



Impact of eutrophication on arsenic cycling in freshwaters

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ABSTRACT

Many arsenic-bearing freshwaters are facing with eutrophication and consequent algae-induced anoxia/hypoxia events. However, arsenic cycling in eutrophic waters and its impact on public health are poorly understood. Laboratory simulation experiments are performed in this study to investigate the effect of algal blooms on the cycling of arsenic in a sediment–water–air system. We found that the anoxia induced by the degradation of algal biomass promoted an acute arsenic (mostly As(III)) release within two days from sediment to both the water and atmosphere, and the release effluxes were proportional to the algae dosage. The reduction and methylation of arsenic were enhanced at the sediment–water interface, owing to the significant increase in arsenate reductase genes (*arrA* and *arsC*), and arsenite methyltransferase genes (*arsM*) caused by increased anoxia. The analysis of synchrotron-based X-ray absorption spectroscopy indicated that the concomitantly released natural organic matter (NOM) and sulfur (S) at the sediment–water interface reduced the As(III) release to a certain extent in the later reducing period of incubation, by forming As₂S₃ (43–51%) and As(III)–Fe–NOM (28–35%). Our results highlight the needs for the *in-situ* assessment of volatile arsenic in eutrophic freshwaters with its risk to human and animal health.

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1. Introduction

Algal blooms, affected by eutrophication and climate change, are increasing in frequency, duration, and intensity globally (Huisman et al., 2018). They threaten the ecosystem functioning of freshwaters and public health, by not only their foul odor, but also the mobilization of pollutants (e.g., arsenic, methylated Hg, Fe, methane) during algae-induced anoxia/hypoxia events (Beutel et al., 2008; Gao et al., 2012; Shi et al., 2018). Arsenic (As) is an environmentally ubiquitous and notorious carcinogen (Wang et al., 2016). Due to the continuous anthropogenic nutrient input resulting from rapid industrialization and urbanization, eutrophication is becoming an increasing challenge in many arsenic-polluted inland waters (Dierszowsky and Wilson, 2015; Gao et al., 2012; Hirata et al., 2011; Lin et al., 2016; Rahman and Hasegawa, 2012; Wei et al., 2011). In the summer when algal blooms are likely to erupt,

increased total dissolved arsenic and As(III) levels have been observed in some eutrophic freshwaters, such as the mine-impacted Balmer Lake in Canada, Biwa Lake in Japan, and Dianchi Lake in China (Hasegawa et al., 2010; Martin and Pedersen, 2004; Rahman and Hasegawa, 2012; Yang et al., 2016). However, the mechanism of arsenic biogeochemical cycling in eutrophic waters, especially during algae-induced anoxia/hypoxia events remains poorly understood.

Existing studies based on field sampling and monitoring have indicated the potential correlation between algae-induced anoxia/hypoxia condition and the endogenous release of arsenic into the water column (Martin and Pedersen, 2004; Rahman and Hasegawa, 2012; Yang et al., 2016). The concentrations of total dissolved arsenic (including As(V), As(III), methylarsonic acid (MMA), and dimethylarsinic acid (DMA(V)) released into the water column vary by several orders of magnitude, ranging from 12.2 to 8500 µg/L in different eutrophic freshwaters, depending on the total arsenic levels in sediments and the environmental chemistry (Martin and Pedersen, 2004; Rahman and Hasegawa, 2012; Yang et al., 2016). However, the maximum permissible arsenic level is 10 µg/L if freshwaters are used for drinking water (World Health Organization (WHO)) or urban water supply sources (CJ/T206–2005, China).

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(Mohan et al., 2007). Except for the release into the water column, arsenic can also escape into the atmosphere by forming volatile arsines, such as arsine (AsH_3), monomethylarsine (MeAsH_2), dimethylarsine (Me_2AsH) and trimethylarsine (TMAs), through microbial activities under anaerobic conditions (Webster et al., 2016). Volatile arsenic species have been proven stable for hours during the daytime, and weeks in dark conditions in the atmosphere (Jakob et al., 2010; Mestrot et al., 2011b), thus potentially represent a serious health risks for tourists, fisherman, local residents, and wild animals (Mestrot et al., 2011b). Increasing studies have shown that arsenic volatilization from soils can be stimulated by adding exogenous natural organic matters (NOMs) such as clover, cattle manure and plant straw (Huang et al., 2012; Mestrot et al., 2009, 2011a). In eutrophic freshwater systems, senescent algal blooms serve as an exogenous NOM that is continuously deposited onto arsenic-polluted sediments (Gao et al., 2012; Hasegawa et al., 2009, 2010; Sheng et al., 2012), which may stimulate the arsenic volatilization. However, compared to the widespread concern of various arsenic species in the water column, the release of volatile arsenic compounds in the eutrophic freshwaters is often overlooked, partly owing to the lack of satisfactory methods to measure them in the open lake field (Faust et al., 2016; Mestrot et al., 2009). Therefore, the investigation of arsenic volatilization through laboratory simulation experiments may bridge the knowledge gap in understanding the biogeochemical cycle of arsenic in eutrophic freshwaters.

The endogenous release of arsenic in freshwaters is often influenced by exogenous NOMs, however, the role of the NOMs on arsenic mobility and bioavailability is highly controversial (Langner et al., 2012). NOMs are typically recognized as affecting arsenic mobilization and bioavailability indirectly through microbial activity. The addition of NOMs (as a nutrient) can stimulate the activity of indigenous arsenic metabolism functional microbes to influence arsenic speciation, for example, from As(V) to the more mobile As(III) (Huang et al., 2012). It can also fuel the dissimilatory reducing bacteria (as an active electron donor) to drive the reduction processes of iron and sulfate in anoxic sediments (Meharg et al., 2006; Weber et al., 2010), thereby indirectly controlling arsenic mobility by the interaction of arsenic with the generated ferrous matter (Kirk et al., 2010; Xu et al., 2011) or sulfides (La Force et al., 2000; Langner et al., 2013; Moon et al., 2017). Nevertheless, NOM has been proved to be a sorbent for both As(III) and As(V) to directly control arsenic mobility (Hoffman et al., 2013). In numerous natural wetland systems and peat sediments with abundant NOMs, the enrichments of arsenic are shown not related to the presence of arsenic-bearing minerals, but through the interaction with NOMs (González et al., 2006; Langner et al., 2012; Rothwell et al., 2010). Increasing spectroscopic evidences have highlighted that As(III)/As(V) can bind to NOMs by forming of “As-NOM” or “As-polyvalent cations-NOM” complexes, depending on the intrinsic chemical heterogeneity of the environments (Hoffmann et al., 2013; Langner et al., 2012, 2013). The senescent algal blooms can induce a NOM-rich anoxic sediment–water interface in eutrophic freshwaters, where interactions between NOMs and As(III) could potentially be an important mechanism for arsenic mobilization and sequestration. However, there is not enough spectroscopic evidence to assess the role of As–NOM on arsenic cycling in freshwaters suffering from algal blooms (Gao et al., 2012; Moon et al., 2017).

In this study, we investigated the biogeochemical cycling of arsenic in the microcosmic sediment–water–air system, with low algae dosage (LAD) and high algae dosage (HAD) representing the normal algal blooms level and black bloom eruption level in freshwaters, respectively. Our primary objectives are (i), to illustrate the potential risks of arsenic in aquatic and atmosphere of

freshwaters undergoing eutrophication; (ii), to elucidate the mechanism of arsenic speciation and volatilization during algal biomass degradation; and (iii), to quantify the extent of arsenic binding to NOMs, sulfides and mineral oxides under different redox conditions.

2. Materials and methods

2.1. Sample collection and preparation

Surface sediment (0–10 cm) and water was sampled from Caohai (N 24°57'–25°1', E 102°37'–102°40'), Northeastern basin of Lake Dianchi in Kunming City, Yunnan Province, China. The surface area of Lake Dianchi is 309 km², with an average depth of 4.4 m. It is a typical arsenic-polluted lake with a total arsenic concentration of 6.55–12.2 µg/L in water column and 24.5–152.9 mg/kg in surface sediments (Wei and Zhang, 2012; Zhang, 2013). It has been affected by annual cyanobacterial blooms since the 1990s (Sheng et al., 2012; Zhou et al., 2016). The characteristics of the sampled sediments and water are listed in Supplementary Table S1. Algal blooms scum (*Microcystis aeruginosa*) collected from the same site was freeze-dried, ground with a mortar and served as the origin of NOMs in the incubation experiments. Dried algal biomass was chosen to exclude the arsenic metabolism origin from the fresh algae themselves (Rahman and Hasegawa, 2012).

2.2. Microcosm experiments

Six treatments were performed with three replicates for each. (i) The control group consists of sediments and lake water that represented the blank group. (ii) The LAD group consists of sediments and lake water with an added 0.04 g of dried algal biomass, representing the general algae level during algal blooms season (Shi et al., 2018). (iii) The HAD group consists of sediments and lake water with an added 0.60 g of dried algal biomass (equivalent to 5000 g fresh algae/m²), representing the black blooms condition (Han et al., 2015). (iv) The S-control group consists of sterilized sediments plus lake water, represents the sterilized blank group. (v) The S-HAD group, consists of sterilized sediments and lake water with an added 0.60 g of sterilized dried algal biomass. (vi) The control 2 group consists of 600 mL of lake water with 0.60 g of added dried algal biomass, representing the arsenic release potential of algal biomass itself without a sediment supply. Through a comparison between the control, LAD, and HAD groups, we can obtain arsenic speciation and mobilization at different eutrophication-induced NOM levels. To further clarify the amount of total arsenic released from the sediments, we compared the arsenic mobilization between the control 2 and HAD groups. By comparing among the control, HAD, S-control, and S-HAD groups, the impact of microbial activity on arsenic speciation and mobilization can be evaluated. Except for control 2, all cylindrical plexiglass microcosms (Φ64 mm, length 300 mm) include 220 mL of homogenized sediments and 600 mL of lake water, with a trapping (Huang et al., 2012) of volatile arsenic installed at the top of the sealed microcosm (Supplementary Fig. S1). Details regarding the collection and quantification of volatile arsenic species are presented in Supplementary Information. In the sterilized groups, sediments, water and algal biomass were autoclaved for 20 min at 121 °C, and another 0.2% NaN_3 was added into the water to further inhibit microbial growth.

Each microcosm was stabilized for three weeks before algal biomass addition. All experiments were performed in the dark at 25 °C for 18 days. Overlying water (10 mL) was sampled at approximately 20 mm above the SWI (sediment–water interface) and filtered with 0.45 µm filter. Porewater (5 mL) was sampled with

Rhizons soil moisture samplers (type MOM) from 5 mm above, and 10, 20, 30 and 40 mm below the SWI. All water samples were sampled in an anaerobic glove box at 0, 2, 4, 7, 12, 18 days after algal biomass addition and stored at -20°C until the analyses for sulfates, DOC, Fe, and As. After each sample collection, all microcosms were replenished with the originally filtered water to compensate for the sampling losses. The mixed sediments (0–20, 20–40, and >40 mm) were sampled in an anaerobic glove box and stored at -80°C before chemical extraction, synchrotron-based X-ray absorption spectroscopy collection, and arsenic metabolism functional gene analyses. More details of the analytical methods are shown in Supplementary Information.

2.3. Bulk X-ray absorption spectroscopy

A subset of fresh sediment samples was prepared for bulk arsenic and iron K-edge XAS analyses. The homogenized sediment samples were filled into Plexiglas sample holders in an anaerobic glove box, sealed with Kapton[®] tapes and immediately stored in vacuum bags before analysis. Bulk arsenic K-edge (11867 eV) and iron K-edge (7112 eV) XANES spectra were collected on beamline 1W1B at the Beijing Synchrotron Radiation Facility (BSRF, China). We analyzed the XANES spectra by means of linear combination fitting (LCF) in the E space, over a fit range from -20 to $+30$ eV relative to the adsorption edge with 0.3 eV step size. Suitable reference compounds (Supplementary Table S2) were identified based on the principal component analysis and target-transform testing (PCT-TT) using arsenic and iron K-edge XANES reference spectra. Details about the sample preparation, experimental setups, measurement conditions, and data analysis can be found in Supplementary Information.

2.4. Arsenic metabolism functional genes analysis: DNA extraction and PCR

DNA was extracted from the sediment or water samples using the mericon DNA Bacteria Kit and mericon DNA Bacteria Plus Kit (Qiagen, Germany) according to the manufacturer's instructions. PCR amplifications of *aioA*, *arrA*, *arsC* and *arsM* genes were performed with the primers *AroAdeg1F/AroAdeg1R* and *AroAdeg2F/AroAdeg2R*, *AS1F/AS1R*, *amlt-42-f/amlt-376-r* and *smrc-42-f/smrc-376-r*, and *arsMF1/arsMR2*, separately (Zhang et al., 2015). The abundance of the genes was estimated using the primers described above by quantitative real-time polymerase chain reaction (qPCR) performed on an AB17500 Thermocycler (Applied Biosystems Inc., USA). The details are shown in the Supplementary Information.

3. Results and discussion

3.1. Algae-induced arsenic release to air

Oxygen depletion by the microbial degradation of the sinking algae induced hypoxia/anoxia (dissolved oxygen <1 mg/L and $E_h < -150$ mV) at the SWI from day 2 (Fig. 1A, Supplementary Fig. S4). The water of the HAD group became malodorous and black owing to the generation of black ferrous sulfide precipitates (Han et al., 2015) on day 4 with the anaerobic deterioration, indicating the outbreak of black blooms (Fig. 1A). Accompanying with the algae-induced hypoxia/anoxia, 25.4 and 100 ng of total volatile arsenic (including both TMAs and AsH_3) were released into the atmosphere during the 18-day incubation in the LAD and HAD groups, respectively (Fig. 1B), corresponding to an average flux of 0.431 and $1.73\text{ }\mu\text{g/m}^2\cdot\text{d}$, respectively (Supplementary Table S6). The volatilization effluxes of the total arsenic in the LAD and HAD were 2 and 8 times higher than that of the control, respectively, indicating that the volatilization

capacity of arsenic was significantly improved under more reducing conditions induced by algae blooms degradation. Arsenic volatilization involves arsenic reduction and methylation metabolic pathways (Challenger, 1945; Huang et al., 2012), with the metabolites of TMAs, AsH_3 , MeAsH_2 or Me_2AsH . In this study, only TMAs and AsH_3 were detected and the predominant volatile arsenic species changed from TMAs to AsH_3 , which is the most poisonous arsenic species (Faust et al., 2016), when black blooms occurred in HAD (Fig. 1B). AsH_3 production, as recognized as a fungi or methanoarchaea-induced biotransformation process under strong reducing condition (Pakulska and Czerczak, 2006; Wang et al., 2014), has also been observed in some paddies or peats with organic matter amendment (Mestrot et al., 2011a). Theoretically, AsH_3 can persist for five days under light (Pantsar-Kallio and Korpela, 2000), and 19 weeks under dark conditions (Jakob et al., 2010; Mestrot et al., 2011b), thus enabling its long-distance transportation from the emission source. Therefore, algae-induced anoxia in arsenic-polluted freshwaters may pose greater health risk to the residents nearby through respiratory exposure.

3.2. Algae-induced arsenic release to water

Algal blooms degradation increased the total dissolved arsenic in the overlying water (Fig. 1C). The total dissolved arsenic in the control group remained at $7\text{--}11\text{ }\mu\text{g/L}$ throughout the experiment. In contrast, it increased following the onset of hypoxia/anoxia (Fig. 1A), peaked at day 4, followed by a gradual decrease until the end of the experiment in the LAD and HAD groups. The maximum total dissolved arsenic concentration in water in the LAD ($19\text{ }\mu\text{g/L}$) and HAD ($38\text{ }\mu\text{g/L}$) groups were 2 and 4 times higher than the WHO drinking water limit of $10\text{ }\mu\text{g/L}$, respectively. Decomposed algal biomass can contribute one-tenth of the increased total dissolved arsenic ($3.02 \pm 0.50\text{ }\mu\text{g/L}$) in the overlying water, implying that the excess was resulted from endogenous release related to algae-induced anoxia/hypoxia. This result was supported by the distinct enlargement of concentration gradients for total dissolved arsenic in porewater at a depth of $-20\text{--}5$ mm when algae were added (Supplementary Fig. S5). The calculated dissolved arsenic flux across the SWI was switched from negative in the control group to positive in the LAD and HAD groups over the incubation (Fig. 1D), thus confirming the change from arsenic sink to source for surface sediments ($0\text{--}2$ cm) during the microbial degradation of algal blooms. Integrating the total dissolved arsenic flux data over the 18-day incubation yield a cumulated arsenic release of 3.94 mg/m^2 (in LAD)– 13.2 mg/m^2 (in HAD) into the overlying water (Fig. 1D), corresponding to an average diffusive flux of $0.219\text{--}0.733\text{ mg/m}^2\cdot\text{d}$ (Supplementary Table S6).

With the endogenous release of arsenic during algae-induced hypoxia/anoxia, the predominant arsenic species converted from As(V) into As(III) ($79.8\text{--}97.2\%$) and methylated As (i.e., MMA and DMA) ($2.33\text{--}11.3\%$) in both overlying water (Fig. 1C) and surface sediments (Supplementary Fig. S6). The reduction and methylation rate of arsenic increased with algae dosage, indicating that the NOM-rich anoxic condition was favorable for the production of As(III) and methylated As, as observed in natural eutrophic systems (Hasegawa et al., 2009, 2010; Li et al., 2014). The toxicity sequence of different arsenic species is $\text{AsH}_3 > \text{As(III)} > \text{As(V)} > \text{MMA} > \text{DMA} > \text{TMAO}$ (WHO, 1981), implying that the expansion of algal blooms may enhance the toxic impact of arsenic in the water column.

3.3. Microbially mediated arsenic speciation

Arsenic reduction and methylation processes at sediment–water–air interfaces were detected after algae addition in unsterilized groups (Fig. 1B–C and Supplementary Fig. S4A).

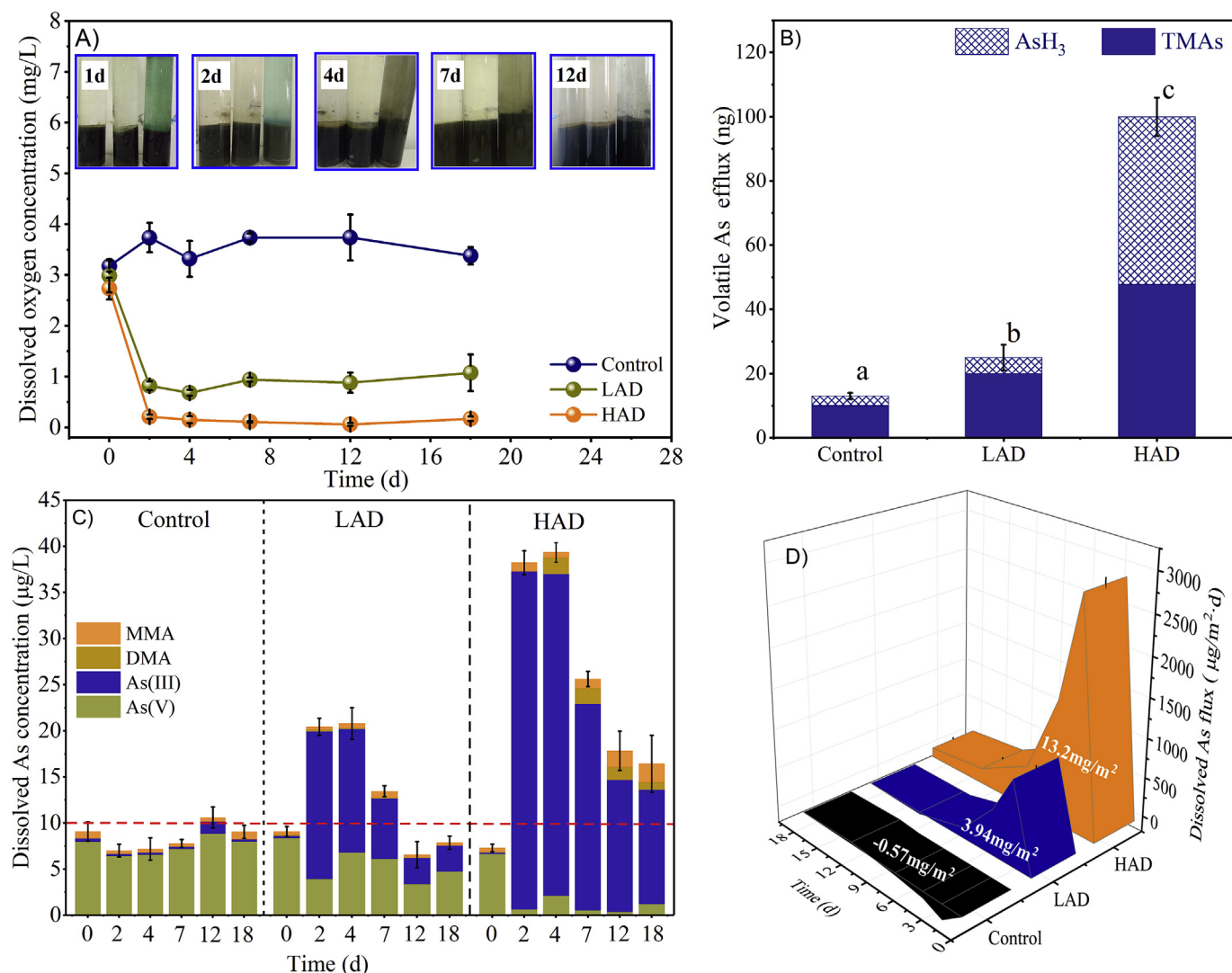


Fig. 1. Arsenic mobilization during the incubation period. A, Dissolve oxygen and visual changes with incubation time. Three columns in each inset indicate Control, LAD and HAD treatment, respectively; B, Volatile arsenic in the air. One-Way ANOVA was used to measure significant differences ($p < 0.05$) between treatments, which marked with various lowercase; C, Dissolved arsenic in the overlying water. The red dashed line indicates the World Health Organization drinking water limit of 10 $\mu\text{g/L}$; D, Dissolved arsenic flux across the sediment–water interface. The data in each bar indicates the cumulated total dissolved arsenic flux during the 18-day incubation. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

However, in sterilized groups, compared to the S-control group, adding high algae dosage in the S-HAD group did not promote arsenic volatilization to air, arsenic reduction and methylation in the overlying water, and arsenic reduction in surface sediments (Supplementary Fig. S7). These implied that the reduction of As(V) to As(III) or AsH₃, and the methylation of As(III) to MMA, DMA or TMAAs during the algae decomposition was primarily a microbially mediated process, which agreed with previous studies (Huang et al., 2012; Mestrot et al., 2011a). To further uncover the arsenic metabolism mechanism during the microbial degradation of algal biomass, the abundance of different arsenic metabolism functional genes (i.e., arsenite oxidation (*aiOA*), arsenate respiratory reduction (*arrA*), arsenate reduction (*arsC*), and arsenite methylation (*arsM*) genes) (Suhadolnik et al., 2017; Zhang et al., 2015) in the overlying water, surface sediments (0–2 cm) and deep sediments (2–4 cm) was analyzed and shown in Fig. 2.

Significant abundance shifts of functional genes were focused on the overlying water column and surface sediments (Fig. 2A and B, respectively), where arsenic reduction and methylation occurred

primarily (Fig. 1C and Supplementary Fig. S6). The copy number of *aiOA* genes decreased significantly when algae were added, indicating the inhibited growth of arsenite oxidative bacteria at the SWI. However, the *arrA* genes notably increased from 3.10×10^6 to 9.54×10^6 copies/L in the water column (Fig. 2A), and from 2.39×10^6 to 4.69×10^6 copies/g in the surface sediments with increasing algae dosage (Fig. 2B), accompanied with the similar notable increase of *arsC* and *arsM* genes. These results demonstrated that the organic carbon enriched anoxic environments (Fig. 1A and Supplementary Table S7) promoted the growth of arsenate reductive bacteria and arsenite methylated bacteria, leading to more formation of arsenite, arsines and methylated arsenic at sediment–water–air interfaces (Fig. 1B and C).

3.4. Geochemically controlled arsenic release and sequestration

The endogenous release of arsenic was paralleled by the release of dissolved Fe(II) and dissolved organic carbon (DOC) from sediments. This was supported by the similar regular patterns for

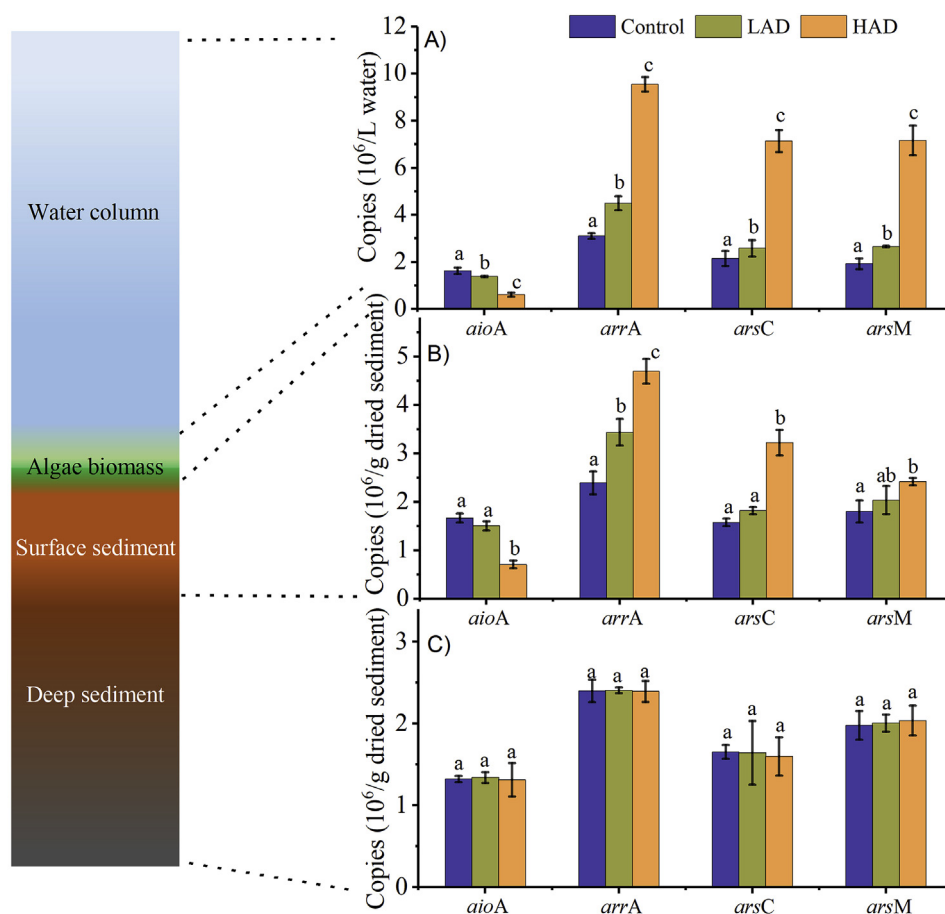


Fig. 2. Abundance of *aioA*, *arrA*, *arsC* and *arsM* genes in the overlying water (A), surface sediments (0–2 cm) (B) and deep sediments (2–4 cm) (C) for treatments with different algae dosage. In each figure, One-Way ANOVA was used to measure significant differences ($p < 0.05$) between treatments, which marked with various lowercase.

dissolved Fe(II) and DOC in the overlying water (Fig. 3A–B), and the increased concentration gradients of porewater dissolved Fe(II) and DOC at the depth of –20–5 mm for treatments with algal biomass compared to the control (Supplementary Fig. S5). DOC is an indicator of organic matter degradation and mineralization (Gao et al., 2012). Highly significant positive correlations ($p < 0.01$) were found between DOC and total dissolved As, DOC and dissolved Fe(II) in the water column throughout the experiment, respectively, and their correlation coefficients increased with increasing algae dosage (Fig. 3D). It clearly implied that the anaerobic degradation of algal blooms in eutrophic freshwaters may develop favorable conditions (e.g., low redox at SWI (Supplementary Fig. S4) and plenty of electron donor (Postma et al., 2012)) for microbial reductive dissolution of arsenic-bearing iron oxides. This facilitated the increase in Fe(II)/TFe and As(III)/TAs in surface sediments (Supplementary Fig. S6), leading to the concurrent release of As(III) and Fe(II) into the overlying water (Figs. 1C and 3B) (Bennett et al., 2012; Bose and Sharma, 2002; Roberts et al., 2009). However, although significantly positive correlations ($p < 0.05$) existed between the total dissolved As and Fe(II) in treatments with algal biomass (Fig. 3D), the correlations degraded slightly from 0.584 in the LAD group to 0.445 in the HAD group, implying that there may be alternative factors other than Fe(II) may exist that affected the As(III) mobilization during black boom eruption.

Much lower dissolved SO_4^{2-} concentrations in the overlying water and porewater profile of –20–5 mm were found in the HAD group than in both the LAD and control groups (Fig. 3C and Supplementary Fig. S5), thus verifying that the microbial sulfate reduction process was enhanced with increased anaerobic degree

induced by a higher algae dosage (Han et al., 2015). The generated sulfide can immobilize As(III) by direct precipitation as arsenic sulfides, such as orpiment (As_2S_3), realgar (AsS), arsenopyrite (FeAsS) and thioarsenic species ($\text{H}_3\text{AsO}_x\text{S}_y$) (La Force et al., 2000; Langner et al., 2013; Moon et al., 2017). It can also interact with the abundant Fe(II) at the anaerobic SWI (Fig. 3B and Fig. S6B) to form iron-sulfide precipitates (FeS or FeS_2 (pyrite)) that can potentially adsorb the released As(III) (Moon et al., 2017). Additionally, in this study, the degradation of algal blooms induced NOM-rich anoxic environments (Fig. 3C and Supplementary Table S7). This implied that NOMs can immobilize As(III), by directly binding to the functional groups of NOMs (e.g., sulfhydryl group or phenolic OH group) to form “NOM-As(III)” complexes, or using polyvalent metal cations (e.g., Fe) as a bridge to form “NOM-polyvalent cations-As(III)” complexes (Hoffmann et al., 2013; Langner et al., 2012, 2013; Mikutta and Kretzschmar, 2011; Sundman et al., 2014). A notable increase in the oxidizable fraction of arsenic, including both NOM- and S-bound arsenic in the surface sediments were found with increasing algae dosage (Fig. 3E), supporting the effect of sulfide and NOMs on arsenic sequestration under NOM-rich anoxic environments, which can be responsible for the gradual decline of total dissolved arsenic in the overlying water at the later period of the incubation (Fig. 1C). To verify and quantify the interactions of arsenic with Fe, sulfides and NOMs under various redox conditions, arsenic and iron K-edge X-ray absorption near-edge structure (XANES) spectra analyses of surface sediments were conducted.

The LCF of the arsenic and iron K-edge XANES spectra of the surface sediments with reference compounds (Fig. 4A and C), and the corresponding fit results are summarized in Fig. 4B and D. With

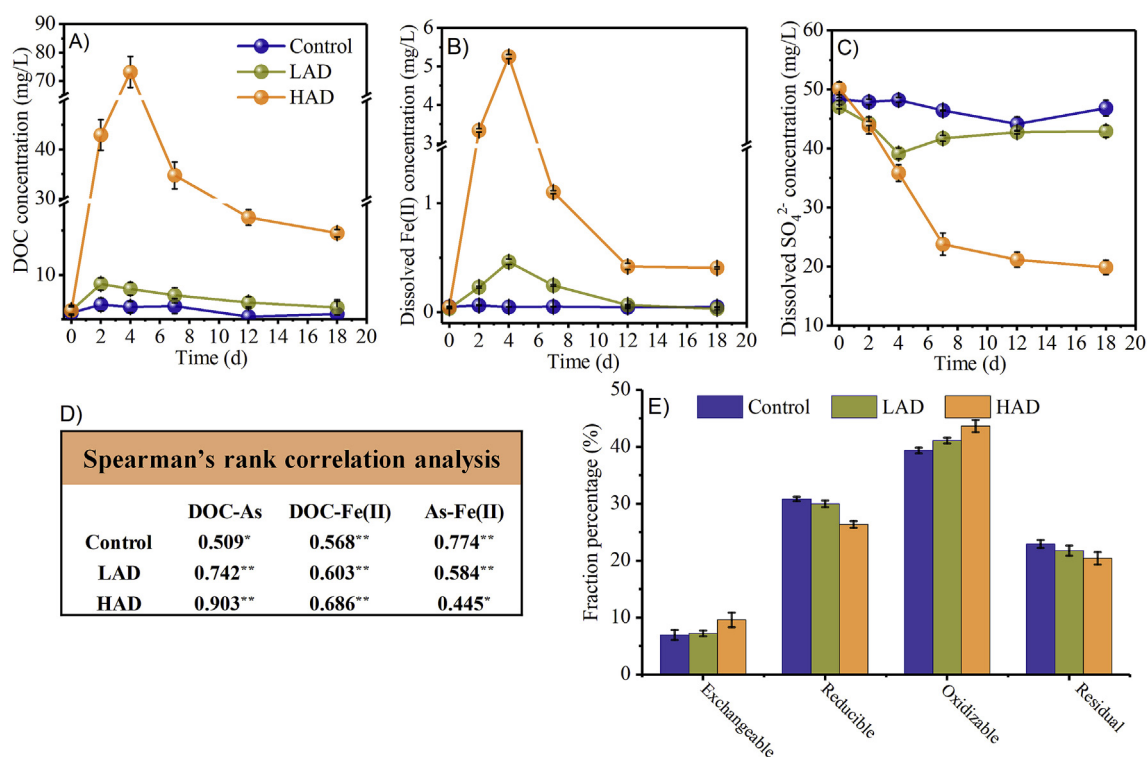


Fig. 3. Geochemistry of arsenic release. A–C, DOC (dissolve organic carbon), dissolved Fe(II) and dissolved SO_4^{2-} in the overlying water; D, Correlation between total dissolved As, dissolved Fe(II) and DOC concentrations during the incubation period. Spearman's rank correlation analysis was done with SPSS version 18.0. Data for each correlation ($n = 24$) consists of measurements taken from the overlying water, $\sim 20\text{--}5\text{ mm}$ of porewater profiles during the 18-day incubation. Values of $P < 0.05$ and < 0.01 indicate significant (*) and highly significant (**), respectively; E, Arsenic fractions in surface sediments through selective extraction.

increasing algae inputs, the proportion of arsenic adsorbed to Ferrihydrite decreased from 38.0% to 14.2% (Fig. 4B), combined with Ferrihydrite fraction decreasing from 31.2% to 21.1% (Fig. 4D), respectively, confirming the primary mechanism of iron redox-controlled arsenic release in freshwaters suffering with degraded algal blooms. However, a notable increase in orpiment (As_2S_3) fraction from 34.3% to 51.2% indicated the formation of As_2S_3 under the algae-induced anoxia condition (Fig. 4B), which even became the principal As(III) sequestration during black blooms eruption. In natural systems, arsenic sulfides are typically formed under high-temperature conditions such as in hot springs (O'Day et al., 2004; Zhu et al., 2014). Instead, our results indicated the microbe-mediated formation of As_2S_3 -like minerals under sulfate-reduced anaerobic environments at the ambient temperature, as observed in previous studies (Bostick et al., 2004; O'Day et al., 2004; Xu et al., 2011; Zhu et al., 2014). Moreover, our results also highlighted particulate NOM as As(III) sequestrators by the formation of ternary complexes of NOM-Fe-As(III) (Fig. 4B and D) during algae-induced hypoxia/anoxia. The NOM-Fe-As(III) fraction can even account for approximately 35% of the solid-phase arsenic speciation during black blooms eruption in freshwaters (Fig. 4B). It was formed when liberated iron under strong anaerobic conditions was acted as a bridge between negatively charged As(III) and the organic ligands of NOMs at the SWI, as observed in arsenic-polluted deep peat layers where both iron and NOMs are enriched (Hoffmann et al., 2013; Mikutta and Kretzschmar, 2011). In natural systems, polyvalent metal cations can also act as bridges between other oxyanions (e.g., phosphate and selenite) and organic ligands, to immobilize these oxyanions by forming similar ternary complexes (Gerke, 2010; Gustafsson and Johnsson, 1994; Mikutta and Kretzschmar, 2011).

3.5. Conceptual model for arsenic cycling

In arsenic-polluted freshwaters that are coupled with eutrophication (Gao et al., 2012; Rahman and Hasegawa, 2012), the mobilization of arsenic across the sediment–water–air could be triggered by algal blooms (Fig. 5). The anaerobic degradation of the senescent algae stimulated the reductive dissolution of As(V)/As(III)-bearing iron oxides in the surface sediments, causing a rapid release of Fe(II)/Fe(III) and arsenic to the water column. Algae-induced hypoxia/anoxia favored the activity of indigenous arsenate reductive bacteria (*arsC* and *arrA* genes) and arsenite methylated bacteria (*arsM* gene), thus promoting the production of As(III), MMA and DMA in the overlying water. Known as the final products of arsenic microbial reduction and methylation (Bentley and Chasteen, 2002), small amounts of AsH_3 and TMAs were formed and emitted into the atmosphere, with AsH_3 as the dominant volatile arsenic species. However, the consequent S and NOM-rich environments may serve partially as potential geochemical traps for the released As(III) in the later anoxic period of algal blooms season, by the formation of arsenic sulfides (43.0–51.2%) and NOM-Fe-As(III) (28.3–34.8%).

In natural eutrophic waters, extensive production, sinking, and subsequent microbial decomposition of algal blooms typically lasts for months (Gao et al., 2012; Hasegawa et al., 2009, 2010; Sheng et al., 2012), thus increasing the potential arsenic exposure risks in both water and air. Taking Lake Dianchi (309 km^2) as an example, in the normal algal blooms level, it was estimated that approximately 8.21 t of arsenic, equivalent to 3.28% of total arsenic in surface sediments, could be released into the overlying water within four months (from June to September) of algal blooms season (Sheng et al., 2012). However, during black blooms

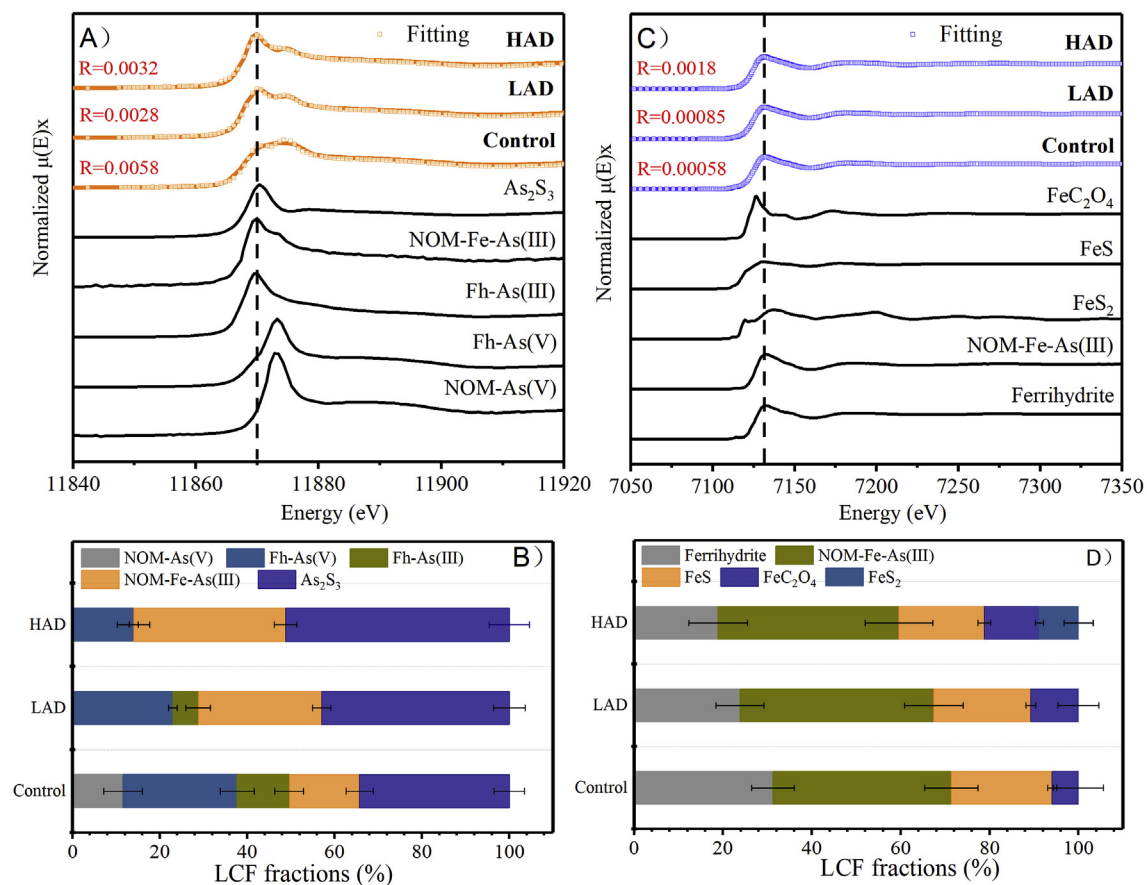


Fig. 4. Arsenic and iron speciation in the surface sediments. A and C, K-edge XANES spectra of arsenic and iron, respectively. R values show the mean square misfit between the data and the fit; B and D, speciation of arsenic and iron in surface sediments, respectively. The component sums were normalized to 100%. Fh-As(III)/As(V) indicates ferrihydrite adsorbed As(III) or As(V).

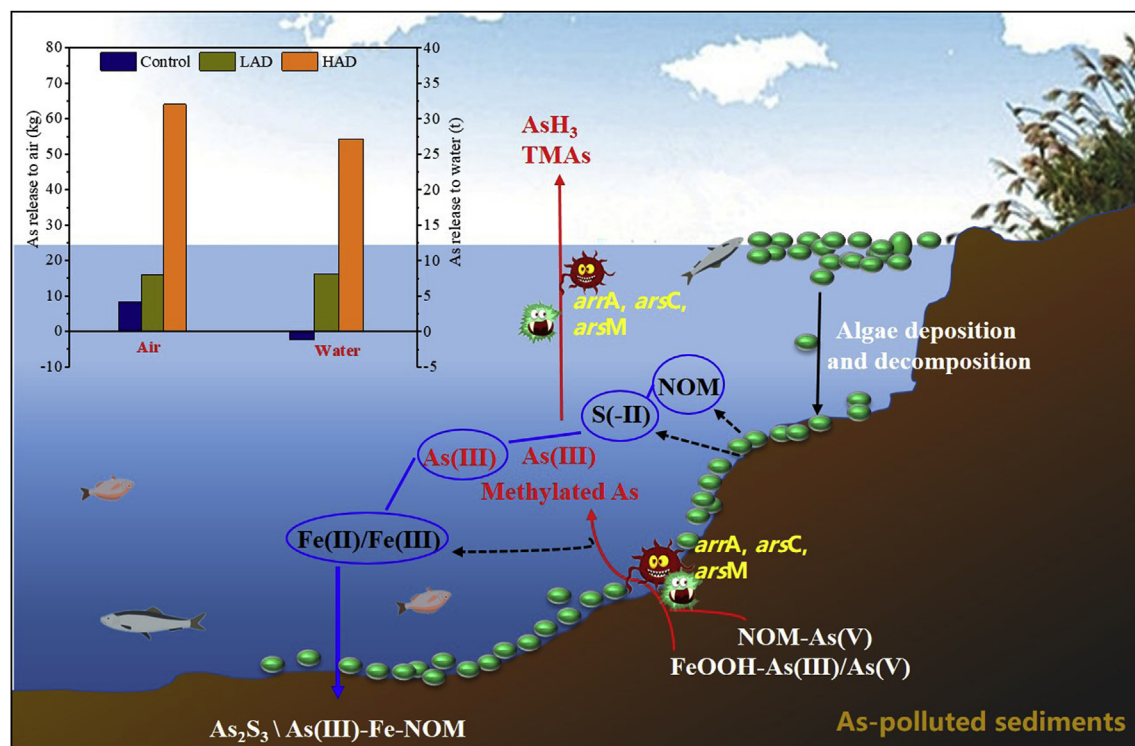


Fig. 5. A conceptual model for cycling of arsenic at sediment-water-air interfaces with algae decomposition in eutrophic waters.

explosion, up to 27.2 t of arsenic—approximately 11% of the surface sediment arsenic capacity, can be released into water (Fig. 5, Supplementary Table S6). The released arsenic in the water column can threaten human health through direct exposure or ingestion of arsenic-accumulated aquatic organisms such as *Caridina diachnensis* (Yang et al., 2017). Moreover, it was estimated that 16.0–64.1 kg of arsenic is likely to be volatilized during the algal blooms season per year, corresponding to 0.0065–0.026% of total arsenic present in the surface sediments (Fig. 5, Supplementary Table S6). This value is close to the volatilization rates (0.002–0.17%) for peat and paddy soils (Mestrot et al., 2011a). Arsenic biovolatilization from paddy and peat soils constitute 2–6% of the global natural arsenic emission (~46500 t/y) (Chilvers, 1987; Mestrot et al., 2011a). However, the relevant contribution estimation from eutrophic freshwaters require further clarification based on worldwide arsenic pollution status in freshwaters and its *in-situ* arsenic volatilization rules.

3.6. Environmental implications

Harmful algal blooms are currently increasing globally, and they are likely to expand further in the coming decades owing to the continued eutrophication and worsening global warming (Huisman et al., 2018). Arsenic endogenous release to water and air induced by the degradation of senescent algal blooms, combined with the anticipated increase in release fluxes related to the intensification of eutrophication in freshwaters, highlights the need for appropriate mitigation strategies. In the short term, combating the algae-induced anoxia/hypoxia by oxygenation (Zhang et al., 2018) may be a logical and feasible method to limit arsenic endogenous release in eutrophic waters. In the long term, controlling arsenic endogenous release by the prevention of algal blooms or eutrophication in aquatic ecosystems will require extensive efforts for nutrient input control (Huisman et al., 2018).

Our results may also provide insight for arsenic dynamics in other wetlands such as paddy fields. Large areas of paddy soils in South and Southeast Asia are contaminated with arsenic (Zhao et al., 2015), where diverse exogenous organic fertilizers, such as rice straw and cattle manure, have been applied as soil amendment to obtain elevated rice yields (Huang et al., 2012). It is generally believed that arsenic accumulation in grains/straw, and arsenic volatilization from rice plants and paddy soil can be promoted strongly during the decomposition of the organic fertilizers (Mestrot et al., 2011a). However, the consequent NOM- and S-rich sediments may act as traps for dissolved As(III) under a reducing condition, and therefore influence arsenic cycling in flooded paddy fields.

4. Conclusion

This study explored the effect of algal degradation on the cycling of arsenic in eutrophic freshwaters. Algae-induced hypoxia/anoxia facilitated a rapid endogenous release of arsenic (As(III) dominant) to both overlying water and air, which may affect drinking water safety, agricultural irrigation, and recreations usage of the affected freshwaters. The reductive dissolution of arsenic-bearing iron oxides in anaerobic surface sediments was responsible for the endogenous release of As(III), although the formation of As₂S₃ and NOM-Fe-As(III) could partially ease this release process. Moreover, the accompanied reduction and methylation of arsenic was attributed to the accumulation of arsenate reductive and arsenite methylated microbes at the SWI. Future studies are required to develop efficient strategies to reduce the toxic impact of arsenic in freshwaters suffering from algal blooms.

Author contributions

G.P., M.Y.Z., G.X.S. and Y.T. conceived the experiments, which were carried out by Y.T.; G.P. provided supervision and support for Y.T.'s PhD study and revised the paper; M.Y.Z. performed synchrotron radiation data analyses and revised the paper; G.X.S. helped with the microbiological data analyses and revised the paper; Y.T. performed data interpretation and drafted the manuscript.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2018.11.046>.

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