



## 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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## Contents

1.	Introduction . . . . .	424
2.	General points on As speciation in solution . . . . .	424
3.	Redox reactions . . . . .	424
3.1.	Oxidation of As(III) . . . . .	425
3.1.1.	Oxygen . . . . .	426
3.1.2.	Iron (hydr)-oxides . . . . .	426
3.1.3.	Manganese (hydr)-oxides . . . . .	427
3.1.4.	Bacterial activity . . . . .	427
3.1.5.	Other oxidants . . . . .	427
3.2.	Reduction of As(V) . . . . .	427
3.2.1.	Sulfides . . . . .	427
3.2.2.	Thio-organic components . . . . .	428
3.2.3.	Biological activity . . . . .	428

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3.3. Reduction of As(III)	428
3.4. Oxidation of As(–I) and As(II)	429
4. Reactions of dissolution/precipitation	429
5. Reactions of adsorption	429
5.1. Sorption onto mineral surfaces	429
5.2. Sorption involving organic matter	431
6. Conclusion	432
Acknowledgments	432
References	432

## 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  $[\text{As}(\text{V}); \text{H}_x\text{As}^+\text{VO}_4^{3-x}]$  with  $x = 0$  to 3] are 11.53, 6.97 and 2.20 whereas the  $\text{pK}_a$  values of arsenite  $[\text{As}(\text{III}); \text{H}_x\text{As}^+\text{VO}_3^{3-x}]$  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),  $\text{H}_2\text{As}^+\text{VO}_4^-$ ,  $\text{HAs}^+\text{VO}_4^{2-}$  and  $\text{H}_3\text{As}^+\text{VO}_3$  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  $\text{As}^{+III}(\text{CO}_3)^{2-}$ ,  $\text{As}^{+III}(\text{CO}_3)^+$  and  $\text{As}^{+III}(\text{CO}_3)(\text{OH})^-$  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

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