/\text{NO}_3/\text{SO}_4$ could accelerate the microbial activity due to the supplement of high ranking electron acceptors and promote the iodine release from the sediment into shallow groundwater.

Keywords: Vertical mixing; Water-sediment interaction; Groundwater; Iodine; Datong basin

1. Introduction

Iodine is an essential micronutrient for human beings, but excessive intake causes health problems, including goiter, cretinism, thyroid autoimmunity and even thyroid cancers. Cases of iodine enrichment in groundwater have been widely reported in coastal area, such as Japan ([Shimamoto et al., 2011](#)), Denmark ([Andersen et al., 2002](#)), North China Plain ([Zhang et al., 2013a](#)), as well as in inland basins, such as La Pampa plain

(Smedley et al., 2002), Datong basin (Li et al., 2013) and Taiyuan basin (Tang et al., 2013). In areas affected by waterborne iodine poisoning, groundwater typically provides the dominant source for water supply, therefore understanding the mechanisms of iodine mobilization in the source aquifers is critical both for sustainable water resource management and for effective actions to diminish iodine poisoning.

Due to the absorption capability of iodine, natural organic matter is commonly considered as the primary pool of solid iodine (Hansen et al., 2011; Shetaya et al., 2012; Xu et al., 2012). And the involved biogeochemical processes have been consequently regarded as the dominant control on the iodine cycle in aquatic environments (Amachi et al., 2007; Amachi et al., 2005). The behavior and speciation states of iodine depend mainly on the redox condition of the groundwater environment (Li et al., 2014; Otosaka et al., 2011). Changes of redox condition from oxidizing to reducing promote the reduction of iodate or organic-iodine, thereby lowering the absorption ability of iodine onto the organic matter or metal oxides and hydroxides (Dai et al., 2009; Hu et al., 2012; Shimamoto et al., 2010; Xu et al., 2015). In the Datong basin, high iodine concentrations up to 1890 $\mu\text{g/L}$ have been detected in the shallow groundwater from the discharge area where the groundwater condition is characterized by lower flow rate, long residence time and (sub)reducing conditions (Li et al., 2014; Li et al., 2013). Recently, periodic irrigation practices using deep groundwater and surface water as the irrigation sources have the potential to change the shallow groundwater environment through water table fluctuation (Li et al., 2016). The variation of the groundwater environment might further influence the geochemical cycling of iodine in the shallow aquifer due to the sensitivity

of iodine species to the redox potential of groundwater system. However, the effects of irrigation practices on iodine mobilization are still not well studied.

Stable isotope signatures (^2H , ^{18}O , and $^{87}\text{Sr}/^{86}\text{Sr}$) have been recently documented to be useful proxies for tracing groundwater recharge sources and flowpaths in meteorological, hydrological, and hydrogeological systems (e.g. (Peng et al., 2010b; Schiavo et al., 2009; Stichler et al., 2008)). The comparison of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ compositions of water samples to Global Meteoric Water Line (GMWL) reported by Craig (1961) can provide valuable information on water origin and regional hydrological setting (Peng et al., 2012). Strontium isotope signatures could provide an opportunity to trace the major contributing sources to the ultimate geochemical composition of the groundwater due to its advantage of hardly being fractionated by phase separation, evaporation or biological assimilation (Sánchez et al., 2010; Skrzypek et al., 2013). This study, therefore, aims to identify the effects of water-sediment interaction and irrigation practices on iodine enrichment in shallow aquifers of the Datong basin based on $\delta^2\text{H}$, $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ signatures and hydrogeochemical features of natural high iodine groundwater.

2. Study area

2.1 Geological setting

The Datong basin, located in northern China, is a NW-SE oriented Cenozoic rifted basin, which experienced multiple periods of lithospheric extensions and associated volcanism since the late Pleistocene (Chen et al., 1992). The active Cenozoic volcanism mainly occurs in the northern part of the basin. Subsidence associated with rifting

resulted in the formation and development of a lake that persisted from the Miocene to the Quaternary. As a result of this extended history, the Quaternary lacustrine sediments of the Datong basin commonly have high contents of humic substances (Li et al., 2013). Due to the variations in sedimentation rate, the thickness of Cenozoic sediments in the south and north centers of the Datong Basin are quite different: 3500 m and 1500 m, respectively (Cheng, 1983). The Sanggan River system and piedmont alluvial fans developed over the basin-scale in the Last Glacial (about 70 ka) (Wang et al., 2008; Zhou et al., 1991). Currently, in most of the Datong Basin, the lacustrine strata are overlain by alluvial plain, pluvial fans, and wind-blown deposits that accumulated under arid/semi-arid glacial period conditions (Gu et al., 2015).

The major types of rocks and sediments in the Datong basin can be classified into four groups (Li et al., 2009; Xie et al., 2011): (1) Archean metamorphic complex (granites and gneiss with greenstone terrain) in the east margin (Heng Mountain); (2) Cambrian to Ordovician limestone and dolomite with clastic rocks, mainly located in the southwest margin (Hongshou Mountain), (3) Carboniferous to Permian coal-bearing clastic rocks in the northwest margin containing varying amounts of inter-bedded sandstone, siltstone and shale, and (4) late Pliocene to Holocene basin sediments (alluvial and fluvial gravel, sand and silt) (Fig. 1).

2.2 Hydrological setting

With an arid/semi-arid climate, the annual average precipitation of the Datong basin is between 225 and 400 mm with 75 to 85% of rainfall occurring in July and August, and annual evaporation is above 2000 mm. Groundwater table changes from >20 m below the

land surface in the margin area to approximately 2~3 m in the central area with fluctuations caused by irrigation activities (Li et al., 2016). Except for some poor saline soils in the central area, most of the soils in the Datong basin have been cultivated for agriculture for centuries. Two upstream reservoirs and many ditches were built for irrigation practices which are conducted in March and September each year. As a result, the Sanggan River, as the main surface water, has temporary water flow only after intense rainfall events or between irrigation periods.

Basin-scale groundwater flow is generally in accordance with the topography from the northwest piedmont to the southeast area and from the basin margin to the central area (Xie et al., 2013). Generally, the Quaternary aquifers in the Datong basin can be divided into three parts with depths: upper (< 50 m), intermediate (50~160 m), and lower (> 160 m) aquifers (Guo and Wang, 2004). The upper aquifer consists of inter-bedded coarse sand, gravel and clay formed in late Pleistocene and Holocene, and is mainly recharged by vertical infiltration of meteoric and/or irrigation water. The intermediate aquifer was separated into several parts by the multiple clay units in brown, gray or dark colors, and generally contains several 2~10 m thick aquifers which are the main source of drinking and irrigation water for residents. The lower aquifer is made up of fine sand and silt formed in the early Pleistocene and Pliocene, and has the lowest specific capacity in comparison to the upper and intermediate aquifers. The laterally flowing groundwater from the fractured bedrock along the basin margins are the main recharge sources for the intermediate and lower aquifers. Evapotranspiration and artificial extraction for drinking and irrigation proposes are the two major forms of groundwater discharge at the Datong

basin. The depth for groundwater sampling in this study varies from 16 to 100 m in the upper and intermediate aquifers (Table 1).

3. Methods

3.1 Sampling and chemical analysis

A total of 29 water samples (26 groundwater, 2 surface water and 1 rain sample) were collected from Datong basin in August 2013 (Fig. 1 and Table 1). Prior to sampling groundwater, the wells were purged for at least 10 min using a high flow-rate pump. Total dissolved solid (TDS), redox potential (Eh), temperature (T) and pH were monitored *in situ* using HACH Instruments' portable meters. Samples were collected in HNO₃-washed polyethylene containers after infiltration using 0.45 µm membranes. The samples for cation and trace element analysis were acidified using ultra-purified HNO₃ to pH<2, and samples for anion, dissolved organic carbon (DOC), total iodine and Sr isotope analysis were stored in 50 mL polyethylene bottles directly after sampling. The samples for hydrogen and oxygen isotope analysis were collected without filtration.

Alkalinity measurements were performed using a titration method within 24h after sampling. Groundwater DOC concentrations were measured using the high-temperature catalytic combustion method with a TOC analyzer after inorganic carbon was removed using dilute HCl (2 mol/L) (Multi N/C 3100 TOC; Analytik Jena AG). Anions were analyzed using Ion Chromatography (IC) (Metrohm 761 Compact). Cation and trace elements including total iodine concentration were determined using ICP-AES (IRIS Intrepid II XSP) and ICP-MS (PerkinElmer ELAN DRC-e), respectively. An agreement

of below $\pm 5\%$ error was fulfilled in laboratory hydrochemical analysis. Charge balance errors for all groundwater samples were below 9% (QA-QC).

A 122 m depth borehole named DXZ was drilled in the central part of Datong basin in September 2012 and sediment samples were collected using capped PVC pipe and stored at 4°C until analysis (Li et al., 2013) (Fig. 1). Three bedrock samples were collected and stored in zip lock bags. A subset of sediment and rock samples was air-dried and crushed to pass through 0.125 mm sieves for further analysis. Sediment TOC was determined using an element analyzer (Vario TOC, Elementar). Major elements compositions (SiO_2 , Fe_2O_3 , TiO_2 , Al_2O_3 , CaO , P_2O_5 , MgO and MnO) were determined using an XRF spectrometer (model RIX2100; Rigaku, the Wood lands, TX). Sediment iodine was extracted using 10% dilute ammonia after being pressurized for decomposition at 190 °C for 19 h, which was developed and tested by Bing et al. (2004) and Xu et al. (2010), respectively, and further measured using ICP-MS (PerkinElmer ELAN DRC-e) with the average error less than $\pm 5\%$. All the chemical analysis work above was done at the State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan.

3.2 Isotope analysis

$\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures of all water samples were measured in China University of Geosciences (Wuhan) using Finnigan MAT 253 mass spectrometer and reported in standard delta notation relative to V-SMOW. Oxygen isotopes were determined via equilibration with H_2O - CO_2 at 25°C for 24 h and analyzed by continuous-flow mass spectrometry using a Thermo Finnigan Gas Bench. Hydrogen isotopes were measured

using an automated Finnigan MAT H/Device by reacting with Cr at 850°C. Precisions for both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are $\pm 1.0\text{‰}$ and $\pm 0.1\text{‰}$, respectively.

Strontium isotope signatures of 25 water samples (23 groundwater and 2 surface water), 7 sediments and 3 rocks were measured using thermal ionization mass spectrometry (TIMS) at the Center for Isotope Geochemistry, University of California, Berkeley. Isotope separations for approximately 1 μg strontium were performed on ion exchange columns using Eichrom Sr Spec resin. 100 ng of separated Sr (in a solution of 3N HNO_3) are loaded with TaCl onto a single Re filament. During the analysis period of our samples, the composition and reproducibility of the NBS 987 strontium standard was 0.71024 ± 1 . $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were reported with 2 s.d. internal errors.

4. Results

4.1 Hydrochemistry, $\delta^2\text{H}$, $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ signatures of water samples

4.1.1 Groundwater Chemistry

The physio-chemical parameters of water samples are listed in [Table 1](#). The groundwater TDS had a range of 298.1~10150 mg/L (median value: 1057 mg/L), and the high TDS values mostly occur in shallow groundwater with depth less than 25~30 m. The groundwater pH was near-neutral to weak alkaline (7.26~9.28). Concentrations of groundwater HCO_3 were very high, reaching up to 2120 mg/L with a median value of 635 mg/L. Groundwater Na concentrations ranged from 9.2 to 1960 mg/L with the median value of 429 mg/L, and Ca concentrations were between 2.86 and 454 mg/L. Na- HCO_3 water is the dominant type of groundwater, and the Ca- HCO_3 type water mainly occurs in the east margin of the study area. Additionally, high NO_3 concentration up to

897 mg/L was detected in shallow groundwater, which might be related to agricultural activity.

The iodine concentration in groundwater ranged from 14.4 to 2180 µg/L, with 48% of the samples failing to meet the national standard for drinking water of China (150 µg/L). As reported in our previous studies, high iodine groundwater (> 150 µg/L) occurs in both shallow and deep aquifers of the Datong basin (Fig. 2) (Li et al., 2014; Li et al., 2013). By contrast, the two upstream reservoir water samples had relatively lower iodine concentrations (64.2 and 90.3 µg/L, respectively).

4.1.2 Hydrogen and oxygen isotope signatures

The results of isotope signatures (^2H , ^{18}O and $^{87}\text{Sr}/^{86}\text{Sr}$) of water samples from the Datong basin are presented in Table 1. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of groundwater ranged from -90.2 to -55.6 ‰ and from -12.1 to -6.5 ‰, respectively. All groundwater can be divided into two groups according to the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values: Group I is characterized by enrichment of light isotope with the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ranging from -90.2 to -82.9 ‰ and from -12.1 to -10.7 ‰, respectively; Group II, by contrast, has heavier hydrogen and oxygen isotope signatures, changing between -76.0 and -55.6 ‰ and between -10.1 and -6.5 ‰, respectively. The distinctive hydrogen and oxygen isotope signatures of these two group samples might reflect the impact of vertical mixing processes in the study area.

The two upstream reservoir water samples are characterized by heavier $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values (mean values: -55.1 ‰ and -6.65 ‰, respectively) in comparison with those of the groundwater samples (Table 1). The rain water collected during the sampling

campaign had the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values ranging from -87.2 ‰ to -10.31‰, respectively, which fall within the ranged of groundwater $\delta^2\text{H}$ and $\delta^{18}\text{O}$.

4.1.3 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios

Groundwater samples from the Datong basin had a wide range of Sr concentrations varying from 0.21 to 8.64 mg/L. High concentrations of Sr are mainly observed in shallow saline groundwater samples collected from wells less than 30 m. The $^{87}\text{Sr}/^{86}\text{Sr}$ values in groundwater changed between 0.70872 and 0.72155. The groundwater samples from the eastern part of Datong basin had a wider range of Sr isotope values (0.71046~0.72155) than that from the western part (0.70872~0.71143). And an evident decreasing trend of Sr isotope signatures was observed in the eastern area from the margin areas to the central part of the basin (Fig. 1), which was related to water-rock interaction along the groundwater flow path. The two surface water samples had $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.71024 and 0.71034, and Sr concentrations of 0.88 and 1.02 mg/L, respectively, which were very close to those of groundwater samples from the central area.

4.2 Sediment geochemistry and $^{87}\text{Sr}/^{86}\text{Sr}$ signatures

The geochemistry and $^{87}\text{Sr}/^{86}\text{Sr}$ signatures of sediment samples from the Datong basin are presented in Table 2 and Fig. 3. The lithology of sediments from the borehole was light grey to black clay and sand, which were mainly composed of SiO_2 (35.9~83.8 wt.%), Al_2O_3 (7.30~15.8 wt.%) and CaO (3.31~29.0 wt.%). High content of organic carbon (OC) was observed in clayey sediment with the maximum of 6.25 wt.% (Fig. 3c). Sr contents of sediments ranged from 140 to 1150 mg/kg and had a good correlation with

total organic carbon (TOC) ($r^2=0.875$) (Fig. 3d). The $^{87}\text{Sr}/^{86}\text{Sr}$ values of sediments varied from 0.71107 to 0.71612, which are slightly higher than that of the groundwater sample DT13-04 (0.71047) from the same sampling site and evidently lower than those of bedrock samples (Cambrian shale: 0.74094, Permian sandstone: 0.72358 and Permian siltstone: 0.73558).

The iodine contents of sediment ranged from <0.01 to 1.81 mg/kg, which is close to that of reported for soils from inland area (0.89~1.16 mg/kg) (Fordyce et al., 2003), but lower than that of soil samples from coastal areas, such as Norway (up to 15.7 mg/kg, (Frontasyeva and Steinnes, 2004)) and the mean content of worldwide soils (approximately 5.1 mg/kg, Johnson, 2003). The high iodine contents in sediment from the Datong are mainly observed at depths of ~15 m and ~90 m (Fig. 3e). The highest iodine content (1.81 mg/kg) was observed in the grey clayey sediment with depth of 89.1 m, and the groundwater DT13-04 collected from its upper aquifer (67~86 m) had the iodine concentration of 934 $\mu\text{g/L}$, indicating that the iodine-rich sediment serves as the primary source of groundwater iodine. The depth profiles of sediment TOC and iodine show that the sediments with high TOC contents generally had high iodine contents (Fig. 3c, e), suggesting that organic matter could be the important host of iodine in aquifer sediments as documented in our previous studies (Li et al., 2014; Li et al., 2013).

5. Discussion

5.1 Hydrochemistry of high iodine groundwater

Cationic ratios (Mg/Na vs. Ca/Na molar ratios in Fig. 4) of all groundwater samples were in alignment around the silicate and evaporite end-members, indicating the

dominant controls of aquifer matrix on groundwater chemistry (Gaillardet et al., 1999; Hagedorn and Whittier, 2015). As shown in Fig. 4, the four groundwater samples from the west margin with higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are plotted near the silicate end-member, and therefore their hydrochemical and Sr isotope features are considered to be related to the metamorphic granites and gneiss from the Heng mountains which generally had relatively high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Karim and Veizer, 2000; Negrel and Roy, 1998; Negrel et al., 1988; Palmer and Edmond, 1992). Along the groundwater flowpath from the basin margin to central area, the Mg/Na and Ca/Na molar ratios gradually decrease to those of the evaporite end-member under the effects of hydrolysis of aluminosilicate minerals (Fig. 4) (Wang et al., 2009). As a result, the groundwater samples from the discharge area had the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios close to that of sediment samples, and therefore, the evolution of regional groundwater chemistry is mainly controlled by the water-sediment interaction along groundwater flowpath.

According to the hydrogeological setting and decreasing trend of groundwater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from the margin area to central area, a groundwater flowpath (#1 in Fig. 1) was selected for the hydrochemical modeling and the evaluation of water-rock interaction effects on iodine enrichment in groundwater from the central area. Variations of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, TDS, iodine, strontium, DOC and HCO_3 concentrations of the five groundwater samples along the model flowpath are shown in Fig. 5. Accordingly, sample DT13-01 from the margin area and DT13-04 from the discharge area are selected to represent ‘initial’ and ‘final’ solutions to conduct inverse geochemical modeling using PHREEQC (Parkhurst and Appelo, 1999), and the result of inverse modeling is shown in Table 3. The TDS range of the five samples was 298.1~1410 mg/L (Fig. 5b), which is

significantly lower than that of saline groundwater (3000~11330 mg/L) reported in Li et al. (2016), indicating that their hydrochemistry are mainly controlled by the water-sediment interaction such as cation exchange and mineral dissolution-precipitation rather than the saline processes (Table 3). As shown in Fig. 1, high iodine groundwater mainly occurs in the central part of the Datong basin, and an increasing trend of groundwater iodine from 17.5 to 934 $\mu\text{g/L}$ was observed along the groundwater flowpath (Fig. 5c). Coincidentally, the DOC varied in the same way (Fig. 5f). As mentioned above, the sediments with high TOC contents generally had high Sr and iodine contents, suggesting that the OC-rich clayey sediments might serve as the primary pool for both elements. In the discharge area of the Datong basin, due to water-sediment interaction including the biodegradation of sediment organic matter, soluble Sr and iodine enriched in radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ signature can be introduced into groundwater, thereby causing the observed elevation of Sr isotope ratios in discharge area (Fig. 5a and Fig. 5e). As a result, the degradation of organic matter might introduce CO_2 as the final stage of organic carbon into groundwater, which forms HCO_3 in solution and leads to the elevation of groundwater HCO_3 in the central area. The occurrence of microbially derived CO_2 is supported by the results of modeling using PHREEQC which showed a positive mole transfer of CO_2 along the groundwater flowpath (Table 3). Meanwhile, because all groundwater samples are oversaturated with respect to calcite and dolomite (Table 1), the precipitation of calcite and/or dolomite would absorb the soluble Sr due to preferential incorporation of Sr into carbonate minerals. As the dissolution and adsorption processes proceed, the addition and removal of groundwater Sr between the groundwater and sediment strongly affect the groundwater Sr concentration and isotope signatures until the

equilibrium is reached. In this study, such an equilibrium assumption is demonstrated by two observations. Firstly, more radiogenic Sr isotopes in groundwater DT13-04 (0.71046) and sediment DXZ-06 (0.71107) from the same sampling site coincidentally occur. Secondly, during the equilibrium process, biodegraded organic matter from the sediment should be introduced into groundwater. As a result, groundwater samples with DOC contents higher than 10 mg/L generally had lower $^{87}\text{Sr}/^{86}\text{Sr}$ compositions (0.71046~0.71095) (Fig. S1). More importantly, during the degradation of iodine-rich organic matter, the iodine sorbed on the clayey sediment would be mobilized into aqueous phases. The difference between groundwater Sr and iodine is that the iodide, which is the major iodine species in the reducing environment of the Datong basin (Li et al., 2014), is difficult to re-incorporated into the precipitated carbonate minerals (Zhang et al., 2013b). Therefore, under the effects of water-sediment interactions, a relatively narrow range of groundwater Sr concentration was observed (Fig. 5d), while the groundwater iodine concentration exhibited a sharp increase in the discharge area (Fig. 5c).

5.2 Vertical mixing process and its influence on iodine enrichment

As shown in Table 3, along the groundwater flowpath, cation exchange among Na, Ca and Mg causes the addition of Na and removal of Ca and Mg, thereby increasing in (Na+K)/(Ca+Mg) weight ratio with decrease of groundwater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Fig. 6). Meanwhile, several groundwater samples had lower (Na+K)/(Ca+Mg) weight ratios and $^{87}\text{Sr}/^{86}\text{Sr}$ signatures, which evidently deviate from the water-rock interaction trend. The two reservoir samples had similar hydrochemical and isotopic characteristics to those

deviating groundwater samples as shown in Fig. 6. The vertical mixing process using the upstream reservoir water as the main irrigation source can introduce surface water into shallow groundwater, which is further supported by groundwater $\delta^2\text{H}$ and $\delta^{18}\text{O}$ signatures.

The plot of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ for all water samples is shown in Fig. 7, where the global meteoric water line (GMWL) (Craig, 1961) and the local meteoric water line (LMWL) (EAEA/WMO, 2007) were also presented. It can be seen that all groundwater samples from the Datong basin fell below the GMWL and below the LMWL. The regression line for the Datong groundwater samples is $\delta^2\text{H}=6.018\delta^{18}\text{O}-16.35$ ($r^2=0.936$). The precipitation sample from Datong basin lies below to the three regression lines, which might be related to evaporation.

Two groups with distinctive $\delta^2\text{H}$ and $\delta^{18}\text{O}$ features were identified, and Fig. 7a shows that the Group II samples fall along the line between the upstream reservoir water sample and the Group I samples, suggesting the Group II samples are mixtures. During the irrigation, the upstream reservoir water, as the main irrigation source, is delivered into the shallow groundwater (Li et al., 2016). The depth profile of water $\delta^{18}\text{O}$ further suggests that the contribution from reservoir water could explain the higher $\delta^{18}\text{O}$ values observed in shallow groundwater (Fig. 7b). The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ features can therefore be used to construct a balance model to estimate the contributions from the two end-members, as applied in previous studies (Halder et al., 2013; Peng et al., 2012; Peng et al., 2010a). The equations in terms of δ values can be expressed as follows:

$$\delta^{18}O_{II} = \delta^{18}O_I \times R_I + \delta^{18}O_{RW} \times R_{RW}$$

$$R_I + R_{RW} = 1$$

where R_I and R_{RW} are the weighted contributions from Group I and reservoir water groundwater, respectively. The mean values of $\delta^{18}O$ in the reservoir water and Group I samples were -6.65 ‰ ($\delta^{18}O_{RW}$) and -11.5 ‰ ($\delta^{18}O_I$), respectively. By this calculation, the contribution of reservoir water to Group II approximately varies from 29% to 93%, gradually decreasing with the well depth. The shallow groundwater is heavily influenced by the surface irrigation activities. Notably, the contribution of rainfall was neglected in this two end-members model. As shown in Fig. 7c, the lowest d value of precipitation can act as an end-member leading to the decrease in d values of shallow groundwater, and therefore, the contribution of reservoir water might be overestimated by the two end-members model.

As shown in Fig. 7b, the vertical mixing process mainly influences the shallow groundwater with well depths less than 30 m, and these groundwater samples have iodine concentrations of 17.4~2180 µg/L. From the results of the mixing model, it can be found that the two groundwater samples (DT13-17 and DT13-19), located near the upstream reservoir DT13-28, are dominantly recharged by the upstream reservoir water (Fig. 1 and Fig. 7). The iodine concentrations in these two samples were 143 and 31.1 µg/L, respectively, indicating the dilution effect of reservoir water infiltration on groundwater iodine in the shallow aquifer.

The DOC concentration of the upstream reservoir is 11.1 mg/L (Table 1), higher than that of 68% of the groundwaters, and under the effect of vertical infiltration of upstream water, the additional organic carbon could potentially be introduced into shallow groundwater, causing the elevation of groundwater DOC as shown in Fig. 8a. The downward migration of organic carbon from the surface might provide additional

energy sources to drive the microbial activity, which has been documented as a major mechanism affecting the iodine behavior (Amachi, 2008; Amachi et al., 2010). In addition, the vertical mixing process also introduces O₂, NO₃ and SO₄-rich irrigation water into shallow aquifers, leading to the elevation of shallow groundwater Eh values, NO₃ and SO₄ concentrations (Fig. 8b and Fig. S2). The change of redox potential in shallow groundwater further affects the iodine enrichment and mobilization in shallow aquifers. As reported in our previous studies, (sub)oxidizing condition favors the enrichment of groundwater iodine (Li et al., 2014). The supplement of free oxygen and/or agricultural NO₃, ranking at the top of the electron acceptor ladder, provide more energy to the microorganisms, causing the acceleration of degradation of organic matter and the subsequent release of iodine (Arndt et al., 2013; Rivett et al., 2008). Consequently, the co-occurrence of oxidizing condition and high iodine concentrations were observed in the shallow groundwater.

5.3 Conceptual model of iodine enrichment in the groundwater system

Based on the spatial distribution of groundwater iodine concentrations and the patterns of isotope signatures, we put forward a conceptual model to illustrate how water-sediment interaction and vertical infiltration facilitate iodine mobilization (Fig. 9). The phreatic zone is particularly vulnerable to vertical irrigation practices, and therefore its iodine level in groundwater mainly depends on the recharged water. As observed in the Datong basin, the groundwater dominantly affected by irrigation practices has lower iodine concentrations owing to the low level of iodine in upstream reservoir water. In shallow groundwater, the major factor affecting the iodine mobilization is the vertical

transport of organic matter and electron acceptors during irrigation period, which accelerates the microbial oxidation of iodine-bearing clay-organic complexes, releasing iodine into groundwater. The turbulence of irrigation water tends to change the redox potential of the aquifer from sub-reducing to oxidizing, which favors iodine enrichment in groundwater (Li et al., 2014). For (medium)deep confined aquifers, the vertical mixing process has limited effect. Similar to shallow groundwater, the organic/iodine-rich clayey sediments act as the primary iodine carrier in the aquifer matrix due to the preferential adsorption of iodine onto organic matter. In these aquifers, the combined influence of intense water-rock interactions and autochthonous microbial activities, as identified from Sr isotope signatures and HCO_3^- concentrations, is considered to be the major factor responsible for the elevation of groundwater iodine concentration. Due to the low affinity of iodide onto carbonate minerals, the re-precipitation of carbonate minerals would not cause the retrieval of iodine back onto the sediment, and iodine may persist in groundwater. However, the hydrobiogeochemical mechanism of iodine release from the organic-rich sediment is still an open question, and needs more detailed investigation.

6. Conclusions

At the Datong basin, groundwater iodine concentrations vary from 14.4 to 2180 $\mu\text{g/L}$, while iodine contents in sediments are <0.01 to 1.81 mg/kg. High iodine groundwater mainly occurs in the central area of the basin, and can be observed at all well depths. Organic-clayey sediments serve as the primary pool of sediment iodine. Groundwater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vary from 0.70872 to 0.72155, and decrease from the basin margin to its central area, in accordance with the regional groundwater flow direction.

The hydrochemical compositions and Sr isotope features of groundwater and sediment samples suggest the water-sediment interactions, including intense microbial activity, affects the hydrochemistry during flow. Biodegradation of organic matter associated with clayey sediment interlayers and the low affinity of iodide are the primary factors explaining the observed sharp increase of groundwater iodine concentration in the discharge area. The evident stratification of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ signatures of surface water and groundwater samples reflects the significance of vertical mixing process. The results of two end-member mixing model show that the groundwater samples most affected by upstream reservoir water contain relatively low iodine concentrations. For high iodine groundwater in shallow aquifers, the input of organic carbon and electron acceptors during irrigation periods is considered to be the main factor favorable for degradation of iodine-bearing clay-organic complexes, thereby leading to iodine release into groundwater.

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Figure Caption

Fig. 1 Topographic and simplified geological map and sampling location of water samples at the Datong basin.

Fig. 2 The depth profile of groundwater iodine in the Datong basin.

Fig. 3 Depth profiles of SiO₂ (a), CaO (b), TOC (c), Sr (d) and iodine (e) contents of the borehole DXZ from the iodine-affected area in the Datong basin shown in Fig. 1.

Fig. 4 Plot of Mg/Na vs. Ca/Na molar ratios in the water samples from the Datong basin.

Fig. 5 Variations of ⁸⁷Sr/⁸⁶Sr ratios (a), TDS (b), iodine (c), strontium (d), HCO₃ (e) and DOC (f) concentrations along the groundwater flowpath from the basin margin to the central area (#1 in Fig. 1).

Fig. 6 The plots of (Na+K)/(Ca+Mg) vs. ⁸⁷Sr/⁸⁶Sr for water samples from the Datong basin.

Fig. 7 The plot of δ¹⁸O and δ²H of water samples from the Datong basin with the Global Meteoric Water Line (GMWL; data from (Craig, 1961)) and Local Meteoric Water Line (LMWL; data from EAEA/WMO, 2007), and the depth profiles of Group II δ¹⁸O (b) and *d*-excess (c) of groundwater from the Datong basin. The *d*-excess of water is defined as $d = \delta^2\text{H} - 8 \times \delta^{18}\text{O}$ (Dansgaard, 1964).

Fig. 8 The potential effects of vertical mixing process on iodine mobilization in the shallow groundwater. The depth profile of sediment iodine refers to the DXZ borehole shown in Fig. 1.

Fig. 9 The conceptual model for major processes and factors controlling iodine mobilization in shallow groundwater systems.

618 **Table Caption**

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620 basin.

621 Table 2 Chemical and isotopic compositions of sediment ssamples from the Datong basin.

622 Table 3 Results of mass transfer calculation using PHREEQC.

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Figure Captions

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

The diagram illustrates the iodine cycle in a subsurface environment, showing the flow of water and the release of iodine from clay minerals. The vertical axis represents depth, with the **Land Surface** at the top. The subsurface is divided into three main zones: **Phreatic** (shallow), **Shallow Groundwater**, and **(Medium)deep Groundwater**.

Key Processes and Features:

- Upstream Reservoir Water:** Water enters from the top, moving downwards through the Phreatic zone.
- Vertical Mixing:** Indicated by a downward arrow in the Phreatic zone.
- Dilution:** Indicated by an upward arrow in the Phreatic zone, leading to a **Relatively lower iodine concentration**.
- Clay minerals rich in Iodine and organic matter (s):** Two horizontal layers are shown, one in the Phreatic zone and one in the (Medium)deep Groundwater zone.
- Introduction of organic carbon and electron acceptors, O_2/NO_3 :** Indicated by a downward arrow from the Phreatic zone into the Shallow Groundwater zone.
- Oxidizing condition:** Indicated by a downward arrow from the introduction of organic carbon.
- Iodine Release:** Indicated by a red arrow pointing from the clay minerals in the Shallow Groundwater zone.
- Abiotic chemical reduction and Enhanced microbial degradation:** Indicated by a dashed red arrow pointing from the clay minerals in the Shallow Groundwater zone towards the Iodine Release.
- Limited effects:** Indicated by a downward arrow from the Shallow Groundwater zone into the (Medium)deep Groundwater zone.
- Na- HCO_3 type Groundwater:** Indicated by a green arrow pointing upwards from the (Medium)deep Groundwater zone.
- Carbonate minerals precipitation:** Indicated by a green arrow pointing upwards from the Na- HCO_3 type Groundwater.
- CO₂ occurrence:** Indicated by a green arrow pointing upwards from the (Medium)deep Groundwater zone.
- Microbial degradation and Intense water-rock interaction:** Indicated by a green arrow pointing upwards from the (Medium)deep Groundwater zone.
- Iodine Release:** Indicated by a red arrow pointing from the clay minerals in the (Medium)deep Groundwater zone.
- More radiogenic Sr isotopes:** Indicated by a green arrow pointing upwards from the clay minerals in the (Medium)deep Groundwater zone.

Table 1

Table 1 Chemical and isotopic compositions of groundwater samples from the Datong basin.

ID	water type	Depth m	pH	Eh mV	TDS mg/L	⁸⁷ Sr/ ⁸⁶ Sr	σ	δ ² H ‰ V-SMOW	δ ¹⁸ O ‰ V-SMOW	d ^c ‰ V-SMOW	DOC mg/L	Iodine μg/L	Calcite SI ^a	Dolomite SI	F mg/L	Cl mg/L	NO ₃ mg/L	SO ₄ mg/L	HCO ₃ mg/L	K mg/L	Na mg/L	Ca mg/L	Mg mg/L	Si mg/L	Sr mg/L
DT13-01	Ca-HCO ₃	-- ^e	8.59	37.7	365.4	0.72138	0.00057	-66.6	-9.4	8.6	3.15	17.5	1.191	2.190	< 0.01	11.5	31.4	111	221	4.39	9.18	68.2	19.4	5.74	0.32
DT13-02	Ca-HCO ₃	--	7.3	-35	1113	0.71728	0.00083	-73.9	-9.8	4.5	2.67	75.9	0.6499	1.091	< 0.01	123	< 0.01	404	543	3.31	27.3	221	61.6	8.21	1.27
DT13-03	Na-HCO ₃	--	8.07	--	298.1	--	--	-82.9	-11.3	7.5	--	19.1	0.6709	1.424	0.21	14.6	< 0.01	3.18	388	0.87	43.2	27.5	14.6	6.27	0.47
DT13-04	Na-HCO ₃	75	8.3	-102	1220	0.71046	0.00089	-87.4	-11.8	7.0	38.1	934	0.1964	1.428	1.01	171	< 0.01	12	1310	0.30	366	3.30	15.1	4.39	0.26
DT13-05	Na-HCO ₃	25	7.96	-56	856.4	0.71246	0.00054	-90.2	-11.9	5.0	5.48	175	0.4225	1.535	0.37	208	< 0.01	50.1	635	< 0.01	225	17.8	38.4	6.03	0.53
DT13-06	Na-HCO ₃	50	8.47	--	1001	--	--	-87.2	-11.5	4.8	--	444	0.2905	1.785	0.46	185	< 0.01	17.6	903	1.13	324	2.94	19.5	4.94	0.25
DT13-07	Na-Cl	100	9.28	--	2191	--	--	-68	-9	4.0	--	830	-0.0412	0.767	< 0.01	917	< 0.01	357	352	73.1	623	11.0	35.2	21.1	0.34
DT13-08	Mg-Cl	60	7.44	-16	7187	0.71095	0.00055	-68.3	-9.1	4.5	15.6	1030	0.5126	2.087	< 0.01	2400	897	1680	879	2.90	1010	125	634	6.14	8.64
DT13-09	Na-HCO ₃	52	7.97	-6.9	420.5	0.71143	0.00323	-71.9	-9.1	0.9	1.96	79	0.3541	1.005	1.20	27.6	34.8	62.3	334	0.85	82.6	24.1	21.2	6.62	0.80
DT13-10	Na-HCO ₃	19	8.28	-2.7	1410	0.71147	0.00060	-85.8	-11.3	4.6	7.56	479	0.5176	1.706	2.61	173	< 0.01	179	1230	1.02	418	8.23	16.6	5.51	0.30
DT13-12	Na-HCO ₃	52	8.53	-39	980.8	0.71070	0.00056	-88.4	-12.1	8.4	26.9	151	0.2801	1.656	1.11	113	< 0.01	13.2	1080	0.37	297	2.85	14.8	4.41	0.21
DT13-13	Na-HCO ₃	48	7.88	-53	1413	0.71668	0.00057	-76	-10.1	4.8	4.52	201	0.6771	1.825	0.65	178	11.9	246	1014	1.39	399	30.1	39.3	5.07	0.61
DT13-14	Na-HCO ₃	50	7.76	-11	965.1	0.71575	0.00093	-74	-9.8	4.4	3.43	96.1	0.642	1.627	0.69	104	7.26	191	756	2.33	184	49.7	48.7	5.71	0.92
DT13-16	Na-HCO ₃	18	8.13	-33	1950	0.71477	0.00057	-69.5	-9	2.5	7.29	50.1	0.5637	1.924	4.17	313	27.4	448	1090	1.45	560	14.3	39.3	5.00	0.61
DT13-17	Na-SO ₄	20	7.28	28.1	8324	0.71091	0.00121	-55.6	-6.5	-3.6	12.9	143	0.6563	1.706	< 0.01	1140	655	4210	571	3.77	1060	454	515	5.58	7.63
DT13-19	Mg-HCO ₃	28	7.7	72.5	1172	0.71089	0.00118	-59.8	-7	-3.8	3.7	31.1	0.4387	1.662	1.70	195	319	114	514	1.06	105	48.9	132	5.93	3.70
DT13-20	Na-Cl	20	8.07	71.1	6275	0.71595	0.00079	-73.2	-9.2	0.4	37.1	2180	0.9421	2.723	< 0.01	1780	87.6	1410	2120	27.5	1780	33.2	100	5.28	1.18
DT13-21	Na-HCO ₃	25	8.03	29.3	801.9	0.71505	0.00058	-71	-9	1.0	2.79	151	0.6268	1.891	0.92	105	55.2	86.4	642	2.34	154	26.9	51.4	4.38	0.81
DT13-22	Ca-HCO ₃	30	7.81	12.9	659.9	0.71870	0.00108	-71.3	-9.6	5.5	3.09	21.1	0.4608	1.023	< 0.01	171	< 0.01	138	316	3.98	31.1	104	53.5	7.39	0.99
DT13-23	Ca-HCO ₃	60	7.75	-10	405.2	0.72155	0.0007	-71.8	-9.5	4.2	1.53	14.4	0.5529	1.127	0.26	18.1	7.00	44.3	456	2.56	19.7	58.2	27.1	7.21	0.56
DT13-24	Mg-HCO ₃	30	7.26	46.3	1906	0.71142	0.00041	-65.8	-8.2	-0.2	4.43	17.4	0.3211	1.263	< 0.01	359	373	384	655	0.15	190	95.4	177	6.13	4.87
DT13-25	Na-SO ₄	--	8.93	16.5	2120	0.71067	0.00078	-87	-10.7	-1.4	2.02	158	0.9540	2.543	< 0.01	566	< 0.01	784	299	5.70	539	25.8	49.6	5.78	1.52
DT13-26	Na-HCO ₃	16	8.1	3.8	749.8	0.70979	0.00080	-65.6	-7.9	-2.4	2.2	125	0.448	1.526	1.58	115	76.2	148	383	1.34	151	23.1	43.7	5.64	0.68
DT13-27	Na-Cl	30	7.63	-89	10150	0.71060	0.00057	-65.3	-7.9	-2.1	17.2	439	0.8737	2.611	< 0.01	3300	< 0.01	3520	755	6.03	1970	228	751	7.73	6.81
DT13-29	Mg-HCO ₃	--	8.29	--	472.7	0.71039	0.00078	-66.9	-8	-2.9	2.71	18.8	0.4203	1.678	2.60	24.1	11.9	102	409	1.09	74.4	13.6	41.2	5.21	0.87
DT13-30	Na-NO ₃	35	7.91	-36	943.7	0.70872	0.00094	-63.5	-7.6	-2.7	2.19	30.9	0.3090	1.148	< 0.01	144	360	47.7	302	1.97	155	33.7	50.5	8.35	1.05
DT13-31	--	--	8.63	--	431.2	0.71024	0.00071	-58.8	-7.2	-1.2	11.1	64.2	--	--	0.71	49.6	8.95	173	160	5.05	38.8	52.3	23.2	3.80	0.88
DT13-28	--	--	--	--	508.2	0.71034	0.00062	-51.4	-6.1	-2.6	--	90.3	0.9645	1.926	0.60	71.5	< 0.01	198	183	6.63	57.5	53.1	30.3	0.93	1.02

SI: Saturation index;
WR: Weight ratio;
 $d = \delta^2\text{H} - 8 \times \delta^{18}\text{O}$;
RW: Reservoir water;
--: No record or not measured.

Table 2

Table 2 Chemical and isotopic compositions of selected sediment samples from the Datong basin

ID	Lithology	Depth m	⁸⁷ Sr/ ⁸⁶ Sr	Iodine mg/kg	TOC %	SiO ₂ %	CaO %	Al ₂ O ₃ %	Fe ₂ O ₃ %	MgO %	Na ₂ O %	K ₂ O %	MnO %	P ₂ O ₅ %	TiO ₂ %
DXZ-02	Greyish-green silt	8.5	0.71319	0.834	0.33	61.66	7.37	11.14	3.97	2.30	1.87	2.22	0.06	0.14	0.57
DXZ-06	Green-brown clay	15.2	0.71107	1.087	5.22	28.57	29.01	7.30	3.09	2.08	0.56	1.21	0.08	0.11	0.36
DXZ-17	Grey silt	32.6	0.71223	0.537	1.59	53.23	13.08	10.05	4.09	2.20	1.25	1.95	0.09	0.16	0.50
DXZ-29	Dark grey fine sand	55.6	0.71612	0.184	0.50	61.60	6.23	12.08	4.32	2.04	1.56	2.45	0.06	0.11	0.73
DXZ-40	Grey silt	72.1	0.71472	0.596	0.06	59.98	7.45	12.30	4.42	2.42	1.73	2.41	0.1	0.16	0.61
DXZ-52	Grey clay	90	0.71299	1.463	2.10	42.54	13.29	13.48	5.73	3.58	0.77	2.38	0.11	0.19	0.59
DXZ-62	Grey silt	108	0.71524	0.322	0.06	67.26	5.03	10.88	3.61	1.79	1.76	2.20	0.05	0.09	0.66

Table 3

Table 3 Results of mass transfer calculation using PHREEQC

ID	Solution fractions	
DT13-01	1	
DT13-04	1	

Phase	mole transfer (mol)	
Calcite	0.007492	CaCO ₃
CO ₂ (g)	0.01433	CO2
MgX ₂	-0.00003662	MgX ₂
NaX	0.01708	NaX
Quartz	0.0002374	SiO ₂
CaX ₂	-0.008505	CaX ₂
Gypsum	-0.0008571	CaSO ₄ ·2H ₂ O
Celestite	-6.819E-07	SrSO ₄
Halite	0.003092	NaCl
Kaolinite	0.0002011	Al ₂ Si ₂ O ₅ (OH) ₄
Illite	-0.0001749	K _{0.6} Mg _{0.25} Al _{2.3} Si _{3.5} O ₁₀ (OH) ₂

Negative values mean phase removal from groundwater, while positive means phase dissolution.