



## Review

## Arsenic behavior in river sediments under redox gradient: A review

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## HIGHLIGHTS

- In surface sediments, the fate of As is controlled by abiotic and biotic reactions.
- Studies dedicated to experimental speciation of As in pore waters remain scarce.
- The role of reduced sulfur species on As speciation is still not fully understood.
- Alternative sampling and *in situ* measurement techniques must be developed.

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## ABSTRACT

The fate of arsenic – a redox sensitive metalloid – in surface sediments is closely linked to early diagenetic processes. The review presents the main redox mechanisms and final products of As that have been evidenced over the last years. Oxidation of organic matter and concomitant reduction of oxidants by bacterial activity result in redox transformations of As species. The evolution of the sediment reactivity will also induce secondary abiotic reactions like complexation/de-complexation, sorption, precipitation/dissolution and biotic reactions that could, for instance, lead to the detoxification of some As species. Overall, abiotic redox reactions that govern the speciation of As mostly involve manganese (hydr)-oxides and reduced sulfur species produced by the sulfate-reducing bacteria. Bacterial activity is also responsible for the inter-conversion between As(V) and As(III), as well as for the production of methylated arsenic species. In surficial sediments, sorption processes also control the fate of inorganic As(V), through the formation of inner sphere complexes with iron (hydr)-oxides, that are biologically reduced in buried sediment. Arsenic species can also be bound to organic matter, either directly to functional groups or indirectly through metal complexes. Finally, even if the role of reduced sulfur species in the cycling of arsenic in sediments has been evidenced, some of the transformations remain hypothetical and deserve further investigation.

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## 1. Introduction

The behavior of arsenic in aquatic systems has been the subject of intense researches due to its potential toxicity towards organisms and human life (see for instance, the particularly alarming situation in Bangladesh in relationship with the contamination of drinking water; Argos et al., 2010; Berg et al., 2001). Unraveling the complexity and dynamic of As speciation in both oxic and anoxic environments has prompted a considerable research effort. Naturally present in the earth's crust (ranking as the 20th most abundant element) (Dowdle et al., 1996), arsenic is generally more concentrated in groundwaters, and important efforts have been made to limit the concentration of As in drinking water especially from wells (the recommended limit of arsenic in drinking-water by the World Health Organization is currently  $10 \mu\text{g L}^{-1}$ ; Burgess et al., 2010). The concentration of As has increased in numerous continental water systems due to anthropogenic activities linked to painting, mining, copper smelting, production of glass and electronic wastes, waste disposal, use of certain pesticides and herbicides (and wood preservative), animal feeding, or burning of fossil fuel (Santelli et al., 2001; Drahota et al., 2009).

Extended research on the behavior of As in freshwater systems has been carried out with a focus on evaluating the sources of contamination (Razo et al., 2004; Tessier et al., 2011), baseline concentration determination (Chen et al., 2001; Chen and Kandasamy, 2008), chemical speciation of As both in water and organisms (Šlejko et al., 2004; Raber et al., 2012; Cullen, 2014), seasonal effects on As behavior (Fattorini et al., 2008; Howard et al., 1995), and the impact of eutrophication processes on the mobility of As (Azizur Rahman and Hasegawa, 2012). However, less attention has been paid to the fate of As in the surface sediments of freshwater ecosystems, especially regarding its speciation. Indeed, due to the difficulty of handling anoxic sediments and of determining As species in pore waters, most studies are focused on the determination of the total As concentration (O'Day et al., 2004; Alves et al., 2011) associated with a modeling approach that mainly includes thermodynamic equilibrium calculations and reactive transport modeling (Sracek et al., 2004; Smith and Jaffé, 1998; Dang et al., 2014). Below the water–sediment interface, reduction of iron (hydr)oxides, oxidation of organic matter and bacterial activity generally result in an increase of As concentration in pore waters (Sullivan and Aller, 1996; Widerlund and Ingri, 1995). Since it is well known that sediments act as an efficient trap for particulate pollutants, early diagenetic processes may liberate dissolved species that can diffuse back to the overlying waters (Belzile and Tessier, 1990). Because of the complexity of the water–sediment composition, its heterogeneity and the poor spatial and temporal resolution of the dissolved As profiles that could be experimentally obtained, quantification of these fluxes still remain uncertain even if sediments act as a source of dissolved As for the overlying waters in some systems (Chaillou et al., 2003).

As the cycling of As in surface sediments is still not fully understood, several studies have focused on single reactions with the aim of providing further information on the reaction mechanisms, as well as thermodynamic and kinetic data. Reactions of interest include abiotic mechanisms such as sorption (e.g. arsenic adsorption on ferrihydrite,

Raven et al., 1998 or iron sulfides, Bostick and Fendorf, 2003), oxidation–reduction processes (e.g. redox transformation of As by Fe(II)-activated goethite, Wilkin et al., 2003a) or complexation (e.g. the evidence of new As species in complexes between As(V) and polysulfides, Couture and Van Cappellen, 2011). Reactions driven by bacterial communities were also considered (e.g. oxidation of As(III), Silver and Phung, 2005, or formation of methylated species, Bentley and Chasteen, 2002).

The main purpose of this paper is to review the geochemical and biological transformations of arsenic that might occur in surface sediments, both in the liquid and solid phases. A particular focus will be the redox abiotic and biotic transformations of arsenic, the sorption processes of As species, as well as the role played by organic matter on the mobility of As in sediments. The main reactions of precipitation/dissolution of As species will be addressed. Some general pathways will be summarized, such as affinity of As(V) towards iron (hydr)-oxides, bacterial methylation of As(III) and As(V) and precipitation of As with reduced sulfide species. Finally, we will discuss the stability of other As species that have only been evidenced from model solutions or thermodynamic equilibrium calculations, with an emphasis on the stability of As(V) in sulfidic environments.

## 2. General points on As speciation in solution

In solution, inorganic arsenical species at oxidation states +III and +V form oxo-anions that can be more or less protonated. The successive  $\text{pK}_a$  values of arsenate species  $[\text{As}(\text{V}); \text{H}_x\text{As}^{+\text{V}}\text{O}_4^{-3+x}$  with  $x = 0$  to 3] are 11.53, 6.97 and 2.20 whereas the  $\text{pK}_a$  values of arsenite  $[\text{As}(\text{III}); \text{H}_x\text{As}^{+\text{V}}\text{O}_3^{-3+x}$  with  $x = 0$  to 3] are successively 13.40, 12.13 and 9.22 (Prohaska and Stinger, 2005). For pH values commonly found in the sediments ranging between 5 and 9 (Boyd, 1995; Mudroch et al., 1998),  $\text{H}_2\text{As}^{+\text{V}}\text{O}_4^-$ ,  $\text{HAs}^{+\text{V}}\text{O}_4^{2-}$  and  $\text{H}_3\text{As}^{+\text{V}}\text{O}_3$  represent the main free inorganic As species (Table 1). In acid mine drainage (AMD), pH values can drop down to 2 or less and the inorganic As(III) and As(V) species are fully protonated. Although the behavior of As in these very peculiar systems will not be detailed in this review, some articles and reviews focus specifically on arsenic in AMD (Johnson and Hallberg, 2005; Cheng et al., 2009).

As(III) can also form carbonate complexes  $\text{As}^{+\text{III}}(\text{CO}_3)^{2-}$ ,  $\text{As}^{+\text{III}}(\text{CO}_3)^+$  and  $\text{As}^{+\text{III}}(\text{CO}_3)(\text{OH})^-$  in anaerobic environments (Silver and Phung, 2005). However, these species are thermodynamically unstable, so that even at slightly basic pH and with  $[\text{HCO}_3^-]$  closed to  $200 \text{ mg L}^{-1}$ , As–carbonate complexes only represent a few percent of the total arsenic (Bentley and Chasteen, 2002; Oremland et al., 2000; Han et al., 2007a).

## 3. Redox reactions

Arsenic behavior in surface sediments is partly controlled by redox reactions. In aquatic systems, including the overlying water and sedimentary compartment, the main As oxidation states in the liquid and solid phases are V, III, and to a lesser extent II and –I. The main redox couples possibly involved in the redox speciation of As are:  $\text{O}_2/\text{H}_2\text{O}$ ,  $\text{Mn}(\text{IV})/\text{Mn}(\text{II})$ ,  $\text{NO}_3^-/\text{N}_2$ ,  $\text{NO}_3^-/\text{NO}_2^-$ ,  $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ ,  $\text{SO}_4^{2-}/\text{HS}^-$  and  $\text{CO}_2/\text{CH}_4$ . In Fig. 1, a redox potential scale shows at pH 7 what are the main theoretical oxidants of As(III) [ $\text{O}_2$ ,  $\text{MnO}_2$  and  $\text{NO}_3^-$ ] and the main

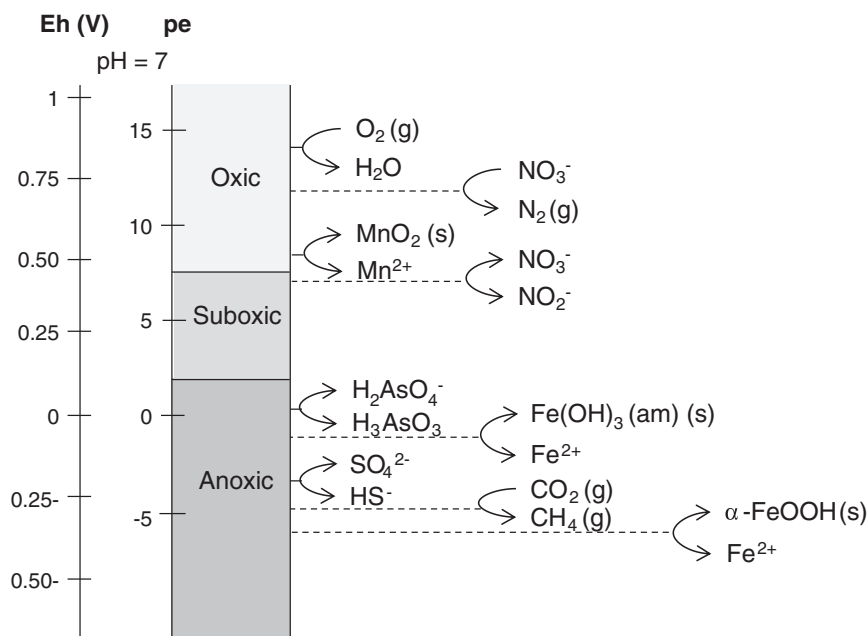
**Table 1**  
Summary of relevant studies dedicated to As behavior in surface sediments.

Matrix				Particulate phase		Surface waters/Porewaters					As speciation		Ref.
Lake	River	Sea	Range of pH	Total As	[As] exchangeable	[As] in porewaters	[As] in surface water	Range of dissolved Fe <sup>2+</sup>	Range of dissolved Mn <sup>2+</sup>	Range of dissolved sulfides	Species detected	Where? And why?	
				μg g <sup>-1</sup>	μg g <sup>-1</sup>	μg L <sup>-1</sup>	μg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>			
	x							<1400	<220				(Smith and Jaffé, 1998)
		x	8.2	<50	<4 (0.1 M NaOH) <12 (0.1 M HCl)	<45		<13,500		<7920			(Dang et al., 2014)
	x	x		<12		<225		<38					(Sullivan and Aller, 1996)
	x			<12		<100		<30	<20				(Widerlund and Ingri, 1995)
x			4–8.4	<1.4		<45		<45					(Belzile and Tessier, 1990)
						<150		<6	<4		As(III), As(V)	As(III) is predominant below the water/sediment interface.	(Chaillou et al., 2003)
x			9.8				<12 10 <sup>3</sup>			<100	As(III), As(V), thio-arsenic components	Shift in As speciation from As(V) to As(III) with the decrease of dissolved oxygen contents.	(Welz and Šucmanová, 1993)
	x						<10				As(III), As(V), DMAA <sup>III</sup> , DMAA <sup>V</sup> , MMAA <sup>III</sup> , MMAA <sup>V</sup>	Organic As species can be the main species in oxic zones	(Rey et al., 2004)
		x			<45 10 <sup>-3</sup> (1 M CH <sub>3</sub> COONa)		<10			<5500	As(III), As(V), DMAA <sup>III</sup> , DMAA <sup>V</sup> , MMAA <sup>III</sup> , MMAA <sup>V</sup>	Phytoplankton produces methylated As species in surface waters. Seasonal variation between inorganic and organic As species is observed in the exchangeable fraction of surface sediment (0–2 cm). Organic As species are linked to the degradation of organic matter, the reductive dissolution of (oxo)-hydroxides and/or bacterial methylation.	(Han et al., 2007b)
x							<3		<5 10 <sup>-2</sup>	<2	As(III), As(V), MMAA <sup>V</sup> , DMAA <sup>V</sup>	Methylated species are more present in summer than inorganic species due to the intensive phytoplankton activity.	(Mudroch et al., 1998)
		x		<35		<30					As(III), As(V), MMAA <sup>V</sup> , DMAA <sup>V</sup> , TMAO	Inorganic As species are more abundant than organic As ones.	(Boyd, 1995)
		x				<3					As(III), As(V)	As(III) becomes the main species under anoxic conditions	(Cutter, 1992)
x						<7 10 <sup>3</sup>	<45	<50	<20		As(III), As(V)	Inorganic As(III) is more abundant than inorganic As (V) under anoxic conditions.	(Aggett and Kriegman, 1988)
					<250 (1 M HCl)	<1500					As(III), As(V), MMAA <sup>V</sup> , DMAA <sup>V</sup>	The abundance of As species decreases with the depth in the following order: As(III) > As(V) > organic As species.	(Riedel et al., 1987)

theoretical reducers of As(V) [HS<sup>-</sup>, CH<sub>4</sub>, Fe<sup>2+</sup>]. In the following sections, identification of chemical oxidants and reducers able to change the redox speciation of As in surface sediments will be presented. In addition, several of these redox transformations are partly controlled by bacterial activity; for instance, the inter-conversion between As(III) and As(V) or the formation of organic As(V) and As(III) species. These aspects will also be addressed.

### 3.1. Oxidation of As(III)

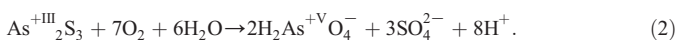
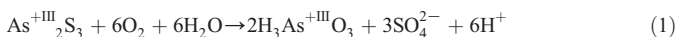
According to the literature, only manganese (hydr)-oxides and the bacterial activity are able to oxidize quantitatively As(III) in the range of pH generally encountered in aquatic environments (i.e. pH 5–9, order of magnitude) (Anderson et al., 1992; Lafferty et al., 2010a).



**Fig. 1.** Redox scale of environmentally relevant redox couples. The Eh and pe values (with  $Eh = 0.059 pe$ ) were calculated at pH 7 with concentrations of all dissolved constituents equal to 1 M except for  $Fe^{2+}$  ( $10^{-3}$  M), and  $CO_3^{2-}$  ( $3 \cdot 10^{-3}$  M). Adapted from (Borch et al., 2009).

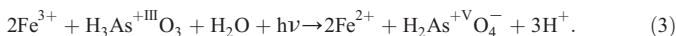
### 3.1.1. Oxygen

Although thermodynamic data predicts that dissolved oxygen can quantitatively oxidize As(III) (Fig. 1), the reaction kinetic is particularly slow with half-times ranging from several months to a year (Smedley and Kinniburgh, 2002; Santini and vanden Hoven, 2004). The oxidative dissolution of  $As_2S_3$  (orpiment) is also known to occur in the presence of dissolved oxygen, thus releasing As(III) in solution accompanied by the oxidation of S(–II) into  $SO_4^{2-}$  (Eq. (1)). However, the subsequent oxidation of As(III) to As(V) did not occur totally with a production of As(V) lower than 40% (Eq. (2)) (Lengke and Tempel, 2002).



### 3.1.2. Iron (hydr)-oxides

Oscarson et al. (1981) have shown that no significant redox reaction occurs between amorphous iron (hydr)-oxides and As(III) after 72 h of mixing at pH 7 in the absence of oxygen. More recently, similar results have been obtained with green rust, goethite, magnetite or ferrihydrite on a time scale of 24 h at pH 7 (Wilkin et al., 2003a; Planer-Friedrich et al., 2010; Planer-Friedrich and Wallschläger, 2009) (without  $O_2$ ). However, the fast oxidation of As(III) mediated by the photochemical reduction of dissolved Fe(III) have been pointed out in several studies (Azizur Rahman and Hasegawa, 2012; O'Day et al., 2004; Kumar and Riyazuddin, 2010) following the process represented in Eq. (3) (McCleskey et al., 2004):



Wang et al. (2013) performed several laboratory experiments with the aim of determining the main parameters [such as pH, concentration of humic acids (HA) and nitrogen] that can affect the photo-oxidation of As(III) to As(V) on natural goethite in suspended solution. They showed that for a reaction time of 6 h, pH values ranging between 3 and 6, and with an initial concentration of As(III) and goethite fixed at  $100 \mu g L^{-1}$  and  $100 mg L^{-1}$ , respectively, the efficiency of the photochemical

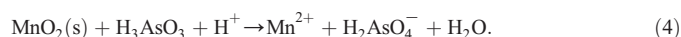
oxidation decreased gradually as pH increased, from 80% at pH 3 to 23% at pH 6. These results indicated that photo-oxidation of As(III) induced by goethite could contribute significantly to As(III) transformation in environmental systems, especially in acidic surface waters. The results are particularly pertinent for acid-mine drainage (AMD), where pH values generally range between 2 and 4 (Bigham et al., 1996). However, the presence of HA in solution resulted in a significant decrease of As(III) photo-oxidation due to the competition between HA and As(III) for active species such as hydroxyl radicals, the affinity of which to HA is high. For example, with  $5 mg L^{-1}$  of HA at pH 3, As(III) photo-oxidation efficiency decreased by 50% (Lafferty et al., 2011). Moreover, the oxidation of As(III) can occur without dissolved oxygen, even if the efficiency of the process is slightly reduced. Several factors explain this reduction, as the absence of some radical species (e.g.  $\cdot O_2^-$ ,  $HO_2\cdot$ ) generated by  $O_2$ . In addition, reaction intermediates can react directly with  $O_2$  during the oxidation of As(III) into As(V) (Buxton et al., 1988). The complexation reactions between Fe(III) and some ligands can also affect the photochemical oxidation of As(III). For example, Emmett and Khoe (2001) have established that  $Fe(III)OH^{2+}$  in acidic solution was not the only species that could generate radical species capable of transforming As(III) to As(V). In a solution containing  $Cl^-$ , the  $Fe(III)Cl^{2+}$  complex is also a source of free-radical chlorine able to catalyze photo-oxidation of As(III).

Furthermore, Ona-Nguema et al. (2010) have demonstrated that the oxidation of As(III) to As(V) by magnetite or ferrihydrite in the presence of dissolved Fe(II) can occur at neutral pH under oxic conditions. This oxidation can be interpreted as the result of a Fenton-type reaction involving Fe(II) oxidation by molecular oxygen leading to the formation of hydroxyl radicals or other highly oxidant species (e.g.  $\cdot O_2^-$  and  $H_2O_2$ ). The latter are then able to oxidize As(III) into As(V) which can in turn adsorb onto iron (hydr)-oxides produced during the oxidation reaction. In aquatic environments, the oxidation of Fe(II) and As(III) can take place simultaneously, as for instance, during sediment particle resuspension in the water column (Bostick et al., 2005). This study points out that the preservation of natural samples can be complicated for speciation analysis. Amstaetter et al. (2010) reported oxidation of As(III) to As(V) under anoxic conditions in the simultaneous presence of goethite and Fe(II) at neutral pH. In this case, reactive  $Fe(III)^*$  species are suggested to be formed after the sorption of dissolved Fe(II) on

Fe(III) phases, and this intermediate then transforms into goethite (crystallization). During the crystallization process, it is supposed that As(III) forms a ternary complex  $[\equiv\text{Fe(III)}-\text{Fe(III)}^*-\text{As(III)}]$  before its oxidation (Wilkin et al., 2003a).

### 3.1.3. Manganese (hydr)-oxides

As presented in Eq. (4), the oxidation of As(III) to As(V) by manganese (hydr)-oxides occurs in three main steps (Lafferty et al., 2010a): (i) formation of an inner-sphere complex between As(III) and a surface site of Mn(IV) (hydr)-oxides; (ii) oxidation of As(III) to As(V) combined with generation of  $\text{Mn}^{2+}$ ; and (iii) successive desorption of As(V) and  $\text{Mn}^{2+}$ . The kinetic rate of the reaction is initially fast, but slows down significantly due to passivation of the manganese-(hydr)-oxide surface (see next paragraph). Scott and Morgan (1995) showed that for pH ranging from 4 to 8, with an initial concentration of As(III) and with manganese (hydr)-oxides fixed respectively at  $100 \mu\text{mol L}^{-1}$  and  $0.25 \text{ g L}^{-1}$ , the half-concentration of As(III) is oxidized within 10 min whereas the remaining part disappears after 80 min.



Passivation of the manganese-(hydr)-oxide surface by adsorption of As(V) and  $\text{Mn}^{2+}$  accounts in part for the rapid decrease in the reaction rate with time. Depending on the surface charge of the manganese (hydr)-oxides, it decreases the number of active surface sites (Lafferty et al., 2011). Another mechanism may involve monodentate internal complexation between  $\equiv\text{Mn(IV)}$  and As(III), and/or  $\text{Mn}^{2+}$  that induces partial changes of the oxidation state of a fraction of the Mn(IV) surface sites into Mn(III) (Lafferty et al., 2010a,b). Even if this reduction does not prevent from the oxidation of As(III) into As(V) (Eq. (5)), the reactivity of  $\equiv\text{Mn(III)}$  surface sites is found to be less important than that of  $\equiv\text{Mn(IV)}$ .



Other abiotic processes can also limit the oxidation rate of As(III), as a competition of various species onto Mn (hydr)-oxide reactive adsorption sites (e.g.  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$ , Lafferty et al., 2011) or formation of surface precipitates that inhibit the reactivity of Mn (hydr)-oxides (e.g. aluminum and iron (hydr)-oxides, calcite, organic matter coating). It is worth noting that the presence of dissolved oxygen does not interfere with the oxidation kinetics of As(III) into As(V) onto Mn (hydr)-oxides (Oscarson et al., 1983).

### 3.1.4. Bacterial activity

Bacteria species, e.g.: *Alcaligenes faecali*, *Agrobacterium tumefaciens*, and *Rhizobium* sp., are able to synthesize arsenite oxidases, which permit the enzymatic oxidation of As(III) into As(V) (Anderson et al., 1992; Inskip et al., 2007). Oxidase enzymes can be either periplasmic ( $\alpha$ -Proteobacteria) or bound to external membrane (*A. faecali*) (Emerson and Moyer, 1997). Bacterial oxidation allows bacteria to obtain an electron source required for their metabolism, and can be viewed as a process of detoxification since inorganic As(V) is less toxic than inorganic As(III).

### 3.1.5. Other oxidants

As for nitrate and sulfate, the literature does not contain any information concerning their ability to oxidize chemically As(III) to As(V), although oxidation by such oxidants does seem to be thermodynamically possible, as shown in Fig. 1.

## 3.2. Reduction of As(V)

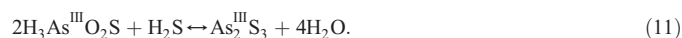
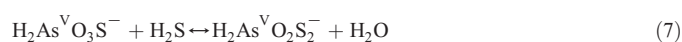
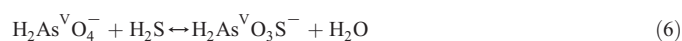
The reduction process of As(V) to As(III) is mainly effective in the presence of sulfides and a bacterial activity. Fe(II), Mn(II),  $\text{NO}_2^-$  and

$\text{NH}_4^+$  are not recognized as relevant As(V) reducing agents in aquatic systems.

### 3.2.1. Sulfides

Although the formation of stable thio-arsenical species may increase the apparent solubility of As (Welz and Šucmanová, 1993), As speciation in sulfidic waters is still poorly understood due to the difficulty to implement reliable analytical procedures (Razo et al., 2004; Delnomdedieu et al., 1994; Suess et al., 2011). Some studies have established the existence of both thioarsenites ( $\text{AsO}_3 - x\text{S}_x^{3-}$  with  $x = 0$  to 4) and thioarsenates ( $\text{AsO}_4 - x\text{S}_x^{3-}$  with  $x = 0$  to 4) as important aqueous species (O'Day et al., 2004; Wilkin et al., 2003b; Millero et al., 1987), but the existence of thioarsenates may result from an analytical artifact. For example, Planer-Friedrich et al. (2010) have experimentally observed that thioarsenite can be decomposed into inorganic As(III) under anaerobic conditions, or into thioarsenate under aerobic conditions during IC-ICP-MS analysis when using a highly alkaline eluent. Using thermodynamic equilibrium calculations, Couture and Van Cappellen (2011) suggested the presence of stable thioarsenates in sulfidic pore waters via oxidation of As(III) by elemental sulfur. Other results suggest that in sulfide-containing solutions without any oxidants, As(III) undergoes disproportionation to thioarsenates and elemental arsenic (Stauder et al., 2005).

Dissolved hydrogen sulfide can reduce As(V) into As(III). These experiments were performed in anoxic condition at pH 4 in the presence of inorganic As(V) and sulfides at initial concentrations of  $133 \mu\text{M}$  and  $266 \mu\text{M}$ , respectively (Rochette et al., 2000). Several intermediate forms of thioarsenic species are produced during the reaction (Eqs. (6)–(11)), and these can remain in solution for several days. Once the production of As(III) occurs,  $\text{As}_2\text{S}_3$  (orpiment) can precipitate depending on the concentrations of dissolved sulfides (Eq. (11)) (Rochette et al., 2000). However, these reduction mechanisms should be consolidated by additional studies on arsenic speciation in sulfidic waters.



Sun (2010) performed several laboratory experiments to show the main factors — such as pH, presence of Fe(II),  $\text{S}^\circ$  and  $\text{O}_2$  — which can affect the reduction of As(V) to As(III) in sulfidic aquatic systems. Without oxygen, a faster reduction rate of As(V) was observed at pH 4 compared with pH 7 (and pH 10), with half-reaction times of 40 h and > 140 h, respectively. This difference can be explained by the fact that  $\text{H}_2\text{S}$  species, which is prevalent at  $\text{pH} < 7$ , is more reactive than  $\text{HS}^-$ . As for  $\text{S}^\circ$ , its



association with sulfides to form polysulfides would promote reductants much stronger than  $S^{2-}$  (Sun, 2010), resulting in a faster reduction of As(V).

It is well known that in anoxic water and porewater,  $Fe^{2+}$  precipitates quickly with sulfides to produce iron sulfides (e.g. troilite, mackinawite, greigite) that subsequently turn into pyrite under various kinetic rates. Since the reduction of As(V) by Fe(II) has never been commented upon and does not seem to be promoted based on thermodynamic calculations, the loss of soluble As(V) by the addition of  $Fe^{2+}$  is instead attributed to its sorption and/or co-precipitation with iron sulfide minerals. Besides, the fact that the reduction rate of As(V) slows down progressively can be attributed to sulfide oxidation in aerobic media, enhanced by the formation of Fe(III) (Millero et al., 1987; Millero, 1991) and to the possible partial reoxidation of As(III) during the oxidation of  $Fe^{2+}$  (see Section 3.1). The presence of oxygen does not re-oxidize As(III) into As(V). However, oxygen has been demonstrated to immediately oxidize thioarsenites into thioarsenate (Razo et al., 2004), thus inhibiting any eventual reduction process of As(V) to As(III).

### 3.2.2. Thio-organic components

Delnomdedieu et al. (1994) have observed that glutathione (GSH) can cause the reduction of both As(V) into As(III), and monomethyl arsenic(V) acid (MMAA<sup>V</sup>) into monomethylarsine (MMA<sup>III</sup>). The redox reaction is further enhanced by the formation of a stable complex between glutathione and As(III) at pH values below 7.0–7.5. The capacity to form such stable As(III)–thiol complexes is also used in analytical methods, where L-cysteine is commonly used to transform As(V) to As(III) (Cullen and Reimer, 1989; Thomas et al., 2004). Furthermore, cysteine is one of the molecular constituents of arsenate reductase, used by some bacteria to reduce As(V) into As(III) (Gihring and Banfield, 2001).

### 3.2.3. Biological activity

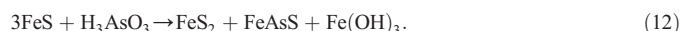
The biological transformations of both inorganic and organic As(V) species into As(III) species can be achieved through the bacterial activity that occurs in aquatic systems, through either detoxification or dissimilatory reduction. Because of the inherent toxicity of arsenic, which depends on the species (As(III) > As(V) > MMAA<sup>V</sup> > DMAA<sup>V</sup>; Prohaska and Stinger, 2005) and its structural analogy with orthophosphate species, numerous micro-organisms have developed detoxification processes to convert absorbed As – especially inorganic As that is recognized as the most toxic species – into other less toxic organic species and/or into species that can be more easily extracted from the biological cell through the “As(III)-efflux system” (Gihring and Banfield, 2001). The methylation of inorganic As is thought to be a process of detoxification which can be performed by some mushrooms and bacteria in sediment (Cullen and Reimer, 1989). In the case of As(V) methylation, the first step consists in the conversion of

As(V) into As(III), followed by one or several methylation steps (Fig. 2) to form less toxic organo-arsenical species, such as MMAA<sup>V</sup> [monomethyl arsenic(V) acid], DMAA<sup>V</sup> [dimethyl arsenic(V) acid], TMAO (trimethylarsenic oxide) and eventually trimethylarsine [As<sup>+III</sup>(CH<sub>3</sub>)<sub>3</sub>] (Cullen, 2014; Thomas et al., 2004; Kosmulski, 2011). It is worth noting that under anaerobic conditions, some bacteria, fungi and yeasts are able to transform methylated As species into volatile As forms, such as arsine (As<sup>+III</sup>H<sub>3</sub>) and other methylated arsine species (Bissen and Frimmel, 2003a; Suess and Planer-Friedrich, 2012). Significant levels of organic As species can be found seasonally in surface water (Mudroch et al., 1998; Rey et al., 2004; Han et al., 2007b). However, these species represent generally less than 5% of the total As in interstitial water (Boyd, 1995) or in the As mobile fraction of the sediment (Huerga et al., 2005).

The second bacterial transformation aimed at limiting As(V) toxicity is the dissimilatory reduction, also known as bacterial respiration. This has been described for some bacterial metabolisms in various compartments of the geosphere, e.g. aquifers, freshwaters, alkaline and salt lakes, and hydrothermal springs (Dowdle et al., 1996; Oremland et al., 2000; Ma and Lin, 2012). The bacterial respiration of As is a process in which the reduction of As(V) dissolved or adsorbed onto the mineral surface is coupled with the oxidation of a wide variety of electron donors (e.g. H<sub>2</sub>, lactate, malate) (Laperche et al., 2003). Currently, no bacteria species is known to use strictly As(V) as an electron acceptor, and other oxidants like Cr(VI), Fe(III), NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and U(VI) can be employed by these bacteria as well. In fact, these microorganisms are considered as opportunists and can harness energy from one electron acceptor rather than another if the species reduction is thermodynamically more favorable and its bioavailable concentration is high enough (Fendorf et al., 2010). It is also worth noting that the detoxification process can occur in oxygenated water, explaining partly the presence of As(III) even in oxic media (contrary to thermodynamic predictions).

### 3.3. Reduction of As(III)

Arsenopyrite [Fe(II)As(-I)S(-I)] and realgar [As(II)S(-II)] are often present in sediments and soils (Nicholas et al., 2003). The unusual oxidation states of As in these minerals, i.e. -I and +II, appear to result from the reduction of As(III) by iron sulfide minerals (pyrite, troilite, greigite, etc.). Bostick and Fendorf (2003) suggest a formation mechanism of FeAsS in which As(III) may adsorb on a sulfide precipitate, before being reduced into As(-I), as illustrated Eq. (12). However, this mechanism still needs to be confirmed.



Native As is a product of low-temperature epithermal mineralization (50–200 °C) under sulfur deficient and strongly reducing conditions. In low-temperature sedimentary conditions (0–50 °C) there is frequently

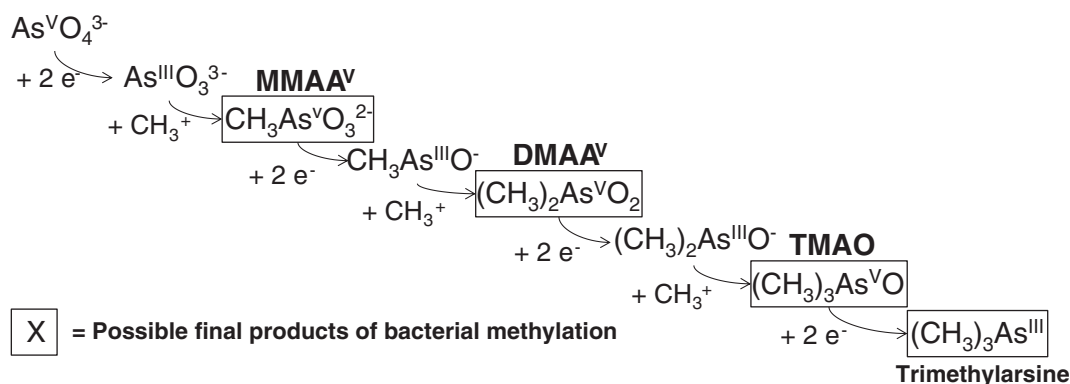
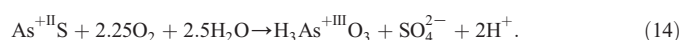
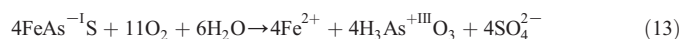


Fig. 2. Hypothetical scheme of bacterial methylation, where enzymatic species are not included in the reactions.

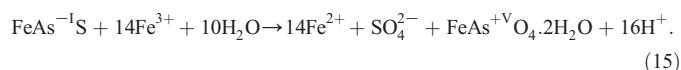
much more sulfur and iron available than arsenic, so that As is incorporated into arsenian pyrite or orpiment rather than occurring under the native form (Nordstrom and Archer, 2003). Concerning As(–III), no information concerning its possible presence in river sediment is recorded in the literature.

#### 3.4. Oxidation of As(–I) and As(II)

Lengke and Tempel (2002, 2003) and Walker et al. (2006) have demonstrated that dissolved oxygen was able to oxidize  $\text{As}^{+II}\text{S}$  and  $\text{FeAs}^{-I}\text{S}$  at pH values close to 7 (Eqs. (13) and (14)). The oxidation would take place on the mineral surfaces, leading to the formation of As(III) that is further desorbed (Lengke and Tempel, 2003).



In oxygen-free solutions, the oxidation of FeAsS by Fe(III) in mine wastes produces “scorodite” ( $\text{Fe}^{III}\text{As}^{\text{V}}\text{O}_4$ ) as shown in Eq. (15) (Alves et al., 2011). This oxidation is only limited by the ferric iron available in solution unless iron-oxidizing bacteria (e.g. *Acidithiobacillus ferrooxidans*, *Thiobacillus ferrooxidans*) are present to reoxidize directly the Fe(II) present in arsenopyrite into Fe(III) (Belzile and Tessier, 1990; Chaillou et al., 2003; Raven et al., 1998).



#### 4. Reactions of dissolution/precipitation

Since the sedimentary particles contain sulfur, alkaline and transition metals in high proportion (for some, >1%), the solubility of As in pore waters may be partly controlled by the formation of several precipitates with these elements. The topic has been studied extensively and some reviews provide an overall view of the reactions of precipitation/dissolution involving As (Smedley and Kinniburgh, 2002; Drahotka et al., 2009; Mandal and Suzuki, 2002).

Although As(V) is known to form many insoluble compounds with various metals such as Cr, Pb or Cu [ $\text{CrAs}^{+V}\text{O}_4$ ,  $\text{Pb}_3(\text{As}^{+V}\text{O}_4)_2$ ,  $\text{Cu}(\text{As}^{+V}\text{O}_4)_2$ , etc.], the concentration of metals in porewaters is generally too low to achieve the solubility product of the precipitates. It appears that only scorodite ( $\text{FeAs}^{+V}\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) and magnesium arsenite [ $\text{Mg}_3(\text{As}^{+V}\text{O}_4) \cdot 8\text{H}_2\text{O}$ ] for As(V), and various associations between reduced As and sulfides ( $\text{As}^{+III}_2\text{S}_3$ ,  $\text{As}^{+II}\text{S}$  and  $\text{FeAs}^{-I}\text{S}$ ) can precipitate. For more information, see the reviews on arsenic dissolution/precipitation, e.g. Smedley and Kinniburgh (2002), Drahotka et al. (2009), and Mandal and Suzuki, (2002). In addition, numerous studies in the field of water treatment have shown that inorganic As(V) can co-precipitate under certain physico-chemical conditions (e.g. pH and specific solubility of the precipitating agent) with  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{CaCO}_3$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{FeCl}_3$ ,  $\text{Mg}(\text{OH})_2$  and  $\text{MnO}_2$  (Bissen and Frimmel, 2003a,b; Clara and Magalhaes, 2002). Masscheleyn et al. (1991) have noticed that the solubility of arsenic is strongly dependent on redox potential (Eh) variations in the subsurface environment. Generally, the solubility of As tends to increase with decreasing Eh values (Ye et al., 2013). Indeed, since As(V) is the dominant species in oxic sediment and overlying waters (+200 to +500 mV), it is efficiently adsorbed and/or (co)-precipitated with various minerals, particularly iron and manganese (hydr)-oxides. Further reduction of these (hydr)-oxides under moderately reducing conditions (0 to +100 mV) results in the partial dissolution of As(V) in porewaters. However, when the sediment turns strongly anoxic (0 to –200 mV), reduction of As(V) into As(III) occurs, combined with the production of sulfides. As As(III)–S(–II) complexes are very stable in

solution, the concentration of As may still increase unless the solubility product of  $\text{As}_2\text{S}_3$  is achieved.

#### 5. Reactions of adsorption

Arsenic can adsorb on various solid phases encountered in sediments, including aluminum, iron and manganese (hydr)-oxides, clays and organic matter. The distribution between the liquid and the solid phases depends on arsenic concentration, arsenic speciation, competing ions, pH, and adsorption properties of the solid surface, e.g. coating or isomorphic substitution (Fendorf et al., 2010; Bissen and Frimmel, 2003b; Wang et al., 2009).

Usually, adsorption mechanisms can be described as non-specific adsorption (outer-sphere surface complexation) and specific adsorption (inner-sphere surface complexation). Note that the sphere of hydration is only maintained for the non-specific adsorption. Inner-sphere complexes are characterized by coordinated covalent bonds which are more stable than the electrostatic interactions of the outer-sphere complexes. The formation of inner-sphere complexes is the main mechanism for the sorption of As(III) and As(V) (Cheng et al., 2009; Arai et al., 2005; Catalano et al., 2008; Manning et al., 1998; Grossl et al., 1997) as illustrated in Fig. 3, and involves specific functional groups at the mineral surface, such as hydroxyl groups (Komárek et al., 2013).

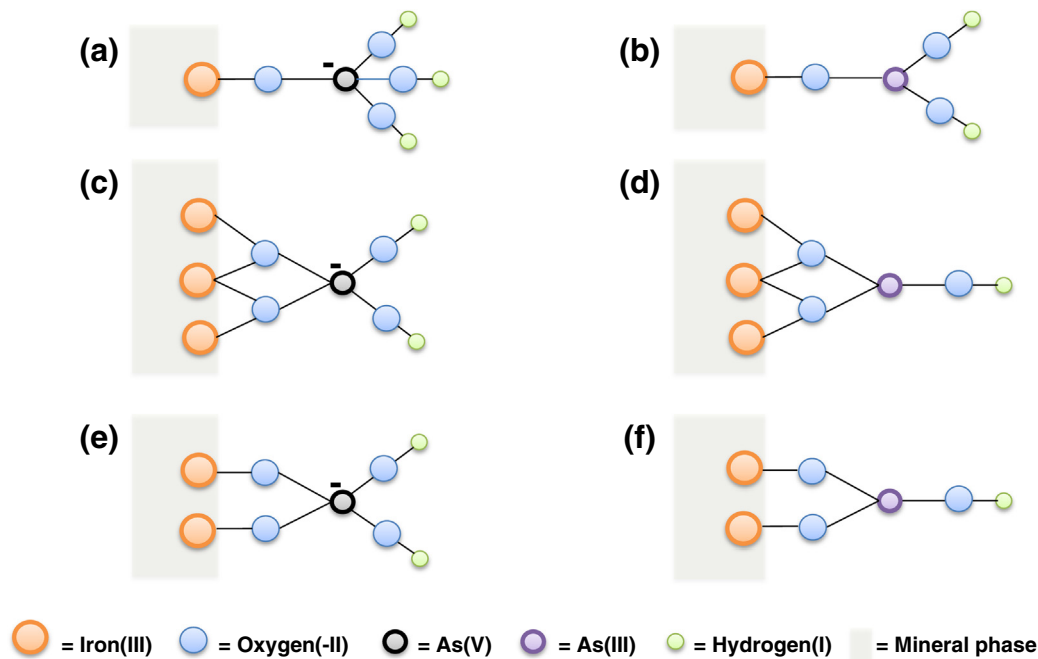
##### 5.1. Sorption onto mineral surfaces

Because of the amphoteric nature of mineral surfaces, the surface charge of hydroxyl groups is positive when the pH is below pH of zero charge (point of zero charge), and negative when  $\text{pH} > \text{pH}$  of zero charge. It can be described in Eqs. (16) and (17), where  $\equiv\text{X}$  corresponds to a surface site:



A positive surface charge commonly promotes the complexation of anionic arsenical species such as As(V),  $\text{DMAA}^{\text{V}}$  and  $\text{MMAA}^{\text{V}}$  that are negatively charged for pH values higher than 2.2, 3.4 and 1.6 respectively. The variations of surface charge, as a function of pH for some minerals present in sediments, are represented in Fig. 4. This indicates the minerals capable of adsorbing those anionic arsenical species in the range of pH observed in sediments. It includes all the minerals from  $\alpha\text{-MnO}_2$  (for acidic pH values in sediments around 5) to magnesium oxides. Sorption processes of As(III) are more complex because  $\text{H}_3\text{As}^{+III}\text{O}_3$ , which is the main species at pH 5–9, is electrically neutral. As(III) is essentially adsorbed on iron (hydr)-oxides, and its adsorption is not pH-dependent and not as strong as As(V). Dixit and Hering (2003) observed in batch experiments [50 mM As(III) or As(V) mixed with 30  $\text{mg L}^{-1}$  hydrous ferric oxides] that sorption of As(V) onto iron (hydr)-oxides is more favorable below a pH of zero charge of oxides ranging between 7 and 10 (Kosmulski, 2011). As(III) exhibits a different behavior since its adsorption capacity is almost constant (around 80%) in the range of pH 5–9.

At pH 4, Fendorf et al. (2010) showed experimentally that the affinity of As(V) for several minerals decreases as follows: iron (hydr)-oxides (40 to 2100  $\text{mmol kg}^{-1}$ ) > aluminum (hydr)-oxides (20 to 1700  $\text{mmol kg}^{-1}$ ) > manganese (hydr)-oxides (16  $\text{mmol kg}^{-1}$ ) > aluminosilicates (0.4 to 0.5  $\text{mmol kg}^{-1}$ ). These results confirm that Fe and Al (hydr)-oxides are the main host phases for As(V) adsorption in sediments. Moreover, the amorphous forms of iron (hydr)-oxides allow for a better retention of arsenic than for crystallized ones (Bowell, 1994). It has also been shown that whatever the pH, inorganic As(V) remains the most impacted species by sorption processes with a retention capacity on

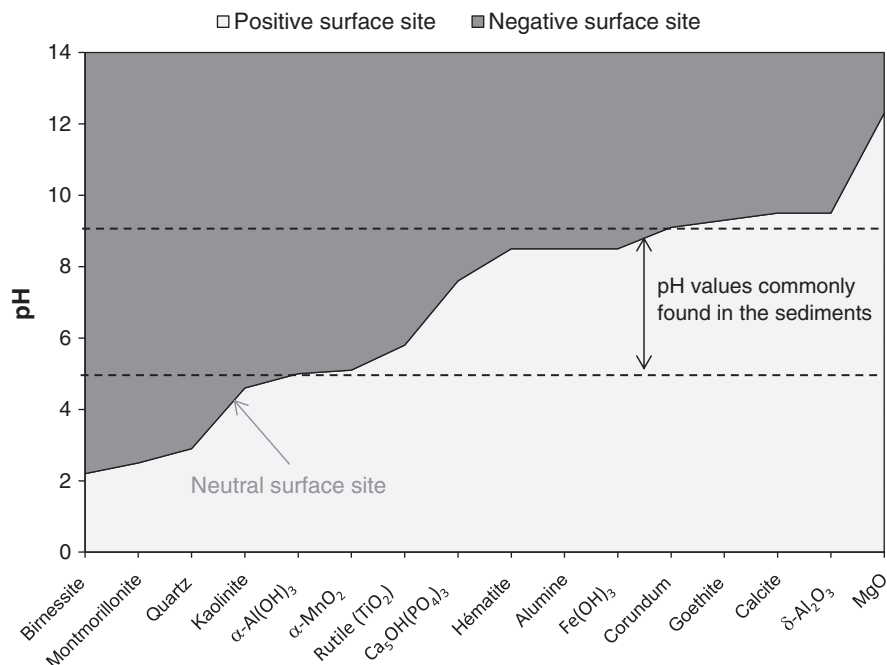


**Fig. 3.** Schematic representation of As (III and V) configurations on metal (hydr)-oxide surfaces: (a, b) mononuclear monodentate inner-sphere complexation; (c, d) mononuclear bidentate inner-sphere complexation; (e, f) binuclear bidentate inner-sphere complexation.

minerals that decreases in acidic media in the following order:  $\text{As(V)} \geq \text{DMAA}^{\text{V}} = \text{MMAA}^{\text{V}} > \text{As(III)}$ . Above pH 6–7, this ranking of retention capacity turns to:  $\text{As(V)} > \text{As(III)} \geq \text{MMAA}^{\text{V}} = \text{DMAA}^{\text{V}}$  (Xu et al., 1991; Redman et al., 2002).

Several anions ( $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{SO}_4^{2-}$ , etc.) found in porewaters with concentrations ranging between  $\mu\text{M}$  and  $\text{mM}$  levels (Kim et al., 2000), can also affect the sorption of As species on mineral solid phases. Isotherm experiments performed on a Mg–Al– $\text{CO}_3$  hydroxide have shown that As(V) adsorption capacity decreases generally in the presence of competing anions in the

following order:  $\text{HPO}_4^{2-} > \text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{F}^-$  (Hug and Leupin, 2003). A similar study for As(III), using Fe–Mn (hydr)-oxides as adsorbent, demonstrated that several anions decrease the sorption capacity of As(III) as follows:  $\text{HPO}_4^{2-} > \text{SiO}_3^{2-} > \text{CO}_3^{2-} > \text{SO}_4^{2-}$  (Zhang et al., 2007). In both cases,  $\text{HPO}_4^{2-}$  appears to be the main competing ion due to its chemical similarity with arsenic. That explains why  $\text{HPO}_4^{2-}$  is often used as an extracting agent of As in single-step extraction (Orero Iserete et al., 2004; Georgiadis et al., 2006) or sequential extraction (Keon et al., 2001; Wenzel et al., 2001; Paul et al., 2009) for soils or sediments.



**Fig. 4.** Evolution of the surface charge of common minerals found in sediments as a function of pH (values extracted from (Cheng et al., 2009)).



5.2. Sorption involving organic matter

Natural organic matter represents an important phase in sediments, but its chemical and structural composition is highly variable and only partially characterized, e.g. aromaticity, elemental composition, nature and content of functional groups or molecular size. Some functional groups (–OH, –COOH, –NH<sub>2</sub>, –SH) are known to potentially influence As sorption. First, As can adsorb on organic solid phases combined with the help of some cations (primarily Al, Fe and Mn) forming cationic bridges between the anionic As species and the negative surface charge of the particulate organic matter (Redman et al., 2002; Mikutta and Kretzschmar, n.d.; Buzek et al., 2013). Secondly, direct interactions

between As and some functional groups, such as –SH, –COOH, –C<sub>6</sub>H<sub>4</sub>OH and –NH<sub>2</sub>, can also occur. For example, Bennett et al. (2011) developed a selective DGT (Diffusive Gradient in Thin film) for As(III) based on the affinity between As(III) and –SH group, by using a 3-mercaptopropyl-functionalized silica gel. Other studies have demonstrated that As(III) can form stable complexes with dissolved thio-organic components (cysteine, dithiothreitol, glutathione, etc.) (Neuberger and Helz, 2005; Buschmann et al., 2006).

Buschmann et al. (2006) evaluated the affinity of all the inorganic As species for dissolved humic substances using dialysis experiments at different pH values ranging between 4 and 9. They concluded that As(V) was always bound more strongly than As(III) whatever the pH

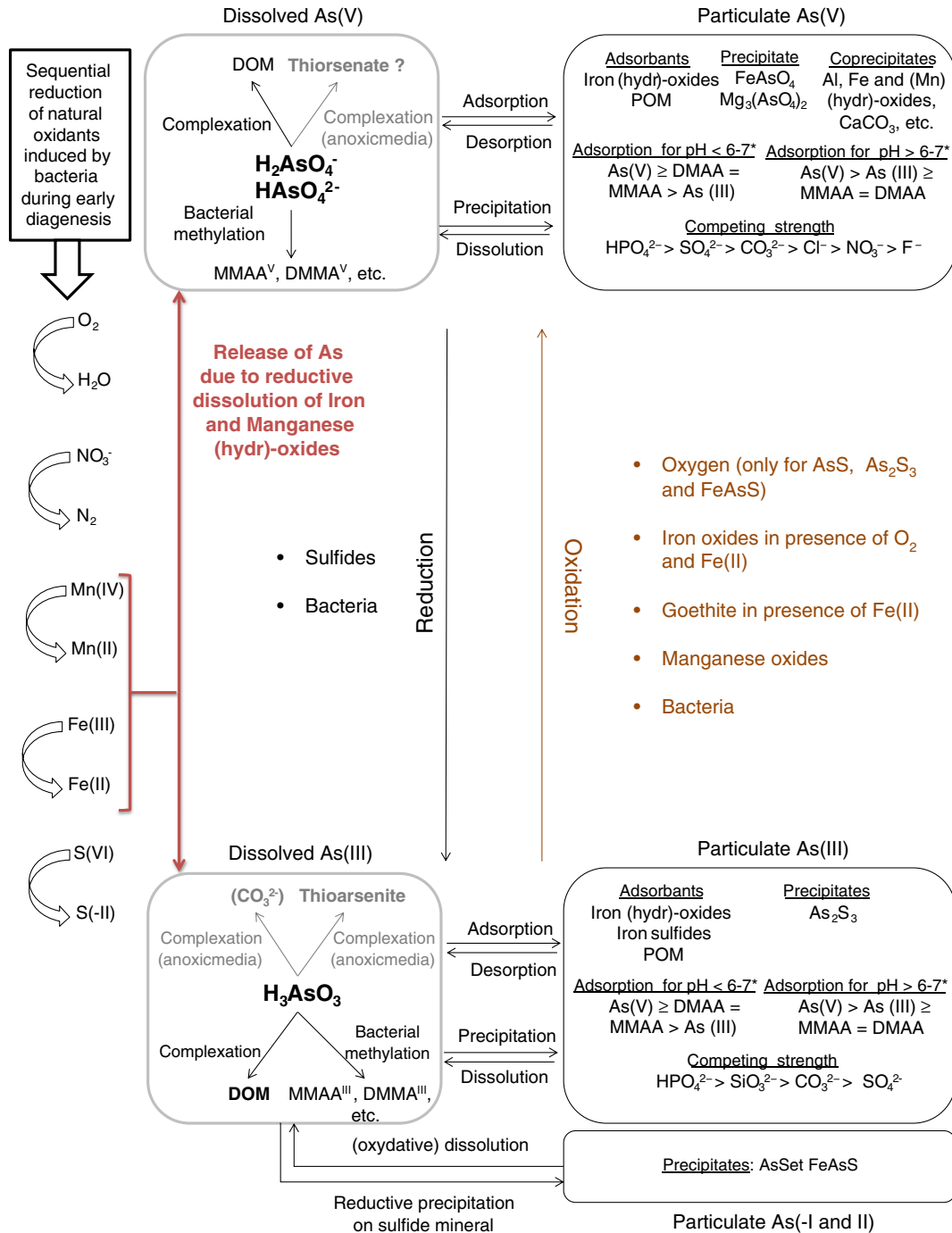


Fig. 5. Summary of arsenic reactions in surface sediment during early diagenetic processes. Abbreviations: DOM: dissolved organic matter; POM: particulate organic matter; MMAA<sup>V</sup>: monomethyl As(V) acid; DMMA<sup>V</sup>: dimethyl As(V) acid; \* results obtained under oxic conditions.

value with a maximum capacity around pH 7. For example at pH 7.2, the distribution coefficient of As(III) and As(V) was around 3000 and 18,000 L kg<sup>-1</sup>, respectively. For As(III) that forms neutral hydroxo complexes [As(OH)<sub>3</sub>] up to pH 9, the phenolate group is a stronger ligand than the carboxylate one. The binding capacity is influenced by H<sup>+</sup> competition for humic functional groups at low pH values and OH<sup>-</sup> competition for As(III) at high pH values. Moreover, the neutral As(OH)<sub>3</sub> species might also partly bind to humic acids by hydrophobic interactions. In contrast to As(III), As(V) is negatively charged for pH > 4.6. Even if both reagents (humic acids and arsenates) are negatively charged, strong binding involving a liberation of water has been pointed out (Santini and vanden Hoven, 2004).

## 6. Conclusion

In surface sediments, the fate of arsenic is controlled by abiotic and biotic reactions, including complexation/de-complexation, sorption, precipitation/dissolution, redox, detoxification and respiration reactions. This review presents the main mechanisms that have been discovered over the last few years in sediments during early diagenetic processes, as summarized in Fig. 5. It has been clearly established that sorption processes on iron hydroxides, the presence of organic matter and the sulfides phases and bacterial activity represent critical points for understanding the dynamic of arsenic under redox gradients that commonly occur in the first centimeters of river sediments.

Although numerous processes have been clearly established by experiments or deduced from thermodynamic equilibrium calculations, dedicated studies to experimental speciation of As in pore waters remains scarce (see summary, Table 1), and additional works are needed to validate the mechanisms occurring at the pore scale and establish the speciation in sediments. More precisely, the role of reduced sulfurs on both As speciation and mobility is still not fully understood, although they should control the mobility of both As(III) and As(V) compounds in anoxic and sulfidic conditions. Additionally, since these transformations may occur within the first cm of the sedimentary column which is mainly under anoxic conditions, alternative sampling and *in situ* measurement techniques must be developed with the aim of increasing the spatial resolution and limiting the changes in pore water composition that could occur during the sampling or/and the treatment in the laboratory.

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## References

Aggett J, Kriegman MR. The extent of formation of arsenic(III) in sediment interstitial waters and its release to hypolimnetic waters in Lake Ohakuri. *Water Res* 1988;22(4):407–11.

Alves G, Magalhães JM, Salaün P, Van den Berg CM, Soares HM. Simultaneous electrochemical determination of arsenic, copper, lead and mercury in unpolluted fresh waters using a vibrating gold microwire electrode. *Anal Chim Acta* 2001;703(1):1–7.

Amstaetter K, Borch T, Laresse-Casanova P, Kappler A. Redox transformation of arsenic by Fe(II)-activated goethite (α-FeOOH). *Environ Sci & Technol* 2010;44(1):102–8.

Anderson GL, Williams J, Hille R. The purification and characterization of arsenite oxidase from *Alcaligenes faecalis*, a molybdenum-containing hydroxylase. *J Biol Chem* 1992;267(33):23674–82.

Arai Y, Sparks DL, Davis JA. Arsenate adsorption mechanisms at the allophane–water interface. *Environ Sci Technol* 2005;39(8):2537–44.

Argos M, Kalra T, Rathouz PJ, Chen Y, Pierce B, Parvez F, et al. Arsenic exposure from drinking water, and all-cause and chronic-disease mortalities in Bangladesh (HEALS): a prospective cohort study. *Lancet* 2010;376(9737):252–8.

Azizur Rahman M, Hasegawa H. Arsenic in freshwater systems: influence of eutrophication on occurrence, distribution, speciation, and bioaccumulation. *Appl Geochem* 2012;27(1):304–14.

Belzile N, Tessier A. Interactions between arsenic and iron oxyhydroxides in lacustrine sediments. *Geochim Cosmochim Acta* 1990;54(1):103–9.

Bennett WW, Teasdale PR, Panther JG, Welsh DT, Jolley DF. Speciation of dissolved inorganic arsenic by diffusive gradients in thin films: selective binding of As(III) by 3-mercaptopropyl-functionalized silica gel. *Anal Chem* 2011;83(21):8293–9.

Bentley R, Chasteen TG. Microbial methylation of metalloids: arsenic, antimony, and bismuth. *Microbiol Mol Biol Rev* 2002;66(2):250–71.

Berg M, Tran HC, Nguyen TC, Pham HV, Schertenleib R, Giger W. Arsenic contamination of groundwater and drinking water in Vietnam: a human health threat. *Environ Sci & Technol* 2001;35(13):2621–6.

Bigam JM, Schwertmann U, Pfaf G. Influence of pH on mineral speciation in a bioreactor simulating acid mine drainage. *Appl Geochem* 1996;11(6):845–9.

Bissen M, Frimmel FH. Arsenic — a review. Part II: oxidation of arsenic and its removal in water treatment. *Acta Hydrochim Hydrobiol* 2003a;31(2):97–107.

Bissen M, Frimmel FH. Arsenic — a review. Part I: occurrence, toxicity, speciation, mobility. *Acta Hydrochim Hydrobiol* 2003b;31(1):9–18.

Borch T, Kretzschmar R, Kappler A, Cappellen PV, Ginder-Vogel M, Voegelín A, et al. Biogeochemical redox processes and their impact on contaminant dynamics. *Environ Sci & Technol* 2009;44(1):15–23.

Bostick BC, Fendorf S. Arsenite sorption on troilite (FeS) and pyrite (FeS<sub>2</sub>). *Geochim Cosmochim Acta* 2003;67(5):909–21.

Bostick B, Fendorf S, Brown G. In situ analysis of thioarsenite complexes in neutral to alkaline arsenic sulphide solutions. *Mineral Mag* 2005;69(5):781–95.

Bowell RJ. Sorption of arsenic by iron oxides and oxyhydroxides in soils. *Appl Geochem* 1994;9(3):279–86.

Boyd CE. *Bottom soils, sediment, and pond aquaculture*. 348. Springer; 1995.

Burgess W, Hoque M, Michael H, Voss C, Breit G, Ahmed K. Vulnerability of deep groundwater in the Bengal Aquifer System to contamination by arsenic. *Nat Geosci* 2010;3(2):83–7.

Buschmann J, Kappeler A, Lindauer U, Kistler D, Berg M, Sigg L. Arsenite and arsenate binding to dissolved humic acids: influence of pH, Type of Humic Acid, and Aluminum. *Environ Sci Technol* 2006;40(19):6015–20.

Buxton GV, Greenstock CL, Helman WP, Ross AB. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (•OH/•O<sup>-</sup>) in aqueous solution. *J Phys Chem Ref Data* 1988;17(2):513–886.

Buzek F, Cejkova B, Dousova B, Jackova I, Kadlecova R, Lnenickova Z. Mobilization of arsenic from acid deposition — the Elbe River catchment, Czech Republic. *Appl Geochem* 2013;33:281–93.

Catalano JG, Park C, Fenter P, Zhang Z. Simultaneous inner- and outer-sphere arsenate adsorption on corundum and hematite. *Geochim et Cosmochim Acta* 2008;72(8):1986–2004.

Chaillou G, Schäfer J, Anschutz P, Lavaux G, Blanc G. The behaviour of arsenic in muddy sediments of the Bay of Biscay (France). *Geochim et Cosmochim Acta* 2003;67(16):2993–3003.

Chen C-T, Kandasamy S. Evaluation of elemental enrichments in surface sediments off southwestern Taiwan. *Environ Geol* 2008;54(6):1333–46.

Chen M, Ma LQ, Hoogeweg CG, Harris W. Arsenic background concentrations in Florida, USA surface soils: determination and interpretation. *Environ Forensic* 2001;2(2):117–26.

Cheng H, Hu Y, Luo J, Xu B, Zhao J. Geochemical processes controlling fate and transport of arsenic in acid mine drainage (AMD) and natural systems. *J Hazard Mater* 2009;165(1–3):13–26.

Clara M, Magalhaes F. Arsenic. An environmental problem limited by solubility. *Pure Appl Chem* 2002;74(10):1843–50.

Couture R-M, Van Cappellen P. Reassessing the role of sulfur geochemistry on arsenic speciation in reducing environments. *J Hazard Mater* 2011;189(3):647–52.

Cullen WR. Chemical mechanism of arsenic biomethylation. *Chem Res Toxicol* 2014;27:457–61.

Cullen WR, Reimer KJ. Arsenic speciation in the environment. *Chem Rev* 1989;89(4):713–64.

Cutter GA. Kinetic controls on metalloid speciation in seawater. *Mar Chem* 1992;40(1–2):65–80.

Dang DH, Tessier E, Lenoble V, Durrieu G, Omanović D, Mullot J-U, et al. Key parameters controlling arsenic dynamics in coastal sediments: an analytical and modeling approach. *Mar Chem* 2014;161:34–46.

Delnomdedieu M, Basti MM, Otvos JD, Thomas DJ. Reduction and binding of arsenate and dimethylarsinate by glutathione: a magnetic resonance study. *Chem Biol Interact* 1994;90(2):139–55.

Dixit S, Hering JG. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility. *Environ Sci Technol* 2003;37(18):4182–9.

Dowdle PR, Laverman AM, Oremland RS. Bacterial dissimilatory reduction of arsenic (V) to arsenic (III) in anoxic sediments. *Appl Environ Microbiol* 1996;62(5):1664–9.

Drahota P, Rohovec J, Filippi M, Mihaljevič M, Rychlovský P, Červený V, et al. Mineralogical and geochemical controls of arsenic speciation and mobility under different redox conditions in soil, sediment and water at the Mokrsko-West gold deposit. *Czech Republic. Sci Tot Environ* 2009;407(10):3372–84.

Emerson D, Moyer C. Isolation and characterization of novel iron-oxidizing bacteria that grow at circumneutral pH. *Appl Environ Microbiol* 1997;63(12):4784–92.

Emett MT, Khoe GH. Photochemical oxidation of arsenic by oxygen and iron in acidic solutions. *Water Res* 2001;35(3):649–56.

Fattorini D, Notti A, Di Mento R, Cicero AM, Gabellini M, Russo A, et al. Seasonal, spatial and inter-annual variations of trace metals in mussels from the Adriatic Sea: a regional gradient for arsenic and implications for monitoring the impact of off-shore activities. *Chemosphere* 2008;72(10):1524–33.

- Fendorf S, Nico PS, Kocar BD, Masue Y, Tufano KJ. Chapter 12—arsenic chemistry in soils and sediments. In: Balwant S, Markus G, editors. *Developments in soil science*. Elsevier; 2010. p. 357–78.
- Georgiadis M, Cai Y, Solo-Gabriele HM. Extraction of arsenate and arsenite species from soils and sediments. *Environ Pollut* 2006;141(1):22–9.
- Gihring TM, Banfield JF. Arsenite oxidation and arsenate respiration by a new *Thermus* isolate. *FEMS Microbiol Lett* 2001;204(2):335–40.
- Grossl PR, Eick M, Sparks DL, Goldberg S, Ainsworth CC. Arsenate and chromate retention mechanisms on goethite. 2. Kinetic evaluation using a pressure-jump relaxation technique. *Environ Sci Technol* 1997;31(2):321–6.
- Han M-J, Hao J, Christodoulatos C, Korfiatis GP, Wan L-J, Meng X. Direct evidence of arsenic(III)—carbonate complexes obtained using electrochemical scanning tunneling microscopy. *Anal Chem* 2007a;79(10):3615–22.
- Han M-J, Meng X, Lippincott L. Determination of configuration of arsenite–glutathione complexes using ECD. *Toxicol Lett* 2007b;175(1):57–63.
- Howard A, Comber S, Kifle D, Antai E, Purdie D. Arsenic speciation and seasonal changes in nutrient availability and micro-plankton abundance in Southampton Water. UK. *Estuar Coast Shelf Sci* 1995;40(4):435–50.
- Huerga A, Lavilla I, Bendicho C. Speciation of the immediately mobilisable As (III), As (V), MMA and DMA in river sediments by high performance liquid chromatography–hydride generation–atomic fluorescence spectrometry following ultrasonic extraction. *Anal Chim Acta* 2005;534(1):121–8.
- Hug SJ, Leupin O. Iron-catalyzed oxidation of arsenic (III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction. *Environ Sci Technol* 2003;37(12):2734–42.
- Inskip WP, Macur RE, Hamamura N, Warelow TP, Ward SA, Santini JM. Detection, diversity and expression of aerobic bacterial arsenite oxidase genes. *Environ Microbiol* 2007;9(4):934–43.
- Johnson DB, Hallberg KB. Acid mine drainage remediation options: a review. *Sci Total Environ* 2005;338(1–2):3–14.
- Keon NE, Swartz CH, Brabander DJ, Harvey C, Hemond HF. Validation of an arsenic sequential extraction method for evaluating mobility in sediments. *Environ Sci Technol* 2001;35(13):2778–84.
- Kim M-J, Nriagu J, Haack S. Carbonate ions and arsenic dissolution by groundwater. *Environ Sci Technol* 2000;34(15):3094–100.
- Komárek M, Vaněk A, Ettler V. Chemical stabilization of metals and arsenic in contaminated soils using oxides – a review. *Environ Pollut* 2013;172:9–22.
- Kosmulski M. The pH-dependent surface charging and points of zero charge: V. Update. *J Colloid Interface Sci* 2011;353(1):1–15.
- Kumar AR, Riyazuddin P. Preservation of inorganic arsenic species in environmental water samples for reliable speciation analysis. *TrAC Trends Anal Chem* 2010;29(10):1212–23.
- Lafferty BJ, Ginder-Vogel M, Sparks DL. Arsenite oxidation by a poorly crystalline manganese-oxide 1. Stirred-flow experiments. *Environ Sci Technol* 2010a;44(22):8460–6.
- Lafferty BJ, Ginder-Vogel M, Zhu M, Livi KJT, Sparks DL. Arsenite oxidation by a poorly crystalline manganese-oxide. 2. results from x-ray absorption spectroscopy and x-ray diffraction. *Environmental Science & Technology* 2010b;44(22):8467–72.
- Lafferty BJ, Ginder-Vogel M, Sparks DL. Arsenite oxidation by a poorly-crystalline manganese oxide. 3. Arsenic and manganese desorption. *Environ Sci Technol* 2011;45(21):9218–23.
- Laperche V, Bodéan F, Dictor MC, Baranger P. Guide méthodologique de l'arsenic appliqué à la gestion des sites et sols pollués. BRGM/RP-52066-FR 2003;90.
- Lengke MF, Tempel RN. Reaction rates of natural orpiment oxidation at 25 to 40 °C and pH 6.8 to 8.2 and comparison with amorphous As<sub>2</sub>S<sub>3</sub> oxidation. *Geochim Cosmochim Acta* 2002;66(18):3281–91.
- Lengke MF, Tempel RN. Natural realgar and amorphous AsS oxidation kinetics. *Geochim Cosmochim Acta* 2003;67(5):859–71.
- Ma Y, Lin C. Arsenate immobilization associated with microbial oxidation of ferrous ion in complex acid sulfate water. *J Hazard Mater* 2012;217:238–45.
- Mandal BK, Suzuki KT. Arsenic round the world: a review. *Talanta* 2002;58(1):201–35.
- Manning BA, Fendorf SE, Goldberg S. Surface structures and stability of arsenic(III) on goethite: spectroscopic evidence for inner-sphere complexes. *Environ Sci Technol* 1998;32(16):2383–8.
- Masscheleyn PH, Delaune RD, Patrick WH. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. *Environ Sci Technol* 1991;25(8):1414–9.
- McCleskey RB, Nordstrom DK, Maest AS. Preservation of water samples for arsenic(III/V) determinations: an evaluation of the literature and new analytical results. *Appl Geochem* 2004;19(7):995–1009.
- Mikutta, C. and R. Kretzschmar, *Spectroscopic Evidence for Ternary Complex Formation between Arsenate and Ferric Iron Complexes of Humic Substances*. *Environmental Science & Technology*. 45(22): p. 9550–9557.
- Millero FJ. The oxidation of H<sub>2</sub>S in the Chesapeake Bay. *Estuar Coast Shelf Sci* 1991;33(5):521–7.
- Millero FJ, Hubinger S, Fernandez M, Garnett S. Oxidation of H<sub>2</sub>S in seawater as a function of temperature, pH, and ionic strength. *Environ Sci Technol* 1987;21(5):439–43.
- Mudroch A, Azcue JM, Mudroch P. *Manual of bioassessment of aquatic sediment quality*. CRC Press; 1998.
- Neuberger CS, Helz GR. Arsenic (III) carbonate complexing. *Appl Geochem* 2005;20(6):1218–25.
- Nicholas D, Ramamoorthy S, Palace V, Spring S, Moore J, Rosenzweig RF. Biogeochemical transformations of arsenic in circumneutral freshwater sediments. *Biodegradation* 2003;14(2):123–37.
- Nordstrom DK, Archer D. Arsenic thermodynamic data and environmental geochemistry. In: Welch A, Stollenwerk K, editors. *Arsenic in ground water*. Springer US; 2003. p. 1–25.
- O'Day PA, Vlassopoulos D, Root R, Rivera N. The influence of sulfur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions. *Proc Natl Acad Sci U S A* 2004;101(38):13703–8.
- Oremland RS, Dowdle PR, Hoeft S, Sharp JO, Schaefer JK, Miller LG, et al. Bacterial dissimilatory reduction of arsenate and sulfate in meromictic Mono Lake, California. *Geochim Cosmochim Acta* 2000;64(18):3073–84.
- Orero Iserete L, Roig-Navarro AF, Hernández F. Simultaneous determination of arsenic and selenium species in phosphoric acid extracts of sediment samples by HPLC–ICP–MS. *Anal Chim Acta* 2004;527(1):97–104.
- Ona-Nguema G, Morin G, Wang Y, Foster AL, Juillot F, Calas G. XANES evidence for rapid arsenic(III) oxidation at magnetite and ferrihydrite surfaces by dissolved O<sub>2</sub> via Fe<sup>2+</sup>-mediated reactions. *Environ Sci Technology* 2010;44(14):5416–22.
- Oscarson DW, Huang PM, Defosse C, Herbillon A. Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments. *Nature* 1981;291(5810):50–1.
- Oscarson DW, Huang PM, Hammer UT, Liaw WK. Oxidation and sorption of arsenite by manganese dioxide as influenced by surface coatings of iron and aluminum oxides and calcium carbonate. *Water Air Soil Pollut* 1983;20(2):233–44.
- Paul CJ, Ford RG, Wilkin RT. Assessing the selectivity of extractant solutions for recovering labile arsenic associated with iron (hydr)oxides and sulfides in sediments. *Geoderma* 2009;152(1–2):137–44.
- Planer-Friedrich B, Wallschläger D. A critical investigation of hydride generation-based arsenic speciation in sulfidic waters. *Environ Sci Technol* 2009;43(13):5007–13.
- Planer-Friedrich B, Suess E, Scheinost AC, Wallschläger D. Arsenic speciation in sulfidic waters: reconciling contradictory spectroscopic and chromatographic evidence. *Anal Chem* 2010;82(24):10228–35.
- Prohaska T, Stügender G. Speciation of arsenic. *Handbook of elemental speciation II – species in the environment, food, medicine and occupational health*. John Wiley & Sons, Ltd.; 2005. p. 69–85.
- Raber G, Stock N, Hanel P, Murko M, Navratilova J, Francesconi KA. An improved HPLC–ICPMS method for determining inorganic arsenic in food: application to rice, wheat and tuna fish. *Food Chem* 2012;134(1):524–32.
- Raven KP, Jain A, Loepfert RH. Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes. *Environ Sci Technol* 1998;32(3):344–9.
- Razo I, Carrizales L, Castro J, Díaz-Barriga F, Monroy M. Arsenic and heavy metal pollution of soil, water and sediments in a semi-arid climate mining area in Mexico. *Water Air Soil Pollut* 2004;152(1–4):129–52.
- Redman AD, Macalady DL, Ahmann D. Natural organic matter affects arsenic speciation and sorption onto hematite. *Environ Sci Technol* 2002;36(13):2889–96.
- Rey NA, Howarth OW, Pereira-Maia EC. Equilibrium characterization of the As (III)–cysteine and the As (III)–glutathione systems in aqueous solution. *J Inorg Biochem* 2004;98(6):1151–9.
- Riedel GF, Sanders JG, Osman RW. The effect of biological and physical disturbances on the transport of arsenic from contaminated estuarine sediments. *Estuar Coast Shelf Sci* 1987;25(6):693–706.
- Rochette EA, Bostick BC, Li G, Fendorf S. Kinetics of arsenate reduction by dissolved sulfide. *Environ Sci Technol* 2000;34(22):4714–20.
- Santelli CM, Welch SA, Westrich HR, Banfield JF. The effect of Fe-oxidizing bacteria on Fe-silicate mineral dissolution. *Chem Geol* 2001;180(1):99–115.
- Santini JM, vanden Hoven RN. Molybdenum-containing arsenite oxidase of the chemolithoautotrophic arsenite oxidizer NT-26. *J Bacteriol* 2004;186(6):1614–9.
- Scott MJ, Morgan JJ. Reactions at oxide surfaces. 1. Oxidation of As(III) by synthetic birnessite. *Environ Sci Technol* 1995;29(8):1898–905.
- Silver S, Phung LT. Genes and enzymes involved in bacterial oxidation and reduction of inorganic arsenic. *Appl Environ Microbiol* 2005;71(2):599–608.
- Šlejko Z, Bajc Z, Doganoc DZ. Arsenic speciation patterns in freshwater fish. *Talanta* 2004;62(5):931–6.
- Smedley PL, Kinniburgh DG. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl Geochem* 2002;17(5):517–68.
- Smith SL, Jaffé PR. Modeling the transport and reaction of trace metals in water-saturated soils and sediments. *Water Resour Res* 1998;34(11):3135–47.
- Sracek O, Bhattacharya P, Jacks G, Gustafsson JP, Brömsen Mv. Behavior of arsenic and geochemical modeling of arsenic enrichment in aqueous environments. *Appl Geochem* 2004;19(2):169–80.
- Stauder S, Raue B, Sacher F. Thioarsenates in sulfidic waters. *Environ Sci Technol* 2005;39(16):5933–9.
- Suess E, Planer-Friedrich B. Thioarsenate formation upon dissolution of orpiment and arsenopyrite. *Chemosphere* 2012;89(11):1390–8.
- Suess E, Wallschläger D, Planer-B. Stabilization of thioarsenates in iron-rich waters. *Chemosphere* 2011;83(11):1524–31.
- Sullivan K, Aller R. Diagenetic cycling of arsenic in Amazon shelf sediments. *Geochim Cosmochim Acta* 1996;60(9):1465–77.
- Sun F. Arsenic chemistry with sulfide, pyrite, zero-valent iron and magnetite. Department of Civil and Environmental Engineering; 2010. p. 110. [i.e., espèces thioarseniées].
- Tessier E, Garnier C, Mullet J-U, Lenoble V, Arnaud M, Raynaud M, et al. Study of the spatial and historical distribution of sediment inorganic contamination in the Toulon Bay (France). *Mar Pollut Bull* 2011;62(10):2075–86.
- Thomas DJ, Waters SB, Styblo M. Elucidating the pathway for arsenic methylation. *Toxicol Appl Pharmacol* 2004;198(3):319–26.
- Walker FP, Schreiber ME, Rimstidt JD. Kinetics of arsenopyrite oxidative dissolution by oxygen. *Geochim Cosmochim Acta* 2006;70(7):1668–76.

- Wang S-L, Liu CH, Wang MK, Chuang YH, Chiang PN. Arsenate adsorption by Mg/Al-NO<sub>3</sub> layered double hydroxides with varying the Mg/Al ratio. *Appl Clay Sci* 2009;43(1):79–85.
- Wang Y, Xu J, Zhao Y, Zhang L, Xiao M, Wu F. Photooxidation of arsenite by natural goethite in suspended solution. *Environ Sci Pollut Res* 2013;20(1):31–8.
- Welz B, Šucmanová M. L-Cysteine as a reducing and releasing agent for the determination of antimony and arsenic using flow injection hydride generation atomic absorption spectrometry—part 1. Optimization of the analytical parameters. *Analyst* 1993;118(11):1417–23.
- Wenzel WW, Kirchbaumer N, Prohaska T, Stingeder G, Lombi E, Adriano DC. Arsenic fractionation in soils using an improved sequential extraction procedure. *Anal Chim Acta* 2001;436(2):309–23.
- Widerlund A, Ingri J. Early diagenesis of arsenic in sediments of the Kalix River estuary, northern Sweden. *Chem Geol* 1995;125(3):185–96.
- Wilkin RT, Wallschläger D, Ford RG. Speciation of arsenic in sulfidic waters. *Geochem Trans* 2003a;4(1):1–7.
- Wilkin R, Wallschläger D, Ford R. Speciation of arsenic in sulfidic waters. *Geochem Trans* 2003b;4(1):1.
- Xu H, Allard B, Grimvall A. Effects of acidification and natural organic materials on the mobility of arsenic in the environment. *Water Air Soil Pollut* 1991;57–58(1):269–78.
- Ye S, Laws EA, Gambrell R. Trace element remobilization following the resuspension of sediments under controlled redox conditions: City Park Lake, Baton Rouge, LA. *Appl Geochem* 2013;28:91–9.
- Zhang G, Qu J, Liu H, Liu R, Wu R. Preparation and evaluation of a novel Fe–Mn binary oxide adsorbent for effective arsenite removal. *Water Res* 2007;41(9):1921–8.