Science of the Total Environment 544 (2016) 158–167

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

# Cl/Br ratios and chlorine isotope evidences for groundwater salinization and its impact on groundwater arsenic, fluoride and iodine enrichment in the Datong basin, China

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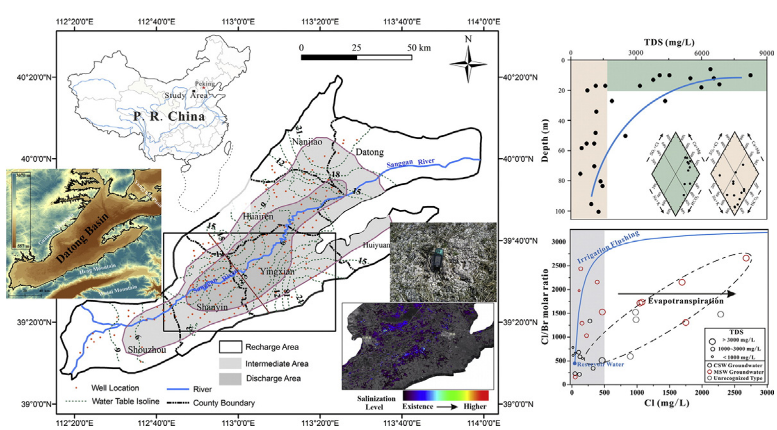
## HIGHLIGHTS

- Natural high arsenic, fluoride and iodine groundwater co-occur with saline water.
- Groundwater Cl/Br ratio and Cl isotope were used to study saline water.
- Groundwater salinization processes retard the groundwater arsenic enrichment.
- Intense evapotranspiration could restrict the groundwater fluoride concentration.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 4 July 2015
Received in revised form 29 August 2015
Accepted 29 August 2015
Available online xxxx

Editor: D. Barcelo

*Keywords:*
Groundwater salinization
Cl/Br molar ratio
Cl isotopes
Groundwater As/F/I enrichment

## ABSTRACT

In order to identify the salinization processes and its impact on arsenic, fluoride and iodine enrichment in groundwater, hydrogeochemical and environmental isotope studies have been conducted on groundwater from the Datong basin, China. The total dissolved solid (TDS) concentrations in groundwater ranged from 451 to 8250 mg/L, and 41% of all samples were identified as moderately saline groundwater with TDS of 3000–10,000 mg/L. The results of groundwater Cl concentrations, Cl/Br molar ratio and Cl isotope composition suggest that three processes including water-rock interaction, surface saline soil flushing, and evapotranspiration result in the groundwater salinization in the study area. The relatively higher Cl/Br molar ratio in groundwater from multiple screening wells indicates the contribution of halite dissolution from saline soil flushed by vertical infiltration to the groundwater salinization. However, the results of groundwater Cl/Br molar ratio model indicate that the effect of saline soil flushing practice is limited to account for the observed salinity variation in groundwater. The plots of groundwater Cl vs. Cl/Br molar ratio, and Cl vs $\delta^{37}$Cl perform the dominant effects of evapotranspiration on groundwater salinization. Inverse geochemical modeling results show that evapotranspiration may cause approximately 66% loss of shallow groundwater to account for the observed hydrochemical pattern. Due to the redox condition fluctuation induced by irrigation activities and evapotranspiration, groundwater salinization processes have negative effects on groundwater arsenic enrichment. For groundwater iodine and fluoride

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http://dx.doi.org/10.1016/j.scitotenv.2015.08.144

enrichment, evapotranspiration partly accounts for their elevation in slightly saline water. However, too strong evapotranspiration would restrict groundwater fluoride concentration due to the limitation of fluorite solubility.


## 1. Introduction

Groundwater salinization has been a world-wide concern not only for sustainable exploration of water resource but also for protection of natural ecosystems (Mehta et al., 2000; Pisinaras et al., 2010). For instance, capillary rise of salt driven by shallow saline groundwater could cause salinization of root zones and further decline in plant productivity (Kobryn et al., 2015). Comparably, groundwater salinization is a more severe problem in arid and semi-arid regions where the groundwater plays an essential role in supporting ecosystems and providing invaluable water resource (Alaghmand et al., 2013; Jones et al., 2009). In the southwest Australia, Caccetta et al. (2010) evaluated that the land salinity driven by saline groundwater has covered almost one million hectares of land in 1996 and a further 5.4 million hectares are at risk of future salinization.

Generally, the spatial variation of groundwater salinity can be directly reflected by hydrochemical compositions (Mondal et al., 2010). However, if there are several contributors involved into groundwater salinization, it is usually difficult to sufficiently discern them only based on the major ion chemistry. For instance, if the groundwater was affected by natural halite (NaCl) and edible salt (NaCl), due to their chemical similarity, their relative importance can hardly be distinguished.

As the useful indicators, Cl/Br molar ratio and Cl stable isotope have been widely used to demonstrate the origination and transport processes of solutes in groundwater (Beekman et al., 2011; Katz et al., 2011; Lüders et al., 2002; Richard et al., 2011). Due to the conservative behavior of groundwater Cl and Br, several original sources of water salinity have distinct ranges of Cl/Br molar ratios (Davis et al., 1998). For instance, seawater has a Cl/Br molar ratio of approximately 600 (Richard et al., 2011), while evaporite minerals such as halite could have Cl/Br molar ratio up to approximately $10^4$ since the exclusion of larger Br ion from the mineral structure (Cartwright et al., 2004). For water Cl stable isotope, besides the mixing and physical processes (e.g. ion filtration (Amundson et al., 2012) and diffusion (Eggenkamp, 2014)), geological water-rock interaction and phase separation could produce isotopic variation (Beekman et al., 2011; Yamanaka et al., 2014). Numerous studies have already investigated Cl stable isotopes as tracers of fluid circulation in various contexts (Lavastre et al., 2005; Li et al., 2015). Thus, groundwater Cl chemical and isotopic signatures can help to provide useful information on salt transport in groundwater system.

The Datong basin in the northern of China is an inland Cenozoic rifted basin, where high concentrations of geogenic arsenic, fluoride and/or iodine enrichment in groundwater have been reported by us recently (Li et al., 2014; Su et al., 2013; Xie et al., 2014). Li et al. (2012) found that high arsenic and/or fluoride groundwater usually co-occurred with saline groundwater in shallow aquifers of the Datong basin. In addition, high groundwater iodine concentrations were also reported to occur in shallow groundwater (Li et al., 2014). Therefore, the better knowledge of groundwater salinization might provide some valuable information for the understanding of groundwater arsenic, fluoride and/or iodine enrichment in the Datong basin.

Therefore, in this study, shallow groundwater salinization processes were investigated by incorporating groundwater chemistry, Cl/Br molar ratio and Cl stable isotope with the following major objectives: (1) to identify the factors controlling groundwater salinity in the shallow aquifers of the Datong basin; (2) to apply groundwater Cl/Br molar ratio and Cl isotope to examine the dominant processes on groundwater salinization, and its impact on the groundwater arsenic, fluoride, and/or iodine enrichment.

## 2. Hydrogeological background

The Datong basin located in northern China, is a NW–SE Cenozoic rifted basin, with Heng Mountain to the east, Guancen Mountain to the south, and Yangyuan plain to the north (Fig. 1). The Heng Mountain mainly consists of Archean metamorphic rocks, while the Guancen Mountain is composed of Cambrian/Ordovician limestone and Carboniferous/Permian clastic rocks. During geologic time, the Datong basin is developed from a fossil lake, and the resulting sediments range in age from later Pliocene to Holocene. The deposited sediments consist of interstratified layers of unconsolidated sand, gravel, silt and clay with varying extent and thickness (Fig. 2).

According to the sediment lithology, three major aquifers were recognized in the study area, which can be divided in depths as upper (< 50 m), intermediate (50–160 m), and lower (>160 m) aquifers, respectively. The upper aquifer consists of interbedded coarse sand, gravel and clay formed in late Pleistocene and Holocene. An evident dark clay layer rich in natural organic matter can be observed around 20 m in most of central area (Fig. 2). Clay units in brown, gray or little dark colors separate the intermediate aquifer into several parts (Li et al., 2013). The lower aquifer is made up of fine sand and silt formed in early Pleistocene and Pliocene.

The depth for water sampling in this study varies from 6 to 100 m, which are mostly positioned in the upper and intermediate aquifers (Table 1). The upper aquifer is mainly recharged by vertical infiltration of meteoric water, while the laterally penetrating groundwater from the fractured bedrocks along the basin margins are the main recharge sources for the intermediate and lower aquifers. Evapotranspiration and artificial abstraction for drinking and irrigation proposes are the major discharge sources. 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.

Basin-scale groundwater flow directions are generally from the northwest piedmont to the southeast area and from the basin margin to the center area. The ephemeral Sanggan River is the main surface water in Datong basin (Fig. 1), but the upstream reservoir, which has been built for decades as the major irrigation source, has substantially changed the river situation (Fig. S1). Each year, there are two periodic and large-scale irrigation activities in March and September, respectively. Additionally, soil salinization has been known as one of the most significant problems in the Datong basin. Results of remote sensing techniques indicated that approximately 25–30% of the whole basin is covered by saline soil (Fig. 1).

## 3. Methods

### 3.1. Sampling and chemical analysis

The basin-scale investigation of water table, involving a total of 191 groundwater wells, was carried out using piezometers in August 2010 (Fig. 1). No significant rainfall occurred during the survey period.

Based on the survey result of groundwater table, a total of 27 groundwater samples were collected in August 2012 (Fig. 2) along the flow path from recharge area to discharge area. According to the sampling well structures, the wells can be mainly divided into two types: multiple screening wells (MSW) and confined screening wells (CSW). The groundwater from MSW is the mixture of water from all aquifers screening the well depth, while the groundwater from CSW is mainly from the specific confined aquifers (Fig. 2). Twelve samples were