

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

3 Wenjing Shi<sup>a</sup>, Wenjie Song<sup>b</sup>, Jinli Zheng<sup>a</sup>, Yu Luo<sup>a</sup>, Geer Qile<sup>a</sup>, Sijie Lü<sup>a</sup>, Xiangmeng  
4 Lü<sup>a</sup>, Bin Zhou<sup>c</sup>, Changwei Lü<sup>a,d,\*</sup>, Jiang He<sup>a,d,\*</sup>

5 <sup>a</sup> School of Ecology and Environment, Inner Mongolia University, Hohhot 010021, China

6 <sup>b</sup> Pioneer College, Inner Mongolia University, Hohhot 010021, China

7 <sup>c</sup> Tianjin Academy of Eco-Environmental Sciences, Tianjin, 300191, China

8 <sup>d</sup> Institute of Environmental Geology, Inner Mongolia University, Hohhot 010021, China

9

10 **ABSTRACT**

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

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<sup>1</sup> Corresponding Authors. Tel:+86-471-4992210; Fax: +86-471-4992210

\* E-mail: [lcw2008@imu.edu.cn](mailto:lcw2008@imu.edu.cn); [ndjhe@imu.edu.cn](mailto:ndjhe@imu.edu.cn)

20 sediment-overlying water system. The reduction process mediated by DFeRB and  
21 SRB significantly promotes reduction of As (V) and endogenous release of As.  
22 However, in the DFeRB and SRB mediated reduction, the main driving process and  
23 their key explanatory factors that dominated As mobility were obviously different.  
24 DFeRB presented significant effects on the reductive dissolution and re-distribution of  
25 Fe (III) oxyhydroxides and As-containing Fe (III) minerals as well as  
26 adsorption-desorption, which in turn influenced the transformation of iron species and  
27 the release and ecotoxicity of As. Meanwhile, the environmental factors that affect As  
28 mobility depend on  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in DFeRB-induced reduction, which have two main  
29 pathways: the process of As mobilization mediated by DFeRB, and the process  
30 influenced by IP of competitive adsorption and anion exchange. Significantly  
31 different from DFeRB, the effects of SRB on As behavior mainly by influencing  
32 adsorbed As, pyrite and As sulfides in sediment as well as the formation of sulfide  
33 during sulfate reduction. The main pathways on As mobilization were the direct  
34 effects of SRB,  $\text{S}^{2-}$  and  $\text{Fe}^{2+}$ . In addition, the role of  $\text{NH}_4^+$ -N for the driving process of  
35 As mobility is more pronounced for SRB-induced reduction.  $\text{NO}_3^-$ -N is an essential  
36 factor affecting As mobility, but the effects of  $\text{NO}_3^-$ -N on As was a non-significant  
37 pathways. This work is helpful to provide insight into the environmental effects of  
38 DFeRB and SRB on biogeochemical cycle of As.

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

41

## 42 **1 Introduction**

43 Arsenic (As) is an environmentally ubiquitous and notorious carcinogen [C  
44 Wang *et al.*, 2016] and As contamination is of great environmental concern [Lan *et al.*,  
45 2018]. The mobility, bioavailability and toxicity of As are strongly associated with its  
46 speciation in sediment and aquatic environment, which largely controlled by redox  
47 processes [Bettoschi *et al.*, 2018; Duan *et al.*, 2017; Mohapatra *et al.*, 2018; Xue *et al.*,  
48 2017]. For instance, As (III) presents higher mobility and toxicity than As (V) due to  
49 its higher solubility and stronger binding ability with dimercapto or carboxyl groups  
50 on enzyme protein molecule forming stable complex or ring compound to inhibit  
51 enzyme activity [Han, 2019]. Meanwhile, other major redox sensitive elements such  
52 as iron (Fe) and sulfur (S) also affect As mobilization and toxicity during their redox  
53 process [Frohne *et al.*, 2011; Han, 2019]. The redox transformation and mobilization  
54 of As has been proven to be primarily mediated by microorganisms [Cai *et al.*, 2019;  
55 J H Huang, 2018; Xu *et al.*, 2016]. Therefore, the reduction process mediated by  
56 DFeRB and SRB is considered to be the most important mechanism affecting the  
57 mobilization of As, which is intrinsically linked to the biogeochemical cycles of Fe  
58 and S [Colombo *et al.*, 2014; Mejia *et al.*, 2016; Mirjam *et al.*, 2007]. However, the  
59 driving process and their explanatory factors governing As mobility and ecotoxicity  
60 during the coupling biogeochemical cycles of As/Fe/S mediated by DFeRB and SRB  
61 remains poorly understood.

62 Previous studies have shown that DFeRB and SRB can induce the reduction of  
63 Fe and S [Das and kerkar, 2017; Kirk *et al.*, 2010; Ko *et al.*, 2019; Sun *et al.*, 2017],  
64 then control the mobility and fate of As by the coupling effects with Fe and S [Han,  
65 2019; Karimian *et al.*, 2018; J Sun *et al.*, 2016]. It might be due to the presence of As  
66 in iron and sulfur minerals played a leading role in the distribution of As in polluted

67 sedimentary environments [Zhang *et al.*, 2018], and the occurrence of As in the water  
68 column was mainly related to the dissolution of As-bearing minerals [Deng *et al.*,  
69 2018; Erika E. Rios-Valenciana, 2020]. Moreover, sediments could act as source and  
70 sink for As, in which physicochemical and/or microbial factors played significant  
71 roles in As behavior [Xu *et al.*, 2011]. However, recent studies mainly focus on  
72 adsorption-desorption of As from As-bearing minerals [Cheng *et al.*, 2016; Xue *et al.*,  
73 2017; Zhu and Elzinga, 2015], the effect of oxidative dissolution of Fe and S minerals  
74 on As mobility [Couture *et al.*, 2015; E. Zanzo, 2017; H.S. Moon, 2017; Jeong *et al.*,  
75 2010; Kocar *et al.*, 2010] and the effect of As on the formation of Fe or S minerals  
76 under the DFeRB and SRB mediated reduction process [Peng *et al.*, 2017; J Song *et al.*,  
77 *et al.*, 2015; V.T.H. Phan, 2018]. There are few reports on how DFeRB and SRB  
78 influence As mobility and ecotoxicity by affecting As pools in the sediment. The  
79 variation of As pool in the sediment is also intrinsically linked with the multiple  
80 factors, such as temperature (Temp), microorganism activities, organic matter (OM),  
81 ammonia nitrogen ( $\text{NH}_4^+\text{-N}$ ), nitrate nitrogen ( $\text{NO}_3^-\text{-N}$ ) and so on. The release of As  
82 into the water column is regulated by not only the mentioned factors but also As pool.

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

92 biogeochemical cycle of As.

93

## 94 **2 Materials and methods**

### 95 2.1 Sampling

96 The surface sediments were collected from Lake Wuliangshuai (WLSH)  
97 (40°59'N, 108°51'E) in Inner Mongolia plateau, China in July, 2018. The sediments  
98 were sampled applying a SA Beeker collector (Eijkelkamp), and sealed immediately  
99 to ensure anaerobic environment and stored in dark immediately after collection, then  
100 transported to the laboratory and stored at 0-4°C. The lake locates in the cold and arid  
101 area with a long ice-bound period (November to March). The chemical characteristics  
102 of the sediments and overlying water from WLSH were listed in Table S1 and S2. The  
103 other basic information about the lake were described in Supporting Materials (SM).

104

### 105 2.2 Experimental design and methods

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

114 soil environment. The sediment samples and deionized water were autoclaved at 121°C  
115 for 15 min before the incubation experiments. And 0.1% chloroform was added into  
116 group A to further inhibit microbial growth. The incubations were inoculated with 4%  
117 (v/v) of inoculums in each culture bottle in group B and C. All experiments were  
118 performed in anaerobic conditions in the sterile console. During the incubation,  
119 overlying water were sampled from the bottles on days 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11,  
120 12, 13, 14, 15, 17, 19, 21, 23, 25, 27 and 30, meanwhile the pH was measured in situ  
121 and biological activity was also determined. After, overlying water were collected, the  
122 samples were filtered through 0.45µm filters, and then the concentrations of total Fe  
123 (TFe), Fe<sup>2+</sup>, S<sup>2-</sup>, total As (TAs), As (III), inorganic phosphorus (IP), total phosphorus  
124 (TP), dissolved organic matter (DOC), total nitrogen (TN), NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N were  
125 determined. The sediment samples were collected at 1, 2, 8, 15, 23 and 30 days, and  
126 then the concentrations of sulfide, TFe, Fe<sup>2+</sup>, TAs, As (III), TP, TN, OM and IP were  
127 measured. Meanwhile, the sequential extraction procedure [Keon *et al.*, 2001] was  
128 performed to obtain the information of arsenic pool in the sediment, including loosely  
129 adsorbed As (S1), strongly adsorbed As (S2), As coprecipitated with AVS, carbonates,  
130 Mn oxides, and very amorphous Fe oxyhydroxides (S3), As incorporated in  
131 amorphous iron oxides (S4), As coprecipitated in crystalline iron oxides (S5), As  
132 oxides and arsenic coprecipitated with silicates (S6), As coprecipitated with pyrite  
133 (S7), and As sulfides (S8) (Table S3).

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

136 were ultrapure water (Milli-Q, Millipore,  $\geq 18.2 \text{ M}\Omega \text{ cm}$ ). In all cases, blank samples  
137 were included and the samples obtained at each time point were analyzed and tested  
138 2-3 times to ensure the accuracy of analysis. The standard deviations of all analytical  
139 methods were within 5%. The recovery ranged from 86% to 117%.

140

### 141 2.3 Data Analysis

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

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

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

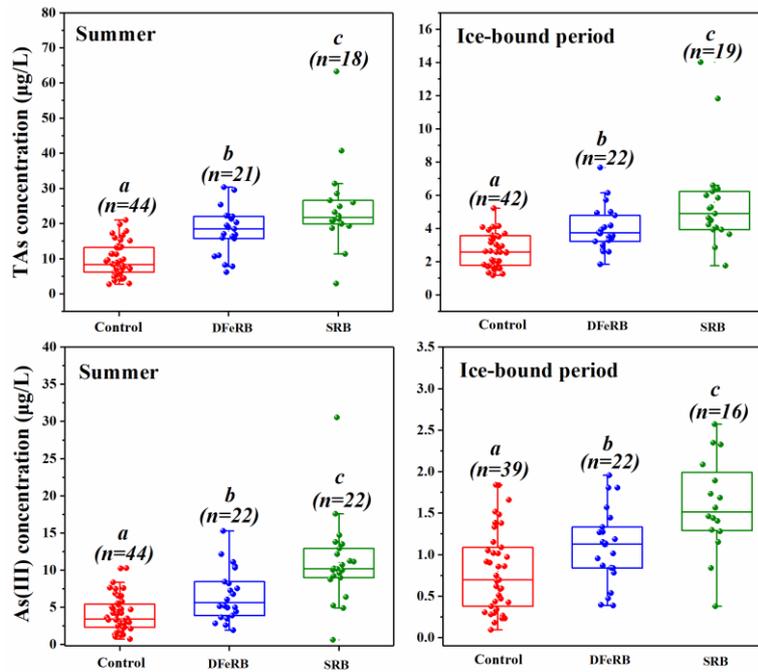
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## 160 **3 Results**

### 161 **3.1 Arsenic reductive release induced by DFeRB and SRB**

162 The results showed that the reduction and release of As induced by DFeRB and  
163 SRB were significantly higher than control group both in summer and ice-bound  
164 period ( $P < 0.05$ ) (Fig.1 and S1). Accompanying with microbial-induced reduction  
165 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  
166 group DFeRB as well as 29.24 and 49.91  $\mu\text{g}/\text{m}^2\cdot\text{d}$  in group SRB during summer,  
167 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  
168  $\mu\text{g}/\text{m}^2\cdot\text{d}$  in group SRB during ice-bound period, respectively (Table.S4). These  
169 release rates were found higher than control groups (1.1-2.3 times), which indicated  
170 the mediating effects of DFeRB and SRB during the reductive release process of As.

171 Our monitoring results found the concentrations of dissolved TAs and As (III)  
172 increased rapidly in the overlying water both in summer and ice-bound incubation  
173 periods (Fig.1 and S1). It indicated that the fractions of As bound to sediments were  
174 destabilized, which suggested the fractions transformation of As in sediments was  
175 happened and enhanced by the mediating effects of DFeRB and SRB during the  
176 incubation, whether in summer or ice-bound periods. Information on the changes in  
177 As concentrations in aqueous phase mediated by DFeRB and SRB were provided in  
178 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  $p < 0.05$ .

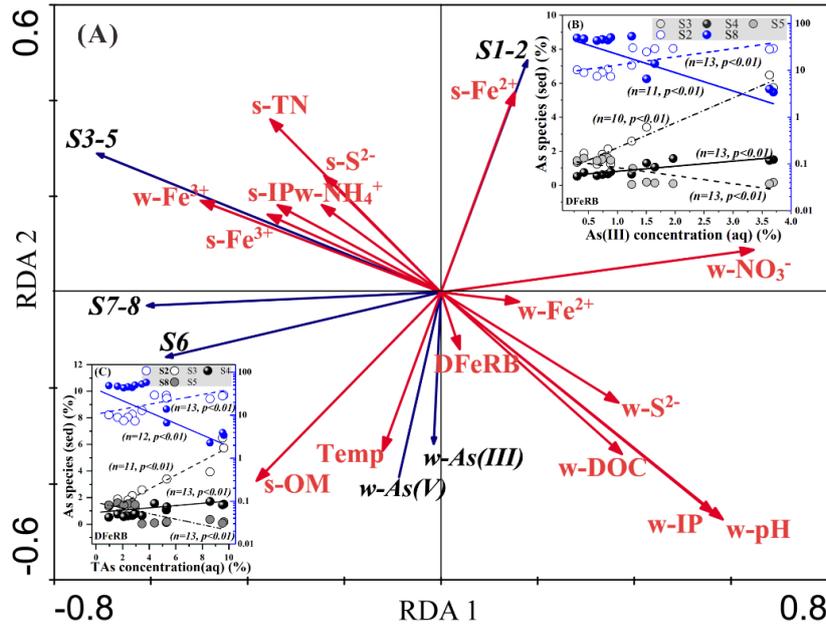
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### 180 3.2 Factors associating with As releases

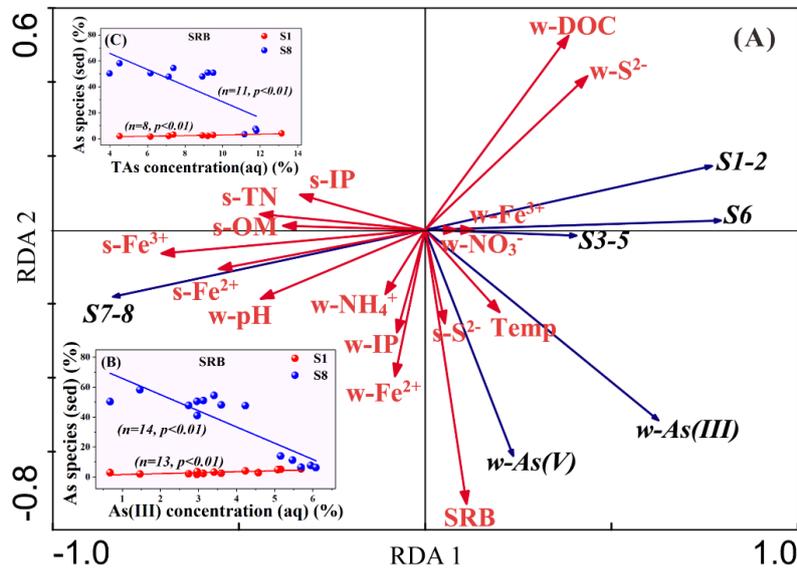
181 RDA which based on the correlation between environment factors and As  
 182 fractions in sediments and water phase were detailed in SM. According to the  
 183 sequential extraction, S1 and S2 were labile pool which contained adsorbed As; S3,  
 184 S4 and S5 were moderately labile pool and closely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

193 obviously different.

194 DFeRB and SRB positively correlated with As(V) (Fig.2 and 3), As (III) and  
195 TAs in water phase (Fig. S3 and S4). It indicated that DFeRB and SRB can  
196 potentially promote the reduction of As (V) to As (III). DFeRB present significant  
197 effected on S1-2 and S3-5 in sediment, meanwhile,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  presented  
198 significant effected on S1-2 and S3-5, respectively (Fig.2), accordingly, the  
199 correlations were observed between DFeRB and  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  (Fig.4 and S3). Moreover,  
200 S1-2 and S3-5 in sediment significantly associated with As (III) and As (V) in water  
201 phase (Fig.2), As (III) and TAs in water phase, corresponding to significant  
202 correlations with S2, S3, S4 and S5 in sediment phase in group DFeRB (Fig.2 (B) and  
203 (C)). These illustrated that As level in water were to a certain extent depended the  
204 effects of DFeRB on S3-5 and S1-2, in which  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  were the most important  
205 factors. In group SRB,  $\text{S}^{2-}$  in water and sediment (w- $\text{S}^{2-}$  and s- $\text{S}^{2-}$ ) significantly  
206 associated with S1-2 and S7-8 (Fig.3 and 5), as well as the correlation between SRB  
207 and  $\text{S}^{2-}$  (Fig.3 and S4).  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  presented close relations with S1-2 and S7-8  
208 (Fig.3), and As (III) and TAs in water phase closely correlated with S1 and S8 in  
209 sediment phase (Fig.3). It demonstrated that SRB significantly influenced S7-8 and  
210 S1-2 in sediment via  $\text{S}^{2-}$ , 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.  $\text{NH}_4^+$  and  $\text{NO}_3^-$  represent  $\text{NH}_4^+$ -N and  $\text{NH}_3^-$ -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.  $\text{NH}_4^+$  and  $\text{NO}_3^-$  represent  $\text{NH}_4^+$ -N and  $\text{NH}_3^-$ -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

236 [Fan *et al.*, 2017]. As adsorbed on iron (hydr)oxides surface will release during the  
237 reductive dissolution of iron (hydr) oxides induced by DFeRB. Therefore, the positive  
238 and negative relationships of S1-2 with  $Fe^{2+}$  and  $Fe^{3+}$ , respectively, were found in  
239 RDA (Fig.2 and 4(A)), suggesting that the reduction of  $Fe^{3+}$  to  $Fe^{2+}$  which limited the  
240 adsorption ability of iron (hydr)oxides for As [Cheng *et al.*, 2016], corresponded to  
241 the release As adsorbed on iron (hydr)oxides surface due to S1-2 contains adsorbed  
242 As. Furthermore, DFeRB presented effects to S8 in some extent in sediments due to  
243 *Shewanella putrofaciens* could lead to As dissolved from As sulfides or even  
244 methylated quickly, inducing the repartition of As [Hansel *et al.*, 2004; C Wang *et al.*,  
245 2016] (Fig.2).

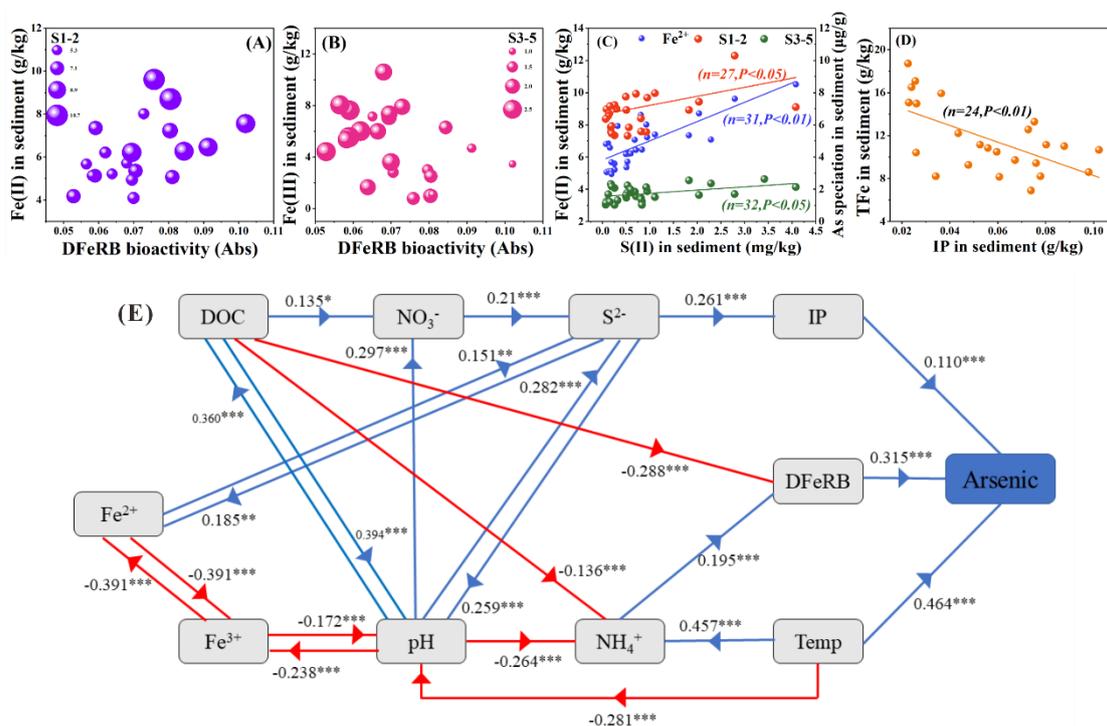
246 In overlying water, DFeRB presented significant positive correlation with As (V),  
247 As (III), TAs (Fig.2 and Fig.S3). It indicated that reduction of As(V) to As(III) may  
248 also cause its release since As(III) is well known for its higher solubility and weaker  
249 affinity to various minerals in aquatic environment [Fan *et al.*, 2018; J H Huang,  
250 2018]. Moreover, the reduction of  $Fe^{3+}$  and As (V) mediated by DFeRB can enhance  
251 As dissociation and release from the host minerals and elevated As levels in water  
252 column [S Wang *et al.*, 2012]. Thus, the interplay between DFeRB mediated As(V)  
253 reduction and Fe(III) (hydr)oxide reduction also influence the mobilisation and  
254 ecotoxicity of As.

## 255 **SRB**

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

261 amorphous and crystalline Fe(III)(oxy)hydroxide minerals quickly [Y Song *et al.*,  
 262 2015], and promote the convert of Fe(III) (oxy)hydroxides to Fe sulfides (e.g. FeS,  
 263 FeS<sub>2</sub>), which reduced the affinity of iron minerals to As [Flynn *et al.*, 2014; Zhang *et*  
 264 *al.*, 2018], can accelerate under the SRB mediating effects due to more reducing agent  
 265 generation (sulfide). Meanwhile, SO<sub>4</sub><sup>2-</sup> reduction process may promote As mobility  
 266 thanks to the formation of thioarsenic species with weakly adsorption properties and  
 267 high solubility [Y Song *et al.*, 2015; Stucker *et al.*, 2014]. On the other hand, some  
 268 insoluble sulfide mineral-like phases, such as orpiment (As<sub>2</sub>S<sub>3</sub>), realgar (AsS) and  
 269 arsenopyrite-like phase (FeAsS), which can sequester As [Burton *et al.*, 2013b; Luo *et*  
 270 *al.*, 2013], will be formed during the sulfate reduction mediated by SRB. Then, the  
 271 newly formed secondary minerals (e.g. siderite, vivianite, green rust, magnetite or  
 272 mackinawite), can also sequester As via precipitation, adsorption or structural  
 273 incorporation, then constraining As release [Xu *et al.*, 2016].

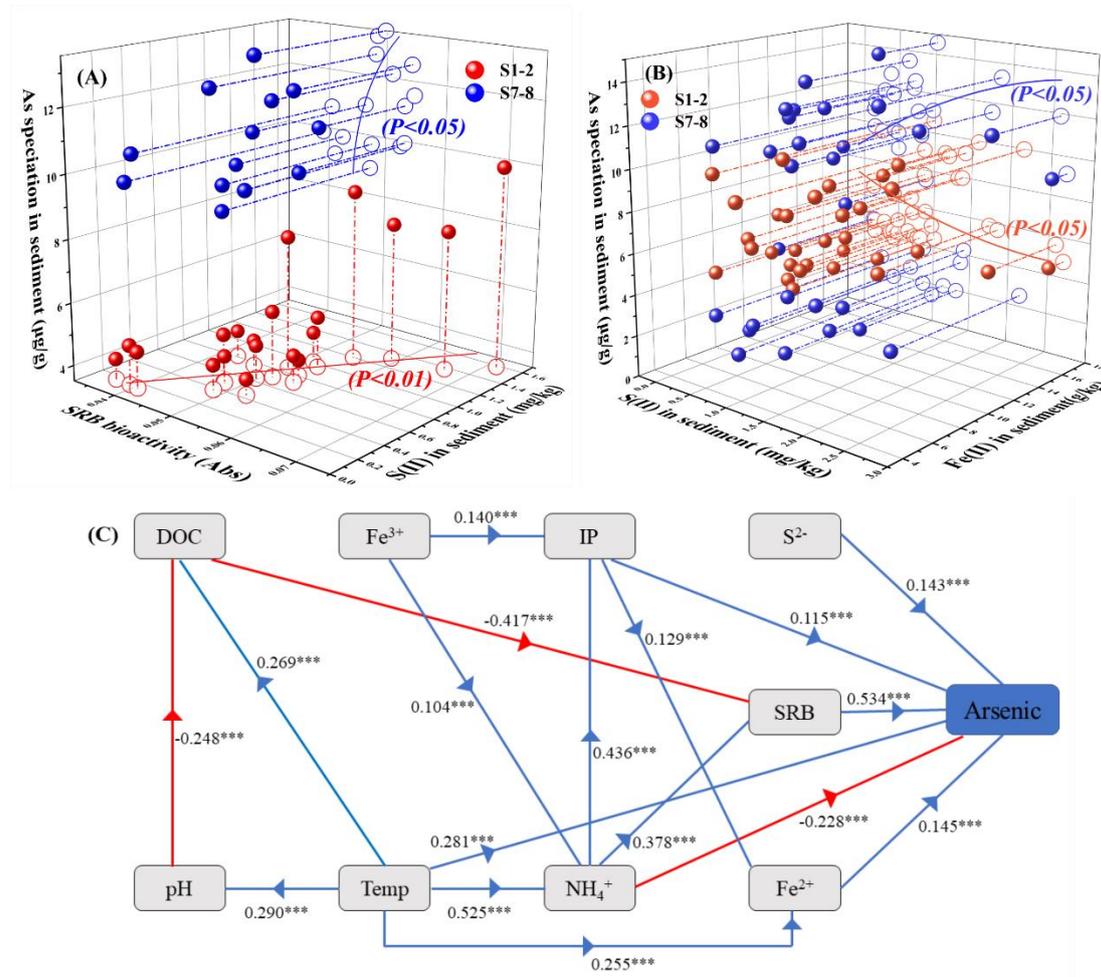
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**Fig.4** (A) Influence of Fe<sup>2+</sup> in sediment and DFeRB-bioactivity on S1-2 in sediment (B) Influence of Fe<sup>3+</sup> in sediment and DFeRB-bioactivity on S3-5 in sediment (C) Correlation

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 ( $\lambda$ ) 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.

275



**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 ( $\lambda$ ) 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

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

289 PLS results demonstrated that DOC influences As release coupling with microbe  
290 (Fig.4(E) and 5(C)), the negative influence indicated that the consumption of DOC  
291 was used to provided energy for the bioactivity of DFeRB and SRB. It can also fuel  
292 the microbe (as an active electron donor) to drive the reduction processes of iron and  
293 sulfate in anoxic sediments [F-A Weber, Hofacker, A.F., Voegelin, A., Kretzschmar, R,  
294 2010], thereby indirectly influencing As mobility by the interaction of As with the  
295 generated ferrous matter [Kirk et al., 2010; Xu et al., 2011] or sulfides [H.S. Moon,  
296 2017; Langner, 2013]. RDA analysis showed that OM presented effects on S7-8 and  
297 S1-2 in group DFeRB and on S7-8 in group SRB. It indicated that the effects of OM  
298 on As mobility were coupled with its effects on Fe oxyhydroxides and sulfur species  
299 in the DFeRB induced reduction process while mainly were coupled with sulfur  
300 species in the SRB induced reduction process. The Fe(III) in As-bearing iron minerals  
301 may act as an electron acceptors during the oxidation process of OM through  
302 anaerobic microbial respiration, resulting in the reductive dissolution of the Fe  
303 minerals and concurrent release of As and Fe from sediments [Borch, 2010; Zeng,  
304 2019]. Sulfate can also cause As desorption from sediments due to its effect on Fe

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

311 DFeRB are reported as fermentation bacteria, which can produce acid to  
312 decrease the environment pH, and gradually stabilized when reaching the lower limit  
313 of the fermentation process. In theory, pH should negatively correlate with DFeRB,  
314 which was coincident with the results of PLS (Fig.4 and Fig.S3). Whereas  $\text{SO}_4^{2-}$   
315 reduction process will increase pH to some degree [Li *et al.*, 2018], because sulfate  
316 reduction is a proton-consuming reaction [Alam and McPhedran, 2019]; and  $\text{CO}_3^{2-}$   
317 and  $\text{HCO}_3^-$  ions produced from OM degradation can also increase pH. Additionally,  
318 pH fluctuations were associated with the accumulation of biogenic HS due to SRB  
319 activity [Fan *et al.*, 2017]. It showed SRB positively correlated with pH (Fig.5 and  
320 Fig.S4). The variety of pH significantly affected the dissolution of main adsorption  
321 phases of As then influence the release of As [Honma *et al.*, 2016]. Therefore, there  
322 were interaction effects between pH and the reduction of DFeRB and SRB in the  
323 environment, thus affecting As mobilization.

324

#### 325 4.1.3 $\text{Fe}^{3+}$ , $\text{Fe}^{2+}$ and $\text{S}^{2-}$

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

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

334 Fe(III) (hydr)oxides is one of the most important sorbents in sediment [*Q Sun et*  
335 *al.*, 2016], even can play a governing role for As behavior.  $\text{Fe}^{3+}$  reduction mediated by  
336 DFeRB can promote the reductive dissolution of Fe (oxy)hydroxide [*Fan et al.*, 2018;  
337 *J H Huang*, 2018], then the dissociation of As from the host minerals. Meanwhile, the  
338 dissolution of Fe can lead to the desorption of As bound to poorly crystalline minerals  
339 [*Usman et al.*, 2012; *Yang et al.*, 2015], thus elevating As levels in water phase.  
340 Additionally, As(III) was released with the reduction of Fe(III) (hydr)oxides due to  
341 As(III) is more soluble and poor affinity towards Fe host mineral phases [*Cheng et al.*,  
342 2016]. Accordingly, in group DFeRB, a major controlling phase of iron oxides for As  
343 repartitioning onto sediments was confirmed in this study based on the significant  
344 positive correlations of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  with S1-2 and S3-5 in sediment, respectively  
345 (Fig.2 and 4).

346  $\text{S}^{2-}$  can be involved in Fe(III) reduction and consequent precipitation of  
347 amorphous FeS, then enhanced As mobilization [*Xu et al.*, 2016], which consistent  
348 with our results that  $\text{S}^{2-}$  positively correlated with S3-5, S1-2 and  $\text{Fe}^{2+}$  in sediment  
349 phase (Fig.4(C)). Meanwhile,  $\text{S}^{2-}$  may compete adsorption sites with As (III) and  
350 result in As desorption from Fe oxyhydroxides surface [*Kocar et al.*, 2010]. In  
351 addition,  $\text{S}^{2-}$  also can act as a strong reductant and participate in Fe(III) reduction,  
352 which accelerates Fe oxyhydroxides dissolution and subsequent As (III) release.  
353 However, there also had an adsorption stage in the presence of sulfides [*Yang et al.*,  
354 2015] during the reductive dissolution of iron(hydr)oxides. Because As could

355 adsorbed and precipitated not only by secondary Fe(II)-bearing minerals[*Q Sun et al.*,  
356 2016; *Vink et al.*, 2017], but also co-precipitation with sulfur [*Yang et al.*, 2015]. It  
357 was consistent with the variations of As concentration in overlying water in group  
358 DFeRB (Fig.S1). PLS results also proved that iron and sulfur were closely related to  
359 each other in group DFeRB (Fig.4).

360 The associations of  $S^{2-}$ ,  $Fe^{2+}$  and  $Fe^{3+}$  with As fractions indicated that S7-8 was a  
361 major controlling phase in partitioning As onto sediment in group SRB (Fig.3 and  
362 Fig.5(B)). The link of As fractions in sediments and water column (Fig.3 and 5)  
363 suggested that SRB not only can enhance As release but also make As be retained or  
364 transformed to more stable binding speciation in sediment. PLS analysis (Fig.5)  
365 demonstrated that sulfide generated by SRB can promote the convert of Fe(III)  
366 (oxy)hydroxides to Fe sulfides (e.g. FeS,  $FeS_2$ ), which has weaker affinity to As and  
367 thus increase the release of As [*Xu L*, 2016]. Furthermore, large amounts of  $S^{2-}$  was  
368 produced in reduction process mediated by SRB, sulfide can sequester As by forming  
369 the precipitation of secondary arsenic sulfide minerals [*Burton et al.*, 2013a; *Luo et al.*,  
370 2013], such as ferrous sulfide or secondary pyrite, which can also re-immobilized As  
371 via adsorption or co-precipitation, further complicating the system [*Alam and*  
372 *McPhedran*, 2019].

373

#### 374 4.1.4 IP

375 PLS results demonstrated that one of the main pathways for the  $Fe^{3+}$  and  $Fe^{2+}$  to  
376 influence As behavior was influenced by IP in group DFeRB (Fig.4). As and  
377 phosphorus have a competitive effect in adsorption and transportation behavior due to  
378 their similar chemical structure and chemical properties [*Che et al.*, 2020; *Junbo et al.*,  
379 2018], thereby increasing the mobility of As [*Junbo et al.*, 2018]. Previous

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

395 However, in group SRB, the direct effecting pathways for As mobility were S<sup>2-</sup>  
396 and Fe<sup>2+</sup> coupling with SRB, although IP also could influence As release. This may be  
397 due to large amounts of S<sup>2-</sup> produced and gradually predominate, and SO<sub>4</sub><sup>2-</sup> also can  
398 competitive adsorption to sites on the Fe oxyhydroxides with inorganic As [Li *et al.*,  
399 2018]. In addition, some studies showed that sulfate reduction is more influential  
400 influenced directly by iron than PO<sub>4</sub><sup>3-</sup> [Schoepfer *et al.*, 2019].

401

#### 402 4.1.5 NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N

403 The correlation analysis indicated NH<sub>4</sub><sup>+</sup>-N was significant parameters  
404 influencing As mobility (Fig.4, 5, S3 and S4). One of the main pathways for the Fe<sup>3+</sup>

405 and  $\text{Fe}^{2+}$  to affect As mobility was mediated by DFeRB in group DFeRB, which  
406  $\text{NH}_4^+$ -N was involved in this process (Fig.4).  $\text{NH}_4^+$ -N provide a nutrient for  
407 bioactivity, thus promoting As mobility [Kurosawa *et al.*, 2013]. Previous studies  
408 showed that ammonium oxidation was coupled directly to Fe(III) reduction via the  
409 microbially catalyzed Feammox process [Ding *et al.*, 2017; S B Huang *et al.*, 2015;  
410 Shan *et al.*, 2018]. Microbially catalysed Feammox process could potentially mobilize  
411 As via the reductive dissolution of sedimentary Fe(III) minerals [Xiu *et al.*, 2020].  
412 Moreover, Feammox process would widen the range of metabolic pathways driving  
413 As mobilization in high As groundwater systems [Xiu *et al.*, 2020]. In addition, the  
414 negative correlations between  $\text{NH}_4^+$ -N and DOC was found in this work (Fig.4 and  
415 Fig.S3) may provide effective evidences that the denitrification occurred together with  
416 OM degradation [Che *et al.*, 2020], which explained why  $\text{NH}_4^+$ -N was an indicator for  
417 As mobility under anoxic conditions. The role of  $\text{NH}_4^+$ -N for the driving process of  
418 As mobility was more pronounced in group SRB, not only direct effects, but also  
419 indirectly effects through SRB (Fig.5). The direct effects of  $\text{NH}_4^+$ -N on As mobility  
420 was negative path, indicating that  $\text{NH}_4^+$ -N may be promote As immobilization in  
421 group SRB, but the complicated interrelationships need further studies.

422 It was reported that nitrate has become an increasingly abundant potential  
423 electron acceptor for Fe(II) oxidation, even nitrate-dependent iron oxidation [Roden,  
424 2012; Tai and Dempsey, 2009; K A Weber *et al.*, 2007]. Nitrate-dependent iron  
425 oxidation results in the anoxic production of Fe (III) oxyhydroxides at circumneutral  
426 pH [Senko *et al.*, 2005]. Typically, the end product is a poorly ordered Fe(III)  
427 oxyhydroxide, although other Fe(III) oxide minerals may form depending on whether  
428 microbes are involved and the growth conditions [Senko *et al.*, 2005].  
429 Nitrate-dependent Fe(III) oxyhydroxide production can control dissolved

430 concentrations of As by sorption [Hemond and Lin, 2010]. Simultaneously, Fe(III)  
431 oxyhydroxides produced in this process are much more readily available for microbial  
432 iron reduction due to higher surface areas and possibly lower degree of order in their  
433 crystal structure [Bethke C. M., 2011]. In addition, *Shewanella* can act as a variety of  
434 electron acceptor for anaerobic respiration under anoxic condition, including  
435 dissolved nitrates and insoluble iron oxide matrix [W Zhang et al., 2013], and lead to  
436 competition between nitrate reduction and Fe (III) reduction. Therefore, the pathway  
437 of  $\text{NO}_3^-$ -N to affect As mobility was through  $\text{S}^{2-}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  et al. in group DFeRB  
438 (Fig.4). In group SRB, however,  $\text{NO}_3^-$ -N presented an effect on As (III) and As(V) in  
439 water phase (Fig.3), but the effects of  $\text{NO}_3^-$ -N on As was a non-significant pathways  
440 in the PLS model (Fig.5). This may be owing to a large amount of  $\text{S}^{2-}$  produced  
441 mediated by SRB, and the stronger affinity of sulfur to iron. In addition, SRB growth  
442 can successfully remediated the sulfide production, especially with nitrate addition  
443 [Kamarisima et al., 2018].

444

#### 445 **4.2 Environmental implication**

446 Taking Lake WLSH as an example, it was estimated that approximately totally  
447 1.60 t TAs including 0.48 t As(III) mediated by DFeRB as well as 1.94 t TAs  
448 including 0.96 t As(III) mediated by SRB could be released from sediments to the  
449 overlying water within 8 months/year (3 months in summer and 5 months in  
450 ice-bound period) (Table S4). The flux of As (III) mediated by DFeRB and SRB were  
451 1.1 and 2.2 times higher than control group, and the flux of TAs mediated by DFeRB  
452 and SRB were 1.54 and 1.87 times higher than control group, respectively (Table S4).  
453 It indicated that DFeRB and SRB have a significant effect on the As release to water  
454 column. Although SRB presented significant effects on S7-8 in sediments which

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

458 In terms of seasons, the flux of TAs and As(III) mediated by DFeRB and SRB  
459 higher than control group both in summer and ice-bound period, and summer higher  
460 than that in ice-bound period (Table S4). However, it is noteworthy that the water  
461 storage capacity of WLSH will increase due to the ecological replenishment from the  
462 Yellow River in April or May. It was estimated that approximately  $1.70 \text{ mg/m}^3$  TAs  
463 including  $0.54 \text{ mg/m}^3$  As(III) in summer and  $1.44 \text{ mg/m}^3$  TAs including  $0.37 \text{ mg/m}^3$   
464 As(III) in ice-bound period mediated by DFeRB could be released to the overlying  
465 water (Table S6). Approximately  $1.88 \text{ mg/m}^3$  TAs including  $1.10 \text{ mg/m}^3$  As(III) in  
466 summer and  $2.21 \text{ mg/m}^3$  TAs including  $0.71 \text{ mg/m}^3$  As(III) in ice-bound period  
467 mediated by SRB could be released to the overlying water (Table S6). The increase of  
468 As in the overlying water during ice-bound period mediated by DFeRB and SRB was  
469 slightly weaker than that in summer, even higher than summer. Furthermore, RAC  
470 values showed that As mediated by DFeRB and SRB posed a medium or high risk to  
471 aquatic environment, max in ice-bound period even higher than summer (Fig.6 and  
472 Table.S7). It indicated that the potential ecological risk of As mediated by DFeRB  
473 and SRB during the ice-bound period still could not be neglected. Additionally,  
474 eutrophication has becoming an increasing challenge in many As-polluted water due  
475 to the continuous anthropogenic nutrient input resulting from rapid industrialization  
476 and urbanization [Tang *et al.*, 2019], As mobility could be increased by IP owing to  
477 the competitive effect in adsorption and transportation process. Meanwhile,  
478 approximately 20-34% of S2 could be released into overlying water mediated by  
479 DFeRB and SRB in summer and ice-bound period. Therefore, except S1, 20-34% of

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

488

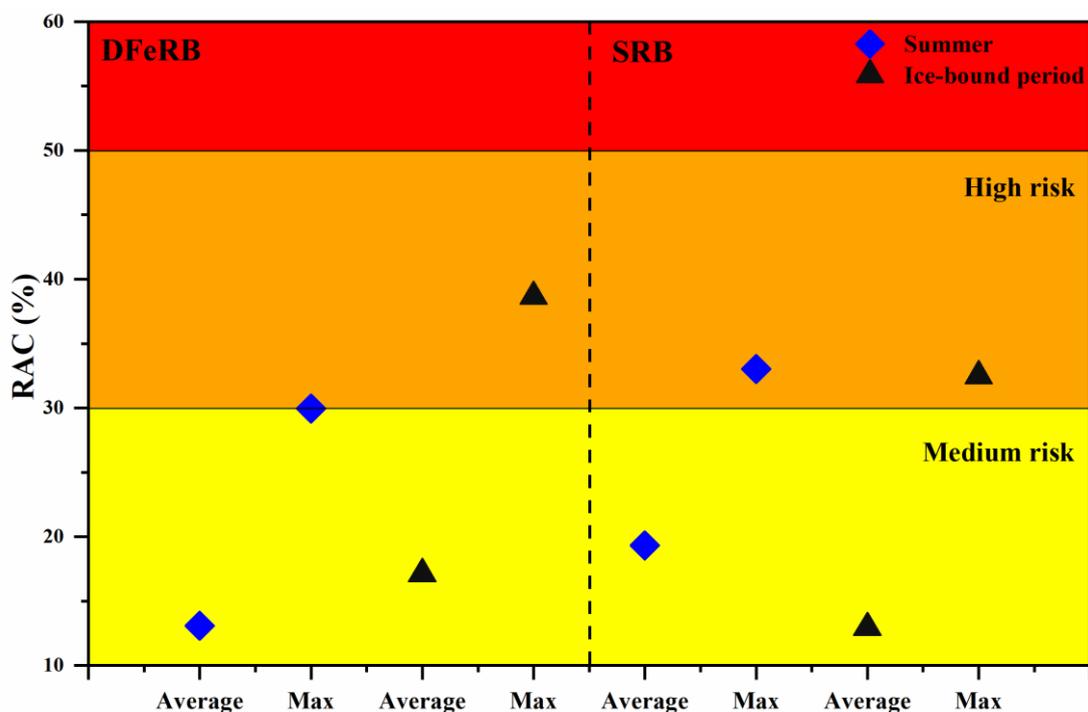


Fig.6 Risk assessment code (RAC) of As mediated by DFeRB and SRB (n=6)

489

## 490 5 Conclusions

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

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

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

516

## 517 **Acknowledgements**

518 This research was supported by the National Natural Science Foundation of China  
519 (No. 41763014, 41163006, 41003049) and Science Fund for Distinguished Young  
520 Scholars of Inner Mongolia (2019JQ05).

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