Hydrobiogeochemistry of redox-sensitive components: A special issue in tribute to Zhaoli Shen

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ABSTRACT

Professor Zhaoli Shen, Emeritus Professor in the China University of Geosciences and Foreign Academician of the Russian Academy of Engineering, was one of the greatest pioneers in hydrogeochemical studies in China and beyond. He left us forever on April 4, 2020, at the age of 88. In this *Zhaoli Shen Tribute Issue*, twenty-three submissions were accepted which focus on hydrobiogeochemistry of redox-sensitive components in groundwater systems and can be classified into five themes: (1) Interaction among water, gas, rock, and microbes in aquifer systems; (2) Natural organic matter and its role in redox-sensitive component mobility; (3) Isotopic signatures of redox-sensitive component sources and biogeochemical processes; (4) Roles of hydrogeochemical and hydrogeological processes in the distribution of redox-sensitive components; and (5) Removal of redox-sensitive contaminants. This special issue thus highlights the importance of hydrobiogeochemical processes in controlling the cycling of redox-sensitive elements in aquifer systems.

1. Introduction

Redox-sensitive components, including trace elements (such as As, Cr, U, V, Mo) and major ions (such SO_4^{2-}, NO_3^-, NH_4^+), are ubiquitous in groundwater, and their mobility is highly dependent on redox conditions of aquifer systems (Borch et al., 2010; Guo et al., 2014, 2016a, 2020; Wang et al., 2019, 2020; O'Connor et al., 2022). When they have high concentrations in drinking groundwater, most of them pose negative impacts on human health. There are strict drinking water guidelines for those components from international organizations and in relevant regulations in different countries/regions. For example, both the WHO and EU have set 10 μg/L of As as the drinking water guideline (Guo et al., 2014). Therefore, distribution and mobility of those redox-sensitive components in groundwater have received much concern from both government agencies and scientific communities.

Redox-sensitive components can be reduced or oxidized with the presence of reductants (such as organic matter, sulfides, CH_4) or oxidants (such as dissolved oxygen, NO_3^-, MnO_2) in aquifer systems. The reductants and the oxidants are either dissolved in groundwater or in the state of solid or gas. Those redox processes are usually mediated by specific microbes in groundwater systems (Xiu et al., 2022; Kappler et al., 2021; Guo et al., 2015), which greatly increase the rates of the redox reactions. Therefore, these processes usually involve interactions among water, gas, rock, organics, and microbes in aquifer systems. Although tremendous studies have been carried out on geochemical interactions between groundwater and rock/sediments (Appelo and Postma, 2005; Erban et al., 2013; Gillispie et al., 2019; Khan et al., 2019; Radloff et al., 2017; Wang et al., 2021), our knowledge about the hydrobiogeochemical interaction among water, gas, rock, organics, and microbes in aquifer systems is still limited (Xiu et al., 2020, 2021).

Natural organic matter (NOM), generally including dissolved organic matter (DOM) and sedimentary organic matter (SOM), widely occurs in aquifer systems, and is crucial in triggering reduction of redox-sensitive components (such as Fe oxides, As(V)) as an electron shuttle or an electron donor (Islam et al., 2004; Rowland et al., 2007; Guo et al., 2019; Kulkarni et al., 2017; Schittich et al., 2018). Characteristics of NOM are

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closely related to its capacity of providing electrons. Labile organic matter, being considered as aliphatic/proteins and carbohydrates, is readily metabolized by microorganisms and provides electrons for reduction of redox-sensitive components (Rowland et al., 2007; Qiao et al., 2020; Lawson et al., 2016; Yan et al., 2020). NOM is a complicated component in aquifer systems, and its characteristics are poorly understood. Optical and molecular techniques help us to better reveal the characteristics of NOM and its roles in redox-sensitive component mobility.

Understanding the sources and biogeochemical processes of redox-sensitive components in groundwater systems is critical not only for locating drinking groundwater resources with safer-level concentrations of redox-sensitive components, but also for remediating sites contaminated by redox-sensitive components. Environmental stable isotopes have been universally used to effectively trace sources and geochemical processes of dissolved components (Guo et al., 2016b; Glok-Galli et al., 2022; Frisbee et al., 2022; Ren et al., 2022; Wright et al., 2021). Generally, there are two types of stable isotopes: one is conservative, which inherits isotopes from the source (such as Sr); the other is easily subject to fractionation during (bio)geochemical processes (including redox processes, adsorption-desorption, dissolution-precipitation, and so on) (such as, C, N, S, O) (Fritz and Fontes, 1980; Clark and Fritz, 1997). Especially, microbes would preferentially metabolize isotopically light elements during redox processes, which produces heavy isotope-depleted components (Clark and Fritz, 1997). Based on this observation, stable isotopes are powerful tools in revealing biogeochemical cycling of redox-sensitive components (Guo et al., 2013; Xiong et al., 2022; Tao et al., 2022). Therefore, multiple isotopes are required to evaluate sources and biogeochemical processes of redox-sensitive components in aquifer systems.

Professor Zhaoli Shen, Emeritus Professor in the China University of Geosciences and Foreign Academician of the Russian Academy of Engineering, was one of the greatest pioneers in hydrogeochemical studies in China and beyond. He left us forever on April 4, 2020, at the age of 88. His intellectual legacies are profound and pass on through generations of hydrogeochemists. In this special issue as a tribute to Prof. Shen, twenty-three submissions were accepted which focus on hydrobiogeochemistry of redox-sensitive components in groundwater systems. The following themes are included: (1) Interaction among water, gas, rock, and microbe in aquifer systems; (2) Natural organic matter and its role in redox-sensitive component mobility; (3) Isotopic signatures of redox-sensitive component sources and biogeochemical processes; (4) Roles of hydrogeochemical and hydrogeological processes in distribution of redox-sensitive components; and (5) Removal of redox-sensitive contaminants. This article, prepared in the format and style of a Perspective, also serves as an extended preface for this special issue, introducing the highlights of the papers in this meaningful collection.

Zhaoli Shen in a field trip to the Yellowstone National Park.

2. Themes of this special issue

2.1. Interaction among water, gas, rock, and microbe in aquifer systems

Groundwater system is a complex system, which contains water, gas, rock/sediment, and microbes. Interactions among water, gas, rock, and microbe largely determine evolution of groundwater quality. Although water-rock interaction has been largely considered in hydrogeochemical investigations (Appelo and Postma, 2005; Erban et al., 2013; Gillispie et al., 2019; Khan et al., 2019; Radloff et al., 2017; Wang et al., 2021), the involvement of microbes and gases in the interaction has been dramatically underestimated.

Guo L. et al. (2022) investigated the co-variation of the exogenous input of NO_3^- and the change of microbial community along a flow path in the southern North China Plain. They found that, along the flow path, relative abundances of *Proteobacteria* and *Epsilonbacteraeota* increased, but overall microbial diversity decreased. Microbial community and co-occurrence networks were dominantly regulated by concentrations of NO_3^-, NO_2^- and DOC, indicating that exogenous NO_3^- and organic carbon played the dominant role in shaping microbial community. They suggest that microbial community distribution is intimately related to exogenous inputs of NO_3^- and DOC, and likely outweighs the effect of groundwater circulation or water-rock interaction on biogeochemical processes (Guo L. et al., 2022). The related biogeochemical processes were evidenced by multiple isotopic and groundwater chemical data in riverbank filtration systems (Chen Y.X. et al., 2022). By using $\delta^2H–H_2O$, $\delta^{18}O–H_2O$, $\delta^{15}N–NO_3$, and $\delta^{18}O–NO_3$ in groundwater and $\delta^{15}N–TN$ and $\delta^{15}N–IEF-NH_4$ in aquifer sediments, they found that denitrification, organic nitrogen mineralization, and dissimilatory nitrate reduction to ammonium (DNRA) are the important biogeochemical processes controlling N species in groundwater.

Nitrate - metal reducing bacteria - ferrihydrite interactions were investigated with anaerobic simulation experiments to reveal migration and transformation of dissolved As and Fe by Liu E.Y. et al. (2022), who found that the presence of NO_3^- decreased the reduction rate of Fe(III), but promoted biological reduction of As(V) due to the increase in bacterial growth. Nitrate decreased As release by inhibiting the reduction of As-bearing ferrihydrite, indicating that the presence of NO_3^- alleviated As contamination in groundwater.

Cao and Yu (2022) investigated gas-rock interaction affected by geochemical properties and pore structure of shale. They observed that clay had a great effect on the adsorption amounts of CH_4 and CO_2. Methane was more likely adsorbed in micropores, while CO_2 was more likely adsorbed in macropores. The amount of adsorbed CO_2 was 2–7 times higher than that of CH_4, indicating that CO_2 injection was promising for shale gas extraction in the study area.

Due to the complex nature, equilibrium of water-rock interaction was not apparently reached even in paleo-groundwater hundreds of millions of years old (Alexeev et al., 2022). In the brine-kimberlite system, with groundwater salinity of up to 400 g/L and kimberlite breccias mainly consisting of quartz, calcite, serpentine, chlorite, and mica, equilibrium simulation showed that groundwaters remained unsaturated with respect to almost all groups of kimberlite-forming minerals, in spite of the high salinity and a very long-term water-rock interaction. One of the proposed reasons is that gases (CO_2) and products of deep genesis (e.g., HCl, H_2SO_4, HNO_3, and HF) act as an acidic neutralizing reagent, which leads to disequilibrium of groundwater with aluminosilicates (Shvartsev, 2000).

2.2. Natural organic matter and its role in redox-sensitive component mobility

NOM would act as an electron shuttle or an electron donor to trigger hydrobiogeochemical processes in groundwater system. Molecular characteristics of NOM determine its specific role. Zhao et al. (2022) identified molecular characteristics of groundwater DOM and water extractable SOM (WEOM) from aquifer systems by using Fourier transform-ion cyclotron resonance-mass spectrometry (FT-ICR-MS). They found a positive correlation between DOC in WEOM and DOC at depth-matched groundwater and large proportion of common compounds in DOM and WEOM, and proposed that WEOM is the key carbon

source in groundwater. In comparison with DOM, WEOM contained relatively higher abundance of low molecular weight and thermodynamically favorable components for microbial oxidation (aminosugars and carbohydrates), which is in line with the observation by Qiao et al. (2020). Accordingly, Zhao et al. (2022) suggested that organic matter is processed into stable components after being mobilized from aquifer sediment into groundwater, and highlighted the synergic effects of aquifer SOM and processing pathway on molecular compositions of groundwater DOM.

DOM in groundwater varied with the recharge of surface water. Yu et al. (2022) monitored variations in geochemical parameters in surface water and porewater near a wetland for around one year. They found that DOC of porewater obviously increased when levels of surface water rose during waterlogging period. Fluorescence indices and PARAFAC modeling indicated that porewater DOM mainly derived from SOM during the drought period and from both surface water DOM and SOM during the waterlogging period. Surface water infiltration introduced DOM and stimulated the release of SOM into the porewater, which led to higher concentrations of dissolved As and Fe in the waterlogging period by triggering reductive dissolution of Fe(III) oxides.

As consequences of redox processes, degradation of NOM changes geochemical parameters of groundwater. Li Y.P. et al. (2022) predicted the spatial distribution of geogenic P in groundwater from alluvial-lacustrine sedimentary aquifers in the central Yangtze River basin by employing three machine learning-based regression models, and found that NH_4–N and Fe^{2+} were the two most important factors associated with P enrichment in groundwater. Since NH_4^+ was formed during mineralization of nitrogen-containing NOM, and Fe^{2+} was produced from the reductive dissolution of Fe(III) oxides (Huang et al., 2021; Gao et al., 2020; Du et al., 2021), P enrichment in groundwater would be related to both degradation of P-containing NOM and reductive dissolution of P-bearing Fe(III) oxides (Li Y. et al., 2022; Zhou J. et al., 2022).

2.3. Isotopic signatures of redox-sensitive component sources and biogeochemical processes

Multiple stable isotopes have been used to trace sources of redox-sensitive components and evaluate biogeochemical processes of those components in aquifer systems. Mao et al. (2022) employed multiple stable isotopes (δ^{15}N–NO_3^-, δ^{18}O–NO_3, and ^{87}Sr/^{86}Sr) and hydrochemical data to elucidate sources and biogeochemical evolution of NO_3^- in groundwater. They observed that the dissolved components in recharge zones were mainly controlled by natural processes, while human activities predominantly altered the natural background levels of groundwater in transition zones and discharge zones, where groundwater NO_3^- was mainly sourced from sewage and NH_4^+ fertilizer and manure affecting the local groundwater quality. In addition to δ^{15}N–NO_3^- and δ^{18}O–NO_3, Cao et al. (2022) utilized δ^{15}N–NH_4^+ and δ^{18}O–H_2O to identify nitrogen sources and elucidate the mechanisms of nitrogen transformation in groundwater systems. Results showed that the main sources of nitrogen in the watershed were from NH_4^+ fertilizers, NO_3^- fertilizer, and soil organic nitrogen. The volatilization and nitrification were the main processes controlling changes of nitrogen isotopes in the water.

Zhang et al. (2021) used hydrochemical data and multiple stable isotopes (viz., δ^{34}S–SO_4^{2-}, δ^{18}O–SO_4^{2-}, δD–H_2O and δ^{18}O–H_2O) to trace sources of groundwater SO_4^{2-} and to quantitively evaluate the contribution of multiple potential sources to SO_4^{2-} pollution in karst water being combined with a Bayesian isotope mixing model. Results showed that SO_4^{2-} in the surface water was mainly derived from evaporite dissolution (33%), sewage (19%), soil sulfate (15%), and sulfide oxidation (10%), while that in the groundwater was predominantly sourced from soil SO_4^{2-} (32%) and sewage (31%). From the recharge area to the discharge area, the proportions of sewage and evaporite dissolution to groundwater SO_4^{2-} increased, while those of soil SO_4^{2-} and

sulfide oxidation decreased. In comparison, the source of SO_4^{2-} in karst geothermal water was sole (Bao et al., 2022). Using multiple isotopes, including ^{87}Sr/^{86}Sr, δ^{34}S–SO_4^{2-}, δ^{18}O–SO_4^{2-}, δ^{18}O–H_2O, δ^2H–H_2O, δ^{13}C-DIC, and ^{14}C-DIC in geothermal water, they evaluated the origin and evolution of dissolved SO_4^{2-} in the Tangquan Karst geothermal system. They showed that geothermal water SO_4^{2-} was mainly derived from dissolution of gypsum and other evaporite minerals in the carbonate reservoir. They constrained the origin of SO_4^{2-} with δ^{34}S–SO_4^{2-} from 27.6‰ to 34.2‰ and δ^{18}O–SO_4^{2-} from 14.3‰ to 18.4‰, indicating open karst geothermal systems (Bao et al., 2022).

Zhang et al. (2022) employed hydrochemistry and multiple stable isotopes (i.e., ^{87}Sr/^{86}Sr, δ^2H–H_2O, δ^{18}O–H_2O, and δ^{34}S–SO_4^{2-}) to elucidate groundwater salinization processes in a coastal area of Beihai, China. They observed that variations in TDS of groundwater corresponded to spatiotemporal variations in ^{87}Sr/^{86}Sr, δ^2H–H_2O, and δ^{34}S–SO_4^{2-}, and proposed that groundwater salinity resulted from seawater intrusion and infiltration of high-productivity mariculture pond water.

2.4. Roles of hydrogeological and hydrogeochemical processes

Hydrogeological and hydrogeochemical processes are two important aspects of hydrobiogeochemical studies. Integrated water chemistry and isotope methods were used to identify the recharge sources and migration paths of an intermittent karst spring in China (Guo X.L. et al., 2022). Results showed that the karst water system consisted of an upper aquifer system dominated by dolomite and a lower aquifer system dominated by limestone. The base flow of the karst system exhibited the hydrochemical characteristics of the upper dolomite aquifer system, but the groundwater after the rain and siphon period showed the mixed hydrochemical characteristics of the lower limestone aquifer system. Those two aquifer systems and three groundwater migration paths formed complex hydrological dynamic characteristics with different groundwater sources. Those hydrogeological characteristics would be recorded by travertine of the karst water system. Sun et al. (2022) used a ^{230}Th-dated travertine δ^{18}O record at Zhangjia Ravine on the eastern margin of the Tibetan Plateau to characterize sub-annual–biannual-resolved Asian Summer Monsoon dynamics. They showed that δ^{18}O sequence was characterized by high-frequency fluctuations at decadal to centennial scales with several abrupt changes. It indicated that the Preboreal oscillation event was triggered by a freshwater outburst, which led to/resulted in a sudden release of thousands of cubic kilometers of meltwater to the North Atlantic Ocean.

The aquifer system and the groundwater flow path are dependent on sedimentation sequences in sedimentary basins. Liu H.Y. et al. (2022) employed rare earth elements (REE) as tracers to elucidate sedimentary provenance and depositional processes. Results illustrated that sediments originated from greywackes and experienced an incipient to intermediate chemical weathering. During sedimentation processes, REE fractionation occurred from the piedmont to the littoral of the plain, reflected by the fact that LREE were preferentially enriched over HREE with an accumulation of REE in the piedmont and the central plain.

Wang et al. (2022) used a multicriteria approach combining hydrodynamic, hydrochemical, and stable isotopic tools to investigate the impact of karst medium heterogeneity (i.e., karst hydrogeology) on groundwater hydrogeochemistry in a mountainous area of Hubei Province, Central China. They showed that groundwater was typically characterized by HCO_3–Ca·Mg type in the shallow aquifer and by SO_4–Ca·Mg type in the deep aquifer. With increasing circulation depth, water-rock interaction and the heterogeneity of the karst medium increased Ca^{2+}, Mg^{2+}, Sr^{2+}, and SO_4^{2-} concentrations in groundwater, which mainly resulted from dissolution of calcite, dolomite, and gypsum.

Zhi et al. (2022) employed ionic ratios to explore the hydro-biogeochemical processes of high As groundwater. According to hydrogeological conditions and ionic ratios in groundwater, three

hydrogeochemical zones were recognized approximately along flow paths (i.e., weathering–fresh water zone (Zone I), evaporation–saline water zone (Zone II), and seawater mixing–reduction zone (Zone III)). High As concentrations were mainly observed in Zone III with relatively high concentrations of Fe^{2+}, NH_4^+ and TDS and low NO_3^- and SO_4/Cl, indicating that both reductive dissolution of Fe(III) oxides and high salinity contributed to As enrichment in groundwater (Zhi et al., 2022).

Zhou Y.Z. et al. (2022) collected groundwater samples along hydrogeological profiles in a high As groundwater area in the Manas River Basin, Xinjiang, China, which were analyzed for inorganic As species, DOC, DIC, major ions, $\delta^{18}O$–H_2O and δD-H_2O. Results showed significant positive correlations between groundwater As and phosphate and between groundwater As and carbonate and significant negative correlations between groundwater As and the sulfate/chloride ratio and between DOC and the sulfate/chloride along the south-north groundwater flow path. They suggested that both competitive desorption and sulfate reduction mediated by microorganisms have been important processes in mobilizing As in the groundwater system.

Both hydrogeological and hydrogeochemical processes regulate distribution of redox-sensitive components (such as As) in groundwater. In order to reveal their relative importance in As mobility in aquifer systems, Feng et al. (2022) took groundwater samples from three hydrogeological transects and different aquifer sediment samples from the Yinchuan basin (China) for hydrochemical and isotopic analyses. Results showed that the hydrogeochemical characteristics played a leading role in controlling As concentrations in each transect, where both reductive dissolution of Fe(III) oxides and desorption of As contributed to As enrichment. However, at the basin scale, hydraulic gradients and groundwater flow conditions were the dominant factors controlling As distribution, where groundwater in aquifers with higher hydraulic gradients generally had lower As concentrations (Feng et al., 2022).

2.5. Removal of redox-sensitive contaminants

Hydrobiogeochemistry of groundwater systems affects efficiency and duration of remediation of redox-sensitive contaminants. Barron et al. (2022) explored the efficiency of nitrate-Fe(II) treatments in mitigating dissolved As concentrations by using laboratory-scale experiments on sediment and groundwater from a severely polluted coastal aquifer. They showed that more than 99% of dissolved As was removed in selected experiments. Pre- and post-experimental characterization of iron (Fe) mineral phases indicated that more than 90% amorphous Fe (III) oxides were transformed into increased crystalline, recalcitrant oxide and sulfide phases, with the formation of limited magnetite. The higher Fe(II) amendment induced a more complete transformation of the amorphous Fe phases and more stable retention of As in the solid phase, in which the addition of labile organic carbon (lactate) as a reductant had no effect on As stability.

Barnie et al. (2022) investigated adsorption and reduction of Cr(VI) by kerogen with different degrees of geochemical alteration using an anaerobic thermal simulation technique. They found the molecular characteristics transition of kerogen from aliphatic to aromatic and aromatic to aliphatic at 300 and 600 °C, respectively. The adsorption, which was controlled by the carboxylic groups, of Cr(VI) on kerogen increased with an increase in ignition temperature, which was controlled by the carboxylic groups. However, Cr(VI) reduction capacities decreased with an increase in ignition temperature due to the decreasing of phenolic moieties and hydroxyl groups, which were the main electron donors for Cr(VI) reduction. After reduction, Cr(III) was complexed by the oxidized phenol sites. It highlighted that the kerogen with different functional groups, aliphaticity, and aromaticity can sequestrate Cr by means of adsorption, reduction, and complexation.

Chen L.P. et al. (2022) monitored the long-term performance of a zeolite permeable reactive barrier (PRB) for in-situ remediation of ammonium-contaminated groundwater in riverside source fields. During the stable stage (from 2012 to 2015), NH_4–N in remediated groundwater decreased below the national standard limit of 0.5 mg/L due to the strong adsorption capacity of the zeolite for NH_4^+. During the semi-stable stage (from 2016 to 2017), the PRB system maintained a relatively high NH_4–N removal efficiency by means of strong nitrification. However, during the unstable stage (2018–2019), NH_4–N of remediated groundwater exceeded 0.5 mg/L because of NH_4^+ desorption and weak nitrification, which was evidenced by gene analysis of groundwater. This study highlighted time-dependent decay in the PRB performance for NH_4–N removal, which should be a matter for concern and suggests the need for frequent monitoring in related field applications.

3. Conclusions

Hydrobiogeochemistry of redox-sensitive components involves coupling of biogeochemical processes with hydraulic dynamics in groundwater systems. Interdisciplinary integration of hydrodynamic, hydrochemical, molecular biological, molecular organic, and stable isotopic tools is critical for understanding the hydrobiogeochemical behavior and cycling of redox-sensitive components. Currently, studies mainly focused on (1) Interaction among water, gas, rock, and microbes in aquifer systems; (2) Natural organic matter and its role in redox-sensitive component mobility; (3) Isotopic signatures of redox-sensitive component sources and biogeochemical processes; (4) Roles of hydrogeological and hydrogeochemical processes in distribution of redox-sensitive components; and (5) Removal of redox-sensitive contaminants. To ensure sustainable and safe supply and effective protection of groundwater resources, catchment-scale and site-scale investigations need to be combined with laboratory-scale experimental and modeling works to better characterize the hydrobiogeochemical processes controlling the fate and transport of redox-sensitive components in aquifer systems which fundamentally affect the quality and ecological service value of groundwater.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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References

Alexeev, S.V., Alexeeva, L.P., Trifonov, N.S., 2022. Equilibrium-non-equilibrium of the brine-kimberlite system in the Udachnaya pipe, Russia, based on physicochemical modeling. Appl. Geochem. 141, 105219.

Appelo, C.A.J., Postma, D., 2005. Geochemistry Groundwater and Pollution, second ed. Balkema Publ.

Bao, Y.F., Pang, Z.H., Huang, T.M., Li, Y.M., Tian, J., Luo, J., Qian, T.Q., 2022. Chemical and isotopic evidences on evaporite dissolution as the origin of high sulfate water in a karst geothermal reservoir. Appl. Geochem. 141, 105419.

Barnie, S., Zhang, J., Duncan, A.E., Osei-Marfo, M., Adenutsi, C.D., Chen, H.H., 2022. The adsorption and reduction mechanism of Cr(VI) by kerogen with different

degrees of geochemical alteration using a thermal simulation method. Appl. Geochem. 141, 105261.

Barron, A., Sun, J., Passaretti, S., Sbarbati, C., Barbieri, M., Colombani, N., Jamieson, J., Bostick, B.C., Zheng, Y., Mastrocicco, M., Petitta, M., Prommer, H., 2022. In situ arsenic immobilisation for coastal aquifers using stimulated iron cycling: lab-based viability assessment. Appl. Geochem. 141, 105155.

Borch, T., Kretzschmar, R., Kappler, A., Van Cappellen, P., Ginder-Vogel, M., Voegelin, A., Campbell, K., 2010. Biogeochemical redox processes and their impact on contaminant dynamics. Environ. Sci. Technol. 44 (1), 15–23.

Cao, M.D., Yin, X.J., Zhang, J., Jin, M.G., Huang, X., 2022. Sources and transformations of nitrogen in an agricultural watershed on the Jianghan Plain, China: an integration of $\delta^{15}N$–NH_4^+, $\delta^{15}N$–NO_3, $\delta^{18}O$–NO_3 and a Bayesian isotope mixing model. Appl. Geochem. 141, 105329.

Cao, B., Yu, Q.C., 2022. Comparing the adsorption of carbon dioxide and methane in Carboniferous shale from the Qaidam Basin, China. Appl. Geochem. 141, 105368.

Chen, L.P., Wang, C.Y., Zhang, C., Zhang, X., Liu, F., 2022. Eight-year performance evaluation of a field-scale zeolite permeable reactive barrier for the remediation of ammonium-contaminated groundwater. Appl. Geochem. 141, 105372.

Chen, Y.X., Su, X.S., Wan, Y.Y., Lyu, H., Dong, W.H., Shi, Y.K., Zhang, Y.W., 2022. Nitrogen biogeochemical reactions during bank filtration constrained by hydrogeochemical and isotopic evidence: a case study in a riverbank filtration site along the Second Songhua River, NE China. Appl. Geochem. 141, 105272.

Clark, I., Fritz, P., 1997. Environmental Isotopes in Hydrogeology. Lewis Publisher, New York.

Du, Y., Deng, Y.M., Liu, Z.H., Huang, Y.W., Zhao, X.W., Li, Q.H., Ma, T., Wang, Y.X., 2021. Novel insights into dissolved organic matter processing pathways in a coastal confined aquifer system with the highest known concentration of geogenic ammonium. Environ. Sci. Technol. 55, 14676–14688.

Erban, L.E., Gorelick, S.M., Zebker, H.A., Fendorf, S., 2013. Release of arsenic to deep groundwater in the Mekong Delta, Vietnam, linked to pumping-induced land subsidence. Proc. Natl. Acad. Sci. USA 110, 13751–13756.

Feng, S., Guo, H.M., Sun, X.M., Han, S.B., Li, Y., 2022. Relative importance of hydrogeochemical and hydrogeological processes on arsenic enrichment in groundwater of the Yinchuan Basin, China. Appl. Geochem. 141, 105180.

Frisbee, M.D., Caffee, M.W., Camberato, J.J., Michalski, G., 2022. Using multiple isotopic and geochemical tracers to disentangle the sources of baseflow and salinity in the headwaters of a large agricultural watershed. J. Hydrol. 609, 127769.

Fritz, P., Fontes, J.Ch., 1980. Handbook of Environmental Isotope Geochemistry: the Terrestrial Environment, vol. 1. Elsevier, New York.

Gao, Z.P., Jia, Y.F., Guo, H.M., Zhang, D., Zhao, B., 2020. Quantifying geochemical processes of arsenic mobility in groundwater from an inland basin using a reactive transport model. Water Resour. Res. 56, e2019WR025492 https://doi.org/10.1029/2019WR025492

Gillispie, E.C., Matteson, A.R., Duckworth, O.W., Neumann, R.B., Phen, N., Polizzotto, M. L., 2019. Chemical variability of sediment and groundwater in a Pleistocene aquifer of Cambodia: implications for arsenic pollution potential. Geochem. Cosmochim. Acta 245, 441–458.

Glok-Galli, M., Vadillo-Pérez, I., Jiménez-Gavilán, P., Ojeda, L., Urresti-Estala, B., Martínez, D.E., 2022. Application of hydrochemical and multi-isotopic ($^{87}Sr/^{86}Sr$, $\delta^{13}C$-DIC, δ^2H-H_2O, $\delta^{18}O$-H_2O) tools to determine contamination sources and processes in the Guadalhorce River Basin, southern Spain. Sci. Total Environ. 828, 154424.

Guo, H.M., Liu, Z.Y., Ding, S.S., Xiu, W., Hao, C.B., Hou, W.G., 2015. Arsenate reduction and mobilization in the presence of indigenous aerobic bacteria obtained from high arsenic aquifers of the Hetao basin, Inner Mongolia. Environ. Pollut. 203, 50–59.

Guo, H.M., Jia, Y.F., Wanty, R., Jiang, Y.X., Zhao, W.G., Xiu, W., Shen, J.X., Li, Y., Cao, Y. S., Wu, Y., Zhang, D., Wei, C., Zhang, Y.L., Cao, W.G., Foster, A., 2016a. Contrasting distributions of groundwater arsenic and uranium in the western Hetao basin, Inner Mongolia: implication for origins and fate controls. Sci. Total Environ. 541, 1172–1190.

Guo, H.M., Zhou, Y.Z., Jia, Y.F., Tang, X.H., Li, X.F., Shen, M.M., Lu, H., Han, S.B., Wei, C., Norra, S., Zhang, F.C., 2016b. Sulfur cycling-related biogeochemical processes of arsenic mobilization in the western Hetao basin, China: evidence from multiple isotope approaches. Environ. Sci. Technol. 50 (23), 12650–12659.

Guo, H.M., Liu, C., Lu, H., Wanty, R., Wang, J., Zhou, Y.Z., 2013. Pathways of coupled arsenic and iron cycling in high arsenic groundwater of the Hetao basin, Inner Mongolia, China: an iron isotope approach. Geochem. Cosmochim. Acta 112, 130–145.

Guo, H.M., Li, X.M., Xiu, W., He, W., Cao, Y.S., Zhang, D., Wang, A., 2019. Controls of organic matter bioreactivity on arsenic mobility in shallow aquifers of the Hetao Basin, P.R. China. J. Hydrol. 571, 448–459.

Guo, H.M., Chen, Y., Hu, H.Y., Zhao, K., Li, H.T., Yan, S., Xiu, W., Coyte, R.M., Vengosh, A., 2020. High hexavalent chromium in groundwater from a deep aquifer in the Baiyangdian basin of the North China Plain. Environ. Sci. Technol. 54 (16), 10068–10077.

Guo, H.M., Wen, D.G., Liu, Z.Y., Jia, Y.F., Guo, Q., 2014. A review of high arsenic groundwater in Mainland and Taiwan, China: distribution, characteristics and geochemical processes. Appl. Geochem. 41, 196–217.

Guo, L., Xie, Q., Sheng, Y.Z., Wang, G.C., Jiang, W.J., Tong, X.X., Xu, Q.Y., Hao, C.B., 2022. Co-variation of hydrochemistry, inorganic nitrogen, and microbial community composition along groundwater flowpath: a case study in Linzhou-Anyang area, Southern North China plain. Appl. Geochem. 141, 105296.

Guo, X.L., Chen, Q.L., Huang, H., Wang, Z.J., Li, J.W., Zhou, H., 2022. Water source identification and circulation characteristics of intermittent karst spring based on hydrochemistry and stable isotope—an example from Southern China. Appl. Geochem. 141, 105309.

Huang, Y.W., Du, Y., Ma, T., Deng, Y.M., Tao, Y.Q., Xu, Y., Leng, Z.C., 2021. Dissolved organic matter characterization in high and low ammonium groundwater of Dongting Plain, central China. Ecotoxicol. Environ. Saf. 208, 111779.

Islam, F.S., Gault, A.G., Boothman, C., Polya, D.A., Charnock, J.M., Chatterjee, D., Lloyd, J.R., 2004. Role of metal reducing bacteria in arsenic release in bengal delta sediments. Nature 430, 68–71.

Kappler, A., Bryce, C., Mansor, M., Lueder, U., Byrne, J.M., Swanner, E.D., 2021. An evolving view on biogeochemical cycling of iron. Nat. Rev. Microbiol. 19 (6), 360–374.

Khan, M.R., Michael, H.A., Nath, B., Huhmann, B.L., Harvey, C.F., Mukherjee, A., Choudhury, I., Chakraborty, M., Ullah, M.S., Ahmed, K.M., Goodbred, S.L., Schlosser, P., Bostick, B.C., Mailloux, B.J., Ellis, T., van Geen, A., 2019. High-arsenic groundwater in the southwestern Bengal Basin caused by a lithologically controlled deep flow system. Geophys. Res. Lett. 46, 13062–13071.

Kulkarni, H.V., Mladenov, N., Johannesson, K.H., Datta, S., 2017. Contrasting dissolved organic matter quality in groundwater in Holocene and Pleistocene aquifers and implications for influencing arsenic mobility. Appl. Geochem. 77, 194–205.

Lawson, M., Polya, D.A., Boyce, A.J., Bryant, C., Ballentine, C.J., 2016. Tracing organic matter composition and distribution and its role on arsenic release in shallow Cambodian groundwaters. Geochem. Cosmochim. Acta 178, 160–177.

Li, Y., Yu, C., Zhao, B., Chen, D., Ye, H.L., Nagel, C., Shao, W., Oelmann, Y., Neidhardt, H., Guo, H.M., 2022. Spatial variation of dissolved phosphorus and interactions with arsenic in response to changing redox conditions in floodplain aquifers in the Hetao basin, Inner Mongolia. Water Res. 209, 117930.

Li, Y.P., Du, Y., Deng, Y.M., Fan, R.Y., Tao, Y.Q., Ma, T., Wang, Y.X., 2022. Predicting the spatial distribution of phosphorus concentration in Quaternary sedimentary aquifers using simple field parameters. Appl. Geochem. 141, 105349.

Liu, E.Y., Xie, Z.M., Fang, J.H., Wang, J., Yang, Y., Chen, M.N., 2022. Nitrate-mediated biomigration and transformation of As/Fe in arsenic-bearing ferrihydrite. Appl. Geochem. 141, 105204.

Liu, H.Y., Guo, H.M., Pourret, O., Wang, Z., Sun, Z.X., Zhang, W.M., Liu, M.H., 2022. Distribution of rare earth elements in sediments of the North China Plain: a probe of sedimentation process. Appl. Geochem. 141, 105089.

Mao, H.R., Wang, G.C., Liao, F., Shi, Z.M., Huang, X.J., Yan, X., 2022. Geochemical evolution of groundwater under the influence of human activities: a case study in the southwest of Poyang Lake Basin. Appl. Geochem. 141, 105299.

O'Connor, A.E., Canuel, E.A., Beck, A.J., 2022. Drivers and seasonal variability of redox-sensitive metal chemistry in a shallow subterranean estuary. Front. Environ. Sci. 9, 613191 https://doi.org/10.3389/fenvs.2021.613191.

Qiao, W., Guo, H.M., He, C., Shi, Q., Xiu, W., Zhao, B., 2020. Molecular evidence of arsenic mobility linked to biodegradable organic matter. Environ. Sci. Technol. 54, 7280–7290.

Radloff, K.A., Zheng, Y., Stute, M., Weinman, B., Bostick, B., Mihajlov, I., Bounds, M., Rahman, M.M., Huq, M.R., Ahmed, K.M., Schlosser, P., van Geen, A., 2017. Reversible adsorption and flushing of arsenic in a shallow, Holocene aquifer of Bangladesh. Appl. Geochem. 77, 142–157.

Ren, K., Pan, X.D., Yuan, D.X., Zeng, J., Liang, J.P., Peng, C., 2022. Nitrate sources and nitrogen dynamics in a karst aquifer with mixed nitrogen inputs (Southwest China): revealed by multiple stable isotopic and hydro-chemical proxies. Water Res. 210, 118000.

Rowland, H.A.L., Pederick, R.L., Polya, D.A., Pancost, R.A., van Dongen, B.E., Gault, A. G., Bryant, C., Anderson, B., Charnock, J.M., Vaughan, D.J., Lloyd, J.R., 2007. Control of organic matter type of microbially mediated release of arsenic from contrasting shallow aquifer sediments from Cambodia. Geobiology 5, 281–292.

Schittich, A.R., Wünsch, U.J., Kulkarni, H.V., Battistel, M., Bregnhøj, H., Stedmon, C.A., McKnight, U.S., 2018. Investigating fluorescent organic-matter composition as a key predictor for arsenic mobility in groundwater aquifers. Environ. Sci. Technol. 52 (22), 13027–13036.

Shvartsev, S.L., 2000. Chemical composition and strontium isotopes of brines in the Tunguska basin connecting with its formation. Geochemistry 11, 1170–1184.

Sun, H.L., Shen, C.C., Wu, C.C., Chen, B., Yin, J.J., Yan, H., Dong, Z.G., An, D.J., Tang, S., Zhang, Q.M., 2022. Subannual-to-biannual-resolved travertine record of Asian Summer Monsoon dynamics in the early Holocene at the eastern margin of Tibetan Plateau. Appl. Geochem. 141, 105305.

Tao, Y.Q., Du, Y., Deng, Y.M., Huang, Y.W., Leng, Z.C., Ma, T., Wang, Y.X., 2022. Carbon and iron isotope approach elucidates the enrichment of geogenic phosphorus in alluvial-lacustrine sedimentary aquifers. J. Hydrol. 607, 127517.

Wang, Y.X., Li, J.X., Ma, T., Xie, X.J., Deng, Y.M., Gan, Y.Q., 2021. Genesis of geogenic contaminated groundwater: as, F and I. Critical Rev. Environ. Sci. Technol. 51, 2895–2933.

Wang, Y.X., Pi, K.F., Fendorf, S., Deng, Y.M., Xie, X.J., 2019. Sedimentogenesis and hydrobiogeochemistry of high arsenic Late Pleistocene-Holocene aquifer systems. Earth Sci. Rev. 189, 79–98.

Wang, Z.J., Guo, X.L., Kuang, Y., Chen, Q.L., Luo, M.M., Zhou, H., 2022. Recharge sources and hydrogeochemical evolution of groundwater in a heterogeneous karst water system in Hubei Province, Central China. Appl. Geochem. 141, 105165.

Wright, M.T., Izbicki, J.A., Jurgens, B.C., 2021. A multi-tracer and well-bore flow profile approach to determine occurrence, movement, and sources of perchlorate in groundwater. Appl. Geochem. 129, 104959.

Xiong, Y.J., Du, Y., Deng, Y.M., Ma, T., Wang, Y.X., 2022. Feammox in alluvial-lacustrine aquifer system: nitrogen/iron isotopic and biogeochemical evidences. Water Res. 222, 118867.

Xiu, W., Lloyd, J., Guo, H.M., Dai, W., Nixon, S., Bassil, N.M., Ren, C., Zhang, C.R., Ke, T. T., Polya, D.A., 2020. Linking microbial community composition to hydrogeochemistry in the western Hetao Basin: potential importance of ammonium as an electron donor during arsenic mobilization. Environ. Int. 136, 105489.

Xiu, W., Tiantian, K., Lloyd, J., Shen, J., Bassil, N., Song, H., Polya, D., Zhao, Y., Guo, H. M., 2021. Understanding microbial arsenic-mobilization in multiple aquifers: insight from DNA and RNA analyses. Environ. Sci. Technol. 55, 15181–15195.

Xiu, W., Wu, M., Nixon, S.L., Lloyd, J.R., Bassil, N.M., Gai, R., Zhang, T., Su, Z., Guo, H. M., 2022. Genome-resolved metagenomic analysis of groundwater: insights into arsenic mobilization in biogeochemical interaction networks. Environ. Sci. Technol. 56 (14), 10105–10119.

Yan, L., Xie, X.J., Wang, Y.X., Qian, K., Chi, Z.Y., Li, J.X., Deng, Y.M., Gan, Y.Q., 2020. Organic-matter composition and microbial communities as key indicators for arsenic mobility in groundwater aquifers: evidence from PLFA and 3D fluorescence. J. Hydrol. 591, 125308.

Yu, C., Guo, H.M., Zhang, C.R., Chen, D., Ye, H.L., 2022. Variations and driving mechanism of dissolved arsenic in sediment porewater near wetland. Appl. Geochem. 141, 105185.

Zhang, J., Jin, M.G., Cao, M.D., Huang, X., Zhang, Z.X., Zhang, L., 2021. Sources and behaviors of dissolved sulfate in the Jinan karst spring catchment in northern China identified by using environmental stable isotopes and a Bayesian isotope-mixing model. Appl. Geochem. 141, 105109.

Zhang, Y.P., Li, Q.H., Luo, Y.X., Yan, L., Peng, K., Liu, Z.M., Wang, Y.X., 2022. Groundwater salinization in a subtropical region, Beihai, southern China: insights from hydrochemistry and multiple isotopes (H, O, S, Sr). Appl. Geochem. 141, 105323.

Zhao, Q., Gan, Y.Q., Deng, Y.M., Zhou, H.R., Zhao, H.M., 2022. Identifying carbon processing based on molecular differences between groundwater and water-extractable aquifer sediment dissolved organic matter in a Quaternary alluvial-lacustrine aquifer. Appl. Geochem. 141, 105199.

Zhi, C.S., Cao, W.G., Wang, Z., Li, Z.Y., Ren, Y., 2022. Genesis of as in the groundwater with extremely high salinity in the Yellow River Delta, China. Appl. Geochem. 141, 105229.

Zhou, J., Du, Y., Deng, Y.M., Tao, Y.Q., Leng, Z.C., Ma, T., Wang, Y.X., 2022. Source identification of groundwater phosphorus under different geological settings in the central Yangtze River basin. J. Hydrol. 612, 128169.

Zhou, Y.Z., Tu, Z., Zhou, J.L., Han, S.B., Sun, Y., Liu, X.S., Liu, J.T., Liu, J.W., 2022. Distribution, dynamic and influence factors of groundwater arsenic in the Manas River Basin in Xinjiang, P.R. China. Appl. Geochem. 141, 105441.

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