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Short Communication

Inhibition of methanogenesis leads to accumulation of methylated arsenic species and enhances arsenic volatilization from rice paddy soil

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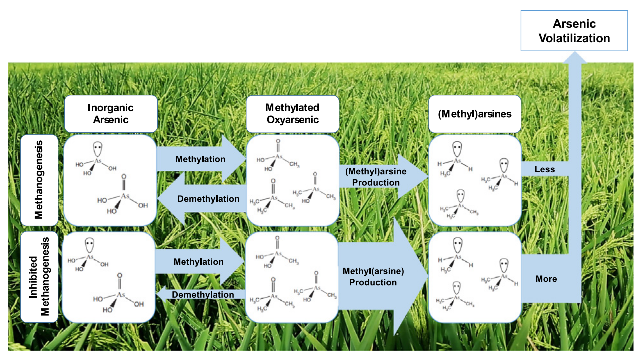
HIGHLIGHTS

- Inhibition of methanogenesis increases accumulation of aqueous methylated arsenic species.
- Inhibition of methanogenesis increases biovolatilization of volatile (methyl)arsine species.
- Trimethylarsine is the dominant volatile arsenic species released.
- 3 mM sulfate amendment decreased arsenic volatilization.

GRAPHICAL ABSTRACT



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ABSTRACT

Flooded soils are important environments for the biomethylation and subsequent volatilization of arsenic (As), a contaminant of global concern. Conversion of inorganic to methylated oxyarsenic species is thought to be the rate-limiting step in the production and emission of volatile (methyl)arsines. While methanogens and sulfate-reducing bacteria (SRB) have been identified as important regulators of methylated oxyarsenic concentrations in anaerobic soils, the effects of these microbial groups on biovolatilization remain unclear. Here, microcosm and batch incubation experiments with an Arkansas, USA, rice paddy soil were performed in conjunction with metabolic inhibition to test the effects of methanogenic activity on As speciation and biovolatilization. Inhibition of methanogenesis with 2-bromoethanesulfonate (BES) led to the accumulation of methylated oxyarsenic species, primarily dimethylarsinic acid (DMAs(V)), and a four-fold increase in As biovolatilization compared to a control soil. Our results support a conceptual model that methanogenic activity suppresses biovolatilization by enhancing As demethylation rates. This work refines understanding of biogeochemical processes regulating As biovolatilization in anaerobic soil environments, and extends recent insights into links between methanogenesis and As metabolism to soils from the mid-South United States rice production region.

1. Introduction

Inorganic arsenic (As) is a non-threshold carcinogen that is widely distributed in the environment and is a common contaminant in water and food, notably rice (Zhao et al., 2010; Fendorf et al., 2010; Smedley and Kinniburgh, 2002). The biogeochemical processes controlling As mobilization and bioavailability in rice paddy soils include redox reactions of iron, manganese, and arsenic (Masscheleyn et al., 1991; Ying et al., 2012); microbe-mediated methylation-demethylation reactions (Reid et al., 2017; Jia et al., 2013; Lafferty and Loeppert, 2005); and interactions between As and dissolved organic matter (Buschmann et al., 2006; Bauer and Blodau, 2009). While these processes have been extensively studied (Wang et al., 2020a; Roberts

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et al., 2011; Williams et al., 2006; Xu et al., 2008; Zhao et al., 2013; Hussain et al., 2021), aspects of As speciation and fate in rice paddies remain poorly understood. A notable example is As biovolatilization and the underlying microbial processes involved in the production of volatile (methyl)arsine species (hereafter referred to as “arsines”) in soils (Mestrot et al., 2013a; C. Chen et al., 2017; Lin et al., 2019). Arsines can be produced by a wide range of bacteria and fungi (Mestrot et al., 2013a; Bentley and Chasteen, 2002; Yin et al., 2011; Čerňanský et al., 2009), and As volatilization has been observed in natural and engineered systems including rice paddies (Mestrot et al., 2011), seawater (Savage et al., 2018), landfills (Pinel-Raffaitin et al., 2007), wetlands (Vriens et al., 2014), and biogas digesters (Mestrot et al., 2013b; Webster et al., 2016a). Biovolatilization of As has gained attention as a potential contaminant elimination mechanism in soils and sediments (Chen et al., 2014; P. Chen et al., 2017; Wang et al., 2014), as well as for its role as the source of approximately 20% of the As flux to the atmosphere (Galloway et al., 1982), where it can be transported long distances before being deposited to the surface (Savage et al., 2019; Wai et al., 2016). Exposure to atmospheric As has also recently been identified as a human health risk (Zhang et al., 2020).

Volatilization typically accounts for <1 to 3.5% of the As budget in soils (Mestrot et al., 2011). Organic matter (OM) amendments (Yan et al., 2019) and reducing conditions increase volatilization from soils through stimulation of anaerobic microbial activity (Pinel-Raffaitin et al., 2007), but the role of specific microbial functional groups in As biovolatilization remains unclear. It is thought that biotransformation of inorganic As (iAs) into methylated oxyarsenic species (hereafter referred to as methylated species), mediated by arsenite S-adenosylmethionine methyltransferase (ArsM) enzymes (Qin et al., 2006) or through side reactions with methyltransferases and cofactors involved in methylotrophic methanogenesis (Thomas et al., 2011; Wuerfel et al., 2012), is the rate-limiting step for the production of arsine species and their subsequent volatilization (Mestrot et al., 2011). It follows that conditions that favor the accumulation of methylated species should also lead to greater volatilization.

Accumulation of methylated As depends on rates of arsenic methylation as well as demethylation, and while there has been significant attention to As methylation (Reid et al., 2017; Jia et al., 2013; Zhao et al., 2019; J. Zhang et al., 2015; S.-Y. Zhang et al., 2015; Viacava et al., 2020; Chen et al., 2021), there remains a significant knowledge gap around As demethylation in anaerobic systems (Sierra-Alvarez et al., 2006). In a notable recent report, Chen et al. (2019) used exogenous ^{13}C-labeled dimethylarsinic acid (DMAs(V)) and metabolic inhibition to demonstrate that sulfate-reducing bacteria (SRB) in rice paddy soils were associated with As methylation while methanogens were active demethylators (Chen et al., 2019). This study did not demonstrate clear linkages between microbial functional groups and As biovolatilization, however, possibly due to limited monitoring of arsines. This and other recent studies on effects of sulfate-reducing and methanogenic metabolisms on As methylation-demethylation reactions have been based on rice paddy soils collected in Asia (Reid et al., 2017; Chen et al., 2021; Chen et al., 2019), and to our knowledge these insights have not yet been tested in rice paddy soils from the mid-south United States, the major rice producing region of the United States. The conclusions of these studies on the role of methanogens also differ from prior research demonstrating that methanogenesis can be an important driver of As biovolatilization, suggesting that methanogenesis also drives biomethylation (Webster et al., 2016a; Meyer et al., 2008).

The objective of the present study was to evaluate relationships between methanogenesis and As biovolatilization. We hypothesized that inhibition of methanogenesis will increase As biovolatilization via diminished As demethylation and subsequent accumulation of methylated As species. A series of metabolic inhibition experiments were performed in flooded soil microcosms and batch soil slurries, using a rice paddy soil collected from Arkansas, USA, where roughly half of the U.S. rice crop is produced. The biogeochemical evolution of the soil solution was monitored in conjunction with As volatilization and pore water As speciation to examine links among methanogenesis, aqueous As speciation, and volatilization.

2. Materials and methods

2.1. Soil properties and experimental apparatus

Rice paddy soil was collected from the United States Department of Agriculture Dale Bumpers National Rice Research Center in Stuttgart, Arkansas, USA. Soil was air-dried and sieved to a 500–1000 μm particle size, and 485 g of soil were mixed with 2% (w/w) ground oak and maple leaves from Ithaca, NY, as an OM source, and added to acid-washed conical flasks. This soil had received amendments of a monomethylarsonic acid (MMAs(V)) pesticide for at least twenty years prior to being collected (Somenahally et al., 2011). Additional details on the physiochemical characterization of the soil are available elsewhere (Maguffin et al., 2020). Organoarsenical pesticides were widely applied to soils in the southern United States (Bednar et al., 2002), so this soil context has broad relevance for the mid-South U.S. rice production region. Total As in the soil was determined using a modified version of EPA Method 3051-6010. Arsenic species associated with poorly-crystalline Fe and Al (oxyhydr)oxide phases was determined using an acid ammonium oxalate (AAO) extraction (Keon et al., 2001). Rhizon Flex pore water samplers (Rhizosphere Research Products) were inserted into the soil and the flask was wrapped in aluminum foil to simulate the subsurface environment. Rhizons consisted of a 5 cm porous sampler with a 0.15 μm pore size that was connected to a polyvinylchloride/polyethylene sampling tube. Importantly, they did not have a stainless steel strengthener. An air pump was used to continuously flow laboratory air through an inlet adapter into the microcosm headspace at a rate of approximately 95 ml/min (Fig. S1). A chemo-trap was placed in-line before the microcosm to exclude inputs of volatile As from the laboratory air. Platinum-cured silicone tubing connected the flask exhaust to a chemo-trap that captured volatile arsines emitted from the microcosm soil. Microcosms were mounted in a fume hood at 20 ± 2 °C for nine weeks. Chemo-traps were prepared following methods in Mestrot et al. (2009). Briefly, a silica gel was impregnated with a 1% $AgNO_3$ solution, purged with N_2 gas, and then heated overnight at 70 °C (Fig. S2). Chemo-traps were replaced weekly and were stored at 4 °C with both ends capped until extraction.

2.2. Soil microcosm experiments

350 ml of synthetic porewater containing 2 mM KCl, 0.5 mM $MgCl_2$, 1 mM $NaHCO_3$, 4 mM sodium acetate, and 10 μM As (as sodium arsenite (As(III))) was used to flood the soil. Arsenite is the dominant form of As in flooded rice paddy soils (Somenahally et al., 2011), and additional As(III) was added to the system to provide an appropriate comparison for experiments in which exogenous DMAs(V) was added. The pH was adjusted to 7.0 ± 0.2 using HCl or NaOH before adding the synthetic porewater to the flask. Four experimental conditions were implemented in addition to the control (Table 1). In the sulfate (SO_4^{2-}) case, the initial SO_4^{2-} concentration was increased to stimulate SRB activity. 2-bromoethanesulfonate (BES), a coenzyme-M analog, was used as an inhibitor of methanogenesis (Zinder et al., 1984). Experiments with DMAs(V) in the synthetic porewater instead of As(III) were used to evaluate effects of exogenous methylated As on biovolatilization rates. All conditions were performed in duplicate with the exception of the BES + DMAs(V) case, for which only one microcosm was tested due to a malfunction with the duplicate microcosm.

Porewater was collected via the rhizon sampler twice per week. Aliquots were filtered through 0.22 μm membrane syringe filters and prepared for wet chemical analysis, including preservation of an aliquot in 0.01 M nitric acid for inductively coupled plasma – mass spectrometry (ICP-MS). Arsines were extracted from chemo-traps by collecting the

Table 1
Summary of experimental conditions.

Condition	Amendment to synthetic porewater[a]
Soil microcosm experiments	
Control	–
Sulfate	3 mM Na_2SO_4
BES	5 mM 2-bromoethanesulfonate
DMAs(V)[b]	10 μM DMAs(V)
DMAs(V)[b] + BES[c]	10 μM DMAs(V) and 5 mM 2-bromoethanesulfonate
Soil slurry batch experiments	
Control	–
BES	5 mM 2-bromoethanesulfonate

[a] Unless noted otherwise, synthetic porewater contained 10 μM sodium arsenite.
[b] 10 μM DMAs(V) added instead of As(III).
[c] This condition was only tested in one replicate; all others were tested in duplicate.

silica gel in a centrifuge tube, adding 5 ml 1% HNO_3 solution, and heating in a hot water bath at 90 °C for 3 h. The solution was then filtered and stored at 4 °C until chemical analysis. With this technique, arsines retained on the chemo-trap are converted to their pentavalent methylated oxyarsenic derivatives, which are measured via HPLC-ICP-MS. (Mestrot et al., 2009) Blanks with unused chemo-traps or labware without silica gel were used to assess potential contamination from labware or reagents. The methane flux from the soil was measured weekly. Microcosms were disconnected from the air pump and sealed. Headspace samples were collected at 0, 15, 30, 45, and 60 min, injected into pre-evacuated 20 ml crimp-sealed serum vials, and stored in the dark until gas chromatography (GC) analysis.

2.3. Soil slurry batch experiments

A soil slurry consisting of 20 g of the air-dried and sieved Arkansas soil, 2% ground leaves (w/w), and 60 ml of the same synthetic porewater used in microcosm experiments (pH 7.0 ± 0.2) were incubated in crimp-sealed serum vials with butyl rubber stoppers. Vials were purged with N_2 after being sealed. Experimental conditions are summarized in Table 1. An azide-sterilized control was also performed. Each condition was performed in triplicate, with the exception of the azide-sterilized control for which only one vial was tested. The vials were wrapped in foil and incubated on an orbital shaker with a speed of 200 rpm at 25 °C. Slurry samples were collected using an N_2-flushed needle and plastic syringe, centrifuged for 1 min, filtered with a 0.22 μm membrane filter, preserved in HNO_3, and frozen at −20 °C. At the end of the batch experiment, headspace from each vial was collected for GC analysis to confirm that BES effectively inhibited methanogenesis.

2.4. Chemical analyses

Elemental concentrations in porewater and chemo-trap extracts were determined with an Agilent 7800 ICP-MS with a helium collision cell and rhodium or germanium as in-line internal standards. Quality control was assessed with periodic analysis of traceable standards, matrix blanks, and repeat samples. Arsenic speciation analysis was performed using HPLC-ICP-MS (Agilent Infinity II HPLC hyphenated to Agilent 7800 ICP-MS) with a Hamilton PRP X-100 column and a 50 mM ammonium carbonate eluent at pH 8.9. Samples were oxidized with hydrogen peroxide prior to analysis, so As(III) was oxidized to arsenate (As(V)), and the sum of As(III) and As(V) is reported as inorganic As (iAs) (Zhao et al., 2019). The As peak eluting at the solvent front after oxidation of As(III) in pore water samples consisted of neutral and cationic As species that were not retained on the anion exchange column. These likely included cationic TMAs(V)O, but we did not perform additional analysis with cation-exchange chromatography to positively identify the peak as TMAs(V)O. In the chemo-trap extracts, we identify the non-retained species as TMAs(V)O since prior research has confirmed the identity of this peak with cation-exchange chromatography (Mestrot et al., 2009). See SI for more details of the speciation method. Chemo-trap extracts were analyzed for As speciation only for the highest As fluxes. Dissolved organic carbon (DOC) concentrations were measured with a Shimadzu TOC-L Total Organic Carbon Analyzer (NPOC method). Sulfate was measured with anion exchange chromatography (Dionex ICS-2100). Gas samples were analyzed using a Shimadzu GC-2014 with a flame ionization detector and a Porapak Q column. CH_4 concentrations in the headspace over time were fit with a linear regression to determine the CH_4 flux (Reid et al., 2013).

3. Results and discussion

3.1. Soil properties

The total As concentration in the microcosm soil was 14 mg/kg and the AAO-extractable As concentration was 11.4 ± 0.4 mg/kg, indicating that roughly 80% of the As in the soil was associated with amorphous iron and/or aluminum oxide phases (Fig. S3) (Keon et al., 2001). 96% of the AAO-extractable As was As(V), while 4% was MMAs(V). So while this soil does have a legacy of MMAs(V) amendment, a relatively small fraction of the extractable As was in the form of MMAs(V). Concentrations of other elements in the soil are listed in Table S1 and elsewhere (Maguffin et al., 2020).

3.2. Biogeochemical evolution of microcosms

The evolution of porewater redox chemistry for a representative subset of experimental conditions is described in Fig. 1A–C. All conditions followed a similar sequence, with As release into porewater closely associated with Fe solubilization. Sulfate reduction was concurrent with Fe solubilization. Initial SO_4^{2-} concentrations were 0.5 and 3.3 mM in the control and sulfate-amended soils, respectively. SO_4^{2-} concentrations were depleted by days 10 and 15. BES did not have a measurable impact on dissolved As, Fe, or Mn. In As(III)-amended microcosms, mean pore water As concentrations ranged from 3 to 4 μM between days 15 and 30. Microcosms with DMAs(V)-amended pore water had higher As concentrations of ~8 μM during this period (Fig. 1C). Even though a large fraction of the total As in the soils was AAO-extractable (Table S3), only a small fraction of the AAO-extractable pool was measured in pore water.

CH_4 fluxes in the control microcosm began to increase around day 20 (Fig. 1D), corresponding to a peak in DOC (Fig. S4). CH_4 fluxes peaked between days 40 and 45. BES amendment completely inhibited CH_4 fluxes (Fig. 1E) and also led to higher DOC in the second half of the experiment compared to other experimental conditions (Fig. S4). Higher DOC was probably due to the organic carbon content of BES itself along with accumulation of volatile fatty acids (VFAs), since inhibition of methanogenesis leads to higher hydrogen partial pressures that make syntrophic VFA oxidation thermodynamically unfavorable (Webster et al., 2016b; Metje and Frenzel, 2007).

3.3. Arsenic volatilization in soil microcosms

Because air was continuously pumped through the microcosm headspace and through the chemo-trap, chemo-trap extracts represent the cumulative volatilization flux over a seven day period. Fig. 1D shows that As and CH_4 fluxes were concurrent in the control microcosm, first increasing after day 20, peaking between days 35 and 45, and then decreasing after day 45. While the temporal patterns in the control suggest a potential relationship between methanogenesis and As volatilization, the inhibition of methanogenesis with BES (Fig. 1E) significantly increased As volatilization four-fold compared to the control soil. Soils amended with DMAs(V) and DMAs(V) + BES also had As fluxes that were significantly greater than the control (Fig. 2; Table S3). DMAs(V)- and BES-amended soils had similar cumulative

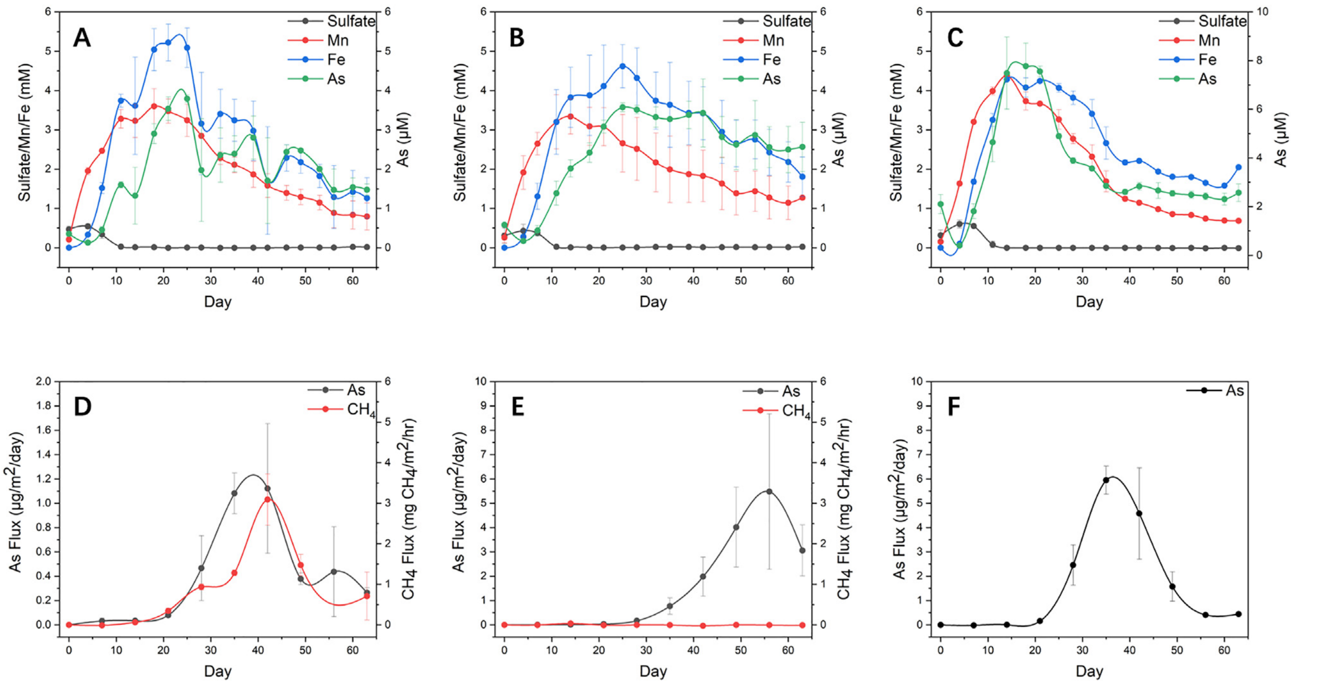

Fig. 1. Biogeochemical evolution of porewater and gas fluxes in soil microcosms in a representative subset of experimental conditions: Porewater in (A) Control; (B) BES-amended; and (C) DMAs(V)-amended microcosms. Fluxes of As and CH_4 in (D) Control; (E) BES-amended; and (F) DMAs(V)-amended microcosms. CH_4 fluxes were not measured in the DMAs(V)-amended microcosms. Symbols show the mean of duplicate microcosms and error bars show the range. Note the different right-hand y-axis scale in panel C compared to A–B for dissolved As, and different left-hand side y-axis scale for As flux in panel D compared to E and F. All experiments were performed in duplicate.

fluxes over the nine week experiment. Their time courses were different, however, with volatilization from DMAs(V)-amended soils increasing early and then largely stabilizing after day 50, while fluxes from BES-amended soils began to increase later and were still increasing at the termination of the experiment on day 65. BES and DMAs(V) appeared to exhibit synergistic effects on As fluxes, with soils amended with DMAs(V) + BES having a cumulative flux roughly eight-fold higher than DMAs(V) or BES alone, and more than thirty-fold greater than the control. However, we caution that this result is based on a single microcosm due to a malfunction with the duplicate, so this result requires further confirmation. Arsenic volatilization from sulfate-amended soils was lower than from the control.

Arsenic extracted from selected chemo-traps consisted almost entirely of TMAs(V)O (Fig. 3), indicating that As was primarily emitted from the soil in the form of trimethylarsine (Mestrot et al., 2009). There was little variation in arsine speciation between conditions, with the volatilization flux from DMAs(V)-amended microcosms also consisting of TMAs(V)O with negligible contribution of DMAs(V). This suggests that exogenous DMAs(V) experienced an additional biomethylation step in the soil prior to volatilization. This result differs somewhat from prior studies, where addition of MMAs(V) or DMAs(V) to soils or microbial cultures enhanced the production of the corresponding mono- and dimethylarsine species, respectively (Mestrot et al., 2011; Viacava et al., 2020).

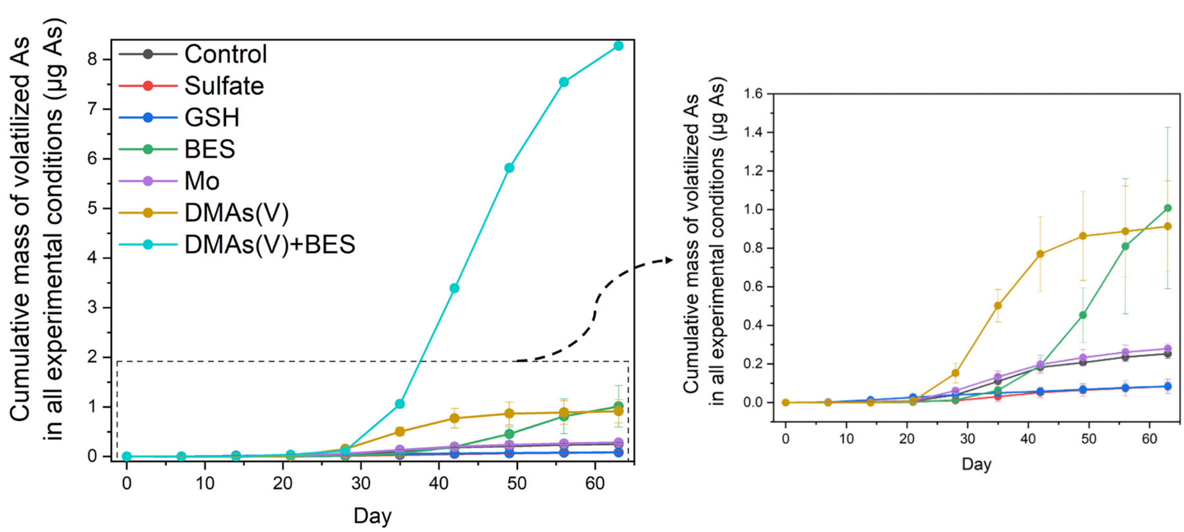

Fig. 2. Cumulative mass of volatilized As in all experimental conditions. Symbols represent the average of duplicate experiments and error bars show the range. All experiments were performed in duplicate with the exception of the DMAs(V) + BES case.

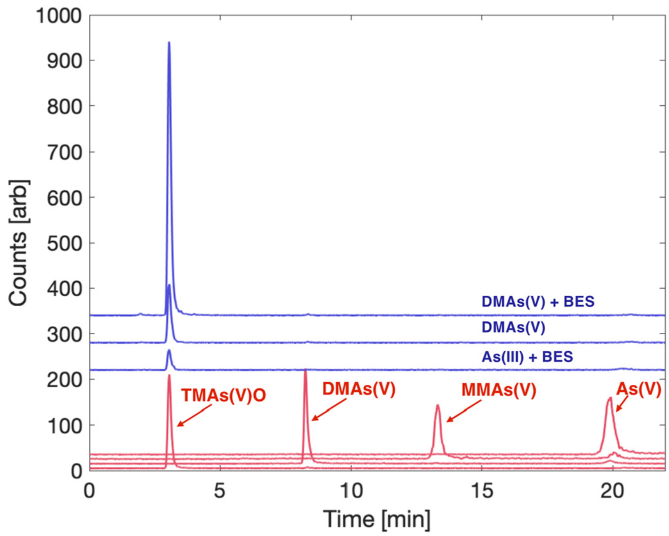

Fig. 3. HPLC-ICP-MS chromatograms of chemo-trap extracts from selected soil microcosms. Gaseous arsines emitted from soil are converted to their methylated oxyarsenic derivatives during chemo-trap extraction. Standards are shown in red and samples are in blue.

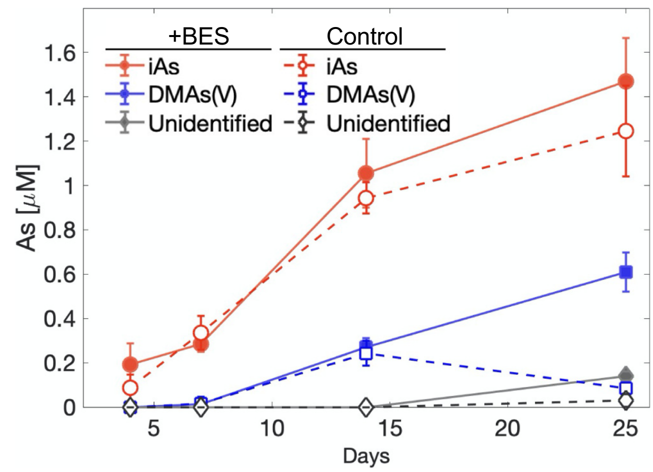

Fig. 4. Arsenic speciation in BES-amended and unamended control batch experiments. Symbols show the mean and error bars show the standard deviation of triplicate experiments. "Unidentified" refers to neutral or cationic As species that could not be definitively identified using anion-exchange chromatography. MMAs(V) was not detected in any samples and is not included in this figure.

Cumulative volatilized As represented a small fraction of the total As in soil (Table S4). Volatilization was more significant when normalized by soluble As (Table S3). In the control, volatilization represented 0.68% of pore water As, and in the BES + DMAs(V) case volatilization represented more than 7% of pore water As. Greater volatilization did not correspond to a decrease in porewater concentrations, however. Dissolved As in the BES + DMAs(V) case was higher than in experimental conditions amended with As(III), probably due to lower adsorption of DMAs(V) to soil mineral surfaces than As(III) (Lafferty and Loeppert, 2005; Shimizu et al., 2010).

3.4. Batch experiments: effects of BES on aqueous As speciation

After noting the significant impact of BES on As biovolatilization, a follow-up set of batch experiments with slurries of the Arkansas Paddy soil were performed to link biovolatilization fluxes to the effects of BES on aqueous As speciation. The sum of As species (ΣAs) determined via HPLC-ICP-MS agreed with total As measurements via ICP-MS within 15% (Fig. S8). DMAs(V) in the control and BES-inhibited slurries increased from days 4 to 14, corresponding to the overall mobilization of As (Figs. 4 and S7). On day 14, DMAs(V) represented 20 ± 4% and 20 ± 2% of ΣAs in control and BES-inhibited experiments, respectively. By day 25, DMAs(V) concentrations decreased in the control while continuing to increase in the BES-inhibited experiments (Fig. 4). A small amount of non-retained neutral and/or cationic species, potentially containing TMAs(V)O and other unidentified species, was also observed, accounting for 2.3 ± 1.8% and 6.3 ± 0.8% of ΣAs in the control and BES-inhibited slurries, respectively. MMAs(V) was not detected in any of the control or BES-inhibited samples, indicating that any MMAs(V) released into the aqueous phase from dissolution of iron (oxy)hydroxide phases was quickly transformed into another species. On day 25, methylated As species represented 34 ± 4.1% of the ΣAs in the BES-inhibited experiments and just 9 ± 2.8% in the control, showing that the inhibition of methanogenesis significantly enhanced the accumulation of methylated As.

3.5. Links among methanogenesis, aqueous arsenic speciation, and biovolatilization

Our observation that BES inhibition of methanogenesis enhances As biovolatilization from flooded rice paddy soils is a novel result. While inhibition of methanogenesis has been previously shown to increase accumulation of aqueous DMAs(V) (Chen et al., 2019), this study is the first to our knowledge that directly links inhibited methanogenesis with greater As biovolatilization.

In this study, the four-fold higher As volatilization when porewater was amended with 10 μM DMAs(V) rather than 10 μM As(III) is consistent with a role for As(III) methylation as a rate-limiting step in arsine production. The earlier onset of significant As volatilization in the DMAs(V)-amended soil compared to the control and BES-amended soil (Fig. 2) also illustrates the effect of exogenous DMAs(V) addition in bypassing the need for a rate-limiting biomethylation step, which was still required before volatilization could commence in control and BES-inhibited soils. The effect of exogenous DMAs(V) in boosting volatilization rates compared to iAs amendments has been shown previously (Mestrot et al., 2011), though the current study provides new details on the time course of As volatilization in the presence of exogenous DMAs(V) and also shows that trimethylarsine rather than dimethylarsine was the primary emitted species. Our data also reveals that greater As volatilization in DMAs(V)-amended soils may be partly due to greater As solubility in soils amended with DMAs(V) compared to As(III) (Fig. 1), probably due to a lower extent of DMAs(V) adsorption onto mineral surfaces (Lafferty and Loeppert, 2005; Shimizu et al., 2010).

BES inhibition has recently been linked to the accumulation of aqueous DMAs(V) in the paddy soil solution (Chen et al., 2019), and ^{13}C-labeled DMAs(V) was used to show that methanogens actively demethylated DMAs(V) by utilizing the methyl groups of DMAs(V) as a carbon substrate to produce CH_4. Methylotrophic methanogens were observed in the soils, leading the authors to conclude that methylotrophic methanogens were able to utilize the methyl group in DMAs(V) as a substrate for CH_4 production (Chen et al., 2019). Arsenic speciation measurements in our batch experiments are consistent with those conclusions. The decrease in DMAs(V) in control soil from day 14 to 25 is consistent with rates of demethylation outpacing rates of methylation, while the increase in DMAs(V) in BES-inhibited soil from day 14 to 25 can be explained by faster methylation than demethylation. The decrease in DMAs(V) in the control between days 14 and 25 can be attributed to demethylation rather than volatilization because cumulative volatilization accounted for <1% of soluble As during the nine week control microcosm experiment, suggesting that volatilization is unlikely to account for >10% of As over a nine day period in the batch experiment.

Taken together, our microcosm and batch results support a conceptual model where inhibiting methanogenesis leads to the accumulation of methylated As species via diminished demethylation, thereby leading to greater As volatilization. This emphasis on demethylation as a critical control on accumulation of methylated As species, and their subsequent conversion to arines, is distinct from much of the research on As methylation, which has primarily focused on biomethylation rates as the factor limiting methylated As concentrations in the environment (Lafferty and Loeppert, 2005; Vriens et al., 2014; Wang et al., 2014). Prior experimental work that has combined BES inhibition studies and measurement of volatile As species did not report significant arsine production, but this may be due to the chemo-trapping being performed over a period of ~24 h (Sierra-Alvarez et al., 2006) rather than the continuous measurements performed in the present study.

The finding that methanogenesis suppresses As biovolatilization is notable since some prior research has suggested that methanogens may be important drivers of biovolatilization. Also, one mechanism for As methylation and arsine production is driven by methyltransferases and co-factors involved in methylotrophic methanogenesis (Thomas et al., 2011; Wuerfel et al., 2012). In a recent survey of aerobic and anaerobic microorganisms, Viacava et al. (2020) found that methanogens were more efficient methylators than other anaerobes, though the relative contribution of methanogenic intermediates vs. ArsM was not clear. In a study of anaerobic digester sludge and cow dung, Webster et al. (2016a) used BES inhibition to show that most of the As volatilization was caused by methanogenic activity, in apparent disagreement with our findings. One explanation for these divergent conclusions is that soil microcosms contained a broader range of terminal electron acceptors (e.g., Fe(III), sulfate) than the organic materials studied in Webster et al. (2016a) and thus supported a greater diversity of metabolisms that could be associated with As methylation. While prior studies indicate that methanogens can play important roles in As biovolatilization in some settings, our results demonstrate that in a paddy soil biomethylation and biovolatilization were associated in large part with non-methanogenic pathways.

3.6. Effects of sulfate reduction on volatilization

There has been significant interest in the role of SRB as drivers of As methylation and volatilization (Reid et al., 2017; Chen et al., 2019; Wang et al., 2015). Inhibition of both *arsM* transcription and DMAs(V) production by molybdate and monofluorophosphate inhibitors (Chen et al., 2019), as well as correlations between *arsM* and *dsrB* (dissimilatory bisulfite reductase β-subunit) transcript numbers (Wang et al., 2019), have suggested that SRB activity drives methylation, and is therefore expected to be associated with volatilization as well. Here, we explored the effects of SRB on As biovolatilization by stimulating SRB activity with sulfate amendments. Addition of 3 mM sulfate led to lower absolute As volatilization and lower volatilization after normalization by pore water As mass (Table S3). The lower pore water-normalized flux suggests that the diminished volatilization was not simply due to lower As solubility, which could have been caused by precipitation of iron sulfide minerals that scavenge As (Wolthers et al., 2005; Burton et al., 2014). It is possible that a 3 mM sulfate amendment was not sufficient to adequately stimulate SRB activity to impact As methylation and volatilization, though a recent study found that a larger addition of 10 mM sulfate in an acidic fen soil also suppressed As biovolatilization (Huang et al., 2018). Because we did not evaluate the effects of sulfate amendment on As speciation in batch soil slurry experiments, we cannot comment on whether sulfate increased formation of aqueous methylated As species in this Arkansas rice paddy soil, as has recently been shown in rice paddy soils in China (Chen et al., 2021; Chen et al., 2019). We further caution that thioarsenic species may have been formed in sulfidic porewater (Wang et al., 2020b; Fisher et al., 2008), and that these thioarsenic species may not be readily converted to arsines.

3.7. Implications for arsenic volatilization from wetland soils

This study confirms prior research showing that As biovolatilization represents a small fraction of the total soil As (tAs) pool in wetlands (Table S4) (Mestrot et al., 2011; Vriens et al., 2014; P. Chen et al., 2017; Huang et al., 2012; Huang et al., 2018). The flux of 250 $\pm$ 20 ng of volatile As over the nine week experiment in the control soil is comparable to prior measurements in UK (Mestrot et al., 2011) and Swiss (Vriens et al., 2014) peat soils (Table S4). Because most of the As in the soil system remains associated with the solid phase, however, volatilization is more significant when normalized by the pore water As mass, reaching 0.68% in the control and 7.3% in the BES + DMAs(V) case. Substantially higher pore water-normalized volatilization fluxes have also been reported previously (Huang et al., 2012). The addition of exogenous As(III) in the synthetic porewater most likely increased the volatilization flux, as has been shown elsewhere (Huang et al., 2018) (Table S4). While the volatilization rates described here are relatively small from the perspective of the soil As budget, the changes in volatilization rates observed under different experimental conditions were significant (e.g., the more than four-fold increase in volatilization rates with BES inhibition compared to the control). This points to the relevance of these results for understanding variability in biovolatilization as a source of atmospheric As, of which biogenic emissions represent roughly 20% (Galloway et al., 1982).

This study is the first to our knowledge to link inhibited methanogenesis to greater As biovolatilization, revealing the importance of methanogenesis-driven demethylation as an underlying control of As biovolatilization rates. The traditional paradigm for understanding the accumulation of methylated As species and/or As biovolatilization has focused on biomethylation rates as the limiting factor, while this study suggests that demethylation may play an equally important role in controlling environmental abundances of methylated As and As volatilization. Our finding that methanogenic activity suppressed methylated As accumulation and As biovolatilization, presumably via faster demethylation (Chen et al., 2019), extends recent insights into the role of methanogens in As metabolism to rice paddy soil from the mid-south U.S. Methanogens are known to be involved in the demethylation of selenium species (Oremland and Zehr, 1986) and have also recently been linked to demethylation of mercury in rice paddies (Wu et al., 2020), underscoring a broader role for methanogens in the control of methylated metal(loid) species in the environment. Research is underway on understanding how concentrations of methyl-group containing substrates for methylotrophic methanogens (e.g., methylamine; methanol) (Zalman et al., 2018) impact As demethylation in anaerobic soils.

CRediT authorship contribution statement

Xuhui Zhang: Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Visualization. **Matthew C. Reid:** Conceptualization, Investigation, Resources, Writing – review & editing, Visualization, Supervision, Funding acquisition.

Declaration of competing interest

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

Additional figures, table, and description of geochemical modeling are presented in Supporting Information. Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.151696.

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