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Relevance of the microbial community to Sb and As biogeochemical cycling in natural wetlands

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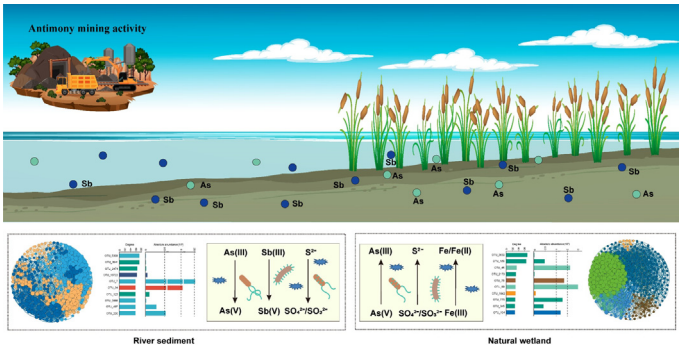
HIGHLIGHTS

- River and wetland sediments showed different status of Sb/As fractions and nutrients.
- Sb/As fractions and nutrients explained the changes of microbial compositions.
- Microbes in the river sediment were involved in Sb/As and sulfide oxidation.
- Microbes in the wetland were involved in Sb/As, sulfate, and Fe(III) reduction.

GRAPHICAL ABSTRACT



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ABSTRACT

Mining activities lead to elevated levels of antimony (Sb) and arsenic (As) in river systems, having adverse effects on the aquatic environment and human health. Microbes inhabiting river sediment can mediate the transformation of Sb and As, thus changing the toxicity and mobility of Sb and As. Compared to river sediments, natural wetlands could introduce distinct geochemical conditions, leading to the formation of different sedimentary microbial compositions between river sediments and wetland sediments. However, whether such changes in microbial composition could influence the microbially mediated geochemical behavior of Sb or As remains poorly understood. In this study, we collected samples from a river contaminated by Sb tailings and a downstream natural wetland to study the influence of microorganisms on the geochemical behavior of Sb and As after the Sb/As-contaminated river entered the natural wetland. We found that the microbial compositions in the natural wetland soil differed from those in the river sediment. The Sb/As contaminant components (Sb(III), As(III), As(V), As_{exe}) and nutrients (TC) were important determinants of the difference in the compositions of the microbial communities in the two environments. Taxonomic groups were differentially enriched between the river sediment and wetland soil. For example, the taxonomic groups *Xanthomonadales*, *Clostridiales* and *Desulfuromonadales* were important in the wetland and were likely to involve in Sb/As reduction, sulfate reduction and Fe(III) reduction, whereas *Burkholderiales*, *Desulfobacterales*, *Hydrogenophilales* and *Rhodocyclales* were important taxonomic groups in the river sediments and were reported to involve in Sb/As oxidation and sulfide oxidation. Our results suggest that microorganisms in both river sediments and natural wetlands can affect the geochemical behavior of Sb/As, but the mechanisms of action are different.

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1. Introduction

Antimony (Sb) and arsenic (As) are considered to be global contaminants and have been listed as priority pollutants by the US Environmental Protection Agency (Callahan et al., 1979) and the European Union (Communities, 1976). Extensive mining and smelting activities discharge Sb and As in adjacent river systems, causing serious harm to people (He et al., 2012). In general, Sb and As co-occur in sulfide ores and co-contaminate mining areas (Sun et al., 2017). Due to their chemical similarities, Sb and As share the same oxidation states (trivalent and pentavalent states) in natural environments (Filella et al., 2002). Both Sb and As in pentavalent states were predominantly found in relatively oxic environments and trivalent states in anoxic environments (Filella et al., 2002). The toxicities of Sb and As were dependent upon oxidation states (Filella et al., 2002). The trivalent state of Sb and As (Sb(III) and As (III)) was considered much more toxic and carcinogenic potential than pentavalent states (Sb(V) and As(V)) (Filella et al., 2002). In addition, the mobility of Sb and As was strongly dependent on their oxidation states (Vodyanitskii, 2013). Therefore, it is necessary to investigate the transformation of Sb and As in the surrounding river systems.

Existing evidence has shown that microorganisms inhabiting river sediment have important roles in Sb and As biotransformation processes (He et al., 2019). For instance, Sb(III)-oxidizing bacteria such as *Acinetobacter* and *Pseudomonas* and Sb(V)-reducing bacteria such as *Sinorhizobium* have been identified from Sb-contaminated sediments (Hamamura et al., 2013; Nguyen et al., 2019). In addition, microbially mediated Sb(V) reduction was observed in Sb mining areas and uncontaminated environments (Kulp et al., 2013). A prior study showed that microorganisms with anaerobic metal-reducing capacity could mobilize sedimentary As from an As-contaminated watershed in West Bengal (Islam et al., 2004). Furthermore, microbial-mediated anaerobic As(III) oxidation has been reported in the bottom water from Mono Lake (Oremland et al., 2002). Microbially mediated Sb and As transformation could reduce the toxicity, mobility, and bioavailability of Sb and As and eventually influence their accumulation or transfer in river systems (Sundar and Chakravarty, 2010). Therefore, microbially mediated transformations of Sb and As could be targeted as promising methods for remediating environments contaminated by Sb and As. Recent evidence has showed that the distribution of microorganisms involved in Sb and As biotransformation processes is shaped by physical and chemical properties in the environment. However, the understanding of the biogeochemical cycling of Sb and As in river systems has not been well elaborated (Filella et al., 2002). It is still less clear whether microbially mediated Sb and As cycling changes with distinct geochemical conditions in river systems.

Wetlands account for 6–11% of the world's land area and undergo many important geochemical cycling processes, such as the cycling of carbon and other major and trace elements (Vriens et al., 2014). Compared to river sediment, natural wetlands could introduce distinct geochemical conditions, i.e., pH, total organic carbon (TOC), and iron content (Soldatova et al., 2021), leading to the formation of distinct sedimentary microbial compositions between river sediments and wetland sediments (Mateos et al., 2006). Importantly, these bacteria have also been reported to be involved in metal(loid) biochemical cycling processes (Aguinaga et al., 2018; Zhang et al., 2017). As a result, it is proposed that the sedimentary microbial community structure may be different when rivers flow into wetlands, leading to differences in microbial Sb/As cycling. However, the changes in microbially mediated Sb/As cycling when rivers flow into wetlands remain poorly understood.

In this study, we examined the changes in microbially mediated Sb/As cycling that occur when rivers flow into wetlands in an Sb/As-contaminated river system. Here, we aimed to investigate (i) the differences in Sb/As and other environmental variables between river sediment and wetland environments; (ii) the relationship between environmental variables and the microbial community; and (iii) the difference in the microbial mediated Sb/As cycling between river sediment and natural wetland systems. These findings can provide new insights into the migration and transformation of Sb/As in river systems.

2. Materials and methods

2.1. Site description and sampling

This watershed was located in Dushan County, Southwest China and receives underground drainage from an Sb tailing reservoir and flows approximately 1 km into a natural wetland (Fig. S1). We selected a total of four sampling sites in this study and distributed these sites into two areas according to whether they entered the wetland. The sampling site before the watershed flows into the natural wetland was denoted BP. The other three sampling sites in the natural wetland were denoted according to their location within the wetland: front (SH1), middle (SH2), and back (SH3) (Fig. S1). A total of 21 samples were collected for this study. Six river sediment samples were collected from BP, and 5 wetland soil samples were collected from SH1, SH2 and SH3, respectively. The water depth of this watershed is approximately 0.5 m. The Eh of all samples ranged from −120.3 to −347.5 mV. We used a columnar sediment sampler to collect the surface (0–10 cm) sediments (approximately 300 g) at each sampling site and placed the sediments in ice bags in situ. After being transferred to the laboratory, all samples were immediately stored in a freezer for geochemical analysis (< −20 °C) and DNA extraction (<−80 °C).

2.2. Analysis of geochemical parameters

All samples were freeze-dried in the laboratory for 48 h before chemical analysis and then sieved (2 mm) to remove the plant roots, gravel and leaves. The samples were thoroughly grounded and then sieved with a 200 mm mesh prior to chemical analysis. The pH of the sediment samples was determined using a pH meter (HACH, Loveland, USA) after mixing 10 g of soil with 25 mL of MQ water in a 50 mL conical flask (Xiao et al., 2021b). To determine the concentrations of nitrate and sulfate, we mixed a 10 g soil sample with 50 mL of MQ water, stirred the mixture for 5 min and equilibrated it for 4 h. After centrifugation (3500 rpm) and filtration, sulfate and nitrate concentrations were determined using ion chromatography (Dionex ICS-40, Sunnyvale, CA, USA) (Xiao et al., 2016b). We used an elemental analyzer (Vario Macro Cube, Elementar, Hanau, Germany) to determine the levels of total carbon (TC), total hydrogen (TH), total nitrogen (TN), total sulfur (TS), and total organic carbon (TOC), where the TOC was measured after using 10% HCl to remove the inorganic carbon. Using spectrophotography (UV-9000s, Shanghai METASH) with 1,10-phenanthroline at 510 nm, the levels of total Fe and Fe(II) were tested (Tamura et al., 1974).

2.3. Analysis of Sb and As

After completely digesting a 50 mg sediment sample with a mixed acid (5 mL of 10 M HF and 15 mL of 15 M HNO_3), we used inductively coupled plasma mass spectrometry (ICP-MS) (Agilent, 7700x, Santa Clara, CA, USA) to determine the levels of total Sb (Sb_{tot}) and total As (As_{tot}) (Xiao et al., 2016b). The standard soil reference material (GBW07310) was utilized to control the quality. A modified five-step sequential extraction procedure was applied in this study to extract the Sb and As in the sediment samples (Gault et al., 2003; Wenzel et al., 2001). Five extractable Sb and As fractions were classified into (1) the easily exchangeable fraction (M_{exe}, extracted by 0.05 M $(NH_4)_2SO_4$, where M stands for Sb or As); (2) specifically sorbed surface-bound fraction (M_{srp}, extracted by 0.05 M $NH_4H_2PO_4$); (3) amorphous hydrous oxides of iron-aluminum fraction (M_{amr}, extracted by 0.2 M ammonium oxalate buffer (pH 3.0)); (4) crystalline Fe and Al oxide-bound fraction (M_{cry}, extracted by 0.2 M ammonium oxalate buffer

(pH 3.0) and 0.1 M ascorbic acid); and (5) sulfides and organics-bound fraction (M_{sob}, extracted by 5% (w/v) $KClO_4$ in concentrated HCl). Detailed information on the extraction conditions, reaction times, and regents was in accordance with our previous study (Xiao et al., 2016b) and is provided in Table S10. In the current study, we only considered the easily exchangeable fraction (M_{exe}) and specifically sorbed surface-bound fraction (M_{srp}) due to their bioavailability to soil microorganisms (Sun et al., 2019). After each extraction stage, the supernatant was centrifuged at 3000 rpm for 15 min. The concentrations of Sb and As were determined by ICP-MS (Agilent, 7700x, California, USA). The redox species of Sb and As (M(III) and M (V), where M represents Sb or As) in sedimentary pore water were extracted by citric acid solution (100 mM, pH = 2.08). The redox species of Sb and As were determined by hydride generation atomic fluorescence spectrometry (HG-AFS; AFS-920, Jitian, Beijing) (Sun et al., 2017). M(III) and M(V) were obtained by using proportional equations corresponding to two different measurement conditions, which followed the modified procedure proposed by Chen et al. (2014) and Gonzalvez et al. (2009). Specifically, M(III) was directly determined by feeding sample extracts diluted with HCl. Total M was determined by pre-reduction with thiourea and ascorbic acid for 30 min. M(V) was obtained by subtracting M(III) from total M. Notably, this method cannot test for organic species of Sb and As. According to standard quality control procedures, we used standard quality control procedures using internationally certified reference materials (SLRS-5), internal standards (Rh at 500 mg/L), and duplicates, which was better than ±10% (Xiao et al., 2021a). In this study, we used the term "Sb and As contaminants" to refer to the total Sb/As (M_{tot}), bioaccessible Sb/As fractions (M_{exe} and M_{srp}), and redox species Sb/As as described above.

2.4. 16S rRNA gene sequencing analysis

DNA of sedimentary soil microbes was extracted by a MoBio Power Soil DNA Extraction Kit (MO BIO Laboratories, Carlsbad, CA, USA) following the manufacturer's instructions. The concentration and purity of the extracted DNA were examined by running the extracts on a 1.2% agarose gel. We used the universal primers 515F (GTGCCAGC MGCCGCGGTAA) and 926R (CCGTCAATTCMTTTRAGTTT) to amplify the V4-V5 region of bacterial 16S rRNA genes (Xiao et al., 2016b). We then sequenced the purified PCR amplicons on an Illumina MiSeq instrument at Novogene (Beijing) Co., Ltd. The obtained paired-end reads were merged by using FLASH (Magoč and Salzberg, 2011) and then filtered by QIIME (Bokulich et al., 2013). After comparison with the GOLD database, we obtained raw sequences and then removed chimeric sequences by using UCHIME (http://www.drive5.com/usearch/manual/uchime_algo.html) (Haas et al., 2011). Operational taxonomic units (OTUs) were obtained after clustering based on 97% similarity. The phylogenetic taxonomy was assigned by using the RDP classifier (Version 2.2, http://sourceforge.net/projects/rdp-classifier/) and the Green Genes database (http://greengenes.lbl.gov/cgi-bin/nph-index.cgi) (Wang et al., 2007).

2.5. Statistical analysis

Analysis of variance (ANOVA) was used to determine differences in microbial diversity indices between the BP and SH groups, including the Shannon, ACE and Chao1. In this study, p values < 0.05 were considered statistically significant. We analyzed the enrichment or depletion of OTUs between the two environmental habitats by using the "tidyverse" and "DESeq2" packages in R software (Love et al., 2014). To identify differences in microbial composition, we drew Venn diagrams, alpha diversity (Shannon, ACE, and Chao1) boxplots, and principal coordinate analysis (PCoA) plots by using microbiome analysis and visualization in R (Liu et al., 2021; Zhang et al., 2019). Permutational multivariate analysis of variance (PERMANOVA) using the Bray-Curtis distances was used to determine differences in microbial communities among group. Random forest (RF) analysis was then used to determine the major edaphic predictors of microbial properties in sedimentary soils (Liu et al., 2018). The random forest analysis is an ensemble tree-based method that combines multiple decision trees (classification or regression) to give a prediction (Breiman, 2001). In this study, the random forest type was regression model and the number of decision trees was 1000. Two co-occurrence networks were constructed to confirm the interaction between environmental variables and specific OTUs by using the interaction platform Gephi (Berry and Widder, 2014). Both co-occurrence networks were constructed based on OTUs that were significantly enriched in wetland sediment (SH, 340 OTUs) and river sediment (BP, 363 OTUs). The correlations were visualized when they met the criteria $0.6 < |r| < 1$ and $p < 0.05$. RF analysis was conducted to further evaluate the link between the enriched OTUs and the geochemical cycles of Sb and As and sorted by Importance to visualize the top 30 important OTUs (Liu et al., 2018).

3. Results

3.1. Distribution of geochemical parameters in the watershed

The distribution of the Sb demonstrated zone-specific trends. As shown in Fig. 1, the content of Sb was higher in the wetland system than that in the river sediment. Specifically, the contents of Sb_{tot} were higher in the wetland system, averaging 5175.8 ± 2087.3 mg/kg, than in the river sediment, averaging 2668.2 ± 641.4 mg/kg (Table S1). The bioaccessible Sb included easily exchangeable (Sb_{exe}) and specifically sorbed surface-bound Sb (Sb_{srp}). The concentrations of Sb_{exe} ranged from 19.2 to 30.8 mg/kg in river sediment and from 17.9 to 52.7 mg/kg in wetland ecosystems. The concentrations of Sb_{srp} ranged from 48.5 to 69.3 mg/kg in river sediment and from 38.9 to 106.9 mg/kg in wetland ecosystems. Notably, the average proportion of bioavailable Sb in the wetland system (2.02%) was relatively lower than that in river sediment (3.27%) (Table S1). Moreover, the contents of Sb(III) and Sb(V) in pore water were determined. The average levels of Sb(III) in the wetland (ranging from 120.2–461.9 mg/kg) were higher than those in the river sediment (ranging from 118.3–196.2 mg/kg) (Fig. 1 and Table S1). Furthermore, the proportions of redox species of Sb and As in the pore water of sediment were relatively low. Notably, the proportions of redox species of Sb in BP were 7.0–17.6%, whereas they were 2.1–20.5% in SH (Table S1).

In addition to Sb, the contents of As_{tot} and its bioaccessible fractions were determined. As shown in Fig. 1, the contents of As_{tot} were higher in the wetland system, averaging 127.7 ± 402.7 mg/kg, than in the river sediment, averaging 76.8 ± 125.7 mg/kg (Table S1). The concentrations of As_{exe} ranged from 0.3 to 0.4 mg/kg in river sediment and from 0.3 to 0.6 mg/kg in wetland ecosystems. The concentrations of As_{srp} ranged from 0.5 to 0.7 mg/kg in river sediment and from 2.3 to 6.1 mg/kg in wetland ecosystems. The average proportion of bioavailable As in the wetland system (2.11%) was relatively higher than that in river sediment (1.06%) (Table S1). The levels of As(III) (ranging from 4.8–18.5 mg/kg) and As(V) (ranging from 1.8–7.2 mg/kg) in the wetland were higher than those in the river sediment (Fig. 1). Moreover, the average levels of As(III) (average 12.53 mg/kg) and As(V) (average 3.71 mg/kg) in the natural wetland ecosystem were 19.6 and 14.3 times those in river sediment, respectively (Table S1). Within the natural wetland, the concentrations of As_{tot} were higher in SH1 (278.8–402.7 mg/kg) than in SH2 (166.2–271.6 mg/kg) and SH3 (127.7–212.4 mg/kg), whereas Sb_{tot} was not significantly different among them. The contents of oxidation species of Sb (Sb(III) and As(III)) were higher in SH2 than in SH1 and SH3. Moreover, the bioavailable Sb and As fractions (including Sb_{exe}, Sb_{srp}, As_{exe} and As_{srp}), Sb(V), and As (V) were not significantly different among SH1, SH2 and SH3 (Fig. S3 and Table S1).

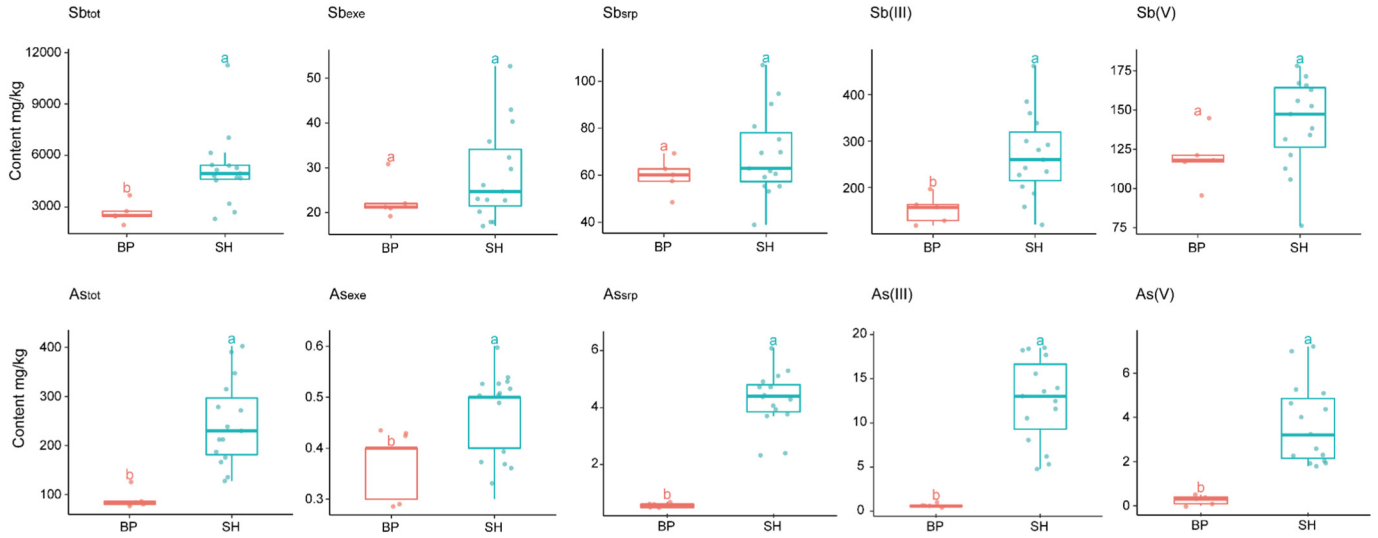

Fig. 1. The contents of Sb and As between BP and SH groups. The group name of SH refers to wetland ecosystem; BP refers to river sediment. Different lowercase letters indicate the significant difference between two groups, whereas same letter indicate no significant difference between groups. The numbers of replicated samples in this figure are 5 in BP and 15 in SH. Abbreviations: Sb_{tot}/As_{tot} (total content of Sb/As); Sb_{exe}/As_{exe} (easily exchangeable forms of Sb/As); Sb_{srp}/As_{srp} (specifically sorbed forms of Sb/As).

As shown in Fig. S2, the levels of nutrient parameters (TOC, TN, TC), Fe(II), and Fe_{tot} in the wetland ecosystem were significantly higher than those in the river sediment. Specifically, TOC averaged 0.42 ± 0.26% in BP and 1.09 ± 0.46 % in SH, and TN averaged 0.04 ± 0.05% in BP and 0.1 ± 0.04% in SH (Table S1). Furthermore, the contents of Fe_{tot} and Fe (II) in pore water were higher in samples taken from wetlands than in those taken from river sediment systems. As shown in Fig. S2, Eh, pH, and SO_4^{2-} in all sediment samples were not significantly different between the river sediment and natural wetland ecosystems. Sb and As contaminant fractions were significant correlated to TC, TOC, and TN (Fig. S9).

3.2. General information for the 16S rRNA gene sequencing analysis

A total of 1,268,912 high-quality sequences were obtained from 21 sediment samples. After filtering the raw reads, we obtained 1,157,841 valid reads, with the number of reads per sample varying from 34,246 to 93,749, which were clustered into 13,219 OTUs for microbial community analysis (97% identity) (Table S2). Notably, in the current study, we chose 3572 representative OTUs (over 95% of the total number of reads) for further analysis. Alpha diversity indices, including the Shannon, Chao1 and ACE, were significantly different between the two different environments and were significantly higher in the wetland system than in the river sediment (Fig. 2 and Table S3). A Venn diagram was used to illustrate the shared and unique OTU distribution between BP and SH (OTUs relative abundance > 0.05%). As shown in Fig. S4, the Venn diagram showed that BP had 39 unique OTUs (account for 9%), whereas SH had 143 unique OTUs (account for 33%). Notably, 258 OTUs (account for 59%) were shared between BP and SH (Fig. S4). The PCoA based on the Bray-Curtis distances of the microbial communities demonstrated a disparity between BP and SH (Fig. S5 and Table S4). PERMANOVA using the Bray-Curtis distances was in agreement with the PCoA that there are significant differences in microbial communities between BP and SH ($p = 0.001$) (Table S11). To further identify the distribution of OTUs inhabiting BP and SH, we used linear analysis to test the enrichment of OTUs in BP and SH. The results showed that 363 OTUs were significantly enriched in BP, and consisted mainly of *Betaproteobacteria*, *Deltaproteobacteria* and *Chloroflexi*, whereas 340 OTUs were significantly enriched in SH, and consisted mainly of *Firmicutes*, *Alphaproteobacteria*, *Gammaproteobacteria*, *Acidobacteria*, *Actinobacteria* and *Cyanobacteria* (Fig. 3 and Table S5). Within the natural wetland, the PCoA of Bray-Curtis distances revealed that the cluster of SH1 separated with SH2 and SH3, indicating that the microbiota among them were different. PERMANOVA using the Bray-Curtis distances supports the PCoA results that there are significant differences in microbial communities among SH1, SH2 and SH3 (all groups $p < 0.05$) (Table S11). Moreover, Shannon revealed a significant difference between SH1 and SH2, and microbiota

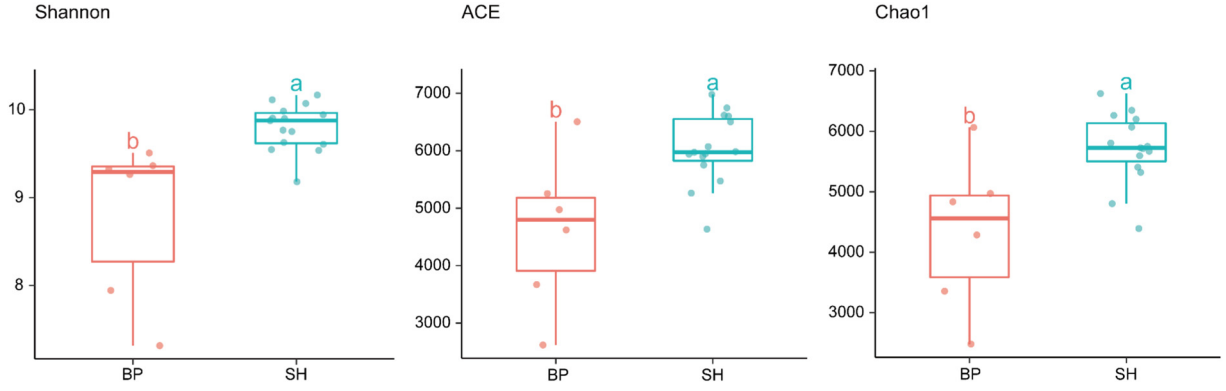

Fig. 2. The distribution of alpha diversity indices between BP and SH groups. The group name of SH refers to wetland ecosystem; BP refers to river sediment. Different lowercase letters indicate the significant difference between two groups, whereas same letter indicate no significant difference between groups. The numbers of replicated samples in this figure are 6 in BP and 15 in SH.

of SH2 had higher diversity than SH1 and SH3. Furthermore, ACE and Chao1 were showed no difference among SH1, SH2 and SH3 (Fig. S10 and Tables S3 and S4).

3.3. Relevance of the microbial communities to fractionated Sb and As

In the current study, we performed various analyses to understand the relationship between sediment physicochemical properties and microbial community structure. First, RF analysis showed that bioavailable Sb/As (including As(III), Sb(III), As(V), Sb(V), As_{exe} and As_{srp}) and TC were important predictors of microbial diversity (Fig. 4 and Table S6). Among them, As(III) and Sb(III) best explained the differences in the microbial diversity indices, including the Shannon and Chao1, respectively (Fig. 4). Second, two bacterial networks were constructed to further identify the link between bacteria and edaphic factors (Fig. 5 and Table S7). The results showed that the topological parameters displayed obvious differences between the two constructed bacterial networks. Specifically, the numbers of edges were 6616 and 7574 in the BP and SH networks, respectively. The average degree and closeness centrality parameters were higher in the wetland than in the river sediment. In contrast, the betweenness centrality and clustering were lower in the wetland network than in the river sediment network. Notably, the OTUs with the top 10 degree values fell into different phyla. Specifically, the taxonomic compositions at the phylum level of those OTUs in the BP network were *Actinobacteria*, *Chloroflexi*, *Proteobacteria* and *TPD-58*, and those in the SH network were *Firmicutes*, *Proteobacteria*, *Clostridia* and *Bacteroidetes* (Fig. 5). To further determine the relationship between microbial attributes and redox species of Sb/As, we performed RF analysis to identify the importance of the OTUs significantly enriched in the wetland for the redox species of Sb and As (Fig. 6 and Table S8). The results showed that the 30 most important predictors of Sb(III) and As(III) were predominantly affiliated with *Acidimicrobiales*, *Rhizobiales*, *iii1-15*, *Chroococcales*, *Solirubrobacterales*, *Pirellulales*, *0319-7L15* and *Acidimicrobiales*, *Legionellales*, *Rhizobiales*, *Gaiellales*, *iii1-15*, *Sphingomonadales*, and *Syntrophobacterales*, respectively. In addition, the 30 most important predictors of Sb(V) and As(V) were predominantly affiliated with *Acidimicrobiales*, *Clostridiales Chloroflexales*, *Rhizobiales*, *Xanthomonadales*, *Gaiellales*, *Legionellales*, *Pirellulales*, *Rhodospirillales* and *Acidimicrobiales*, *Rhizobiales*, *Xanthomonadales*, *iii1-15*, *Sphingomonadales*, *Pirellulales*, *Solirubrobacterales*, and *0319-7L15*, respectively. Notably, among these OTUs, most were also identified as OTUs that were significantly correlated with Sb and As from the SH bacterial network (blue in the RF model) (Figs. 5 and 6). Furthermore, our results showed that most of these OTUs positively correlated with Sb/As contaminants (Fig. S8).

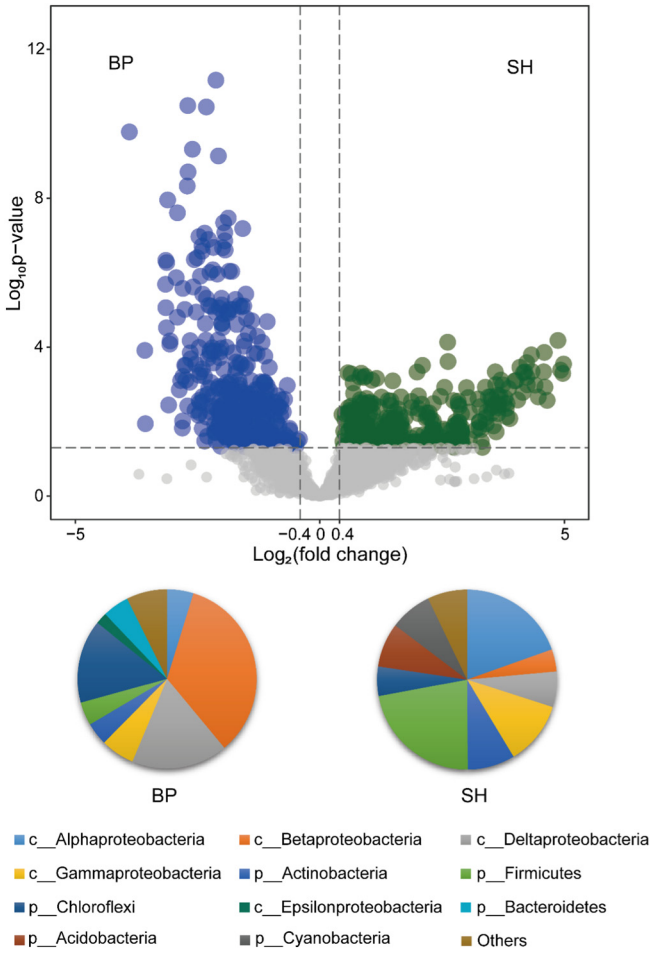

Fig. 3. Volcano plot showing OTUs enriched in BP and SH. Each dot represents a single OTU and OTUs significantly enriched in BP and SH are represented by blue and green, respectively. Pie charts show the bacteria taxonomic composition of those OTU that are significantly enriched in BP and SH groups. The numbers of replicated samples in this figure are 6 in BP and 15 in SH.

4. Discussion

4.1. Sb and As in the watershed

This watershed was characterized by elevated Sb (as high as 1942.9–3688.3 mg/kg) and As concentrations (as high as 76.8–125.7 mg/kg), which were remarkably higher than the background concentrations of Sb (0.80–3.00 mg/kg) (He et al., 2012) and As (4.10–12.46 mg/kg) (Xu et al., 2017) in China's river sediment. The elevated contents of Sb and As in the watershed were mainly due to the reception of Sb-rich tailings from an Sb tailing pond along the Xiaohe River. In general, the concentrations of sedimentary Sb and As decrease dramatically over the distance to the tailings pond (Wang et al., 2011). In the current study, however, the levels of total Sb and As in river sediment (BP), which is closer to the tailings pond, were significantly lower than those in the natural wetland ecosystem (SH) (Fig. 1). This result suggests that natural wetland ecosystems have a significant role in the immobilization of Sb and As in the watershed, which is in accordance with previous studies (Filella et al., 2002). In general, the mobility and bioaccessibility of metal(loid) were correlated with the binding type with the sample matrix (Savonina et al., 2012). In the current study, we used sequential extraction to obtain the bioaccessible Sb and As in sediments. Overall low levels of bioaccessible Sb and As have also been reported in previous studies (Flynn et al., 2003; Gal et al., 2007), indicating that Sb and As are relatively immobile in the river environments. Notably, the averaged contents of bioavailable Sb were relatively higher in the wetland ecosystem, whereas bioavailable As were relatively lower in river sediments (Table S1). This result was consistent with a recent study conducted by Xu et al. (2020b), which showed that this phenomenon was mainly due to microbial mediated Sb and As cycling. In this study, the averaged proportions of Sb(III) and As(III) were higher relative to Sb(V) and As(V) in river sediment and wetland ecosystems (Table S1). This may be because all sediment samples were characterized by low Eh (below −100 mV) (Ascar et al., 2008). Surprisingly, the contents of Sb(V) and As(V) were elevated in whole samples where Eh was negative (Table S1). This phenomenon was also reported by Xu et al. (2020b) who proposed that this may partially be due to microbially mediated Sb and As cycling.

The other environmental variables demonstrated zone-specific pattern. For instance, both TC, TN, and TOC were higher in the wetland ecosystem than in the river sediments (Fig. S2 and Table S1). This is expected, as TC, TN, and TOC contents are often higher in wetland ecosystems than in river sediments due to the growth of plants (Sung et al., 2015). These environmental variables were significant correlated to Sb and As contaminant fractions (Fig. S9), suggesting their important

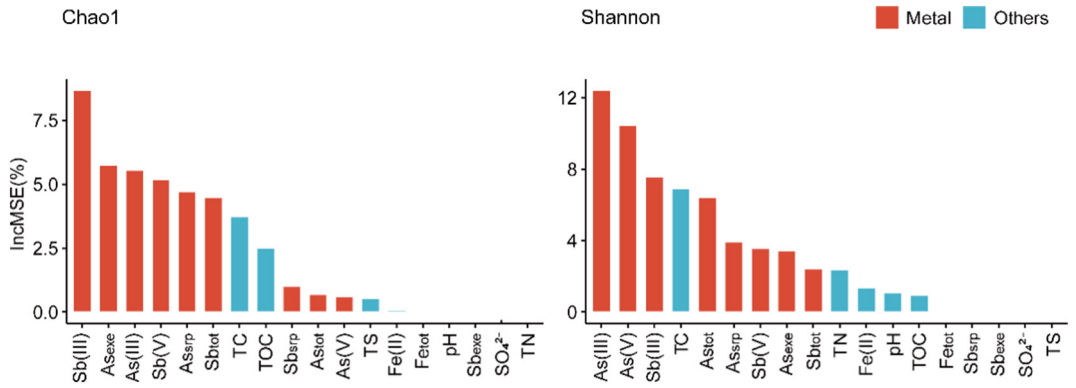

Fig. 4. RF analysis of microbial diversity indices (Shannon and Chao1) predicted by metal(loid)s, nutrients and other chemical parameters for bacterial community between BP and SH. The numbers of replicated samples in this figure are 5 in BP and 15 in SH.

roles on Sb and As geochemical cycling. This result was consistent with prior studies that the TN and TOC could impact the geochemical behavior of Sb and As via adsorption and complexation in the river sediment (Filella et al., 2002). More important, TN and TOC could facilitate microbial growth and indirectly impacts the geochemical behavior of Sb and As (Y. Li et al., 2021b). Notably, we also identified that the distribution of As_{tot}, Sb(III), and As(III) differed within natural wetland ecosystems, suggesting the heterogeneity within wetlands. The

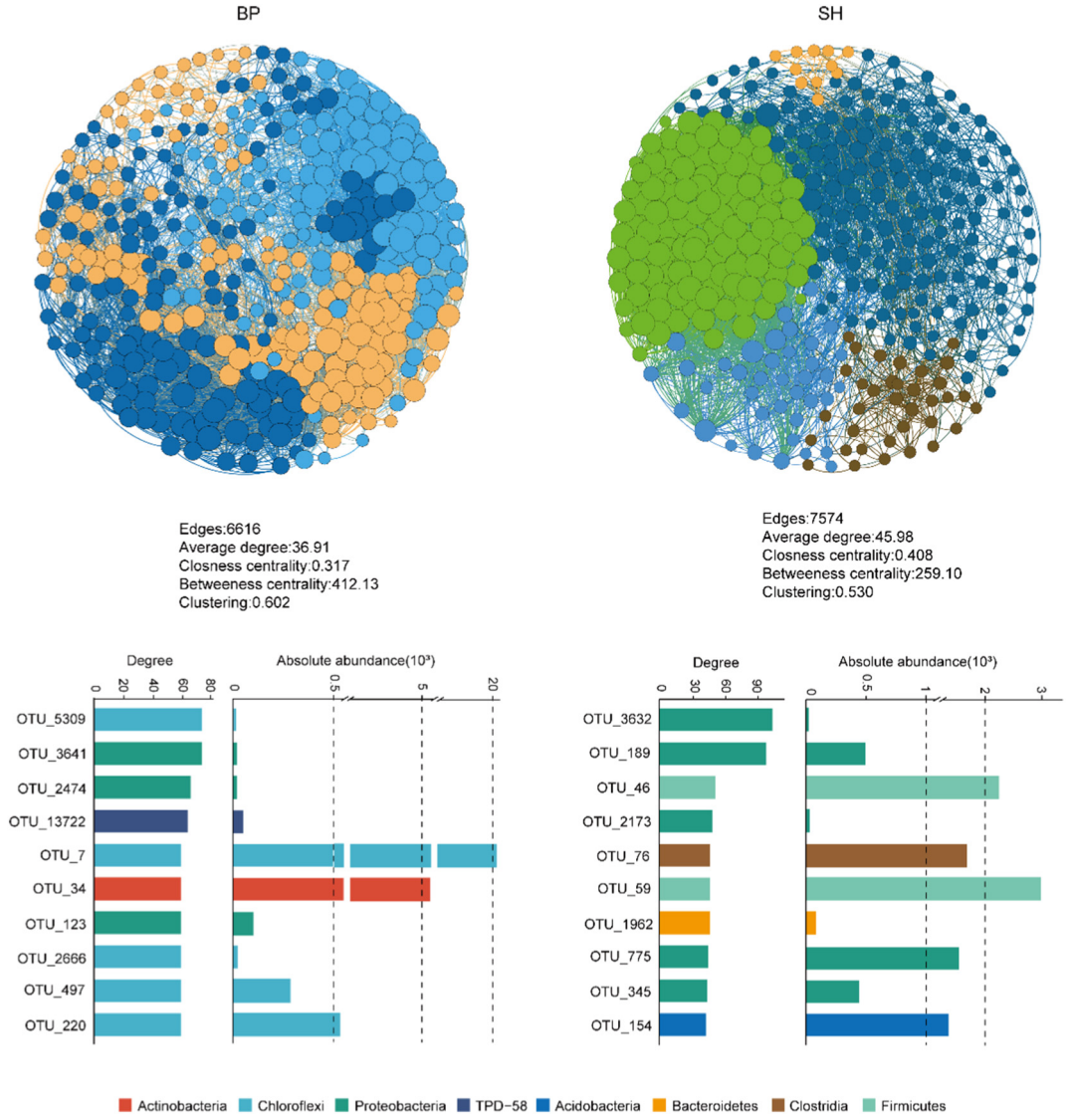

Fig. 5. Microbial co-occurrence network of BP and SH. The parameters of structure of networks (edges, average degree, closeness centrality, betweenness centrality, and clustering) were shown. The top 10 degree of OTUs and their absolute abundance were showed (each OTUs were colored by phyla). The numbers of replicated samples in this figure are 5 in BP and 15 in SH.

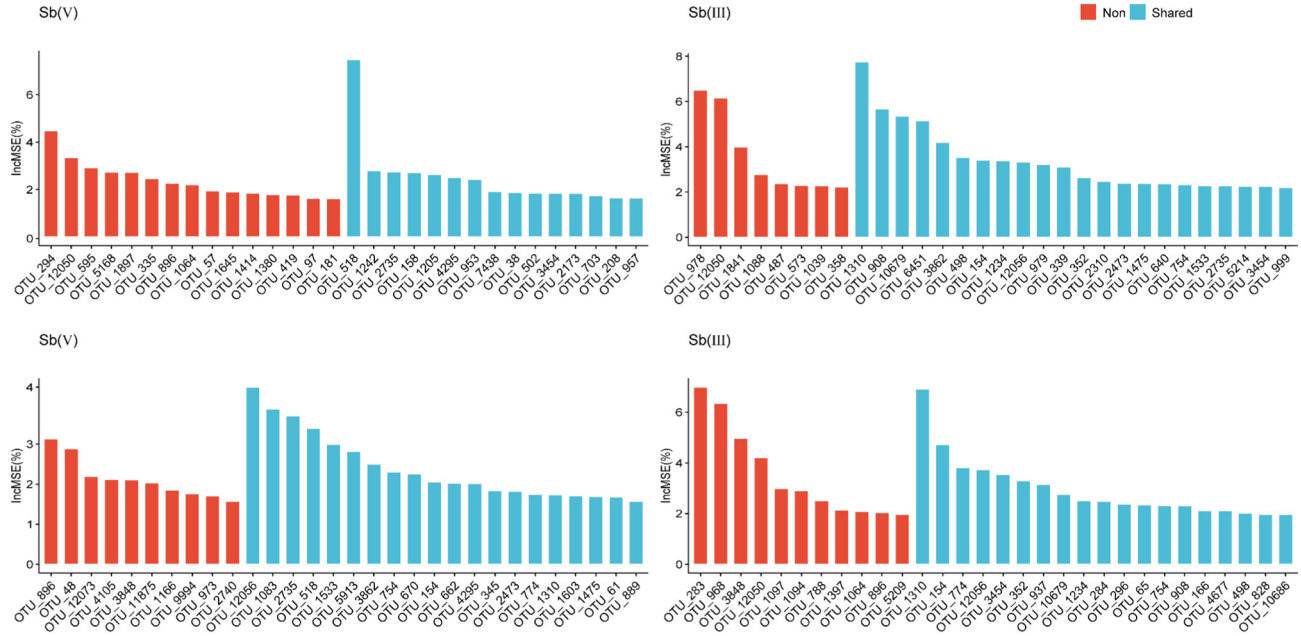

Fig. 6. RF analysis of redox state of Sb/As (Sb(III), As(III), Sb(V), As(V)) predicted by the top 30 OTUs based importance in SH group. The numbers of replicated samples in this figure are 5 in BP and 15 in SH.

changes in environmental variables further shape the microbial community, which is critical for Sb and As biogeochemical cycling in the environment (Mateos et al., 2006; Gao et al., 2021).

4.2. Relevance of environmental variables on the overall microbial community

Previous studies have shown that sedimentary bacteria respond differently to distinct environments in river systems (Zhang et al., 2020), adopting different survival strategies to improve their fitness (Goddard and Bradford, 2003). Recent evidence has shown that such changes in the sedimentary microbial community may potentially play important roles in Sb/As biogeochemical cycling in certain environments (Y. Li et al., 2021a). Indeed, we identified that the microbial alpha diversity was significantly higher in natural wetland soils than in river sediment (Fig. 2 and Table S3), which is consistent with a prior study showing that sedimentary microbial diversity indices could be increased when rivers enter a constructed wetland (Cao et al., 2017). Existing evidence suggests that the distributional patterns of microbial communities may be relevant to the differences in plant growth in natural wetland ecosystems (Wang et al., 2010). Generally, the status of chemical factors in sedimentary soils can be altered by the growth of plants, and microbial communities can sensitively respond to these variations (Shahzad et al., 2015). Consistent with this, we determined differences in nutrient and Sb/As statuses between the SH and BP groups (Figs. 1 and S2) and such changes could reasonably explain the distinct distribution of the sedimentary microbial community. This idea was also supported by the fact that TC and metal(loid) parameters (such as Sb(III), As(III), Sb(V), As(V) and As_{exe}) parameters were important predictors of the bacterial community composition (Fig. 4 and Table S6).

Likewise, the prevalence of the dominant bacterial taxa is also a reflection of the changes in the nutrient and metal(loid) statuses of the sedimentary soils. For example, taxonomic classification of the significantly different OTUs at the phylum level demonstrated that *Firmicutes* and *Alphaproteobacteria* were significantly enriched in SH, whereas *Beta-* and *Deltaproteobacteria* were enriched in the BP sedimentary soil samples (Fig. 3 and Table S5). These taxonomic groups are believed to be ubiquitous and abundant bacterial phyla and are generally found in different metal(loid)-affected environments, such as soils (Xiao et al., 2021a, W. Sun et al., 2020), river sediments (Xu et al., 2020a, 2020b), and tailings (Sun et al., 2017; X. Sun et al., 2020). It has been reported that *Beta-* and *Deltaproteobacteria* are versatile heterotrophs with an oligotrophic lifestyle (Trivedi et al., 2013), whereas *Alphaproteobacteria* and *Firmicutes* are able to utilize a variety of carbon sources for fast-growth (i.e., copiotrophs) (Trivedi et al., 2013). The enrichment of *Beta-* and *Deltaproteobacteria* was consistent with their colonization ability in nutrient-limited river sedimentary samples, and these taxa can contribute to improving the soil nutrient status (Inceoglu et al., 2010). Overall, these results suggested that natural wetlands affect the selective enrichment of sedimentary soil microbes.

4.3. Microbially mediated Sb/As cycling differs between river sediment and natural wetlands

As discussed above, natural wetlands could form distinct environments with different nutrients and metal(loid) statuses compared to river systems, which subsequently influence the selective enrichment of sedimentary microbes. To determine whether these changes influence Sb and As biogeochemical cycling, we tested the linkage between the microbial community and Sb and As. In this study, we observed that Sb and As components play important roles in the distribution of sedimentary microbial community structure (Figs. 4 and S6). The interactions between Sb and As contaminants and microorganisms could be involved in multiple processes, mainly microbially mediated redox processes and biotic adsorption by microorganisms, which could potentially alter their toxicity and mobility (Xu et al., 2020a). Importantly, we identified that the OTUs in module 0 (Oxford blue) related to Sb/As fractions in the natural wetland were widely identified in various plant roots or rhizosphere soils and reported to promote plant growth via nutrient cycling, i.e., nitrogen fixation (*Rhizobiales*, order level), nitrification (*Xanthomonadaceae*, family level) and denitrification (*Proteiniclasticum*, genus level) (Fig. 5 and Table S7). Therefore, our results suggest that the assemblage of microorganisms is mainly influenced by plant colonization in natural wetlands. This result is consistent with prior studies showing that the microbial composition in a wetland was mainly regulated by the resident plants (Zhang et al., 2010; Zhao et al., 2012). Importantly, we also identified that the enriched OTUs at SH1, SH2, and SH3 were affiliated with

Xanthomonadales (order level), and *Rhizobiales* (order level), suggesting their different distributional patterns within wetland systems. Notably, these groups have been widely reported in various Sb/As-contaminated environments (Tomczyk-Zak et al., 2013). For instance, *Xanthomonadales* was correlated with two bioavailable fractions of As and Sb (Fig. S7 and Table S9). Although members of *Xanthomonadales* have previously been described as As-metabolizing bacteria and encode As(V) reductase-arsC (Yuan et al., 2020), *Xanthomonadales* has also been found to be substantially correlated with Sb fractions in environments (J. Li et al., 2021; Nguyen et al., 2019). In this study, the OTUs with the top 50 degree values in module 0 affiliated with *Xanthomonadales* from the SH bacterial network, such as OTU_2173 and OTU_61, demonstrated a significant correlation with Sb and As, which were also important predictors of Sb(V) and As(V), respectively (Figs. 5 and 6). Given that Sb and As share some physicochemical and toxic properties, we hypothesized that *Xanthomonadales* might be capable of bearing and utilizing certain Sb components (Xu et al., 2020b). Furthermore, we identified that some important OTUs may indirectly affect the biogeochemical behavior of Sb and As. For instance, *Clostridiales* was positively correlated with the As_{tot} fractions (Fig. 7 and Table S9). Members of *Clostridiales*, such as *Clostridium*, are widely reported to be sulfate- and sulfur-reducing species (Davis et al., 2012). *Clostridiales* was believed to be well adapted to As and Sb contamination. Extensive studies have demonstrated that microbially mediated sulfate- and sulfur-reducing species generate S^{2-}, which thereby quickly precipitates As and Sb to form As_2S_3 and Sb_2S_3 from water (Kirk et al., 2004; Wang et al., 2013). Furthermore, we identified that members of *Desulfuromonadales* were widely reported as Fe(III)-reducing bacteria (Tang et al., 2020). Usually, microbially mediated Fe reduction is strongly related to the distribution of Sb and As in river environments. The statistical analysis consistently showed that the absolute abundance of *Desulfuromonadales* was significantly correlated with As_{tot}, As_{exe}, and As_{srp} (Figs. 7 and S7). Taken together, these results suggested that the plant-induced assemblage of microorganisms was involved in As(V) reduction, sulfate reduction, and Fe(III) reduction, which could directly or indirectly immobilize Sb and As in the natural wetland ecosystem.

Compared to natural wetlands, river sediment lacks plants and exhibits a distinct geochemical status (Figs. 1 and S2). It is therefore believed that the microbial composition in river sediment may differ from that in natural wetlands, thereby resulting in different microbial mediated Sb and As cycling compared to that in natural wetland systems. Indeed, we revealed that the OTUs with the top 50-degree values in both modules 1 and 2 (Oxford blue and orange) that were related to Sb/As fractions in the river sediment were distinct compared to those in the natural wetland system (Fig. 5 and Table S7). Among these OTUs, those belonging to *Burkholderiales*, *Desulfobacterales*, *Hydrogenophilales* and *Rhodocyclales* exhibited extensive interactions with Sb and As contaminants (Fig. 5 and Table S7). More importantly, these OTUs were identified as important predictors of the distribution of Sb and As fractions. Therefore, it is reasonable to suggest that these OTUs play a significant role in microbially mediated Sb and As cycling in river sediments. Members of *Burkholderiales* are capable of sulfide oxidation and have been widely identified in Sb- and As-contaminated environments (Y. Li et al., 2021a). Recent evidences have shown that microbially mediated sulfide oxidation is usually coupled with the mobilization of Sb and As in river sediments (Loni et al., 2020; Tsaplina et al., 2013). In the current study, we demonstrated that there was a significant negative correlation between the absolute abundance of *Burkholderiales* and As_{exe} (Fig. 7 and Table S9). Furthermore, the OTUs affiliated within *Burkholderiales* were strongly correlated with Sb and As components (Fig. S7 and Table S9). Notably, moderately thermophilic and acidophilic *Thiobacillus*, a member of *Hydrogenophilales*, has been extensively reported to be a genus of sulfur-oxidizing bacteria (SOB). It is particularly intriguing that Fe(III) can catalytically oxidize As(III) in the presence of *Thiobacillus ferrooxidans* (Mandl and Vyskovsky, 1994). Recently, arsenate oxidase and reductase were found in a *Thiobacillus*-affiliated bin (X. Sun et al., 2020). In this study, the absolute abundance of *Thiobacillus* was negatively correlated with As(III) (Figs. 7 and S7). These results indicate a potentially important role for *Thiobacillus* in the cycling of As. Moreover, our previous report showed that *Thiobacillus* spp. was present in Sb tailings (Xiao et al., 2016a). *T. ferrooxidans* has been reported to be capable of oxidizing Sb(III)-bearing minerals (Silver and Torma, 1974). A study by Lialikova (1972) demonstrated that *T. ferrooxidans* was only able to utilize the released energy from Sb(III) oxidation to grow autotrophically. Consistent with this, the absolute abundance of *Thiobacillus* also exhibited a significant negative correlation with the Sb(III) content in the current study (Figs. 7 and S7). These results suggested that *Thiobacillus* may be important in the cycling of Sb and As in river sediment. Moreover, *Desulfovibrio* (genus level) and *Dechloromonas* (genus level) were characterized as abundant groups in Sb- and As-rich environments (Hery et al., 2015). Some highly similar genes for As metabolism, such as arrA and acr3, were observed in the genomes

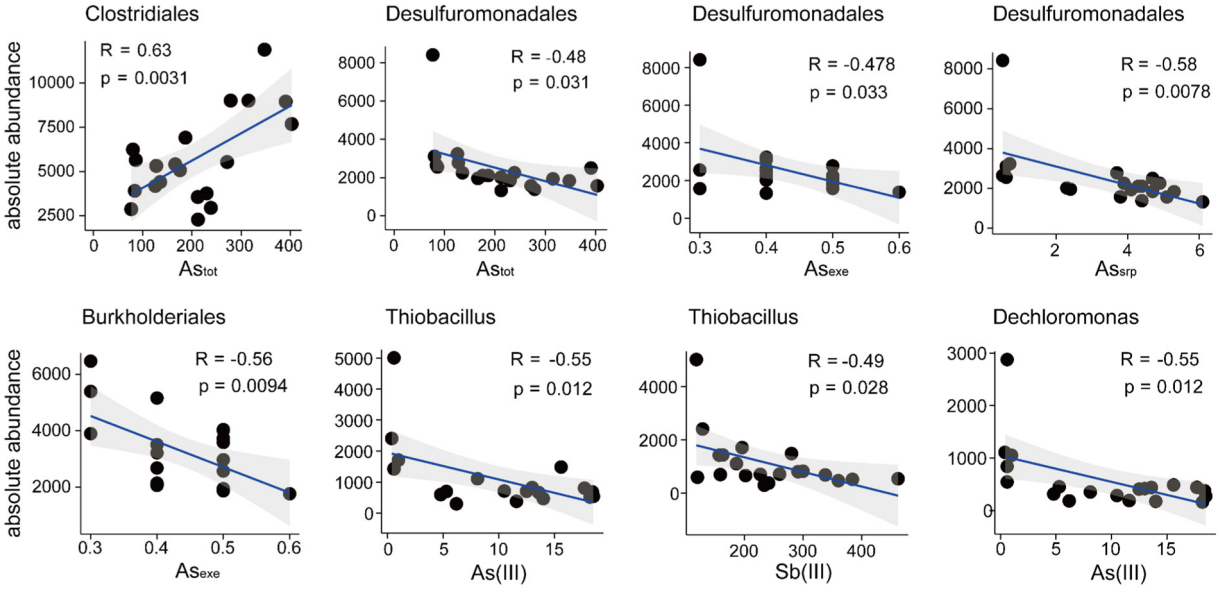

Fig. 7. Pearson's correlations between important bacteria and Sb/As contaminated fractions. The numbers of replicated samples in this figure are 5 in BP and 15 in SH.

of certain *Desulfovibrio* spp. (Hery et al., 2015). Consistent with this, we demonstrated a significant negative correlation between the absolute abundance of *Desulfovibrio* and the content of As_{tot} (Fig. 7 and Table S9). Another study reported that members of *Dechloromonas*, containing the aroA gene, were capable of growing by linking As(III) oxidation with ClO_3^- reduction (Sun et al., 2011). Consistent with this, we demonstrated that the absolute abundance of *Dechloromonas* was significantly negative correlated with As(III) (Figs. 7 and S7). Collectively, these results suggested that members of the taxonomic groups *Burkholderiales*, *Desulfobacterales*, *Hydrogenophilales*, and *Rhodocyclales* can tolerate high levels of Sb/As contamination in river sediments and participate in sulfide oxidation and As(III) and Sb(III) oxidation to directly or indirectly mobilize Sb and As in river sediment.

5. Conclusions

In the current study, we analyzed the changes in the microbial community and microbially mediated potential Sb and As cycling that occur when rivers flow into wetlands in Sb- and As-contaminated river systems. Our results suggested that there are distinct geochemical conditions between river systems and natural wetlands, which significantly impact the distribution of sedimentary microbial communities in the two environments. This study identified that microbial-mediated Sb and As cycling was shifted when rivers flowed into wetlands. Importantly, the microorganisms inhabiting natural wetlands could immobilize Sb and As via Sb/As reduction, sulfate reduction and Fe(III) reduction. The findings of this study have important implications for future bioremediation of Sb/As-contaminated rivers by constructing natural wetland ecosystems. Notably, we acknowledged that this study investigated the microbe-mediated Sb and As cycling based on statistical analysis, and further experimental studies are needed to confirm these processes. Despite this limitation, this study improves our understanding of microbially mediated Sb and As cycling in wetland environments and provides important information for the bioremediation of Sb/As in river systems.

CRediT authorship contribution statement

Jinmei Deng: Writing – original draft, Writing – review & editing, Investigation. **Tangfu Xiao:** Writing – review & editing, Project administration, Funding acquisition. **Wenjun Fan:** Formal analysis, Writing – review & editing. **Zengping Ning:** Writing – review & editing. **Enzong Xiao:** Writing – review & editing, Resources, Project administration, Supervision.

Declaration of competing interest

The authors declare that they have no current or potential competing financial interests.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.151826.

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