



Geochemical characteristics and fluoride distribution in the groundwater of the Zhangye Basin in Northwestern China

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ABSTRACT

To better understand geochemical processes leading to the fluoride enrichment in the groundwater of the Zhangye basin, chemical parameters, stable isotopic compositions, tritium and radiocarbon data were obtained for groundwater samples (depth 10 m–250 m) from three hydrogeological environments: Longshou and Qilian piedmont and the central fine soil plain. Groundwater ($n = 7$ out of a total of 8 samples) with high fluoride concentration (> 1.0 mg/l) is found in the piedmont of the Longshou Mountains, with a maximum value of 3.06 mg/l. Fluoride concentrations in the groundwater also gradually increase from the piedmont of the Qilian Mountains from 0.15 to 0.45 mg/l ($n = 7$) to the fine soil plain from 0.21 to 2.78 mg/l ($n = 23$) located in the center of the Zhangye Basin. The high fluoride concentration in groundwater correlates with the prevalence of $\text{SO}_4\text{--Cl--Na--Mg}$ and alkaline conditions. Isotope and tritium analyses indicate that streams and rivers rapidly recharge the groundwater in the piedmont of the Qilian Mountains and the fine soil plain. In contrast, the high fluoride groundwaters in the piedmont of the Longshou Mountains display ^{14}C ages older than 8 ka, indicating a longer water–rock interaction time. Using the ionic ratio plot and the Gibbs' diagram, evaporation and dissolution of fluorine-rich minerals are shown to be major factors resulting in the elevated fluoride concentrations. The results have implications for managing groundwater resources for drinking water supply to ensure public safety in the Zhangye Basin and other inland arid basins in northwestern China.

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1. Introduction

Occurrence of fluoride in groundwater has drawn worldwide attention due to its considerable impact on human health. Insufficient or excessive intake of fluorine can result in a number of health issues. Small concentrations of fluoride have beneficial effects on the teeth by hardening the enamel and reducing the incident of tooth decay (Fung et al., 1999). Chronic exposure to elevated concentrations of fluoride in drinking water above the World Health Organisation guideline value of 1.5 mg/l often results in endemic diseases such as dental and skeletal fluorosis (World Health Organisation, 2004). At least 25 countries in the world have reported occurrences of fluorosis due to chronic exposure to high fluoride in drinking water. Examples include East Africa (Gaciri and Davies, 1993), Mexico (Grimaldo et al., 1995), India (Jack et al., 2005), and China (Wang et al., 2004). In northern China, approximately 50 million people are exposed to high fluoride groundwater above the Chinese drinking water standard for fluoride of 1.0 mg/l. About 60% of the exposed population suffer from dental fluorosis, and about 10% suffer from skeletal fluorosis (Dai et al., 2007).

Fluoride-rich minerals such as fluorite, topaz, fluorapatite, and cryolite have been suggested as the important fluoride source, especially in granitic terrains (Chae et al., 2007). In addition, specific hydrogeochemical settings also play a very significant role in the fluoride enrichment of groundwater; for instance, high alkalinity and low calcium favor high fluoride content (Guo and Wang, 2007; Meenakshi and Maheshwari, 2006). Evaporation and ion exchange have been invoked to explain increased fluorine levels in shallow groundwater, such as those observed in Northern China (Liu and Zhu, 1991).

The Zhangye Basin is located in the middle reaches of the Heihe River which is one of the largest and most intensely exploited inland river in the semi-arid and arid regions of NW China. During the last several decades, there has been misuse and poor management of surface water for irrigation using traditional multichannel design (Wang and Gao, 2002). Over the last two decades, Groundwater has become increasingly important as domestic (drinking) water supply due to rapid population growth and socio-economic development. It has been estimated that more than 17,000 people are drinking high F groundwater, with 3800 dental fluorosis patients and 650 skeletal fluorosis patients identified in the Zhangye Basin (He et al., 2008). To utilize and protect valuable groundwater resources effectively and to safeguard the health of people, it is important to understand the occurrence and the hydrochemical characteristics of high F groundwater, and its evolution processes.

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The main objectives of this study are as follows: 1) to delineate the spatial distribution of F enrichments in the groundwater from the Zhangye Basin, 2) to use isotopic tracers to illustrate sources of recharge for the high F groundwater, 3) to evaluate hydrogeochemical factors and processes contributing to occurrence of high F in the groundwater.

2. Regional geology and hydrogeology

The Zhangye Basin is a northwest trending basin about 70 km long and 40–60 km wide (Fig. 1). The mean annual air temperature is about 7.1 °C. The climate is semiarid continental. The annual mean precipitation between 1951 and 2005 was 128.2 mm, with 78% of rain falling between June and September. The annual surface evaporation is 2020.2 mm. The basin has an altitude of about 1500 m above sea level (masl) and is flat compared to the surrounding mountains with altitudes ranging from 2000–5000 masl (Qilian Mountains to the southwest) and 1600–3000 masl (Longshou Mountains to the northeast). There are three major geomorphologic units: the Qilian and Longshou Mountains, and the middle oases plain of Zhangye

(Chen, 1997). The bedrock of both mountains consists of Sinian schist, gneiss, limestone, metamorphic sandstone, Palaeozoic tuff, limestone, metamorphic sandstone, inter-bedded Jurassic and Tertiary sandstone, and shale (Fig. 2). Yingluoxia Gorge divides the drainage basin of the Heihe River into the upper recharge and the middle runoff areas where the Zhangye Basin is located. Discharge of the Heihe River at Yingluoxia has been about 1.6×10^9 m³/a since 1985 (Gao et al., 2004). The Shandan River, a major tributary, converges with the main branch of the Heihe River in the study area (Fig. 1).

The middle oasis plain is composed of alluvial fans of the Qilian Mountains, a fine soil plain currently used for farming, and smaller diluvial fans of the Longshou Mountains (Fig. 1). The unconsolidated Quaternary diluvial and lacustrine sediment deposits form the main aquifers (Fig. 2). From southwest to northeast along transect I–II (Fig. 2), the sediments gradually become finer, changing from coarse-grained gravel pebbles with a thickness of up to 1000 m, to fine-grained sand and silt with a thickness of 50–200 m (Chen, 1997; Fan, 1991). With this change of lithology, a simple unconfined aquifer near the foot of the Qilian Mountains gradually changes into multi-layered

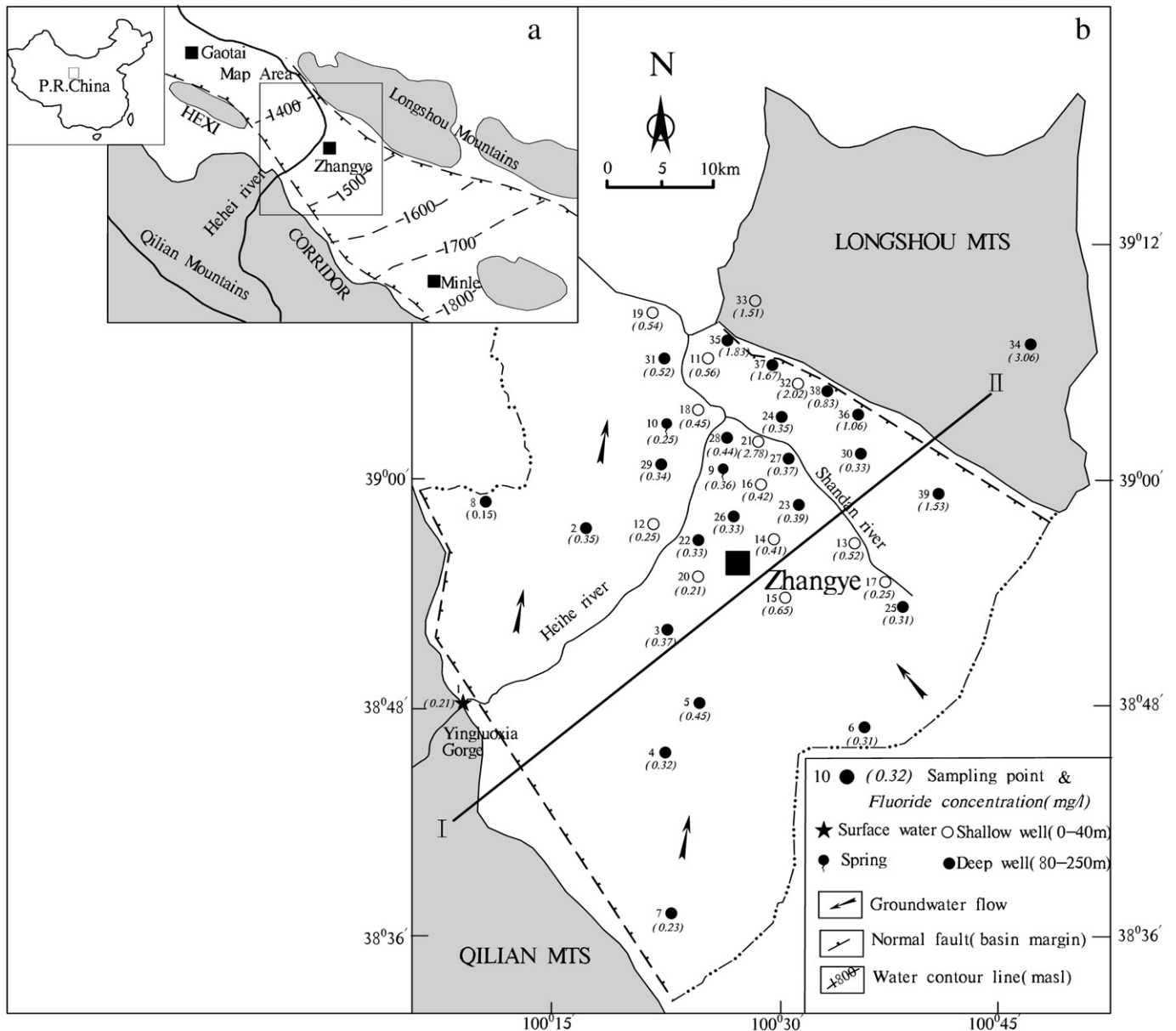


Fig. 1. Geographic location of the study: (a) location map of the Zhangye Basin; (b) the study area, sample sites, and groundwater F⁻ concentrations.

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