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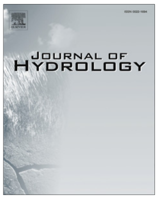

Research papers

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 (^{2}H, ^{18}O and ^{87}Sr/^{86}Sr) 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}Sr/^{86}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 ^{2}H 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 O_2/NO_3/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.

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, 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 μg/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, 2013). Recently, periodic irrigation practices using deep groundwater and surface water as the irrigation sources have the potential to change the shallow ground-

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water 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 (^{2}H, ^{18}O, and ^{87}Sr/^{86}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 δ^{18}O and δ^2H 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 δ^2H, δ^{18}O and ^{87}Sr/^{86}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 75–85% 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, grey 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 HNO_3-washed polyethylene containers after infiltration using 0.45 μm membranes. The samples for cation and trace element analysis were acidified using ultra-purified HNO_3 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 24 h 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 ±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