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Zhang , S.-Y., Williams, P. N., Luo, J., & Zhu, Y.-G. (2017). Microbial mediated arsenic biotransformation in wetlands. *Frontiers of Environmental Science & Engineering*, 11(1). <https://doi.org/10.1007/s11783-017-0893-y>

**Published in:**  
Frontiers of Environmental Science & Engineering

**Document Version:**  
Peer reviewed version

**Queen's University Belfast - Research Portal:**  
[Link to publication record in Queen's University Belfast Research Portal](#)

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**Microbial mediated arsenic biotransformation in wetlands**

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1 **Abstract**

2 Arsenic (As) is a pervasive environmental toxin and carcinogenic metalloid. It ranks  
3 at the top of the US priority List of Hazardous Substances and causes worldwide  
4 human health problems. Wetlands, including natural and artificial ecosystems (i.e.  
5 paddy soils) are highly susceptible to As enrichment; acting not only as repositories  
6 for water but a host of other elemental/chemical moieties. While macro-scale  
7 processes (physical and geological) supply As to wetlands, it is the micro-scale  
8 biogeochemistry that regulates the fluxes of As and other trace elements from the  
9 semi-terrestrial to neighboring plant/aquatic/atmospheric compartments. Among these  
10 fine-scale events, microbial mediated As biotransformations contribute most to the  
11 element's changing forms, acting as the 'switch' in defining a wetland as either a  
12 source or sink of As. Much of our understanding of these important microbial  
13 catalyzed reactions follows relatively recent scientific discoveries. Here we document  
14 some of these key advances, with focuses on the implications that wetlands and their  
15 microbial mediated transformation pathways have on the global As cycle, the  
16 chemistries of microbial mediated As oxidation, reduction and methylation, and future  
17 research priorities areas.

18 **Keywords**

19 Arsenic, wetland, microbes, switch

20

## 1 **1 Introduction**

2 Arsenic (As) exists in four oxidation states (-III, 0, +III, and +V), and is present in  
3 both inorganic and organic forms. Commonly found in highly auriferous regions, As  
4 also associates with the mineral ores of other metals such as iron, copper, and lead [1].  
5 Speciation in addition to concentration is fundamental to the understanding of As  
6 toxicity, mobility and fate in the environment [2]. In the biosphere, arsenate ( $\text{As}^{\text{V}}$ ) and  
7 arsenite ( $\text{As}^{\text{III}}$ ) are the most abundant inorganic As species. Under aerobic conditions,  
8  $\text{As}^{\text{V}}$  dominates, is typically strongly absorbed to iron oxy-hydroxide minerals, and  
9 exhibits limited mobility/bioavailability [3]. Conversely, under anaerobiosis, a shift in As  
10 speciation to the trivalent form means the element is both more toxic and inherently  
11 more labile [3].

12 Common organic As species found in our bodies as well as in waters, soils, feeds  
13 and foods include monomethylarsenate ( $\text{MMAs}^{\text{V}}$ ), dimethylarsenate ( $\text{DMAs}^{\text{V}}$ ),  
14 trimethylarsine oxide ( $\text{TMAOs}$ ), arsenosugars and arsenobetaine (AsB) (Table 1).  
15 They can be introduced into the environment due to microbial mediated  
16 biomethylation [4] and via anthropogenic activities, such as pesticide/fertilizer  
17 applications. Historically, the organic arsenical Roxarsone (2-nitrophenol-4-arsonic  
18 acid), has been added to poultry feeds as a growth promoter, however this has been  
19 largely phased out due to both animal and environmental health concerns [5]. Most,  
20 but not all, of the organic As species are considerably less toxic compared to their  
21 inorganic As counterparts. Typically, they are found **with** high concentrations in  
22 marine organisms. Arsenosugars constitute the main organo-As species found in algae,

1 while in other marine dwellers, from lobsters to white fish, the toxin is packaged as  
2 the inert and very stable/unreactive AsB [6]. In freshwaters and soils/sediments,  
3 generally MMAs<sup>V</sup>, DMAs<sup>V</sup> and volatile TMAsO are the most commonly detected  
4 organic As species [7].

5 As the interface between terrestrial and aquatic ecosystems, wetlands occupy  
6 between 5.3 and 12.8 million km<sup>2</sup> of the earth's surface [8]. Defined by their  
7 inundation by water and constant transition between wet and dry states, oxygen  
8 availability is typically very heterogeneous resulting in regions of water and sediment  
9 where anaerobism is commonplace [9]. Because of their wide distribution, high  
10 productivity, and rich biodiversity, wetlands have been viewed as having a major  
11 influence on many global biogeochemistries, including the carbon and nitrogen cycles  
12 [10, 11] in addition to impacting on As transfer [2].

13 Owing to their depositional characteristics, wetlands are also highly susceptible  
14 to contamination by heavy metals and other toxic trace elements. Macro-scale  
15 processes (physical and geological events), which include anthropogenic activities,  
16 wet, dry deposition, erosion, volcanism, and weathering are essential in determining  
17 As loading in these environments (Figure 1). Even seemingly 'pristine' wetland  
18 habitats/ecosystems, with Yellowstone National Park being a prime example [12], can  
19 be 'naturally' enriched in As. However, anthropogenic activities such as mining,  
20 smelting, urban waste and wastewater discharges, fertilizer and pesticide use also  
21 contribute significantly to the build-up of As stores in wetland [13]. Often,  
22 disconnected from the surrounding geology, these human induced redistributions of

1 As can be the hardest to predict and hence pose perhaps the greatest hazard to human  
2 health.

3 Despite the importance of macro-scale processes in determining As loading into  
4 wetlands, it is micro-scale biogeochemistry, which includes desorption, dissolution  
5 [14] and microbial mediated  $\text{As}^{\text{V}}$  reduction,  $\text{As}^{\text{III}}$  oxidation and methylation [2] that  
6 mainly regulate the fluxes of As from the semi-terrestrial to either aquatic or  
7 atmospheric compartments (Figure 1). Recent advances in molecular methods have  
8 enabled great leaps in our understanding of microbial mediated As biotransformations.  
9 This review summarizes the role of wetland microbiology within the global As cycle,  
10 and the distribution and behavior of As in water submerged soils and sediments.  
11 Moreover, it provides a detailed overview of the key transformation **biochemistries**,  
12 ranking the events in order of priority and discussing their interactions within a  
13 chemically complex and heterogeneous localized environment. Finally, an outlook for  
14 future research areas and introduction to emerging new technologies for measuring As  
15 cycling in wetlands is presented.

16

## 17 **2 Distribution and behavior of As in wetlands**

### 18 **2.1 Overview**

19 Wetlands can be broadly classified as either '*natural*', which includes marine, **coastal**  
20 zone and inland wetlands, or '*artificial*' wetlands such as paddy soils. Although, the  
21 true state of most systems is perhaps as a mixture/intermediary of the two. The  
22 definition of what constitutes, as a 'contaminated sediment' is similarly quite open to

1 interpretation, as the acceptable quality criteria for As in wetland soils varies between  
2 countries (Table 2). For example, the Canadian Council of Ministers of the  
3 Environment (CCME), have set interim quality guidelines (ISQGs) for  
4 marine/estuarine sites at  $7.24 \text{ mg kg}^{-1}$  dry weight [15], whereas trigger thresholds in  
5 China are marked slightly higher, so a site is only given contamination status when  
6 concentrations of  $20 \text{ mg kg}^{-1}$  are breached [16]. An alternative method to evaluate the  
7 quality of a wetland, is to consider the As concentration in extractable waters.  
8 Recently reported incidences where detected As in overlying surface waters exceeded  
9 the US Environmental Protection Agency's (EPA) maximum containment level of As  
10 in drinking water ( $10 \text{ } \mu\text{g L}^{-1}$ ) are summarized in Table 3.

11 Perhaps the focal point of As contamination in wetlands, where to date most of  
12 the scientific research attention has been directed lies in southeast Asia [17-21]. Here  
13 the As source originally derived from eroded Himalayan rock, now resides as buried  
14 lens of sediment making up the Bay of Bengal Delta. These near-surface alluvia are  
15 the cause of As release to aquifers, and threaten tens of millions of people consuming  
16 these waters [22]. In samples collected from fifteen selected Bhaluka wetlands in  
17 Bangladesh, the concentration of As in the waters ranged from 7 to  $80 \text{ } \mu\text{g L}^{-1}$ , with 93%  
18 found exceeding WHO recommended permissible limits [23]. For further information  
19 on the Bangladesh As crisis, refer to reviews by Meharg *et al.* [24] and Meharg &  
20 Zhao [25].

21 Paddy field contamination in the region is also a serious problem, here high soil  
22 As concentrations are linked to the quality of the groundwaters used for irrigation [20].

1 This problem was uncovered in 2003, when seventy-one soils collected from three  
2 districts, revealed a range of As concentrations in soils spanning 3.1 mg kg<sup>-1</sup> (*baseline*)  
3 up to 42.5 mg kg<sup>-1</sup> [20]. While a later study by Stroud *et al.* [26], reported an even  
4 greater variation in total As concentrations in twelve paddy soils from Bangladesh,  
5 again similar baselines of 4 mg kg<sup>-1</sup>, but this time the inputs of As from irrigation  
6 caused soils to reach 138 mg kg<sup>-1</sup>. This highlights the ease in which As can  
7 accumulate in agricultural-wetland soils, which then leads to the direct transfer to  
8 food supply chains [20, 27].

9 China, meanwhile, is another country that has extensively studied the problem of  
10 As build-up in wetlands [28-31]. Here though the main inputs derive not from  
11 groundwaters, but instead take many different forms/guises. Although, often difficult  
12 to characterize due to the mixing of multiple and varying sources, they do share a  
13 commonality, in that inputs have intensified as the country had modernized. For  
14 example, freshwater and salt marsh sediments in the Yellow river delta, before the  
15 Xiaolangdi reservoir was built, were already As enriched, recording values of 30 mg  
16 kg<sup>-1</sup>. However, after it was constructed, changes to the sediment flows coupled with  
17 increased human settlement and activity in the area, resulted in further As deposition  
18 taking the concentration up to 45 mg kg<sup>-1</sup> [32], equivalent to a 4.5-fold increase from  
19 baseline levels for soils in the Yangtze river delta [33].

20 Like Bangladesh, paddy field contamination is also a topic of importance in  
21 China, with numerous studies highlighting this as a prominent issue, see Table 3  
22 [28-31, 34]. However, total As concentrations only tell part of the story. Here As



1 species are essential to understand the bioavailability and uptake of As in rice. Based  
2 on soil pore waters collected from Bangladesh and Chinese paddy soils, As<sup>III</sup> is the  
3 dominant species, accounting for 66-100% of the total As [26]. Methylated As species  
4 (DMAs<sup>V</sup> and MMAs<sup>V</sup>) are also commonly detected in rice soils [34]. Although the  
5 uptake of organic As into rice is not as rapid as As<sup>III</sup>, once inside roots they quickly  
6 translocate to the above-ground tissues [25]. Volatile TMAs<sup>III</sup> has also been recently  
7 detected in field studies of paddy soils from Spain and Bangladesh, albeit only at  
8 trace-concentrations [35].

9 Far from just being confined to Asia, the problem of As contamination in  
10 **wetlands** is a feature on other continents as well. For example, concentrations of total  
11 As in twenty-five surface sediments (0-4 cm) collected from wetlands in  
12 Massachusetts in the U.S., ranged from 20 to 2100 mg kg<sup>-1</sup> [36]. In southwest Spain,  
13 the contamination by As in the Guadalquivir marshes, arising from the mine-tailing  
14 spill in Aznalcollar, led to severe wetland soil pollution, with far reaching biological  
15 effects for local wildlife, a subject covered in depth by a number of related  
16 publications (Table 3) [37-39].

17

## 18 **2.2 Biogeochemistry of As transformation and transport in wetlands**

19 The predominant form of As in soil prior to flooding is As<sup>V</sup>. Bound commonly to iron  
20 (oxy)hydroxides, due in equal measure to it's high affinity for the species and  
21 abundance in most soils, the labiality and subsequently toxicity of As<sup>V</sup> is relatively  
22 low [40]. Saturating the system with water causes soil redox potentials to rapidly

1 decrease, in response to the depletion of electron acceptors, such as oxygen, nitrate,  
2 manganese oxides and iron oxides/hydroxides. When Eh drops to below -200 mV  
3 porewater As<sup>V</sup> concentrations decline as the species is transformed to As<sup>III</sup> [25]. In the  
4 short-term, buffering can occur, because in these highly reducing conditions iron  
5 oxides/hydroxides are solubilized, releasing As<sup>V</sup>. However, As<sup>III</sup> development will  
6 dominate overtime [25, 41, 42]. This phenomenon can be further enhanced, by the  
7 direct reduction of soil reservoirs of As<sup>V</sup>. Due to As<sup>III</sup> being less strongly bound to soil  
8 particle surfaces than As<sup>V</sup>, it partitions more readily into solution phase, increasing the  
9 overall bioavailability of the toxin [40, 43].

10       Organic carbon (OC) has also been shown to mobilize As in aquifers in south  
11 Bangladesh [44], while high concentrations of dissolved organic matter (DOM) in soil  
12 porewaters can compete with surface absorbed As<sup>V</sup> and As<sup>III</sup> displacing them into  
13 solution [21, 25]. Other important chemistries that control As transport, include the  
14 grouping of interactions that As has with sulfur rich minerals [45]. Under highly  
15 reducing conditions, and in the presence of dissolved sulfide, As<sup>III</sup> can form stable  
16 complexes, for example, orpiment (As<sub>2</sub>S<sub>3</sub>) or realgar (As<sub>4</sub>S<sub>4</sub>) [36]. Immobilizing As  
17 by controlling redox conditions, to favor As-S precipitation, is a **practice** used in  
18 constructed **wetlands** for reducing As bioavailability [46]. However, the sites still  
19 require careful management, as oxidation of the sediment can result in the dissolution  
20 of sulfides and re-mobilization of As<sup>III</sup> back into the environment [47, 48].

21

22

### 3 Mechanisms of microbial mediated As biotransformation in wetlands

Compared to chemical change, microbial mediated As redox reactions occur far more rapidly [49]. Study has showed As<sup>V</sup> reduction in soils to be significantly suppressed when  $\gamma$ -irradiated, highlighting the dominant role the microbiota play in this in situ As transfer step [40]. Microbial activity can be increased/simulated by enhancing the availability of OC sources, a response that differs between species/communities. This in turn contributes to different rates and forms of As biotransformation, impacting on both inorganic and methylated As trends [28]. Indeed, most methylated As species detected in wetlands are originally derived from microbial mediated As reactions [31, 35], because plants are not efficient at methylating inorganic As [50]. These different As species with their ranging properties/characteristics define the manner that As is transferred back and forth from the main land and aquatic stores [51-54]. Some volatile As is released into the atmosphere, in the form of AsH<sub>3</sub>, CH<sub>3</sub>AsH<sub>2</sub> (MeAsH<sub>2</sub>), (CH<sub>3</sub>)<sub>2</sub>AsH (Me<sub>2</sub>AsH), and (CH<sub>3</sub>)<sub>3</sub>As (TMAAs<sup>III</sup>). However compared to the land and water exchanges the fluxes are relatively minor [28, 35].

The evolution of such effective and diverse microbial mediated As biotransformation systems arose because they protect against As toxicity. The pathways of how microbes deal with As have been extensively studied in the last couple of decades, revealing various genes and enzymes responsible for As biotransformation and its biotransportation out of cells [50, 55-57]. The main systems used in As biotransformation by microbes in wetlands are further summarized below.

### 1 3.1 As<sup>III</sup> oxidation in wetlands

2 Rapid As<sup>III</sup> oxidation in the environment is mediated by metabolic microbial  
3 processes [1, 58], which are catalyzed by As<sup>III</sup> oxidase (Aio). This enzyme is encoded  
4 by *aioA* and *aioB* genes for the two subunits AioA (AoxB) and AioB (AoxA) [55, 59].  
5 Microbial mediated As<sup>III</sup> oxidation is considered as one of the primary As  
6 detoxification mechanisms for microbes because it can oxidize As<sup>III</sup> to the less toxic  
7 As<sup>V</sup> [55]. The high abundance of *aioA* genes in paddy soils under flooding conditions  
8 further suggests the importance of this pathway [31, 60]. As<sup>III</sup> oxidizing bacteria in  
9 paddy soils mainly assign to the following family groupings: *Phyllobacteriaceae*,  
10 *Bradyrhizobiaceae*, *Methylobacteriaceae*, *Rhizobiales*, *Burkholderiales* and  
11 *Comamonadaceae* [60, 61].

12 In other types of wetland, for example coastal sediments, a high diversity of  
13 *aioA*-like genes have also been detected. The most abundant *aioA*-like genes derived  
14 from *Roseobacter litoralis* Och 149 [62]. As<sup>III</sup> oxidizing bacteria isolated from natural  
15 and constructed wetlands in the Republic of Korea showed that they were all able to  
16 grow in the presence of high concentrations of As<sup>III</sup> (10 mM). The bacterium  
17 identified as *Pseudomonas stutzeri* strain GIST-BDAN2 showed an especially high  
18 activity of As<sup>III</sup> oxidation (completely oxidized 1 mM As<sup>III</sup> to As<sup>V</sup> within 25-30 h) and  
19 possessed both the *aoxB* and *aoxR* genes [63]. Three As<sup>III</sup> oxidizing bacteria including  
20 *Agrobacterium tumefaciens*, *Pseudomonas fluorescens*, and *Variovorax*  
21 *paradoxus*-like organisms were also isolated from the same Madison River Valley  
22 soils that also supported large populations of As<sup>V</sup> reducing bacteria [64]. This

1 highlights the close overlay of the microbial catalyzed oxidation and reduction  
2 pathways, and how this dichotomy functions as the principal 'switch' which controls  
3 As fate in a specific site or zone within a site.

4

### 5 **3.2 As<sup>V</sup> reduction in wetlands**

6 Microbial mediated As<sup>V</sup> reduction segregates into two functional schemes, the  
7 respiratory and the detoxification pathway. The respiratory pathway is catalyzed by  
8 the As<sup>V</sup> respiratory reductase (ArrA) complex, which consists of a large catalytic  
9 subunit (ArrA) and a small subunit (ArrB) [65-67]. It can mediate anaerobic  
10 dissimilatory As<sup>V</sup> reduction and couple this with energy production [68-70]. A more  
11 universal system of As<sup>V</sup> detoxification reduction, is catalyzed by the cytoplasmic As<sup>V</sup>  
12 reductase (ArsC), which is present in both aerobic and anaerobic microbes [71]. The  
13 *arsC* gene occurs in the *ars* operons next to the *arsB* gene that functions as an As<sup>III</sup>  
14 membrane pump in most bacteria [56], controlling cytoplasmic As<sup>V</sup> reduction, and  
15 thereafter As<sup>III</sup> efflux.

16 In wetland sediments, microbial mediated As<sup>V</sup> reduction is considered to be a  
17 crucial mechanism controlling As<sup>V</sup> mobilization [72], and contributing factor leading  
18 to As contamination of ground water, as has happened in south and southeast Asia [22,  
19 73]. Due to the anaerobic conditions encountered in wetlands, dissimilatory As<sup>V</sup>  
20 respiring bacteria are quite commonplace. The dissimilatory As<sup>V</sup> reduction gene *arrA*  
21 has been detected in various wetlands, including paddy soils [60, 61], coastal  
22 sediments from south China [62], and estuarine sediments from Chesapeake Bay in

1 the U.S. [74]. Zhang *et al.* [34] revealed that *arrA* sequences detected in paddy soils  
2 were analogous to those found in *Geobacter* species, which have been frequently  
3 found in As rich sediments before [72, 75]. Similarly, *Geobacter* are prominent in  
4 Japanese paddy soil [54]. Observations of *Geobacter* species OR-1 have revealed that  
5 in addition to As, ferrihydrite is also being used as an electron acceptor, thus  
6 catalyzing the dissolution of As from As<sup>V</sup>-absorbed ferrihydrite, by promoting ferrous  
7 iron formation [54]. Moreover, As K-edge X-ray absorption near-edge structure  
8 analysis demonstrated the OR-1 can also reduce soil/solid bound As<sup>V</sup> directly. In  
9 addition to *Geobacter*-related bacteria, other microbiota, such as *Shewanella* species,  
10 that utilize the coupling/uncoupling of iron and As reduction as a means of acquiring  
11 energy, are also capable of dissimilatory As<sup>V</sup> reduction [76, 77].

12         Similar to *arrA*, *arsC* has also been frequently detected in paddy soils [60, 61]  
13 and coastal sediments [62]. The As<sup>V</sup> reducing microbes with the most active  
14 detoxification pathways in paddy soils mostly belonged to typically rhizospheric  
15 bacteria groups, such as *Rhizobiales* and *Pseudomonadales* [61]. Study of pure culture  
16 bacteria from Madison River Valley soils revealed five isolates, *Agrobacterium*  
17 *tumefaciens*, *Flavobacterium* sp., *Microbacterium* sp. and two *Arthrobacter* sp.-like  
18 organisms capable of rapidly reducing As<sup>V</sup> under aerobic conditions, with the later  
19 found to possess new putative *arsC* genes [64]. Seventeen As-resistant bacteria  
20 isolated from Mandovi and Zuari estuarine water systems revealed *arsA* (ATPase),  
21 *arsB* and *arsC* genes on their plasmid DNA. While, *arsC* genes were individually  
22 detected in thirteen bacterial isolates, including the genera's *Halomonas* and

1 *Acinetobacter* [78]. Using genome sequencing of *Bacillus* bacterium isolated from  
2 Andean wetlands in northern Chile, the *arsC* gene function was found as  
3 detoxification As<sup>V</sup> reduction [79]. Together with the As<sup>V</sup> respiring bacteria, these  
4 detoxification As<sup>V</sup> reducing microbes catalyze the reduction of both the soil absorbed  
5 As<sup>V</sup> and dissolved As<sup>V</sup> in solution into As<sup>III</sup>.

6

### 7 **3.3 As<sup>III</sup> methylation and volatilization in wetlands**

8 Organic As is introduced primarily into the environment via the microbial catalyzed  
9 methylation of As<sup>III</sup>. The As<sup>III</sup> S-adenosylme-thionine methyltransferase (ArsM),  
10 which is responsible for As<sup>III</sup> methylation has recently been found to be common to  
11 many different microbes [12, 80-82]. It is encoded by *arsM* genes, and **catalyzes** the  
12 generation of less toxic organic As species, such as MMAs<sup>V</sup>, DMAs<sup>V</sup> and TMAO.  
13 The volatile As gas including MeAsH<sub>2</sub>, Me<sub>2</sub>AsH and TMAs<sup>III</sup> could also be generated  
14 during the biomethylation processes. To date, TMAs<sup>III</sup> is the most commonly detected  
15 volatile As species in the natural environment [28, 35] and under *in vitro* conditions  
16 during pure culture [81-83].

17 In microcosm experiments using As contaminated paddy soils, Huang *et al.* [28]  
18 and Jia *et al.* [29] found evidence of both microbial mediated As<sup>III</sup> methylation and  
19 volatilization. Recently discovered universal primers for the amplification of *arsM*  
20 genes have uncovered *arsM* sequences as being widespread in numerous paddy soils  
21 [29, 61]. Continued investigation reveals these *arsM* sequences mainly derive from  
22 the phyla *Gemmatimonadales*, *Firmicutes*, *Actinobacteria*, and *Proteobacteria* and the

1 domain *Archaea* [61]. By applying a metagenomic approach, Cai *et al.* [62] also  
2 found *arsM* genes in coastal sediments, but the dominant bacteria species involved in  
3 As<sup>III</sup> methylation were not identified in this study. Furthermore the ability to  
4 methylate and volatilize As<sup>III</sup> has been discovered in three cyanobacteria species that  
5 are common in paddy soils [82], and a small free-living eukaryote *Ostreococcus tauri*  
6 found in coastal waters [83]. In general, to the best of our knowledge, the study of  
7 As<sup>III</sup> methylation and volatilization in wetlands is still rather limited, but given the  
8 rapid advance in our understanding of the importance of this aspect of the As  
9 biogeochemical cycle, this is an area that will likely be of increasing interest in the  
10 future.

11

### 12 **3.4 Environmental factors affecting As biotransformation microbes**

13 Various environmental factors affecting the diversity, behavior and metabolism of As  
14 biotransformation microbes have been observed in wetlands. One of the most  
15 important is the As concentration of the soils/sediments with As biotransformation  
16 microbe abundance found to correlate positively with As concentration in paddy soils  
17 [61]. Similarly, *arsM* gene abundance and the concentration of methylated As in  
18 paddy soil solutions also exhibit a strong positive correlation [29]. The amount and  
19 form of OM in wetlands is also key, for example, several experiments carried out in  
20 microcosms using paddy soils have demonstrated that the amendment of OM  
21 promotes the activity of As<sup>III</sup> oxidizing bacteria [28]. The application of rice straw can  
22 increase the community diversity of As<sup>III</sup> oxidizing bacteria [60], and the activity of



1 As<sup>III</sup> methylation microbes in paddy soils [28, 29]. Straw also has an impact on As<sup>V</sup>  
2 detoxification reducing microbes, acting to moderately simulate their activity, but  
3 greatly enhance the total abundance of As<sup>V</sup> reducers [28].

4 The concentration of SO<sub>4</sub><sup>2-</sup> in paddy soils strongly influences microbial  
5 community compositions, modifying both As<sup>III</sup> oxidation and As<sup>V</sup> detoxification  
6 reduction activity. It is postulated that this is due to the possible sharing of microbial  
7 groups of sulfur oxidation and As redox [61]. The microbial community composition  
8 of bacteria/archaea involved in As biotransformations is also particularly sensitive to  
9 iron concentrations. This is reasonable, especially considering that the  
10 absorption-desorption dynamics of iron /oxyhydroxides and As<sup>V</sup> influence the  
11 concentration and species of bioavailable As in wetlands [41, 42]. For the microbial  
12 communities carrying out As<sup>III</sup> methylation, it is the available NO<sub>3</sub><sup>-</sup>-N, NH<sub>4</sub><sup>+</sup>-N, that  
13 appears to be the most sensitive environmental parameter influencing community  
14 composition [61]. Other factors, such as pH, redox potential, alkalinity, temperature  
15 and dissolved oxygen, also contribute and influence As biotransformation microbial  
16 abundance and activity [46]. However, investigation into this topic is still in its  
17 infancy. Much remains to be done to improve our understanding of how we can  
18 optimize the function of microbial mediated As biotransformations by changing the  
19 management of local wetland environments. A significant hurdle, blocking this goal  
20 has been the lack of suitable methods to observe and measure the dynamic  
21 environmental conditions, at scales appropriate to the biota driving the change.  
22 However, with the development of new multi-parameter, visualization tools such as

1 diffusive gradients in thin films (DGT)/planar optode sandwich sensors [84, 85] and  
2 advanced radiography and isotope imaging, *in situ* mapping of As and other key  
3 elements is now possible. Employing these technologies concurrently with 2D  
4 enzyme activity plots (zymography) and microbial imaging, i.e. fluorescence *in situ*  
5 hybridization (FISH) or oligonucleotides labeled probes with light emitting  
6 chromophores [86], offers further exciting possibilities to unravel the complex  
7 environment-biota interactions impacting on wetland As release.

8

#### 9 **4 Concluding remarks and perspectives**

10 Microbes act as the ‘switch’ turning a wetland from an As sink to source through As<sup>V</sup>  
11 reduction, As<sup>III</sup> oxidation, As<sup>III</sup> methylation, and As volatilization processes (Figure 1).  
12 As<sup>V</sup> reducing bacteria/archaea can enhance As mobilization from sediments to water  
13 [54, 75], while As<sup>III</sup> oxidizing microbes act to decrease As mobility and bioavailability  
14 [3]. The two groups of As<sup>V</sup> reducers and As<sup>III</sup> oxidizers act in tandem, controlling the  
15 direction/path of the inorganic As cycle. While wetland As<sup>III</sup> methylators create  
16 organic As species (MMAs<sup>V</sup>, DMAs<sup>V</sup>, TMAs<sup>III</sup>), they also generate volatile As,  
17 promoting its release into the atmosphere [2].

18 Considering the key role wetlands play in delivering essential ecosystems  
19 services and the large area they occupy, the microbial mediated As biotransformations  
20 they host/support remain indispensable components of a ‘safe’ global As  
21 biogeochemical cycle, one that functions in the best interests of humankind. Failure to  
22 live in balance with As’ complex biogeochemistry can have devastating consequences,

1 from the release of As from near-surface wetland sediments to underground drinking  
2 water supplies [72], to its transfer into rice plants [41].

3 Better management of wetland resources for optimized microbial control of As  
4 could potentially yield huge gains in public and environmental health. However more  
5 research is needed to improve our understanding of how to make best use of these  
6 microbial mediated reactions. We recommend research attention is immediately  
7 directed at gaps in our understanding of wetland As cycling, such as microbial  
8 organic-As degradation, as the literature available on this topic is scant. Furthermore,  
9 continued improvements to the technologies available to study *in situ*, both the  
10 chemistry and biology of the mercurial wetland environment is needed.

11

## 12 **Acknowledgements**

13 The authors declare no conflicts of interest and financial disclosures. We would like to  
14 thank the Chinese Academy of Sciences President's International Fellowship Initiative  
15 (CAS-PIFI 2016VEC001) and China Postdoctoral Science Foundation (No.  
16 212400241).

17

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- 9    Chinese).
- 10

1 Table 1. Structure of prevalent As species in the environment.

Species	Structure of As speciation
Arsenite, As <sup>III</sup>	$\begin{array}{c} \text{HO}-\text{As}-\text{OH} \\   \\ \text{OH} \end{array}$
Aesenate, As <sup>V</sup>	$\begin{array}{c} \text{O} \\    \\ \text{HO}-\text{As}-\text{OH} \\   \\ \text{OH} \end{array}$
Methylarsonate, MMAs <sup>V</sup>	$\begin{array}{c} \text{O} \\    \\ \text{HO}-\text{As}-\text{OH} \\   \\ \text{CH}_3 \end{array}$
Dimethylarsinate, DMAs <sup>V</sup>	$\begin{array}{c} \text{O} \\    \\ \text{H}_3\text{C}-\text{As}-\text{OH} \\   \\ \text{CH}_3 \end{array}$
Thrimethylarsine oxide, TMAO	$\begin{array}{c} \text{O} \\    \\ \text{H}_3\text{C}-\text{As}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$
Aesenosugars	
Arsenobetaine, AsB	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_3\text{C}-\text{As}^+-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})\text{OH} \\   \\ \text{CH}_3 \end{array}$

2

3

Table 2. The quality guidelines for As contamination in wetlands from different countries.

Sediment quality guidelines in various countries	Countries	Level	Arsenic concentration (mg kg <sup>-1</sup> )	References
Hongkong ISQVs	China	ISQV-low	8.2	[87]
		ISQV-high	70	
Sediment Quality Criteria	China	Class I	20	[16]
		Class II	65	
Canadian Environmental Quality Guideline	Canada	ISQGs	7.24	[15]
		PEL	41.6	

ISQV, interim sediment quality value; ISQGs, interim sediment quality guidelines; PEL: probable effect level.

Table 3. Summary of recently detected arsenic contaminated wetlands.

Wetland types	Country	Sampling Location	As concentration (mg kg <sup>-1</sup> / μg L)	References
Coastal wetlands	China	Yellow River delta	38	[32]
			45	
	Yangtze River delta	10	[33]	
Inland wetlands	U.S.	Massachusetts	20-2100	[36]
	Spain	Guadalquivir	20	[38]
		Fatehpur	72-114	
Paddy soils	Bangladesh	Dhumrakandi	62-138	[26]
		Paranpur	73-77	
		Faridpur	34	
	India	De Ganga	17	
	China	Chenzhou	60	[61]

		Qiyang	79	
		Anqing	19	
		Jiaxing	20	
		Yingtian	16	
		Jingzhou	19	
		Changde	16	
		Jiangmen	25	
		Guilin	21	
		Guiyang	21	
		Zhanjiang	18	
<hr/>				
Wetland waters	Bangladesh	Malabar	60	[23]
		Gerajan	80	
		Dohuria	11-14	
<hr/>				

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Behi	11
Porabait	26
Barakhaillah	20
Jora	11
Uhila	18
Barakuri	11
Jerukuri	11
Bigaira	11

---

**Figure caption**

Figure 1. Sources of As introduced to wetland, microbial mediated As biotransformation in wetland, and genes responsible for As<sup>V</sup> respiratory reduction, As<sup>V</sup> detoxification reduction, As<sup>III</sup> oxidation, and As<sup>III</sup> methylation.