Science of the Total Environment 487 (2014) 123–129

Contents lists available at ScienceDirect

Science of the Total Environment

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

Hydrogen and oxygen isotopic composition of karst waters with and without acid mine drainage: Impacts at a SW China coalfield

Jing Sun [a], Changyuan Tang [a], Pan Wu [b,*], William H.J. Strosnider [c]

[a] *Graduate School of Horticulture, Chiba University, Matsudo, 271-8510 Chiba, Japan*
[b] *College of Resources and Environmental Engineering, Guizhou University, Huaxi, 550004 Guiyang, Guizhou, China*
[c] *Environmental Engineering Program, Center for Watershed Research & Service, Saint Francis University, 117 Evergreen Drive, Loretto, PA 15940, USA*

HIGHLIGHTS

- Elucidating $\delta^{18}O_{H_2O}$ and $\delta^2H_{H_2O}$ dynamics benefits remediation strategies.
- Isotopic compositions with and without acid mine drainage were very different.
- Isotopic variability was affected by pyrite oxidation and Fe hydrolysis.
- The observation was supported by three-component mixing modeling.
- Results present models for isotopic fractionation of mine drainage in karst settings.

ARTICLE INFO

Article history:
Received 17 December 2013
Received in revised form 10 March 2014
Accepted 1 April 2014
Available online 3 May 2014

Editor: Eddy Y. Zeng

Keywords:
Isotopic characteristics
Water mixing model
Acid mine drainage
Karst waters

ABSTRACT

Karst water resources, which are critical for the support of human societies and ecological systems in many regions worldwide, are extremely sensitive to mining activities. Identification and quantification of stable isotope ($\delta^2H_{H_2O}$ and $\delta^{18}O_{H_2O}$) composition for all sources is essential if we are to fully understand the dynamics of these unique systems and propose successful remediation strategies. For these purposes, a stable isotope study was undertaken in two similar watersheds, one impacted by acid mine drainage, and the other not. It was found that the majority of $\delta^2H_{H_2O}$ and $\delta^{18}O_{H_2O}$ values of acid mine drainage (AMD), AMD-impacted and Main channel mix waters plotted above the local meteoric water line (LMWL), while the non-AMD-impacted water was below the LMWL. The AMD and AMD-impacted water had a similar composition of $\delta^{18}O_{H_2O}$ and heavier $\delta^2H_{H_2O}$ than that of the other waters as a result of pyrite oxidation and Fe hydrolysis. The non-AMD-impacted and spring waters were the background waters in the study area. The composition of $\delta^2H_{H_2O}$ and $\delta^{18}O_{H_2O}$ for the former was influenced by the re-evaporation and water–rock interaction, and that for the latter was controlled by re-condensation. Along the water flow, the Main channel mix water is recharged by AMD-impacted, non-AMD-impacted and spring waters. The composition of $\delta^2H_{H_2O}$ and $\delta^{18}O_{H_2O}$ for the Main channel mix water was coincident with the characteristics of water mixing, supported by three-component mixing modeling of upstream spring, non-AMD-impacted and AMD-impacted waters. The composition of $\delta^2H_{H_2O}$ and $\delta^{18}O_{H_2O}$ for the Main channel mix water was mainly affected by the AMD-impacted water. These results help elucidate the impact of AMD on $\delta^2H_{H_2O}$ and $\delta^{18}O_{H_2O}$ compositions for karst waters and demonstrate the utility for impact assessments and remediation planning in these unique systems.

1. Introduction

As a crucial resource of drinking water, karstic aquifers have become an important field for hydrogeological study (Sun et al., 2012). Because of their unique nature, carbonate aquifers are especially vulnerable to anthropogenic contamination, and their use as drinking water resources requires careful a priori assessment of their chemical and physical characteristics (Schiavo et al., 2009). Hence, it has been extremely difficult to develop a systemic understanding of karst systems, especially those affected by acid mine drainage (AMD).

In a review compilation, Schulte et al. (2011) indicated that over the last few decades data on inorganic and organic constituents and ionic fluxes in river basins were complemented by isotopic tracer studies. The main purpose of most of these studies was to identify the sources and cycling of water and solutes in river systems. A proper assessment of hydrogeochemical characteristics involves the identification and quantification of all sources. Despite the importance of such processes,

* Corresponding author. Tel./fax: +86 851 4733001.
E-mail addresses: sunjingchiba@gmail.com (J. Sun), pwu@gzu.edu.cn (P. Wu).

http://dx.doi.org/10.1016/j.scitotenv.2014.04.008
0048-9697/

quantitative assessment studies are lacking (Cánovas et al., 2012). Such studies require the implementation of tools to identify and evaluate the different sources and mixing processes shaping the hydrogeochemistry of these unique systems.

In general, isotopic tracers in conjunction with other conservative tracers (e.g., chloride) have been used to quantify multiple contributions to stream/river flow. That is helpful for understanding interactions of different water sources. These studies have been beneficial for providing new insights into hydrological processes, as well as for associated transport of water and redefining hydrological models on catchment scale (e.g., Kendall and MacDonnell, 1998; Barth and Veizer, 2004; Ladouche et al., 2001). Often, end-members with distinct hydrochemical characteristics cannot be collected (Carrera, 2004). In addition, their concentrations vary in time and space. For these cases, it is possible to quantify the proportional contributions of different sources (Barth and Veizer, 2004). This method is based on the modeling of mixing waters from mass balance of solutes and accounts for the uncertainty of end-members.

As a result, the Xingren coalfield, which is host to one of the more renowned coalfields in China as well as a vast karst region, was chosen for this investigation. In the study area, karst waters with AMD impacts were characterized by low pH values (2.8–4.4) and high levels of Fe (mean, 283 mg/L), SO_4 (mean, 2217 mg/L), Cu (mean, 127 μg/L), As (mean, 676 μg/L) and Zn (mean, 2017 μg/L), respectively (Sun et al., 2012, 2013). In comparison, karst waters without AMD impacts showed neutral pH, together with low levels of Fe, SO_4 and heavy metals. There has been much research on the migration and transfer of constituents of concern in karst waters, paddy soil, and sediments of reservoirs and rivers (e.g., Wu et al., 2009; Tang et al., 2009; Xie et al., 2011; Tao et al., 2012; Sun et al., 2009, 2013).

The main objectives of this study were: (1) to elucidate $\delta^2H_{H_2O}$ and $\delta^{18}O_{H_2O}$ dynamics in karst waters with and without AMD impacts, especially the variability of $\delta^2H_{H_2O}$ in AMD-impacted waters; and (2) to evaluate water flux with the three-component mixing technique. These determinations were preceded by chemical analyses (Sun et al., 2013). Research on the dynamics of $\delta^{18}O_{H_2O}$ and $\delta^2H_{H_2O}$ in AMD-impacted waters is scarce (e.g., Seal II et al., 2008; Schulte et al., 2011; Halder et al., 2013; Li et al., 2014). The authors have not encountered a similar study in a karst system anywhere in the literature.

2. Site description

The study area is located in the Xingren coalfield of Guizhou Province (105°1′–105°2′ E, 25°3′–25°4′ N) (Fig. 1). The climate is of the subtropical warm–moist type with annual average temperature of 15.2 °C and precipitation of 1320.5 mm, respectively (Wu et al., 2009). About 84% of the annual precipitation falls in the wet season from May to October (Wu et al., 2009). Most of the paddy fields are irrigated by the AMD-impacted waters in the study area during the growing season.

There are two reservoirs, Shitouzhai Reservoir and Maoshitou Reservoir, in the study area (Fig. 1). The Shitouzhai Reservoir is an area without the effects of mining. However, there are many coal pits upstream of the Maoshitou Reservoir, from which AMD flows continually. High-As coal was mined in the study area since the 1940s. In 1976, mining activities were forbidden by the local government due to chronic As poisoning to the exposed population (Li et al., 2005).

For ease of discussion, we categorized the Maoshitou stream and Main channel waters with low pH value and high levels of Fe, SO_4 and heavy metals (Sun et al., 2013) as the “AMD-impacted” water and “Main channel mix” water, respectively, and will refer to the Shitouzhai stream as the “non-AMD-impacted” water. The Main channel mix water is contributed to by the Shitouzhai and Maoshitou Reservoirs (Fig. 1). It becomes an underground river in the area between sites M3 and M4, and flows out from the study area after the tributary joins at site M5. Springs are in the vicinity of the Maoshitou stream and main channel.

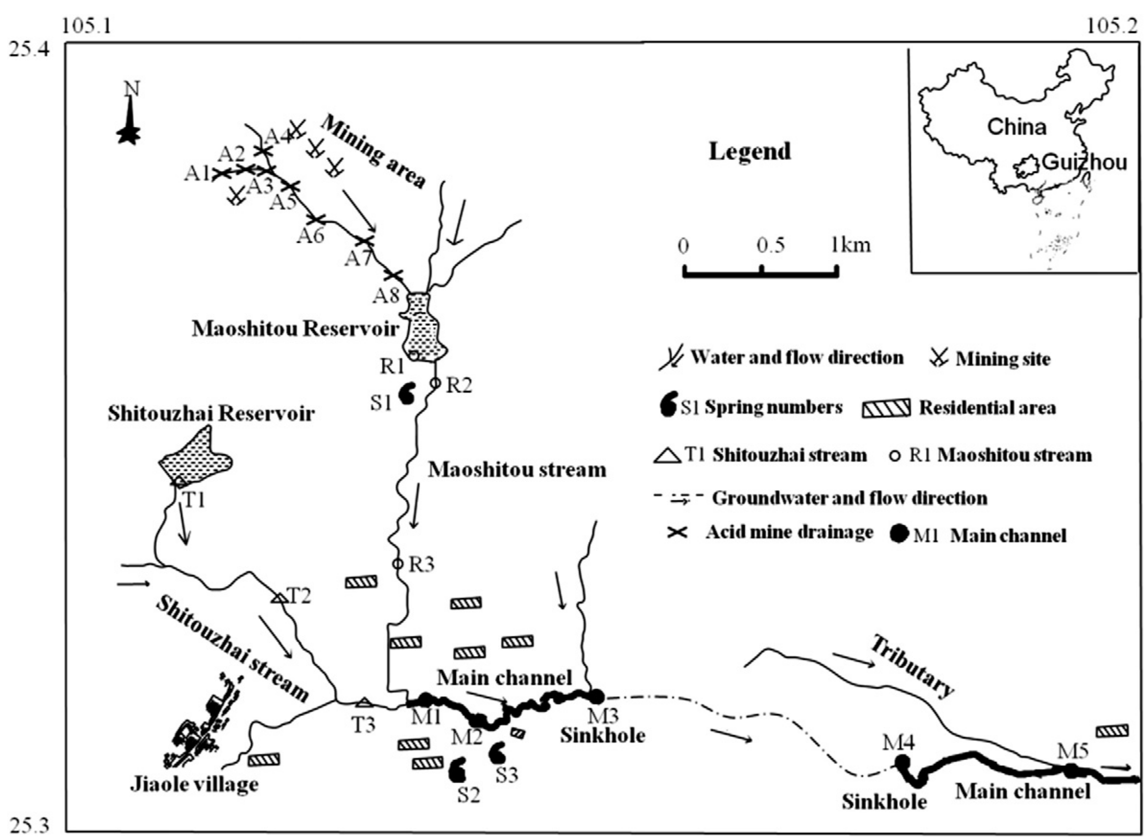

Fig. 1. The map of the study area and sampling points.