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# Impact of Microorganisms on Arsenic Biogeochemistry: A Review

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**Abstract** Microorganisms are abundant in many surface and near-surface geochemical environments. They interact with arsenic through a variety of mechanisms, including sorption, mobilisation, precipitation and redox and methylation transformation; sometimes, this is to their benefit, while other times it is to their detriment, substantially affecting the fate and transport of arsenic in the environment. Here, an attempt was made to review the current state of knowledge concerning microbial influences on arsenic transformation and retention processes at the water–solid interface with the goal to elucidate the ability of microorganisms to react with arsenic, and to quantify the role of microorganisms in the biogeochemical arsenic cycle. Such knowledge is indispensable for comprehensive understanding arsenic behaviour in the environment and support accurate assessment of the threat of arsenic contamination to human and environmental health, as well as for the development of novel technologies for arsenic bioremediation.

**Keywords** Arsenic · Microorganism · Biogeochemistry · Redox transformation · Methylation

## 1 Introduction

Arsenic (As) is one of the most toxic elements and a non-threshold class 1 carcinogen (Vahidnia et al. 2007). There is increasing evidence of cancer risk associated with chronic exposure of low levels of As (Cantor, 1996). Today, elevated As concentrations represent a major water quality and health problem for millions of people worldwide (Bundschuh et al. 2012; Nordstrom 2002; Smedley and Kinniburgh 2002). Naturally high concentrations of As in surface and ground waters may be due to geothermal sources or from the dissolution of As-bearing minerals in soils and sediments, whereas anthropogenic inputs result from emissions of mining and smelting activities (Bissen and Frimmel 2003; Fendorf et al. 2010a; Smedley and Kinniburgh 2002). In comparison, immobilisation of As in the environment occurs predominately by sequestration to soil and sediment solid phases (Fendorf et al. 2010b; Smedley and Kinniburgh 2002).

Although the possibility of a "new As form of life" is highly controversial, the significance of As in life science has drawn much public attention (Parke 2013; Wolfe-Simon et al. 2011). Microorganisms constitute the majority of all living matter on Earth (Toner et al. 2006) and, as such, form a foundational component of the entirety of Earth's environment, along with the lithosphere, soils, oceans and the atmosphere. Microorganisms play a major role in driving, along with the inanimate Earth, biogeochemical cycles, which involve the most fundamental underlying aspects of our entire environment, namely electron and elemental transfer among all of the compartments of the Earth's environmental systems (Tamaki and Frankenberger, 1992). The result is the unmistakable influence of microorganisms on, for example nitrogen and carbon cycling, mineral growth and dissolution, biological nutrient fluxes, and on a larger scale, ocean and atmospheric chemistry.

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Modification of microbial composition and activity can have consequences on local, regional and global scales.

The fate of As released into geochemical environments is determined by a complex interplay among processes of As mobilisation, sequestration and transformation, most of which are directly or indirectly driven by microbial activity. There are already plenty of researches focussing on understanding the behaviour of As in different compartments of the surface and subsurface environment (see review articles, e.g. Cullen and Reimer 1989; Mandal and Suzuki 2002; Smedley and Kinniburgh 2002). On the other hand, many efforts were focussed on characterising the ability of microorganism to interact with As, e.g. respiratory oxidation and reduction and methylation, and the corresponding physiological mechanisms (see review articles e.g. Dhuldhaj et al. 2013; Lloyd and Oremland 2006; Mukhopadhyay et al. 2002; Paez-Espino et al. 2009; Silver and Phung 2005; Slyemi and Bonnefoy 2012; Tsai et al. 2009). Studies on microbial diversity in natural samples to estimate As behaviour are also abundant (e.g. Fan et al. 2008; Meyer-Dombard et al. 2013; Tomczyk-Żak et al. 2013). However, comparably few studies have been aimed at truly understanding the linkage between microbial activities and As geochemistry in the environment, especially for the natural system. These studies were achieved by investigating As geochemistry in parallel with microbiology and molecule ecology in more depth instead of only comparing the sterile control or just adding organic substances to stimulate certain microbial activities, thereby enabling identification of the link between microorganisms and As geochemistry with strong evidence. For example, Islam et al. (2004) showed that As release from the sediments of West Bengal delta occurred along with Fe(III) and arsenate (As(V)) reduction in the presence of *Clostridium* species (involved in As(V) reduction), and *Geobacter* species (involved in Fe(III) reduction). Both Fe(III) and As(V) reduction were stimulated by spiking additional acetate and at the same time as a remarkable shift in the microbial population, with increased numbers of the family *Geobacteraceae* from 11 to 70 % of total clones analysed. The linkage of microorganism-driven As(V) reduction with As mobilisation in paddy soils was evidenced by the highly frequent presence of respiratory As(V) reductase gene (*arrA*) and, on the other hand, by the observation of As released in the sterile soil inoculated with an As(V) reducing bacterium, *Geobacter* sp. OR-1, which was isolated from the same soil (Ohtsuka et al. 2013). Methylation of As in paddy soils was suggested to be a microbial-mediated process based on the high phylogenetic diversity of microorganism containing *arsM* genes in soils and the positive correlation between the concentrations of methyl As species and the abundance of the *arsM* gene in the soil (Jia et al. 2013). One of the most careful studies done on the linkage between As geochemistry and microbial activities may be that by Demergasso et al. (2007). The involvement of microbial activities in the precipitation process of As sulphides in Andean salt flats in northern Chile was demonstrated from several different aspects: (1) the enrichment and isolation of microbial cultures with As precipitation capacity from As mineral samples, (2) the high abundance of As-precipitating bacteria found in the Andean minerals and brines, (3) the similarities in stoichiometry between natural and laboratory obtained biogenic sulphide minerals, and (4) the consistent depletion in $\delta^{34}S$ values for natural versus laboratory obtained sulphides.

The aforementioned studies on natural systems clearly revealed that microorganisms are the major player to drive the As cycling in the surface environment. In comparison, the model incubations under well-defined experimental conditions are able to better define the influence of microbial processes on As biogeochemical behaviour, the current state of knowledge of which will be reviewed in the following sections. Thus, the goal of this review article is to provide a comprehensive overview on the interplay between microorganisms and As geochemistry, which includes physical interactions with microbial cells, microorganism-mediated chemical transformation and processes induced by other microbial processes. This review provides a junction between the geochemical behaviour of As, microorganism-mediated process reactions and microbial matrix-mediated interactions with As. The knowledge generated here on As behaviour in the environment is essential for accurate assessment of the threat of As contamination to human and environmental health, as well as for the development of novel technologies for bioremediation of As-contaminated soils and sediments.

## 2 Microbial Intracellular and Extracellular Sequestration

There seems to be no specific As uptake pathway for microorganisms since As does not play any metabolic or nutrimental role in the cell cytoplasm (Tsai et al. 2009). Arsenic enters cells via existing transporting systems, such as phosphate transport for As(V), due to the similar

chemical structure (Tsai et al., 2009). Arsenite (As(III)) mostly presents as the noncharged form at environmental and physiological pH. Thus, the aquoporin transporter may be responsible for As(III) entering cells. Therefore, microorganisms develop different strategies to detoxify intracellular cells by either excluding As from the cell or binding As in cells (Fig. 1). The extracellular polymeric substance (EPS) matrix on the cell surface can act as a molecular sieve, sequestering cations, anions, apolar compounds and particles from the water phase (Flemming and Wingender 2010). The EPS contains apolar regions, groups with hydrogen-bonding potential, anionic groups (e.g. in uronic acids and proteins) and cationic groups (e.g. in amino sugars) (Poli et al. 2011). Owing to this stickiness of the matrix, particles and nanoparticles can be trapped and accumulated. Interestingly, heavy metals such as $Zn^{2+}$, $Cd^{2+}$ and $Ni^{2+}$ bind to the cell walls of bacteria, whereas hydrophobic compounds such as benzene, toluene and xylene are present in the matrix (Flemming and Wingender 2010). Thus, it is plausible that microorganisms have physical interactions with As both intra- and extracellularly. In this section, the potential of microbial intra- and extracellular physical interaction is discussed, including biosorption, bioaccumulation and the influence of the cell surface on As sorption.

## 2.1 Biosorption

To date, most knowledge related to the retention of trace elements on the microbial cell surface is focussed on cationic elements (Gadd 2009). Recent growing interest in the biosorption of As species with microorganisms has enabled an insight in more depth into the interaction between As and the microbial cell surface (Giri et al. 2013; Miyatake and Hayashi 2011; Prasad et al. 2011; Yan et al. 2010). The sorption of As(III), As(V) and monomethylarsonic acid has been evidenced with *Bacillus subtilis* (Hossain and Anantharaman 2006), *Bacillus cereus* (Giri et al. 2013), *Acidithiobacillus ferrooxidans* ($q_{max}$, 0.19 mg $g^{-1}$ for As(III) and 0.22 mg $g^{-1}$ for monomethylarsonic acid at pH 4) (Chandraprabha and Natarajan 2011; Yan et al. 2010), *Rhodococcus* sp. WB-12 ($q_{max}$, 77.3 mg $g^{-1}$ for As(III) at pH 7.0) (Prasad et al. 2011), *Halobacterium saccharovorum*, *Halobacterium salinarium* and *Natronobacterium gregoryi* (Williams et al. 2013). Sorption of As to bacterial cell surface was indicated in the form of electrostatic interaction involving hydroxyl, amide and amino groups on the microorganism surface (Giri et al. 2013; Prasad et al. 2011; Yan et al. 2010). Such interaction is pH dependent and was explained by variable surface charge behaviour with changing pH (Giri et al. 2013). In the case of living *Bacillus cereus*, the highest As(III) adsorption content was at pH 7.5 (Giri et al. 2013). Similarly, characterising the pH dependent As(V) and As(III) sorption behaviour onto dry *B. cereus* W2 and *Rhodococcus* sp. WB-12 showed the highest adsorption extents for both As species at around pH 7 (Miyatake and Hayashi 2011; Prasad et al. 2011). Thermodynamic characterisation based on the investigations from 15 and 20 to 40 °C of living *B. cereus* and *A. ferrooxidans* BY-3 revealed that this sorption process is

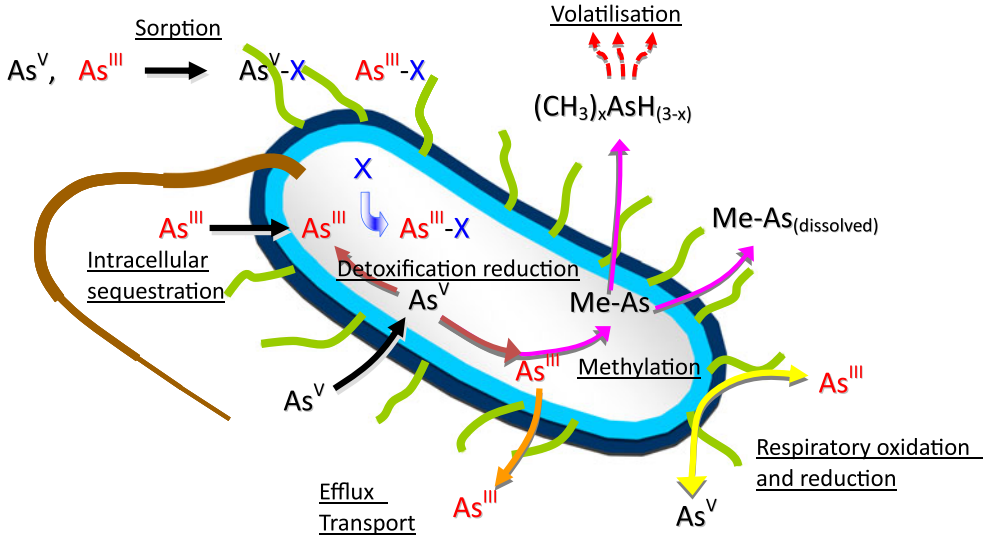


**Fig. 1** Overview of the interaction between microorganism and arsenic compounds

spontaneous and endothermic with a usually higher sorption extent observed at higher temperatures (Giri et al. 2013; Yan et al. 2010). On the other hand, As(III) and As(V) adsorption capacities onto dry *B. cereus* W2 cells first increased from 20 to 30 °C and thereafter decreased from 30 to 60 °C (Miyatake and Hayashi 2011). Whether the living status of microbial cells plays a role in such discrepancies is not clear. Giri et al. (2013) proposed the formation of an inner-sphere complex between As(III) and the surface of *B. cereus* in the neutral pH range; however, further research is required to prove this hypothesis. Among different As species, monomethylarsonic acid sorption was favoured over As(III) at the surface of *A. ferrooxidans* (Yan et al. 2010). Chandraprabha and Natarajan (2011) highlighted another As binding mechanism to the cell surface via the precipitation of As(V) by Fe(II) present in the EPS of ferrous grown *A. ferrooxidans*. The formation of nano-particled amorphous Fe (hydr)oxides precipitating on the cell surface by adding Fe(III) may also largely increase the As(III) and As(V) sorption capacity via the formation of inner-sphere complexes (Yang et al. 2012).

### 2.2 Microbial Competitive Adsorption

Microbial cells attached to minerals facilitate a series of reactions ranging from the retardation of toxins adsorbed to their surface, to the accelerated weathering of minerals (Dong 2010). Recently, microbial attachment to minerals was identified as an important factor leading to the increased solubility of As(V) via competition between As(V) and bacterial phosphate and carboxylate groups for Fe(III)-(oxyhydr)oxide surface sites (Huang et al. 2011a). Conversely, Kim et al. (2010) indicated a negligible influence of the bacterial cells of *Enterococcus faecalis*, *Escherichia coli* and *B. subtilis* on As(III) and As(V) adsorption to Fe-impregnated granular activated carbon. One potential explanation is the lower cell density ($10^8$ CFU $mL^{-1}$) used in the study by Kim et al. (2010) compared to that used in Huang et al. (2011a) ($5\times10^9$ cells $mL^{-1}$). Whether the difference of bacterial strains plays an important role, however, remains an open question.

### 2.3 Bioaccumulation

Although there is wide distribution of As-resistant microorganisms in the environment, comparably small amounts of microorganisms are known to hyperaccumulate As (non-genetically engineered microorganisms) (Xie et al. 2013). Different from biosorption, bioaccumulation infers intracellular accumulation of As in, e.g. cell membranes and cytoplasm instead of at the cell surface (Joshi et al. 2009; Takeuchi et al. 2007; Xie et al. 2013). Usually, an effective strategy to bind As intracellularly is required to tolerate high amounts of As in cells aside from the classical *ars* operon detoxification, which pumps As out of the cell after reduction. Microorganisms may take advantage of several different strategies to bind As in cells such as the formation of As(III) complexes with chelating proteins or peptides containing thiol groups. For example, the metalloregulatory protein ArsR offers high affinity and selectivity toward As(III), which was used in engineered bacterial cells to accumulate As (Kostal et al. 2004). In the case of *Bacillus* sp. strain DJ-1, which accumulates As levels of up to 9.8 mg $g^{-1}$ (dry weight), this occurs by binding As with the DNA protection during starvation protein using not only interaction with thiol but also ionic interactions with amino acids (Joshi et al. 2009).

## 3 Microbial Arsenic Transformation

Major transformations of As in the environment include microbial oxidation, reduction, methylation and demethylation (Fig. 1). These transformation reactions have an enormous impact on the environmental behaviour of As, as the different chemical forms of As exhibit different mobility [methyl As(III)>>methyl As(V)>As(III)> As(V)] (Lafferty and Loeppert 2005), toxicity [methyl As(III)>As(III)>As(V)>methyl As(V)] (Petrick et al. 2000) and susceptibility to plant uptake [e.g. uptake by the rice root As(III)>monomethyl As(V)>dimethyl As(V)] (Abedin et al. 2002). Generally, As transformation in the environment is mostly biotic (Meng et al. 2003). Abiotic transformation of As has been shown to be substantially slower and is believed to be less important than microbially mediated reduction (Ahmann et al. 1997; Jones et al. 2000; Newman et al. 1997b). For example, the reduction of As(V) by sulphide was kinetically much slower than As(V) reduction by *Desulfotomaculum auripigmentum* strain OREX-4, and thiosulphate and sulphite showed negligible reductions of As(V) (Newman et al. 1997b). *Thermus aquaticus* and *Thermus thermophilus* have been shown to oxidise As(III) to As(V) 100-fold faster than abiotic controls in laboratory experiments (Gihring et al. 2001). The

mechanisms and physiological aspects related to microbial As transformation have been detailed in many review articles (Kruger et al. 2013; Lloyd and Oremland 2006; Mukhopadhyay et al. 2002; Paez-Espino et al. 2009; Silver and Phung 2005). Thus, this section will focus on the knowledge concerning the interplay between microbial As transformation and its geochemical behaviour.

### 3.1 Arsenite Oxidation

Microbial As(III) oxidation is a potential detoxification process that allows microorganism to tolerate higher As(III) levels (Paez-Espino et al. 2009; Tamaki and Frankenberger 1992). Additionally, As(III) oxidation may serve as an electron donor for microbial respiration in combination with $O_2$ or nitrate under oxic and anoxic conditions (Paez-Espino et al. 2009). Arsenite oxidation is catalysed by a wide range of microorganisms, e.g. *Alcaligenes faecalis*, *Hydrogenophaga* sp., *A. ferrooxidans*, *T. aquaticus*, *T. thermophilus*, etc. (Gihring et al. 2001; Oremland and Stolz 2003; Stolz et al. 2006; Wang and Zhao 2009). The major impact of microbial oxidation of As(III) to As(V) is to reduce As mobility in the environment as the affinity of As(V) to mineral solids is usually higher than that of As(III) (Dixit and Hering 2003; Huang et al. 2011c; Smedley and Kinniburgh 2002). Microbial As(III) oxidation has been proposed for As removal from polluted water (Cavalca et al. 2013; Ito et al. 2012). Arsenic immobilisation enhanced by the simultaneous microbial oxidation of As(III) and Fe(II) has been considered as a potential bioremediation strategy of As in anoxic environment. This is based on the formation of Fe(III) (hydr)oxides, which adsorbed As(V) formed from As(III) oxidation (Inskeep et al. 2004; Sun 2008).

### 3.2 Arsenate Reduction

Reduction of As(V) generally indicates an increase in As mobility in the natural environment, as As(III) is generally more mobile than As(V) (Ahmann et al. 1997; Smedley and Kinniburgh 2002). Microbial reduction of As(V) may occur via respiratory reduction, as microorganisms use As(V) as the terminal electron acceptor in anaerobic respiration (Lloyd and Oremland 2006; Mukhopadhyay et al. 2002; Stolz et al. 2002, 2006), e.g. bacteria (*Sulfurospirillum barnesii, Bacillus arsenicoselenatis, Bacillus selenitireducens, Sulfurospirillum arsenophilum*, *Desulfotomaculum auripigmentum*, *Chrysiogenes arsenatis* and *Desulfomicrobium* strain Ben-RB) (Macy et al. 2000; Newman et al. 1998, 1997b; Stolz and Oremland 1999) and hyperthermophilic archaea (*Pyrobaculum arsenaticum* and *Pyrobaculum aerophilum*) (Huber et al., 2000). Another mechanism of microbial reduction of As(V) to As(III) is through detoxification (Langner and Inskeep 2000; Stolz et al. 2002). Arsenic detoxification has been documented in *E. coli*, *Staphylococcus aureus* and *Staphylococcus xylosis*, and is controlled by *ars* genes that encode for As(V) (Cervantes et al. 1994; Tamaki and Frankenberger 1992). Arsenate detoxifying reducing bacteria were found to play a major role in As mobilisation under oxic conditions. In the flooding soil amended with citrate, strong As mobilisation was observed at the beginning of incubation when oxic conditions prevailed (Eh>250 mV) (Corsini et al. 2010). The predominant As(III) appearance in soil solution appeared to be due to the detoxifying activity of As-resistant bacteria with *ars* genes, which were identified as *Bacillus* and *Pseudomonas* spp. Nevertheless, As(V) became prevalent as a consequence of As liberation driven by reductive dissolution of Mn and Fe (hydr)oxides by *Geobacter* spp. and inhibiting the growth and activity of As(V)-resistant bacteria. Apparently, there was a lack of As(V) respiratory reducing bacteria in the aforementioned soils. Studies of *Shewanella* strain ANA-3 with or without ArrA suggest that ArsC does not contribute significantly to total As(V) reduction when soluble As(V) concentrations are in the low micromolar range and the reduction kinetics of As(V) was much faster via respiration than detoxification (Campbell et al. 2006; Malasarn et al. 2004).

Respiratory As(V) reduction has been shown to be capable of mobilising solid associated As(V), including adsorbed and mineral As(V) (Babechuk et al. 2009; Huang et al. 2011c; Zobrist et al. 2000). The rate of As(V) reduction is known to be influenced by the binding forms in which As(V) became associated with the mineral phases and coupled strongly with As(V) adsorption and desorption rates. The microbial As(V) reduction rate was found to decrease in the order: dissolved >>As(V) added to ferrihydrite suspensions at the start of the incubation>As(V) reacted with ferrihydrite for 24 h before incubation>As(V) co-precipitated during ferrihydrite synthesis (Zobrist et al. 2000). Microbial As(V) reduction kinetics studies undertaken in mineral suspensions without growth medium highlight that the presence of mineral sorbents resulted in pronounced decreases in reduction

rates and the magnitude of this effect increased with increasing sorbent concentration and sorption capacity (Huang et al. 2011d). Due to the very low affinity of As(III) to Al (hydr)oxides, As(V) reduction to As(III) will largely enhance the solubility of As at the water–Al (hydr)oxide interface. Reductive dissolution of Al-ferrihydrite by *Shewanella* sp. ANA-3 results in the enrichment of Al sites and As(V) reduction accelerates As release due to the low affinity of As(III) on these non-ferric sites (Masue-Slowey et al. 2011).

Malasarn et al. (2008) characterised in detail the location of *Shewanella* sp. strain ANA-3 As(V) respiratory reductase, showing that the enzyme localises to the periplasm in intact cells. Since direct contact between enzyme and substrate is necessary for reaction, this finding suggests that microbial respiratory reduction of solid associated As(V) is infeasible. However, the authors have verified the release of As(V) reductase from ANA-3 into the surrounding environment and the fact that this remains active for a while, which is suggested to be a general phenomenon of As(V) respiratory-reducing bacteria. The presence of cell-free ARR in the environment may be relevant if electron donors with sufficiently low redox potentials are present to allow the enzyme to catalyse As(V) reduction. Redox active small molecules, including natural products, could possibly serve this purpose, although this hypothesis has yet to be tested. Respiratory As(V) reduction may inhibit or be inhibited by the other redox processes. Nitrate inhibited As(V) reduction by nitrate reduction as a preferred respiratory electron acceptor rather than as a structural analogue of As(V). Bacterial sulphate reduction was completely inhibited by As(V) reduction as well as by As(III) (Dowdle et al. 1996). *D. auripigmentum* strain OREX-4 was shown to be able to respiratory-reduce As(V) and sulphate, but was found to prefer sulphate (Newman et al. 1997b).

### 3.3 Methylation

Biogenic As volatilisation was budgeted as the input at 26,000 t year$^{-1}$, accounting for 58 % of natural emissions and 36 % of total As emission (Chilvers and Peterson 1987). Arsenic methylation was demonstrated by different aerobic and anaerobic microorganisms (Table 1) (Kuehnelt and Goessler 2003). Until 2006, there have been more than 125 bacterial and 16 archaeal ArsM homologues identified (Qin et al. 2006) and more microorganisms capable of As methylation are expected. Microbial methylation allows the transformation of aqueous- or solid-associated inorganic As into gaseous arsines and leaves from the living medium, which is usually regarded as a detoxification (Jia et al. 2013). The gaseous arsines are highly mobile in comparison to aqueous As and may undergo long-distance transport in the atmosphere (Mukai et al. 1986). The formation of aqueous trivalent and pentavalent methyl As were also reported and was considered mobilisation due to the lower adsorption affinity of methylated As than inorganic As (Huang and Matzner 2006; Lafferty and Loeppert 2005). Low redox potentials (i.e. reducing conditions) promote the production and mobilisation of methylated As (Frohne et al. 2011). Under reducing conditions, the reductive dissolution of Fe/Mn (hydr)oxide mineral sorbents and the reduction of As(V) to As(III) may increase the levels of dissolved As in soils and sediments (Bennett et al. 2012; Du Laing et al. 2009) and thereby enhance subsequent microbial methylation of As. Cullen et al. (1994) identified the extracellular As metabolites in the growth medium of *Apiotrichum humicola* and *Scopulariopsis brevicaulis* and the methylation was as follows: inorganic As→monomethylarsonic acid→dimethylarsinic acid→trimethylarsine oxide. Monomethylarsonic acid was shown to be an intermediate, which is hardly excreted due to its low permeability and rapid intracellular metabolism. Dimethylarsinic acid was 10 times more permeable to the membranes than monomethylarsonic acid and thus explains the generally much lower concentrations of monomethylarsonic acid in most natural environments compared to dimethylarsinic acid (Blodau et al. 2008; Fauser et al. 2013; Hasegawa et al. 2009; Huang and Matzner 2007). Intracellular methylation of As(V) in *Trichoderma asperellum*, *Penicillium janthinellum* and *Fusarium oxysporum* revealed the formation As(III), monomethylarsonic acid and dimethylarsinic acid in cells and highlights the fact that intracellular As(V) reduction progresses more easily than methylation (Su et al., 2012). Instead of aqueous methyl As, numerous studies showed the formation of gaseous methyl arsines such as *Methanobacterium bryantii* (McBride 1971), *Methanobacterium formicium*, *Clostridium collagenovorans*, *Desulfovibrio gigas* and *Desulfovibrio vulgaris* (Michalke et al. 2000). Trivalent methyl As (monomethylarsonous acid and dimethylarsinous acid) were proposed to be the intermediates of As methylation according to Challenger's pathway, and have been detected in both environmental samples (Huang et al. 2011b; McKnight-Whitford et al. 2010)

and human cells (Hippler et al. 2011). However, both monomethylarsonous acid and dimethylarsinous acid have not yet been found during microbial As methylation. As indicated, the ability to methylate As(III), As(V) or methyl As and the chemical forms of methyl As produced seems to be microorganism dependent (Table 1). To date, As(III) S-adenosyl-methionine methyltransferase has been the most frequently investigated methylation pathway for As(III) (Qin et al. 2006; Yuan et al. 2008), showing methyl arsines as the products. Nevertheless, the summary in Table 1 highlights that most microorganisms are able to methylate As using As(V) as starting compounds and dissolved methyl As may be the product instead of methyl arsines. This suggests that either microorganisms have the ability to reduce As(III) or use other methylation pathways for methylation directly using As(V). Although several methylation pathways have been proposed (Mestrot et al. 2013; Wu 2005; Wuerfel et al. 2012), the current state of knowledge is still not able to explain the occurrence of methyl As of different chemical forms in nature and their linkage to the different enzymatic systems involved in microbial methylation; e.g. As(V) reductase, monomethylarsonic acid reductase, As(III) methyltransferase and monomethylarsonous acid methyltransferase (Wu 2005).

### 3.4 Demethylation

Demethylation may occur under oxic and anoxic conditions but is usually faster under oxic conditions (Huang et al. 2007). Elimination of the organic moieties not only increases the general toxicity of As but also decreases its mobility. Thus, demethylation is apparently not suitable for the purpose of remediation and therefore draws relatively few research interests. Although microbial As demethylation has been broadly evidenced in the natural environment (Huang et al. 2007; Khokiattiwong et al. 2001; Millward et al. 1996; Sierra-Alvarez et al. 2006), characterisation of microbial demethylation and investigation of microbial community involved is scarce. Yoshinaga et al. (2011) identified *Burkholderia* and *Streptomyces* species in contaminated soils as being responsible for monomethylarsonic acid reduction and monomethylarsonous acid demethylation. Only a mixed culture could perform the complete process of demethylation, demonstrating that monomethylarsonic acid demethylation to As(III) is a two-step process. *Mycobacterium neoaurum* was found to demethylate both monomethylarsonic acid and monomethylarsonous acid to mixtures of As(V) and As(III) (Lehr et al. 2003). Arsenic demethylation usually refers to the degradation of aqueous methylated As. In the atmosphere, the gaseous methylated arsines undergo rapid photooxidative degradation (Mestrot et al. 2011). Whether the microorganisms present in the atmosphere are able to carry out As demethylation is still an open question.

## 4 Influence of Other Microbial Redox Reactions on Arsenic Geochemistry

Almost all of the natural redox reactions may influence As environmental behaviour. They may shift the redox equilibrium between As(III) and As(V), and may also dissolve and precipitate minerals, substantially changing the mobility of As. The most well-known processes among all are microbial Fe and S reduction and oxidation. Figure 2 shows a schematic presentation of the interaction among As, Fe and S oxidation and reduction. The redox transformation of Fe, S and As is predominately driven by microorganisms, but abiotic As transformation coupled with Fe and S redox transformation may also occur. Formation of Fe(II) and Fe(III) (hydr)oxides, sulphide and As(V) minerals during biogeochemical cycling will be the major sink for the solution As. Discussion about the known interplay between other microbial redox reactions and As behaviour are given in the following sections and detailed information is summarised in Table 2.

### 4.1 Nitrate Reduction

Nitrate reduction may not only inhibit As(V) reduction (see Section 3.2) (Dowdle et al. 1996) but can also influence As cycling under anoxic conditions. For example, nitrate-respiring sediments could reduce As(V) to As(III) once all of the nitrate has been removed (Gibney and Nusslein 2007). In urban lakes, microbial oxidation of Fe(II) and As(III) facilitated by nitrate may be a significant process leading to the formation of particulate ferric-oxide and As(V); an important consequence of enriched nitrate is therefore the presence of As(V) associated with hydrous ferric oxide colloids (Senn and Hemond 2002). Injecting nitrate may support the anoxic oxidation of Fe(II) and As(III) in the subsurface as a means to immobilise As in the form of As(V) adsorbed onto biogenic Fe(III) (hydr)oxides (Sun et al. 2009).

**Table 1** Metabolites of arsenic methylating microorganisms documented in the literature

| Microorganism | As(III) | $CH_3AsH_2$ | $(CH_3)_2AsH$ | $(CH_3)_3As$ | MMA(V) | DMA(V) | TMAO | Starting As | References |
|---|---|---|---|---|---|---|---|---|---|
| *Achromobacter* sp. | X | X | X | | X | X | | MMA(V) | (Shariatpanahi et al. 1983) |
| *Aeromonas* sp. | X | X | X | X | X | X | | MMA(V) | (Shariatpanahi et al. 1983) |
| *Alcaligenes* sp. | X | X | X | | X | X | | MMA(V) | (Shariatpanahi et al. 1983) |
| *Enterobacter* sp. | X | X | X | | X | X | | MMA(V) | (Shariatpanahi et al. 1983) |
| *Nocardia* sp. | X | X | X | X | X | X | X | MMA(V) | (Shariatpanahi et al. 1983) |
| *Pseudomonas putida*[a] | | | | | | | | As(V) | (Maeda et al. 1990) |
| *Xanthomonas* sp.[a] | | | | | | | | As(V), Methyl As(V)[b] | (Maeda et al. 1992) |
| *Klebsiella oxytoca*[a], | | | | | | | | As(V), Methyl As(V)[b] | (Maeda et al. 1992) |
| *Flavobacterium–Cytophaga* spp. | | | | X | | | | As(III), As(V) | (Turpeinen et al. 1999) |
| *Methanobrevibacter smithiia* | | X | X | X | | | | As(V) | (Meyer et al. 2008) |
| *Clostridium collagenovorans* | X ($AsH_3$) | | | X | | | | As(V) | (Michalke et al. 2000). |
| *Desulfovibrio gigas* | X ($AsH_3$) | | | X | | | | As(V) | (Michalke et al. 2000). |
| *Desulfovibrio vulgaris* | X ($AsH_3$) | | | X | | | | As(V) | (Michalke et al. 2000). |
| *Fusarium oxysporum* | X | | | | X | X | | As(V) | (Su et al. 2012) |
| *Penicillium janthinellum* | X | | | | X | X | | As(V) | (Su et al. 2012) |
| *Trichoderma asperellum* | X | | | | X | X | | As(V) | (Su et al. 2012) |
| *Methanobacterium formicicum* | X ($AsH_3$) | X | X | X | | | | As(V) | (Michalke et al. 2000) |
| *Proteus* sp. | X | X | X | | | | | As(V) | (Shariatpanahi et al. 1981) |
| *Corynebacterium* sp. | X | | X | X | | | | As(V) | (Shariatpanahi et al. 1981) |
| *Flavobacterium* sp. | X | | X | | | | | As(V) | (Shariatpanahi et al. 1981) |
| *Escherichia coli* | X | X | X | | | | | As(V) | (Shariatpanahi et al. 1981) |
| *Pseudomonas* sp. | X | X | X | X | | | | As(V) | (Shariatpanahi et al. 1981) |

Genetically engineered microorganisms are not included

*As(III)* arsenite, *As(V)* arsenate, *$CH_3AsH_2$* monomethylarsine, *$(CH_3)_2AsH$* dimethylarsine, *$(CH_3)_3As$* trimethylarsine, *MMA(V)* monomethylarsonic acid, *DMA(V)* dimethylarsinic acid, *TMAO* trimethylarsine oxide

[a] Mono-, di-, and tri-metyhlated arsenic, valence state not specified

[b] Including MMA(V), DMA(V) and arsenobetaine

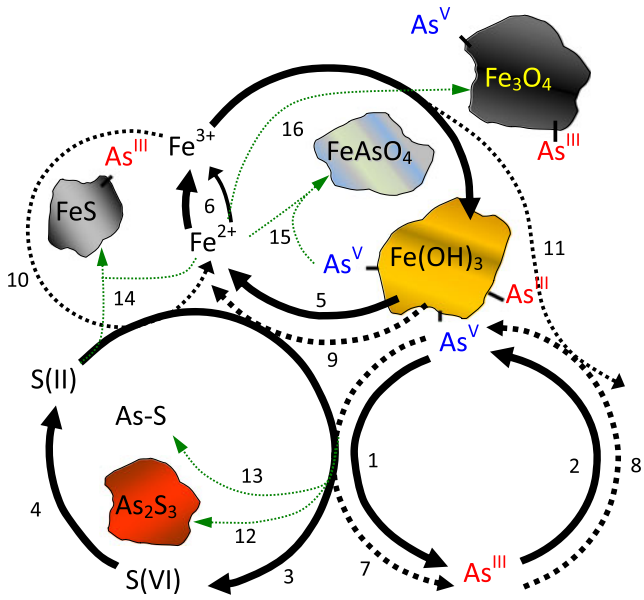


**Fig. 2** Overview of the interaction between microbial (*solid lines*) and microorganism mediated processes (*dash lines*) of Fe, S and As redox transformation influencing As compounds. (*1*) microbial As(V) reduction; (*2*) microbial As(III) oxidation; (*3*) microbial sulphide oxidation; (*4*) microbial sulphidisation; (*5*) microbial Fe(III) reduction; (*6*) microbial Fe(II) oxidation; (*7*) sulphide induced As(V) reduction; (*8*) abiotic As(III) oxidation; (*9*) sulphide-induced Fe(III) reduction; (*10*) ferric ion-induced sulphide oxidation; (*11*) ferric ion-induced As(III) oxidation; (*12*) arsenic sulphide precipitation; (*13*) formation of aqueous thioarsenic complexes; (*14*) iron sulphide precipitation; (*15*) ferrous arsenate precipitation; (*16*) formation of secondary Fe(II) minerals

### 4.2 Iron Reduction

There are a number of microorganisms known to be responsible for reducing Fe in the reducing environment. The most famous are *Geobacter* spp. and *Shewanella* spp. (Lovley et al. 2004). Generally, reductive As mobilisation is attributed to microbial Fe reductive dissolution, which is concluded mostly based on field observations (Corsini et al. 2010; Cummings et al. 1999; Huang and Matzner 2006; Islam et al. 2004; Tadanier et al. 2005). Corsini et al. (2010) demonstrated that microbial Fe reduction was the major process that caused As mobilisation in flooded soils when microbial As(V) respiratory activity was lacking. Microbially mediated reduction of Fe(III) (hydr)oxides was shown to be capable of promoting As mobilisation from a crystalline ferric arsenate as well as from sorption sites (Cummings et al. 1999). Tadanier et al. (2005) suggested microbially-mediated deflocculation of Fe(III) (hydr)oxide nanoparticles from an initially aggregated particulate configuration to smaller filterable colloids as the dominant mechanism of As mobilisation. Nevertheless, As mobilisation via reductive dissolution of Fe (hydr)oxides, especially amorphous phases with very high As adsorption capacity, is doubtful when looking into the results from a series of lab model experiments: Simulating microbial Fe reduction with ascorbic acid indicated that adsorbed As(V) was not released until the surface area of ferrihydrite and goethite became too small (Pedersen et al. 2006). It is thus plausible that increased As mobilisation at the water-ferrihydrite interface via Fe(III) reductive dissolution was indicated to be only relevant at high As(V) to ferrihydrite ratios (Jiang et al. 2013). On the other hand, several model experiments have shown that the formation of secondary Fe(II) (hydr)oxides, e.g. magnetite ($Fe_3O_4$), vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$] siderite ($FeCO_3$) and bobierrite [$Mg_3(PO_4)_2{\cdot}8H_2O$] during microbial reduction may trap released As again, depending on the composition of the working solution (Burnol et al. 2007; Coker et al. 2006; Herbel and Fendorf 2006; Islam et al. 2005). Additionally, As(V) bound more strongly after $Fe^{2+}$ catalysed ferrihydrite and lepidocrocite [$\gamma$-FeO(OH)] transformation into more crystalline Fe(III) oxide phases or magnetite, leading to the incorporation of As into the structure of the crystalline product (Pedersen et al. 2006). Similar to ferrihydrite, no apparent As mobilisation was observed during reduction of schwermannnite due to the formation of biogenic minerals (Cutting et al. 2012). Recently, incubations with different *Shewanella* strains

**Table 2** Investigation concerning microbial processes affecting arsenic mobility in model experimental systems

| Microorganism | Microbial reactions | Experimental conditions | Remarks | References |
|---|---|---|---|---|
| *Geobacter metallireducens* | Fe(III) reduction | Batch incubation, 56 mM Fe ferrihydrite, 0–100 μM As(V), pH 7-7.5 | As mobilisation via microbial reductive deflocculation to nanometer sized colloid | (Tadanier et al. 2005) |
| *Shewanella alga* BrY | Fe(III) reduction | Batch incubation, 10 mM scorodite, 10 mM lactate, $10^{10}$ cells $mL^{-1}$, pH 6.1–7.5 | As mobilisation via respiratory reduction of Fe(III) to Fe(II) | (Cummings et al. 1999) |
| *Geobacter sulfurreducens* | Fe(III) reduction | Batch incubation, 10 mM ferrihydrite, pH 7.1, 20 mM acetate, 100 μM As(III) or As(V), 20 °C | No As mobilisation during reduction of ferrihydrite to magnetite | (Coker et al. 2006) |
| *Geobacter sulfurreducens* | Fe(III) reduction | Batch incubation, 10 mM ferrihydrite, pH 7.1, 20 mM acetate, 100 μM As(III) or As(V), 20 °C | Capture of solution As by biogenic magnetite, siderate and vivianite | (Islam et al. 2005) |
| *Geobacter sulfurreducens* | Fe(III) reduction | Batch incubations, 0.1 g As(V) bearing schwertmannite (0–4.13 wt.%), 20 mM acetate, 10 μM anthraquinone-2,6-disulfonate, 20 °C, pH 7.1 | Limited As mobilisation due to formation of biogenic minerals | (Cutting et al. 2012) |
| Strain FRB1 | Fe(III) reduction and As (V) reduction | Batch incubation, ca. 5.5 mM Fe ferrihydrite, 0.17–0.84 mM As(V), P-rich medium, $1.1–7.6\times10^{7}$ cells $mL^{-1}$, | As reduction due to its reduction, Fe(III) reduction precipitate vivianite and bobierrite | (Burnol et al. 2007) |
| *Sulfospirillium barnesii*<br>*Bacillus benzoevorans* HT-1 | As(V) and Fe(III) reduction;<br>As(V) reduction | Flow-through reactor experiment, As(V) and As(III) loading on ferrihydrite coated quartz, 0.28 mM lactate pH 7.2 | Maximum As release before Fe(III) reduction | (Herbel and Fendorf, 2006) |
| *Shewanella putrefaciens* CN-32 or *Sulfurospirillum barnesii*<br>*Bacillus benzoevorans* HT-1 | As(V) and Fe(III) reduction<br>As(V) reduction | Flow-through reactor experiment | As(V) reduction enhanced As release; As(V) retained within column solids under Fe(III) reducing conditions | (Kocar et al. 2006) |
| *Shewanella* sp. ANA-3 | As(V) and Fe(III) reduction | Batch incubation, 1.9–2.8 g $L^{-1}$ hydrous ferric oxide, pH 8.0, 20 mM As(V), 14 mM lactate, 500 cells $mL^{-1}$ | As(III) adsorption accelerate microbial HFO reduction, As(V) respiratory reduction was faster than detoxification reduction | (Campbell et al. 2006) |
| *Shewanella* sp. ANA-3 | As(V) and Fe(III) reduction | Flow-through reactor experiment, ferrihydrite, goethite and hematite coated quartz sand (98–141 mg $kg^{-1}$ Fe), $10^{8}$ cells $g^{-1}$ ferrihydrite sand, 3 mM lactate, pH 7.1 | As(III) is desorbed more rapidly and extensively from all oxides; As(V) reduction appears to be the dominant process controlling As release when decoupling with Fe(III) reduction | (Tufano et al. 2008) |
| *Shewanella putrefaciens* CN-32 | As(V) and Fe(III) reduction | Flow-through reactor experiment, As(III) loading of 4.48 mmol $kg^{-1}$ and $10^{7}$ cells $g^{-1}$ on the ferrihydrite-coated sands, 0.08–7.7 mM lactate, pH 7.1 | As(III) retention during Fe reduction is temporally dependent on secondary precipitation of iron phases (magnetite) | (Tufano and Fendorf 2008) |
| *Shewanella* sp. ANA-3 | As(V), Mn(IV) and Fe(III) reduction | Flow-through reactor experiment, As(V) presorbed ferrihydrite-and birnessite-coated sand aggregate, 3 mM lactate, ca. $8\times10^{9}$ cells $g^{-1}$ sand, pH 7.1 | As, Mn, and Fe to migrate from the reduced aggregate interiors to the aerated exterior region; Mn oxide induced As(III) oxidation in the presence of $O_2$ | (Ying et al. 2013) |
| *Shewanella* sp. ANA-3 | Fe(III) and As(V) reduction | Flow-through reactor experiment, Al-substituted ferrihydrite, pH 7.1, 1 mM lactate, $10^{8}$ cells $g^{-1}$ sand | Enrichment of Al site after reductive dissolution of Al-ferrihydrite and As(V) reduction accelerates As release | (Masue-Slowey et al. 2011) |
| *Shewanella oneidensis* MR-1, *Shewanella* | Fe(III) and As(V) reduction | Batch incubation, 50 mM ferrihydrite, 5 mM As(V), 20 mM pyruvate or $Fe_3(AsO_4)_2$, 30 °C | As(V) reduction to As(III) preventing from precipitation with Fe(II) and transformation of ferrihydrite to siderite re-release As | (Jiang et al. 2013) |

**Table 2** (continued)

| Microorganism | Microbial reactions | Experimental conditions | Remarks | References |
|---|---|---|---|---|
| sp. HN-41, *Shewanella putrefaciens* 200 | | | As(V) and Fe(III) respiratory reducing strain releases As(III) and Fe(II) from $Fe_3(AsO_4)_2$ faster than Fe(III) reducing strains | |
| *Shewanella putrefaciens* CN-32 | As(V) and Fe(III) reduction | Batch incubation, 3.33 g $L^{-1}$ Pb-As jarosite, pH 7.4, $1.3\times10^8$ cells $mL^{-1}$, 27 °C | As released due to As(V) reduction | (Smeaton et al. 2012) |
| *Shewanella putrefaciens* CN-32 | As(V) reduction | Batch incubation, 0.2–20 g $L^{-1}$ ferrihydrite, goethite, boehmite, medium free working solution, 10 μM As(V), 25 μM lactate, 25 °C, $5\times10^9$ cells $mL^{-1}$, pH 7 | As mobilisation. As(V) sorption behaviour controlled As(V) reduction rates | (Huang et al. 2011c) |
| *Sulfurospirillum barnesii* | As(V) reduction | Batch incubation, ferrihydrite and $Al(OH)_3$ with As(V) pre-sorbed and co-precipitated, medium free working solution, 1 mM lactate, pH 7.3, $1–3\times10^9$ cells $mL^{-1}$, 25 °C | Dissolution of ferrihydrite was not required to reduce adsorbed As(V); As(V) reduction kinetics was influenced by the method in which arsenate associated with the mineral | (Zobrist et al. 2000) |
| *Clostridium* sp. CN-8 | As(V) reduction (detoxification pathway) | Batch incubation, 10 mM ferrihydrite, 0–5 mM As(V), $5\times10^8$ cells $mL^{-1}$, 23 °C, pH 6.8 | No reduction of adsorbed As(V) | (Langner and Inskeep 2000) |
| Strain MIT-13 | As(V) reduction | Batch incubation, sediment spiked with ferric and ferrous arsenate (2.61 and 2.87 mM As, respectively), $1\times10^8$ cells $mL^{-1}$, 22 °C | Microbial Fe(III) reduction may be not important to the dissolution and reduction of solid-phase arsenate in the presence of microbial As(V) reducing activity | (Ahmann et al. 1997) |
| *Shewanella* sp. ANA-3 | As(V) reduction<br>Mn(IV) induced As(III) oxidation | Donnan cell experiment, birnessite 5 g $L^{-1}$, $1.9\times10^9$ cells $mL^{-1}$, 510 μM As(V), 3 mM lactate, 25 °C, pH 7.1 | Precipitation of rhodochrosite inhibited cycling between microbial As(V) reduction and As(III) oxidation by birnessite | (Ying et al. 2011) |
| *Desulfotomaculum auripigmentum OREX-4* | Sulphidisation, As(V) reduction | Batch incubation, 10–20 mM lactate, 1–10 mM sulphate and As(V), pH 6.8 | Reduction rates of As(V) to As(III) and S(VI) to S(-II)and pH are critical for $As_2S_3$ precipitation intra- and extra-cellularly | (Newman et al. 1997a) |
| *Shewanella* sp. HN-41 | Sulphidisation, As(V) reduction | Batch incubation, 5 mM As(V), 20 mM lactate, 10 mM thiosulphate, 30 °C, pH 7.5 | Formation of amorphous $As_2S_3$ and AsS and $As_4S$ | (Lee et al. 2007) |
| *Desulfovibrio vulgaris* | Sulphidisation and As(V) reduction<br>Sulphidisation induced Fe(III) reduction | Flow-through reactor experiment, 80 and 400 mg $kg^{-1}$ As(V) on ferrihydrite-coated quartz (0.1 mg $kg^{-1}$), 600–800 μM sulphate, 800–1,000 μM lactate, pH 7.5, $10^8–10^9$ cells $mL^{-1}$ | Iron sulphide (sulphidisation zone) and magnetite and green rust formation (downstream); Fe(III) inhibited formation of As sulphide; No As mobilisation | (Kocar et al. 2010) |
| *Desulfovibrio vulgaris* | Sulphidisation and As(V) reduction<br>Fe(III) reduction by S(-II) | Batch incubation, 0.08–10 mM sulphate, 0.1–5 g $L^{-1}$ ferrihydrite, 225–9,900 ppm As(III) and As(V) | Formation of magnetite, elementary S and trace Fe and As sulphide. Limited As mobilisation | (Saalfield and Bostick 2009) |
| *Acidovorax* sp. *strain* BoFeN1 | Fe(II) oxidation | Batch incubation, 10–15 mM Fe(II), As(III) or 50–500 μM As(V), 28 °C | As immobilisation via formation of goethite and ferrihydrite at low and high As levels, respectively | (Hohmann et al. 2011) |
| *Acidovorax* sp. *strain* BoFeN1 | Fe(II) oxidation | Scanning transmission X-ray microscopy study, 5 mM acetate, 6 mM Fe(II), 1 mM As(V) | As immobilisation via formation of goethite, ferrihydrite, and carbonate green rust | (Hitchcock et al. 2012) |
| *Acidithiobacillus ferrooxidans* | Fe(II) and S(-II) oxidation | Batch incubation, 5 g $L^{-1}$, realgar with and without 4.5 g of $FeSO_4{\cdot}7H_2O$ and 0.1 g of S added, $1.2\times10^7$ cells $mL^{-1}$ | As mobilisation and $As_4S_4$ and $As_4S_3$ precipitation without addition of Fe(II) and S; As mobilisation and $S_8$ formation with addition of S; No As mobilisation in the | (Chen et al. 2011) |

**Table 2** (continued)

| Microorganism | Microbial reactions | Experimental conditions | Remarks | References |
|---|---|---|---|---|
| | | | presence of Fe(II) and jarosite, magnetite, $FeAsO_3$, sulphur formed | |
| *Acidithiobacillus ferrooxidans* | Fe(II) and S(-II) oxidation | Batch incubation, arsenopyrite, pH 1.8 | Orpiment, jarosite, sulphur and arsenolite formed and no As mobilisation | (Marquez et al. 2012) |
| *Thiobacillus ferrooxidans* | Fe(II) oxidation | Fermenter experiment; enagite; 1–6 %*v/v* $CO_2$; 35 °C and pH 2.4, $2.6\times10^7$–$1.2\times10^8$ cells $mL^{-1}$ | ~0.8 g $L^{-1}$ As released | (Acevedo et al. 1998) |
| *Acidithiobacillus ferrooxidans* | Fe(II) and S(-II) oxidation | Stirr tank reactor experiment; arsenopyrite, 28 °C, pH 0.9-2.3 | Sulphur, FeOOH and jarosite precipitated and no As mobilisation | (Fantauzzi et al. 2011) |
| *Leptospirillum ferrooxidans* | Fe(II) oxidation<br>Fe(II) oxidation induced As(III) oxidation | Batch incubation, 2.5 g $L^{-1}$ arsenopyrite and Batch incubation, enargite, pH 1.8, 30 °C, $10^8$ cells $mL^{-1}$ | Arsenic mobilisation and formation of Fe(III) (hydr)oxides, ferric sulphate and unknown As oxide | (Corkhill et al. 2008) |

suggested that microbial Fe(III) reduction is able to immobilise As via the formation of $Fe_3(AsO_4)_2$ precipitation and that the parallel As(V) reduction to As(III) prevents precipitation with Fe(II) (Jiang et al. 2013). In summary, the model experiments showed highly controversial results of the influence of microbial Fe reduction on As mobility, although most field studies highlight As mobilisation as a consequence of microbial reductive dissolution of Fe(III) (hydr)oxides. Recently, a study of As behaviour in wetland soils allowed the first explanation of this discrepancy. It showed that the presence of organic matter reduced or inhibited the formation of secondary Fe(II) minerals during reductive dissolution of Fe(III) (hydr)oxide and that As was not taken up and was thereby strongly solubilised (Davranche et al. 2013). It appears that the complexity of the natural system provides plenty of possibilities to influence the transformation of Fe (hydr)oxides with a consequent effect on As mobility, which should be more comprehensively investigated in future model experiments.

Abiotic reduction of As(V) by Fe(II) produced by microbial Fe(III) reduction is unlikely. In an abiotic control experiment, Zobrist et al. (2000) checked for possible As(V) reduction in the presence of Fe(II) in ferrihydrite suspensions, but detected no As(III) in solution or sorbed to the solid phase. Similarly, Amstaetter et al. (2010) observed no reduction of As(V) under strictly anoxic conditions by "Fe(II)-activated" goethite, i.e. goethite with adsorbed Fe(II). Surprisingly, however, the authors did observe oxidation of As(III) to As(V) by Fe(II)-activated goethite under anoxic conditions, suggesting that Fe(II) on the goethite surface formed a highly reactive, As(III)-oxidising surface site of unknown nature.

### 4.3 Manganese Oxidation and Reduction

The information concerning the interaction between Mn oxidation and reduction and As is less than Fe redox transformation, probably because Mn oxides are usually a minor component compared to Fe (hydr)oxides in soils and sediments. Microbial Mn oxidation and reduction may act on As mobilisation similar to Fe(III) reduction since Mn(IV) oxides are also effective sorbents for As(V) (Ajith et al. 2013; Smedley and Kinniburgh 2002; Ying et al. 2012). The major difference with Fe (hydr)oxides is that Mn-oxides are quite reactive, with respect to As(III) oxidation to As(V), which substantially changes the As mobility. To date, As(III) oxidation by

biogenic Mn oxides has been evidenced in bacteria and fungi (Liao et al. 2013; Ozaki et al. 2013; Tani et al. 2004; Ying et al. 2011). An interesting study based on Donnan cell experiments highlighted the potential cycling between microbial As(V) reduction and abiotic As(III) oxidation by bernessite ($MnO_2$) (Ying et al. 2011). Such As redox cycling ceased until the passivation of bernessite surface by precipitating rhodochrosite ($MnCO_3$). Whether the As cycling between microbial As(V) reduction and Mn oxide oxidation play a significant role in the natural environment is questionable. The simultaneous presence of Mn oxides and microbial As(V) reduction in the natural environment seems unlikely. As shown in redox priority sequence, the priority of As(V) reduction is generally lower than the reduction of Mn oxides, i.e. As(V) reduction may begin in the redox condition after Mn oxides have been completely reduced.

### 4.4 Sulphidisation

Although microbial reduction of S compounds into sulphide is frequently regarded as a process to trap solution As (O'Day et al. 2004), $As_2S_3$ precipitation is sensitive to environmental conditions. Usually, $As_2S_3$ precipitation favours acidic over basic conditions and microorganism-mediated precipitation of $As_2S_3$ may occur both extracellularly and intracellularly (Newman et al. 1997a). Microorganism-mediated $As_2S_3$ precipitation is a function of the ability of microorganisms to reduce As and S compounds to appropriate concentrations of As(III) and sulphide. The precipitation of $As_2S_3$ occurs in anoxic waters essentially when dissolved sulphide and As(III) production exceeds their solubility products. On the other hand, investigation of precipitation of $As_2S_3$ by *D. auripigmentum* and *Desulfotomaculum propionicus* demonstrated that *D. propionicus* reduce S(VI) too rapidly, leading to formation of $H_xAsS_6^{x-3}$ rather than $As_2S_3$ precipitates (Newman et al. 1997a). When Fe concentrations are much higher than sulphide concentrations, As sequestration becomes controlled by Fe because aqueous sulphide is rapidly depleted during the formation of iron sulphide minerals (Kocar et al. 2010; Saalfield and Bostick 2009). The findings related to the influence of Fe–S redox interaction during microbial sulphidisation on As mobility are controversial and at the same time show the high complexity of the natural system. Kocar et al. (2010) and Saalfield and Bostick (2009) both concluded As sequestration by the residual ferrihydrite and secondary Fe(II) minerals (magnetite) during sulphidisation. On the other hand, Burton et al. (2011) reported that sulphide-driven reductive dissolution of ferrihydrite and its replacement by mackinawite (FeS) resulted in the substantial mobilisation of As into the pore water. Formation of poorly sorbing aqueous thioarsenic species during microbial sulphidisation may cause the additional enhancement of As mobilisation (Burton et al. 2013). Accordingly, the change of not only the mineral composition but also As speciation needs to be carefully considered when evaluating and predicting subsurface As mobility in the presence of sulphidisation.

### 4.5 Iron Oxidation

Due to the high adsorption capacity to As, the formation of Fe(III) (hydr)oxides is undoubtedly capable of trapping As from the solution phases. Microorganism-mediated Fe(III) (hydr)oxide is known to be responsible for As immobilisation in acid mine drainage (see also Section 4.6) (Duquesne et al. 2003; Ma and Lin 2012) and the presence of free $Fe^{3+}$ ion enable to oxidise As(III) to As(V) abiotically (Huang and Kretzschmar 2010). Furthermore, microbial Fe oxidation has been broadly applied for As remediation in anoxic environments (Hohmann et al. 2010; Kleinert et al. 2011; Liu et al. 2013a). Different from the abiotic Fe(III) (hydr)oxides, the presence of cell organic matter in biogenic Fe(III) (hydr)oxides seems to decrease As adsorption capacity, probably due to competitive adsorption (Hohmann et al. 2011; Kleinert et al. 2011).

### 4.6 Bioleaching

Arsenic bioleaching is usually referred to as biooxidation of As containing sulphide minerals, e.g. arsenopyrite (FeAsS), enargite ($Cu_3AsS_4$) and realgar ($As_4S_4$) by acidophilic Fe oxidation microorganisms such as *A. ferrooxidans*, *Leptospirillum ferrooxidans*, *Thiobacillus ferrooxidans* and *Thiobacillus caldus* (Acevedo et al. 1998; Corkhill et al. 2008; Dopson and Lindstrom 1999; Marquez et al. 2012). Usually, bioleaching is more efficient than abiotic oxidation (Corkhill et al. 2008). Bioleaching of As-containing sulphide minerals usually occurs via the microbial transformation of ferrous to ferric ions with the subsequent chemical oxidation of sulphides by $Fe^{3+}$ (Marquez et al.

2012). It has been indicated that a close contact between microorganisms and the mineral is needed for leaching (Arredondo et al. 1994). Thus, the $Fe^{3+}$ produced may also become a constitute of extracellular polymeric substances supporting microbial attachment to mineral surface and the biooxidation process. The presence of microorganism such as *T. caldus* may support bioleaching by metabolise $S^0$ built upon the surface of the mineral, allowing microbial and chemical access to the mineral (Dopson and Lindstrom 1999). Another potential pathway is the microbial oxidation of sulphides parallel releasing As(III) in solution (Chen et al. 2011). Some microorganisms, like *A. ferrooxidans*, are able to oxidise As(III) to As(V) and thereby decrease As mobility (Zhang et al. 2007). Additionally, the oxidation of As(III) to As(V) could be catalysed by microbial oxidising $Fe^{2+}$ presented to conserve energy (Chen et al. 2011). Bioleaching may elevate As concentrations in solution up to several grams per litre (Acevedo et al. 1998). On the other hand, the release of As may be suppressed by formation of the secondary mineral precipitates such as jarosite [$KFe_3(OH)_6(SO_4)_2$], magnetite ($Fe_3O_4$), ferric arsenate [$Fe_2(AsO_4)_3$], scorodite ($FeAsO_4{\cdot}2H_2O$), schwertmannite [$Fe_8O_8(OH)_6(SO_4){\cdot}nH_2O$], ferric hydroxide [$Fe(OH)_3$] and ferric phosphate [$Fe_2(PO_4)_3$] (Chen et al. 2011; Corkhill et al. 2008; Duquesne et al. 2003). Arsenolite ($As_2O_3$) may also be created during bioleaching of arsenopyrite. Although it is highly water soluble, this presents as fine particles embedded in the jarosite matrix, which prevents its dissolution (Marquez et al. 2012). Therefore, the mobility of As after bioleaching seems to be determined by the environmental matrix. For example, bioleaching of realgar with *A. ferrooxidans* by adding $Fe^{2+}$ led to the formation of jarosite, whereas adding sulphur and $Fe^{2+}$ suppressed the formation of jarosite (Chen et al. 2011). The presence of highly concentrated As(III) and As(V) inhibited bioleaching due to the toxic effect (Breed et al. 1996).

## 5 Influence of Microbial Redox Transformation on Arsenic Mobility in Natural Soils and Sediments

Few attempts were made to outline the influence of microbial activities on As mobilisation from soils and sediments by inoculating pure cultures. For example, inoculating a native As(V)-reducing strain MIT-13 in the sediment of the Aberjona watershed demonstrated the potential of microbial As(V) reduction to release As associated with sediment solids (Ahmann et al. 1997). Incubations of lake sediments with *Shewanella alga* BrY demonstrated Fe(III) reduction releasing As(V) without reducing it (Cummings et al., 1999). The latest studies with Fe(III) reducing *Shewanella* strains of different As(V) reducing activities showed very different As mobilisation behaviour from ferrihydrite and natural soils. In the incubations with ferrihydrite, As mobilisation was only observed in the incubation with the strain capable of As(V) reduction, whereas As release from the natural soils was detected in all incubations. Such discrepancy suggests that the soil matrix substantially changed the geochemical behaviour of As and Fe species and, furthermore, to implicate the knowledge obtained from the model experiments to the natural system, it is indispensable to include the effects caused by the matrix from the natural samples, which much more focus should be placed on in the future research.

## 6 Arsenic Mobilisation and Immobilisation via Non-redox Reaction-Induced Mineral Dissolution and Precipitation

### 6.1 Mineral Dissolution

Microorganisms have developed several different strategies to dissolve insoluble minerals to obtain the nutrients encompassed. The most well-known case is probably the production of siderophores, which are small, high-affinity Fe-chelating compounds secreted by microorganisms (Gadd 2004). In addition to Fe, siderophores can also bind to the other metals such as Al, Mn, Mg, Cr, etc. Different from reductive dissolution of Fe(III) (hydr)oxides, the complexation of $Fe^{3+}$ retards the formation of secondary minerals and As solubilisation is thus plausible. *Pseudomonads* strains isolated from mining sites produced siderophores, which could promote mineral dissolution and mobilisation of the more toxic As(III) species in the environment (Matlakowska et al. 2008). Nair et al. (2007) indicated that the siderophore secreted by *Pseudomonas azotoformans* is capable of complexation with As(III) and As(V) and thereby extracted not only the bioavailable fraction but also bound As in soils. Mineral dissolution may also occur via the by-product of microbial metabolites. Phosphate-limited cells of *Burkholderia fungorum* mobilise ancillary As from

apatite as a by-product of mineral weathering for nutrient acquisition (Mailloux et al. 2009). Microbial oxidative degradation of glucose to gluconic acid by *B. fungorum* in intimate contact with apatite ($Ca_5(PO_4)_3(F,Cl,OH)$) is a likely cause of As release from the mineral structure into the water. In the absence of secondary precipitates, the mobility of As in this case will simply be determined by the amount and adsorption capacity of the compounds. Microorganisms may also secrete organic compounds for other purposes; e.g. *Shewanella* spp. are able to produce Fe(III) solubilising ligands to initialise respiration of insoluble Fe(III) (hydr)oxides (Taillefert et al., 2007). There may be more mechanisms of As mobilisation via microorganism-induced mineral dissolution, but these have not yet been identified. For instance, Frey et al.(2010) highlighted the potential of HCN-producing microorganisms to dissolve minerals, which might be a probable mechanism to release mineral-associated As. Therefore, microorganisms seem to be more involved, directly or indirectly, in mineral dissolution-induced As release than we currently know, which might be a potential focus of future research.

### 6.2 Biomineralisation

Aside from the influence of biogenic Fe, Mn and sulphide minerals (see also Fe reduction and oxidation and sulphidisation), a range of biogenic minerals may immobilise As in solution. For example, calcite precipitated by the As(III) tolerant soil bacterium *Sporosarcina ginsengisoli* CR5 was able to shift soil As from the exchangeable fraction to the carbonated fraction (Achal et al. 2012). Another biomineralisation process to immobilise As is the formation of As precipitates, e.g. scorodite and As sulphide (see bioleaching and sulphidisation). There are more than 300 As minerals known to occur in nature (Drahota and Filippi 2009). For example, in an As-contaminated perched aquifer affected by mining activity, free $Ca^{2+}$ availability was found to control As mobility in the aquifer through the diagenetic precipitation of calcium arsenates $[Ca_5H_2(AsO_4)_4{\cdot}cH_2O]$ preventing further mobilisation of As in Ca-rich environments (Martinez-Villegas et al. 2013). For decades, it has been a common practice to stabilise As wastes as metal arsenate compounds (i.e. ferric arsenate, calcium arsenate and magnesium arsenate) (Bothe and Brown 1999; McNeill and Edwards 1997), and to dispose of them in slags, tailings and residue dumps (Robins 1981). The significance, mechanism and environmental implication of many microbial minerals have been reviewed (Benzerara et al. 2011). In comparison, the occurrence of most microbial As minerals is still not clear.

## 7 Biofilm

Most microorganisms can form biofilms, and over 99 % of all microorganisms on earth live in these biological structures (Costerton et al. 1987). Biofilms allow the coexistence of microniches of different physiological requirements, enabling the simultaneous, but spatially separated occurrence of opposing redox processes in the same biofilm environment (Labrenz et al. 2000; van Hullebusch et al. 2003). This important role of biofilm in As biogeochemistry was evidenced by the potential enrichment of As in biofilm. The concentrations of As in rock biofilm reached up to 60 mg $kg^{-1}$ (dry weight) (Drewniak et al. 2008). A recent research based on X-ray absorption spectroscopic analysis focussed on As biotransformation in the mix cultured biofilm spiked with 50–1,000 ppm As(III) and As(V) (Yang et al. 2011). Interestingly, there might be simultaneous As oxidation and reduction in biofilms, although the extent of As(III) oxidation was apparently higher than that of As(V) reduction. Aside from As redox transformation, As methylation was also indicated, as shown by the appearance of monomethylarsonous acid and trimethylarsine oxide after 20 and 90 days of incubation. The addition of Se seemed to stimulate As redox transformation and methylation in biofilms. The oxidation of As(III) and the formation of trimethylarsine oxide was especially suggested as a useful application of the aforementioned biofilm for As(III) removal and detoxification in As(III) contaminated aquatic environments. It has also been demonstrated that As treatment can lead to changes in microbial biofilm structure. Another study concerning rock biofilm from an ancient gold and As mine highlighted the simultaneous presence of As-oxidising and As-reducing bacteria and evidenced the ability of siderophores in biofilm porewater to mobilise As from the rock (arsenopyrite) (Tomczyk-Żak et al. 2013). Still, the knowledge concerning biofilm As is scant. Further research on As-biofilm interactions and biofilm As transformations is required in the future with the objective of defining the role of biofilms in As biogeochemistry.

## 8 Conclusion and Outlook

The past research has clearly indicated the significant influence of microorganisms on the environmental fate and transport of As, regardless of whether the contribution is direct or indirect. Figure 1 summarises the potential pathways of the direct interactions between microbial cells and As, including physical sequestration and chemical transformation. Accordingly, taking the soil as an example, in which the microbial density may reach up to $10^{10}$ cells $g^{-1}$ (Torsvik et al. 2002), the presence of microbial cells in the environmental media may already change As adsorption affinity to mineral surfaces due to the cell surface functional group competition, intracellular sequestration and cell surface biosorption. Microbial transformation of As, Fe, S and Mn simultaneously affects the mobility of As in nature, while the mobility of As depends largely on the chemical forms of As Fe, S and Mn. Therefore, biotransformation could be considered the major driving force of the As biogeochemical cycle. Table 3 outlines the influence of different microbial processes on As mobility at the water-mineral interface. The influence of microbial processes acting directly on As can be clearly concluded. For example, As reduction and methylation increase the mobility of As, whereas oxidation and demethylation decrease As mobility. In comparison, for those processes indirectly associated with As such as Fe and S redox transformation, their influence on As environmental mobility is usually ambiguous. As indicated in the schematic presentation of the interaction among Fe, S and As redox cycling (Fig. 2), which was proposed based on the literature information, the interplay between Fe and S redox transformation and As biogeochemical behaviour is complicated. Iron and S redox transformation may cause the precipitation of secondary minerals [e.g. Fe(II) and Fe(III) (hydr)oxides, $FeAsO_4$, FeS, $As_2S_3$] for trapping As in solution. On the other hand, they may mobilise As via the reductive dissolution of Fe(III) hydroxides, oxidation of As-containing sulphides and the formation of dissolved thioarsenic complexes. Additionally, their redox products ($S^{2-}$ and free $Fe^{3+}$) are able to induce abiotic As redox transformation. Apparently, the mobility of As is governed by whether the formation of secondary minerals takes place or not. In addition, the interplay between Fe and S redox transformation shifts the extent of their influence on As mobilisation. For example, the presence of much larger amounts of Fe(III) hydroxides in soils and sediments inhibit the interaction between S redox cycling with As (Kocar et al. 2010).

The soil matrix has been shown to be capable of completely changing the mobility of As associated with

**Table 3** Summary of microbial processes influencing arsenic mobility in the surface environment

| Processes | Comments |
|---|---|
| Mobilisation | |
| Arsenic reduction | As(III) more mobile than As(V) |
| Arsenic methylation | (Gaseous) Methyl As mobile than inorganic As |
| Competitive adsorption | |
| Immobilisation | |
| Arsenic oxidation | As(III) more mobile than As(V) |
| Demethylation | (Gaseous) Methyl As more mobile than inorganic As |
| Biomineralisation | Adsorption and formation of As containing minerals |
| Biosorption | Extracellular sequestration |
| Bioaccumulation | Intracellular sequestration |
| Iron oxidation | Formation of Fe(III) (hydr)oxide for As sorption |
| Mobilisation and immobilisation | |
| Iron reduction | Mobilisation: reductive dissolution of Fe (hydr)oxide<br>Immobilisation: secondary mineral sequestration |
| Sulphidisation | Mobilisation: formation of aqueous As-S complexes<br>Immobilisation: formation of As sulphide precipitates |
| Bioleaching | Mobilisation: oxidative dissolution<br>Immobilisation: secondary mineral sequestration |

**Table 4** Microorganism based arsenic bioremediation proposed in the literature to date

| Micorbial process/comments | References |
|---|---|
| *Biosorption* | |
| • Fe(III) treated *Baccilus subtulis* has 11 times higher As(V) sorption capacity than that of the native bacteria | (Yang et al. 2012) |
| • The maximum biosorption capacity of living cells of *Bacillus cereus* for As(III) was found to be 32.42 mg $g^{-1}$ at pH 7.5, at optimum conditions of contact time of 30 min, biomass dosage of 6 g $L^{-1}$, and temperature of 30 °C | (Giri et al. 2013) |
| • *Bacillus cereus* Strain W2 retained As(III) and As(V) up to 1.87 mg As $g^{-1}$ of dry cell weight and dry cell removal capacity up to 0.18 mg As $g^{-1}$ | (Miyatake and Hayashi 2011) |
| • The biosorption capacity of the *Rhodococcus* sp. WB-12 for As(III) was 77.3 mg $g^{-1}$ at pH 7.0 using 1 g $L^{-1}$ biomass with the contact time of 30 min at 30 °C | (Prasad et al. 2011) |
| Bioaccumulation | |
| • Engineering of phytochelatin producing, As transporter GlpF co-expressing and an As efflux deletion *Escherichia coli* showed a 80-fold more As accumulation than a control strain, achieving accumulation level of 16.8 μmol $g^{-1}$ (dry cell weight) | (Singh et al. 2010) |
| • *Saccharomyces cerevisiae* was engineered for 3–4-fold greater As(III) uptake and accumulation by over-expression of transporters genes FPS1 and HXT7 responsible for the influx of the contaminant coupled with and without high-level production of cytosolic As sequestors (phytochelatins or bacterial ArsRp) | (Shah et al. 2010) |
| • Engineered *Escherichia coli* expressing ArsR accumulated 50-60 times higher As(III) and As(V) than control | (Kostal et al. 2004) |
| Bioreduction | |
| • The co-presence of anthraquinone-2,6-disulfonate with As(V) respiratory reducing bacteria (*Bacillus selenatarsenatis* SF-1) improved the removal efficiency and can be an effective strategy for remediation of As-contaminated soils | (Yamamura et al. 2008) |
| Biomethylation | |
| • A synergistic degradation system combining two bacteria (*Bacillus* sp. PY1 and *Sphingomonas* sp. PY2) and a fungus (*Fusarium* sp. PY3), isolated from contaminated soils is the most effective approach to degrade pyrene and remove As in contaminated soil | (Liu et al. 2013b) |
| • Engineering the soil bacterium *Pseudomonas putida* expressing the As(III) S-adenosylmethionine methyltransferase gene has the potential for bioremediation of environmental As | (Chen et al. 2013) |
| • Soil microorganism e.g. *Trichoderma* sp., sterile mycelial strain, *Neocosmospora* sp. and *Rhizopus* sp. fungal strains could be used for soil As bioremediation via biovolatilisation | (Srivastava et al. 2011) |
| Biomineralisation | |
| • The nitrate- and sulphate-plus-lactate-amended microcosms with sediment from an aquifer with naturally elevated As levels decreased effective soluble As levels from 3.9 to 0.01 and 0.41 μM via sorption onto freshly formed hydrous ferric oxide and iron sulphide | (Omoregie et al. 2013) |
| • The biogenic Mn oxides generated by *Marinobacter* sp. MnI7-9 oxidised the highly toxic As(III) to As(V) and decreased the concentration of As(III) from 55.02 to 5.55 μM | (Liao et al. 2013) |
| • Arsenic immobilisation by biogenic Fe-mineral formed by *Acidovorax* sp. BoFeN1, an anaerobic nitrate-reducing Fe(II)-oxidising ß-proteobacteria | (Hitchcock et al. 2012) |
| • Microbial calcite precipitated by an As(III) tolerant bacterium *Sporosarcina ginsengisoli* CR5 to retain As | (Achal et al. 2012) |
| • Bioremediation strategy based on injecting nitrate to support the anoxic oxidation of Fe(II) and As(III) in the subsurface as a means to immobilise As in the form of As(V) adsorbed onto biogenic Fe(III) (hydr)oxides | (Sun et al. 2009) |

Fe (hydr)oxide during microbial Fe(III) reduction (Jiang et al. 2013). Thus, many natural substances are expected to exhibit substantial effects on the microbial processes and subsequently change the environmental behaviour of As, either directly or indirectly. One of the best known examples is natural organic matter. Although its presence may partly explain the controversial findings of Fe(III) reduction-induced As releases between lab model studies and field work in the past (Davranche et al. 2013), natural organic matter may also interact with As by (1) serving as an electron donor or carbon source to fuel Fe(III) and As(III) reduction (Lovley et al. 1996) and methylation (Zheng et al. 2013), (2) as an adsorbant to complete As adsorption to the mineral surface (Weng et al. 2009), (3) as a sorbent for As (Thanabalasingam and Pickering 1986) and (4) as an abiotic reductant for As(V) (Palmer and von Wandruszka 2010). This highlights the fact that there are still many unknown factors influencing As fate and mobility in the environment and, at the same time, that the research concerning microbial As is still in its infancy;

therefore, a thorough understanding the true As behaviour in the surface and subsurface environments under the influence of microbial activities is still very challenging.

Researching microorganism–As interactions also provides the opportunity of studying As remediation taking advantage of microbial activities (Wang and Zhao 2009). More and more studies have shown the potential to utilise (genetic engineered) microorganisms to remediate As-contaminated compartments e.g. via bioreduction (Yamamura et al. 2008), biomethylation (Chen et al. 2013; Liu et al. 2013b; Srivastava et al. 2011), biomineralisation (Achal et al. 2012; Hitchcock et al. 2012; Liao et al. 2013; Omoregie et al. 2013; Sun et al. 2009), biosorption (Giri et al. 2013; Miyatake and Hayashi 2011; Prasad et al. 2011; Yang et al. 2012) or bioaccumulation (Kostal et al. 2004; Shah et al. 2010; Singh et al. 2010). Information from some recent publications about As remediation utilising microorganisms is outlined in Table 4. Although microbial transformation may help to release solid-associated As into the gaseous or aqueous phases, no suggestion was given for the follow-up removal/treatment of mobilised As. In comparison, research into As remediation based on intra- and extra-cellular sequestration seems to be deeper. The cell retention capacity of As was largely magnified by manipulating phytochelatin producing, As transporter and As efflux genes (Singh et al. 2010) and overexpressing As-resistance regulatory proteins (Kostal et al. 2004). Although it is very difficult to have an objective comparison of the retention capacity among different methods due to inconsistencies of the experimental conditions, the proposed microorganism-based methods for As removal based on intra- and extracellular sequestration still seem to be unsatisfactory compared to the conventional abiotic methods. Currently, the retention capacity of *Rhodococcus* sp. WB-12 cells is the highest of all microorganisms in the literature, with a value of 77.3 mg $g^{-1}$ for As(III) at pH 7.0 (Prasad et al. 2011) (Table 4). However, this is far from the adsorption capacity of minerals (e.g. 300–375 mg $g^{-1}$ to hydrous ferric oxide) (Raven et al. 1998) and 1,125 mg $g^{-1}$ to amorphous $Al(OH)_3$ (Anderson et al., 1976). The microorganism-based treatment is usually advantageous over minerals due to lower costs of treatment (Wang and Zhao 2009). Thus, more extensive and deeper research into As–microorganism–mineral interactions may help to identify the appropriate conditions for improving the efficiency of microbial As remediation, making it comparable with abiotic methods.

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## Appendix 1

**Table 5** Minerals and their chemical formulas mentioned in this review

| Mineral | Chemical formula |
|---|---|
| Apatite | $Ca_5(PO_4)_3(F,Cl,OH)$ |
| Arsenolite | $As_2O_3$ |
| Arsenopyrote | FeAsS |
| Pb-As Jarosite | $PbFe_3(SO_4,AsO_4)_2(OH)_6$ |
| Birnessite | $MnO_2$ |
| Bobierrite | $Mg_3(PO_4)_2{\cdot}8H_2O$ |
| Boehmite | γ-AlOOH |
| Calcite | $CaCO_3$ |
| Calcium arsenates | $(Ca_5H_2(AsO_4)_4{\cdot}cH_2O$ |
| Enargite | $Cu_3AsS_4$ |
| Ferrihydrite | $Fe_5HO_8{\cdot}4H_2O$ |
| Goethite | α-FeO(OH) |
| Green rust | $[Fe^{II}_{(1-x)}\ Fe^{III}_x\ (OH)_2]^{x+}{\cdot}[(x/n)\ A^{n-}{\cdot}(m/n)\ H_2O]^x$ |
| Hematite | $\alpha$-$Fe_2O_3$ |
| Iron sulphide | FeS |
| Jarosite | $KFe_3(OH)_6(SO_4)_2$ |
| Mackinawite | FeS |
| Magnetite | $Fe_3O_4$ |
| Orpiment | $As_2S_3$ |
| Realgar | $As_4S_4$ |
| Rhodochrosite | $MnCO_3$ |
| Schwertmannite | $(Fe_8O_8(OH)_6(SO_4){\cdot}nH_2O)$ |
| Scorodite | $FeAsO_4{\cdot}2H_2O$ |

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