



Review

A review of arsenic interfacial geochemistry in groundwater and the role of organic matter

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ABSTRACT

Recent discoveries on arsenic (As) biogeochemistry in aquifer-sediment system have strongly improved our understanding of As enrichment mechanisms in groundwater. We summarize here the research results since 2015 focusing on the As interfacial geochemistry including As speciation, transformation, and mobilization. We discuss the chemical extraction and speciation of As in environmental matrices, followed by As redox change and (im)mobilization in typical minerals and aquifer system. Then, the microbial-assisted reductive dissolution of Fe (hydr)oxides and As transformation and liberation are summarized from the aspects of bacterial isolates, microbial community and gene analysis by comparing As rich groundwater cases worldwide. Finally, the potential effect of organic matter on As interfacial geochemistry are addressed in the aspects of chemical interactions and microbial respiring activities for Fe and As reductive release.

1. Introduction

Arsenic (As) poses a severe threat to human health through exposure pathways mainly including drinking As tainted groundwater. Since 1993, WHO has recommended a maximum safe concentration of 10 µg/L As for drinking. Until now, over 100 million people are at risk of exposing to high As groundwater as drinking water source, which can lead to skin keratosis and pigmentation as well as lung and bladder cancer (Cui et al., 2013; Fendorf et al., 2010; Jia et al., 2018; Singh et al., 2015; Smedley and Kinniburgh, 2002; Wang et al., 2019a).

The formation of high As groundwater is primarily involved in three processes (Fig. 1) including competitive desorption by co-existing ions, anoxic reductive dissolution of As containing Fe(III) (hydr)oxides, and oxidative dissolution of As-S-Fe containing minerals (Fendorf et al., 2010; Guo et al., 2014; Polizzotto et al., 2005; Shen et al., 2018; So et al., 2018). Arsenite (As(III)) adsorption on minerals is much less favorable in comparison with arsenate (As(V)), and therefore, As(V) reduction process facilitated As mobilization in groundwater. Arsenic redox transformation and mobilization in groundwater are generally regulated by indigenous microorganisms. Microbial reductive release process of Fe(III) (hydr)oxides is the prevailing mechanism dominating

high As groundwater evolution. Furthermore, for some geological environment, sulfide minerals may be the primary carrier phase for As, and the oxidative release of As-bearing sulfide matrix can be the dominant mechanism. In some regions, various As geochemical processes may contribute equally or jointly to As enrichment in groundwater (Nicholas et al., 2017).

Many great review articles have been published on As geochemical behavior (Cullen et al., 2016; Guo et al., 2014; Singh et al., 2015; Yan et al., 2016), thus we aimed to include the most developed research highlights in recent five years, focusing on As speciation, chemical and microbial transformation, and the critical influence from organic matter in groundwater matrix. Arsenic geochemistry in paddy soil, mine soil, surface water environment, and the corresponding remediation strategies have been extensively investigated (Chen et al., 2017b; Kumarathilaka et al., 2018; Paulelli et al., 2019; Singh et al., 2015; Wang et al., 2015; Yan et al., 2017), and were not included in the current review, except for the related studies with groundwater systems. Future research on As interfacial geochemistry in aquifer system will be prospected based on the current review work.

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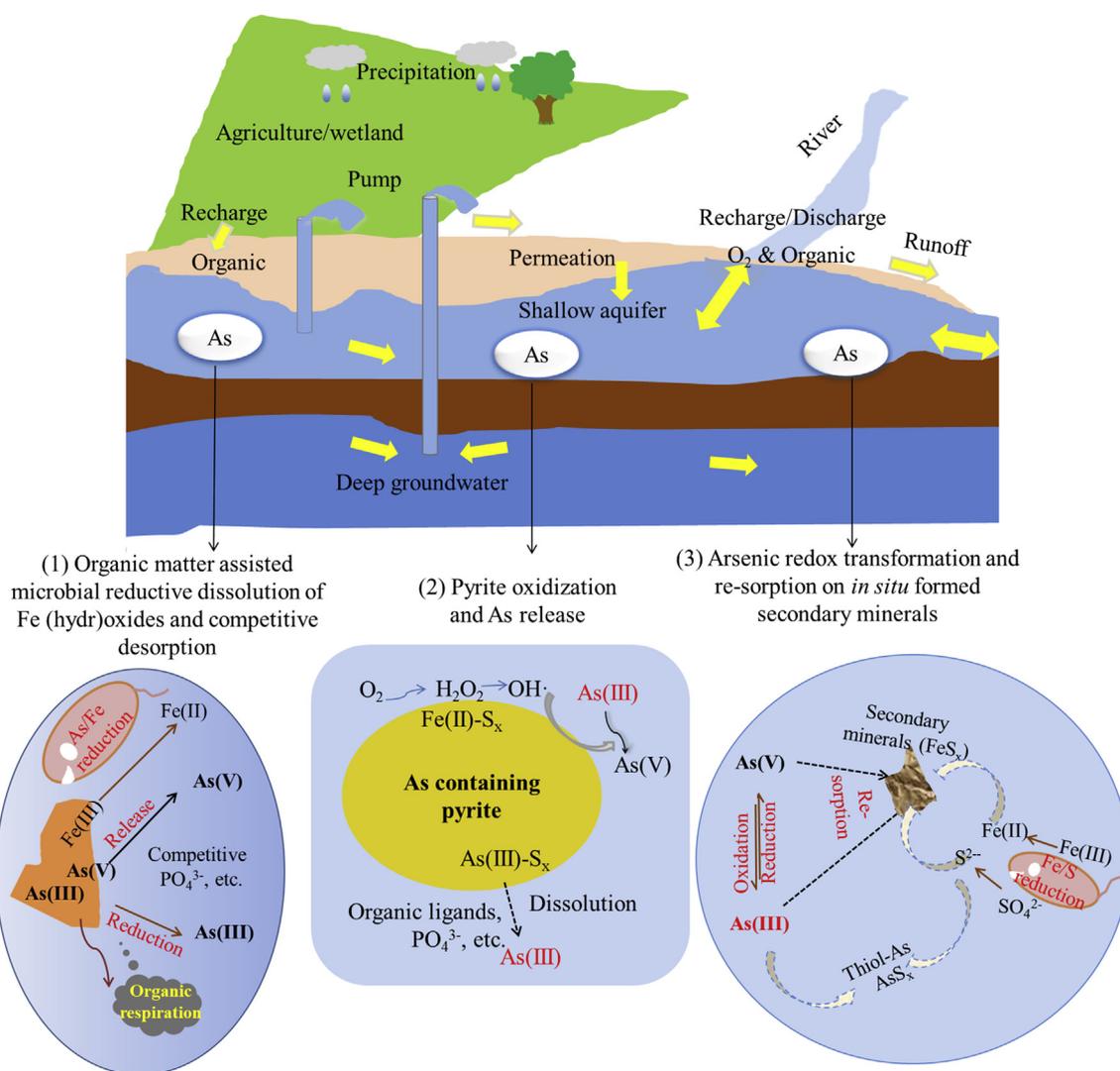


Fig. 1. Summarized mechanisms for As geochemistry in aquifer system: (1) As release in two processes including organic matter mediated microbial reductive dissolution of Fe (hydr)oxides and competitive desorption by phosphate, etc.; (2) Pyrite oxidation process for As release and oxidation, and competitive desorption by organic ligands and phosphate, etc.; and (3) As redox transformation and re-sorption on secondary minerals such as FeS_x and thiol-As species formed during reductive process of Fe(III), As, and/or sulfate. The aqueous As concentration in aquifers can be variable under various geochemical processes.

2. Arsenic speciation, transformation and (im)mobilization in groundwater system

Chemical speciation analysis of As involves operational sequential extraction methods and molecular speciation techniques. Knowledge of the extractable (available) fractions, oxidation state, and surface complexation of As on mineral and soil/sediment can widen our understanding of the interfacial geochemical process. Traditional sequential extraction procedure (SEP) methods can distinguish available and reactive As fractions from the uneasily immobilized part in solid phase (Stuckey et al., 2015a; Varsanyi and Kovacs, 2017). New developed techniques including XPS, FTIR, and particularly X-ray adsorption spectroscopy (XAS) can provide molecular-level information on the *in situ* As oxidation state and possible binding atoms without much sample damage, and have shown great new insights on elucidating As molecular interfacial geochemistry.

2.1. Chemical speciation of As in environmental matrices

Chemical operational species of As can be investigated using SEP, which is a simple and useful method to evaluate the general chemical fractions of As in soil/sediment using selective extract solution for the

corresponding As species bound to specific solid phase (Cui et al., 2018b; Gillispie et al., 2019; Wenzel et al., 2001). An eight-step sequential extraction procedure with more distinct information was used to characterize the operational fraction of As from sediment, which could provide some information of As related fraction on pyrite and amorphous As_2S_3 (Keon et al., 2001; Wang et al., 2018d). Sequential extraction results of As fractions can have some implications on As geochemistry. Brown color sediment samples often show high amount of strongly adsorbed fraction associated with crystalline Fe/Mn/Al oxides fraction and residual fraction, with slight contents of exchangeable fraction. These fractions are often co-precipitated into or adsorbed on the Fe/Mn/Al oxides in the soil matrix, and often show low mobilized ability in groundwater system because of their resistance to the redox change and dissolution. The related aquifer-sediment layers include a Pleistocene aquifer of Cambodia (Gillispie et al., 2019), and sediment profiles from Hong Kong of southern China (Cui et al., 2018b; Li et al., 2017b). This kind of sediment often shows brown/orange color, and the corresponding aquifer often shows low concentration of As, not exceeding 11.5 $\mu\text{g/L}$. On the other hand, some other grey or dark sediment, mostly from reducing aquifer, showed relatively higher contents of extractable (non)specific adsorbed fraction, including 16.5–21.2% in Guide basin, northwestern China (Wang et al., 2018d)

with As concentration from 9.9 to 377 $\mu\text{g/L}$ (average 109 $\mu\text{g/L}$).

Other one-step extraction methods have also been developed to evaluate exchangeable or reducible As fractions. As an efficient competitive anion, phosphate is often selected to desorb As from minerals to extract the ligand-displaceable fraction or strongly adsorbed species (Johnston et al., 2015; Stuckey et al., 2015a). Usually, fresh, freeze-dried, or anaerobic-dried sediment samples are used because air-drying of the sample can cause oxygen exposure and aging, which might change the As speciation. Previous studies employed the phosphate extraction method and indicated that ligand-displaceable As comprised $15 \pm 12\%$ of the total As at the Nawalparasi floodplain in Nepal and 12–26% of total As at the top 6 m of sediment in the Mekong Delta (Stuckey et al., 2015a). A high exchangeable fraction of As in the sediment usually corresponds to elevated concentrations of As in tube wells (Johnston et al., 2015). Using 1 M HCl to extract sediment can produce acid-reactive fractions such as amorphous Fe/Mn oxides, acid-volatile sulfides, and carbonates; the reducible fraction can be obtained using the citrate–bicarbonate–dithionite (CBD) method for Fe and Mn crystalline oxides (Stuckey et al., 2015a). A two-step extraction involved the use of 0.5 M formic acid at pH 3 in a serum bottle with N_2 bubbling to remove O_2 and CO_2 from the solution and headspace, in order to extract reactive components, carbonate and phosphate minerals, as well as adsorbed arsenic, with no Fe(III) (hydr)oxides including ferrihydrite in formic acid (So et al., 2018). The second step used a deoxygenated solution of 0.1 M ascorbic acid and 0.2 M oxalate solution at pH 3 to dissolve the Fe(III) (hydr)oxides present in the sediment and the As. Various chemical extraction methods employed together can provide some operational proportion and highlight the possible extent for As release and reductive dissolution of Fe(III) (hydr)oxides. Nevertheless, chemical extraction is an operationally-defined method, strongly relying on the extraction reagent and procedure. Furthermore, typical sequential extraction cannot distinguish organic or sulfide fractions of trace metals in soil, which is crucial for understanding the geochemical behavior of As. Finally, the information on molecular species that can be obtained using this sequential extraction method is limited.

X-ray adsorption spectroscopy (XAS) can provide valuable information on the As oxidation species in aquifer-sediments. The detected As oxidation states such as As(III), As(V), inorganic As bound with sulfide, and thiol-As(III) reflect the redox potential of the sediment. XAS analysis of the sediment cores in a Pleistocene aquifer of Cambodia (Gillispie et al., 2019), a coastal island of Hong Kong in the Pearl River Delta of southern China (Cui et al., 2018b), and the near surface sediment (< 5 m) of the Jiangnan Plain of Central China (Duan et al., 2017) indicated that the majority of As was strongly adsorbed to aquifer sediments or coprecipitated in oxides in the form of As(V). When the environmental redox potential changes from oxic surface to anoxic deep sediment or reducing region, the dominant species often changes from As(V) to As(III) or a more reducing species such as As-sulfide. For example, in the Jiangnan Plain of Central China (Duan et al., 2017), As(III) constituted 64% of the reducing clay and silty clay layers because of the local reductive environment with low oxygen penetration; and even more reductive As-sulfide (49–63%) become the dominant As species in deep coarse sand aquifers (> 35 m deep). Arsenite or As-S species were also observed as the dominant species in the deeper sediments of the permanent wetlands of the Mekong Delta (Stuckey et al., 2015a, 2015b), while arsenian pyrite was found to be the predominant form in the peat layer of an alluvial sediment profile in Nepal (Johnston et al., 2015). Therefore, the As oxidative species, to some extent, were restricted by the localized redox potential or geochemical processes that varied widely.

In more reducing sediment deposits with a high amount of organic matter, organic sulfur-bound As may be formed, such as a naturally anoxic arsenic-enriched peatland in Switzerland (Langner et al., 2011), wherein covalent bonds between As(III) and organic sulfur groups with an average A-S distance of 2.26 Å have been observed with no

involvement of Fe-(hydr)oxides or Fe sulfide phases, owing to that As was completely sequestered by natural organic matter. Thiol-bound As(III) (40–55%) and arsenopyrite (15–30%) were found to be the dominant species in the mangrove depositional sediment of the Mekong Delta (Wang et al., 2018c). However, when free sulfide was noted to be limited, the predominant As species changed to thiol-bound As(III) and oxygen-bound As(III/V), and siderite was observed instead of pyrite.

Micro XAS (μ -XAS) coupled with micro X-ray fluorescence spectrometry (μ -XRF) techniques can be employed to quantify the spatial distribution of molecular As species in the specific regions of soil/sediment particles. A series of micro regions from several samples were characterized using As μ -XAS speciation mapping analysis for three representative aquifer sediments obtained from the Des Moines Lobe glacial advance (Nicholas et al., 2017). A total of six incident energies including 11,830 eV (pre-edge), 11,868 eV for arsenopyrite, 11,869 eV for orpiment, 11,871.5 eV for As(III), 11,875 eV As(V), and 11,979 eV (post-edge) were included for As speciation analysis, which used hundreds of thousands of points for a sample. The results indicated a very heterogeneous distribution of As and Fe species on sediment particles wherein core OTT3 and TG3 showed a much more higher amount of As-sulfide minerals in aquitard samples, while core UMRB2 showed approximately equal fractions of all four As species. Detailed spatial XAS speciation in the solid phase coupled with analysis of the water chemistry can successfully predict the distinguishable As enrichment mechanism occurring in different layers of the same region.

In addition to solid As speciation, labile As species can reflect the mobilized behavior in the solid phase. Arsenic in groundwater often exists as As(III) and As(V), depending on the redox potential and microbial activities. Recently, thiolated As species such as thioarsenite was detected, which consisted $> 93\%$ of total As in the porewater of peatlands (Besold et al., 2018). Further incubation experiments of solid samples indicated that monothioarsenate was stable for over 41 days in anoxic environments at pH 8.5, which facilitates a stable environment for aqueous As. In contrast, at slightly acidic environments, As(III) is the only As species and favors As mobilization in such environments. Another study also indicated 71% of total As was As(III) at acidic pH (4.0–4.4) in an England peat bog pore water (Mikutta and Rothwell, 2016). Thiolated As has often been found in hot springs (Guo et al., 2017; Wang et al., 2018a). However, few studies have directly detected thiolated As in groundwater systems, including an aquifer contaminated severely by methylated As pesticides (Wallschläger and London, 2008), even though several studies have performed thermodynamic calculations and suggested the possible presence of thiolated As in natural groundwater in the Datong Basin China (Pi et al., 2017) and porewater in surface sediment of the Marque River surface sediment in Northern France (Gorny et al., 2018), where formation of such species is favored by the presence of high concentrations of sulfide. The high instability of thioarsenicals limits its detection in groundwater, which is highly affected by the redox potential, pH, and concentrations of oxygen, sulfur, and Fe. General procedures for groundwater sampling and preservation do not favor the original species of thioarsenicals, either, as thioarsenicals rapidly transform to other As species. Furthermore, appropriate storage and analytical methods for accurate detection of thioarsenicals in groundwater require further investigation.

2.2. Arsenic transformation on typical minerals

Arsenic geochemistry is usually restricted by typical minerals including Fe and Mn (hydr)oxides, and studies have taken such facts into account in recent years. Understanding the interfacial geochemical mechanism relies on accurate analysis of As species and their interactions with the minerals, such as ferrihydrite, goethite, magnetite, hematite, and pyrite, and the complex behavior of As on the typical minerals was summarized in this chapter which can provide valuable insight on As geochemistry in groundwater.

The complex manner of As(III) adsorption on ferrihydrite under

anaerobic conditions has been investigated (Xiu et al., 2018). The results indicated that As(III) formed both bidentate binuclear structure and monodentate mononuclear structure on ferrihydrite in the initial 2 h, which changed to bidentate binuclear structure only after 192 h. Aerobic interactions of As(III) and As(V) with FeS showed that part of the As(III) changed to As(V) and As₂S₃-like species; similarly, partial of the As(V) was reduced to As(III), with small amounts of As₂S₃ observed in the final solid (Niazi and Burton, 2016). A recent study prepared As(III)-containing pyrite (Qiu et al., 2017), in which the amount of Fe-S increased and crystalline pyrite decreased after As substitution. Anaerobic pyrite oxidation was accelerated by Fe(III) at pH 3.0–6.0 and by As(V) at pH 7.0–11.0, and As(III) released owing to pyrite oxidation was adsorbed on the freshly formed secondary Fe (hydr)oxides on pyrite surface systems (Qiu et al., 2017). Other secondary minerals including scorodite and jarosite on the arsenopyrite surface mainly contributed to the limited dissolution of arsenopyrite (Deng et al., 2018a). Active oxygen intermediates including OH[•] and H₂O₂ governed arsenopyrite oxidation under anoxic conditions (Qiu et al., 2018), and the oxygen introduced remarkably increased the radical concentrations and therefore the arsenopyrite oxidation rate (Fig. 1-(2)).

Manganese (hydr)oxides typically contained in sediments may be also involved in As release and transformation in groundwater (Vega et al., 2017). Interactions of As(III) with Mn minerals are complicated, and usually involve electron transfer for As(III) oxidation, surface complexation of As(V) primarily via a bidentate binuclear structure, and surface passivation by the re-adsorbed Mn²⁺ (Lafferty et al., 2010; Manning et al., 2002). To simulate the behavior of natural minerals bearing both Fe and Mn, poorly crystalline δ-MnO₂ was synthesized and its interactions with As(III) were investigated in the presence of dissolved Fe(II) (Wu et al., 2015, 2018). The results indicated that As(III) was oxidized to As(V) as the predominant species on the solid phase at low Fe(II) concentrations (100 μM), while higher Fe(II) concentrations (200–1000 μM) inhibited As(III) oxidation and both As(III) and As(V) were found on the solid phase. The inhibition brought by Fe(II) in As(III) oxidation was also detected for naturally formed MnO₂ using natural aerated As tainted groundwater at a water treatment plant (Gude et al., 2017). Further XAS characterization indicated both As(III) and (V) adsorbed on Fe (hydr)oxides rather than Mn oxide, as a bidentate binuclear corner-sharing complex, suggesting that the formation of Fe(III)-(hydr)oxides plays a very important role in reducing As mobility in systems containing As(III) with birnessite.

Many cations and anions coexist in groundwater with As, and often show potential influence on the As adsorption/desorption behavior on typical minerals. As(III) and As(V) often experience no influence from chloride, fluoride, sulfate, and nitrate species (Cui et al., 2015; Yan et al., 2016; Zhou et al., 2019). Some oxyanions such as phosphate, silicic acid, and carbonate can undergo competitive effect on As adsorption to some extent, and phosphate primarily forms similar surface complexes as those of As by competing for the limited number of binding sites (Kanematsu et al., 2013; Perez et al., 2019; Stolze et al., 2019). Other metalloids such as antimony and selenium strongly influence As retention because they often form strong inner sphere complexes on the mineral surface like As does (Rouwane et al., 2016; Yan et al., 2017). Some cations including Ca can enhance As adsorption on minerals: our recent study employed XAS and observed a surface ternary complex Ca–As(V)–TiO₂ (Hu et al., 2015). The formation of the Ca–As(V)–metal oxide ternary structure increased As(V) retention. The ternary surface complexation of Ca–As(V)–metal oxide like structure significantly enhanced the modeling results, which was also observed during surface complexation modeling of As mobilization during *in-situ* reactions undergone by loaded goethite in an aquifer in the Hetao Basin (Stolze et al., 2019). Integrating the interfacial geochemical findings for real environmental systems to predict As-free groundwater for drinking remains a great challenge as few studies have been performed on this topic.

In reducing groundwater systems, sulfide is often coupled to As with

iron oxide (Zhao et al., 2017). The results indicated that the presence of sulfide significantly decreased the adsorption of As(III) (50%) and As(V) (30%) on ferrihydrite. The reason for this was suggested to be the formation of thioarsenite in solution in the presence of high concentrations of sulfide (Fig. 1-(3)), as determined using geochemical modeling calculations. The comparative adsorption and behavior of thioarsenite and As(III) on several iron minerals such as magnetite, ferrous sulfide, and hematite were further explored (Wang et al., 2018b, 2019b). The results demonstrated a much lower affinity of thioarsenite than As(III) exhibited by the minerals and that the dominant species in solids is As(III) or amorphous As₂S₃. Nevertheless, if more sulfide is provided, a FeS-like mineral may form and will can, to some extent, immobilize aqueous As (Pi et al., 2017).

2.3. Arsenic transformation and (im)mobilization in aquifer-sediment system

Arsenic has been found in investigations undertaken widely on the geochemical processes undergone in aquifer-sediment systems (Fig. 1), and the main mechanism often relies on the reductive process of Fe (hydr)oxides prevailing in sediment, competitive desorption, and the oxidizing dissolution of As-sulfide-like compounds (e.g., orpiment or pyrite) (Fendorf et al., 2010; Guo et al., 2014; Polizzotto et al., 2005; Sathe et al., 2018; Shen et al., 2018). In this chapter, chemical processes related to lowering of the redox potential and competitive anions concerning As enrichment in aquifer-sediment system will be discussed.

The reductive dissolution of Fe minerals in sediment (Fig. 1-(1)) was considered as an As enrichment mechanism in studies of the Holocene aquifer in the Red River floodplain using ascorbic acid/oxalate extraction following formic acid (Postma et al., 2016; So et al., 2018). The results identified two stages for Fe release: the first rapid dissolution stage with high amounts of extractable As and Fe and the second stage, which slowly released Fe(II) only but no As. The extract showed that the As/Fe ratio was in the range of 0.1–1.2 mmol/mol, with the highest value obtained for the youngest sediment layer, consistent with a higher labile As concentration. The data were comparable with the extractable 0.15–0.65 mmol/mol As/Fe ratio for sediments from Bangladesh, Cambodia, and Vietnam (Fendorf et al., 2010; Kocar and Fendorf, 2009), and 0.10–0.82 mmol/mol As/Fe ratio for the Hetao Basin (Shen et al., 2018). Nevertheless, the extraction rates and quantity do not necessarily reflect the extent of As release in groundwater. Determining whether the chemically extractable Fe and As can be involved in the microbial reductive dissolution require further investigation.

Anaerobic reductive dissolution of Fe(III) (hydr)oxides contributing to As release was further demonstrated using incubated aquifer sediments, including those in Florida (Jin et al., 2016) and the central Yangtze River Basin (Duan et al., 2019; Schaefer et al., 2017). In Florida, all of the anaerobic cases showed that As was released via reductive dissolution in the anaerobic periods, which was promoted by labile dissolved organic matter (DOM) addition, but refractory DOM (i.e., soil extracts) showed no influence (Jin et al., 2016). Therefore, aquifer storage and recovery should be carefully taken considered to reduce the amount of labile DOM-containing shallow water into the aquifer. In the Yangtze River Basin sediment (Duan et al., 2019), anoxic incubations resulted in As release into the solution and the geogenic organic matter in sediment was sufficiently reactive to support microbial reduction of As(V) and Fe (III) without an exogenous carbon source, justifying the high As concentrations throughout the aquifer (Schaefer et al., 2017).

Sulfur is widely involved in As geochemistry in groundwater, both in the form of sulfur-bearing minerals like pyrite and through sulfate reduction. Oxidizing dissolution of As-containing sulfide compounds including pyrite, arsenopyrite, or orpiment has been identified an As enrichment mechanism recently (Fig. 1-(2)). Although reductive dissolution of Fe minerals usually leads to As enrichment in the upper part

of the shallow aquifer (< 25 m deep), the following depth of 25–30 m showed significantly low As concentrations at the Datong Basin, northern China (Pi et al., 2018). The variation in the extent of As enrichment according to the depth is often due to the availability of organic matter and sulfate, which is efficient electron acceptors for microbial activities. Elevated sulfate contents in shallow groundwater can trigger As desorption by competitive adsorption sites on Fe minerals in sediments (Cui et al., 2018b; Li et al., 2018). Reduction of sulfate to sulfide can result in high As concentration in the groundwater due to the possible formation of a more mobile phase such as inorganic As-S and thiol-As. Higher concentrations of sulfide may precipitate with Fe (II) by forming pyrite-like minerals and finally immobilize As (Phan et al., 2019; Xie et al., 2015; Xu et al., 2016). If the secondary formed pyrite is not sufficient for As immobilization, a moderate level of aqueous As can still be observed (Pi et al., 2017).

Nitrate is another potential contaminant in groundwater along with the surface water recharge, particularly that arising from agricultural activities. Along with widespread agricultural development, nitrate has become an increasingly abundant pollutant in groundwater and can be a potential electron acceptor for Fe(II) oxidation, and this redox couple on As biogeochemistry has been studied for a sand and gravel aquifer (Smith et al., 2017). Long-term (15-year) geochemical monitoring of the constant injection of nitrate in a wastewater-contaminated aquifer on Cape Cod showed Fe(II) oxidation coupled with nitrate reduction. In addition, Fe(III) (hydr)oxides were produced *in situ* resulting from Fe oxidation, and therefore dissolved concentrations of As decreased as a potential remediation strategy, which can also be a feasible method for groundwater As(III) oxidation and removal along with nitrate reduction (Cui et al., 2018a). However, a case reported in Emsland, Germany (Houben et al., 2017) found contaminated As in the local groundwater, and the oxidation of As-containing authigenic pyrite was considered the potential source of aqueous As, possibly owing to the use of agricultural nitrate as an electron acceptor, because of complicated reactions in the groundwater system. Further work is needed for elucidation.

Other competitive anions including carbonate could also contribute to As enrichment in a carbonate-rich unsaturated aquifer in Argentina (Dietrich et al., 2016). PHREEQC calculations of the exchangeable extraction process suggested that As desorption was attributable to the high pH and carbonate arising from calcite dissolution. The influence of carbonate on As release was also identified in sandy aquifer systems in the Mannar Island, Sri Lanka (Amarathunga et al., 2019; Bandara et al., 2018) and Doñana National Park, Spain (Kohfahl et al., 2016). Bandara et al. (2018) analyzed the varying $\delta^{13}\text{C}_{\text{DIC}}$ values (−19.4‰ to −6.5‰) of the high concentrations of dissolved inorganic carbon (DIC, 2.11–0.9 mmol/L) and indicated that these isotope values are typical of carbonate dissolution, which contribute to the dissolution of Fe/Mn (hydr)oxides.

It should be noted that As enrichment may be caused by various mechanisms collectively. One typical case was observed in the Des

Moines Lobe glacial advance region involving three aquifer cores (Nicholas et al., 2017). The area near the first core showed a higher redox potential and lower pH values in the elevated As groundwater than those needed for low As concentrations with sub-equal Fe and sulfate, suggesting competitive desorption as the primary mechanism. The wells near the second core with elevated As showed a lower redox potential, lower pH, higher Fe(II) content, and lower sulfate concentrations, consistent with reductive dissolution-induced As enrichment, similar to that noted in upstream of the Ganges River basin in Nepal (Yadav et al., 2015). The area near the third core with high As concentrations showed a higher redox potential, lower pH, and higher Fe and sulfate concentrations. The corresponding sediment samples contained much higher concentrations of As-bearing sulfide minerals (arsenopyrite and orpiment-like material), and therefore the oxidative dissolution processes of Fe sulfides could have contributed to As enrichment in the nearby wells. The study provides a good case showing that the particular environmental geochemical conditions at aquifer-aquitarad interfaces facilitate a series of geochemical reactions leading to changes in the minerals and subsequent As release into groundwater. Nevertheless, the exact relationship between those parameters requires further explanation. The critical roles and exact contributions of microbial activity for As release mechanisms (chemical or microbial) also need further elucidation because a recent study showed that the chemically controlled reducing potential contributed to one half of As release from contaminated soil samples (Rajpert et al., 2018).

2.4. Microbial role in As transformation and mobilization

Indigenous microorganisms in the groundwater play a key role in the reductive dissolution of Fe (hydr)oxides and As transformation and release (Fendorf et al., 2010; Zhu et al., 2017). Microbial As(V) reduction to As(III) directly affects the As mobility as As(III) is more mobile and subsequently limits As adsorption on sediment minerals. Besides direct bacterial redox reactions involving As, microbial redox metabolism of Fe, carbon, sulfur, and nitrogen also affect the redox potential of the environment and consequently indirectly influence geochemical changes concerning As. This chapter primarily discussed the bacterial processes, including reduction, oxidization, reductive dissolution of Fe (hydr)oxides, and As sequestration by the secondary mineral formation.

2.4.1. Arsenic reducing bacteria isolated from aquifer system

Recently, many As-reducing bacterial species have been isolated or enriched from groundwater or aquifer sediments (Table 1). Anaerobic As-reducing bacteria include *Desulfuromonas* genus WB3, which bears a dissimilatory As(V) reductase and was isolated from the Bengal Basin (Osborne et al., 2015). Anaerobic As-resistant *Staphylococcus* sp. As-3 with *arsC* from sediments in the Chianan Plain Taiwan reduced 32% of 5 mM As(V), and could interact with arsenopyrite (FeAsS) and mobilize

Table 1
Recent As(V) reducing bacterial isolates for both soluble and solid phase As.

Bacterial species	Redox condition	Gene	Soluble As(V)	Solid phase As(V)	Location	References
<i>Desulfuromonas</i> genus	Anaerobic	<i>arrA</i>	4.05 mM in ~28 h	No test	Bengal Basin in West Bengal	Osborne et al. (2015)
<i>Staphylococcus</i> sp.	Anaerobic	<i>arsC</i>	1.6 mM in 96 h	Arsenopyrite	Chianan Plain, Taiwan	Rathod et al. (2019)
<i>Bacillus</i> JQ and <i>Desulfitobacterium</i> DJ-3	Anaerobic	<i>arsC</i>	5 mM in 30 h	As(V) on goethite	Inner Mongolia, China	Cai et al. (2016)
<i>Exiguobacterium</i> DJ-4	Anaerobic	<i>arrA</i>	5 mM in 30 h	As(V) on goethite	Inner Mongolia, China	Cai et al. (2016)
<i>Pseudoxanthomonas</i> strain	Aerobic	<i>arsC</i>	2.5 mM in 96 h	No test	West Bengal, India	Mohapatra et al., 2018b
<i>Pseudomonas</i> sp. M17-1	Aerobic	<i>arrA</i> & <i>arrC</i>	0.1 mM in 6 h	Scorodite, and As(V) on goethite and in sediment	Hetao basin, China	Guo et al. (2015)
<i>Bacillus</i> sp. M17-15	Aerobic	<i>arrA</i> & <i>arrC</i>	0.1 mM in 24 h	Scorodite, and As(V) on goethite and in sediment	Hetao basin, China	Guo et al. (2015)
<i>Microbacterium</i> sp. AE038-20	Aerobic	–	0.001 mM in 50 h	No test	Tucuman, Argentina	Maizel et al., 2018a
<i>Pantoea</i> sp. IMH	Aerobic	<i>arsC</i>	1 mM in 60 h	No role in As(V) in solid waste	Shanxi, China	Tian et al. (2015)

As into a soluble phase as As(III) and As(V) (Rathod et al., 2019). One dissimilatory As(V)-respiring bacterium *Aeromonas* sp. JH155 was isolated from sediment in the Jiangnan Plain (Chen et al., 2017a), and it could completely reduce 2.0 mM As(V) into As(III) in 72 h, and efficiently promote the reduction and release of mineral As into the aqueous phase.

Aerobic As(V)-reducing bacteria, including six *Actinobacteria* strains, were isolated in groundwater from Tucuman, Argentina (Maizel et al., 2018): they could grow in media with 20 mmol/L As(III) or 200 mmol/L As(V). Among them, *Brevibacterium* sp. strain AE038-4 and *Microbacterium* sp. strain AE038-20 were capable of aerobic As(V) reduction and can probably facilitate As mobility in groundwater systems. From high As aquifers of the Hetao Basin, China, two strains of aerobic As-resistant bacteria *Pseudomonas* sp. M17-1 and *Bacillus* sp. M17-15 were isolated and found to bear *arr* and *ars* genes, respectively (Guo et al., 2015). KAs 5-3(T) was isolated from As-contaminated groundwater in the West Bengal, India, which bore As(V) reductase (*arsC*) capable of As-detoxification and nitrate and nitrite reductase (*narG* and *nitS*) for denitrification, and could be involved in coupled cycles involving both As and nitrate (Mohapatra et al., 2018).

Usually a large number and variety of bacterial species exist in aquifers and sediments. In a recent study, more than 170 strains were isolated from As contaminated groundwater in Barasat and Chakdaha of West Bengal, India (Paul et al., 2015). Sixty percent of the strains showed As(V)-reducing ability and much fewer isolates showed As(III)-oxidizing ability. In total, more than 50% of the strains possessed the As(V)-reducing gene *arsC*, and nearly 10% contained the As(III) oxidizing gene *aiob*.

Besides As-reducing bacteria, some other Fe-reducing and S-related isolates have also been reported to indirectly influence As geochemical changes. The related bacterial activities may release Fe(II) and sulfide and, therefore, secondary Fe(II/III)-bearing mineral phases can be generated including Fe sulfide minerals, vivianite from Fe(II), and the aqueous-phase phosphate (Muehe et al., 2016). The released As can often be re-immobilized on secondary minerals including Fe(II)-S minerals and vivianite, and thereafter As release into water can be inhibited. Iron (III) (hydr)oxide minerals formed *in situ* from Fe(II) oxidation by nitrate reduction can be a route for both As and nitrate removal from tainted groundwater (Smith et al., 2017). A novel bacterium (*Clostridium* sp. strain PXL2) isolated from anoxic activated sludge can efficiently oxidize Fe(II), which is associated with the reduction of nitrate. PXL2 formed nanosized and poorly crystalline Fe(III) oxides encrusted on the cells by exhausting the nitrate (Li et al., 2016). The Fe(III) (hydr)oxides formed *in situ* following Fe oxidation and therefore the concentrations of dissolved As decreased; this can be implemented as a potential remediation strategy.

In summary, different groundwater sites may harbor distinct As related microbial species. High As groundwater often bears either anaerobic or aerobic As reducing bacteria. Anaerobic As(V)-reducing microorganisms often occur in more reducing environments or deep groundwater and play a key role in As releasing behavior. Aerobic As(V)-reducing bacteria often prevail in shallow or surface groundwater, whereas some oxygen penetrates during surface water recharge or groundwater pumping. Both kinds of bacteria can reduce aqueous As(V) to As(III) and thus increase As mobility. The summarized above show that microbial As redox behavior in the groundwater system is very complex and depends on various bacterial species in different locations.

2.4.2. Interaction between bacterial isolates and As in solid phase

How microbial activities govern As release in an aquifer can be understood by gaining comprehensive understanding of the interactions between bacteria and As-bearing solid phase, which is often affected by relevant environmental conditions. It has been widely reported that Fe-reducing bacteria usually release the sequestered As during Fe(III) reduction. Such bacteria, particularly *Shewanella* strains, can reduce Fe minerals such as clay minerals, arsenopyrite, and scorodite and Fe

containing solid waste and, consequently, the As contained in the solid phase is released (Ghorbanzadeh et al., 2015; Tian et al., 2015; Wang et al., 2016). The reductive dissolution of As-containing Fe (hydr)oxides in an aquifer by Fe-reducing bacteria usually increases As concentration in groundwater.

The interactions between As-reducing bacteria and solid phase As remain complicated (Table 1). Anaerobic As(V)-reducing bacteria often show a much higher ability to reduce aqueous As(V) than the sorbed As(V) on minerals or solid fractions in the soil/sediment. The extent of the release and reduction of As(V) strongly depends on the As(V) desorption rate. The As reducing bacteria, such as *S. putrefaciens* CN-32 strain, have to interact with Fe minerals probably via bacterial phosphate or carboxylate groups and promote As(V) desorption to a soluble phase, which is followed by the reduction of dissolved As(V) (Huang et al., 2011). Determining whether microorganisms can directly reduce the adsorbed or sequestered As(V) in soil/sediments accurately and, if so, to what extent is crucial for understanding the sequence of reductive dissolution of Fe minerals and As(V) reduction and subsequent groundwater As enrichment mechanism. The role of anaerobic As(V)-reducing bacteria on the adsorbed As(V) was verified in a few recent works. Our recent study tested the ability of the anaerobic As(V)-reducing strain *OhILAs* bearing the *arrA* gene to treat As-containing Fe waste, which showed no reduction and release of As(V) from the waste residues (Tian et al., 2015). By comparing the As(V) reduction rate and desorption rate from minerals, Michaelis-Menten kinetic data illustrated that the Arr enzyme encoded by *arrA* showed exceptionally fast aqueous As(V) reduction with a maximum rate of 29 s^{-1} , which is several orders of magnitude faster than the rate of As(V) desorption (2×10^{-7} to $1 \times 10^{-5} \text{ s}^{-1}$) from the soil (Glasser et al., 2018; Zhang and Selim, 2005), suggesting that As(V) desorption is the rate-limiting step in As mobilization. In other words, bacterial As(V) reduction in the solid fraction relies on efficient As(V) desorption.

From high As aquifers of the Hetao Basin in China, *Pseudomonas* sp. M17-1 and *Bacillus* sp. M17-15, bearing *arr* and *ars* genes, respectively, can contribute to As(V) reduction from the adsorbed fraction in goethite and sediments using acetate as the carbon source (Guo et al., 2015). Three anoxic As(V) reducing bacteria including JQ (*arsC* gene) and DJ-3 (*arsC* gene) and DJ-4 (*arrA* gene) can reduce high concentrations of dissolved As(V) (5 mM) within 3 day in the order DJ-3 (100%) > DJ-4 (97.2%) > JQ (56.8%) (Cai et al., 2016). Furthermore, in comparison with control groups, these bacteria also facilitated the release and reduction of As(V) from goethite in the order DJ-4 (90.5%) > DJ-3 (64.5%) > JQ (18.8%). However, the interactions involved in the three strains releasing adsorbed As(V) needs elucidation.

Sulfate-reducing bacteria can reduce adsorbed As(V) employing the sulfide generated by sulfate reduction as determined using *in situ* ATR-FTIR technique in our recent publications (Luo et al., 2017, 2018). The biogenic sulfide significantly affects As transformation. Further aquifer-sediment microcosm assays indicated that sulfate facilitates microbial release of As and Fe since that some bacteria including *Citrobacter* sp. JH001 can catalyze the dissolution, reduction and release of As and Fe from the sediments using sulfate (Wang et al., 2017). The same incubation indicated that, not only the bacterial sulfate-reducing activity, but also the As(V)-respiring reductase gene abundance collectively significantly increased after sulfate addition, suggesting complicated As enrichment processes in groundwater.

In real environments offering changing redox potentials, many bacterial processes involve As, Fe, and S, and the geochemistry becomes more complicated. One recent study simulated a real flowing system using aquifer sediment samples for 110 days (Moon et al., 2017). During the reduction phase, the amount of As(III) in the effluent rapidly increased due to reductive dissolution of iron minerals by the inoculated iron-reducer, genus *Geobacter*. Furthermore, As(V) reduction induced by *Desulfosporosinus* and *Anaeromyxobacter* as well as the *Geobacter* inoculum facilitated As release initially. Then,

Desulfosporosinus (33%) dominated in the column, which reduced sulfate to sulfide and a ferrous sulfide precipitate formed. The amount of As released gradually decreased due to the re-adsorption on the secondary minerals. Arsenic sequestration by ferrous sulfide minerals was also demonstrated in our recent studies using sulfate-reducing bacteria (Luo et al., 2017, 2018). Therefore, the biogenic sulfide process strongly affects the As(V) releasing behavior.

2.4.3. Microbial community and gene analysis for groundwater As enrichment

Recent gene sequencing techniques have greatly advanced the study of As enrichment geochemistry, particularly in gaining information on uncultured microorganisms. The abundance of functional genes controlling As reduction for a scenario can be obtained, which is useful since the respective abundance of each gene to some extent reflects the corresponding microbial activities. Furthermore, coupled use of incubation and bacterial sequence information can determine the microbial role in As transformation and mobilization precisely.

Various microbial communities involving in As redox transformation, Fe/Mn reduction, and sulfate reduction have been identified using sequencing techniques for various As enrichment groundwater samples worldwide, including the Chianan Plain in Taiwan (Das et al., 2016a), the Hetao Basin in China (Li et al., 2015, 2017c), and the Jiangnan Plain in China (Chen et al., 2017a; Deng et al., 2018b). Usually, different sites have shown identical bacterial diversity species undertaking distinct As biogeochemical behavior. Richness and diversity of microbial communities in high As sediment are usually higher than those in corresponding groundwater (Li et al., 2015). Arsenic rich groundwater and sediments shows both dissimilatory Fe(III)-reducing and As(V)-reducing bacterial species in Bangladesh, identified using 16S rRNA gene analysis (Gnanaprakasam et al., 2017). The results obtained for water chemistry, solid characterization, and microbial community for shallow aquifers of the Datong Basin revealed that bacterial mediated reductive desorption of As(V) as the main pathway towards As mobility and Fe (III) reduction coupled with sulfate reduction as a secondary process contributing to As enrichment (Zhang et al., 2018). Analysis of 16S rRNA genes indicated that deep sediments contain diverse microbial communities shaped by environmental factors such as As, sulfate, nitrate, Fe and the pH.

Owing to limited abundance of As-reducing bacteria in groundwater systems (Davolos and Pietrangeli, 2013), microbial enrichment processes such as those using a carbon source for culture have often been employed before amplification of *arrA*. It was observed that microbial enrichment processes may drastically shift the original community structure. One study successfully amplified *arrA* gene sequences from unaltered Cambodian near-surface sediments without prior enrichment (Ying et al., 2015). The results indicated that a large majority (> 70%) of the community was phylogenetically distinct from that previously recorded in Cambodia. And the dominant sequence was similar to that of *Geobacter* species, which are capable of As(V) respiration, a process that contributes to As mobilization. Further work may identify how and to what extent the microbial enrichment changes the original microbial communities and species.

Arsenate reductase genes have been thoroughly investigated to determine their relationships with groundwater As contamination, for example, the high As groundwater system in the Chianan Plain, Taiwan (Das et al., 2016a, 2016b). The abundance of the dissimilatory *arrA* gene indicated that the amount of *arrA* gene increased with labile carbon addition and groundwater As enrichment is enhanced by the dissimilatory As reduction process, which was also determined on the basis of the changing microbial community.

More recently, based on current comprehensive profiling of microbial As related genes, a high-throughput AsChip was developed containing 81 primer sets targeting 19 As related genes (Zhao et al., 2019). The AsChip was successfully applied in the Hetao Basin, indicating that diverse and functional As genes may act on As biogeochemical

processes in groundwater (Li et al., 2017c). Therefore, in future research, AsChip techniques can largely help quantify As genes in studies on environmental geochemistry.

Currently, not much is known about As methylation processes in As-rich groundwater. Recent studies have indicated involvement of methylated As and thioarsenicals in As geochemistry, as reviewed in recent papers (Cullen et al., 2016; Fan et al., 2018; Yang and Rosen, 2016). However, few studies detected methylated As in a groundwater aquifer: one investigated a methylated As pesticide contaminated site (Wallschläger and London, 2008) and another studied microbial As-methylating activities using microcosm assays using As-rich sediments in the Jiangnan Plain (Zeng et al., 2018). The results indicated that most groundwater samples showed microbial As methylation capability with different *arsM* genes identified, demonstrating a wide variety of As-methylating microorganisms in groundwater systems. The role of microbial As methylation in groundwater As geochemistry, however, remains largely unknown and requires future study.

3. Role of organic matter in As interfacial geochemistry

Organic matter, consisting of complicated heterogeneous components with various functional groups, usually interact with As, catalyze As reduction and oxidation, and act as efficient carbon sources for microbial activities. Many recent studies have investigated the characteristics of the dissolved organic carbon and its relationship with other water chemistry parameters in As contaminated groundwater. Co-occurrence of very high DOM levels with high concentrations of dissolved As and Fe in reducing groundwater has often been observed, such as in aquifers in West Bengal in India (Mukherjee et al., 2018; Vega et al., 2017), Cambodia (Lawson et al., 2016), the Gangetic Plain in India (Kumar et al., 2016; Mukherjee et al., 2018), the Datong Basin in China (Pi et al., 2015), and the Jiangnan Plain in China (Yu et al., 2018). The DOM significantly influences the As biogeochemistry, but its critical role in affecting As enrichment mechanisms, including their characteristics, sources, and reactivity still requires further elucidation. The chemical change on speciation transformation and release of As undergone by microbial respiration of organic matter should be distinguished from reductive Fe (hydr)oxide dissolution. Therefore, recent related studies have been summarized as below.

3.1. Effect of organic matter on As geochemistry: chemical interactions

Many studies have demonstrated that aqueous As(III) and As(V) can bind to organic matter. Recent EEM-PARAFAC analysis showed obvious quenching effects of fluorescent DOM components in the presence of As(III), suggesting that As(III) may undergo stronger complexation with humic-like substances than As(V) (Gao et al., 2016). Another study quantified the complex by subtracting the amount of labile As uncomplexed with HA using differential pulse amperometry and showed lower complexation percentages of As(III) (12.0–27.0%) in comparison with that observed for As(V) (20.6–61.7%) (Ren et al., 2017), consistent with a previous study using HA and FA (Fakour and Lin, 2014). It is believed that As(III) reacts with peat-derived organic matter by exchanging hydroxylic/phenolic groups (Hoffmann et al., 2013) or by binding sulfhydryl groups (Besold et al., 2018; Catrouillet et al., 2015), forming As(III)-NOM complex. However, no adsorption of As(III) was observed in the case of Brazilian tropical peat, with only As(V) noted as having been adsorbed (de Oliveira et al., 2015). Another study showed that the binding capacity of HA with As increased with decreasing molecular weight, probably due to the different structural compositions and molecular properties involved (Ren et al., 2017).

The interactions between Fe, As, and organic matter remain unresolved. The complexation among As, Fe, and HA components relies on the molecular sizes, structural composition, and molecular properties of the DOM components. The possible formation of ternary Fe(III)-As(V)-DOM complexes are strongly affected by pH, and the respective

concentrations and ratios of the three components. A previous work suggested no formation of Fe(III)-As(V)-DOM complexes using Suwannee River fulvic acid (SRFA) and Suwannee River natural organic matter (SRN) with As(V) and Fe(III) at different concentrations and ratios (Sundman et al., 2014). The results showed that the predominant species were mononuclear Fe(III)-OM complexes, Fe(III) (hydr)oxides, precipitated FeAsO₄ solids, and precipitated Fe(OH)_{1.5}(AsO₄)_{0.5} solid because the Fe(III)-OM complexes showed much higher stability and strongly controlled the ternary reactions and speciation at pH 3.0–7.0. Nevertheless, recent studies observed ternary complex of As(III)-Fe-organic matter formed in Fe- and OM-rich waters (Besold et al., 2018; Catrouillet et al., 2016). Such ternary complex was also observed in 0.2 μm–30 kDa fractions of a wetland organic soil matrix, representing the most concentrated fraction of Fe and OM (Guenet et al., 2017), where As(V) and Fe(III) reacted with DOM with nanosized Fe aggregates or dispersed Fe in organic matter acting as the bridge for such ternary complex. Pahokee peat humic acid and fulvic acid were employed to study the interactions of Fe(III) (1 wt%) and As(V) (molar Fe/As at ~10) at pH 7 (Mikutta and Kretzschmar, 2011). The results suggested that at least 70% of aqueous As(V) was bound to Fe(III)-HA complexes via inner-sphere complexation, with most of the Fe being present as in oligomeric Fe(III) clusters. The use of (HP)SEC-ICP-MS illustrated the formation of a bridged As(III/V)-Fe-DOM complex, and HA comprised a higher amount of the NOM-As(V) complex compared to FA (Gao et al., 2016; Li et al., 2017a; Martin et al., 2017). One recent study extracted humic acid and its ternary complex with Fe and oxyanions from a real soil sample using DI water (Peel et al., 2017). In the extract, the ternary complex of humic acid with Fe(III) and As(V/III) was identified against a prepared standard using SEC-ICP-MS. Increasing addition of Fe(III) resulted in increasing As(III) retention (Hoffmann et al., 2013), because the presence of Fe(III) favored the formation of ternary complexes by metal bridging such as As(III)-Fe-NOM (de Oliveira et al., 2015).

Arsenic speciation and sequestration may be significantly affected by Fe mineral transformation process mediated by NOM. Incubation of ferrihydrite with adsorbed As(V) under HA addition was performed at pH 10 (Hu et al., 2018). The results showed Fe mineral transformation from ferrihydrite to hematite and goethite, resulting in lower amount of extractable As(V). HA addition also slowed down the mineral transformation rate owing to adsorption of HA on the mineral surface and subsequent slowing down of the transformation of sequestered As to an extractable fraction. Similarly, for an As(III)-Fe-DOM system (Chen and Sparks, 2018), the DOM led to a decrease in the ferrihydrite transformation to goethite and lepidocrocite irrespective of As(III) addition. Coexistence of As(III) and DOM favored lepidocrocite formation over goethite, which may occur in aquifer sediment and change the reductive dissolution of Fe minerals.

Besides the traditional organic matter, other organic matrices including biochar may release available carbon to the soil and induce further chemical/microbial reductive dissolution of Fe minerals and thereafter enhance As mobility (Kim et al., 2018; Qiao et al., 2018). Furthermore, biochar also can show As adsorption owing to surface functional groups containing C and O and transformation of As(V) to As(III) (Niazi et al., 2018). Therefore, various organic amendments with different leachable organic carbon can be judiciously selected for remediating As-contaminated soils.

In summary, different sources of natural organic matter with various molecular structures show distinct physicochemical properties with different kinds of surface groups, and will thus strongly influence the speciation change and complexation behavior of As and Fe. When considering the groundwater system, it is believed that terrestrially derived fulvic acid from old sediments promotes As-Fe-FA complexation in a reducing environment (Mladenov et al., 2015), which may have enhanced As mobility and facilitated As accumulation in Araihaazar aquifers in Bangladesh. Nevertheless, usually very low concentrations of As and Fe coexist and their long term kinetic

accumulation and interactions with DOM need to be investigated at relevant concentrations in environmental matrices.

3.2. Effect of organic matter on As geochemistry: microbial respiration

Overall, geogenic As transformation, dissolution and mobilization in groundwater is usually influenced by various microbial activities as discussed above, and the key step often relies on reactive bioavailable organic carbon, which mediates microbial biogeochemical cycles of Fe and As. Dissolved organic matter in groundwater can have various sources, including sediment evolution depending on the depositional environment and surface water recharge. Not only the total concentrations of species but also the reactive characteristics of organic matter are important in predicting groundwater As liberation from sediments and have been investigated in recent years globally. Although organic matter is widely accepted as a trigger for microbial As mobilizing activities, the sources and reactivity of organic matter responsible for driving As release remain elusive (Gillispie et al., 2016).

The sources of reactive organic carbon driving the microbial reduction of Fe and As in groundwater depend on distinct environmental deposition and hydrological characteristics of the regions (Eiche et al., 2017; Guo et al., 2019; Kulkarni et al., 2017; Schittich et al., 2018; Wang et al., 2019a). For similar sediment depth layer, the Bengal Basin Holocene aquifer showed a higher As concentration in comparison with oxidized Pleistocene (orange) aquifers (Kulkarni et al., 2017, 2018a). The underlying reason relies on the higher amount of reactive organic matter in the Holocene aquifer, which led to a higher humification index (HIX) and lower freshness index (beta:alpha) values, and higher ratios of terrestrially-derived to microbially-derived components. The DOM in the groundwater mainly contained terrestrially and microbially derived humic substances, and oxidized the quinone-like humic substance (Pi et al., 2015). Similarly, the characteristics and sources of DOM in shallow aquifers near a wetland in the Hetao Basin, China (Guo et al., 2019) were characterized using EEM-PARAFAC, water stable isotopes, and laboratory incubation. The results showed that in comparison with the groundwater near the dry wetland receiving sedimentary OM only, the groundwater near the permanent wetlands received reactive organic matter from both the wetland DOM recharge and the sedimentary DOM, which resulted in a higher bioreactive DOM and consequently higher dissolved As concentrations. In contrast, in the dried wetland, sedimentary OM contributed to most of the corresponding groundwater DOM (Li et al., 2019). Further suggested that in the Hetao Basin groundwater, As accumulation collectively arises from low molecular weight DOM of < 5 kDa fractions and terrestrial-derived humic-like substances with molecular weight at 5–10 kDa, probably in the form of As-Fe-HS complexation.

Related information on the penetration of young organic matter into shallow groundwater was also obtained for the Jiangnan Plain (Yu et al., 2018), Araihaazar in Bangladesh (Whaley-Martin et al., 2016), Cambodia (Richards et al., 2019), West Bengal (Majumder et al., 2016), and permanently water-saturated wetlands in the Mekong Delta (Stuckey et al., 2016). (Stuckey et al., 2016) claimed that the reactive organic carbon in groundwater under wetlands in the Mekong Delta were mainly derived from surface water and are favorable for microbial respiration and reductive dissolution of As containing Fe(III) (hydr) oxides and As release from near-surface sediment, which is not observed within the deeper aquifer with insufficient reactive organic carbon contents. Considering the organic carbon sources (Lawson et al., 2016), isotopes data including tritium and radiocarbon demonstrated that more reactive young organic matter prevailing in Cambodian groundwater, which could be transported from surface recharged through ponds and/or clay windows under natural flow conditions.

Soluble electron transfer shuttles including quinone anthraquinone-2,6-disulfonate (AQDS) and riboflavin (RF) have been considered as efficient electron acceptor for microbial reductive dissolution of Fe(III) minerals (Jiang et al., 2009; Shi et al., 2012). Recent studies further

investigated the role of AQDS and RF in microbial Fe(III) reduction in real soil systems. A soil incubation study indicated that AQDS and RF significantly enhanced the reductive dissolution of Fe and As (Yamamura et al., 2018). (Yamamura et al. (2018)) showed that diverse taxonomic groups were present within Fe(V)-reducing bacteria *Firmicutes* and high diversity and abundance of As(V)-reducing bacterial species capable of using various electron acceptors. However, a recent study indicated a dual role of AQDS in determining As geochemistry using As rich sediments from a mine site in China that low level (0.05 mM) of AQDS resulted in more As liberation in comparison with 0.10 mM AQDS, whereas an inhibitory effect was observed for 1.00 mM (Chen et al., 2017c). The confounding results were explained by higher abundance of As- and Fe-reducing bacteria at 0.05 and 0.10 mM of AQDS, while 1.00 mM incubation of AQDS resulted in higher abundance of As- and Fe-oxidizing bacteria. Not only the HS model quinone, but fulvic acids isolated from a high-As Holocene-aged aquifer in Bangladesh also demonstrated as a high electron accepting capacity (176–245 $\mu\text{mol/g}$) for bacterial Fe(III) reduction, even higher than the AQDS ability (135 $\mu\text{mol/g}$) (Kulkarni et al., 2018b).

Besides characterization of aqueous DOM in groundwater, organic components in shallow sediment samples (0–10 m) from the Jiangnan Plain China showed high CPI values predominantly originating from terrestrial plant input (Ye et al., 2017), probably from local cultivation fields during surface water recharge. A recent study in the Hetao Basin China further determined the organic lipid component and indicated that they originated from terrestrial higher plants in the clay layer and terrestrial higher plants, microorganisms, and petroleum in fine sand samples (Mao et al., 2018). Further investigation of the fine sand using carbon isotopes indicated that the short-chain n-alkyl compounds acted as potential electron donors for bacteria facilitated Fe (hydr)oxide reductive dissolution and As mobilization processes in the shallow aquifers. Further anaerobic incubation using aquifer sediments were performed to confirm whether the sedimentary DOM was sufficient for reductive dissolution of Fe minerals contributing to As release worldwide, including Florida (Jin et al., 2016) and the central Yangtze River Basin (Duan et al., 2019; Schaefer et al., 2017). The initial sediment samples were usually carefully collected from the field, wrapped tightly in tinfoil or sealed with paraffin wax, loaded in sterile plastic bags filled with pure N_2 or a gas-tight box containing anoxic pouches, and kept at 4 °C during transportation to laboratory. The strict collection, preservation, and transport processes prohibited the samples from contacting oxygen and undergoing microbial activities. In Florida, As was released via reductive dissolution at the anaerobic periods, a process that was promoted by labile DOM addition, but refractory DOM (i.e., soil extracts) showed no influence (Jin et al., 2016). Therefore, aquifer storage and recovery should be carefully considered to reduce the introduction of labile DOM containing shallow water into the aquifer. In the Yangtze River Basin sediment (Duan et al., 2019), anoxic incubations resulted in As release into solution and the geogenic sediment organic matter was sufficiently reactive to support microbial reduction of As(V) and Fe (III) without exogenous carbon source, justifying high As concentrations throughout the aquifer (Schaefer et al., 2017).

In summary, the reactive organic matter largely facilitated the microbial release of As from sediment to groundwater. Sedimentary organic matter may provide carbon sources for microorganisms. Moreover, shallow groundwater is usually recharged by surface water and more reactive organic carbon can be imported for accelerating microbial reductive processes, even though the exact contribution of young organic carbon in As release still needs further evaluation. Such changes in the organic matter can potentially influence both the spatial and temporal evolution of groundwater As geochemistry.

4. Concluding remarks and future perspectives

In this review, we have focused on the speciation, transformation, and mobilization of As in aquifer systems, the role of organic matter in

such processes, and As interfacial geochemistry. A summary of extensive previous reports can identify unanswered scientific questions to be addressed.

Interfacial geochemical behaviors of As on minerals have been well interpreted by considering As adsorption/desorption, oxidation/reduction, and precipitation/dissolution and the molecular (ternary) surface complexation. Integrating these results in laboratory simulation has achieved great success. However, simulating As geochemistry in groundwater aquifers remains a challenge, since it involves complicated hydrogeology and complex environmental conditions. Further work is required on this issue, that can be undertaken by considering As geochemistry in conjunction with complicated aquifer sediment systems to predict groundwater As evolution in finding safe groundwater for domestic use.

DOM is central on As release from the chemical view of reducing redox potential after degradation and from microbial standpoint of reductive As release acting as carbon sources. Until now, it largely remains unknown regarding the source of reactive organic carbon, and how much and to what extent young organic carbon can penetrate into the aquifer. The exact contribution from young organic carbon to As release in comparison with the original organic matter from sediment need further investigations, even though young organic carbon is more reactive.

“Emerging As species” such as thiolated or methylated As have been observed recently. Sample preservation and speciation analysis remain challenge that limit their observation. Under certain environmental conditions, these species are predominant. Nevertheless, their environmental process is not well understood. Because the molecular size, charge density, and hydrophobicity of thiolated or methylated As are different from those of inorganic As(III/V), the current knowledge is not sufficient for predicting the environmental interfacial behaviors of these species.

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References

- Amarathunga, U., Diyabalanage, S., Bandara, U.G.C., Chandrajith, R., 2019. Environmental factors controlling arsenic mobilization from sandy shallow coastal aquifer sediments in the Mannar Island, Sri Lanka. *Appl. Geochem.* 100, 152–159.
- Bandara, U.G.C., Diyabalanage, S., Hanke, C., van Geldern, R., Barth, J.A.C., Chandrajith, R., 2018. Arsenic-rich shallow groundwater in sandy aquifer systems buffered by rising carbonate waters: a geochemical case study from Mannar Island, Sri Lanka. *Sci. Total Environ.* 633, 1352–1359.
- Besold, J., Biswas, A., Suess, E., Scheinost, A.C., Rossberg, A., Mikutta, C., Kretzschmar, R., Gustafsson, J.P., Planer-Friedrich, B., 2018. Monothioarsenate transformation kinetics determining arsenic sequestration by sulfhydryl groups of peat. *Environ. Sci. Technol.* 52 (13), 7317–7326.
- Cai, X.L., Zhang, Z.N., Yin, N.Y., Du, H.L., Li, Z.J., Cui, Y.S., 2016. Comparison of arsenate reduction and release by three As(V)-reducing bacteria isolated from arsenic-contaminated soil of Inner Mongolia, China. *Chemosphere* 161, 200–207.
- Catrouillet, C., Davranche, M., Dia, A., Coz, M.B.-L., Demangeat, E., Gruau, G., 2016. Does As(III) interact with Fe(II), Fe(III) and organic matter through ternary complexes? *J. Colloid Interface Sci.* 470, 153–161.
- Catrouillet, C., Davranche, M., Dia, A., Bouhnik-Le Coz, M., Pédrot, M., Marsac, R., Gruau, G., 2015. Thiol groups controls on arsenite binding by organic matter: new experimental and modeling evidence. *J. Colloid Interface Sci.* 460, 310–320.
- Chen, C., Sparks, D.L., 2018. Fe(II)-Induced mineral transformation of ferrihydrite–organic matter adsorption and Co-precipitation complexes in the absence and presence of as(III). *ACS Earth and Space Chemistry* 2 (11), 1095–1101.
- Chen, X., Zeng, X.-C., Wang, J., Deng, Y., Ma, T., Guoji, E., Mu, Y., Yang, Y., Li, H., Wang, Y., 2017a. Microbial communities involved in arsenic mobilization and release from the deep sediments into groundwater in Jiangnan plain, Central China. *Sci. Total Environ.* 579, 989–999.
- Chen, Y., Han, Y.-H., Cao, Y., Zhu, Y.-G., Rathinasabapathi, B., Ma, L.Q., 2017b. Arsenic transport in rice and biological solutions to reduce arsenic risk from rice. *Front. Plant Sci.* 8.
- Chen, Z., Wang, Y., Jiang, X., Fu, D., Xia, D., Wang, H., Dong, G., Li, Q., 2017c. Dual roles of AQDS as electron shuttles for microbes and dissolved organic matter involved in arsenic and iron mobilization in the arsenic-rich sediment. *Sci. Total Environ.* 574,

- 1684–1694.
- Cui, J.L., Shi, J., Jiang, G., Jing, C., 2013. Arsenic levels and speciation from ingestion exposures to biomarkers in shanxi, China: implications for human health. *Environ. Sci. Technol.* 47 (10), 5419–5424.
- Cui, J.L., Jing, C., Che, D., Zhang, J., Duan, S., 2015. Groundwater arsenic removal by coagulation using ferric(III) sulfate and polyferric sulfate: a comparative and mechanistic study. *J. Environ. Sci.* 32, 42–53.
- Cui, J.L., Du, J., Tian, H., Chan, T., Jing, C., 2018a. Rethinking anaerobic As(III) oxidation in filters: effect of indigenous nitrate respirers. *Chemosphere* 196, 223–230.
- Cui, J.L., Zhao, Y.P., Li, J.S., Beiyuan, J., Tsang, D.C.W., Poon, C.S., Chan, T.S., Wang, W.X., Li, X.D., 2018b. Speciation, mobilization, and bioaccessibility of arsenic in geogenic soil profile from Hong Kong. *Environ. Pollut.* 232, 375–384.
- Cullen, W.R., Liu, Q., Lu, X., McKnight-Whitford, A., Peng, H., Popowich, A., Yan, X., Zhang, Q., Fricke, M., Sun, H., Le, X.C., 2016. Methylated and thiolated arsenic species for environmental and health research - a review on synthesis and characterization. *J. Environ. Sci.* 49, 7–27.
- Das, S., Liu, C.C., Jean, J.S., Liu, T.L., 2016a. Dissimilatory arsenate reduction and in situ microbial activities and diversity in arsenic-rich groundwater of Chianan Plain, Southwestern Taiwan. *Microb. Ecol.* 71 (2), 365–374.
- Das, S., Liu, C.C., Jean, J.S., Lee, C.C., Yang, H.J., 2016b. Effects of microbially induced transformations and shift in bacterial community on arsenic mobility in arsenic-rich deep aquifer sediments. *J. Hazard Mater.* 310, 11–19.
- Davolos, D., Pietrangeli, B., 2013. A molecular study on bacterial resistance to arsenic-toxicity in surface and underground waters of Latium (Italy). *Ecotoxicol. Environ. Saf.* 96, 1–9.
- de Oliveira, L.K., Melo, C.A., Goveia, D., Lobo, F.A., Armienta Hernandez, M.A., Fraceto, L.F., Rosa, A.H., 2015. Adsorption/desorption of arsenic by tropical peat: influence of organic matter, iron and aluminium. *Environ. Technol.* 36 (2), 149–159.
- Deng, S., Gu, G., Xu, B., Li, L., Wu, B., 2018a. Surface characterization of arsenopyrite during chemical and biological oxidation. *Sci. Total Environ.* 626, 349–356.
- Deng, Y., Zheng, T., Wang, Y., Liu, L., Jiang, H., Ma, T., 2018b. Effect of microbially mediated iron mineral transformation on temporal variation of arsenic in the Pleistocene aquifers of the central Yangtze River basin. *Sci. Total Environ.* 619, 1247–1258.
- Dietrich, S., Bea, S.A., Weinzettel, P., Torres, E., Ayora, C., 2016. Occurrence and distribution of arsenic in the sediments of a carbonate-rich unsaturated zone. *Environmental Earth Sciences* 75 (2).
- Duan, Y., Schaefer, M.V., Wang, Y., Gan, Y., Yu, K., Deng, Y., Fendorf, S., 2019. Experimental constraints on redox-induced arsenic release and retention from aquifer sediments in the central Yangtze River Basin. *Sci. Total Environ.* 649, 629–639.
- Duan, Y., Gan, Y., Wang, Y., Liu, C., Yu, K., Deng, Y., Zhao, K., Dong, C., 2017. Arsenic speciation in aquifer sediment under varying groundwater regime and redox conditions at Jiangnan Plain of Central China. *Sci. Total Environ.* 607–608, 992–1000.
- Eiche, E., Berg, M., Hönig, S.-M., Neumann, T., Lan, V.M., Pham, T.K.T., Pham, H.V., 2017. Origin and availability of organic matter leading to arsenic mobilisation in aquifers of the Red River Delta, Vietnam. *Appl. Geochem.* 77, 184–193.
- Fakour, H., Lin, T.-F., 2014. Experimental determination and modeling of arsenic complexation with humic and fulvic acids. *J. Hazard Mater.* 279, 569–578.
- Fan, C., Liu, G., Long, Y., Rosen, B., Cai, Y., 2018. Thiolation in arsenic metabolism: a chemical perspective. *Metallomics* 10 (10), 1368–1382.
- Fendorf, S., Michael, H.A., van Geen, A., 2010. Spatial and temporal variations of groundwater arsenic in south and southeast Asia. *Science* 328 (5982), 1123–1127.
- Gao, J., Yang, H., Li, B., 2016. Investigating the roles of dissolved organic matter on arsenic mobilization and speciation in environmental water. *Clean. - Soil, Air, Water* 44 (7), 818–828.
- Ghorbanzadeh, N., Lakzian, A., Halajnia, A., Kabra, A.N., Kurade, M.B., Lee, D.S., Jeon, B.-H., 2015. Influence of clay minerals on sorption and bioreduction of arsenic under anoxic conditions. *Environ. Geochem. Health* 37 (6), 997–1005.
- Gillispie, E.C., Andujar, E., Polizzotto, M.L., 2016. Chemical controls on abiotic and biotic release of geogenic arsenic from Pleistocene aquifer sediments to groundwater. *Environmental Science-Processes & Impacts* 18 (8), 1090–1103.
- 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.
- Glasser, N.R., Oyala, P.H., Osborne, T.H., Santini, J.M., Newman, D.K., 2018. Structural and mechanistic analysis of the arsenate respiratory reductase provides insight into environmental arsenic transformations. *Proc. Natl. Acad. Sci. U. S. A* 115 (37), E8614–E8623.
- Gnanaprakasam, E.T., Lloyd, J.R., Boothman, C., Ahmed, K.M., Choudhury, I., Bostick, B.C., van Geen, A., Mailloux, B.J., 2017. Microbial community structure and arsenic biogeochemistry in two arsenic-impacted aquifers in Bangladesh. *mBio* 8 (6).
- Gorny, J., Billon, G., Noirielle, C., Dumoulin, D., Lesven, L., Made, B., 2018. Redox behaviour of arsenic in the surface sediments of the Marque River (Northern France). *J. Geochem. Explor.* 188, 111–122.
- Gude, J.C.J., Rietveld, L.C., van Halem, D., 2017. As(III) oxidation by MnO₂ during groundwater treatment. *Water Res.* 111, 41–51.
- Guenet, H., Davranche, M., Vantelon, D., Bouhnik-Le Coz, M., Jarde, E., Dorcet, V., Demangeat, E., Jestin, J., 2017. Highlighting the wide variability in arsenic speciation in wetlands: a new insight into the control of the behavior of arsenic. *Geochem. Cosmochim. Acta* 203, 284–302.
- Guo, H., Wen, D., Liu, Z., Jia, Y., 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, H., Li, X., Xiu, W., He, W., Cao, Y., Zhang, D., Wang, A., 2019. Controls of organic matter bioreactivity on arsenic mobility in shallow aquifers of the Hetao Basin, PR China. *J. Hydrol.* 571, 448–459.
- Guo, H.M., Liu, Z.Y., Ding, S.S., Hao, C.B., Xiu, W., 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, Q., Planer-Friedrich, B., Liua, M., Li, J., Zhou, C., Wang, Y., 2017. Arsenic and thioarsenic species in the hot springs of the Rehai magmatic geothermal system, Tengchong volcanic region, China. *Chem. Geol.* 453, 12–20.
- Hoffmann, M., Mikutta, C., Kretzschmar, R., 2013. Arsenite binding to natural organic matter: spectroscopic evidence for ligand exchange and ternary complex formation. *Environ. Sci. Technol.* 47 (21), 12165–12173.
- Houben, G.J., Sitnikova, M.A., Post, V.E.A., 2017. Terrestrial sedimentary pyrites as a potential source of trace metal release to groundwater - a case study from the Emsland, Germany. *Appl. Geochem.* 76, 99–111.
- Hu, S., Shi, Q., Jing, C., 2015. Groundwater arsenic adsorption on granular TiO₂: integrating atomic structure, filtration, and health impact. *Environ. Sci. Technol.* 49 (16), 9707–9713.
- Hu, S., Lu, Y., Peng, L., Wang, P., Zhu, M., Dohnalkova, A.C., Chen, H., Lin, Z., Dang, Z., Shi, Z., 2018. Coupled kinetics of ferrihydrite transformation and as(V) sequestration under the effect of humic acids: a mechanistic and quantitative study. *Environ. Sci. Technol.* 52 (20), 11632–11641.
- Huang, J.-H., Voegelin, A., Pombo, S.A., Lazzaro, A., Zeyer, J., Kretzschmar, R., 2011. Influence of arsenate adsorption to ferrihydrite, goethite, and boehmite on the kinetics of arsenate reduction by *Shewanella putrefaciens* strain CN-32. *Environ. Sci. Technol.* 45 (18), 7701–7709.
- Jia, Y., Xi, B., Jiang, Y., Guo, H., Yang, Y., Lian, X., Han, S., 2018. Distribution, formation and human-induced evolution of geogenic contaminated groundwater in China: a review. *Sci. Total Environ.* 643, 967–993.
- Jiang, J., Bauer, I., Paul, A., Kappler, A., 2009. Arsenic redox changes by microbially and chemically formed semiquinone radicals and hydroquinones in a humic substance model quinone. *Environ. Sci. Technol.* 43 (10), 3639–3645.
- Jin, J., Zimmerman, A.R., Norton, S.B., Annable, M.D., Harris, W.G., 2016. Arsenic release from Floridan Aquifer rock during incubations simulating aquifer storage and recovery operations. *Sci. Total Environ.* 551, 238–245.
- Johnston, S.G., Diwakar, J., Burton, E.D., 2015. Arsenic solid-phase speciation in an alluvial aquifer system adjacent to the Himalayan forehills, Nepal. *Chem. Geol.* 419, 55–66.
- Kanematsu, M., Young, T.M., Fukushi, K., Green, P.G., Darby, J.L., 2013. Arsenic(III, V) adsorption on a goethite-based adsorbent in the presence of major co-existing ions: modeling competitive adsorption consistent with spectroscopic and molecular evidence. *Geochem. Cosmochim. Acta* 106, 404–428.
- Keon, N.E., Swartz, C.H., Brabander, D.J., Harvey, C., Hemond, H.F., 2001. Validation of an arsenic sequential extraction method for evaluating mobility in sediments. *Environ. Sci. Technol.* 35 (13), 2778–2784.
- Kim, H.-B., Kim, S.-H., Jeon, E.-K., Kim, D.-H., Tsang, D.C.W., Alessi, D.S., Kwon, E.E., Baek, K., 2018. Effect of dissolved organic carbon from sludge, Rice straw and spent coffee ground biochar on the mobility of arsenic in soil. *Sci. Total Environ.* 636, 1241–1248.
- Kocar, B.D., Fendorf, S., 2009. Thermodynamic constraints on reductive reactions influencing the biogeochemistry of arsenic in soils and sediments. *Environ. Sci. Technol.* 43 (13), 4871–4877.
- Kohfahl, C., Navarro, D.S.-R., Mendoza, J.A., Vadillo, I., Giménez-Forcada, E., 2016. Algae metabolism and organic carbon in sediments determining arsenic mobilisation in ground- and surface water. A field study in Doñana National Park, Spain. *Sci. Total Environ.* 544, 874–882.
- 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.
- Kulkarni, H.V., Mladenov, N., Datta, S., Chatterjee, D., 2018a. Influence of monsoonal recharge on arsenic and dissolved organic matter in the Holocene and Pleistocene aquifers of the Bengal Basin. *Sci. Total Environ.* 637, 588–599.
- Kulkarni, H.V., Mladenov, N., McKnight, D.M., Zheng, Y., Kirk, M.F., Nemerlut, D.R., 2018b. Dissolved fulvic acids from a high arsenic aquifer shuttle electrons to enhance microbial iron reduction. *Sci. Total Environ.* 615, 1390–1395.
- Kumar, M., Ramanathan, A.L., Rahman, M.M., Naidu, R., 2016. Concentrations of inorganic arsenic in groundwater, agricultural soils and subsurface sediments from the middle Gangetic plain of Bihar, India. *Sci. Total Environ.* 573, 1103–1114.
- Kumarathilaka, P., Seneweera, S., Meharg, A., Bundschuh, J., 2018. Arsenic speciation dynamics in paddy rice soil-water environment: sources, physico-chemical, and biological factors - a review. *Water Res.* 140, 403–414.
- Lafferty, B.J., Ginder-Vogel, M., Sparks, D.L., 2010. Arsenite oxidation by a poorly crystalline manganese-oxide I. Stirred-flow experiments. *Environ. Sci. Technol.* 44 (22), 8460–8466.
- Langner, P., Mikutta, C., Kretzschmar, R., 2011. Arsenic sequestration by organic sulphur in peat. *Nat. Geosci.* 5, 66.
- 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, B.H., Deng, C.N., Zhang, D.Y., Pan, X.L., Al-misned, F.A., Mortuza, M.G., 2016. Bioremediation of nitrate- and arsenic-contaminated groundwater using nitrate-dependent Fe(II) oxidizing *Clostridium sp* strain pxi2. *Geomicrobiol. J.* 33 (3–4), 185–193.
- Li, F., Guo, H., Zhou, X., Zhao, K., Shen, J., Liu, F., Wei, C., 2017a. Impact of natural organic matter on arsenic removal by modified granular natural siderite: evidence of ternary complex formation by HPSEC-UV-ICP-MS. *Chemosphere* 168, 777–785.
- Li, J.-S., Beiyuan, J., Tsang, D.C.W., Wang, L., Poon, C.S., Li, X.-D., Fendorf, S., 2017b. Arsenic-containing soil from geogenic source in Hong Kong: leaching characteristics

- and stabilization/solidification. *Chemosphere* 182, 31–39.
- Li, P., Jiang, Z., Wang, Y.H., Deng, Y., Van Nostrand, J.D., Yuan, T., Liu, H., Wei, D.Z., Zhou, J.Z., 2017c. Analysis of the functional gene structure and metabolic potential of microbial community in high arsenic groundwater. *Water Res.* 123, 268–276.
- Li, P., Wang, Y.H., Dai, X.Y., Zhang, R., Jiang, Z., Jiang, D.W., Wang, S., Jiang, H.C., Wang, Y.X., Dong, H.L., 2015. Microbial community in high arsenic shallow groundwater aquifers in Hetao Basin of inner Mongolia, China. *PLoS One* 10 (5).
- Li, S., Yang, C., Peng, C., Li, H., Liu, B., Chen, C., Chen, B., Bai, J., Lin, C., 2018. Effects of elevated sulfate concentration on the mobility of arsenic in the sediment-water interface. *Ecotoxicol. Environ. Saf.* 154, 311–320.
- Li, X., Guo, H., Zheng, H., Xiu, W., He, W., Ding, Q., 2019. Roles of different molecular weights of dissolved organic matter in arsenic enrichment in groundwater: evidences from ultrafiltration and EEM-PARAFAC. *Appl. Geochem.* 104, 124–134.
- Luo, T., Ye, L., Chan, T., Jing, C., 2018. Mobilization of arsenic on nano-TiO₂ in soil columns with sulfate reducing bacteria. *Environ. Pollut.* 234, 762–768.
- Luo, T., Ye, L., Ding, C., Yan, J., Jing, C., 2017. Reduction of adsorbed As(V) on nano-TiO₂ by sulfate-reducing bacteria. *Sci. Total Environ.* 598, 839–846.
- Maizel, D., Balverdi, P., Rosen, B., Sales, A.M., Ferrero, M.A., 2018. Arsenic-hypertolerant and arsenic-reducing bacteria isolated from wells in Tucumán, Argentina. *Can. J. Microbiol.* 64 (11), 876–886.
- Majumder, S., Datta, S., Nath, B., Neidhardt, H., Sarkar, S., Roman-Ross, G., Berner, Z., Hidalgo, M., Chatterjee, D., Chatterjee, D., 2016. Monsoonal influence on variation of hydrochemistry and isotopic signatures: implications for associated arsenic release in groundwater. *J. Hydrol.* 535, 407–417.
- Manning, B.A., Fendorf, S.E., Bostick, B., Suarez, D.L., 2002. Arsenic(III) oxidation and arsenic(V) adsorption reactions on synthetic birnessite. *Environ. Sci. Technol.* 36 (5), 976–981.
- Mao, R., Guo, H., Xiu, W., Yang, Y., Huang, X., Zhou, Y., Li, X., Jin, J., 2018. Characteristics and compound-specific carbon isotope compositions of sedimentary lipids in high arsenic aquifers in the Hetao basin, Inner Mongolia. *Environ. Pollut.* 241, 85–95.
- Martin, D.P., Seiter, J.M., Lafferty, B.J., Bednar, A.J., 2017. Exploring the ability of cations to facilitate binding between inorganic oxyanions and humic acid. *Chemosphere* 166, 192–196.
- Mikutta, C., Kretzschmar, R., 2011. Spectroscopic evidence for ternary complex formation between arsenate and ferric iron complexes of humic substances. *Environ. Sci. Technol.* 45 (22), 9550–9557.
- Mikutta, C., Rothwell, J.J., 2016. Peat bogs as hotspots for organoarsenic formation and persistence. *Environ. Sci. Technol.* 50 (8), 4314–4323.
- Mladenov, N., Zheng, Y., Simone, B., Bilinski, T.M., McKnight, D.M., Nemergut, D., Radloff, K.A., Rahman, M.M., Ahmed, K.M., 2015. Dissolved organic matter quality in a shallow aquifer of Bangladesh: implications for arsenic mobility. *Environ. Sci. Technol.* 49 (18), 10815–10824.
- Mohapatra, B., Sar, P., Kazy, S.K., Maiti, M.K., Satyanarayana, T., 2018. Taxonomy and physiology of *Pseudoxanthomonas arseniciresistens* sp. nov., an arsenate and nitrate-reducing novel gammaproteobacterium from arsenic contaminated groundwater, India. *PLoS One* 13 (3).
- Moon, H.S., Kim, B.-A., Hyun, S.P., Lee, Y.-H., Shin, D., 2017. Effect of the redox dynamics on microbial-mediated as transformation coupled with Fe and S in flow-through sediment columns. *J. Hazard Mater.* 329, 280–289.
- Muehe, E.M., Morin, G., Scheer, L., Le Pape, P., Esteve, I., Daus, B., Kappler, A., 2016. Arsenic(V) incorporation in vivianite during microbial reduction of arsenic(V)-bearing biogenic Fe(III) (oxyhydr)oxides. *Environ. Sci. Technol.* 50 (5), 2281–2291.
- Mukherjee, A., Fryar, A.E., Eastridge, E.M., Nally, R.S., Chakraborty, M., Scanlon, B.R., 2018. Controls on high and low groundwater arsenic on the opposite banks of the lower reaches of River Ganges, Bengal basin, India. *Sci. Total Environ.* 645, 1371–1387.
- Niazi, N.K., Burton, E.D., 2016. Arsenic sorption to nanoparticulate mackinawite (FeS): an examination of phosphate competition. *Environ. Pollut.* 218, 111–117.
- Niazi, N.K., Bibi, I., Shahid, M., Ok, Y.S., Burton, E.D., Wang, H., Shaheen, S.M., Rinklebe, J., Luetge, A., 2018. Arsenic removal by perilla leaf biochar in aqueous solutions and groundwater: an integrated spectroscopic and microscopic examination. *Environ. Pollut.* 232, 31–41.
- Nicholas, S.L., Erickson, M.L., Woodruff, L.G., Knaeble, A.R., Marcus, M.A., Lynch, J.K., Toner, B.M., 2017. Solid-phase arsenic speciation in aquifer sediments: a micro-X-ray absorption spectroscopy approach for quantifying trace-level speciation. *Geochem. Cosmochim. Acta* 211, 228–255.
- Osborne, T.H., McArthur, J.M., Sikdar, P.K., Santini, J.M., 2015. Isolation of an arsenate-respiring bacterium from a redox front in an arsenic-polluted aquifer in West Bengal, Bengal Basin. *Environ. Sci. Technol.* 49 (7), 4193–4199.
- Paul, D., Kazy, S.K., Gupta, A.K., Pal, T., Sar, P., 2015. Diversity, metabolic properties and arsenic mobilization potential of indigenous bacteria in arsenic contaminated groundwater of West Bengal, India. *PLoS One* 10 (3).
- Paulelli, A.C.C., Martins Jr., A.C., Batista, B.L., Barbosa Jr., F., 2019. Evaluation of uptake, translocation, and accumulation of arsenic species by six different Brazilian rice (*Oryza sativa* L.) cultivars. *Ecotoxicol. Environ. Saf.* 169, 376–382.
- Peel, H.R., Martin, D.P., Bednar, A.J., 2017. Extraction and characterization of ternary complexes between natural organic matter, cations, and oxyanions from a natural soil. *Chemosphere* 176, 125–130.
- Perez, J.P.H., Freeman, H.M., Schuessler, J.A., Benning, L.G., 2019. The interfacial reactivity of arsenic species with green rust sulfate (GR(SO₄)). *Sci. Total Environ.* 648, 1161–1170.
- Phan, V.T.H., Bernier-Latmani, R., Tisserand, D., Bardelli, F., Le Pape, P., Fruttschi, M., Gehin, A., Couture, R.-M., Charlet, L., 2019. As release under the microbial sulfate reduction during redox oscillations in the upper Mekong delta aquifers, Vietnam: a mechanistic study. *Sci. Total Environ.* 663, 718–730.
- Pi, K., Wang, Y., Xie, X., Huang, S., Yu, Q., Yu, M., 2015. Geochemical effects of dissolved organic matter biodegradation on arsenic transport in groundwater systems. *J. Geochem. Explor.* 149, 8–21.
- Pi, K., Wang, Y., Xie, X., Ma, T., Su, C., Liu, Y., 2017. Role of sulfur redox cycling on arsenic mobilization in aquifers of Datong Basin, northern China. *Appl. Geochem.* 77, 31–43.
- Pi, K., Wang, Y., Postma, D., Ma, T., Su, C., Xie, X., 2018. Vertical variability of arsenic concentrations under the control of iron-sulfur-arsenic interactions in reducing aquifer systems. *J. Hydrol.* 561, 200–210.
- Polizzotto, M.L., Harvey, C.F., Sutton, S.R., Fendorf, S., 2005. Processes conducive to the release and transport of arsenic into aquifers of Bangladesh. *Proc. Natl. Acad. Sci. U. S. A.* 102 (52), 18819–18823.
- Postma, D., Pham, T.K.T., So, H.U., Hoang, V.H., Vi, M.L., Nguyen, T.T., Larsen, F., Pham, H.V., Jakobsen, R., 2016. A model for the evolution in water chemistry of an arsenic contaminated aquifer over the last 6000 years, Red River floodplain, Vietnam. *Geochem. Cosmochim. Acta* 195, 277–292.
- Qiao, J.-t., Li, X.-m., Hu, M., Li, F.-b., Young, L.Y., Sun, W.-m., Huang, W., Cui, J.-h., 2018. Transcriptional activity of arsenic-reducing bacteria and genes regulated by lactate and biochar during arsenic transformation in flooded paddy soil. *Environ. Sci. Technol.* 52 (1), 61–70.
- Qiu, G., Gao, T., Hong, J., Tan, W., Liu, F., Zheng, L., 2017. Mechanisms of arsenic-containing pyrite oxidation by aqueous arsenate under anoxic conditions. *Geochem. Cosmochim. Acta* 217, 306–319.
- Qiu, G., Gao, T., Hong, J., Luo, Y., Liu, L., Tan, W., Liu, F., 2018. Mechanisms of interaction between arsenian pyrite and aqueous arsenite under anoxic and oxic conditions. *Geochem. Cosmochim. Acta* 228, 205–219.
- Rajpert, L., Schaeffer, A., Lenz, M., 2018. Redox-stat bioreactors for elucidating mobilization mechanisms of trace elements: an example of As-contaminated mining soils. *Appl. Microbiol. Biotechnol.* 102 (17), 7635–7641.
- Rathod, J., Jean, J.-S., Jiang, W.-T., Huang, I.H., Liu, B.H., Lee, Y.-C., 2019. Micro-colonization of arsenic-resistant *Staphylococcus* sp. As-3 on arsenopyrite (FeAsS) drives arsenic mobilization under anoxic sub-surface mimicking conditions. *Sci. Total Environ.* 669, 527–539.
- Ren, J., Fan, W., Wang, X., Ma, Q., Li, X., Xu, Z., Wei, C., 2017. Influences of size-fractionated humic acids on arsenite and arsenate complexation and toxicity to *Daphnia magna*. *Water Res.* 108, 68–77.
- Richards, L.A., Magnone, D., Sueltenfuss, J., Chambers, L., Bryant, C., Boyce, A.J., van Dongen, B.E., Ballentine, C.J., Sovann, C., Uhlemann, S., Kuras, O., Goody, D.C., Polya, D.A., 2019. Dual in-aquifer and near surface processes drive arsenic mobilization in Cambodian groundwaters. *Sci. Total Environ.* 659, 699–714.
- Rouwane, A., Rabiet, M., Grybos, M., Bernard, G., Guibaud, G., 2016. Effects of NO₃- and PO₄- on the release of geogenic arsenic and antimony in agricultural wetland soil: a field and laboratory approach. *Environ. Sci. Pollut. Control Ser.* 23 (5), 4714–4728.
- Sathe, S.S., Mahanta, C., Mishra, P., 2018. Simultaneous influence of indigenous micro-organism along with abiotic factors controlling arsenic mobilization in Brahmaputra floodplain, India. *J. Contam. Hydrol.* 213, 1–14.
- Schaefer, M.V., Guo, X., Gan, Y., Benner, S.G., Griffin, A.M., Gorski, C.A., Wang, Y., Fendorf, S., 2017. Redox controls on arsenic enrichment and release from aquifer sediments in central Yangtze River Basin. *Geochem. Cosmochim. Acta* 204, 104–119.
- Schittich, A.-R., Wunsch, 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.
- Shen, M., Guo, H., Jia, Y., Cao, Y., Zhang, D., 2018. Partitioning and reactivity of iron oxide minerals in aquifer sediments hosting high arsenic groundwater from the Hetao basin, P. R. China. *Appl. Geochem.* 89, 190–201.
- Shi, Z., Zachara, J.M., Shi, L., Wang, Z., Moore, D.A., Kennedy, D.W., Fredrickson, J.K., 2012. Redox reactions of reduced flavin mononucleotide (FMN), riboflavin (RBF), and anthraquinone-2,6-disulfonate (AQDS) with ferrihydrite and lepidocrocite. *Environ. Sci. Technol.* 46 (21), 11644–11652.
- Singh, R., Singh, S., Parihar, P., Singh, V.P., Prasad, S.M., 2015. Arsenic contamination, consequences and remediation techniques: a review. *Ecotoxicol. Environ. Saf.* 112, 247–270.
- Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* 17 (5), 517–568.
- Smith, R.L., Kent, D.B., Repert, D.A., Bohlke, J.K., 2017. Anoxic nitrate reduction coupled with iron oxidation and attenuation of dissolved arsenic and phosphate in a sand and gravel aquifer. *Geochem. Cosmochim. Acta* 196, 102–120.
- So, H.U., Postma, D., Vi Mai, L., Pham Thi Kim, T., Kazmierczak, J., Dao Viet, N., Pi, K., Koch, C.B., Pham Hung, V., Jakobsen, R., 2018. Arsenic in Holocene aquifers of the Red River floodplain, Vietnam: effects of sediment-water interactions, sediment burial age and groundwater residence time. *Geochem. Cosmochim. Acta* 225, 192–209.
- Stolze, L., Zhang, D., Guo, H., Rolle, M., 2019. Surface complexation modeling of arsenic mobilization from goethite: interpretation of an in-situ experiment. *Geochem. Cosmochim. Acta* 248, 274–288.
- Stuckey, J., Schaefer, M.V., Kocar, B.D., Benner, S.G., Fendorf, S., 2016. Arsenic release metabolically limited to permanently water-saturated soil in Mekong Delta. *Nat. Geosci.* 9 (1), 70–+.
- Stuckey, J.W., Schaefer, M.V., Benner, S.G., Fendorf, S., 2015a. Reactivity and speciation of mineral-associated arsenic in seasonal and permanent wetlands of the Mekong Delta. *Geochem. Cosmochim. Acta* 171, 143–155.
- Stuckey, J.W., Schaefer, M.V., Kocar, B.D., Dittmar, J., Pacheco, J.L., Benner, S.G., Fendorf, S., 2015b. Peat formation concentrates arsenic within sediment deposits of the Mekong Delta. *Geochem. Cosmochim. Acta* 149, 190–205.
- Sundman, A., Karlsson, T., Sjöberg, S., Persson, P., 2014. Complexation and precipitation

- reactions in the ternary As(V)–Fe(III)–OM (organic matter) system. *Geochem. Cosmochim. Acta* 145, 297–314.
- Tian, H., Shi, Q., Jing, C., 2015. Arsenic biotransformation in solid waste residue: comparison of contributions from bacteria with arsenate and iron reducing pathways. *Environ. Sci. Technol.* 49 (4), 2140–2146.
- Varsanyi, I., Kovacs, L.O., 2017. Distribution of dissolved arsenic in a sedimentary environment from the near-surface to a depth of 2500 m, and factors controlling distribution. *Appl. Geochem.* 80, 168–175.
- Vega, M.A., Kulkarni, H.V., Mladenov, N., Johannesson, K., Hettiarachchi, G.M., Bhattacharya, P., Kumar, N., Weeks, J., Galkaduwa, M., Datta, S., 2017. Biogeochemical controls on the release and accumulation of Mn and as in shallow aquifers, West Bengal, India. *Frontiers in Environmental Science* 5.
- Wallschlager, D., London, J., 2008. Determination of methylated arsenic-sulfur compounds in groundwater. *Environ. Sci. Technol.* 42 (1), 228–234.
- Wang, J.N., Zeng, X.C., Zhu, X.B., Chen, X.M., Zeng, X., Mu, Y., Yang, Y., Wang, Y.X., 2017. Sulfate enhances the dissimilatory arsenate-respiring prokaryotes-mediated mobilization, reduction and release of insoluble arsenic and iron from the arsenic-rich sediments into groundwater. *J. Hazard Mater.* 339, 409–417.
- Wang, Y., Liu, X.-h., Si, Y.-b., Wang, R.-f., 2016. Release and transformation of arsenic from As-bearing iron minerals by Fe-reducing bacteria. *Chem. Eng. J.* 295, 29–38.
- Wang, Y., Li, P., Guo, Q., Jiang, Z., Liu, M., 2018a. Environmental biogeochemistry of high arsenic geothermal fluids. *Appl. Geochem.* 97, 81–92.
- Wang, Y., Pi, K., Fendorf, S., Deng, Y., Xie, X., 2019a. Sedimentogenesis and hydrobiogeochemistry of high arsenic Late Pleistocene-Holocene aquifer systems. *Earth Sci. Rev.* 189, 79–98.
- Wang, Y., Wu, X., Wang, S., Xiao, F., Zhang, D., Yao, S., Jia, Y., 2018b. The adsorption behavior of thioarsenite on magnetite and ferrous sulfide. *Chem. Geol.* 492, 1–11.
- Wang, Y., Lin, J.R., Wang, S.F., Zhang, D.N., Xiao, F., Wang, X., Jia, Y.F., 2019b. Adsorption and transformation of thioarsenite at hematite/water interface under anaerobic condition in the presence of sulfide. *Chemosphere* 222, 422–430.
- Wang, Y., Wang, S., Xu, P., Liu, C., Liu, M., Wang, Y., Wang, C., Zhang, C., Ge, Y., 2015. Review of arsenic speciation, toxicity and metabolism in microalgae. *Rev. Environ. Sci. Biotechnol.* 14 (3), 427–451.
- Wang, Y., Le Pape, P., Morin, G., Asta, M.P., King, G., Bartova, B., Suvorova, E., Fruttschi, M., Ikogou, M., Vu Hoai Cong, P., Phu Le, V., Herman, F., Charlet, L., Bernier-Latmani, R., 2018c. Arsenic speciation in Mekong delta sediments depends on their depositional environment. *Environ. Sci. Technol.* 52 (6), 3431–3439.
- Wang, Z., Guo, H., Xiu, W., Wang, J., Shen, M., 2018d. High arsenic groundwater in the Guide basin, northwestern China: distribution and genesis mechanisms. *Sci. Total Environ.* 640, 194–206.
- Wenzel, W.W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E., Adriano, D.C., 2001. Arsenic fractionation in soils using an improved sequential extraction procedure. *Anal. Chim. Acta* 436 (2), 309–323.
- Whaley-Martin, K.J., Mailloux, B.J., van Geen, A., Bostick, B.C., Silvern, R.F., Kim, C., Ahmed, K.M., Choudhury, I., Slater, G.F., 2016. Stimulation of microbially mediated arsenic release in Bangladesh aquifers by young carbon indicated by radiocarbon analysis of sedimentary bacterial lipids. *Environ. Sci. Technol.* 50 (14), 7353–7363.
- Wu, Y., Li, W., Sparks, D.L., 2015. Effect of iron(II) on arsenic sequestration by delta-MnO₂: desorption studies using stirred-flow experiments and X-ray absorption FineStructure spectroscopy. *Environ. Sci. Technol.* 49 (22), 13360–13368.
- Wu, Y., Kukkadapu, R.K., Livi, K.J.T., Xu, W., Li, W., Sparks, D.L., 2018. Iron and arsenic speciation during as(III) oxidation by manganese oxides in the presence of Fe(II): molecular-level characterization using XAFS, mossbauer, and TEM analysis. *ACS Earth and Space Chemistry* 2 (3), 256–268.
- Xie, X., Wang, Y., Li, J., Yu, Q., Wu, Y., Su, C., Duan, M., 2015. Effect of irrigation on Fe(III)-SO₄²⁻ redox cycling and arsenic mobilization in shallow groundwater from the Datong basin, China: evidence from hydrochemical monitoring and modeling. *J. Hydrol.* 523, 128–138.
- Xiu, W., Guo, H., Zhou, X., Wanty, R.B., Kersten, M., 2018. Change of arsenite adsorption mechanism during aging of 2-line ferrihydrite in the absence of oxygen. *Appl. Geochem.* 88, 149–157.
- Xu, L., Wu, X., Wang, S., Yuan, Z., Xiao, F., Ming, Y., Jia, Y., 2016. Speciation change and redistribution of arsenic in soil under anaerobic microbial activities. *J. Hazard Mater.* 301, 538–546.
- Yadav, I.C., Devi, N.L., Singh, S., 2015. Reductive dissolution of iron-oxhydroxides directs groundwater arsenic mobilization in the upstream of Ganges River basin, Nepal. *J. Geochem. Explor.* 148, 150–160.
- Yamamura, S., Sudo, T., Watanabe, M., Tsuboi, S., Soda, S., Ike, M., Amachi, S., 2018. Effect of extracellular electron shuttles on arsenic-mobilizing activities in soil microbial communities. *J. Hazard Mater.* 342, 571–578.
- Yan, L., Hu, S., Jing, C., 2016. Recent progress of arsenic adsorption on TiO₂ in the presence of coexisting ions: a review. *J. Environ. Sci.* 49, 74–85.
- Yan, L., Song, J.Y., Chan, T.S., Jing, C.Y., 2017. Insights into antimony adsorption on {001} TiO₂: XAFS and DFT study. *Environ. Sci. Technol.* 51 (11), 6335–6341.
- Yang, H.-C., Rosen, B.P., 2016. New mechanisms of bacterial arsenic resistance. *Biomed. J.* 39 (1), 5–13.
- Ye, H., Yang, Z., Wu, X., Wang, J., Du, D., Cai, J., Lv, K., Chen, H., Mei, J., Chen, M., Du, H., 2017. Sediment biomarker, bacterial community characterization of high arsenic aquifers in Jiangnan Plain, China. *Sci. Rep.* 7.
- Ying, S.C., Damashek, J., Fendorf, S., Francis, C.A., 2015. Indigenous arsenic(V)-reducing microbial communities in redox-fluctuating near-surface sediments of the Mekong Delta. *Geobiology* 13 (6), 581–587.
- Yu, K., Gan, Y., Zhou, A., Liu, C., Duan, Y., Han, L., Zhang, Y., 2018. Organic carbon sources and controlling processes on aquifer arsenic cycling in the Jiangnan Plain, central China. *Chemosphere* 208, 773–781.
- Zeng, X.C., Yang, Y., Shi, W.X., Peng, Z.F., Chen, X.M., Zhu, X.B., Wang, Y.X., 2018. Microbially mediated methylation of arsenic in the arsenic-rich soils and sediments of Jiangnan Plain. *Front. Microbiol.* 9.
- Zhang, H., Selim, H.M., 2005. Kinetics of arsenate adsorption-desorption in soils. *Environ. Sci. Technol.* 39 (16), 6101–6108.
- Zhang, J.W., Ma, T., Yan, Y.N., Xie, X.J., Abass, O.K., Liu, C.Q., Zhao, Z.Q., Wang, Z.Z., 2018. Effects of Fe-S-As coupled redox processes on arsenic mobilization in shallow aquifers of Datong Basin, northern China. *Environ. Pollut.* 237, 28–38.
- Zhao, Y., Su, J.Q., Ye, J., Rensing, C., Tardif, S., Zhu, Y.G., Brandt, K.K., 2019. AsChip: a high-throughput qPCR chip for comprehensive profiling of genes linked to microbial cycling of arsenic. *Environ. Sci. Technol.* 53 (2), 798–807.
- Zhao, Z., Wang, S., Jia, Y., 2017. Effect of sulfide on As(III) and As(V) sequestration by ferrihydrite. *Chemosphere* 185, 321–328.
- Zhou, Z., Yu, Y.Q., Ding, Z.X., Zuo, M.M., Jing, C.Y., 2019. Competitive adsorption of arsenic and fluoride on {201} TiO₂. *Appl. Surf. Sci.* 466, 425–432.
- Zhu, Y.-G., Xue, X.-M., Kappler, A., Rosen, B.P., Meharg, A.A., 2017. Linking genes to microbial biogeochemical cycling: lessons from arsenic. *Environ. Sci. Technol.* 51 (13), 7326–7339.