

Factors and pathways regulating the release and transformation of arsenic mediated by DFeRB and SRB

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ABSTRACT

Dissimilatory iron reducing bacteria (DFeRB) and sulfate reducing bacteria (SRB) are regarded as the most important microbial communities regulating the mobility, bioavailability and toxicity of arsenic (As) in environment. However, the driving process and their explanatory factors regulating the As transformation and migration mediated by DFeRB and SRB remain poorly understood. The novelty of this work is to explore the driving process and key environmental factors governing As mobilization mediated by DFeRB and SRB on the basis of continuous As speciation and environment parameters monitoring in sediment-water system. The results illustrated that DFeRB and SRB played a critical role in regulating As mobilization in

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sediment-overlying water system. The reduction process mediated by DFeRB and SRB significantly promotes reduction of As (V) and endogenous release of As. However, in the DFeRB and SRB mediated reduction, the main driving process and their key explanatory factors that dominated As mobility were obviously different. DFeRB presented significant effects on the reductive dissolution and re-distribution of Fe (III) oxyhydroxides and As-containing Fe (III) minerals as well as adsorption-desorption, which in turn influenced the transformation of iron species and the release and ecotoxicity of As. Meanwhile, the environmental factors that affect As mobility depend on Fe^{2+} and Fe^{3+} in DFeRB-induced reduction, which have two main pathways: the process of As mobilization mediated by DFeRB, and the process influenced by IP of competitive adsorption and anion exchange. Significantly different from DFeRB, the effects of SRB on As behavior mainly by influencing adsorbed As, pyrite and As sulfides in sediment as well as the formation of sulfide during sulfate reduction. The main pathways on As mobilization were the direct effects of SRB, S^{2-} and Fe^{2+} . In addition, the role of NH_4^+ -N for the driving process of As mobility is more pronounced for SRB-induced reduction. NO_3^- -N is an essential factor affecting As mobility, but the effects of NO_3^- -N on As was a non-significant pathways. This work is helpful to provide insight into the environmental effects of DFeRB and SRB on biogeochemical cycle of As.

Keywords: As, transformation and migration, driving process, environmental explanatory factors, DFeRB and SRB

1 Introduction

Arsenic (As) is an environmentally ubiquitous and notorious carcinogen [C Wang *et al.*, 2016] and As contamination is of great environmental concern [Lan *et al.*, 2018]. The mobility, bioavailability and toxicity of As are strongly associated with its speciation in sediment and aquatic environment, which largely controlled by redox processes [Bettoschi *et al.*, 2018; Duan *et al.*, 2017; Mohapatra *et al.*, 2018; Xue *et al.*, 2017]. For instance, As (III) presents higher mobility and toxicity than As (V) due to its higher solubility and stronger binding ability with dimercapto or carboxyl groups on enzyme protein molecule forming stable complex or ring compound to inhibit enzyme activity [Han, 2019]. Meanwhile, other major redox sensitive elements such as iron (Fe) and sulfur (S) also affect As mobilization and toxicity during their redox process [Frohne *et al.*, 2011; Han, 2019]. The redox transformation and mobilization of As has been proven to be primarily mediated by microorganisms [Cai *et al.*, 2019; J H Huang, 2018; Xu *et al.*, 2016]. Therefore, the reduction process mediated by DFeRB and SRB is considered to be the most important mechanism affecting the mobilization of As, which is intrinsically linked to the biogeochemical cycles of Fe and S [Colombo *et al.*, 2014; Mejia *et al.*, 2016; Mirjam *et al.*, 2007]. However, the driving process and their explanatory factors governing As mobility and ecotoxicity during the coupling biogeochemical cycles of As/Fe/S mediated by DFeRB and SRB remains poorly understood.

Previous studies have shown that DFeRB and SRB can induce the reduction of Fe and S [Das and kerkar, 2017; Kirk *et al.*, 2010; Ko *et al.*, 2019; Sun *et al.*, 2017], then control the mobility and fate of As by the coupling effects with Fe and S [Han, 2019; Karimian *et al.*, 2018; J Sun *et al.*, 2016]. It might be due to the presence of As in iron and sulfur minerals played a leading role in the distribution of As in polluted

sedimentary environments [Zhang *et al.*, 2018], and the occurrence of As in the water column was mainly related to the dissolution of As-bearing minerals [Deng *et al.*, 2018; Erika E. Rios-Valenciana, 2020]. Moreover, sediments could act as source and sink for As, in which physicochemical and/or microbial factors played significant roles in As behavior [Xu *et al.*, 2011]. However, recent studies mainly focus on adsorption-desorption of As from As-bearing minerals [Cheng *et al.*, 2016; Xue *et al.*, 2017; Zhu and Elzinga, 2015], the effect of oxidative dissolution of Fe and S minerals on As mobility [Couture *et al.*, 2015; E. Zanzo, 2017; H.S. Moon, 2017; Jeong *et al.*, 2010; Kocar *et al.*, 2010] and the effect of As on the formation of Fe or S minerals under the DFeRB and SRB mediated reduction process [Peng *et al.*, 2017; J Song *et al.*, 2015; V.T.H. Phan, 2018]. There are few reports on how DFeRB and SRB influence As mobility and ecotoxicity by affecting As pools in the sediment. The variation of As pool in the sediment is also intrinsically linked with the multiple factors, such as temperature (Temp), microorganism activities, organic matter (OM), ammonia nitrogen ($\text{NH}_4^+\text{-N}$), nitrate nitrogen ($\text{NO}_3^-\text{-N}$) and so on. The release of As into the water column is regulated by not only the mentioned factors but also As pool.

Accordingly, to study the association of As mobility and ecotoxicity with environmental factors mediated by DFeRB and SRB. The objectives of this study is (1) to illustrate the release and potential ecotoxicity of As mediated by DFeRB and SRB, (2) to understand the main mechanism regulating As mobility and ecotoxicity mediated by DFeRB and SRB, (3) to identify the driving process and explanatory factors governing As mobility and ecotoxicity, (4) to compare the differences in driving process and their key explanatory factors governing As mobility and ecotoxicity under the DFeRB and SRB mediated reduction. It is of great significance to provide insight into the environmental effects of DFeRB and SRB on

biogeochemical cycle of As.

2 Materials and methods

2.1 Sampling

The surface sediments were collected from Lake Wuliangsu Hai (WLSH) (40°59'N, 108°51'E) in Inner Mongolia plateau, China in July, 2018. The sediments were sampled applying a SA Beaker collector (Eijkelpkamp), and sealed immediately to ensure anaerobic environment and stored in dark immediately after collection, then transported to the laboratory and stored at 0-4°C. The lake locates in the cold and arid area with a long ice-bound period (November to March). The chemical characteristics of the sediments and overlying water from WLSH were listed in Table S1 and S2. The other basic information about the lake were described in Supporting Materials (SM).

2.2 Experimental design and methods

Surface sediments were constructed microcosm incubation experiments with a water-to-sediment mass ratio of 5:1 (100 ml deionized water, 20 g sediment). The experiments were carried out at 30°C and 4°C for 30 days in the dark, respectively, and divided into three groups: (A) control group (sterilized sediment), (B) *Shewanella putrofaciens* group (addition after sediments sterilized) and (C) *Desulfovibrio desulfuricans* subsp. *desulfuricans* group (addition after sediments sterilized). *Shewanella putrofaciens* and *Desulfovibrio desulfuricans* subsp. *desulfuricans* are representative and ubiquitous species of DFeRB and SRB, respectively, in lakes and

soil environment. The sediment samples and deionized water were autoclaved at 121°C for 15 min before the incubation experiments. And 0.1% chloroform was added into group A to further inhibit microbial growth. The incubations were inoculated with 4% (v/v) of inoculums in each culture bottle in group B and C. All experiments were performed in anaerobic conditions in the sterile console. During the incubation, overlying water were sampled from the bottles on days 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 17, 19, 21, 23, 25, 27 and 30, meanwhile the pH was measured in situ and biological activity was also determined. After, overlying water were collected, the samples were filtered through 0.45µm filters, and then the concentrations of total Fe (TFe), Fe^{2+} , S^{2-} , total As (TAs), As (III), inorganic phosphorus (IP), total phosphorus (TP), dissolved organic matter (DOC), total nitrogen (TN), NH_4^+ -N and NO_3^- -N were determined. The sediment samples were collected at 1, 2, 8, 15, 23 and 30 days, and then the concentrations of sulfide, TFe, Fe^{2+} , TAs, As (III), TP, TN, OM and IP were measured. Meanwhile, the sequential extraction procedure [Keon *et al.*, 2001] was performed to obtain the information of arsenic pool in the sediment, including loosely adsorbed As (S1), strongly adsorbed As (S2), As coprecipitated with AVS, carbonates, Mn oxides, and very amorphous Fe oxyhydroxides (S3), As incorporated in amorphous iron oxides (S4), As coprecipitated in crystalline iron oxides (S5), As oxides and arsenic coprecipitated with silicates (S6), As coprecipitated with pyrite (S7), and As sulfides (S8) (Table S3).

All methods for water and sediment samples analysis were detailed in SM. All chemicals used were guaranteed or analytical grade. Water used in the experiments

were ultrapure water (Milli-Q, Millipore, $\geq 18.2 \text{ M}\Omega \text{ cm}$). In all cases, blank samples were included and the samples obtained at each time point were analyzed and tested 2-3 times to ensure the accuracy of analysis. The standard deviations of all analytical methods were within 5%. The recovery ranged from 86% to 117%.

2.3 Data Analysis

All statistical analyzes were conducted using IBM SPSS 25.0 software (IBM Corp., Armonk, NY, USA) and OriginPro 2017. Redundancy analysis (RDA) was performed using Canoco version 4.5 software (Microcomputer Power) to explore the effects of environmental factors on As release and potentially ecotoxicity. Spearman's correlation matrix diagram conducted by R version 3.5.3 (R Foundation for Statistical Computing, Vienna, Austria, 2019).

Risk assessment code (RAC) was calculated to better understand the indication of the mobility of As mediated by DFeRB and SRB in the aquatic environment [Hu *et al.*, 2018], method and categories for RAC were described in SM.

Partial Least Squares (PLS) Path model is the partial least squares approach to structural equation modeling. This study fitted a PLS Path model to explain the driving process of As mobility in sediment-water interface (SWI) including direct and indirect pathways based on 1000 resampled bootstrap *t* test. Multiple conceptual models were considered and tested in the initial PLS model based on 1000 resampled bootstrap *t*-test, and ultimately integrated them into a general model for visualization by eliminating non-significant pathways. The overall fit of the PLS was evaluated in the R package plspm, these statistical analyses were performed using R version 3.5.3.

3 Results

3.1 Arsenic reductive release induced by DFeRB and SRB

The results showed that the reduction and release of As induced by DFeRB and SRB were significantly higher than control group both in summer and ice-bound period ($P < 0.05$) (Fig.1 and S1). Accompanying with microbial-induced reduction process, the average release rates of As(III) and TAs were 14.31 and 45.19 $\mu\text{g}/\text{m}^2\cdot\text{d}$ in group DFeRB as well as 29.24 and 49.91 $\mu\text{g}/\text{m}^2\cdot\text{d}$ in group SRB during summer, respectively; while 2.59 and 10.09 $\mu\text{g}/\text{m}^2\cdot\text{d}$ in group DFeRB as well as 4.97 and 15.52 $\mu\text{g}/\text{m}^2\cdot\text{d}$ in group SRB during ice-bound period, respectively (Table.S4). These release rates were found higher than control groups (1.1-2.3 times), which indicated the mediating effects of DFeRB and SRB during the reductive release process of As.

Our monitoring results found the concentrations of dissolved TAs and As (III) increased rapidly in the overlying water both in summer and ice-bound incubation periods (Fig.1 and S1). It indicated that the fractions of As bound to sediments were destabilized, which suggested the fractions transformation of As in sediments was happened and enhanced by the mediating effects of DFeRB and SRB during the incubation, whether in summer or ice-bound periods. Information on the changes in As concentrations in aqueous phase mediated by DFeRB and SRB were provided in SM.

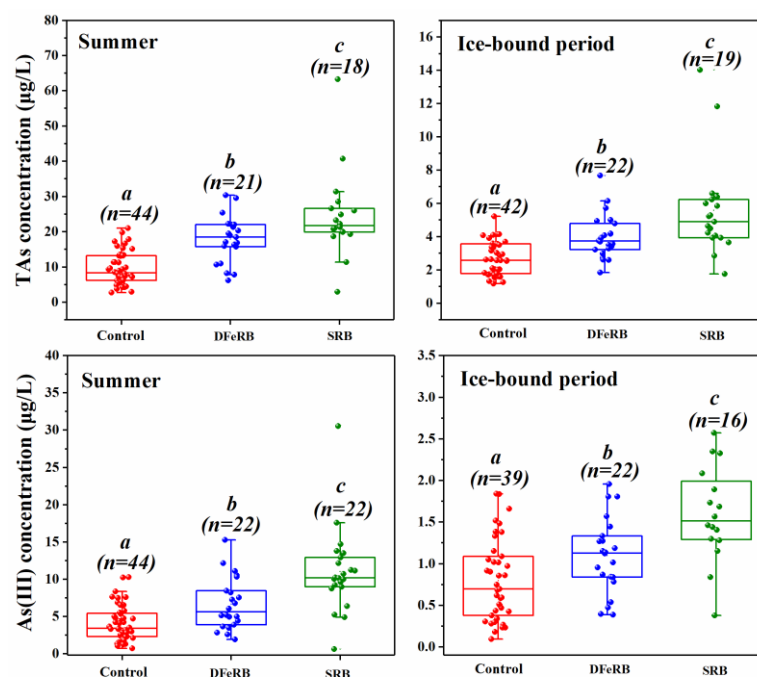


Fig.1 Effect of microbial reduction on the concentration of As (III) and TAs in aqueous phases. Values marked with different lowercase letters differ significantly at p<0.05.

3.2 Factors associating with As releases

RDA which based on the correlation between environment factors and As fractions in sediments and water phase were detailed in SM. According to the sequential extraction, S1 and S2 were labile pool which contained adsorbed As; S3, S4 and S5 were moderately labile pool and closely related to iron species; S6 was As oxides and As coprecipitated with silicates; S7 and S8 were nonlabile pool related to sulfur. Therefore, eight As speciation were classified as S1-2, S3-5, S6 and S7-8 in RDA analysis, in order to better understand the effects of DFeRB and SRB on As mobilization. The results showed DFeRB and SRB, coupling with environmental factors, played important roles in the process of As fractions transformation and in turn the reductive release (Fig.2 and 3). DFeRB and SRB could promote As (V) reduction and then elevated the concentrations of As (III) and TAs in water phase. The most interesting thing is, the effects of DFeRB and SRB on As fractions were

obviously different.

DFeRB and SRB positively correlated with As(V) (Fig.2 and 3), As (III) and TAs in water phase (Fig. S3 and S4). It indicated that DFeRB and SRB can potentially promote the reduction of As (V) to As (III). DFeRB present significant effected on S1-2 and S3-5 in sediment, meanwhile, Fe^{2+} and Fe^{3+} presented significant effected on S1-2 and S3-5, respectively (Fig.2), accordingly, the correlations were observed between DFeRB and Fe^{2+} , Fe^{3+} (Fig.4 and S3). Moreover, S1-2 and S3-5 in sediment significantly associated with As (III) and As (V) in water phase (Fig.2), As (III) and TAs in water phase, corresponding to significant correlations with S2, S3, S4 and S5 in sediment phase in group DFeRB (Fig.2 (B) and (C)). These illustrated that As level in water were to a certain extent depended the effects of DFeRB on S3-5 and S1-2, in which Fe^{2+} and Fe^{3+} were the most important factors. In group SRB, S^{2-} in water and sediment (w- S^{2-} and s- S^{2-}) significantly associated with S1-2 and S7-8 (Fig.3 and 5), as well as the correlation between SRB and S^{2-} (Fig.3 and S4). Fe^{2+} and Fe^{3+} presented close relations with S1-2 and S7-8 (Fig.3), and As (III) and TAs in water phase closely correlated with S1 and S8 in sediment phase (Fig.3). It demonstrated that SRB significantly influenced S7-8 and S1-2 in sediment via S^{2-} , and iron involved in this process.

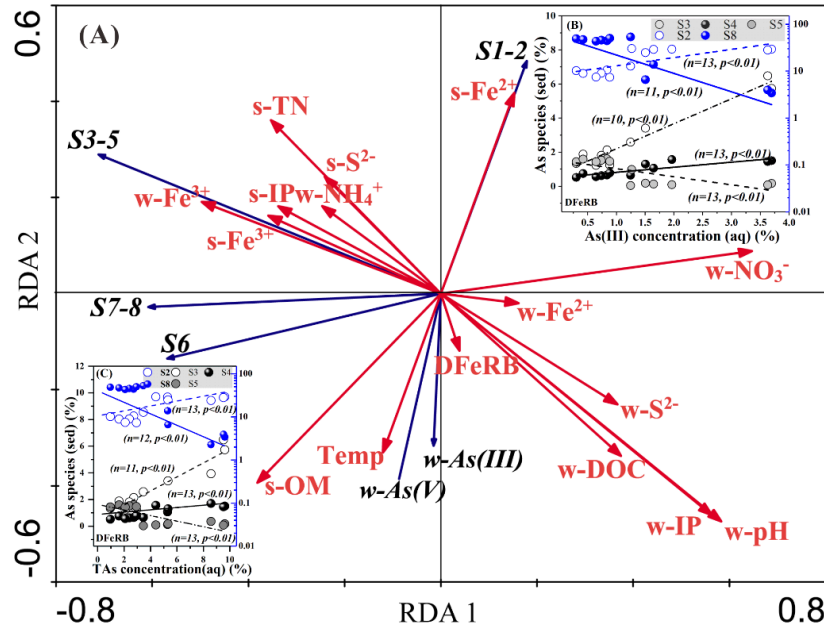


Fig.2 (A) Redundancy analysis (RDA) of As and environmental factors in sediment and water phase in DFeRB environment. w- and s- represent environmental factors in water and sediment phase, respectively. S1-2 (sum of S1 and S2), S3-5 (sum of S3, S4 and S5), S6 (S6) and S7-8 (sum of S7 and S8) represent the As speciation in sediment phase. NH_4^+ and NO_3^- represent $\text{NH}_4^+\text{-N}$ and $\text{NH}_3^-\text{-N}$, respectively. (B) and (C) Correlation analysis between As (III) and TAs concentrations in water phase and As pool concentrations in sediment phase, respectively.

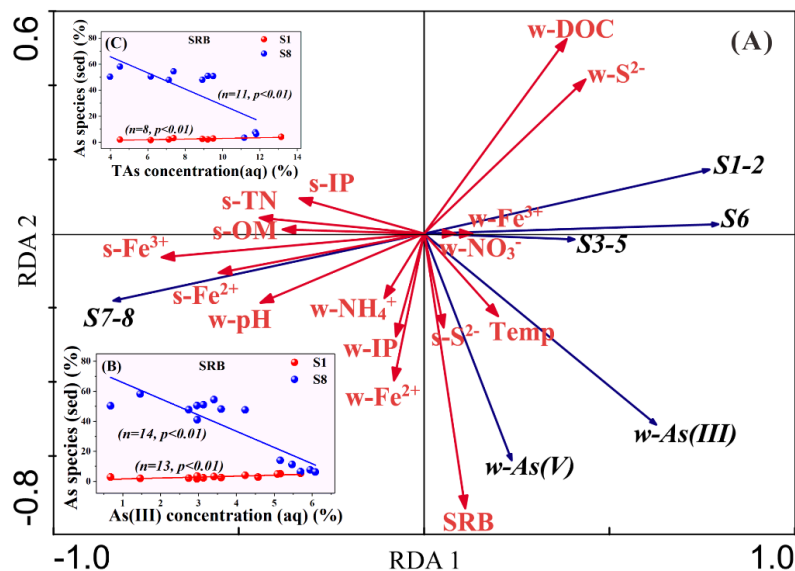


Fig.3 (A) Redundancy analysis (RDA) of As and environmental factors in sediment and water phase in SRB environment. w- and s- represent environmental factors in water and sediment phase, respectively. S1-2 (sum of S1 and S2), S3-5 (sum of S3, S4 and S5), S6 (S6) and S7-8 (sum of S7 and S8) represent the As speciation in sediment phase. NH_4^+ and NO_3^- represent $\text{NH}_4^+\text{-N}$ and $\text{NH}_3^-\text{-N}$, respectively. (B) and (C) Correlation analysis between As (III) and TAs concentrations in water phase and As pool concentrations in sediment phase, respectively.

211

212 **4 Discussion**

213 **4.1 Mechanisms of different factors on As reductive release**

214 The potential pathways of As mobility explained by PLS analysis were detailed in
215 SM.

216 4.1.1 DFeRB and SRB

217 ***DFeRB***

218 Theoretically, Fe(III) (oxy)hydroxides could be transformed to more crystalline
219 minerals (e.g., goethite and lepidocrocite), or Fe(II)/Fe(III) (oxy)hydroxides minerals
220 (magnetite and green rust) due to the catalysis of Fe(II), which results in the weaker
221 binding affinities to As, and the enhancing transformation and release of As [*Y Song et*
222 *al.*, 2015]. Meanwhile, the reductive dissolution of As-bearing Fe(III)
223 oxyhydroxysulfates and hydroxides (e.g. schwertmannite and ferrihydrite) mediated
224 by DFeRB may result in the release of structurally incorporated or surface adsorbed
225 As [*Burton et al.*, 2013b; *Fan et al.*, 2018; *Revesz et al.*, 2016]. According to the
226 sequential extraction procedure, S3-5 were moderately labile pools of As in sediments
227 which closely related to iron species. Accordingly, a significant correlation between
228 DFeRB and fractions of S3-5 were found (Fig.2 and 4(B)); Further, As (III) and TAs
229 in water presented significantly correlations with the fractions of S3, S4 and S5 in
230 sediments in group DFeRB (Fig.2(B) and (C)). It suggested that the transformation
231 between crystalline Fe(III) and poorly crystalline Fe phase can be influenced by the
232 reductive dissolution and re-distribution of Fe(III) oxyhydroxides and As containing
233 Fe (III) minerals mediated by DFeRB, in turn the releasing of As from sediments to
234 overlying water.

235 As is well-known, iron (hydr)oxides are the main carriers of As in environment

[Fan *et al.*, 2017]. As adsorbed on iron (hydr)oxides surface will release during the reductive dissolution of iron (hydr) oxides induced by DFeRB. Therefore, the positive and negative relationships of S1-2 with Fe^{2+} and Fe^{3+} , respectively, were found in RDA (Fig.2 and 4(A)), suggesting that the reduction of Fe^{3+} to Fe^{2+} which limited the adsorption ability of iron (hydr)oxides for As [Cheng *et al.*, 2016], corresponded to the release As adsorbed on iron (hydr)oxides surface due to S1-2 contains adsorbed As. Furthermore, DFeRB presented effects to S8 in some extent in sediments due to *Shewanella putrofaciens* could lead to As dissolved from As sulfides or even methylated quickly, inducing the repartition of As [Hansel *et al.*, 2004; C Wang *et al.*, 2016] (Fig.2).

In overlying water, DFeRB presented significant positive correlation with As (V), As (III), TAs (Fig.2 and Fig.S3). It indicated that reduction of As(V) to As(III) may also cause its release since As(III) is well known for its higher solubility and weaker affinity to various minerals in aquatic environment [Fan *et al.*, 2018; J H Huang, 2018]. Moreover, the reduction of Fe^{3+} and As (V) mediated by DFeRB can enhance As dissociation and release from the host minerals and elevated As levels in water column [S Wang *et al.*, 2012]. Thus, the interplay between DFeRB mediated As(V) reduction and Fe(III) (hydr)oxide reduction also influence the mobilisation and ecotoxicity of As.

SRB

Accordingly, both S1-2 (labile pools) and S7-8 (nonlabile pools) inherently relate to sulfur. It indicated SRB can mediate the transformation of S7-8 and S1-2 in sediments, then influence As levels in water column (Fig.3and 5(A)). These processes included two distinct stages namely release and re-immobilization. On the one hand, sulfide generated by sulfate reduction is a strong reducing agent that can reduce

amorphous and crystalline Fe(III)(oxy)hydroxide minerals quickly [Y Song *et al.*, 2015], and promote the convert of Fe(III) (oxy)hydroxides to Fe sulfides (e.g. FeS, FeS₂), which reduced the affinity of iron minerals to As [Flynn *et al.*, 2014; Zhang *et al.*, 2018], can accelerate under the SRB mediating effects due to more reducing agent generation (sulfide). Meanwhile, SO₄²⁻ reduction process may promote As mobility thanks to the formation of thioarsenic species with weakly adsorption properties and high solubility [Y Song *et al.*, 2015; Stucker *et al.*, 2014]. On the other hand, some insoluble sulfide mineral-like phases, such as orpiment (As₂S₃), realgar (AsS) and arsenopyrite-like phase (FeAsS), which can sequester As [Burton *et al.*, 2013b; Luo *et al.*, 2013], will be formed during the sulfate reduction mediated by SRB. Then, the newly formed secondary minerals (e.g. siderite, vivianite, green rust, magnetite or mackinawite), can also sequester As via precipitation, adsorption or structural incorporation, then constraining As release [Xu *et al.*, 2016].

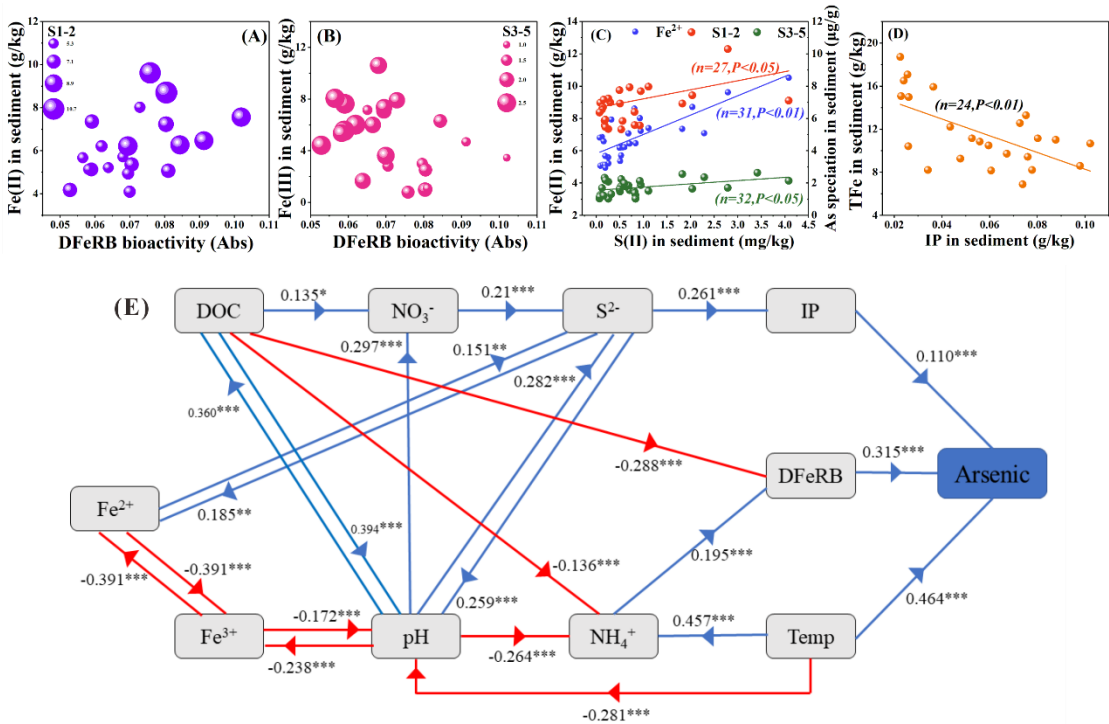


Fig.4 (A) Influence of Fe²⁺ in sediment and DFeRB-bioactivity on S1-2 in sediment (B) Influence of Fe³⁺ in sediment and DFeRB-bioactivity on S3-5 in sediment (C) Correlation

between S^{2-} and Fe^{2+} , S1-2 and S3-5 in sediment (D) Correlation between IP and TFe in sediment (E) The PLS path model for arsenic release in DFeRB environment (n=264). Numbers on the arrows are path coefficients (λ) indicating the effect size of the relationship. Solid blue and red arrows represent positive and negative paths, respectively (*, **, *** indicate significant at $p<0.05$, $p<0.01$, and $p<0.001$, respectively. Significant differences are based on 1000 resampled bootstrap t-test). NH_4^+ represent NH_4^+ -N, NO_3^- represent NO_3^- -N.

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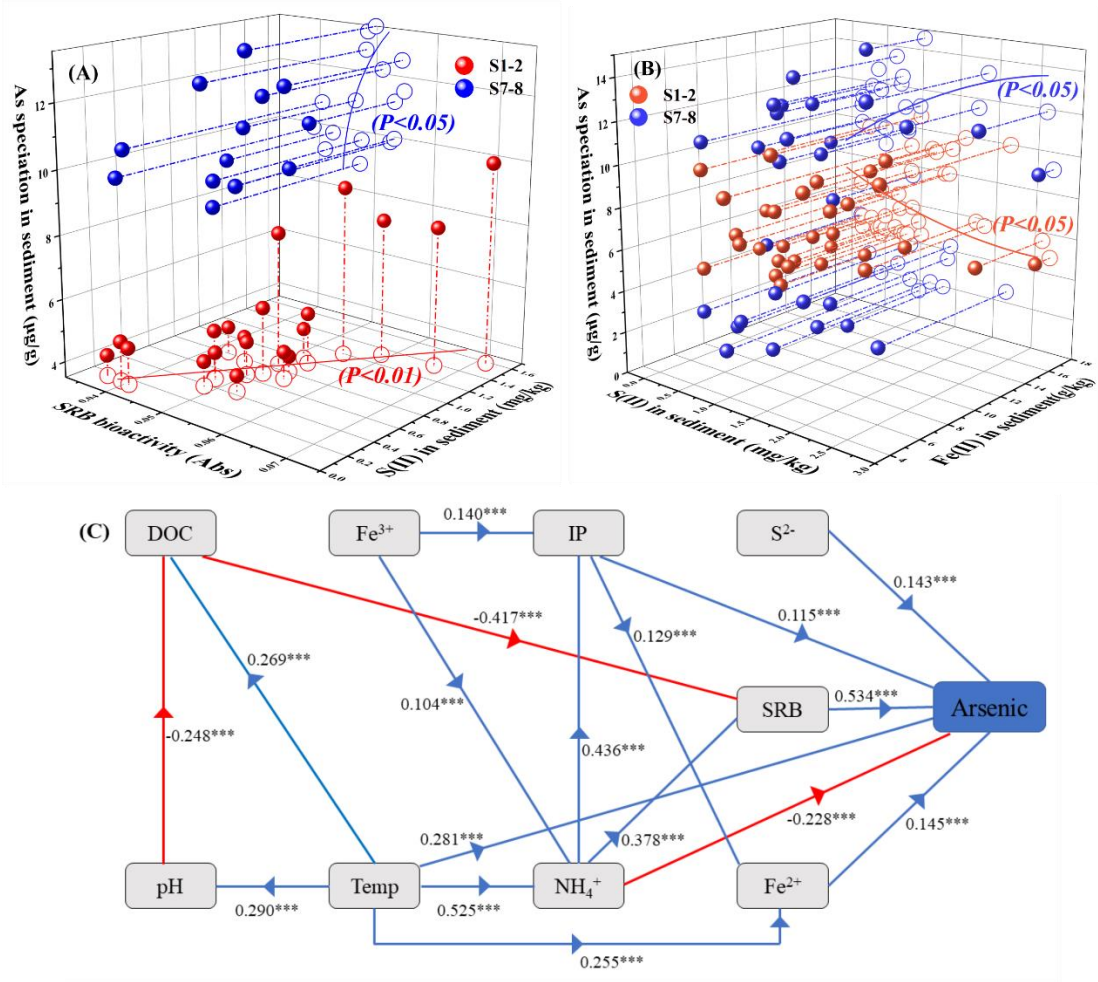


Fig.5 (A) Influence of S^{2-} in sediment and SRB-bioactivity on S1-2 and S7-8 in sediment (B) Influence of S^{2-} and Fe^{2+} in sediment on S1-2 and S7-8 in sediment (C) The PLS path model for arsenic release in SRB environment (n=264). Numbers on the arrows are path coefficients (λ) indicating the effect size of the relationship. Solid blue and red arrows represent positive and negative paths, respectively (*, **, * indicate significant at $p<0.05$, $p<0.01$, and $p<0.001$, respectively. Significant differences are based on 1000 resampled bootstrap t-test). NH_4^+ represent NH_4^+ -N.**

276

277 4.1.2 Temperature, DOC and pH

278 Temperature strongly influence the microbial activity and respiration rates, and

279 the reductive As solubilization in anoxic soils was reported to exhibit a temperature

dependence of similar order [F-A Weber, Hofacker, A.F., Voegelin, A., Kretzschmar, R, 2010], therefore could direct affect As mobilization (Fig.4 and 5). S1-2 and S3-5 in sediments closely related to temperature in SRB environment (Fig.3), indicating that temperature may affect As release and ecotoxicity. There is evidence that dissolution of As-rich hydrous ferric oxides [Majzlan and Juraj, 2011] and As desorption from poorly-crystalline Fe(III)-oxyhydroxides [Martin *et al.*, 2009] are endothermic reactions. Moreover, numerous studies also observed that reductive As solubilization from sediment and soil was highly temperature dependent [Hindersmann and Mansfeldt, 2014; Karhu, 2014].

PLS results demonstrated that DOC influences As release coupling with microbe (Fig.4(E) and 5(C)), the negative influence indicated that the consumption of DOC was used to provided energy for the bioactivity of DFeRB and SRB. It can also fuel the microbe (as an active electron donor) to drive the reduction processes of iron and sulfate in anoxic sediments [F-A Weber, Hofacker, A.F., Voegelin, A., Kretzschmar, R, 2010], thereby indirectly influencing As mobility by the interaction of As with the generated ferrous matter [Kirk *et al.*, 2010; Xu *et al.*, 2011] or sulfides [H.S. Moon, 2017; Langner, 2013]. RDA analysis showed that OM presented effects on S7-8 and S1-2 in group DFeRB and on S7-8 in group SRB. It indicated that the effects of OM on As mobility were coupled with its effects on Fe oxyhydroxides and sulfur species in the DFeRB induced reduction process while mainly were coupled with sulfur species in the SRB induced reduction process. The Fe(III) in As-bearing iron minerals may act as an electron acceptors during the oxidation process of OM through anaerobic microbial respiration, resulting in the reductive dissolution of the Fe minerals and concurrent release of As and Fe from sediments [Borch, 2010; Zeng, 2019]. Sulfate can also cause As desorption from sediments due to its effect on Fe

species transformation [Li *et al.*, 2018]. Furthermore, OM can strongly bind with metals due to the effects of strong adsorption, ion exchange, competition for sporting sites and chelation [Vink *et al.*, 2017], which resulted in the transformation and mobilization of As from sediments to water column. In addition, OM can be used as a catalyst for As mobilization through metal chelation under anaerobic conditions [Machado *et al.*, 2016].

DFeRB are reported as fermentation bacteria, which can produce acid to decrease the environment pH, and gradually stabilized when reaching the lower limit of the fermentation process. In theory, pH should negatively correlate with DFeRB, which was coincident with the results of PLS (Fig.4 and Fig.S3). Whereas SO_4^{2-} reduction process will increase pH to some degree [Li *et al.*, 2018], because sulfate reduction is a proton-consuming reaction [Alam and McPhedran, 2019]; and CO_3^{2-} and HCO_3^- ions produced from OM degradation can also increase pH. Additionally, pH fluctuations were associated with the accumulation of biogenic HS due to SRB activity [Fan *et al.*, 2017]. It showed SRB positively correlated with pH (Fig.5 and Fig.S4). The variety of pH significantly affected the dissolution of main adsorption phases of As then influence the release of As [Honma *et al.*, 2016]. Therefore, there were interaction effects between pH and the reduction of DFeRB and SRB in the environment, thus affecting As mobilization.

4.1.3 Fe^{3+} , Fe^{2+} and S^{2-}

Based on the mentioned above, DFeRB and SRB play an important role in the transformation and migration of As. As the production of DFeRB and SRB reduction, Fe^{2+} and S^{2-} accordingly presented significant correlation with DFeRB and SRB, respectively (Fig.S3 and S4). Moreover, PLS analysis illustrated that one of the main

effecting pathways of Fe^{3+} and Fe^{2+} on As release was mediated by DFeRB in group DFeRB; while the direct effects of S^{2-} and Fe^{2+} in group SRB (Fig.4 and 5). Therefore, the roles and effects of Fe^{3+} , Fe^{2+} and S^{2-} were inherent indicators for the reduction of DFeRB and SRB during of the incubation experiments.

Fe(III) (hydr)oxides is one of the most important sorbents in sediment [Q Sun et al., 2016], even can play a governing role for As behavior. Fe^{3+} reduction mediated by DFeRB can promote the reductive dissolution of Fe (oxy)hydroxide [Fan et al., 2018; J H Huang, 2018], then the dissociation of As from the host minerals. Meanwhile, the dissolution of Fe can lead to the desorption of As bound to poorly crystalline minerals [Usman et al., 2012; Yang et al., 2015], thus elevating As levels in water phase. Additionally, As(III) was released with the reduction of Fe(III) (hydr)oxides due to As(III) is more soluble and poor affinity towards Fe host mineral phases [Cheng et al., 2016]. Accordingly, in group DFeRB, a major controlling phase of iron oxides for As repartitioning onto sediments was confirmed in this study based on the significant positive correlations of Fe^{2+} and Fe^{3+} with S1-2 and S3-5 in sediment, respectively (Fig.2 and 4).

S^{2-} can be involved in Fe(III) reduction and consequent precipitation of amorphous FeS, then enhanced As mobilization [Xu et al., 2016], which consistent with our results that S^{2-} positively correlated with S3-5, S1-2 and Fe^{2+} in sediment phase (Fig.4(C)). Meanwhile, S^{2-} may compete adsorption sites with As (III) and result in As desorption from Fe oxyhydroxides surface [Kocar et al., 2010]. In addition, S^{2-} also can act as a strong reductant and participate in Fe(III) reduction, which accelerates Fe oxyhydroxides dissolution and subsequent As (III) release. However, there also had an adsorption stage in the presence of sulfides [Yang et al., 2015] during the reductive dissolution of iron(hydr)oxides. Because As could

adsorbed and precipitated not only by secondary Fe(II)-bearing minerals[*Q Sun et al.*, 2016; *Vink et al.*, 2017], but also co-precipitation with sulfur [*Yang et al.*, 2015]. It was consistent with the variations of As concentration in overlying water in group DFeRB (Fig.S1). PLS results also proved that iron and sulfur were closely related to each other in group DFeRB (Fig.4).

The associations of S^{2-} , Fe^{2+} and Fe^{3+} with As fractions indicated that S7-8 was a major controlling phase in partitioning As onto sediment in group SRB (Fig.3 and Fig.5(B)). The link of As fractions in sediments and water column (Fig.3 and 5) suggested that SRB not only can enhance As release but also make As be retained or transformed to more stable binding speciation in sediment. PLS analysis (Fig.5) demonstrated that sulfide generated by SRB can promote the convert of Fe(III) (oxy)hydroxides to Fe sulfides (e.g. FeS, FeS_2), which has weaker affinity to As and thus increase the release of As [*Xu L*, 2016]. Furthermore, large amounts of S^{2-} was produced in reduction process mediated by SRB, sulfide can sequester As by forming the precipitation of secondary arsenic sulfide minerals [*Burton et al.*, 2013a; *Luo et al.*, 2013], such as ferrous sulfide or secondary pyrite, which can also re-immobilized As via adsorption or co-precipitation, further complicating the system [*Alam and McPhedran*, 2019].

4.1.4 IP

PLS results demonstrated that one of the main pathways for the Fe^{3+} and Fe^{2+} to influence As behavior was influenced by IP in group DFeRB (Fig.4). As and phosphorus have a competitive effect in adsorption and transportation behavior due to their similar chemical structure and chemical properties [*Che et al.*, 2020; *Junbo et al.*, 2018], thereby increasing the mobility of As [*Junbo et al.*, 2018]. Previous

publications showed that the fraction of P bound to Fe oxyhydroxides was a major fraction, even the dominant fraction [Lü *et al.*, 2016], thereby Fe oxyhydroxides play a key role in the competition between As and P [Gu *et al.*, 2020]. Accordingly, IP and Fe^{3+} in sediment significantly positively correlated with S3-5 in group DFeRB (Fig.2), and correlation between TFe and IP was observed (Fig.4(D)). PO_4^{3-} interactions have been extensively documented with respect to Fe (III) oxides, such as ferrihydrite, goethite and hematite [Schoepfer *et al.*, 2017]. It showed that PO_4^{3-} influence Fe^{3+} reduction directly [Schoepfer *et al.*, 2019], and PO_4^{3-} also can enhance Fe(III) reduction by scavenging the produced Fe(II) [Schoepfer *et al.*, 2019] as well as influencing secondary mineral transformation pathways [Borch, 2010; Schoepfer *et al.*, 2017]. Although it is difficulty for As and IP directly sorption to OM, they can be adsorbed on organic solid phases combining with Fe to form cationic bridges between the anionic As or P species and the negative surface charge of the particulate organic matter [Gorny *et al.*, 2015]. Therefore, IP was an important pathway to influence As release and ecotoxicity.

However, in group SRB, the direct effecting pathways for As mobility were S^{2-} and Fe^{2+} coupling with SRB, although IP also could influence As release. This may be due to large amounts of S^{2-} produced and gradually predominate, and SO_4^{2-} also can competitive adsorption to sites on the Fe oxyhydroxides with inorganic As [Li *et al.*, 2018]. In addition, some studies showed that sulfate reduction is more influential influenced directly by iron than PO_4^{3-} [Schoepfer *et al.*, 2019].

4.1.5 NH_4^+ -N and NO_3^- -N

The correlation analysis indicated NH_4^+ -N was significant parameters influencing As mobility (Fig.4, 5, S3 and S4). One of the main pathways for the Fe^{3+}

and Fe^{2+} to affect As mobility was mediated by DFeRB in group DFeRB, which NH_4^+ -N was involved in this process (Fig.4). NH_4^+ -N provide a nutrient for bioactivity, thus promoting As mobility [Kurosawa *et al.*, 2013]. Previous studies showed that ammonium oxidation was coupled directly to Fe(III) reduction via the microbially catalyzed Feammox process [Ding *et al.*, 2017; S B Huang *et al.*, 2015; Shan *et al.*, 2018]. Microbially catalysed Feammox process could potentially mobilize As via the reductive dissolution of sedimentary Fe(III) minerals [Xiu *et al.*, 2020]. Moreover, Feammox process would widen the range of metabolic pathways driving As mobilization in high As groundwater systems [Xiu *et al.*, 2020]. In addition, the negative correlations between NH_4^+ -N and DOC was found in this work (Fig.4 and Fig.S3) may provide effective evidences that the denitrification occurred together with OM degradation [Che *et al.*, 2020], which explained why NH_4^+ -N was an indicator for As mobility under anoxic conditions. The role of NH_4^+ -N for the driving process of As mobility was more pronounced in group SRB, not only direct effects, but also indirectly effects through SRB (Fig.5). The direct effects of NH_4^+ -N on As mobility was negative path, indicating that NH_4^+ -N may be promote As immobilization in group SRB, but the complicated interrelationships need further studies.

It was reported that nitrate has become an increasingly abundant potential electron acceptor for Fe(II) oxidation, even nitrate-dependent iron oxidation [Roden, 2012; Tai and Dempsey, 2009; K A Weber *et al.*, 2007]. Nitrate-dependent iron oxidation results in the anoxic production of Fe (III) oxyhydroxides at circumneutral pH [Senko *et al.*, 2005]. Typically, the end product is a poorly ordered Fe(III) oxyhydroxide, although other Fe(III) oxide minerals may form depending on whether microbes are involved and the growth conditions [Senko *et al.*, 2005]. Nitrate-dependent Fe(III) oxyhydroxide production can control dissolved

concentrations of As by sorption [Hemond and Lin, 2010]. Simultaneously, Fe(III) oxyhydroxides produced in this process are much more readily available for microbial iron reduction due to higher surface areas and possibly lower degree of order in their crystal structure [Bethke C. M., 2011]. In addition, *Shewanella* can act as a variety of electron acceptor for anaerobic respiration under anoxic condition, including dissolved nitrates and insoluble iron oxide matrix [W Zhang et al., 2013], and lead to competition between nitrate reduction and Fe (III) reduction. Therefore, the pathway of NO_3^- -N to affect As mobility was through S^{2-} , Fe^{2+} and Fe^{3+} et al. in group DFeRB (Fig.4). In group SRB, however, NO_3^- -N presented an effect on As (III) and As(V) in water phase (Fig.3), but the effects of NO_3^- -N on As was a non-significant pathways in the PLS model (Fig.5). This may be owing to a large amount of S^{2-} produced mediated by SRB, and the stronger affinity of sulfur to iron. In addition, SRB growth can successfully remediated the sulfide production, especially with nitrate addition [Kamarisima et al., 2018].

4.2 Environmental implication

Taking Lake WLSH as an example, it was estimated that approximately totally 1.60 t TAs including 0.48 t As(III) mediated by DFeRB as well as 1.94 t TAs including 0.96 t As(III) mediated by SRB could be released from sediments to the overlying water within 8 months/year (3 months in summer and 5 months in ice-bound period) (Table S4). The flux of As (III) mediated by DFeRB and SRB were 1.1 and 2.2 times higher than control group, and the flux of TAs mediated by DFeRB and SRB were 1.54 and 1.87 times higher than control group, respectively (Table S4). It indicated that DFeRB and SRB have a significant effect on the As release to water column. Although SRB presented significant effects on S7-8 in sediments which

means As may be retained or transformed to more stable binding speciation in sediments, the effects of SRB upon the As mobility and ecotoxicity was remain strong.

In terms of seasons, the flux of TAs and As(III) mediated by DFeRB and SRB higher than control group both in summer and ice-bound period, and summer higher than that in ice-bound period (Table S4). However, it is noteworthy that the water storage capacity of WLSH will increase due to the ecological replenishment from the Yellow River in April or May. It was estimated that approximately 1.70 mg/m³ TAs including 0.54 mg/m³ As(III) in summer and 1.44 mg/m³ TAs including 0.37 mg/m³ As(III) in ice-bound period mediated by DFeRB could be released to the overlying water (Table S6). Approximately 1.88 mg/m³ TAs including 1.10 mg/m³ As(III) in summer and 2.21 mg/m³ TAs including 0.71 mg/m³ As(III) in ice-bound period mediated by SRB could be released to the overlying water (Table S6). The increase of As in the overlying water during ice-bound period mediated by DFeRB and SRB was slightly weaker than that in summer, even higher than summer. Furthermore, RAC values showed that As mediated by DFeRB and SRB posed a medium or high risk to aquatic environment, max in ice-bound period even higher than summer (Fig.6 and Table.S7). It indicated that the potential ecological risk of As mediated by DFeRB and SRB during the ice-bound period still could not be neglected. Additionally, eutrophication has becoming an increasing challenge in many As-polluted water due to the continuous anthropogenic nutrient input resulting from rapid industrialization and urbanization [Tang *et al.*, 2019], As mobility could be increased by IP owing to the competitive effect in adsorption and transportation process. Meanwhile, approximately 20-34% of S2 could be released into overlying water mediated by DFeRB and SRB in summer and ice-bound period. Therefore, except S1, 20-34% of

S2 was also considered as indicators of As release risk in RAC calculation in this study. The environment of SWI was mostly in an oxidized state in summer, the released As (III) into water might be oxidized to As(V) and the alkaline condition would also promote the precipitation of As. In a long-time scale, the released As may return into the sediment. However, ice-bound period was characterized as poor reoxygenation, which made the SWI in the anaerobic environment for a long time, resulting As existing as reducing speciation, and increasing its solubility and potential ecotoxicity risks.

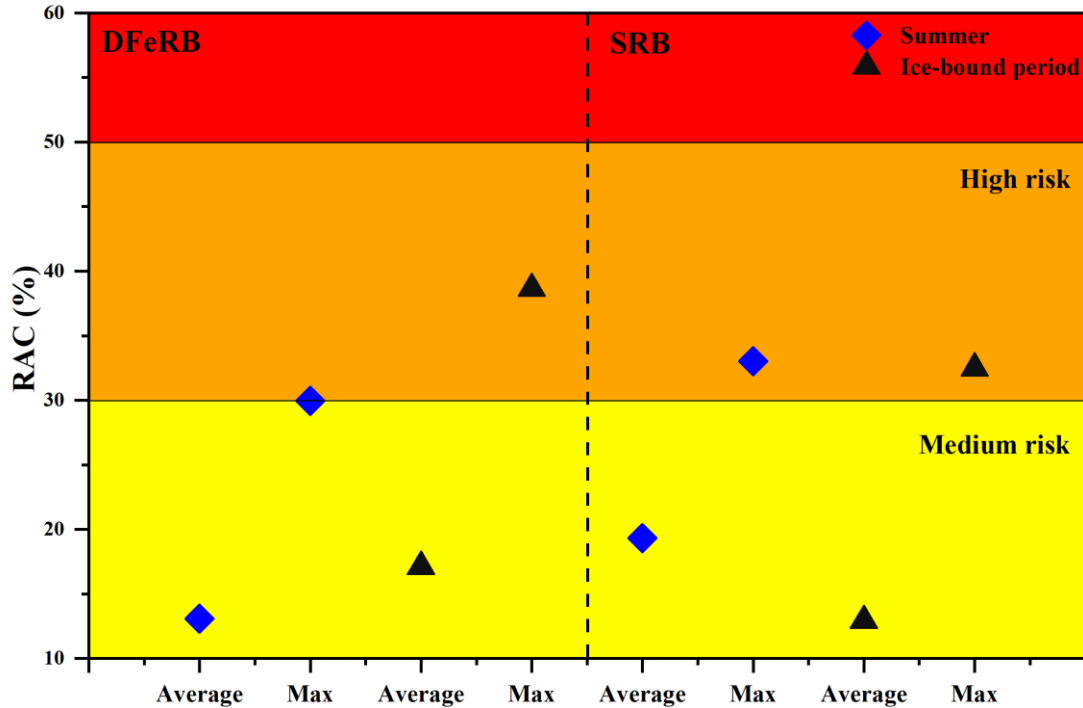


Fig.6 Risk assessment code (RAC) of As mediated by DFeRB and SRB (n=6)

5 Conclusions

DFeRB and SRB play an important role in regulating the transformation and migration of As, but the predominant driving process and their key explanatory factors are obviously different. DFeRB mainly regulating As behavior by prompting

the transformation of iron species, the reductive dissolution and re-distribution of Fe(III) oxyhydroxides and As containing Fe (III) minerals as well as adsorption-desorption. Fe^{3+} and Fe^{2+} were the most important factors in this process, which is intrinsically linked with DFeRB. Fe^{2+} and Fe^{3+} presented significant effects on labile pool and moderately labile pool, respectively. S^{2-} was also the main factors associated with As distribution and mobility in DFeRB-induced reduction, which correlated with moderately labile pool and closely related to Fe^{2+} and Fe^{3+} in sediment. The environmental factors that affect As mobility depend on Fe^{2+} and Fe^{3+} which had two main pathways: one was the process of As release mediated by DFeRB, and the other was the process influenced by IP. Different from DFeRB, SRB showed regulating effects on As behavior by influencing labile pool, pyrite and As sulfides in sediments as well as the formation of S^{2-} during the process of sulfate reduction. The main effecting pathways on As mobilization were the direct effects of SRB, S^{2-} and Fe^{2+} .

In summary, DFeRB and SRB mediated reduction process obviously facilitated reduction of As (V) and endogenous As release, which creating As content at potentially hazardous levels, increasing the risk of As ecotoxicity, whether in summer or ice-bound period. The potential ecological risk of As mediated by DFeRB and SRB during the ice-bound period still could not be neglected. Additionally, although SRB presented significant effects on pyrite and As sulfides in sediments which means As may be retained or transformed to more stable binding speciation in sediments, the effects of SRB upon the As mobility and ecotoxicity was remain strong.

516

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