Impact of Iron Amendment on Net Methylmercury Export from Tidal Wetland Microcosms

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Tidal wetlands can be important sources of methylmercury (MeHg) in aquatic ecosystems. As a result, wetland restoration could increase MeHg concentrations. Previous research has shown that addition of Fe[II] to wetland sediment can reduce MeHg production by decreasing concentrations of bioavailable Hg complexes with dissolved sulfur species. In this study, the potential for reducing MeHg production via an iron amendment was evaluated in laboratory microcosms that used intact sediments from a tidal marsh in San Francisco Bay. The microcosms were maintained under simulated tidal conditions and amended at four iron doses (0, 180, 360, and 720 g-Fe/m^2). Two experiments were conducted: one with devegetated sediments and one with live wetland vegetation. Following iron addition to the devegetated sediments, porewater S[-II] concentrations decreased for each dose relative to the control with the average weekly export of MeHg in the surface water decreased by 82% and 89% for the two highest doses, respectively. Despite substantial variability within treatment groups, similar trends were observed for the vegetated microcosms. The results suggest that iron addition has the potential to provide a landscape-scale control on MeHg released by restored tidal wetlands; however, additional research is required to evaluate the efficacy of this approach under field conditions.

Introduction

During the past 200 years, wetlands have been drained or filled to increase agricultural productivity or to make land more suitable for habitation (*1*). In recognition of the ecosystem services that wetlands provide, this trend has recently been reversed in many locations worldwide.

A potential drawback to wetland restoration, however, is the formation and subsequent bioaccumulation of monomethylmercury (MeHg). MeHg can lower the reproductive success and survival of piscivorous birds and mammals (*2*), as well as benthic omnivores endemic to tidal wetlands (*3*). The primary exposure pathway of MeHg for humans is through the consumption of fish, and most fish advisories are due, at least in part, to elevated levels of MeHg (*4*). Under the anoxic conditions typical of wetland sediments, mercury methylation is primarily mediated by sulfate-reducing bacteria (*5, 6*), although iron-reducing bacteria are also capable of methylation (*7, 8*). Because mercury methylation is predominantly a biotic process, the production rate of MeHg depends on both bacterial activity and the bioavailability of Hg[II]. In the presence of S[-II] produced by sulfate-reducing bacteria, Hg[II] solubility and speciation is controlled by cinnabar ($HgS_{(s)}$). Under these conditions, the uptake and subsequent methylation of Hg[II] depends upon the concentration of uncharged mercury complexes (e.g., HgS^0 and $Hg(HS)_2^0$) that are capable of passively diffusing into bacterial cells (*9, 10*). Dissolved organic matter in sediment porewater affects the bioavailability of mercury by enhancing Hg[II] dissolution and preventing the precipitation of cinnabar (*11*). Organic matter in sediments can also alter Hg[II] speciation and bioavailability, and stimulate microbial activity, which in turn enhances MeHg production (*12*).

Due to their high productivity and anoxic sediments, tidal wetlands typically contain elevated concentrations of MeHg (*13*−*15*). Thus, tidal wetland restoration has the potential to exacerbate existing mercury contamination problems by increasing concentrations of MeHg. In recognition of this potential problem, the merits of wetland restoration without simultaneous control of MeHg have been questioned (*16*). To facilitate the restoration of coastal wetlands without increasing MeHg, landscape-scale controls are needed.

We previously evaluated the use of a ferrous iron (Fe[II]) amendment to lower dissolved sulfide concentrations via the formation of $FeS_{(s)}$, which subsequently decreased the pool of bioavailable neutral mercury-sulfide species (*17, 18*). Studies conducted with pure cultures of a sulfate-reducing bacteria (*Desulfobulbus propionicus* (1pr3)) demonstrated a decrease in net mercury methylation of over 70% without changing microbial metabolic rates during a three-day incubation (*17*). Subsequent studies using sediment with native microbial communities collected from five wetlands around San Francisco Bay again showed that addition of Fe[II] reduced net MeHg production in a 7-day incubation (*18*). This approach has since been reproduced in experiments using sediments from other locations (*19, 20*), but the efficacy of the process has not been demonstrated under the complex conditions encountered in tidal marshes.

In this study, the potential for reducing MeHg production and export was evaluated in microcosms that approximated the conditions encountered in a tidal marsh, using sediments and plants from a tidal wetland that contained elevated concentrations of mercury from historical mining activities (*21*). This is the first study to demonstrate the efficacy of this approach under simulated field conditions and at ambient mercury concentrations. By exposing intact sediment cores to a simulated tidal cycle we were able to extend the studies to several months, preserve vertical stratification of solutes and redox conditions within the sediments, simulate cycling of electron acceptors by tidal cycles, and allow the exchange of H_2S and O_2 with the atmosphere.

Experimental Section

Microcosm Collection and Operation. Intact sediment cores (50 × 25 × 15 cm) were collected from a tidal saltmarsh near Petaluma, CA (38.207°N,122.584°W). The marsh is dominated by pickleweed (*Sarcocornia pacifica*) and has tidal exchange with the Petaluma River, which drains into San Pablo Bay in the San Francisco Bay estuary. Sediment cores were collected for the devegetated experiment in October 2007 and for the vegetated experiment in September 2008. Intact blocks of sediment were extracted using shovels (details in Supporting Information (SI) 1) and placed into acrylic aquariums. Additional sediment was added to the core edges as necessary to prevent pooling of surface waters and minimize short circuiting. Twelve microcosms were collected from the same

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area of the marsh plain that had a similar density of pickleweed.

Microcosms were transported back to the laboratory immediately after collection and connected to a simulated tidal system (details in SI 2). In brief, the microcosms were operated under grow lamps and connected to individual reservoirs containing 5 L of diluted synthetic seawater. A tidal regime was simulated using automated peristaltic pumps that provided two daily uniform high-tide events that brought water to a depth of 1−2 cm over the sediments, with each tide lasting for a total of 3 h. As a result, the sediment surfaces were directly exposed to the atmosphere for 18 h per day.

Iron Sediment Amendment. For the devegetated experiment, microcosms were equilibrated under laboratory conditions for four months before the aboveground vegetation was removed. One hundred grams of dried pickleweed collected from the microcosms was added to the sediment surface. The microcosms were randomly assigned to one of four iron treatment groups ($n = 3$ per group): a control dose (0 g-Fe/m^2), a low dose (180 g-Fe/m^2), a medium dose (360 g-Fe/m^2), and a high dose (720 g-Fe/m^2). These dosing levels were selected such that the dose applied to the medium group would approximately double the reduced iron initially present in the sediments, assuming that all of the measured acid-volatile sulfides (AVS) consisted of $FeS_{(s)}$. These application rates were similar to the ranges used for the suppression of methane production in rice paddies (*22*) and phosphorus removal in treatment wetlands (*23*), and were around an order of magnitude higher than those used to reduce sulfide toxicity in seagrass beds (*24*).

The iron amendment solution consisted of 0.28−1.1 M $FeCl_2$ in a deaerated 1.0−2.0 M $Na_2CO_3/NaHCO_3$ buffer adjusted to pH 7. The amendment occurred over 3 days, with 0.5 L of solution being amended in around 20 min per day, for a total injection volume of 1.5 L per microcosm. Plastic syringes (20 mL) with stainless steel needles were used to inject the solution at a depth of 2.5 cm using a grid pattern of 32 injections per day (a row of four injections across the width, and eight rows down the length) to ensure coverage over the entire area of the sediments. For the control group, a suspension of 1.0 M $CaCO_{3(s)}$ was injected under the same conditions.

For the vegetated experiment, microcosms were allowed to equilibrate to the laboratory conditions for a period of 3 weeks before the iron amendment. The 12 tanks were randomly assigned into four treatment groups ($n = 3$ per group): a control with no iron added and the above-ground vegetation removed (devegetated control), and a control, low, and medium iron dose with the vegetation present at doses of 0, 180, and 360 g-Fe/m^2, respectively. The iron was amended in the same manner as in the devegetated experiment, and the control group also received a suspension of 1.0 M $CaCO_{3(s)}$.

Sample Collection. Surface water and porewater samples were collected from each microcosm every 7 or 14 days (details in SI 3). In brief, surface water samples were collected from the reservoirs following the final high tide of the 7 day exposure period. The volume of surface water remaining in the reservoir was measured to correct for differences in evaporation among microcosms (typically less than 25% for the devegetated microcosms and less than 15% for the vegetated microcosms). Surface water concentrations are reported after normalizing to the initial 5 L reservoir volume. After sample collection, the reservoir was refilled with 5 L of simulated estuarine water (see SI 2). Prior to initiating the experiment, an in situ porewater sampler (10 cm Rhizon Soil Moisture Sampler, Rhizosphere Research Products, Netherlands) was installed in the interior of each microcosm at a depth of 3.5 cm.

Following the final water sample collection, triplicate sediment cores were collected from each microcosm using acrylic tubes (see SI 3). The 6 cm i.d. cores were sectioned at 1 cm resolution to a depth of 10 cm, and sediment analyses were performed on a composite sample of the depth interval for each of the three cores.

Analytical Methods. Water and sediment samples were analyzed for sulfur, iron, and carbon using established methods (details in SI 4). Method detection limits were defined as 3 times the standard deviation of the blanks, unless otherwise noted. For samples with concentrations below the detection limit, one-half of the detection limit was used for calculations.

Total mercury in the surface water was measured by BrCl oxidation, reduction with $SnCl_2$, trapping on gold traps, thermal desorption, and cold vapor atomic fluorescence (CVAFS) detection (*25*). The detection limit was computed for each analytical run and had an average of 0.6 pM for a 100 mL bubbler volume. Relative percent difference between duplicate sample bottles averaged 16 ± 17% ($n = 16$), and recovery of Hg spikes into duplicate samples averaged 97 ± 20% ($n = 10$). MeHg in surface water was measured by acidic chloride distillation (*26, 27*), aqueous phase ethylation, collection on Tenax traps, thermal desorption, GC separation, and detection by CVAFS (*28*). Percent recovery of MeHg spiked into a distillation blank averaged 103 ± 11% ($n = 13$), recovery of MeHg spikes into duplicate samples averaged 95 ± 28% ($n = 17$) with relative percent difference of duplicate samples of 23 ± 21% ($n = 16$), and recovery of distilled NIST mussel tissue standard (NIST SRM 2976) was 93 ± 17% ($n = 11$). The detection limit was defined as 0.9 pM, which was the typical lowest point on the daily calibration curve in a 55 mL sample.

Results

Dissolved Sulfur and Iron in Devegetated Microcosms. Samples were collected over a 17-week period following the iron amendment. A pump failure occurred during Week 6, which resulted in flooded conditions for approximately 72 h. During the 2-week period when the pump system was being repaired (Weeks 7−8), the microcosms received a single daily high tide.

Surface water sulfate concentrations (SI Figure S2) exhibited a decrease of approximately 7 mM during the weeklong exposure period. Dissolved porewater sulfide concentrations were decreased by the addition of Fe[II] (Figure 1(a)). The low dose group typically showed decreases in weekly porewater sulfide concentrations of greater than 70% relative to the control group, and the medium and high dose groups showed decreases of up to 80−90% for most weeks.

The concentration of iron measured in the surface water was similar among the treatment groups, with weekly averages ranging between 0.5 and 27 μM (data not shown). Relatively large differences in the porewater dissolved iron concentrations were observed among the treatment groups (Figure 1(b)), with the high-dose groups exhibiting iron concentrations that were up to 3 orders of magnitude higher than the control. The concentration of porewater iron for both the medium and high treatment groups decreased over the first 12 weeks.

Mercury in Devegetated Microcosms. Total concentration of inorganic mercury in the surface water (defined as the difference between 5 L reservoir normalized concentrations of total mercury and MeHg), was similar among all treatment groups with average concentrations ranging from around 20−50 pM, except for Week 6, when the pump failed and average concentrations increased to as much as 90 pM (SI Figure S3). On the basis of equilibrium predictions (*29*), it is likely that inorganic mercury was associated with chloride

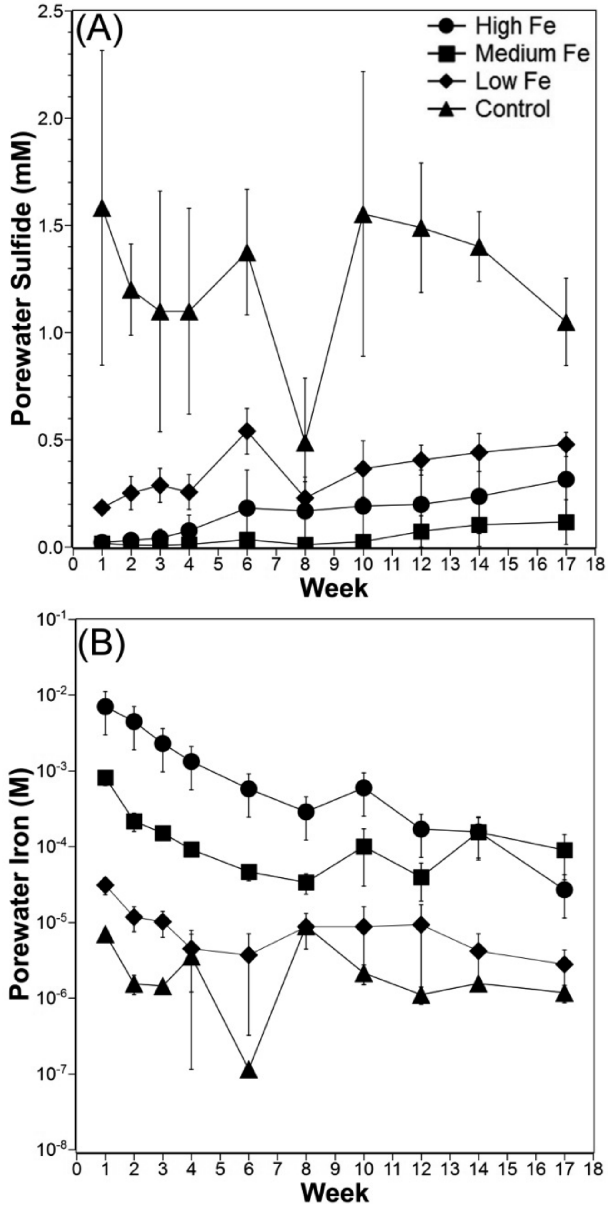

FIGURE 1. Average porewater concentrations in the devegetated microcosms for dissolved sulfide (A) and dissolved iron (B). Values shown are the average concentration of the three replicate microcosms ± standard error for each iron treatment group.

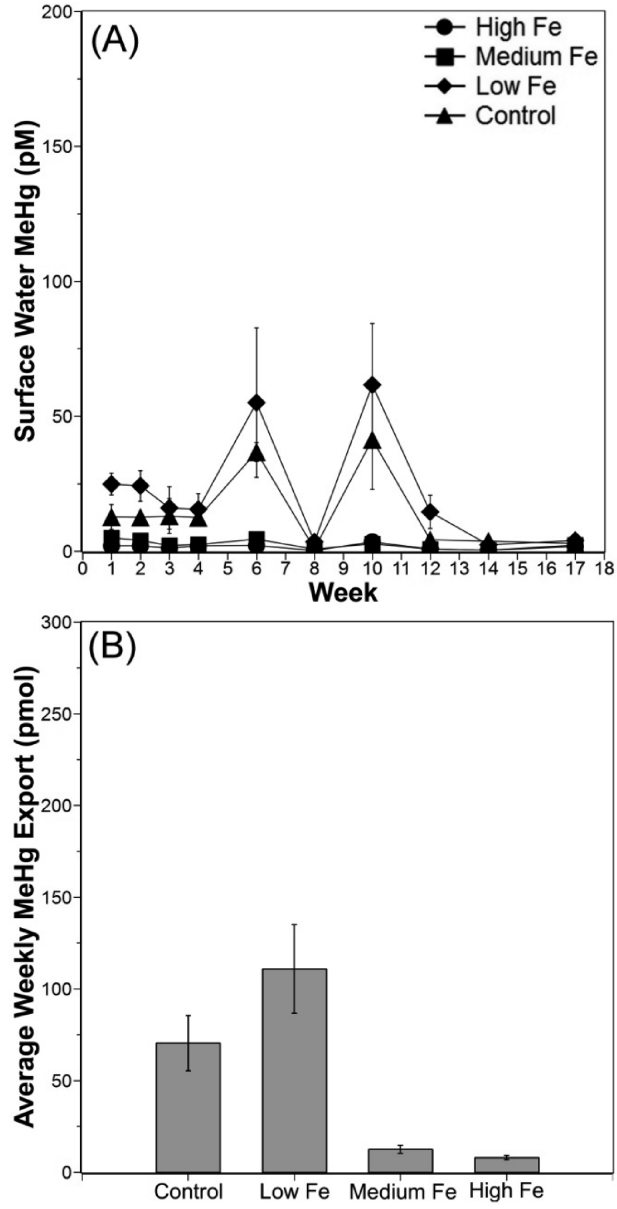

FIGURE 2. (A) Methylmercury measured in the surface water of the devegetated microcosms, normalized to the 5 L reservoir volume, after 7 day exposure to microcosm sediments. (B) Average mass of MeHg exported per week over the experimental period (n = 30 per group). The medium and high dose groups were each significantly different (α = 0.05, p < 0.001) than the control, whereas the low dose group was not significantly different than the control. Values shown are average ± standard error.

or organic matter in the surface water. Dissolved organic carbon (DOC) in the surface water exhibited decreased concentrations for the high dose, and porewater concentrations were fairly constant among treatments (SI Figure S4).

In contrast, methylmercury concentrations in the surface water reservoirs showed clear differences among treatments (Figure 2(a)) with the medium and high groups exhibiting average concentrations less than 5 pM and the low dose and control groups exhibiting average concentrations between 10 and 60 pM. Concentrations of MeHg for the low and control groups were highest during and immediately following the flooded period when the pumps failed. After 12 weeks, the concentrations of MeHg for the low and control groups decreased to levels similar to the medium and high groups.

The average mass of MeHg exported from the sediment porewater to the surface water each week (Figure 2(b)) was significantly higher for the low and control treatments compared to the medium and high treatment groups. A one-way ANOVA ($\alpha = 0.05$, $p < 0.001$) followed by a Tukey's HSD test showed that both the medium and high dose groups were significantly different than the control group. The medium dose exhibited an 82% decrease in weekly MeHg export and the high dose showed an 89% decrease. While the low dose group was 57% greater than the control group (see SI 8), the averages were not significantly different.

Sulfur Minerals in Devegetated Microcosms. The depth profiles of AVS and chromium reducible sulfur (CRS) concentrations at the end of the experimental period (Figure 3) indicated increased formation of AVS for the high dose group at the 2−3 cm depth relative to the other groups. Additionally, all three treatment groups showed elevated concentrations of CRS relative to the control dose over the 2−4 cm depth.

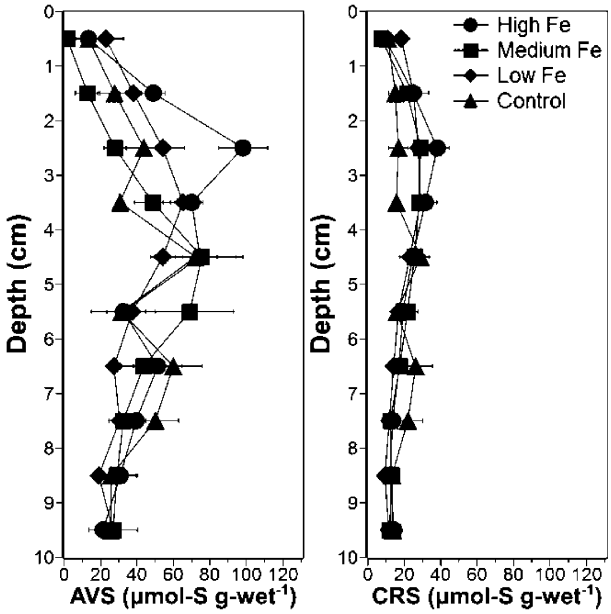

FIGURE 3. Depth profiles of reduced sulfur speciation in the devegetated microcosms collected at the end of the experiment for the top 10 cm of sediments from composite core samples. Values shown as average of triplicate microcosms ± standard error.

Dissolved Sulfur and Iron in Vegetated Microcosms. Samples were collected from the vegetated microcosms over an 8-week period following the iron amendment. Around Week 4, plants in many of the microcosms had lost their vibrant green color. By Week 8, almost all plants were dormant.

Sulfate concentrations remaining in the surface water after one week of tidal exposure decreased by approximately 6−7 mM, which was similar to the decrease observed in the devegetated experiment (SI Figure S5). Patterns in the porewater sulfide concentrations (Figure 4(a)) were not as evident in the vegetated experiment because substantial variability occurred among the triplicate microcosms. On average, the vegetated low and medium dose groups exhibited lower sulfide concentrations than the control, but the variability was large due to a single tank behaving markedly different than the other two (see description in SI 5).

Dissolved iron concentrations in the porewater (Figure 4(b)) exhibited trends similar to those observed in the first experiment with the highest iron doses having the highest concentrations. However, concentrations were around an order of magnitude higher than those measured for the corresponding dose in the devegetated experiment. The vegetated control generally showed lower average iron concentrations than the devegetated control.

Mercury in Vegetated Microcosms. Inorganic mercury concentrations were similar among all groups with average concentrations ranging between 10 and 120 pM (SI Figure S6). During the initial three weeks of the experiment, the low and medium groups had lower average concentrations of MeHg in the surface water than the vegetated control (Figure 5(a)). However, the vegetated control showed considerable variability. By Week 4, average MeHg concentrations were similar for all groups. No significant differences were found between the average weekly export of MeHg (Figure 5(b)) for any of the groups (one-way ANOVA with $\alpha = 0.05$, $p = 0.11$).

Sulfur Minerals in Vegetated Microcosms. Depth profiles analyzed for reduced sulfur speciation showed small increases in AVS for the vegetated treatment groups relative to the control over 2−4 cm depth. No differences were evident at any depth for CRS (SI Figure S7).

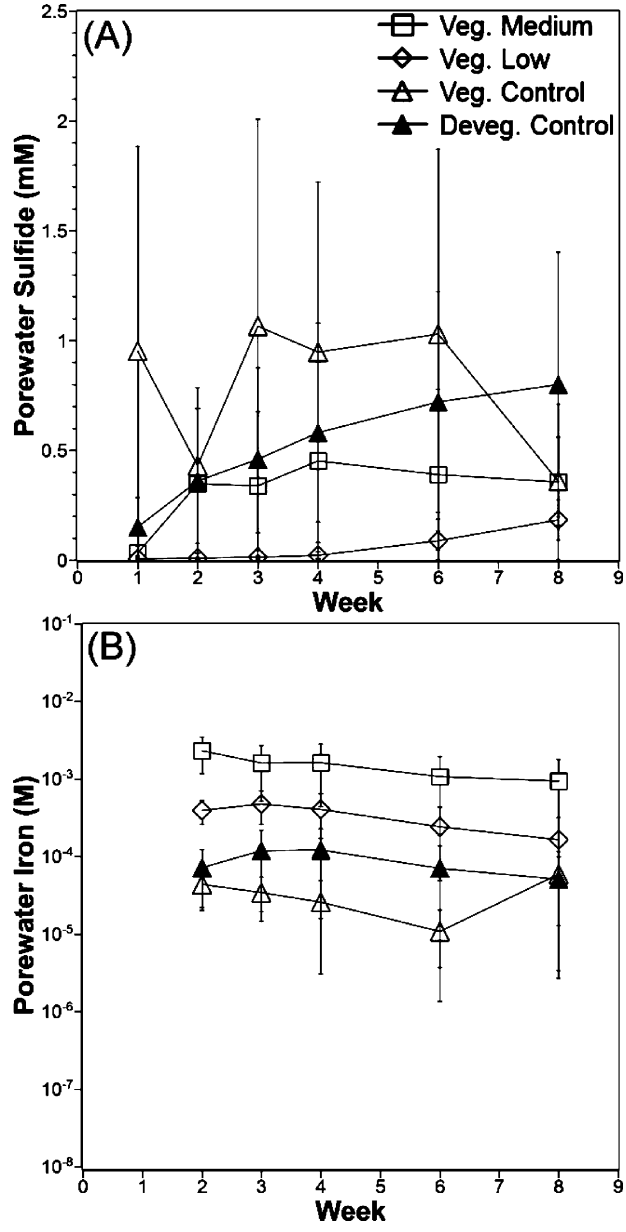

FIGURE 4. Average porewater concentrations in the vegetated microcosms for dissolved sulfide (A) and dissolved iron (B). Values shown are the average concentration of the triplicate microcosms ± standard error for each iron treatment group.

Discussion

These microcosm experiments demonstrated that the amendment of tidal wetland sediments with iron can reduce methylmercury concentrations under simulated field conditions. The findings are consistent with previous mechanistic studies that demonstrated this effect in short incubation experiments (*17*−*20*), and they showed that an iron amendment can be effective for a period of at least 12 weeks under these conditions. This study also provided insight into the fate of iron and S[-II] within the sediments and the role of vegetation. Each of these issues is explored in the following sections.

The effect of iron on sediment biogeochemistry was most evident in the devegetated experiment. Iron addition increased porewater Fe[II] which subsequently lowered the concentration of porewater S[-II] for all of the treatment groups. Coupled with the decrease in porewater iron observed over the first 12 weeks for the medium and high dose groups,

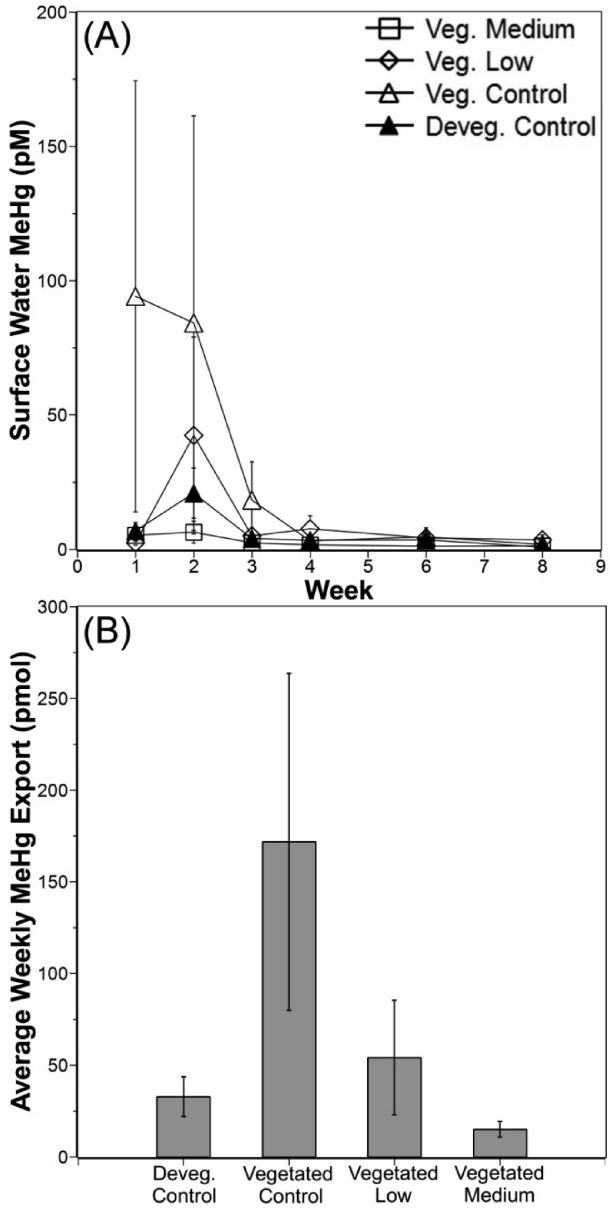

FIGURE 5. (A) Methylmercury measured in the surface water of the vegetated microcosms, normalized to the 5 L reservoir volume, after 7 day exposure to microcosm sediments. (B) Average mass of MeHg exported per week over the experimental period (n = 18 per group). No statistical difference was found between the groups (p = 0.11). Values shown are average ± standard error.

these findings suggest that there was a solid-phase sink for both iron and sulfur in the sediments (e.g., $FeS_{(s)}$ and $FeS_{2(s)}$) (*30*). The presence of these minerals was confirmed through the AVS/CRS measurements and by visual observation of the formation of black sediment layers characteristic of $FeS_{(s)}$. The formation of these minerals could also be important to Hg bioavailability since they can be important scavengers of Hg[II] (*31, 32*), and mercury can coprecipitate with authigenic pyrite in marine sediments (*33*). In both cases, it is possible that mercury could be rendered less bioavailable. If this occurred following an iron amendment, it could provide a long-term means of reducing MeHg production, provided that the minerals are prevented from reoxidizing and releasing the associated mercury. However, it appears that iron−sulfur minerals did not affect the microcosms in this way, since the inorganic mercury concentrations were similar for all groups (SI Figures S3 and S6). It is possible that the high concentrations of porewater DOC (SI Figure S4(b)) inhibited sorption to the minerals by forming complexes with Hg.

Due to the destructive nature of the sampling, sediment cores were collected only after the final water samples were collected, and it is unclear if larger differences in sulfur mineral concentrations existed earlier in the experiment. A mass balance on sulfur in the devegetated experiment indicated between 77 and 105% of the sulfur added during the 17-week experimental period could be accounted for as AVS/CRS in the top 10 cm of the sediment and porewater sulfate (Table S1 in SI 6). If it was assumed that sulfate reduction continued at its average rate within the microcosms over the 6−8 week period between the final water measurement and the sediment core collection, between 63 and 84% of the sulfur was recovered (Table S2 in SI 6). A calculation of potential volatilization of H_2S from the porewater during the daily exposure of the sediment to the air, based on porewater pH and sulfide concentrations (see SI 6), suggests that H_2S volatilization likely accounted for the remaining sulfur. However, it is possible that a portion of the S[-II] in the porewater could have been oxidized by iron (oxyhydr)oxide minerals to S^0 (*34*), which was not detected by our analytical methods.

An approximate mass balance for iron was also calculated by assuming that all of the measured AVS and CRS consisted of $FeS_{(s)}$ and $FeS_{2(s)}$, respectively (SI Table S4). This calculation yields between 38 and 72% recovery of the added iron as iron−sulfur minerals. It is likely that some of the remaining iron was present in the sediments as $FeCO_{3(s)}$ or as an Fe[II]/Fe[III] mineral phase not detected by the AVS/CRS extraction methods. Reoxidation of a portion of the Fe[II] to Fe[III] was possible at the sediment−water interface, and was evident for the medium and high iron doses by the presence of red solids on the sediment surface.

Addition of iron to the devegetated sediments at both the medium and high dose levels significantly reduced the concentrations of MeHg that were exported from the porewater to the surface water (Figure 2). Because the export of inorganic mercury was similar among all of the treatments, it appears that the addition of iron did not substantially inhibit the exchange of mercury species to the surface water. This suggests that the reduction in MeHg export was related to the net production of MeHg in the sediments. In-situ methylation rates were not directly measured; however, the percent of total mercury that is MeHg (%-MeHg), which has been considered an approximation of net MeHg production in coastal sediments (*35*), provides further evidence that iron addition decreased net methylation rates. Consistent with this assumption, weekly average %-MeHg values in the surface water of the devegetated microcosms over the first 12 weeks (excluding the Week 8 pump failure) were higher in the control and low groups than in the medium and high dose groups (SI Figure S8). These values likely reflect porewater concentrations since there were no other sources of mercury in our system. The average %-MeHg values, typically between 5 and 40%, were consistent with porewater values reported in other wetland mesocosm studies (*36, 37*) and in contaminated bay sediments (*38*).

The net export of MeHg decreased after approximately 12 weeks in the devegetated microcosms, and after around 3 weeks in the vegetated microcosms, until there was no difference between the control and treatment groups. The decrease in net MeHg export that occurred after the first 12 or 3 weeks may have been due to the experimental limitations of the microcosms to act as proxies of field conditions over extended periods of time. In the lab, the microcosms were subjected to conditions unlike those encountered in the field. For example, the microcosms were supplied with simulated estuarine water that contained negligible concentrations of DOM and dissolved mercury. Additionally, the movement of

tidal water occurred only on the surface of the microcosms, while under field conditions the water table varies vertically in the sediments as the tides change. Over time, this could have limited advective flushing of reduced species in the microcosms and affected the redox stratification. By disturbing the sediments, we also may have induced a period of high net MeHg production early in the experiment. Field studies have shown pulses of MeHg can occur when reservoirs (*39*) or tidal marshes (*40*) are subjected to new hydraulic conditions. If this was the case for our microcosms, these results suggest that an iron amendment may be able to reduce the size of the MeHg pulses that occur when natural systems are inundated.

The reason for the increased variability in porewater sulfide and MeHg export in the vegetated experiment is unclear, however several factors could have contributed. The laboratory equilibration time to the new hydraulic conditions was reduced from 4 months for the devegetated sediment experiment to only 3 weeks for the vegetated experiment. Additionally, plants can significantly alter the biogeochemistry of saltmarsh sediments through the production of organic acids that can stimulate microbial activity (*41*) and release of oxygen into the rhizosphere (*42*). Therefore, the presence of plants may have introduced extra heterogeneity into the system. While care was taken to select similarly vegetated plots in the field during microcosm collection, the amount of living roots in each microcosm was not quantified. Additionally, the health of individual plants within the microcosms could have contributed to the variability. By around 3−4 weeks into the experimental period, most of the plants had gone dormant, but individual plants declined at different times, which could have resulted in increased variability due to the decreased subsurface activity of the plants.

Even with the increased variability in the vegetated experiment, the trends observed were similar to that of the devegetated sediments, and suggest that an iron amendment could be an effective means of controlling net MeHg export in restored tidal wetlands. Research at the field scale is needed to determine the efficacy of an iron amendment under field conditions, and if an amendment is effective for longer than 12 weeks or if repetitive dosing would be needed. Additionally, unintended consequences of adding iron to the ecosystem, including toxicity to wetland vegetation, must be taken into account to ensure that changes that alter habitat quality do not occur.

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Supporting Information Available

Additional descriptions of microcosm operation (Figure S1), discussion of variability in the vegetated microcosms, additional data from both experiments (Figures S2−S10, Tables S5 and S6), and details of the mass balance calculations (Tables S1−S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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