PENOBSCOT RIVER MERCURY STUDY

Chapter 19

In-situ amendment plot studies

Submitted to Judge John Woodcock
United States District Court (District of Maine)

April 2013

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1 SUMMARY

It has been thought that there are few available remediation options for mercury (Hg) contaminated sediments, short of capping and dredging. Recently, *in-situ* sorbent amendments have attracted recent attention as a low-cost, low-impact approach for remediation of organic-contaminated sediments (Ghosh et al. 2011). This study is one of the first field trials of *in situ* amendments for Hg and methyl Hg methyl remediation.

In this study, the efficacy of *in situ* soil amendments was tested as a potential tool for methyl Hg risk mitigation in the Penobscot system, specifically in tidal salt marshes. Four amendments were tested, activated carbon (formulated into SediMite^{TM} pellets with sand and clay), a pine dust biochars, ferrous chloride ($FeCl_2$), and lime. The carbon treatments were chosen based on previous laboratory studies demonstrating their ability to reduced pore water Hg and methyl Hg concentrations, and uptake by benthic infauna (Gilmour et al. in review). The lime treatment was designed to alter pH, as Hg methylation rates, and % methyl Hg in soils tends to decrease with pH in the Penobscot system (see Penobscot "Mercury Methylation Studies" Report – Chapter 11).

Two study sites in Mendall Marsh were chosen for the study. Field studies of methyl Hg concentrations and production rates in sediments and soils across the Penobscot system pointed to salt marshes as sites of particularly high methyl Hg production and accumulation, and therefore a key target for remediation.

The study design was a fully-crossed small plot study, with five treatments at each of two sites in Mendall Marsh. At each site, four amendment treatments plus an un-amended control treatment were set up in triplicate. Treatments were randomized in each of three rows at each site. Plots were roughly 1 square meter (m^2) in size. Two sites ("West" and "Central") on the main west platform of Mendall Marsh were chosen for study. The sites were chosen to represent two different major habitats in the marsh. Both sites contain elevated Hg levels in surface soils, and produce substantial methyl Hg from that contamination.However the sediment chemistry is somewhat different at each site, with the West site more reducing than Central.

Dosing rates were 1 (kg) of activated carbon (AC), biochar or Fe (as $FeCl_2$) per square meter, and 0.5 kg of lime. Amendments were broadcast by hand onto the plots during a tidal cycle where the marsh was not overtopped by tide.

Plots were initially treated in Sept. 2010, and were sampled four times post-amendment, through Sept. 2012. The study sampling design was based on two objectives. The first was to determine if amendments reduced potential risk from methyl Hg by reducing pore water methyl Hg concentrations and sediment water partition coefficients. A secondary objective was to evaluate the impact of amendments on sediment biogeochemistry.

Carbon amendments were effective in reducing Hg and especially methyl Hg concentrations in pore waters at both study sites in Mendall Marsh. Across all four sampling dates, AC amendments resulted in significant reductions in pore water Hg and methyl Hg at both test sites in the marsh. Biochar significantly reduced methyl Hg concentrations at both sites, and total Hg concentrations at Central. AC, applied after being formulated as SediMite™ pellets, gave the highest and most consistent reduction through time.

AC amendments reduced pore water methyl Hg concentrations at the both sites by >90% at the one month time point and by 60% to 70% on average across all the four time points through two years. At the one year time point, AC plots had about 75% less pore water methyl lHg than control plots at West and 50% less at Central. On average, AC reduced total Hg in pore waters at both sites by 50% to 60%. Biochar was only a little less effective than AC, providing on average 50% to 70% reductions in methyl Hg and 35% to 55% reductions in total Hg.

Lime and $FeCl_2$ additions had inconsistent effects across the sites and through time. On average, across all time points, neither amendment had a significant impact on either total Hg of methyl Hg concentrations.

The treatments were generally well-retained in the plots. In 2011, surface soils in AC plots (0-3 centimeter [cm]) contained more than 10% carbon black on average. It was visually obvious that AC and biochars penetrated deeper into surface soils over time; by Sept. 2012 the average penetration was 2-3 cm. Analysis of metals in soils showed that calcium (Ca) and iron (Fe) were retained in the plots at levels significantly above controls for the 24-month duration of the study.

In general, the AC and bioachar amendments did not have any significant impact on surficial pore water chemistry, including pH, and the concentrations of nutrients, dissolved organic matter, anions, cations or redox-sensitive constituents like Fe and sulfide. Carbon amendments did not significantly impact soil bulk density or porosity. Therefore, the carbon amendments may not have significant impacts on marsh plant growth or food webs, but that would need to be explicitly tested. Vegetation cover was visually assessed in the plots in fall 2011. The major species composition and plant density was similar between control and carbon plots.

In prior laboratory microcosms studies, AC amendments to Hg-contaminated sediments were highly effective in reducing methyl Hg bioaccumulation by benthic invertebrates (Gilmour et al. in review). In these studies, the effectiveness of AC and other amendments in reducing invertebrate bioaccumulation was well-correlated with their effectiveness in decreasing pore water methyl Hg concentrations, and increasing sediment:water partition coefficients. The mechanism of AC remediation appears to be mainly by reductions in methyl Hg bioavailability to worms, rather than by reductions in sediment methyl Hg production or bulk sediment methyl Hg concentration.

AC as a remediation tool for Hg and methyl Hg has been tested in several laboratory studies, and in two other field studies of which the authors are aware. Across these studies, AC was most effective in sediments and soils where sediment:water Hg and methyl Hg partitioning are naturally low. Mendall Marsh soils have some of the lowest observed K_D (dissociation constant) values for both Hg and methyl Hg across a broad literature on Hg in the environment (see the Penobscot “Mercury Methylation Studies” Report – Chapter 11).

In summary, activated carbon amendments could be an effective tool to reducing Hg and methyl Hg risk in contaminated Penobscot Marshes. The next steps in evaluating this tool should be larger-scale plot studies. These studies should include evaluation of animal bioaccumulation, food web structure, plant community structure, and possibly marsh productivity and Hg/methyl Hg flux. Large plot studies (perhaps an acre in size) would also provide a better estimate of the cost of treatment.

2 INTRODUCTION

2.1 Overview

In 2010 we began trials of the potential efficacy of *in situ* soil amendments for mercury (Hg) and methyl Hg remediation in the Penobscot ecosystem. *In-situ* sorbent amendments have attracted recent attention as a low-cost, low-impact approach for remediation of contaminated sediments (Ghosh et al. 2011).

Field studies of methyl Hg concentrations and production rates in sediments and soils across the Penobscot system pointed to salt marshes as sites of particularly high methyl Hg production and accumulation. The large western platform of Mendall Marsh, which is itself the largest wetland system in the tidal Penobscot, was chosen as the study site.

Small plot studies were selected as a first approach to testing *in situ* amendments in Mendall Marsh. Small-scale studies offer advantages in cost and in the ability to replicate treatments, facilitating statistical tests of response. Four amendments were chosen for study – activated carbon (AC), biochar, iron (Fe), and lime, plus a control treatment, yielding five treatments. Activated carbon was formulated as SediMite™ granules, basically millimeter (mm)-sized particles weighted with clay and sand. Arrays of treatment plots were established at two sites in the marsh. The sites were chosen to represent two different biogeochemical conditions found in the marsh. At each site, three sets of plots were established, with each set containing each of the treatments. Overall, each treatment was applied to triplicate plots at each site, for a total of 15 plots per site or 30 total plots. Plot size was 1 square meter (m^2).

Plots were established, and treatments applied, in Sept. 2010. A suite of biogeochemical parameters was examined prior to application, and after 1 month (Oct. 2010), 9 months (June 2011), 1 year (Oct. 2011) and two years (Oct. 2012). Sample and data analysis is complete and reported below.

2.2 Background and Introduction to *in-situ* Sorbent Amendments

In-situ sorbent amendments have attracted recent attention as a low-cost, low-impact approach for remediation of contaminated sediments (Ghosh et al. 2011). Sorbent amendments are designed to increase contaminant binding to sediments, in turn reducing contaminant bioavailability and transport. The goal for this remediation approach is to reduce the bioavailability and mobility of contaminants *in situ*, rather than removing the contaminants *per se*. Sorbent materials, such as AC, biochar, organoclays, and functionalized substrates can be physically mixed into sediments, added to capping materials, or applied directly to sediment or marsh surfaces.

Sorbent amendments have been effective, both in laboratory and field trials, in reducing bioaccumulation and thus risk of hydrophobic organic contaminants (HOCs; Zimmerman et al. 2004; Millward et al. 2005; Werner et al. 2006; Cho et al. 2007, 2009; Beckingham et al. 2011). The main mode of action is a reduction in the pore water concentration of the toxicant that results in reduced uptake in benthic organisms and flux from sediment into water. Porewater concentrations are strong predictors of bioavailability. Based on trials to date, the application of AC to sediment appears to be the most efficient and cost-effective amendment in reducing bioavailability of HOCs. In laboratory trials, AC has generally reduced sediment pore water concentrations of polychlorinated biphenyl (PCBs), polycyclic aromatic hyrdrocarbon (PAHs), dioxins and dichloro-diphenyl trichloroethane (DDT) by 70% to 99%. Bioaccumulation of these contaminants by benthic test organisms was reduced by 70% to 90% (Ghosh et al. 2011).

A pilot-scale field trial at Hunters Point, California, showed that AC that was tilled into a contaminated mud flat has been physically stable and effective in reducing PCB bioaccumulation into benthic infauna for several years (Cho et al. 2007, 2009). Another pilot-scale field trial at Grasse River, New York, demonstrated that AC delivered to surficial sediment in a river was stable and reduced PCB pore water concentrations and uptake in caged oligochaetes (Beckingham et al. 2011). Both field studies observed no impact of AC amendment on existing benthic community which contrasts with laboratory studies that have reported potential negative impacts of AC on benthic organisms (Jonker et al. 2009). Although other remedies may be appropriate for some highly contaminated sites, these pilot studies demonstrate that exposure of HOCs from moderately contaminated sediments may be managed effectively through activated carbon amendment. Subsequent work has confirmed the efficacy of *in situ* AC amendments in remediation of risk from other chlorinated organics (Josefsson et al. 2012; Cornelissen et al. 2012).

Until recently, sorbents have not been have not been widely tested for the remediation of sediment contaminants other than HOCs, including mercury. Methyl Hg has similar partitioning and bioaccumulation characteristics to PCBs. Like PCBs, the main goal in Hg remediation is to reduce risk from its highly bioaccumulative form, methyl Hg (Munthe et al 2007; Wiener et al 2008). AC is commonly used in water treatment for removal of Hg, a soft metal with strong binding constants for ACs (Gomez-Eyles et al. in prep). methyl Hg exhibits other behaviors similar to PCBs, particularly a relatively high K_{ow} (octanol-water partition coefficient) (for a metal; Faust et al. 1992).

Further, the concentration of natural organic matter in sediments is a strong predictor of K_D for both total Hg and methyl Hg (Orginc et al. 2007; Hammerschmidt et al. 2004, 2006; Hollweg et al. 2010). The sediment:water partition coefficient for Hg or methyl Hg can be a strong predictor of bioavailability to benthic fauna (Wang et al. 1998; Williams et al. 2010).

These characteristics led us to believe that AC amendment might be effective in Hg remediation in contaminated sediments and soils, by reducing pore water Hg and methyl Hg concentrations. If AC or other amendments can reduce pore water Hg and methyl Hg concentrations, and/or enhance partitioning to sediments, they should be effective in reducing bioavailability to organisms. The bioaccumulation of methyl Hg by polychaetes (Wang et al. 1998), amphipods (Lawrence and Mason 2001) and sipunculans (Zhong and Wang 2008) is negatively related to sediment organic content.

For moderately contaminated sediments and soils where direct toxicity to invertebrates is not a concern, risk derives mainly from the bioaccumulation of methyl Hg (Wiener and Suchanek 2008). Therefore a reasonable remediation goal in these areas is to reduce methyl Hg bioavailability and bioaccumulation, rather than to reduce total bulk Hg concentrations in sediments or soils.

Currently, there are few remediation options for sediment and soil Hg contamination, short of dredging and capping. Dredging can achieve mass removal of Hg from a site (Hosokawa et al. 1993; Wang et al. 2004), but may resuspend and mobilize contaminants (Bloom and Lasorsa 1999; Kim et al. 2006). *In-situ* capping can be a low cost remediation practice and may result in fewer adverse environmental impacts than dredging (Nichols et al. 1990; Palermo 1998). However, buried contaminants may be transported through the capping layer and enter into the overlying water through various natural processes such as bioturbation, tidal pumping, and groundwater flow (Liu et al. 2001). Regulations may not permit changes in elevation, and where they do, elevation changes may alter community structure. Capping may also impact the magnitude and depth of methyl Hg production (Johnson et al. 2010). Recent field studies show that thin-layer caps that include AC, and AC mixed into surface sediments have limited impact on benthic community structure and density, especially after some re-colonization time (Naslund et al. 2012; Kupryianchyk et al. 2011, 2012).

Sediment and soil amendments can be delivered with little physical disturbance. For example, these materials can be broadcast onto sediments and marsh surfaces. Materials can be formulated into weighted pellets for delivery, potentially improving retention and allowing them to sink into soft substrates, where pellets break up and mix into surface sediments over time via bioturbation and water and sediment movement. Delivered in this way, sorbents can provide a treatment approach that does not substantially disrupt the physical structure of marsh or benthic communities. Application is less energy-intensive and less expensive than traditional dredging or capping approaches to remediation. SediMite™ is a patented technology for this delivery method. Challenges with surface AC amendments include retention and potential impacts on sediment biogeochemistry and benthic communities.

Over the past three years, we have begun to test the efficacy of sorbent amendments for Hg remediation. Initial trials were done in sediment-water microcosms, using sediments from multiple contaminated sites, and using multiple amendment types. Three field trials are complete or underway, including the Penobscot study. One field trial was conducted in 2010 and 2011 in a Hg-contaminated tidal creek in Maryland, funded by the Dept. of Defense. Another trial began in summer 2012 in a Hg-contaminated salt marsh in New Jersey.

2.3 *In-situ* Sorbent Amendments for Hg remediation: Results from prior microcosm studies

We initially evaluated the efficacy of sediment amendments for Hg remediation using sediment:water microcosms. Multiple types of sediment amendments were tested, including AC, for Hg and methyl Hg exposure reduction, using a study design that combines sediment/water microcosms with 14-day bioaccumulation assays. Our key end points were pore water Hg and methyl Hg concentrations and bioaccumulation. The deposit-feeding worm *Lumbriculus* was chosen as a test organism, because of its tolerance for low salinities, and because the organism directly ingests contaminated sediments. Sediments from four contaminated sites were tested, including two estuarine and two freshwater sediments. The effect of amendments on both sediment chemistry and bioaccumulation were examined concomitantly. This design allowed us to examine multiple lines of evidence for exposure reduction including pore water concentrations, sediment water partitioning, and bioaccumulation. It also allowed us to evaluate any impacts of the amendments on net methyl Hg production and sediment biogeochemistry.

Overall, four sets of microcosm studies were conducted, using Hg-contaminated sediments from South River, Virginia, a contaminated lake, estuarine Canal Creek in Chesapeake Bay, and creek sediments from tidal Berry's Creek in New Jersey. The sorbents tested included particulate AC, an organoclay, and proprietary sorbents designed for commercial Hg removal. Particulate AC (TOG 80 × 235 mesh; particle size 75–300 micrometer (µm)), referred to here as AC, was obtained from Calgon Carbon Corporation. For the Canal Creek microcosm study, the AC was formulated as SediMite^{TM} containing 60% AC by weight. SediMite^{TM} is a granular material that has been developed with support from an Environmental Protection Agency Small Business Innovation Research (EPA SBIR) grant and a Strategic Environmental Research and Development Program (SERDP) project (ER-1491) by Charles Menzie (formerly at Menzie-Cura) and Upal Ghosh (UMBC) to deliver a variety of treatment materials (including AC) to sediments contaminated by organic chemicals and metals. An organoclay developed as an adsorption media for mercury, denoted as MRM, was purchased from CETCO. Thiol-SAMMS® (TS), is a thiol-functionalized mesoporous silica purchased from Steward Environmental Solutions and used in a powder form (<45 µm). The uptake capacity of mercury by Thiol-SAMMS® is high, approximately 600 mg/g[40]. Ambersep^{TM} GT74, is a commercial ion exchange resin manufactured by Rohm and Haas Company for Hg removal from solutions and gaseous streams. For the microcosm study, GT74 was crushed with a mortar and pestle and then sieved thru a 60 *µ*m sieve. Isotherm studies were conducted separately to ascertain the effectiveness of Hg and methyl Hg sorption by each amendment (Gomez-Eyles et al. in prep.). In most cases, the binding capacity was enhanced at lower particle sizes.

Sorbent amendments were effective in reducing methyl Hg uptake, and to a lesser extent inorganic Hg uptake, by *Lumbriculus* (Figure 19-1). AC formulated as SediMite™, and Thiol-SAMMS® were the most effective additives. On average, amendments were twice as effective in reducing methyl Hg uptake as inorganic Hg. AC reduced methyl Hg concentrations in pore waters, relative to unamended controls, by 50% to 95%, and reduced bioaccumulation of methyl Hg by *Lumbriculus* by between 30% and 90%. The mechanism appears to be mainly via reductions in methyl Hg bioavailability to worms, rather than by reductions in sediment methyl Hg production or bulk sediment methyl Hg concentration. The effectiveness of amendments in reducing bioaccumulation was well-correlated with their effectiveness in increasing sediment:water partitioning, especially of methyl Hg. Contaminated sediments where natural methyl Hg partitioncoefficients are relatively low appeared to be most effectively treated. A detailed description of the study and results is provided as a separate submitted manuscript (Gilmour et al. in review).

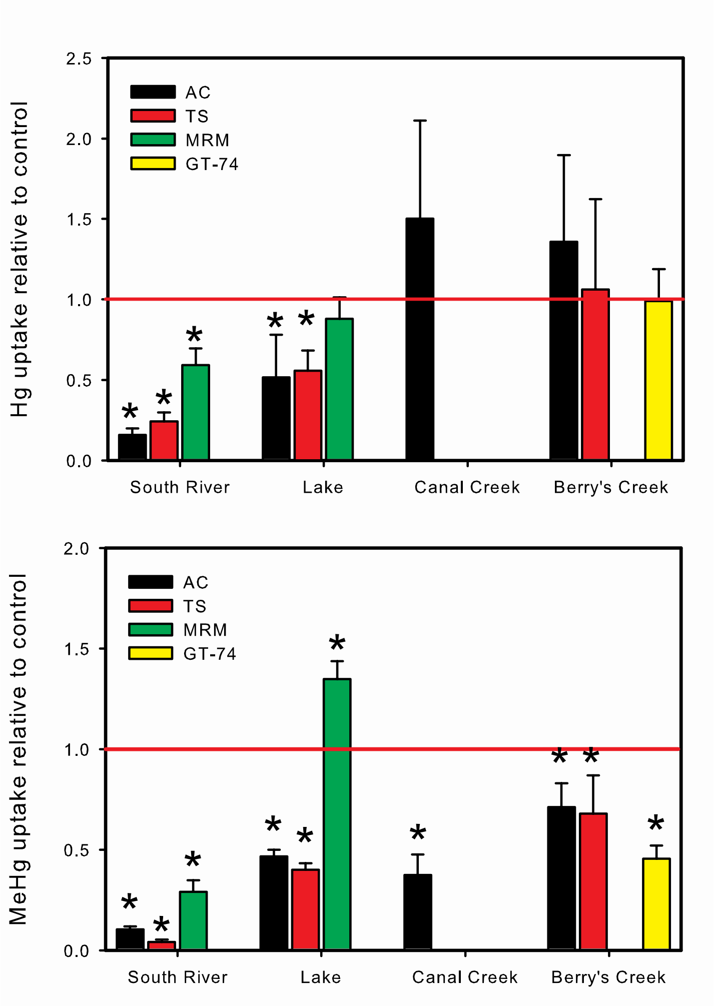


Figure 19-1. Influence of sediment amendments on inorganic Hg (top) and methyl Hg (bottom) uptake by Lumbriculus in a series of microcosm studies. *Lumbriculus* uptake data are shown as a fraction of uptake in unamended control microcosms (shown as red lines). AC = particulate activated carbon (except for Canal Creek, where AC was formulated into SediMite™ pellets); TS = Thiol-SAMMS® ; MRM = Mercury Reduction Medium; GT-74 = Ambersep^{TM} GT74. Starred values are significantly different from controls based on ANOVA (**α** <0.05) and Student-Newman-Keuls comparisons. Bars show the means (± 1 SD) of 5 replicate treatment microcosms, normalized to the mean value of 5 control microcosms, except Canal Creek, where bars show the average of 15 microcosms across three AC treatment levels. Lower values reflect more effective treatment.

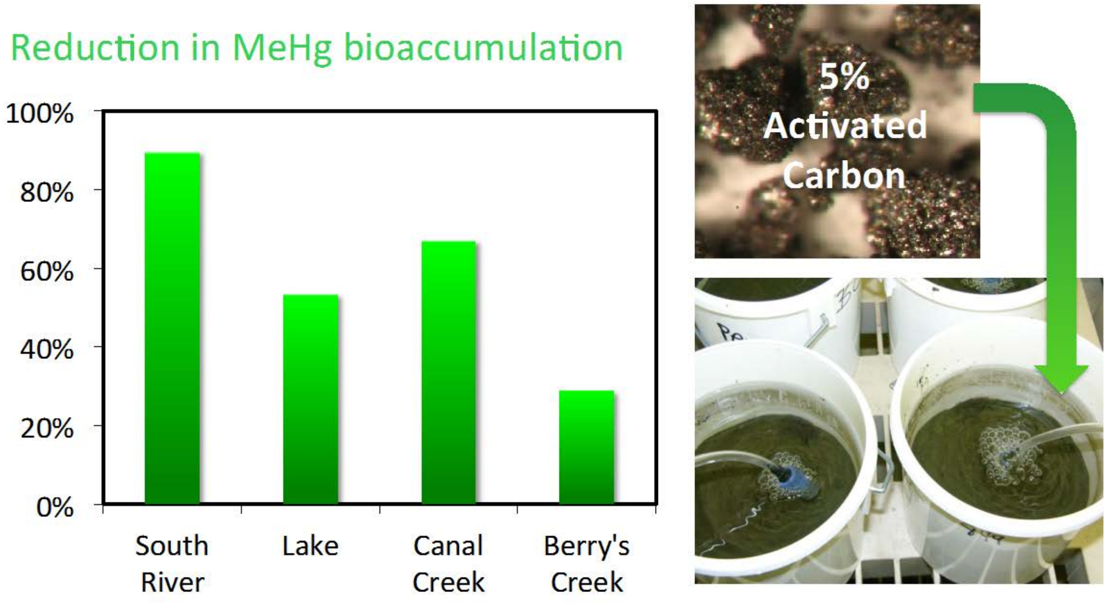


Figure 19-1A. Synthesis of the efficacy of activated carbon amendments in reducing methyl Hg bioaccumulation by benthic infauna, based on data in Figure 19-1.

2.4 Mendall Marsh Small Plot Amendment Study

2.4.1 Study Design and Methods

2.4.1.1 Site Selection

Two sites on the main west platform of Mendall Marsh were chosen for study. Both sites were accessible on foot, on the main, flat part of the marsh, well away from the Marsh River or any major tidal guts. The sites were chosen to represent two different major habitats in the marsh. Both sites contain elevated Hg levels in surface soils, and produce substantial methyl Hg from that contamination.

The site designated “West” is in a relatively low elevation part of the marsh platform. Vegetation is low (~1-2’), and dominated by *Spartina patens* (salt marsh hay), *Agrostis stolonifera* (creeping bentgrass), and *Eleocharis uniglumis* (spike rush). There are many open pools or salt pannes in the area, and soil pore waters were generally highly sulfidic. Salt pannes clearly stayed wet, based on the build-up of classic yellow/white elemental sulfur precipitate and the growth of purple, green, yellow and white sulfur oxidizing bacterial mats in the pannes.

The site designated “Central” is somewhat drier and less reducing than West. It has moderate height (2-3’) vegetation, dominated by *Juncus gerardii* (saltmarsh rush), *Agrostis stolonifera* (creeping bentgrass), *and Schoenoplectus pungens* (three square). There are no standing pools of water in this area. Sulfide is readily measureable in pore waters, but concentrations are lower than at West. Data on the chemistry of each site can found in the results section of the report.

At the west site, plywood sheets were used to stand and kneel on during work on the plots, to minimize disruption and avoid getting stuck in the mud. Soils were hard enough at the Central site that plywood sheets were not needed.

2.4.1.2 Sorbent Amendments

The sorbent amendments used in the plots study are given in Table 19-1. The sorbents tested included particulate AC (formulated into SediMite™), biochar, iron and lime. The two carbon sorbents were chosen based on our isotherm measurements of the sorption behavior of a suite of activated carbons and biochars (Gomez-Eyles et al. in prep). Materials chosen for this study were selected for high binding strengths and ready availability.

SediMite™ is a patented mixture, formulated from a sorbent plus clays and sand as a weighting agent. It is custom made for each application, and can made from any type of carbon sorbent. For this study, SediMite™ was formulated from coconut shell activated carbon (80-235 mesh), obtained from Prominent, Inc. The final material contained 50% AC on a dry weight basis, with the remainder made up of sand and clays. It was produced in the form of cylindrical pellets 3 mm in diameter with an average length of 10 mm. Water was added to form the pellets. They were dried to a final moisture content of about 15% to keep down dust

Lime was Pennington pelletized Quick Lime (mainly $CaCO_3$]) purchased from Lowes. Its density was about 1 g/cc. It was used in the size supplied, about 100 pellets per gram. Prior to use in the plots, the immediate effect of the lime on soil pH was tested by mixing 10 g wet site soil with 10 ml of deionized water and 100 to 500 mg of lime pellets in a container, and following pH over 48 h. This range was chosen to be about 10 times the suggested range of application rates for a 1 pH unit increase in lawn soils. However, the buffering capacity of seawater and carbonate saturated marsh soils is much higher than that of lawn soils. The pH of a site water sample saturated with quick lime was 7.5. The lime additions increased the pH of the soil slurries by 0.1 to 0.4 pH units over 48h. The final lime amendment was chosen to be 500 g per plot. To calculate the lime amendment, we assumed that the lime would affect pH in the upper 1 cm of soil; a plot contains roughly 100,000 cc of soil in the upper 1cm of depth. To match the upper application rate in the slurry test, we used 50 mg/cc of soil, or 500 g of lime per plot.

Iron was added as crystalline $FeCl_2$ $4H_20$ (ferrous chloride tetrahydrate) purchased from Fisher Scientific.

The biochar was pine dust biochar obtained from Jonah Levine at Biochar Engineering Corp. Particle size was sub-mm. The BET surface properties of the char ranged from 125 -350 square meter per gram (m^2/g). BET is an analysis technique for the measurement of the specific surface area of a material (Brunauer et al. 1938). Fixed carbon content was 85% to 95%.

2.4.1.3 Study design and plot siting

At each of the two study locations, 15 plots were established. Plot size was 3’ X 3’ square. Plots were set up in 3 rows of 5 plots each, each row containing one replicate of each treatment (Figure 19-2). The location of each treatment randomized within each row, and the direction and orientation of rows was also randomized within each site. In siting rows, consideration was given to keeping the vegetation mix as similar as possible across rows, to avoiding ditches, and to avoiding the many salt marsh pools at the West site.

Plots were laid out using measuring tape and marker flags. The plots were edged with plastic landscape edging with a sharp lower edge. Edging was installed by cutting through the marsh soil with a saw, inserting the edging and banging it down with a rubber mallet. Edging was ~20 cm deep, and purchased in 6’ lengths cut to needed size. About 10 cm of edging was left above the surface of the soil to limit the horizontal movement of amendments over the marsh surface across adjacent plots.

2.4.1.4 Loading Rates

Amendment dosing for the plot study was based on field and laboratory treatment studies of the use of AC amendments for PCB remediation (see review in Ghosh et al. 2011); and our own microcosm treatability studies of AC remediation of Hg and methyl Hg in other contaminated sediments and soils (Gilmour et al. in review). We did not do a site-specific microcosm treatability study for Mendall Marsh. In early studies of PCBs and Hg, dosing rates were first estimated to roughly match the total organic carbon content of contaminated sediments, typically ~5% of dry weight (dry wt.). However, we found that amendment loadings below the TOC content of sediments were also effective. For example, AC amendment as low as 2.2% of dry wt. was effective in reducing methyl Hg concentrations in pore waters, and uptake by *Lumbriculus,* in contaminated estuarine sediments with about 10% loss on ignition (Gilmour et al. in review).

For this study, the target loading rate for amendments, was 5% AC by dry weight of soil in the target treated zone (which we considered the top 10 cm of soil). The loading rate for SediMite™ was calculated as follows:

Loading rate of SediMite™ for top 10cm.		
Volume of sediment treated per square meter (1 sq. m. x 0.1m)	0.1	m^3
Dry mass of sediment to be treated/sq. m. (measured dry density of soil = ~0.2 kg/L)	20	Kg
Dry mass of AC to be added (5% of dry mass of soil)	1.0	Kg
Weight of SediMite™ per square m, at 5% AC by dry weight of soil (50% AC in dry SediMite™; SediMite™ used had 15% water content)	2.3	Kg

Biochar amendments were calculated the same way, assuming the char was entirely organic carbon. Thus, the mass of organic carbon added to SediMite™ and biochar plots was designed to be the same.

With little experience in the use of either lime or iron to mitigate Hg risk in soils, the loading levels for these amendments were guesses. The lime addition was calculated to increase the pH of the soil by about 1 pH unit if all of the lime remained in place dissolved. The Fe addition level was chosen to match the mass of the organic carbon additions.

Table 19-1: Plot amendments and loading rates.

Treatment	Loading (kg/plot)	Hg in amendment material (ng/g dry wt.)
Control	None	
$FeCl_2.4H_2O$	2.3 (equivalent to 1 kg Fe)	
Lime	0.5	<1
Biochar	1	<1
SediMite™ (Activated Carbon)	2.3	4
Sand	2” cap (150 lbs/plot)	<1
Clay	2” cap (12.5 cubic liters/plot)	7

2.4.1.5 Amendment application

Amendments were applied by hand to plots on the morning of Sept. 23, 2010. Application was made during a tidal cycle where the marsh was not overtopped by tide. A known weight of amendment was prepared for each plot, and these were broadcast by hand over the plots. The fine amendments readily slipped through the vegetation onto the soil surface.

SediMite™ pellets were easy to broadcast by hand. Use of AC in this form avoids problems associated with applying ground activated carbon or biochar, which are statically charged powders unless wetted. Plots were visibly black after application.

The biochar was mixed 1:1 with site water (from a nearby tidal gut) prior to application, in order to avoid the biochar blowing away. It was quite clumpy after wetting. A heavy rake was used to manually even the layer. Plots were visibly black after application.

Once amendments were in place, plots were gently “gardened” by hand with a piercing tool to attempt to allow some of the amendments to enter surface soils. The depth of the tool used was about 10 cm. Small cores taken after the “gardening” showed that the process was not very effective in moving amendments into the soils, i.e. a very small fraction of cores sampled showed any amendment visually below the surface of the soils.

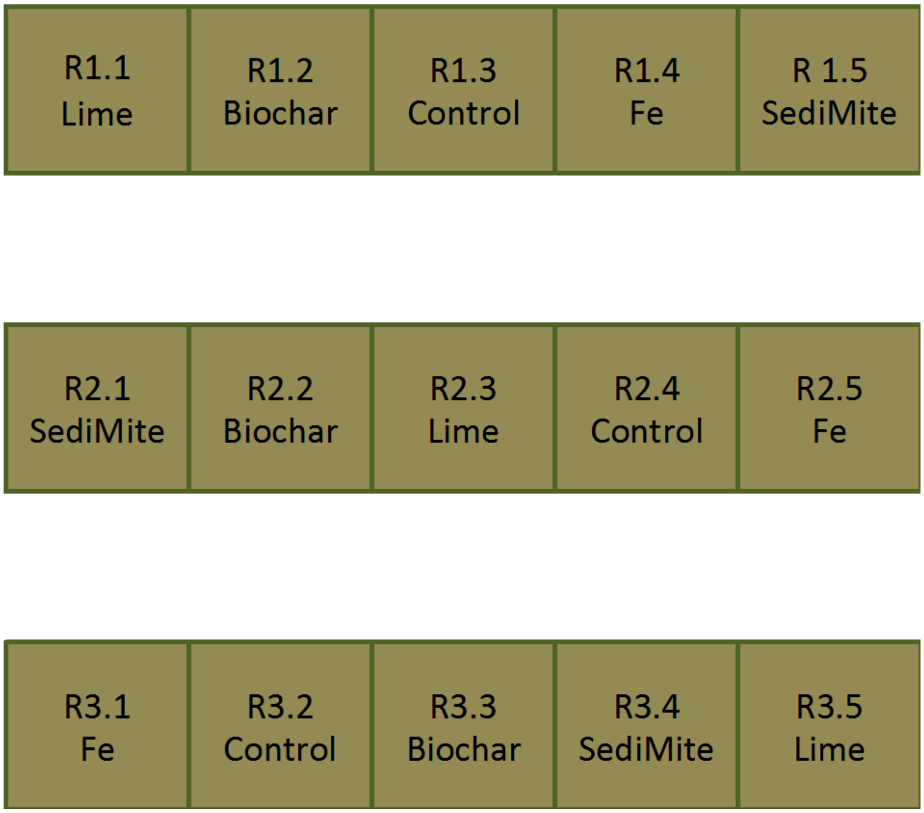
After application, the plots treated with biochar or SediMite™ were visibly black. Lime pellets remained un-dissolved on the sediment surface for at least 24 h. The $FeCl_2$ addition rapidly dissolved in the wet surface of the marsh.

Amendments were applied during a part of the monthly tidal cycle when the marsh was not overtopped with seawater at high tide. However, the marsh surface is always wet, and the marsh also received heavy rain on the night of the application. Visually, the amendments stayed in place in the plots during that night. Biochar and AC plots retained black surfaces, and black color and/or pellets were not visible in adjacent plots of marsh. The SediMite™ pellets had begun to break up after 24 h, and were not visible as pellets when we resampled the plots at 1 month. Over the 2 years we have observed the plots, the amendments appear visually to have been largely retained in the plots. At each sampling point, a variety of measurements were made to assess retention of the amendments in the plots. For Fe and lime amendments, Fe and Ca in soils and pore waters were measured. For the carbon amendments, cores were photographed and the depth of black color measured. The amount of carbon black in the top 3 cm of soil was also measured quantitatively. The depth to which the visible black color has penetrated has increased through time, to almost 2 cm in fall 2012.

2.4.1.6 Study design and plot siting

At each of the two study locations, 15 plots were established. Plot size was 3’ X 3’ square. Plots were set up in 3 rows of 5 plots each, each row containing one replicate of each treatment (Figure 19-2). The location of each treatment randomized within each row, and the direction and orientation of rows was also randomized within each site. In siting rows, consideration was given to keeping the vegetation mix as similar as possible across rows, to avoiding ditches, and to avoiding the many salt marsh pools at the West site.

Plots were laid out using measuring tape and marker flags. The plots were edged with plastic landscape edging with a sharp lower edge. Edging was installed by cutting through the marsh soil with a saw, then inserting the edging manually into the cut with the aid of a rubber mallet. Edging was ~20 cm deep, and purchased in 6’ lengths cut to needed size. About 10 cm of edging was left above the surface of the soil to limit the horizontal movement of amendments over the marsh surface across adjacent plots.



R1.1 Lime	R1.2 Biochar	R1.3 Control	R1.4 Fe	R 1.5 SediMite
R2.1 SediMite	R2.2 Biochar	R2.3 Lime	R2.4 Control	R2.5 Fe
R3.1 Fe	R3.2 Control	R3.3 Biochar	R3.4 SediMite	R3.5 Lime

Figure 19-2. Physical design of remediation plots at each site. The design was the same at both sites. Within each site, rows were oriented in random directions. Plot size is 3’ X 3’.

2.5 Capping study

In addition to the fully designed amendment studies, a small trial of the effect of sand or silt capping was done in single plots at each of the study sites. For this study, the plots were somewhat larger, 4’ X4’. At each site (West and Central), one plot was capped with play sand purchased from Lowes; one plot was capped with a silt/clay mix obtained from a local surface mine, and one plot was left un-amended as a control. This yielded a total of just 6 plots. Loading rates were roughly 100 lbs of material per plot, resulting in about 1-2 inches of cap. Caps were applied in Sept. 2010.

These plots were only sampled once in Oct. 2010, one month after application. Because the capping did not appear to be effective in reducing pore water Hg or methyl Hg in soils below the cap (see results below), and because the some of the soil amendments were effective, the capping study did not continue. However, the capping materials remain in place and could be re-evaulated in 2013 if desired; which would be almost 3 years after the materials were applied.

2.5.1 Plot sampling

Time line. Plots were sampled prior to application of amendments, and then at one month, nine months, 1 year, and 2 years later. Dates are given in Table 2.

Table 19-2: Time line for amendment plots.

Event	**Date**
Plots sited, edging installed	9/20-21/2010
Pre-amendment sampling	9/21-22/2010
Application of amendments	9/23-24/2010
One month sampling	10/18-19/2010
9 month sampling	6/6-7/2011
One year sampling	9/27-29/2011
Two year sampling (control, AC and biochars plots only)	9/24-25/2012

Parameters sampled. The study sampling design was based on two objectives. The first was to determine if amendments reduced potential risk from methyl Hg by reducing pore water methyl Hg concentrations and sediment water partition coefficients. A secondary objective was to evaluate the impact of amendments on sediment biogeochemistry.

A separate evaluation of plant density and community structure in the plots was done by Prof. Aram Calhoun of the University of Maine and Dr. Dianne Kopec (PRMS). The plots are probably too small to assess animal community structure of methyl Hg bioaccumulation; however, amphipod samples were collected from carbon amendment and control plots in Sept. 2012 by Kopec. Results are pending.

Thus our key end points in this study were pore water methyl Hg concentrations and sediment water partition coefficients. Both provide predictive information on the bioavailability of methyl Hg to biota. Additionally, pore water nutrient concentrations may provide information the impact of amendments on nutrient availability for plant growth. Redox indicators like sulfide and Fe can also help assess the potential impact of amendments on plant and animal communities.

The tables below list the analytes sampled and how they were processed and preserved. Sample preparation and analytical methods are given in detail in the SERC project standard operating procedures (SOPs).

Table 19-3: Parameters measured in soil solids. For the plots studies, all samples were taken from 0-3 cm depth cores. All core samples were place in coolers on ice in the field, and frozen within hours of collection.

Parameter	Units
Bulk density, wet	g wet weight/cc
Bulk density, dry	g dry weight/cc
Porosity	ml/cc
Loss on ignition (LOI)	%
Total Hg (THg)	ng/g dry wt.
methyl Hg	ng/g dry wt.
Acid-volatile sulfides (AVS)	µmoles/g dry wt.
Chromium-reducible sulfides (CRS)	µmoles/g dry wt.
Extractable FeII	µmoles/g dry wt.
Extractable FeIII	µmoles/g dry wt.
Elemental Analysis (Al, Ca, Fe, K, Mg, Mn, Na, P, S, Si)	mg/g dry wt.

Table 19-4: Parameters measured in soil pore waters. For the plot studies, all pore water samples were taken from sippers inserted to 2.5 cm. For the volume of pore water sampled, this should represent roughly the 0-5 cm soil depth interval. All samples were filtered to 0.45 µm.

Parameter	Units
Total Hg	ng/L
methyl Hg	ng/L
Sulfide	µM
Anions (Br, Cl, F, NO_2, NO_3, PO_4, SO_4)	µM
Nutrients (NH_4, NO_2+NO_3, PO_4)	µM
Dissolved organic carbon (DOC)	mg C/L
DOC spectral properties:	
Absorbance @ 280 nm (aCDOM 280)	m-1
Absorbance @ 440 nm (aCDOM 440)	m-1
Spectral slope, 275-295 nm	nm-1
Spectral slope, 300-700 nm	nm-1
Spectral slope, 350-400 nm	nm-1
Slope ratio (275-295/350-400)	unitless
Elemental Analysis (Al, Ca, Fe, K, Mg, Mn, Na, P, S, Si)	mg/L

Table 19-5: Filtration and preservation methods for parameters measured in soil pore waters. All samples were filtered with Whatman GD/X filters (0.45 micron).

Parameter	Preservation	Storage
Total Hg	0.5% HCl, refrigerate	PETG bottles,
methyl Hg	0.5% HCl, refrigerate	PETG bottles,
Sulfide	Sulfide anti-oxidant buffer	50 ml polypro tubes, analyze same day
Anions	Refrigerate	15 ml polypro tubes
Nutrients	Freeze	7 ml autosampler vials
Dissolved organic carbon (DOC)	Refrigerate until spectral properties done (24-48 h), then freeze	15 ml polypro tubes
DOC spectral properties	Refrigerate	Analyze within 48 h
Elemental Analysis	0.5% HCl, refrigerate	15 ml polypro tubes

Sampling methods. Study sites were accessed by walking across the marsh from Route 1A. For each sampling period, soils and soil pore water were collected over 1-3 days. Basic field parameters collected included surface soil temperature (~2 cm depth), air temperature, soil surface pH, sampling time, etc. Soil pH was measured with a calibrated Oakton pH spear (designed for wet solid samples); four measurements were made in each plot on each date.

Non-contaminating, Hg clean techniques were used through all stages of sample collection, storage, handling and analysis. Samples were collected using methods that minimized contamination through the use of clean sampling equipment, sample containers, gloves, and plastic bags to prevent sample contact with unclean surfaces. Sample integrity was carefully maintained throughout the sampling process, from field collection to delivery of samples to the laboratory. All samples were stored away from sunlight to limit the effect of photo degradation, biological activity and assure sample integrity. Samples were individually numbered and tracked by each participating laboratory.

Soil interstitial waters (pore waters) were collected for the plot study using stainless steel push point sippers (http://www.mheproducts.com). The benefit of this procedure over other pore water collection method is little disturbance of the sediment/pore water strata and the ability to sample without exposure to the air. This technique is also fast and does not require the use of a glove box. Sippers work well in rooty, porous marsh soils, but are not suitable for fine-grained muds, which clog the slits in the sippers. Manufacturer instructions for use of push points sippers can be found at: www.mheproducts.com/MHE-instructions-ver-2.01.doc. Use of the sippers in SERC projects is described in detail in SOP:

“Extraction of Pore Water From In Situ Sediments Using Push Points.” In each plot, pore waters were extracted from 4 locations. At each location, the first 10 ml of sample was wasted as a rinse, and then next 30 ml were retained. Sulfide samples were filtered and immediately preserved in sulfide-antioxidant buffer in the field. The remaining pore water samples were kept in 60 cc syringes (without headspace) on ice in coolers in the dark until they were filtered and processes in the Winterport laboratory. All four samples were composited for filtration and analysis. Sample filtration and preservation usually occurred in the afternoon after morning collection.

Small surface soil cores were collected by hand using sharpened stainless-steel cork borers (2 cm diameter X 9 cm depth). Cores were placed on a tray and cut to 3 cm depth. Four cores from each plot were sampled and composited, yielding about 36 cc of material. Cores were place in vacuum ziplocks in the field and placed on ice in coolers in the dark. They were frozen upon return to the lab in Winterport, usually within a few hours. Cores were homogenized at SERC (under N_2) prior to analysis.

Table 19-6: **Sample preparation and analysis methods. All sample preparation and analysis performed at SERC unless noted. SERC SOPs are provided in the Appendix. Chesapeake Biological Laboratory(CBL) SOPs are available at: http://nasl.cbl.umces.edu/.**

Parameter	Sample Preparation Method	SERC Sample Prep SOP	Sample Analysis Method	Reference	SERC Analytical SOP
Filtered total Hg in water			OXIDATION, PURGE AND TRAP, AND COLD VAPOR ATOMIC FLUORESCENCE SPECTROMETRY or ICP-MS	EPA 1631	THg FIAS-ICP-MS OR HgT Tekran 2600
Filtered methyl Hg in water (Fmethyl Hg)	Distillation	methyl Hg Distillation Method	Ethylation, GC, CVAF or ICP-MS	EPA 1630	methyl Hg ET-GC-ID-ICPMS OR methyl Hg MERX ET-GC-ID-ICPMS
Total Hg in solids	Hot acid digest	Sediment and Tissue Digestion for Total Mercury	EPA 1631	EPA 1631	THg FIAS-ICP-MS
methyl Hg in solids (methyl Hg-solid)	Distillation	methyl Hg Distillation Method	EPA 1630	EPA 1630	methyl Hg ET-GC-ID-ICPMS OR methyl Hg MERX ET-GC-ID-ICPMS
Filterable sulfide	Preserve in fresh anti-oxidant buffer		Ion selective electrode	Brouwer and Murphy, 1994, Standard Methods 4500G	Analysis Of Dissolved Sulfide Ion In Aqueous Media Using Sulfide Anti-Oxidant Buffer And Sulfide Selective Electrode
Anions			Ion Chromatography	EPA 300.0A	Analysis Of Inorganic Anions In Aqueous Biogeochemical Samples By Ion Chromatography

Table 19-6: Sample preparation and analysis methods. All sample preparation and analysis performed at SERC unless noted. SERC SOPs are provided in the Appendix. Chesapeake Biological Laboratory(CBL) SOPs are available at: http://nasl.cbl.umces.edu/.

Parameter	Sample Preparation Method	SERC Sample Prep SOP	Sample Analysis Method	Reference	SERC Analytical SOP
Nutrients (Nutrient Analytical Services Laboratory at the University of Maryland Chesapeake Biological Laboratory)					
NH_4			phenol/hypochlorite method	Solorzano 1969; USEPA Method 350.1	CBL_Ammonium Method
NO_2+NO_3			cadmium reduction	USEPA Method 352.3	
PO_4			molybdate/ascorbic acid method	USEPA Method 365.1	CBL Orthophosphate Method
Dissolved organic carbon (DOC)			Shimadzu - catalytically-aided platinum 680°C combustion	Suzuki et al. 1992.	Determination Of Dissolved Organic Carbon By High Temperature Catalytic Oxidation And Quantification By A Non-Dispersive Infrared Detector
DOC spectral properties:			uv/vis spectrophotometry	Weishaar et al. 2003	
Elemental Analysis (Al, Ca, Fe, K, Mg, Mn, Na, P, S, Si)	Pore waters		ICP-AES	Lichte et al. 1987, EPA 200.7	ANALYSIS OF TRACE ELEMENTS BY INDUCTIVELY COUPLE PLASMA – ATOMIC
	Solids	Open Vessel Digestion of			

Table 19-6: Sample preparation and analysis methods. All sample preparation and analysis performed at SERC unless noted. SERC SOPs are provided in the Appendix. Chesapeake Biological Laboratory(CBL) SOPs are available at: http://nasl.cbl.umces.edu/.

Parameter	Sample Preparation Method	SERC Sample Prep SOP	Sample Analysis Method	Reference	SERC Analytical SOP
		Siliceous Sediment Samples for Elemental Analysis			EMISSION SPECTROPHOTOMETRY
Acid-volatile sulfides (AVS)			Cold-acid (6N HCl) distillation, sulfide trapping in SAOB, detection by selective ion probe	Fossing and Jorgensen 1989; Brouwer and Murphy 1994; Gilmour et al. 1998	Determination Of Acid-Volatile And Chromium-Reducible Sulfides From Sediments By Sequential Distillation, With SAOB Trapping And Determination Using Sulfide Selective Electrode
Chromium-reducible sulfides (CRS)			Hot-acid (1M Cr(II) in concentrated HCl) distillation, sulfide trapping in SAOB, detection by selective ion probe	Fossing and Jorgensen 1989; Brouwer and Murphy 1994; Gilmour et al. 1998	Same as AVS
Extractable FeII/FeIII	0.5 M HCl extraction and hydroxylamine (NH_2OH) oxidation		Ferrozine-HEPES/UV spectrophotometry at 562 nm	Stookey 1970; Lovley and Phillips 1986	Extraction and Analysis of Reactive Iron in Sediments and Soils by Colorimetric Ferrozine Analysis

2.6 Results of Plot Studies

2.6.1 Impact of soil amendments on Hg and methyl Hg in soil pore waters.

Carbon amendments were effective in reducing Hg and especially methyl Hg concentrations in pore waters at both study sites in Mendall Marsh. Lime and $FeCl_2$ amendments were not. AC applied after being formulated as SediMite™ pellets, gave the highest and most consistent reduction through time (Figures 19-3 and 19-5).

Ambient pore water Hg concentrations in unamended plots were somewhat higher at the Central site (25-70 ng/L); West control plots ranged from 15-25 ng/L. methyl Hg was also higher in Central pore waters (10-40 ng/L) compared to West (5-10 ng/L).

Across all four sampling dates, AC amendments resulted in significant reductions in pore water Hg and methyl Hg at both test sites in the marsh (Table 19-7). Biochar significantly reduced methyl Hg concentrations at both sites, and total Hg concentrations at Central. Biochar and AC amendments also resulted in significant reductions in pore water Hg and methyl Hg at most of the individual sampling time points (Table 19-8)

AC amendments reduced pore water methyl Hg concentrations at the both sites by >90% at the one month time point, and by 60% to 70% on average across all the four time points through two years (Figure 19-6; Table 19-8). At the one year time point, AC plots had about 75% less methyl Hg than control plots at West and 50% less at Central. On average, AC reduced total Hg in pore waters at both sites by 50% to 60%. Biochar was somewhat less effective that AC, but still provided on average 50% to 70% reductions in methyl Hg and 35% to 55% reductions in total Hg.

Lime and $FeCl_2$ additions had inconsistent effects across the sites and through time. On average, across all time points, neither amendment had a significant impact on either total Hg of methyl Hg concentrations. Analysis of metals in soils showed that Fe was retained in the plots at levels significantly above controls for the 24 month duration of the study. The same was true for Ca in the lime-treated plots (see Figures 19-15 and 19-16 and data appendix).

It is worth mentioning that across the two years of this study, pore water THg and methyl Hg concentrations dropped in control and most treatment plots, especially at the West site. Whether this reflects recovery from initial disturbance of plots, or a larger trend across Mendall marsh deserves further analysis.

2.6.1.1 Statistical analysis

To evaluate the efficacy of the various amendments, the target variables were total Hg and methyl Hg in pore water, and the sediment:water partition coefficient for each.

Differences among treatments were assessed by ANOVA by treatment on post-treatment sampling dates. Each site was analyzed separately, using the full data set (i.e. individual values for each plot for n=15 plots and each date). Comparisons among treatments were made using pairwise Student's t-test. Alpha was set at < 0.05 for both

ANOVA and the t-tests. ANOVAs and comparisons by treatment were run for each variable on each sampling date. To assess the effectiveness across the entire study, an analysis across all four sampling dates was run. Statistics were performed using JMP (SAS Institute, Inc.).

All variables were tested for normalcy prior to analysis. Determination of normality is subjective; but here was generally based on visual distribution, and skewness and kurtosis <1. Most variables were log transformed before further analyses. The distribution of log-transformed variables was also evaluated. Full results of ANOVAs and t-test comparisons are given in a separate spreadsheet, and highlighted in tables and graphics below.

Table 19-7A: Overall average Hg and methyl Hg concentrations in surficial (0-5cm) pore waters in Mendall Marsh plot amendment study, and average percent reduction compared to controls. Averages and comparisons are for four sampling dates through Sept. 2012 for controls, biochar and SediMite™ treatments; and for three sampling dates through Sept 2011 for Fe and lime. Average reductions were calculated by averaging the reductions from each individual date. Comparisons among treatments are shown with the connecting letters comparison; treatments not connected by the same letter are significantly different at alpha = 0.05 based on ANOVA/t-test (see text).

Site	Treatment	Filtered total Hg (ng/L)	Avg. % Reduction	Connecting Letters Comparison	Filtered methyl Hg (ng/L)	Avg. % Reduction	Connecting Letters Comparison
CENTRAL	Control	34.2		A	21.8		A
	$FeCl_2$	21.4	35%	AB	14.6	27%	A
	Lime	39.2	10%	A	21.9	18%	A
	Biochar	18.1	52%	B	7.0	66%	B
	SediMite™	13.0	59%	B	5.2	67%	B
WEST	Control	14.1		AB	6.3		A
	$FeCl_2$	14.5	7%	AB	10.3	-49%	A
	Lime	21.1	-35%	A	9.4	-40%	A
	Biochar	9.5	36%	BC	2.8	56%	B
	SediMite™	6.6	51%	C	2.1	66%	B

Table 19-7B: Average partition coefficients for Hg and methyl Hg in surficial soils in the Mendall Marsh plot amendment study, based on the same data, sampling dates, and statistical approach as Table 19-7A.

Site	Treatment	KD total Hg	Avg. % Increased	Connecting Letters Comparison	KD methyl Hg	Avg. % Increase	Connecting Letters Comparison
CENTRAL	Control	2.8E4		AB	3.1E3		C
	$FeCl_2$	1.1E4	83%	AB	2.0E3	133%	BC
	Lime	7.6E3	-4%	B	1.4E3	3%	C
	Biochar	3.9E4	54%	A	9.1E3	256%	A
	SediMite™	3.1E4	47%	AB	5.0E3	365%	AB
WEST	Control	2.0E4		AB	3.7E3		B
	$FeCl_2$	3.0E4	83%	A	7.5E3	56%	B
	Lime	1.1E4	-33%	B	4.0E3	7%	B
	Biochar	4.5E4	94%	A	1.4E4	250%	AB
	SediMite™	3.4E4	79%	A	2.9E4	1136%	A

Table 19-8: Percent reductions in total Hg and methyl Hg in surficial (0-5cm) pore waters in Mendall Marsh plot amendment study, on each of the four individual sampling dates. Negative values represent an increase in concentration. Average reductions were calculated by averaging the reductions in each individual plot. Significant changes relative to control are starred, based on ANOVA and t-test comparisons of pairs at alpha <0.05.

Treatment	Date	West		Central	
		Total Hg	methyl Hg	Total Hg	methyl Hg
Fe	Oct 2010	-54%	-146%	65% *	62% *
	June 2011	13%	-54%	29%	29%
	Sept 2011	62%	53%	11%	-10%
Lime	Oct 2010	-108%	-106%	-12%	-3%
	June 2011	1%	-25%	25%	29%
	Sep. 2011	4%	11%	16%	28%
Biochar	Oct 2010	-16%	36%	40%	69% *
	June 2011	37%	62%	54%	77% *
	Sept 2011	54%	51%	42%	49%
	Sept 2012	68%	76%	70%	69%
AC	Oct 2010	72% *	98% *	67% *	91% *
	June 2011	48% *	71% *	65% *	85% *
	Sept 2011	55%	74% *	45%	43%
	Sept 2012	28%	21% *	61%	50%

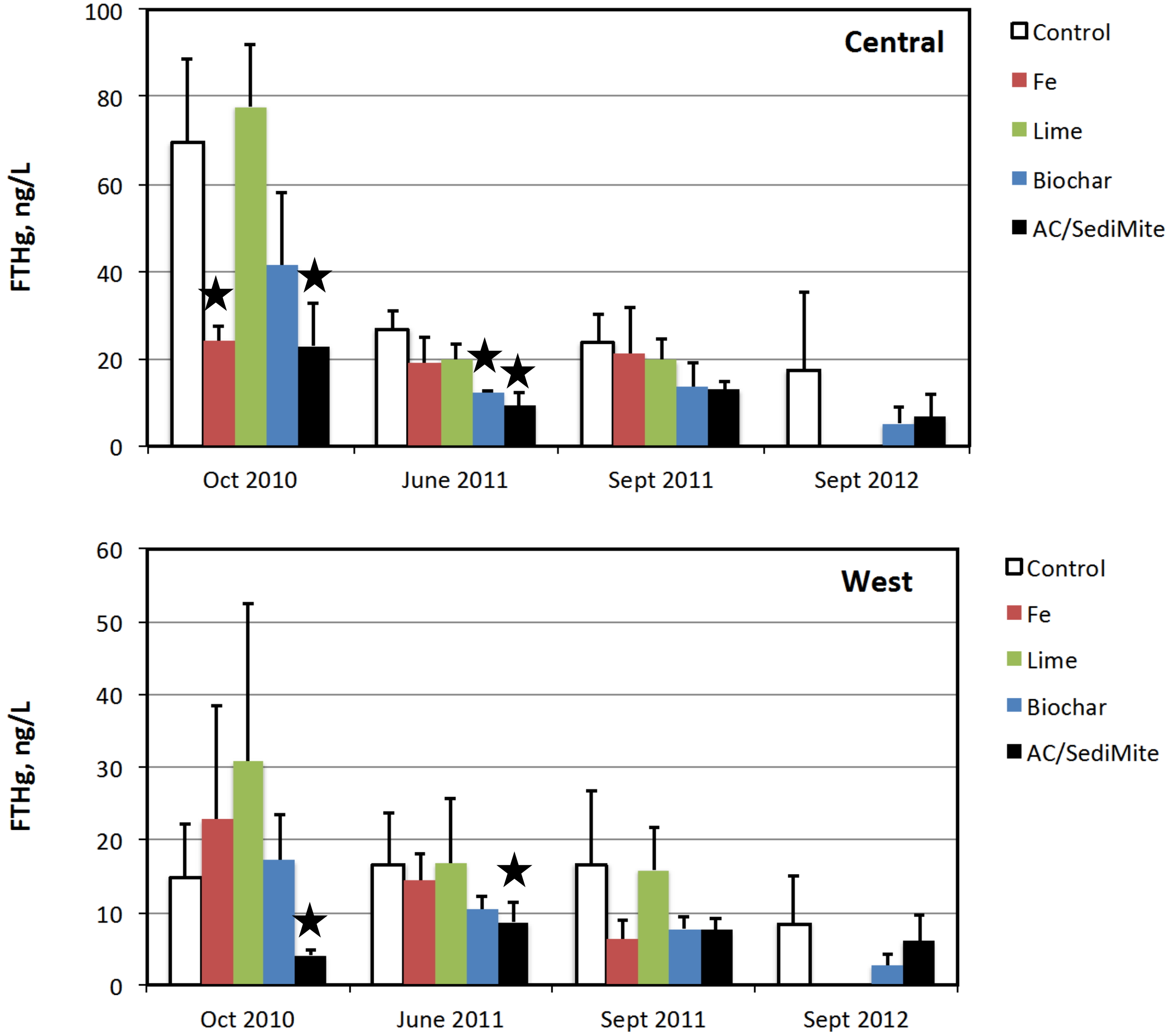


Figure 19-3. Pore water total Hg concentration (filtered total Hg) in surface soils (0-5 cm) of amendment plots over time. Plots were amended in Sept. 2010, one month prior to the first sampling date. All bars are the averages of values from triplicate plots for each treatment, with standard deviation. Samples from individual plots are composites of four samples. Treatments that are significantly different from the control on any individual date ($p<0.05$ by pairwise Student's t-test) are designated with a star.

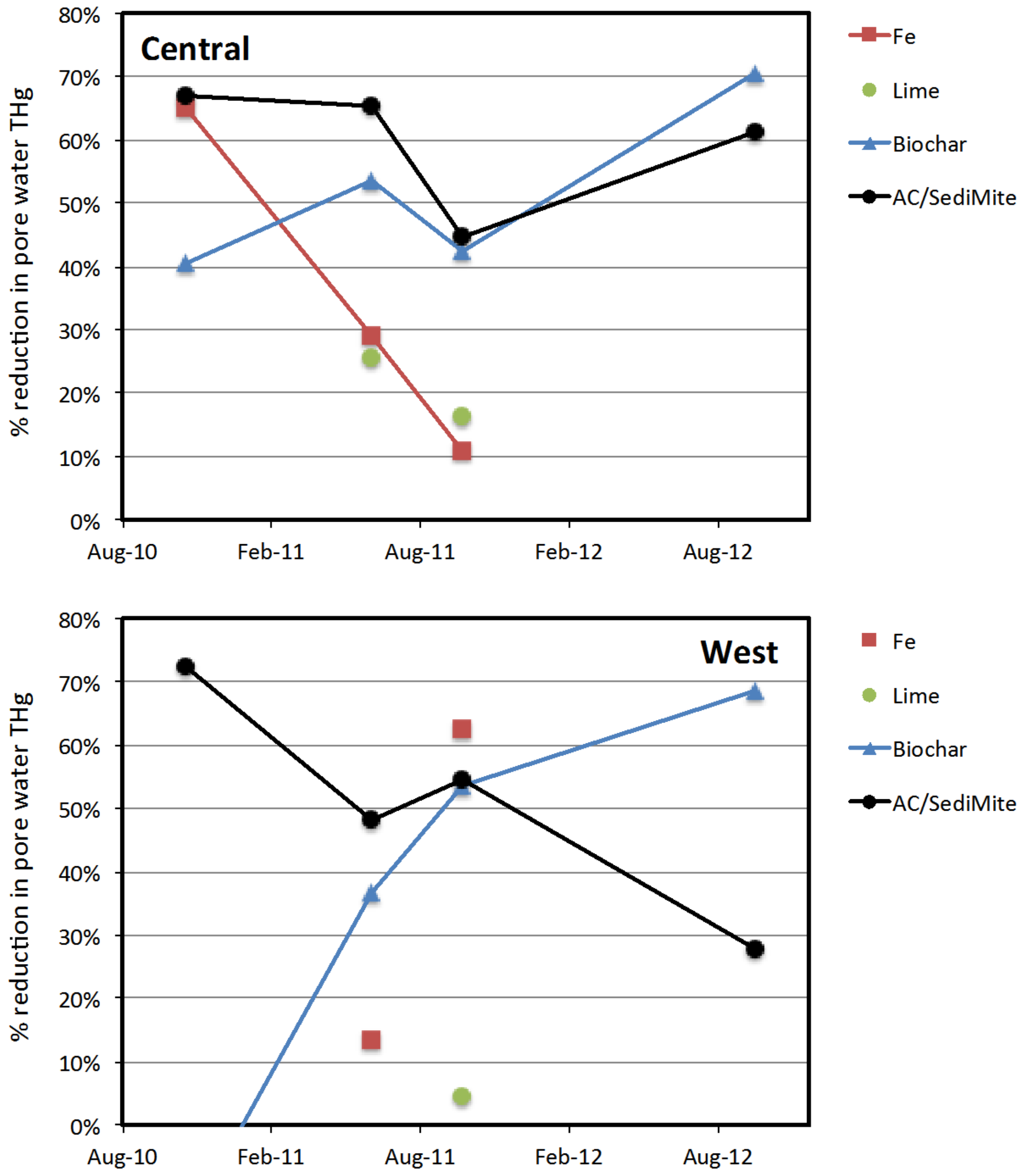


Figure 19-4. The reduction in pore water total Hg concentration in surface soils (0-5 cm) of amendment plots over time, shown as the % reduction relative to untreated control plots at each time point. Each point is the average concentration in three treatment plots at each time point. Average reductions were calculated by averaging the reductions in each individual plot. Error bars not shown, but an estimate of error can be seen in Figure 19-3.

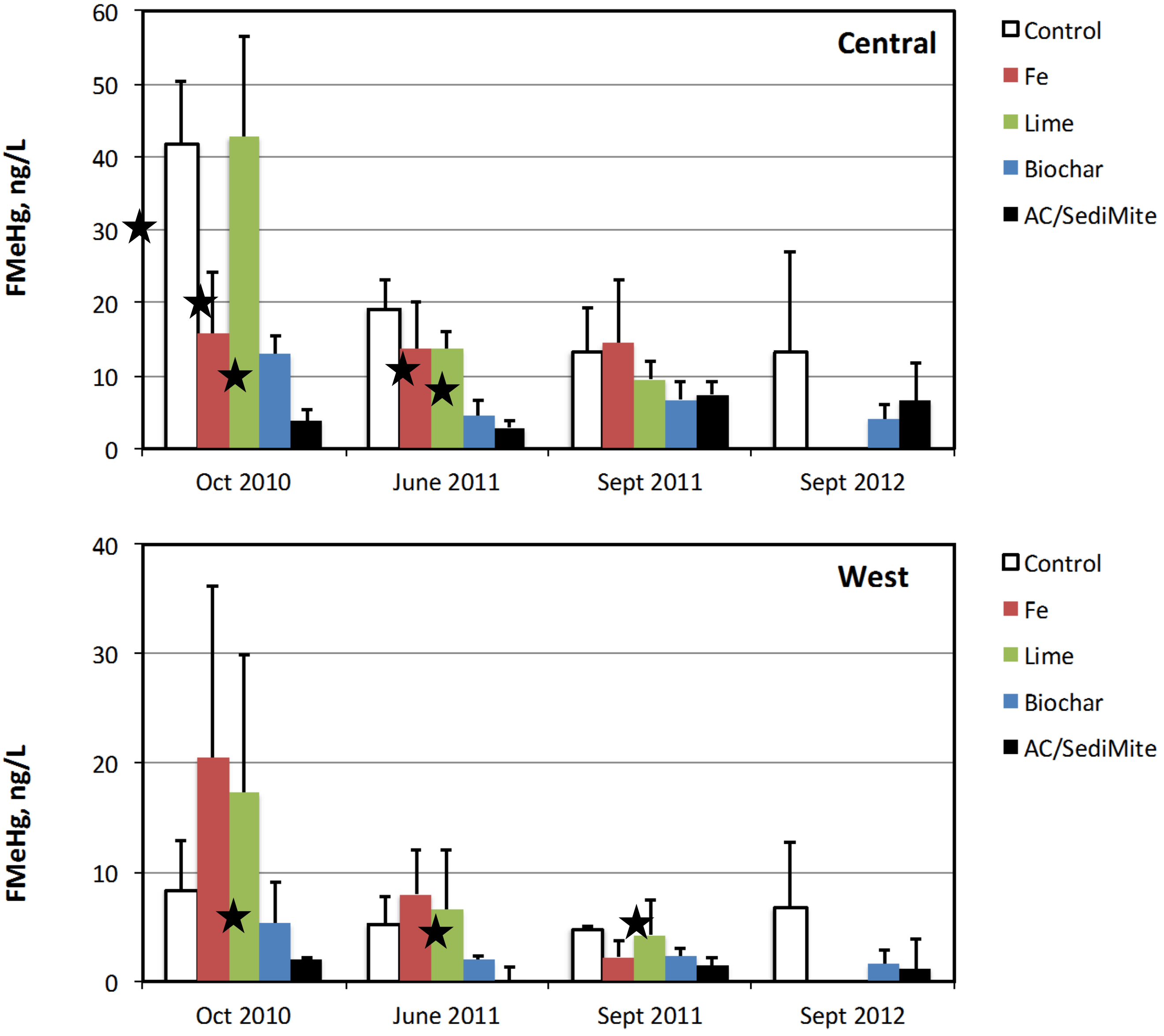


Figure 19-5. Pore water total Hg concentrations in surface soils (0-5 cm) of amendment plots over time. All bars are the averages of values from triplicate plots for each treatment, with standard deviation. Samples from individual plots are composites of four samples. Treatments that are significantly different from the control on any individual date ($p<0.05$ by pairwise Student's t-test) are designated with a star.

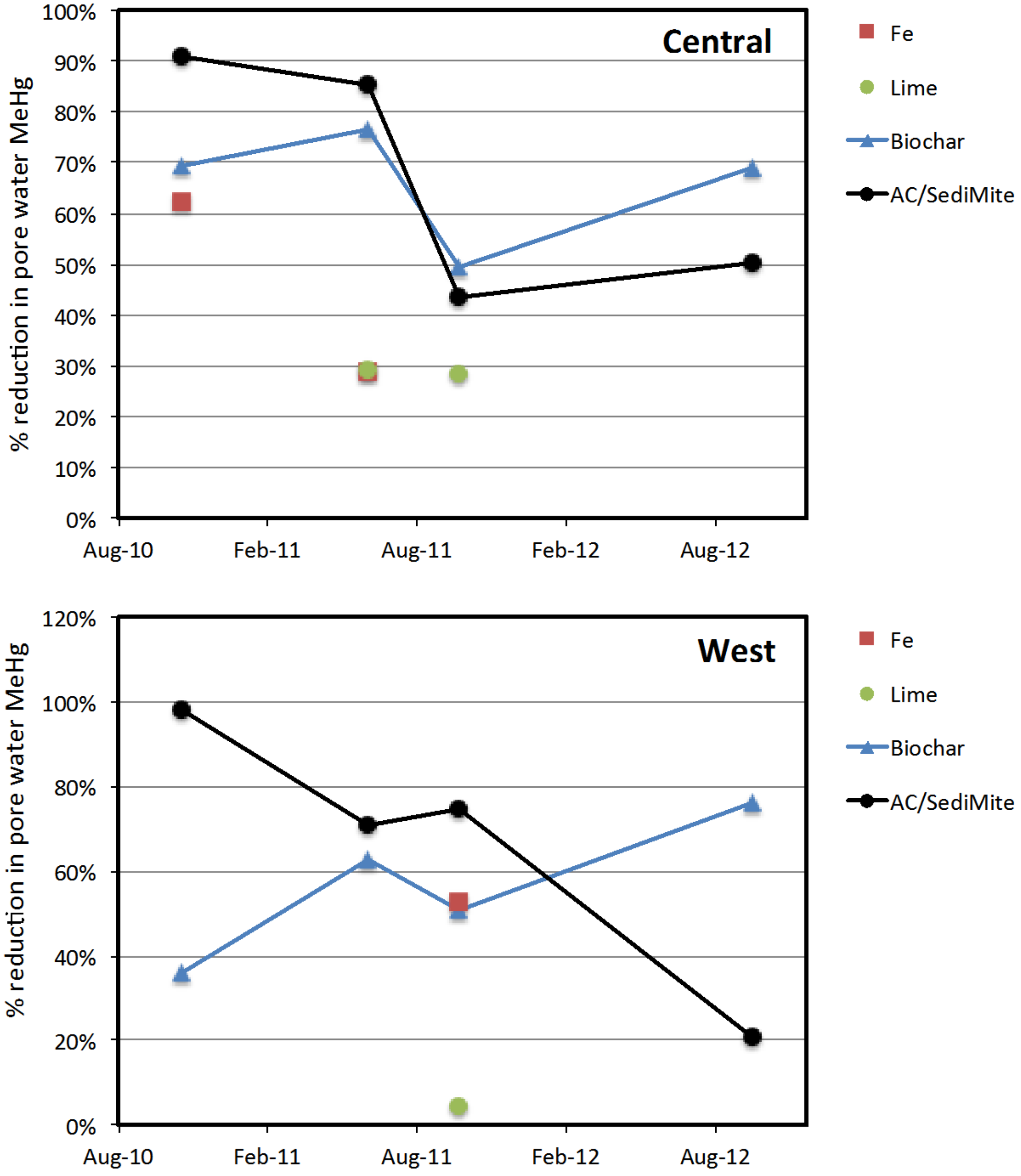


Figure 19-6. The reduction in pore water total Hg concentration in surface soils (0-5 cm) of amendment plots over time, shown as the % reduction relative to untreated control plots at each time point. Each point is the average concentration in three treatment plots at each time point. Average reductions were calculated by averaging the reductions in each individual plot. Error bars not shown, but an estimate of error can be seen in Figure 19-5.

2.6.2 Impact of soil amendments on soil pore water chemistry

We measured a suite of pore water chemistry parameters in order to evaluate the impact of amendments on chemistry that could affect Hg behavior, as well as the function of plants and animals in the marsh.

Pore water chemistry varied substantially among sampling dates, presumably in response to the seasonal and diurnal tidal cycles in the Penobscot. Variability among sampling dates was much larger than between the two study sites in the marsh. Overall, the $FeCl_2$ addition had the largest impact on pore water chemistry, although it was not effective in reducing Hg and methyl Hg. The AC and biochar amendments did not significantly affect any of the pore water variables we measured. Lime raised pore water Ca concentrations in the plots (especially at West; Figure 19-10), but did not significantly impact pH (Figure 19-7).

Salinity at the marsh study sites varied widely across sampling dates, ranging from a high of about 10 parts per thousand (ppt) at the Sept 2010 sampling to a low of 2 ppt in June 2011. On average West was 1-2 ppt higher than Central. Amendments had no effect on pore water salinity (see amendment plot data set).

Soil pH was similar at both sites (Figure 19-7), but varied substantially over time. Fe had the largest effect on soil pH, decreasing concentrations by roughly half a unit. Other amendments did not significantly affect soil pH. Fe had the largest effect on soil pH, decreasing concentrations by roughly half a unit. Other amendments did not significantly affect soil pH.

Both sites were highly sulfidic, with pore water concentrations in surface soils sometimes exceeding 1 mM (Figure 19-8). West averaged somewhat higher pore water sulfide concentrations. Iron additions dramatically decreased pore water sulfide concentrations at both sites, presumably through precipitation of FeS. The iron addition level was substantial enough to provide Fe in excess of sulfide through the first 12 months after sampling (Figure 19-11). None of the other amendments significantly changed pore water sulfide. Within and among-plot sulfide variability was high. Sulfide and other redox-sensitive variables may vary over steep gradients with depth in soils, and around plant roots.

None of the amendments significantly altered concentrations of phosphate and nitrate. Levels of both were very low, only a few uM, and near analytical detection limits. Ammonium concentrations in control plots were more commonly 30-100 uM (Figure 19-12), with higher levels at the more reducing West site. Iron amendments reduced NH_4 concentrations at both sites. At West, NH_4 levels were higher than controls in all of the other amendment plots (lime, biochar and AC), but variability was high and the differences were not significant.

The amendments had no significant consistent impact on the suite of anions and cations other than those described above (see amendment plot data set).

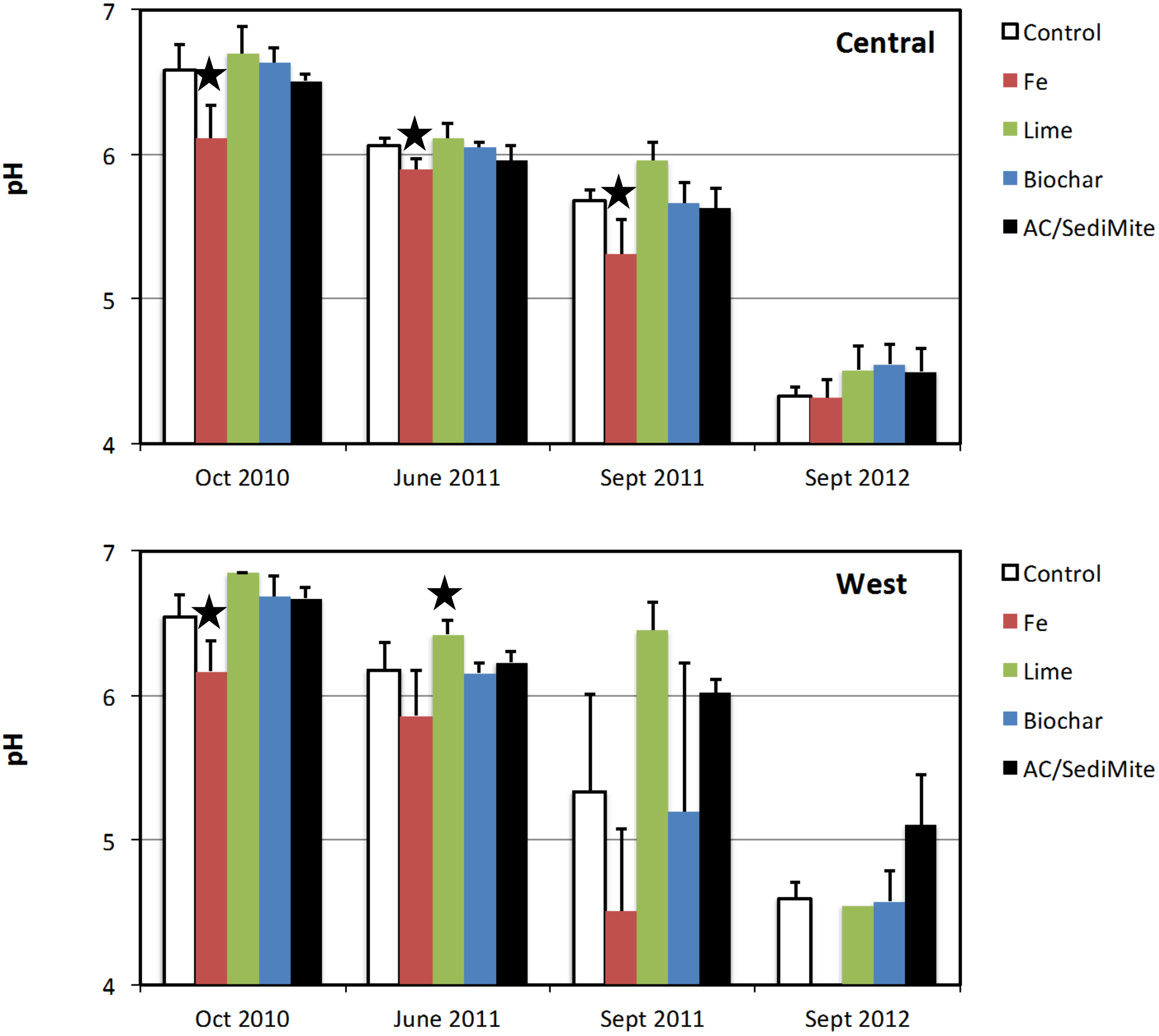


Figure 19-7. Pore pH in surface soils (0-5 cm) of amendment plots over time. Bars shown the averages of values from triplicate plots for each treatment, with standard deviation. Samples from individual plots are composites of four samples. Treatments that are significantly different from the control on any individual date ($p<0.05$ by pairwise Student's t-test) are designated with a star.

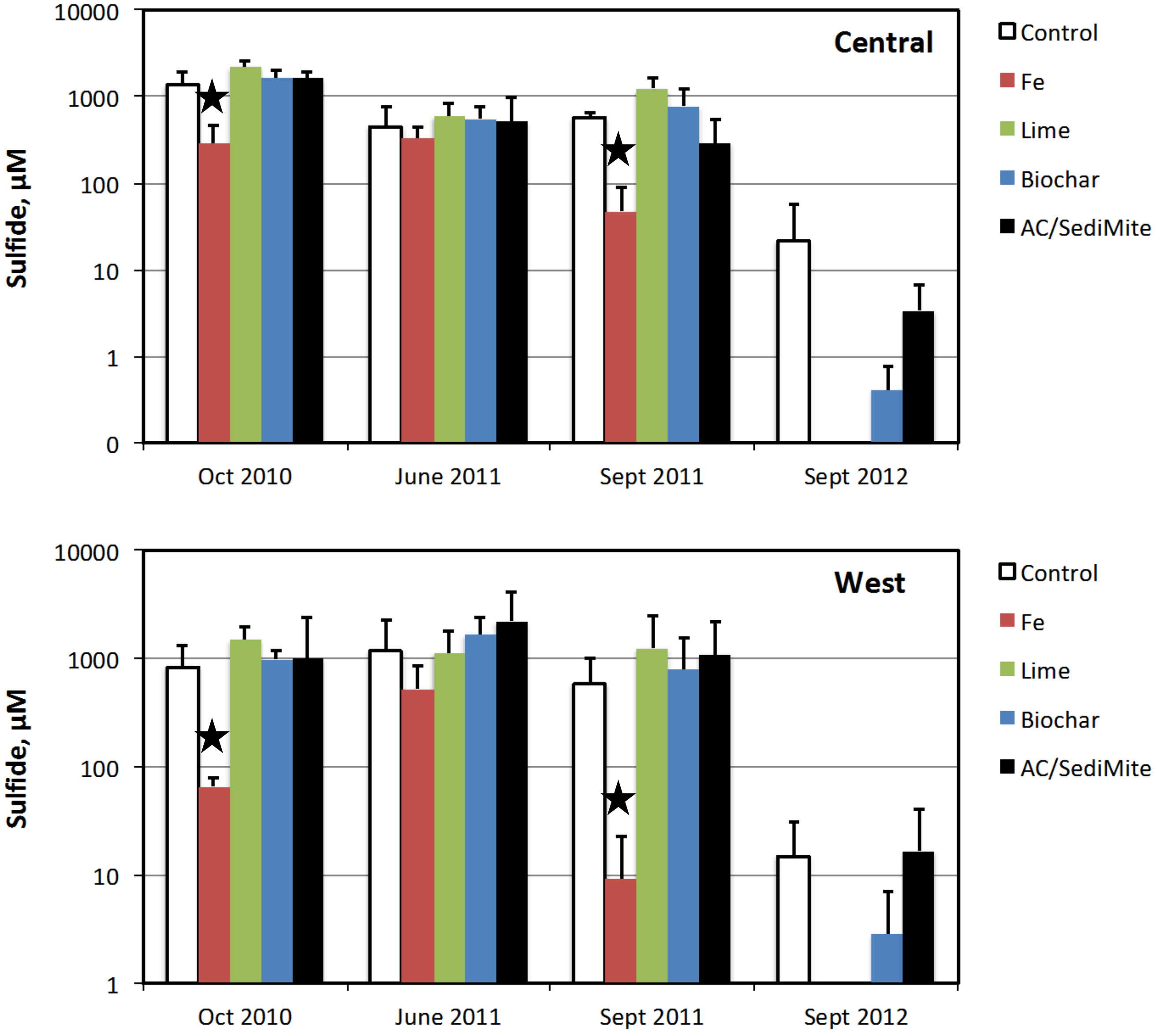


Figure 19-8. Pore water sulfide concentrations in surface soils (0-5 cm) of amendment plots over time. Bars show the averages of values from triplicate plots for each treatment, with standard deviation. Samples from individual plots are composites of four samples. Treatments that are significantly different from the control on any individual date ($p<0.05$ by pairwise Student's t-test) are designated with a star. The plots were also sampled in Sept. 2012 and are pending analysis.

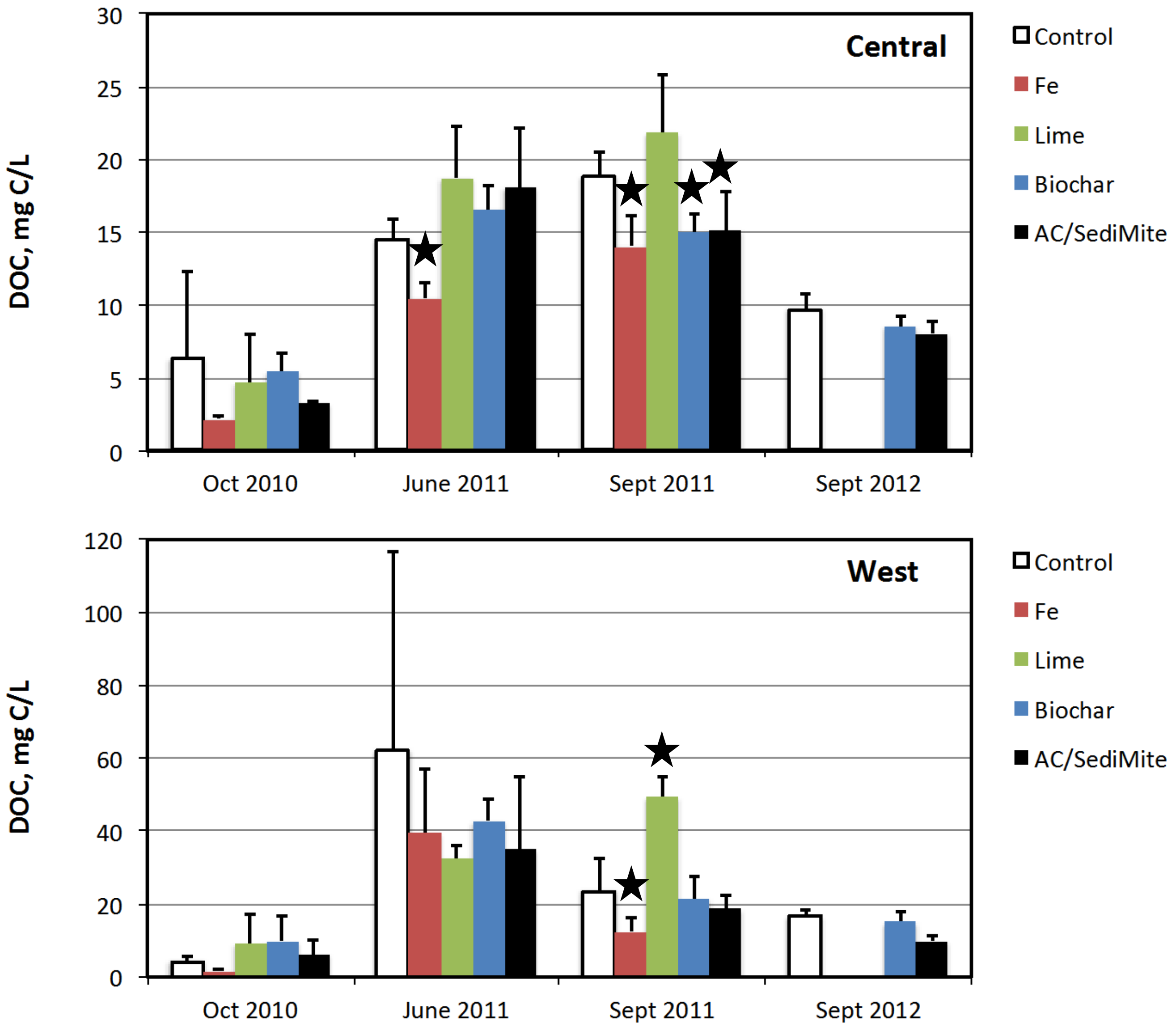


Figure 19-9. Pore water DOC concentrations in surface soils (0-5 cm) of amendment plots over time. Bars shown the averages of values from triplicate plots for each treatment, with standard deviation. Samples from individual plots are composites of four samples. Treatments that are significantly different from the control on any individual date ($p<0.05$ by pairwise Student's t-test) are designated with a star.

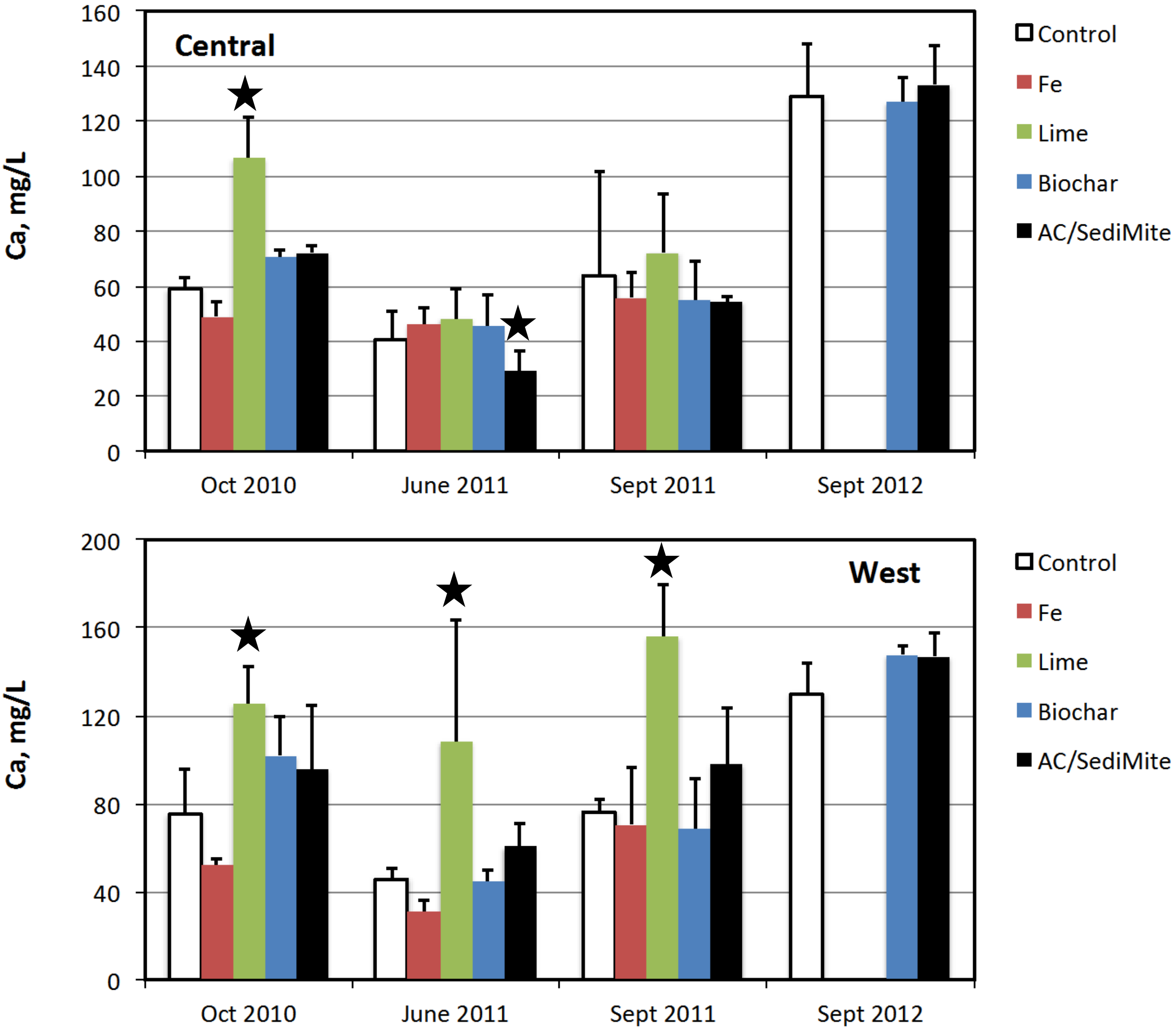


Figure 19-10. Porewater total Ca concentrations in surface soils (0-5 cm) of amendment plots over time. Bars show the averages of values from triplicate plots for each treatment, with standard deviation. Samples from individual plots are composites of four samples. Treatments that are significantly different from the control on any individual date ($p<0.05$ by pairwise Student's t-test) are designated with a star.

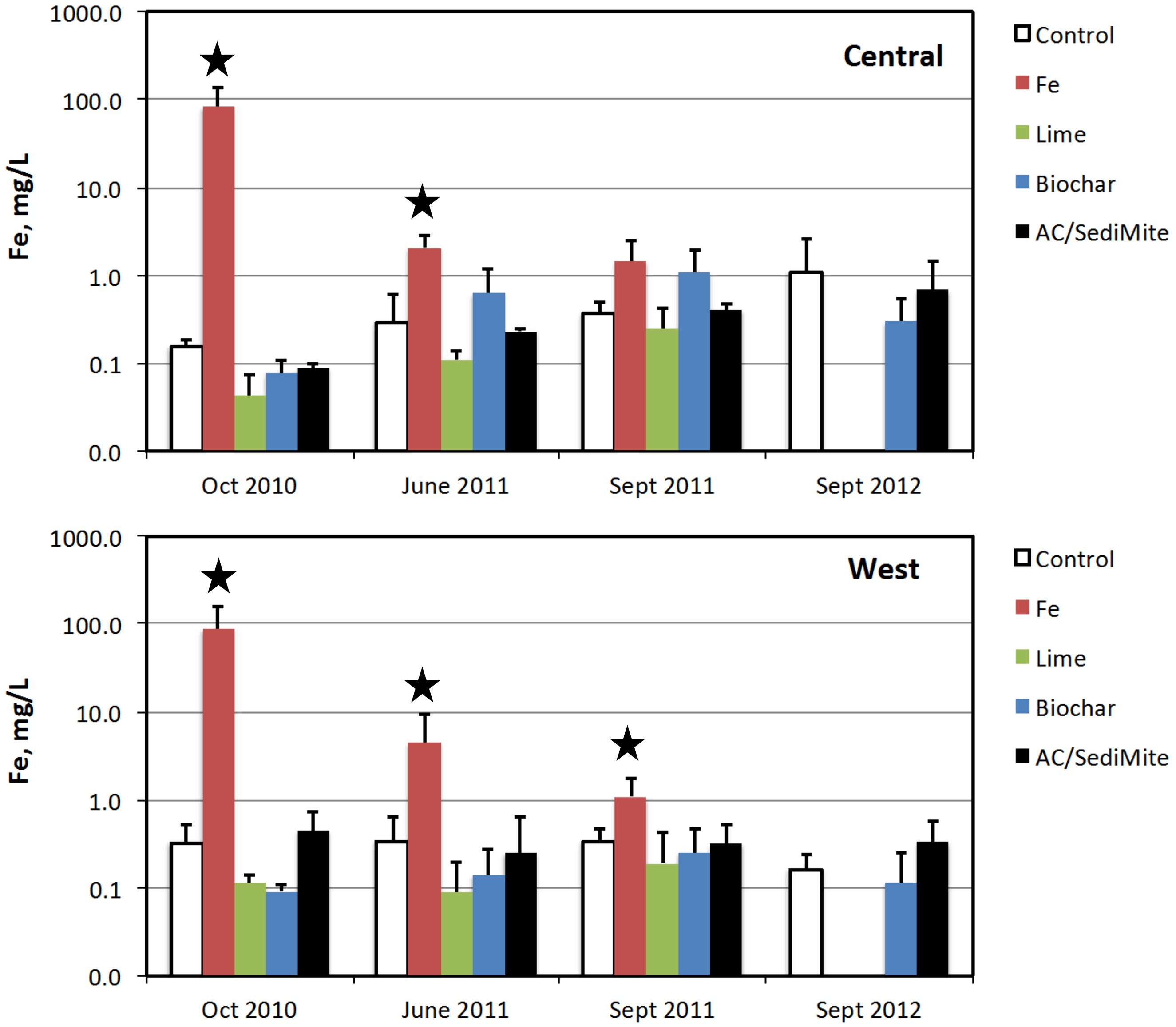


Figure 19-11. Pore water total Fe concentrations in surface soils (0-5 cm) of amendment plots over time. Bars show the averages of values from triplicate plots for each treatment, with standard deviation. Samples from individual plots are composites of four samples. Treatments that are significantly different from the control on any individual date ($p<0.05$ by pairwise Student's t-test) are designated with a star.

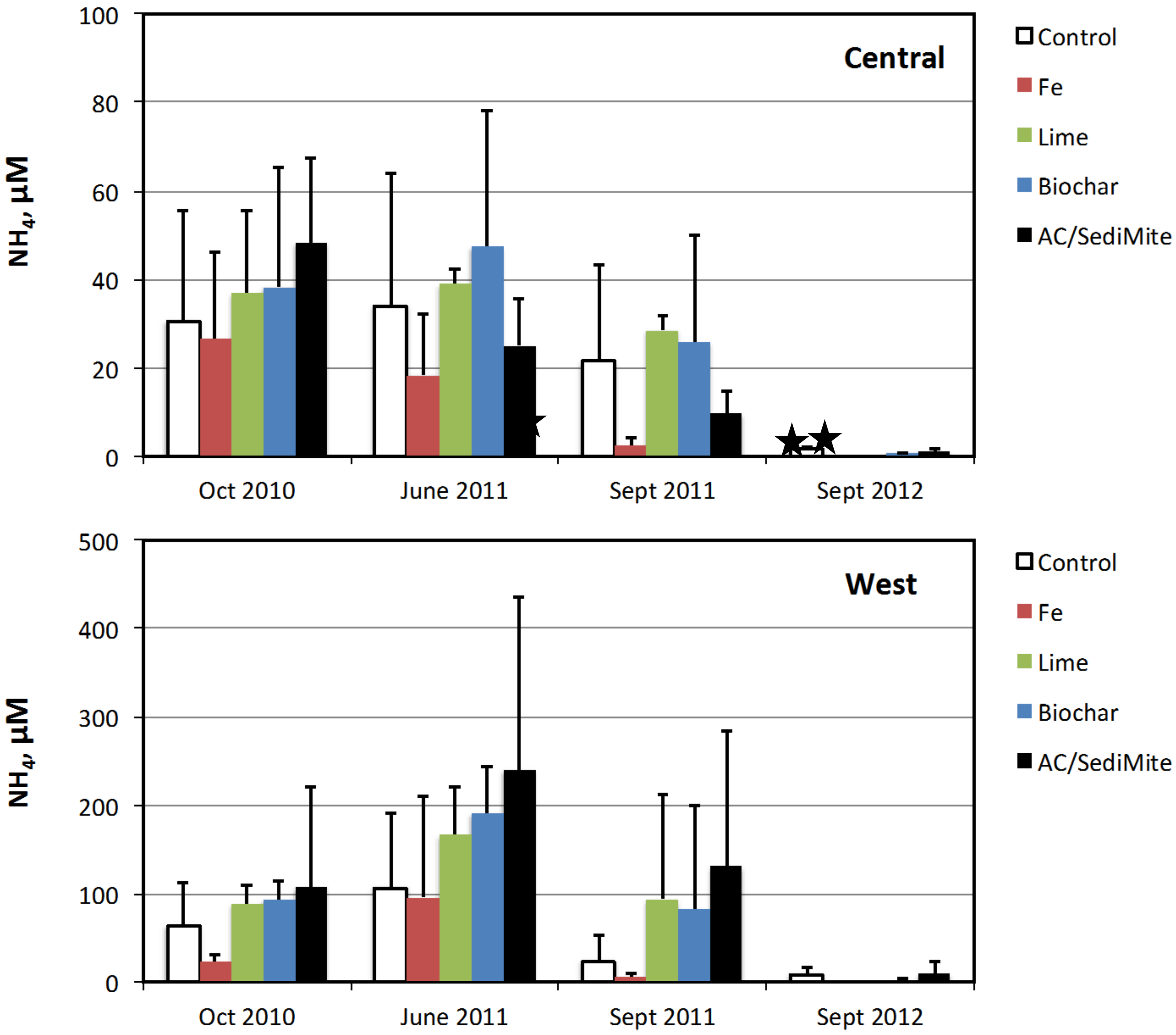


Figure 19-12. Pore water total ammonium concentrations in surface soils (0-5 cm) of amendment plots over time. Bars show the averages of values from triplicate plots for each treatment, with standard deviation. Samples from individual plots are composites of four samples. Treatments that are significantly different from the control on any individual date ($p<0.05$ by pairwise Student's t-test) are designated with a star.

2.6.3 Effect of amendments on solid phase Hg and methyl Hg

Total Hg concentrations in soils at the West and Central plot study sites were about 200 and 250 ng/g respectively (Figure 19-13). Solid methyl Hg concentrations in control plots at both sites ranged from roughly 10-20 ng/g (Figure 19-14).

The carbon amendments, especially the bulkier SediMite™, tended to reduce the concentration of Hg and other solid constituents (probably by dilution). However, the effect was rarely significant. Methyl Hg concentrations in surface soils did not change significantly in response to amendments, except for an increase in biochar plots at Central at the one year time point.

2.6.4 Effect of amendments on other solid phase constituents

The lime and $FeCl_2$ amendments increased the solid pools of Ca and Fe, respectively, in surface marsh soils (Figures 16a-15 and 16a-16). The persistent elevated concentrations of Fe and Ca in the iron and lime treatment plots (respectively) demonstrate that these amendments stayed in place over at least 12 months. The lime amendment significantly raised sediment Ca levels and the Fe addition significantly raised Fe levels. The Ca addition raised total Ca on average in 0-3 cm by about 30 mg/g, to ~35mg/g at Central and 45 mg/g at West. The Fe addition raised total Fe on average in 0-3 cm by about 10 mg/g (to 22 mg/g at West and 28 mg Fe/g at Central).

All of the soil samples from this study have been sent to Dr. Upal Ghosh’s lab at the University of Maryland, Baltimore County, for carbon black analysis. Data should be available in early 2013.

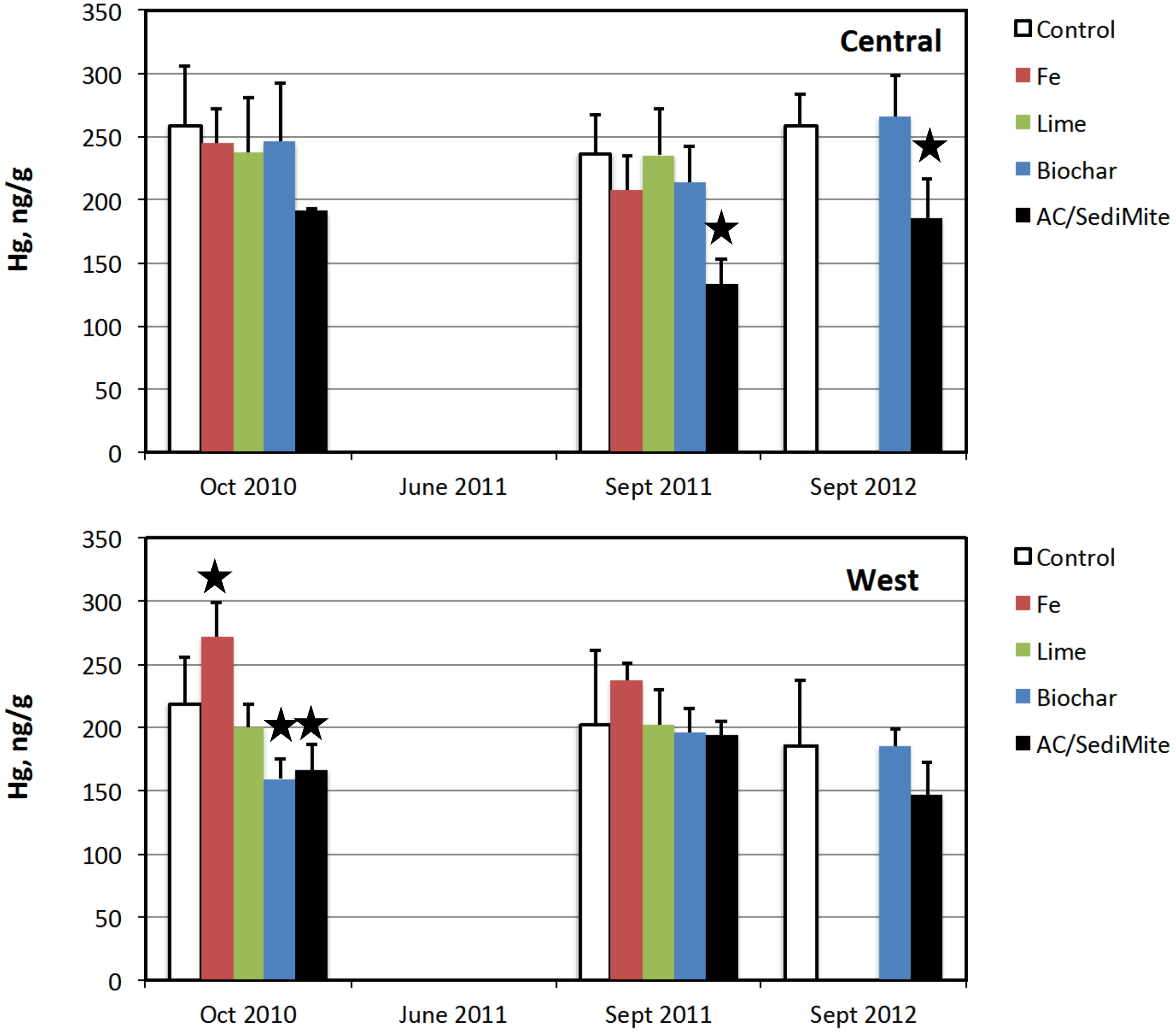


Figure 19-13. Solid-phase total Hg concentrations in surface soils (0-3 cm) of amendment plots over time. All bars are the averages of values from triplicate plots for each treatment, with standard deviation. Samples from individual plots are composites of four samples. Samples from June 2011 are also available (and are in storage) in case future analysis is desired. Treatments that are significantly different from the control on any individual date ($p<0.05$ by pairwise Student's t-test) are designated with a star.

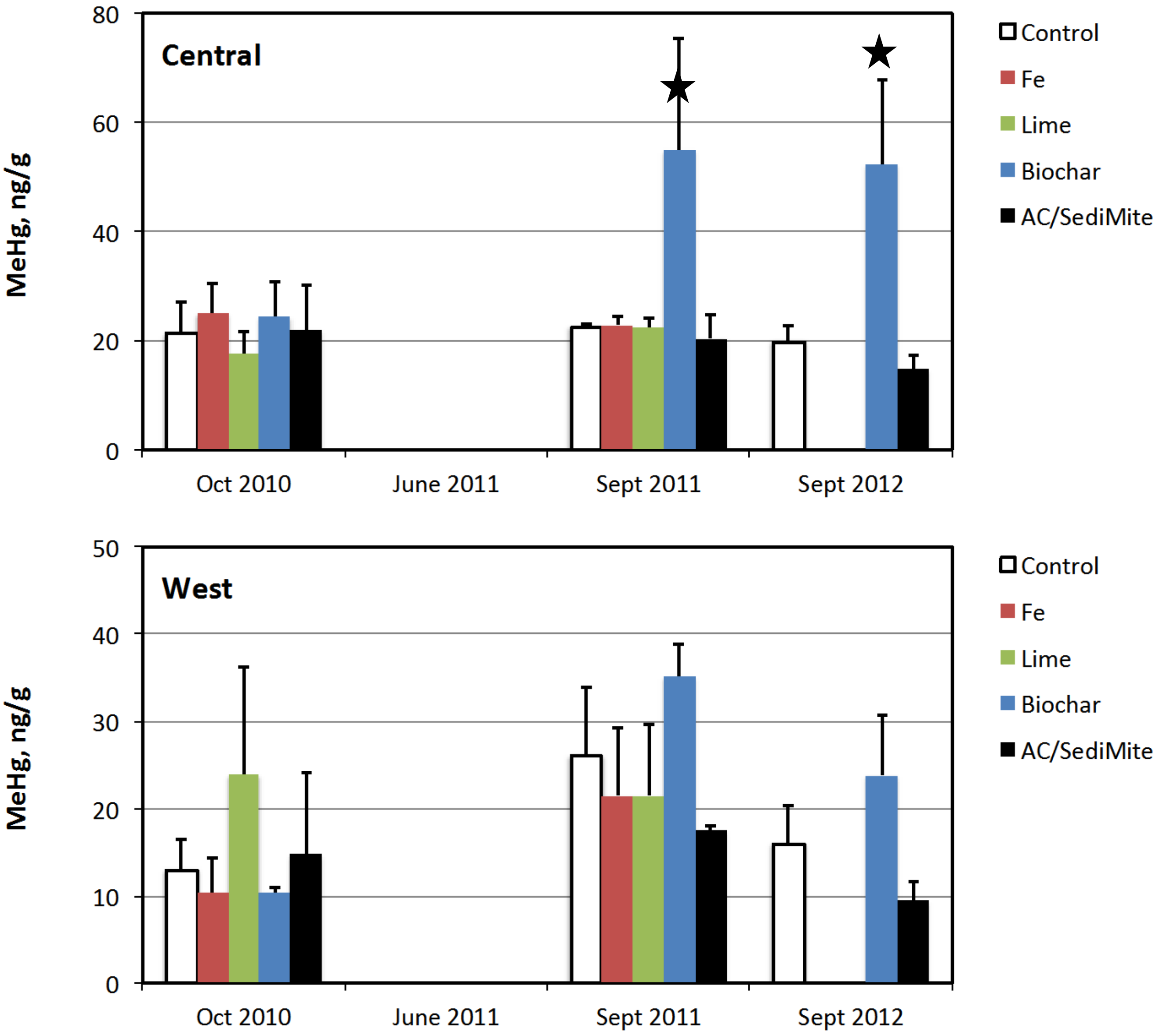


Figure 19-14. Solid-phase methyl Hg concentrations in surface soils (0-3 cm) of amendment plots over time. All bars are the averages of values from triplicate plots for each treatment, with standard deviation. Samples from individual plots are composites of four samples. Samples from July 2011 are also available (and are in storage) in case future analysis is desired. Treatments that are significantly different from the control on any individual date ($p<0.05$ by pairwise Student's t-test) are designated with a star.

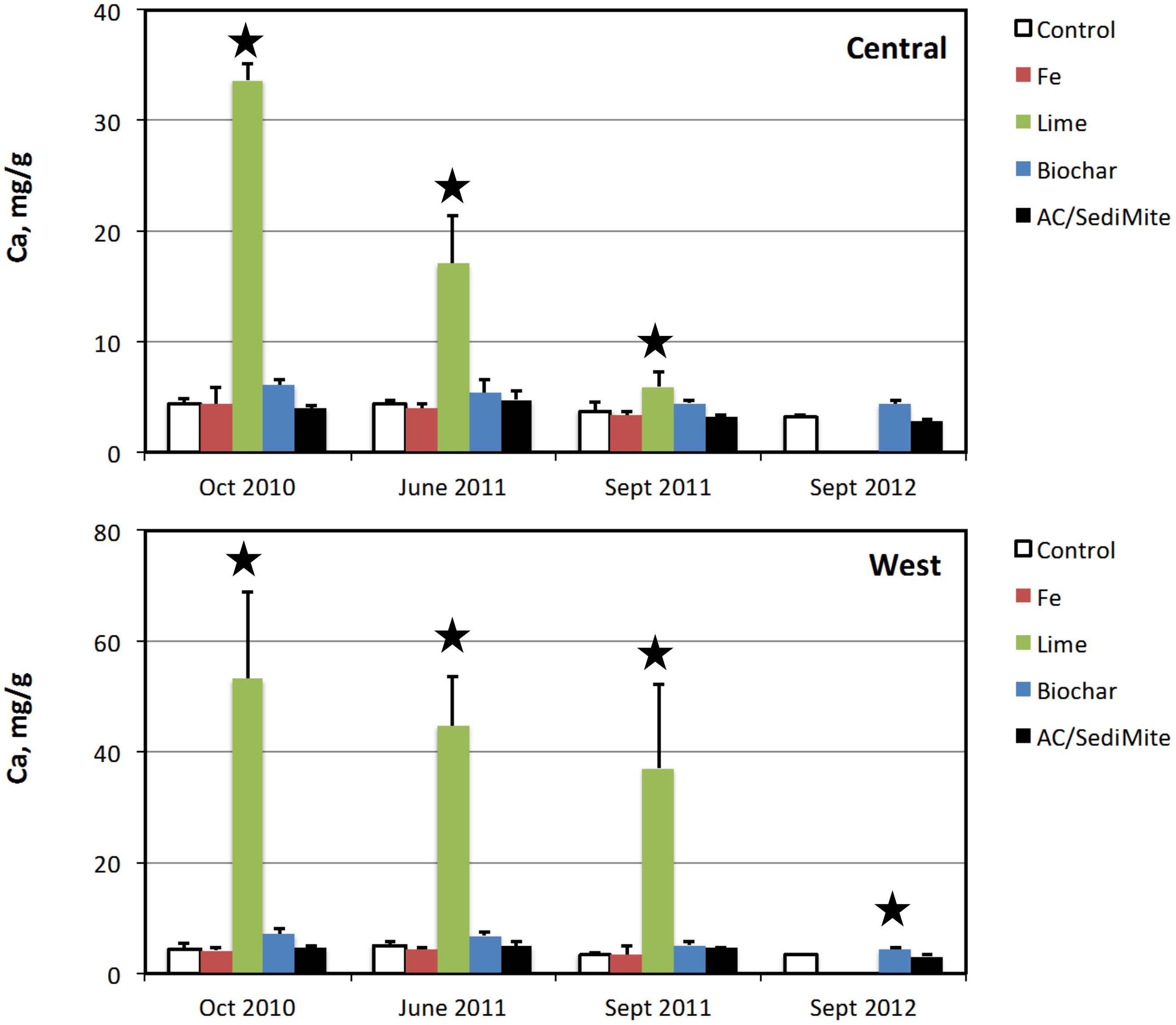


Figure 19-15. Solid-phase Ca concentrations in surface soils (0-3 cm) of amendment plots over time. All bars are the averages of values from triplicate plots for each treatment, with standard deviation. Samples from individual plots are composites of four samples. Samples for Sept. 2011 are in storage in case future analysis is desired. Samples from July 2012 are currently being analyzed. Treatments that are significantly different from the others on any given date ($p<0.05$ by pairwise Student's t-test) are designated with a star.

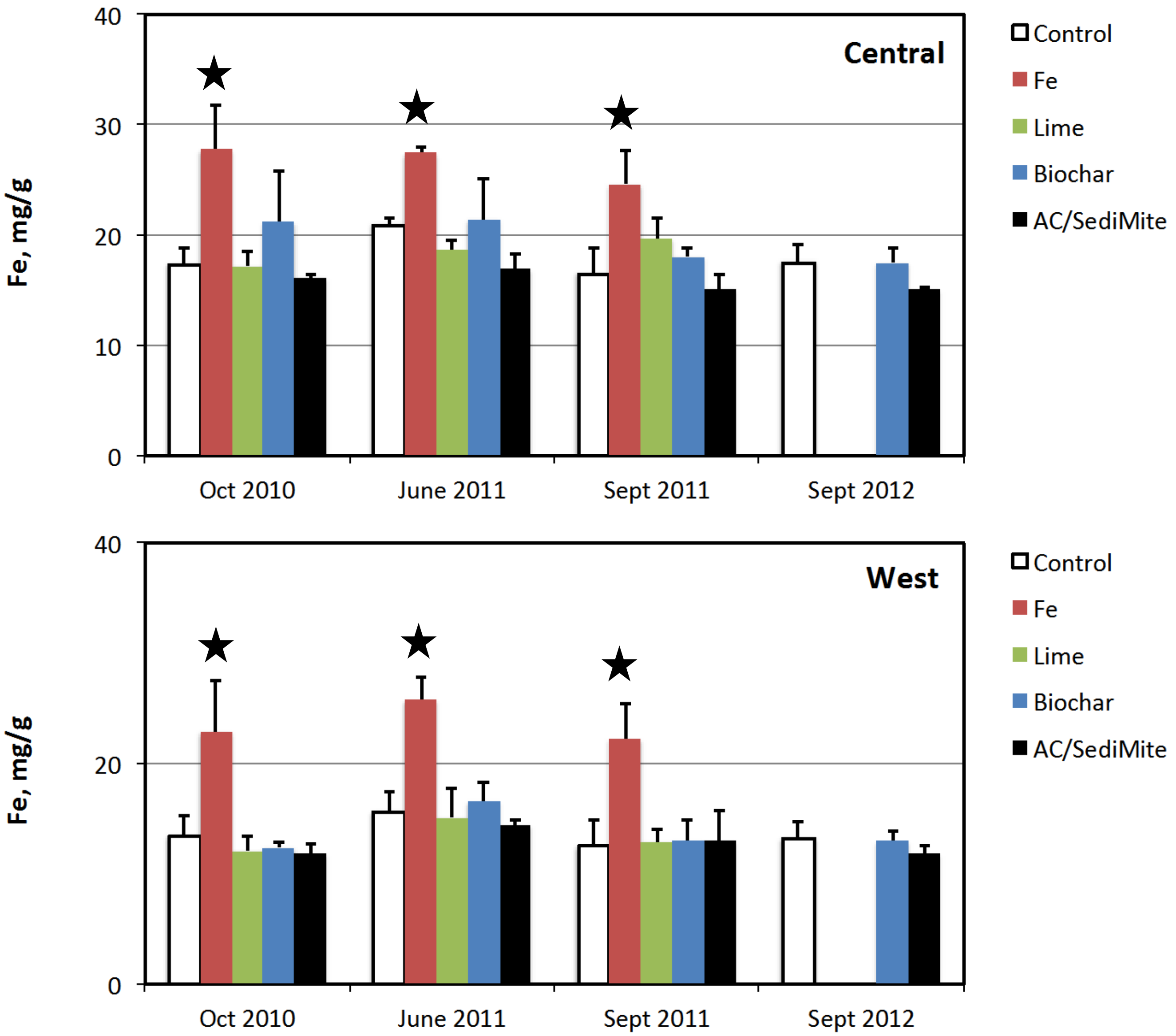


Figure 19-16. Solid-phase Fe concentrations in surface soils (0-3 cm) of amendment plots over time. All bars are the averages of values from triplicate plots for each treatment, with standard deviation. Samples from individual plots are composites of four samples. Samples for Sept. 2011 are in storage in case future analysis is desired. Samples from July 2012 are currently being analyzed. Treatments that are significantly different from the others on any given date ($p<0.05$ by pairwise Student's t-test) are designated with a star.

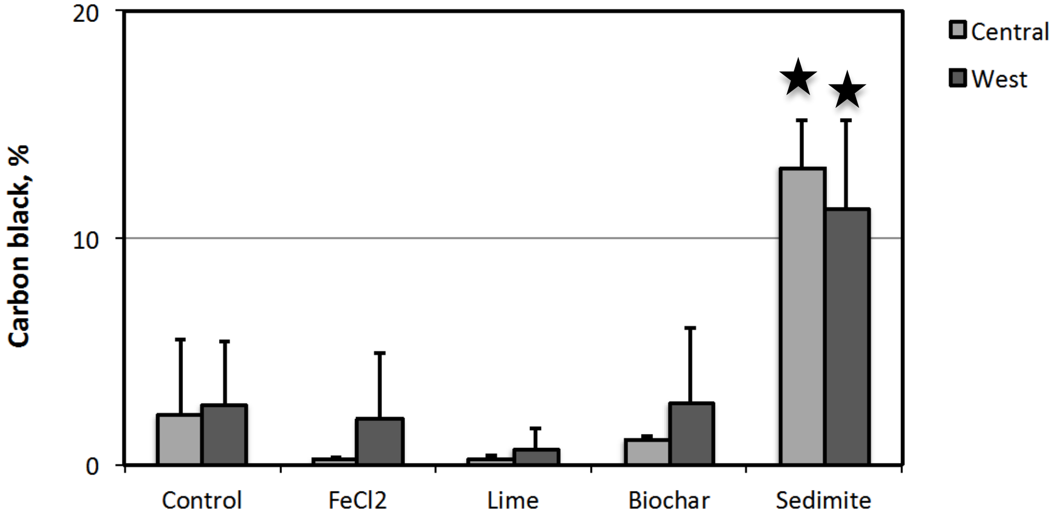


Figure 19-17. Carbon black as a % of solids in surface soils (0-3 cm) of amendment plots in June 2011. All bars are the averages of values from triplicate plots for each treatment, with standard deviation. Samples from individual plots are composites of four samples. Treatments that are significantly different from controls (one way ANOVA; means comparison with Student's t-test, $p<0.05$) are designated with a star.

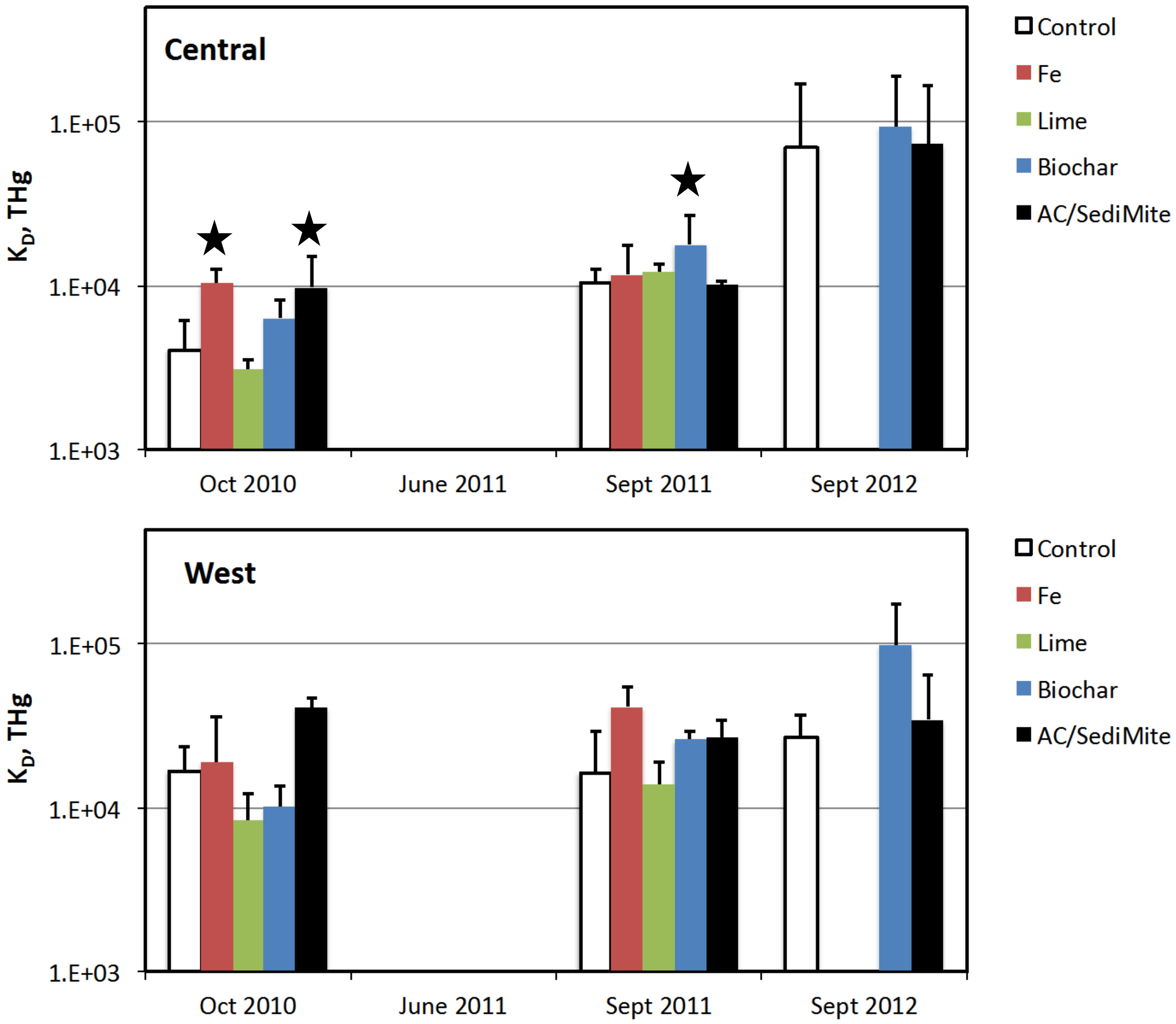


Figure 19-18. Sediment:water partition coefficients (K_D) for total Hg in surface soils (0-3 cm) of amendment plots over time. All bars are the averages of values from triplicate plots for each treatment, with standard deviation. Samples from individual plots are composites of four samples. Samples for Sept. 2011 are in storage in case future analysis is desired. Treatments that are significantly different from the others on any given date ($p<0.05$ by pairwise Student's t-test) are designated with a star

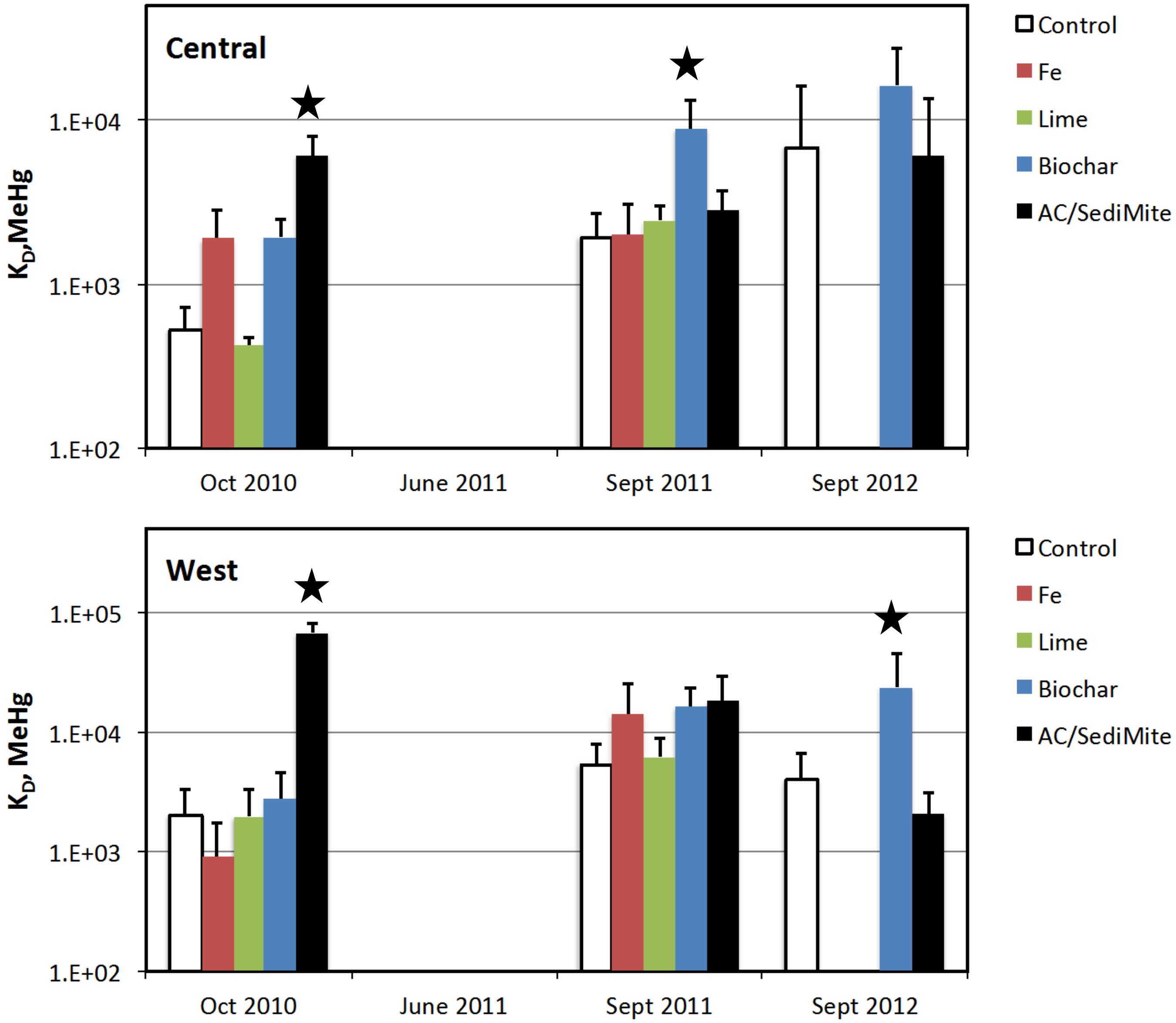


Figure 19-19. Sediment:water partition coefficients (K_D) for methyl Hg in surface soils (0-3 cm) of amendment plots over time. All bars are the averages of values from triplicate plots for each treatment, with standard deviation. Samples from individual plots are composites of four samples. Samples for Sept. 2011 are in storage in case future analysis is desired. Treatments that are significantly different from the others on any given date ($p<0.05$ by pairwise Student's t-test) are designated with a star

2.6.5 Effect of amendments on vegetation cover

In Oct. 2011, Prof. Aram Calhoun of the University of Maine visually assessed the cover in the study plots. Results were reported as percent cover of major species, plus bare ground (Figure 19-20). This was a visual assessment of species and cover, designed to provide an initial assessment of potential impacts of the amendments. The small plot size makes a more quantitative analysis difficult, given the size and physical structure of plant communities. Going forward, any assessment of amendments should include a quantitative determination of above ground vegetation growth, mass and speciation. Consideration of the impacts of amendments on below-ground biomass and marsh growths rates (elevation) are probably also important.

Three-square (*Schoenoplectus pungens*) is the dominant tall vegetation at the Central site, with interspersed rushes. *Agrostis* (creeping bentgrass) is a lower height ground cover. Central is a slightly higher elevation, drier site. Lower rushes and sedges are dominant at West, a very wet part of the marsh.

The lime plots were visibly most affected, with large bare spots, lower and less dense vegetation at both study sites. This effect was still visually obvious in fall 2012. About 1/3 of the area of the lime-amended plots at both sites was bare of cover in fall 2011. At Central, dominant species *Agrostis* and *Schoenoplectus* were much less dense, and the three-square was shorter. At West, vegetation was thinner overall.

Both carbon amendments, and the Fe amendment, appeared to enhance the biomass of vegetation in the plots. At both sites, vegetation was taller and thicker in all of these plots than in control plots, with the most visually obvious enhancement in the iron plots. However, the Fe additions initially inhibited growth; enhance growth was observed at 12 and 24 months. Presumably, the high level of $FeCl_2$ addition burned plants at first, but acted as a nutrient after it was diluted into soils. Iron amendment changes the 12 month species composition somewhat at both sites.

The carbon addition plots, both biochar and SediMite™, looked visually most similar to the control plots, and to the surrounding marsh. At the West site, species composition at 12 months was similar to controls with the exception of less *Agrostis.* At Central, species major species composition was very similar to control plots.

The Oct. 2011 species composition and cover data are not amenable to statistical treatment, as the sum of reported percent cover did not add to 100% for most plots.

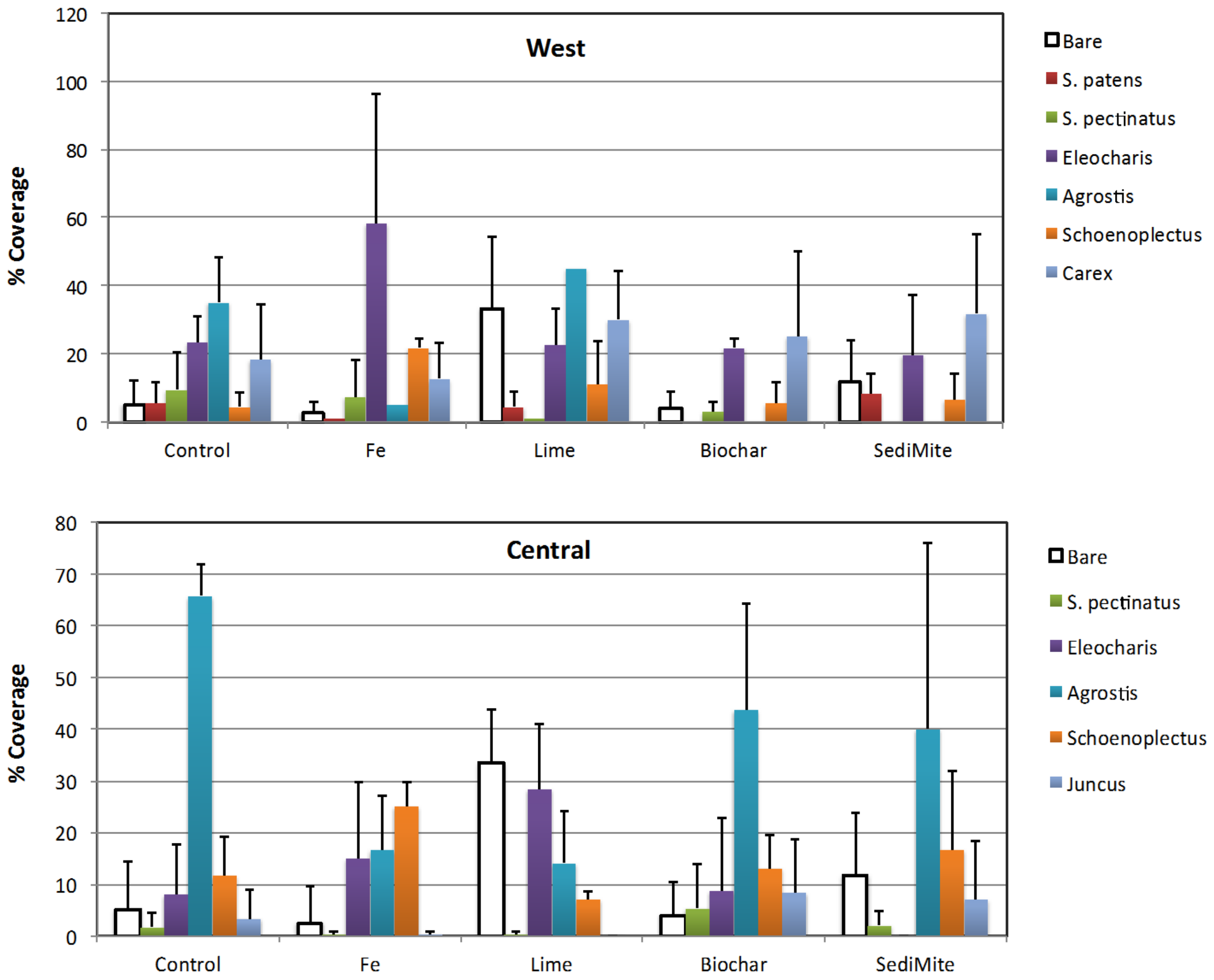


Figure 19-20. Dominant vegetation and percent cover in Mendall Marsh amendment plots, Oct. 2011. Bars are the averages of values from triplicate plots for each treatment, with standard deviation. Species list:

Agrostis stolonifera (creeping bentgrass)
Carex paleacea (salt marsh sedge)
Eleocharis uniglumis (salt marsh spike rush)
Juncus gerardii (black grass)
Schoenoplectus pungens (common three square)
Spartina patens (salt marsh hay)
Spartina pectinata (slough grass)
Typha angustifolia (cattail)

2.7 Results from limited capping study

Small plots in each study area (West and Central) were capped with about 1 inch of either sand or silt/clay in Sept. 2010. Single 4' X 4' plots were capped in each site, and single unamended control plot was marked off nearby. Pore waters and surface soils were sampled one month after application. For pore water sampling, the 0-5 interval sampled included the depth of the cap. Multiple pore water samples were drawn from each plot, but composited for analysis. With this plot and sampling design, there was no replication except across the sites.

At the West site, the single measured total Hg and methyl Hg concentrations in pore waters were higher than in the nearby control plot (Figure 19-21). At the Central site, effects were less pronounced. However, without replication of plots, or repeated sampling through time, these results cannot be evaluated statistically.

Sampling of the capped plots did not continue after Oct. 2012, because some of the soil amendments in the main plot study were effective, However, the capping materials remain in place and could be re-evaluated in 2013 if desired; which would be almost 3 years after the materials were applied.

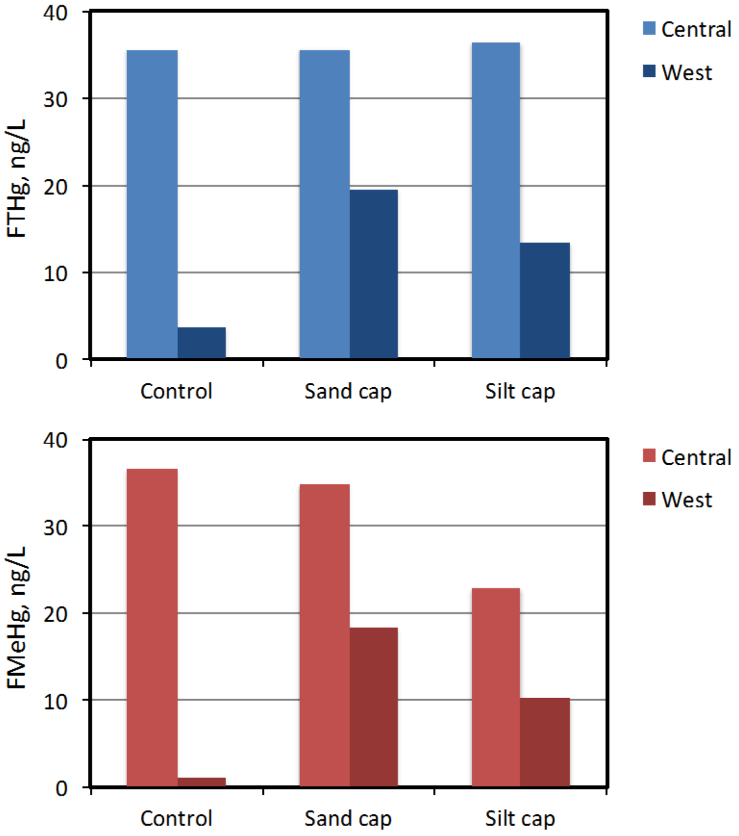


Figure 16-21. Pore water THg and methyl Hg concentrations in the top 5 cm of soils in capped plots, compared to uncapped controls. Samples were taken 1 month after application of the caps. The sampling interval includes the approximately 1" cap. Each bar is based on a composite sample from each plot, but there was no replication of plots, or repeated sampling within each plot.

2.8 Costs of large-scale amendment application

For large-scale production the cost of SediMite^{TM} with 50% AC is approximately $2/lb (a little lower for > million pounds). So we can calculate the material cost of SediMite™ per acre by multiplying with the rate of application we used in the field. At ~5 lb/square meter (the dosing rate used in this trial), that would translate to about 20,000 lb/acre, or about $40,000/acre in material cost. This does not include the cost of application, which is more difficult to estimate as we have no full-scale application experience with SediMite™ in a marsh setting. However, large-scale PCB remediation field trials are underway with SediMite™ in other locations.

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