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Source apportionment of fluorine pollution in regional shallow groundwater at *You'xi* County southeast China

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HIGHLIGHTS

- Systematic study on source apportionment and migration of regional fluorine pollution at *You'xi* County Southeast China.
- Water-rock interaction, mixing of groundwater, and human activity demonstrated to be responsible for fluorine pollution.
- Ratio of soluble ions $(K^+ + Na^+)/Ca^{2+}$ (***R***) applied as a viable factor for prediction of fluorine water availability.

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ABSTRACT

Source apportionment of fluorine pollution in the regional shallow groundwater at *You'xi* County, southeast China, has been analyzed by means of monitoring F^- ion change characteristics in this area. Meanwhile, pollution sources and influencing factors of the shallow groundwater have been uncovered by studying the correlation between F^- and other related ions such as Na^+, Ca^{2+}, Cl^-, NO_3^-, HCO_3^-, as well as $(K^+ + Na^+)/Ca^{2+}$ ratio (***R***) and pH effect. The results show that F^- ions in shallow groundwater at the study area come mainly from the dissolution of fluorinated minerals in a form of fluorite (CaF_2), the so-called water-rock interaction, and there is a higher possibility for the occurrence of fluorine water where the ratio of $(K^+ + Na^{+)}/Ca^{2+}$ exceeds a value of 2.1. Moreover, the release and migration of F^- ions have been favored by the alkaline environment in this study area.

1. Introduction

You'xi County is one of the most important national and provincial bases for commodity grain and agriculture in southeast China. Due to the increasingly serious pollution of surface water, groundwater has become the main source of life supply for local inhabitants in this area. Therefore, the study of regional groundwater quality is of peculiar importance (Li and Zhang, 2011; Schot and Pieber, 2012; Bonte et al., 2013; Ouyang et al., 2013). According to the occurrence, hydraulic characteristics, and physical property, groundwater in the study area includes mainly three types: loose rock pore water, carbonate rock karst water and bedrock fissure water. Loose rock pore water mainly occurs in the pore water of Quaternary alluvial layer of sand, gravel or pebbles in the clay of Quaternary talus residual pores, as water-rich medium. Recharge of loose rock pore water depends greatly on lateral and short flow recharge from creek and river, both in rainy and non-rainy seasons. Karst water, also known as cavern water, refers to groundwater in fracture and caves of soluble rocks. The storage of carbonate rock Karst water is relatively short and the supply is mainly from rainfall and water-rich rocks, in a form of spring in valley and hillside. Bedrock fissure water appears in the bedrock fractures and shattered fault zones, as the pressure of local water. On the other hand, groundwater recharge is realized by means of precipitation, irrigation, subterranean flow, channel leakage and so forth. Quaternary loose rock pore water is capable of partially

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accepting bedrock fissure water supply and river recharge, as well as forming springs or subsurface drainage to *You'xi* River system. Moreover, groundwater dynamics changes significantly with seasons (Jiang et al., 2009; Jaffrezic et al., 2015), which results in water table rise in the rainy season and decline in the dry season. Groundwater pollution may originate from different underground zones, coupled to seasonal and environmental changes (Tareq et al., 2003; Shi et al., 2009).

Fluorine is one of the trace elements that are widely distributed in the natural environment and closely related to human health. Regional fluorosis, which causes damage to teeth, bones, and soft tissues, has been observed where people live in the environment of high fluoride and the chronic poisoning happens as a result of long-term and excessive intake of fluoride (Ghosh et al., 2015). Fluorine distributes widely in nature, mainly in forms of minerals such as fluorite (CaF_2), cryolite (Na_3 [AlF_6]), and apatite ($Ca_5(PO_4)_3F$) (Antipin et al., 2006; Feng et al., 2012; Doherty et al., 2014). Fluorine-rich rocks and deposits are key sources of fluorinated soil and drinking water. Fluorine pollution may also come from discharged water, waste gases, and industrial waste residues, including metal manufacturing, electroplate, and phosphate fertilizer production. In the study area, release of fluoride ions from surface water to groundwater has been possible, as a result of dissolution and hydration of all kinds of fluorine-containing minerals and bedrocks, during the process of water recharge. On the other hand, fluorine-rich medium of Quaternary deposits, sand, and clay form through water transportation and sedimentation during the bedrock weathering and soil forming processes. At the same time, fluorine contents released from bedrock to groundwater under chemical adsorption and sedimentation, present in loose deposits, reallocate and exchange into shallow groundwater. Therefore, fluorine-containing minerals and bedrocks contribute as the main resources of fluorine; whereas Quaternary loose deposits determine the enrichment and distribution of fluoride ions, which has more straightforward and important impact on the origin of fluorine in shallow groundwater.

Mapping of fluorine source apportionment in groundwater is particularly important for evaluation and prediction of F^- content in groundwater, which requires, in principle, an extensive knowledge on dissolubility, transportation and sedimentation of F^- ions (Aboal et al., 2008; Guo et al., 2009; Zhang et al., 2010). This work presents a case study on the source apportionment of fluorine pollution in shallow groundwater at *You'xi* County, southeast China. It has been revealed that multiple factors, including water-rock interaction, mixing of groundwater, and human activity, are responsible for fluorine pollution in the study area. Furthermore, the alkaline environment in this area (appearance of high pH water) favors also the release and migration of F^- ions (Zamana and Bukaty, 2004). This current work focuses on the comprehensive analysis of water quality and the distribution of fluoride ions in groundwater. The results provide not only the technical support for groundwater exploitation, but also the measures to control excessive fluoride in groundwater.

2. Material and methods

2.1. Study area

You'xi County locates at the east longitude between 117°48′–118°39′, north latitude between 25°50′–26°26′ in the middle of Fujian province, southeast China. The total area of *You'xi* County (3463 km^2) ranks the second in counties of Fujian, among which 689.5 thousand acres of mountains, 56 thousand acres of cultivated land, and 110 thousand acres of water and other areas.

2.2. Sample selection

Water samples in the study area were collected from shallow, medium-deep and deep groundwater, respectively. The shallow groundwater was pore phreatic water, which was detected between 1 and 60 m, mostly from upper Pleistocene sub-fine sands; samples of medium-deep layer water were pore-confined water, which was detected between 50 and 130 m, mostly from lower and middle Pleistocene sub-fine sands; deep groundwater samples were also pore-confined water of detection layer about 200 m, which was mostly from sub-Pleistocene sub-sands and Neogene Tertiary middle-sands. The reference groundwater data was extracted from the Geological Environment Monitoring Center, Fujian Province, including sixty-five sampling points, of which thirty-five points were in shallow groundwater, fifteen points were in medium-deep layer and the rest fifteen points were in deep groundwater. Some of these points might coincide, but the selected points were detected specially under the monitor of national and provincial organizations.

2.3. Sampling

The sampling of selected areas (Fig. 1) was carried out using German GARMIN GPS locator geographical coordinates for sampling point positioning. Groundwater samples were stored and tested in polyethylene bottles, prior to rinsing the bottles for three times and pH was measured with a portable pH meter. Cation test of water samples was pre-treated by acidification to pH lower than 2.0 with HCl, whereas anion test of water samples was carried out directly from the sealed polyethylene bottles. For the detection of metal contents in the water samples, ultra-pure HNO_3 was used to adjust solution pH to about 1.0, and then sealed into polyethylene bottles. All water samples were returned to the laboratory within 2 h, kept at 4 °C, and tested within 48 h.

2.4. Sample test

A series of testing methods were applied to identify the

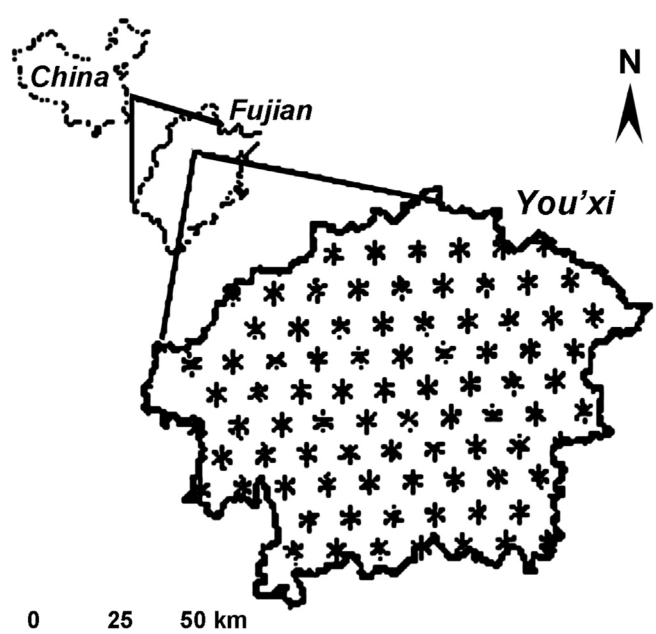

Fig. 1. The sampling sites in this study at *You'xi* County southeast China.