Porewater Methods Development

in support of the

Minnesota Pollution Control Agency's Preliminary Wild Rice Study

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Final Report

Contents

Introduction & Background

As part of an effort to evaluate MPCA's Wild Rice Sulfate Standard, a preliminary field study was conducted in the summer and fall of 2011. While most of this preliminary study involved a survey of chemical and biological parameters across a geographical range of wild rice sites in Minnesota (led by Amy Myrbo of UMTC LacCore), a preliminary investigation into methods applicable for porewater analysis was also completed. This evaluation of porewater sampling methods was undertaken at the University of Minnesota Duluth Civil Engineering Department under the direction of Dr. Nathan Johnson. Redox geochemistry in the rooting zone of aquatic macrophytes is known to be important in some instances due to both the direct toxicity of reduced sulfur as well as effects on other trace chemicals that indirectly affect root growth and function (Gao et al. 2003, Koch et al. 1990). Methods applicable for measuring chemicals in porewaters are necessary to evaluate many of the hypotheses related to the effects of sulfate on wild rice from the MPCA's Study Protocol. Hypotheses 4 are related to factors that remove free sulfide from sediment porewater and Hypotheses 5 are related to factors that reduce the production of sulfide in sediment porewaters.

The interaction between sulfur and iron in reduced environments is complex and can change both spatially and temporally. At environmentally relevant concentrations, iron is a more favorable electron acceptor than sulfate and its oxidized form is predicted thermodynamically to be consumed at shallower layers in the sediment than sulfate (Stumm and Morgan 1996). However, in the complex setting of the rooting zone of aquatic macrophytes, oxygen can be introduced to micro-niche environments around roots which can oxidize both reduced iron and sulfide, confounding the normal depth-dependent sequence of diagenetic reactions (Gao et al. 2003).

The solubility of sulfide and ferrous iron is thermodynamically limited by one of a number of insoluble solid-phase complexes at circumneutral pH. The process of iron-sulfide formation can also be rate limited, and oversaturation of iron-sulfide minerals sometimes occurs when reduced iron and sulfide are being actively produced or cycled. In addition to chemicals directly involved in the hypotheses related to wild rice, the MPCA also expressed a desire to test porewater sampling techniques for obtaining uncontaminated samples for the analysis of mercury and methylmercury.

The objective of the study described herein was to (1) critically review porewater measurement techniques for characterizing important geochemistry related to the effects of sulfate on wild rice, (2) select and test candidate porewater sampling methods at field sites, and (3) test methods in the laboratory for sampling porewater total-and methyl- mercury.

Methods

A variety of methods applicable for measuring dissolved chemicals in sediment porewaters was compiled and is presented in Table 1. Each method was considered in terms of the analytes it was capable of measuring, as well as its temporal and spatial resolution. A qualitative assignment was made for "ease of use" in order to compare methods for use in both (1) a "survey-scale" study involving one-time visits to hundreds of lakes by a team of inexperienced technicians and (2) a "detailed" study involving a team of experienced researchers investigating detailed geochemistry at only a handful of sites.

Analytes were prioritized in Table 2 by the hypotheses that they addressed. The "A-Team," "B-Team," and "C-Team" analytes are chemicals that are important for addressing, respectively, Level A, B, and C Hypotheses in the Sulfate Standard to Protect Wild Rice Study Protocol. Approximate volume requirements for each of the analyses are also included in Table 2. In addition to the synthesis of methods described in literature, conversations with several colleagues having significant experience in sampling pore fluids aided in evaluating and vetting the list of techniques outlined in Table 1 and Table 2.

Table 1. Potential methods for sampling sediment porewater.

		Resolution		
Method	**Applicable Chemical Class**	**Time**	**Space**	**Difficulty of Operation**
*Peepers	Any, dissolved	14-28 d equilibration	1-2 cm	Moderately difficult
†Sippers	Any, dissolved	Instantaneous	5-10 cm	Relatively easy
*Microelectrodes	Redox active, ISE	Instantaneous	0.2-0.5 cm	Difficult
Core / Centrifuge	Any (with preservation)	Instantaneous	2-5 cm	Moderately difficult
DGT/Silver sorbent	Metals/Sulfide, dissolved	Cumulative deployment	1-2 cm	Difficult
SPME	Hydrophobic orgs., dissolved	14-28 d equilibration	2-5 cm	Moderately difficult

* tested method appropriate for detailed study, † tested method appropriate for field survey

Table 2. Analytes relevant for addressing MPCA Wild Rice Study Hypotheses.

Organized by System:

- Sulfide
- Sulfate
- Nitrate
- Ammonium/ammonia
- Phosphorus
- Iron
- Manganese
- Calcium, magnesium, potassium, sodium
- Dissolved organic carbon
- Copper, zinc
- Temperature
- THg & MeHg

Organized by Analysis Class:

Electrode (2 mL) or colorimetric (30 mL):

- Sulfide
- Ammonium/ammonia

Ion Chromatography (2-5 mL):

- Sulfate
- Nitrate
- Phosphate

Microelectrode (non-destructive), color (ferrous–2.5 mL), or ICP (2-10 mL):

- Iron
- Manganese

ICP (2-10 mL):

- Calcium, magnesium, potassium, sodium
- Copper, zinc

TOC analyzer (10 mL):

- Dissolved organic carbon

Electrode (non-destructive):

- Temperature & pH

ICP or CVAFS (100 mL for both):

- THg & MeHg

A-Team:

- Sulfate
- Sulfide
- Iron
- Nitrate
- Calcium, magnesium, potassium, sodium
- THg/MeHg

B-Team:

- Copper, zinc
- Manganese

C-Team:

- Phosphorus
- Ammonium/ammonia
- Dissolved organic carbon

Based on the synthesis of information included in Table 1 and 2, it was determined that sippers were the most applicable method for gathering data on a survey scale. Although the relatively low spatial resolution limits the use of sippers in obtaining data on vertical variations in porewater geochemistry, the ease of implementation by a team of technicians with minimal training was a major advantage. Additionally, the scope of analytes that sippers can be applied to made them ideal for survey-scale sampling. A detailed description of the method for extracting samples without exposure to oxygen and minimal loss of dissolved gas with sippers is given in the methods section.

For more detailed investigations that required higher spatial resolution, two techniques were chosen for testing. Porewater peepers (diffusion equilibrium samplers) were chosen for analytes that require a relatively small volume of sample. Peepers were constructed of polycarbonate and each discrete well is spaced at intervals of ~1.5 cm, with a volume of ~10 mL. This volume allowed for subsamples to be collected for pH and temperature (non-destructive electrode), sulfide (destructive electrode, high concentrations), sulfate and nitrate (IC), and ferrous iron (colorimetric). Owing to its small volume requirement, cation analysis would also be possible with peepers although it was not measured in this preliminary study. These analyses cover all of the MPCA's A-Team analytes excluding mercury. If low sulfide concentrations (<~2-5 µm) are to be measured, a larger volume (~30 mL) is required and would necessitate the composition of adjacent peeper samples. Sufficient volume for other analytes (DOC, total- and methyl- mercury, nutrients, low level sulfide) was not available even at the ~3 cm resolution achieved by combining two adjacent peeper wells. Combining additional adjacent cells (at the expense of vertical resolution) or compositing samples from adjacent peepers would have been necessary to obtain sufficient sample volume for these analytes.

In addition to porewater peepers, voltammetric microelectrodes were also tested as a means of obtaining high vertical resolution samples for some redox-active porewater chemicals. Voltammetric techniques, after Brendel and Luther, 1995, are capable of detecting oxygen, manganese (II), iron (II), and sulfur (II) in porewaters simultaneously. It is also possible to qualitatively detect the presence or absence of dissolved amorphous iron sulfide ($FeS_{(aq)}$). A distinct response for this chemical can be seen in its presence, but quantitative results for this compound are not reliable. Although a powerful technique, its use is presently limited due to the lack of commercial availability of electrodes (fabricated in the lab) and the specialized knowledge required to implement the data collection and analysis.

Field/Lab Trials

August trip to Pastor's Microcosms:

In order to test and refine the application of these chosen analytical methods, two study sites were chosen for testing. The first was the wild rice microcosms maintained by John Pastor at the UMD Farm and provided a convenient and realistic test case. The objectives of this preliminary (reconnaissance) sampling trip to Pastor's microcosms was (a) to test the effectiveness of two porewater measurement techniques (microelectrodes & Rhizons) for iron and sulfide, and (b) to begin to characterize spatial heterogeneity (both vertical and lateral) in porewater geochemistry. A brief outline of the sampling plan for the trip to Pastor's microcosms is given below:

<u>Sampling plan outline for trip to Pastor's Microcosms on 8/30/2011:</u>

- Dissolved ferrous iron and total dissolved (inorganic) sulfide will be measured using triplicate voltammetric microelectrodes spaced ~3-5 cm apart.

- Dissolved sulfide will be sampled with Rhizon filters using evacuated serum bottles and preserved with 2 mL 0.1N ZnAc + 1 mL 0.6N NaOH, later analyzed with ISE in lab
- Ferrous iron will also be sampled with Rhizon filters and serum bottles pre-loaded with reagents for analysis (4x standard 2.5 mL sample size):
- All bottles will need to be weighed pre and post sample collection to accurately determine the volume of sample collected
- In order to quantify both vertical and horizontal heterogeneity: electrodes will be used to measure vertical variation; Rhizons will be used to quantify lateral variation.

- For each microcosm sampled (2 or 3, one control and one sulfate amended microcosm):
    - A minimum of 3 microelectrodes spaced 1-2" apart will be inserted and moved <1 cm at a time to obtain vertical profiles of iron (II), manganese (II), sulfide (II), and oxygen (quantitative), as well as iron-sulfide and organic-bound ferric iron (qualitative).
    - For Rhizon samplers, we will test the ability to collect an uncompromised sample, the length of time necessary to collect a sample, and as a point of comparison to electrode measurements:
        - Sulfide –
            - 3x N2 bottles sealed in N2 atmosphere
            - 1x atmosphere evacuated bottle (to see if N2 atmosphere is necessary)
        - Ferrous iron–
            - 3x N2 bottles sealed in N2 atmosphere
            - 1x atmosphere evacuated bottle
        - Also will want a field matrix spike at or near estimated detection limit to ensure our preservation/quantification is effective.

The focus of this preliminary trip was on sulfide and iron, believed to be the most difficult chemicals to collect uncompromised using porewater sippers. A subsequent trip to a field site near Cloquet, MN was used for a more detailed testing of these and other methods.

October trip to a managed wild rice lake:

In October 2011, a second field trial investigating porewater sampling techniques was undertaken at a managed wild rice lake near Cloquet, MN. The objectives of this follow up field sampling trip to the managed wild rice lake was (a) to test an additional high-resolution porewater sampling method (peepers), and (b) to test peepers and sippers for an expanded suite of analytes, and (c) to characterize spatial heterogeneity in porewater geochemistry (both vertical and lateral) in a field situation. A brief outline of the sampling plan for the follow-up trip to the managed wild rice lake is outlined below:

<u>Sampling plan outline for trip to managed Wild Rice Lake on 11/8/2011:</u>

In order to characterize lateral variability at both a local (few meters) and larger (10s of meters) scale, three sample plots were chosen with a longitudinal (along-shore) spacing of ~10-15m. Each plot was progressively further from shore (5m, 10m, 15m) and all were located greater than 30m from the boat landing on the lake. At each plot, three cores were collected for extracting porewater with sippers and a peeper was inserted into the sediment to leave for 3+ weeks.

- SULFIDE: Dissolved sulfide will be sampled with Rhizon filters using nitrogen-filled, evacuated serum bottles and preserved with 2 mL 0.1N ZnAc + 1 mL 0.6N NaOH

- IRON: Ferrous iron will also be sampled with Rhizon filters and serum bottles pre-loaded with reagents for analysis (4x standard 2.5 mL sample size):
- ANIONS: An additional (no preservative) bottle will be filled for the analysis of anions upon return to the lab.
- Sulfide and iron bottles will need to be weighed pre and post sample collection to accurately determine the volume of sample collected

- Peepers were assembled submerged in a tank of distilled water (>18Mohm) in the lab and left in an upright container (Peeper Keeper) of distilled water purged of oxygen by a continuous flow of nitrogen through a microdiffuser stone for >1 week.
- Peepers were transported to the site sealed in the Peeper Keeper and quickly transferred from the oxygen free water directly to the sediment. 8-10 wells were left exposed to the overlying water after insertion into the sediment.

- After a 3.5 week equilibration time, the team returned to the field site to retrieve the peepers (through the ice) and analyze samples. Samples were composited from adjacent wells where necessary to achieve volumes required to obtain adequate vertical resolution in ferrous iron, sulfide, anions, and cations.

Results

As a predominantly methods-based study on field sample collection techniques, a brief description of each collection method is included here in the results section.

Method descriptions

Sippers

Rhizon soil moisture samplers were purchased from SunValley Solutions, the US distributor for Rhizosphere Research Products, a company based in the Netherlands. Briefly, Rhizons (referred to as sippers) are an in-line filter composed of a hydrophilic membrane (blend of polyvinylpyrrolidine and polyethersulfone) having nominally 0.2 µm pore spaces. Standard Rhizons are available in 5 or 10 cm lengths, and MacroRhizons are 10 cm variants with a larger diameter, greater surface area, and much faster flow rates. Rhizons are inserted into moist or saturated soil and a sample is collected by pulling a negative pressure using a syringe, negative pressure atmosphere, or pump.

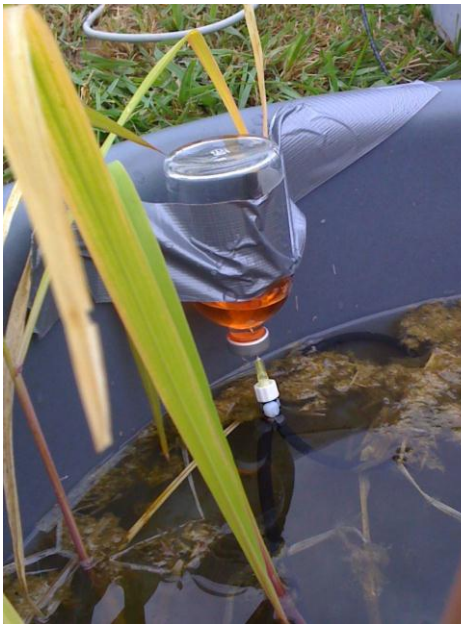

Figure 1. Sipper deployed in Pastor's microcosm

Although originally designed for the field of soil science as tensiometers, sippers have been used for the collection of small-volume porewater samples in aquatic systems

(Seeberg et al. 2005, Shotbolt 2010). The principle advantage of Rhizon sippers is the ability to collect uncompromised samples for redox-active analytes by avoiding any contact with the oxygenated atmosphere. A second advantage is their relative ease of use by untrained workers.

During our trial experiments, Wheaton glass serum bottles (20, 50, or 125 mL with 13x20 IDxOD neck opening) were pre-loaded with Zinc Acetate (ZnAc) preservative for sulfide (if low-level analysis is to be completed later) and sealed under an oxygen-free atmosphere with 1 cm thick Bellco blue butyl-rubber stoppers. A vacuum pump was used to pull the nitrogen out of bottles by connecting the vacuum line to an 18 or 20 gauge disposable hypodermic needle (30 second vacuum time is more than sufficient). A pump capable of pulling a negative gauge pressure of at least 29 inches mercury was used for the field trials. Once in the field, the Rhizon (with needle attached) was put into place in the sediment, the needle was used to puncture the septum on the bottle, and the negative atmosphere in the bottle pulled the sample directly into the bottle. After this process was initiated, the bottles could be secured in place and left unattended to fill with sample.

Two different size sippers were used. The larger MacroRhizons, 10 cm length, had the advantage of pulling sample more quickly and clogging less frequently, but also had a larger dead-space volume and additional connection points. For MacroRhizons, it was important to purge the line of the sipper with sample prior to collecting an aliquot for quantification, particularly if the Rhizons was being reused for multiple samples.

Peepers

Peepers similar to those described in Teasdale et al. (1995) were constructed of half-inch thick, 24x6 inch polycarbonate sheet plastic milled to contain ~35 1 cm deep wells spaced ~1.5 cm apart. Large diameter (~12 inch circular filter paper (0.45 µm polyethersulfone) and a nylon mesh was placed over the wells and secured in place using a face plate with openings corresponding to each well. Nylon mesh (200 µm openings, Industrial Netting) was used to avoid puncturing the filter membrane during insertion and retrieval. Small machine screws were used to seal the face plate tightly against the filter paper and avoid movement of water bypassing filter material or between adjacent wells.

Peepers were assembled in the lab while submerged in distilled water to avoid any bubbles and immediately placed in an upright container filled with distilled water purged of oxygen by a continuous flow of nitrogen. This nitrogen purge continued for >1 week and until peeper deployment.

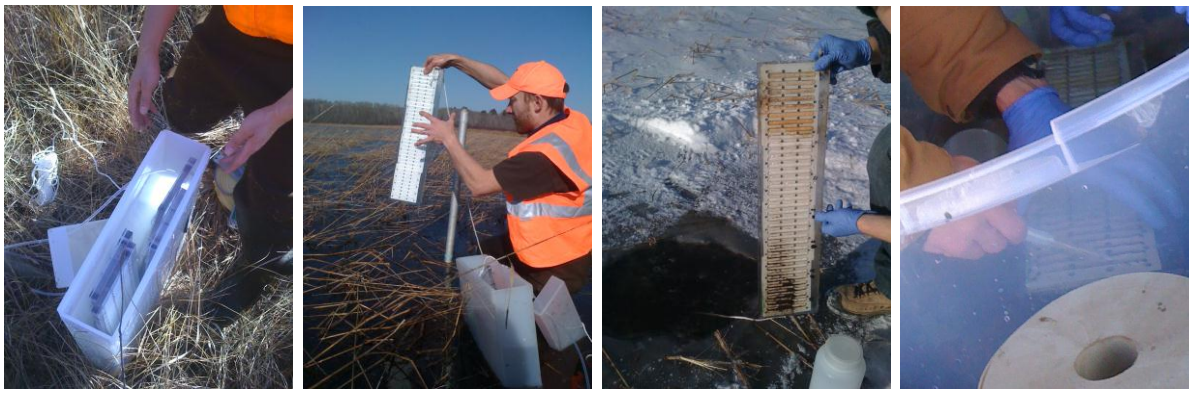

Figure 2. Peeper deployment and retrieval at managed wild rice field site.

Following a 2-3 week deployment (Urban et al. 1997), a plan was made to allocate sample volumes to three different types of sample analysis upon retrieval: ferrous iron, sulfide (with ZnAc preservation), and cations/anions (filtered and split in lab, cations acidified in lab). Additional filtration of anion/cation samples from the field site was necessary due to the large mass of ferric iron present after ferrous iron was oxidized during storage. Samples from adjacent peeper wells were composited where necessary to meet required volumes, with an attempt to maintain close spacing near the sediment-water interface where high-resolution changes in redox-active species were expected.

Peepers were retrieved (through the ice in November) and quickly transported to the back of a minivan where the peepers were submerged in a tub of distilled water (not de-oxygenated) to minimize rates of diffusion which is faster when exposed to air. Excess sediment was wiped and rinsed from the filter/mesh surface using Kimwipes and a laboratory spray bottle. Care was taken to rinse as many particles as possible, but with the consideration that longer exposure to air increases sample oxygen exposure. The filter/mesh surface was dried as thoroughly as possible before being punctured by a hypodermic syringe needle attached to a plastic 10 mL syringe barrel to retrieve ~9-10 mL from each peeper well. This sample was then placed immediately (from the syringe barrel and needle) into sample vials preloaded with preservatives for sulfide (ZnAc or SAOB), ferrous iron (phenanthroline), or cations/anions (unpreserved, filtered/preserved later in lab).

The entire process of retrieval through subsampling all 35 peeper wells took less than 30 minutes for each peeper with a team of 3 or 4 people. Samples were transported to the lab, stored at 4°C, and subsequently analyzed for ferrous iron on a spectrophotometer (immediately), sulfide by ISE (within 48 hours), anions & cations by ion chromatography (within 3 months, longer than recommended storage time).

High sulfide concentrations were not encountered at the managed wild rice lake. However, the potential for dissolved sulfide to oxidize to sulfate in anion samples during storage is known to be important for samples that had significant dissolved sulfide concentrations. Dissolved sulfide can be purged from anion samples prior to storage by acidifying to pH <4 and either bubbling with nitrogen or pulling negative gauge pressure. Hydrochloric acid is preferred over nitric acid due to the ability of nitric acid to oxidize reduced sulfide. If it is necessary to quantify chloride in samples, an unpreserved sample should be split prior to acidification and analyzed separately for chloride.

Electrodes

The method of Brendel and Luther (1995) was used to fabricate electrodes in the lab and calibrate electrodes for oxygen, iron (II), manganese (II), and sulfide (II). Briefly, a 100 µm gold wire connected to coaxial cable is sealed inside a tapered (1 mm tip) epoxy electrode body. The tip of this gold wire is polished with progressively smaller diamond polish with the smallest diameter polish being 0.25 µm.

Mercury is then plated on the tip of the electrode and serves as the surface at which oxidation-reduction reactions involving dissolved oxygen, iron, manganese, and sulfide can be measured in-situ. A scanning potential is applied to the mercury surface relative to a reference electrode and the reaction for each analyte occurs at a distinct electric potential. The electrode response to field measurements is compared to standard addition calibrations performed in a matrix similar to the sampled pore fluids.

Figure 3. Microelectrodes fabricated in the lab and micropositioner deployed in Pastor's microcosm

In order to obtain non-destructive, high-resolution vertical profiles in sediment, an automated micropositioner is used to position the electrodes at increasing depths. Triplicate electrodes spaced at 2-5 cm are typically used and the results averaged to obtain an average concentration at each depth. In-situ field implementation of the microelectrodes was possible at the UMD microcosms since electricity was available. Electrode measurements were not made at the managed wild rice lake.

Total- and methyl- mercury sampling with Rhizons

In case the MPCA determines that it is necessary to measure total- and methyl- mercury in the future, a lab trial characterizing the utility of Rhizon sipper samplers in measuring these parameters. Briefly, blank samples were collected using Rhizons for both inorganic- and methyl- mercury simultaneously, while spikes were performed independently. The procedure used is outlined below.

Blanks included, for both inorganic- and methyl- mercury,

a) Bottle blanks from pulled Rhizon sample (testing desorption from Rhizon during contact with water)
b) Filtered water pulled through Rhizon sample (testing desorption during filtering)

Spike recoveries include, for both inorganic- and methyl- mercury,

c) 2 ppt standard: sample from bottle into which spike was performed (testing spike concentration, desorption from filter)
d) 2 ppt standard: Filtered water pulled through Rhizon filter (testing adsorption to Rhizon during sampling)

Each of these samples was collected in replicate using separate new Rhizon samplers for both freshwater (Cloquet River filtered through a 0.1 µm polyethersulfone filter) and MilliQ water. Samples were collected into an evacuated, acid-washed serum bottle and poured immediately into PETG bottles and preserved with 0.5% trace metal HCl.

Field trial results

Quantification Methods

In all samples in which sulfide was quantified, the ion selective method (Method 4500- S2- G.) was used. In some cases samples were preserved with ZnAc and reconstituted in Sulfide Antioxidant Buffer (SAOB) prior to analysis with ISE. This resulted in a higher estimated detection limit of 10 µM. In other cases, the sample was directly placed in equal volume SAOB which resulted in a lower detection limit of 2-5 µM. A very low detection limit for ZnAc preserved samples (<0.1 µM) was implemented as a part of the MPCA's preliminary field study, but this method was unavailable to the UMD porewater team at the time of sample collection and analysis. Recovery of 10 and 50 µM standards with either method averaged 113% (n=4) with RPD of replicate analyses between 2 and 20%. In general, Zn preserved samples were less consistent than samples that were quantified directly in SAOB.

Ferrous iron was quantified by the phenanthroline method (Method 3500-Fe-I) using reagent volumes adjusted for larger sample sizes. For peeper samples, less than 0.5 mL sample was diluted to 2.5 mL due to high iron concentrations at the field site. The detection limit for undiluted samples was estimated to be 9.5 µm based on the standard deviation of replicate 10 µM analysis (n=4). pH was measured with a silicone-based field pH sensor (IQ 160 Waterproof pH meter with Stainless Steel ISFET Probe, Ben Meadows) calibrated immediately prior to use. Anions were quantified by ion chromatography on a Dionex 1100 with A22 column following acidification and purging of samples expected to have high sulfide.

Inorganic and methyl mercury was quantified using cold vapor atomic fluorescence spectrometry (following ethylation and GC separation for methyl mercury) by an experienced laboratory at the University of Toronto Scarborough using a slight modification from EPA methods 1630 and 1631.

Microcosm results

Results from samples collected by sippers at Pastor's microcosms are tabulated in Appendix A. pH ranged from 6.5 to 7.0 in the sediment and ranged between 7.5 and 8.0 in the overlying water. Total dissolved sulfide concentrations in the sediment porewater were low in both the control (1.8 µM +/ 0.12, n=3) and sulfate amended (4.2 µM +/ 1.8, n=3) microcosms. The difference between the two microcosms was significant (p=0.083) based on this limited data set.

Ferrous iron was measured at 127.5 µm (+/- 0.82, n=2) in the sulfate amended microcosm and 223 µM (+/- 39, n=3) in the control microcosm. One sample from the amended microcosm was compromised due to a failure to purge the line from the sipper prior to collecting a subsequent sample.

Results from voltammetric electrode measurements are included in Appendix B. Electrode measurements in the sulfate amended microcosm were consistent with those made using sipper samplers. Sulfide concentrations below 3 cm ranged from 0.3 µM to 3.7 µM, while iron concentrations ranged from 40 to 150 µM. Distinct depth profiles were observed for both iron (II) and sulfide (II) with very low concentrations in the surficial 2-3 cm, higher concentrations between 4-7 cm, and a low measurement made at 9 cm. The depth of sediment in the microcosms is ~10 cm and there is a 10 cm layer of clean sand in the bottom of the microcosm. A current peak at a potential consistent with that of FeS (aq) was also observed in the amended microcosms. This peak is seen when both iron and sulfide are present in porewaters, but is not quantitative.

Electrode measurements in the control microcosm appeared to have been compromised as the electrode response for iron during calibration was very low. The only response that appeared during scans in the control microcosm was that for FeS, which is not quantitative. Electrode data for this microcosm is included in the appendix, but should be interpreted with caution. Results from sippers above showed slightly lower sulfide concentrations and significantly higher iron concentrations in the porewaters of the unamended (control) microcosm.

Samples for sulfide, pH, and iron collected from the microcosms with sippers are interpreted with respect to the solubility of different iron-sulfide solid phases. Figure 4 shows the ion activity product measured in both the control and sulfate amended microcosms compared to the solubility product of two solid phase iron sulfide minerals. Although iron and sulfide differ amongst the microcosm treatments, these results suggest that, in both microcosms, the sulfur and iron pool are interacting in a way that is consistent with the formation of amorphous iron sulfides in the surficial sediment.

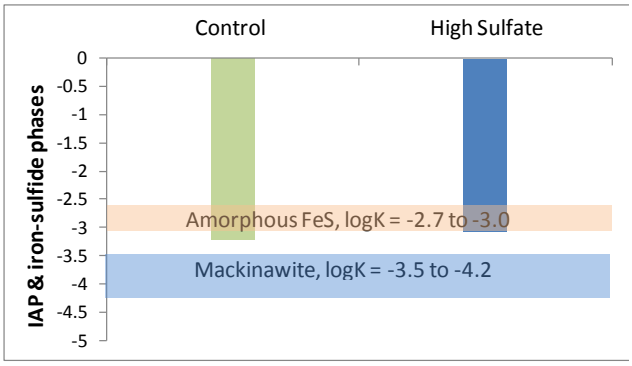

Figure 4. Iron and sulfur solid phase minerals and measurements from control and amended microcosms.

Field site results

pH and ferrous iron quantified in samples from peepers deployed at the field site and retrieved in November 2011 and are shown in Figure 5, Appendix C and Appendix D. pH was very consistent among the three deployed peepers at 6.75 +/- 0.5 in the overlying water and in the surficial 30 cm of sediment. Ferrous iron peaked at near 1000 µM in all three peepers at just above the sediment-water interface (0-5 cm) and dropped to a relatively constant value of 500 µM (~28 mg/L). This response was consistent among all three deployed peepers and little variability was observed among the three different distances from shore. Results from sippers (which collected water from the top 10 cm of sediment) were very consistent for the peeper measurements in surficial sediment. Triplicate cores collected and sampled with Rhizons from 5, 10, and 15 m from shore had an average of 530 (+/- 38, n=3), 435 (+/- 18, n=2), and 494(+/- 33, n=3) µM dissolved ferrous iron, respectively as shown in Figure 5b. Some within-plot variability was observed, but the porewaters at this site were clearly dominated by iron and contained little dissolved sulfide.

Little variation in iron and pH concentrations were observed over the top 10-15 cm of sediment porewaters using peepers during this late-fall sampling event. While this would suggest that the bulk, integrated sample collected by Rhizon filters does not sacrifice much information due to the lack of spatial variability, the slowing of microbial activity during winter months (and the lack of a low-level sulfide method) may not induce an active zone of sulfur/iron cycling in the top 5 cm of sediment in the rooting zone which is present in warmer summer conditions. Subsequent samples collected with peepers at UMD wild rice microcosms during spring 2012 show sharp gradients in sulfide and iron near the sediment-water interface to ~5 cm below. While vertically integrated samples collected with Rhizons would not capture this high-resolution changes to porewater chemicals, they may still provide adequate

information for a coarse, survey-scale assessment. Higher resolution measurements with peepers or electrodes appear necessary to characterize redox processes at a finer scale in wild rice sediments.

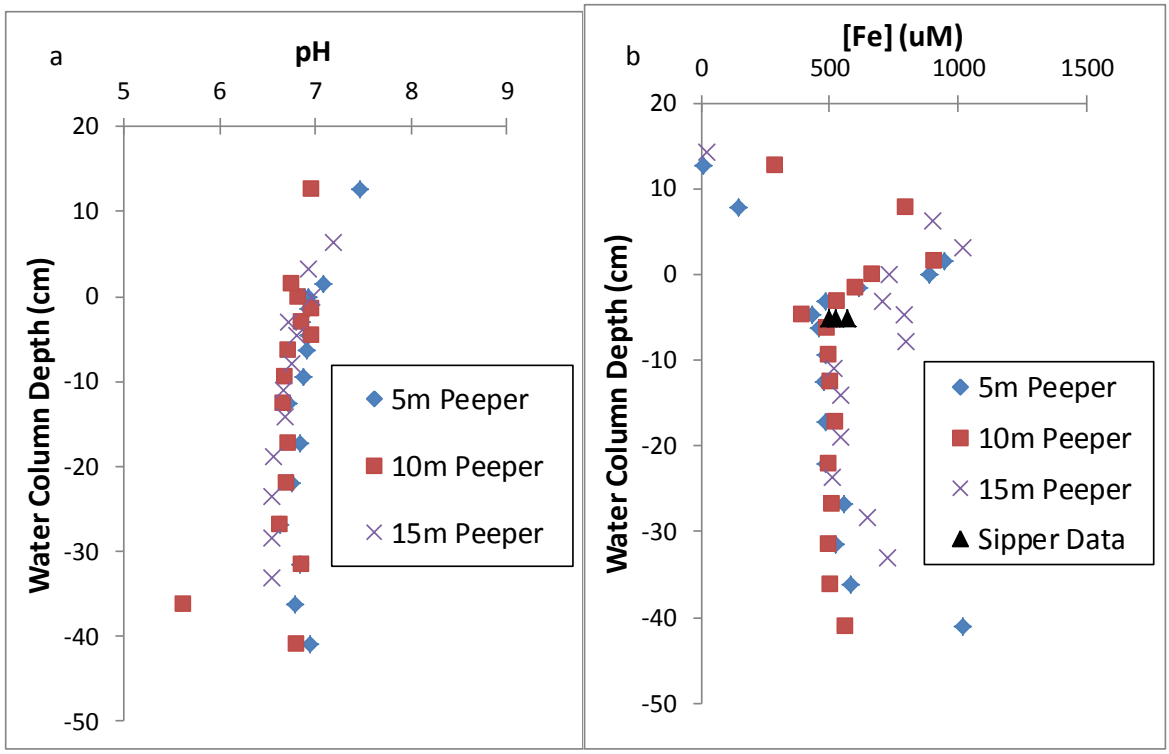

Figure 5. pH and ferrous iron concentrations in peepers deployed at a field site.

An attempt was made to quantify sulfide using an ion selective electrode, but all samples had concentrations well below 10 µM, below the detection limits for the ISE method available at UMD. pH values ranged from 6.5 to 7 and equilibrium calculations with solubility products estimated at microcosms suggest that sulfide concentrations in equilibrium with the measured ferrous iron concentration would be less than or around 0.2uM. A few sulfide samples preserved with ZnAc were sent to the St Croix Watershed Research Station (SCWRS) as a practice for low-level sulfide analysis. Reliable results for these samples were not obtained since they were analyzed during method development. Field samples collected as a part of the field sampling component of the preliminary wild rice study were eventually analyzed by the SCWRS down to less than 0.1 µm sulfide although a sample size of >30 mL was used.

Anions were also quantified in peeper samples from the managed wild rice field site and results are shown in Appendix C. The samples were stored for longer than the recommended holding time and were some of the first to be processed through a new piece of equipment (Dionex Ion Chromatograph). Analytical duplicates were not consistent (3% to 70% RPD for sulfate, 4% to 80% RPD for nitrate). Samples from Peeper 3 (right peeper) were preserved with HCl, while other samples were left at 4°C unpreserved. These limitations make the anion data from this study unreliable and highlight the importance of correctly preserving and analyzing small-volume anion samples.

Total- and Methyl- Mercury results

Results from testing Rhizons for collecting mercury and methyl mercury suggest they can be effective in natural waters although some loss of MeHg was observed from a spike sample. Samples collected in distilled water, however, showed significant interaction with filter material. A limited sample volume resulted in some loss of resolution, especially for methyl mercury samples.

Natural Waters

For *inorganic mercury*, blanks for 0.1 µm filtered Cloquet River water were 2.32 ng/L (+/- 0.05, n=3) in the bottle and 2.57 ng/L (+/- 0.31, n=2) for water after passing through new, unrinsed Rhizons. One of the unspiked inorganic mercury samples filtered through a new Rhizon was quantified at 6.87 ng/L. It is unknown whether this was due to an error during analysis, contamination in sample bottles, or mercury desorption from a new Rhizon. Spikes to filtered Cloquet water showed 4.06 ng/L (+/- 0.08, n=3) in bottles and 4.04 ng/L (+/- 0.31, n=3) in filtered samples. The mean of filtered samples was nearly identical to the bottle spike concentration suggesting little loss during filtering; however, there was more variability in filtered samples.

For *methyl mercury* in filtered Cloquet water, bottle blanks averaged 0.14 ng/L (+/- 0.14, n=3). One bottle blank was below detection limits. Rhizon filtered Cloquet water blanks averaged 0.31 ng/L (+/- 0.32, n=4) which is slightly higher than the native water. This difference, however, is not statistically significant with the number of samples tested. A spike of MeHg to the filtered Cloquet water was quantified at 1.73 ng/L in the bottle from which the sample was filtered. The Rhizon-filtered sample from this spike was quantified at only 0.69 ng/L. No replicates of this analysis were conducted for methyl mercury, though this result, in conjunction with slightly higher methyl mercury quantified in blanks, suggests that a MeHg may be interacting with (desorbing from or adsorbing to) filter material during filtering with new Rhizons.

DI Water

For *inorganic mercury* in DI water, bottle blanks were 0.24 ng/L (+/-0.017,n=3) while filter blanks averaged 0.39 ng/L (+/-0.046, n=3). Though the sample set is limited, this suggests that a small amount of inorganic mercury could be released during filtration with a new Rhizon. Spikes to DI water showed 1.735 ng/L (+/-0.007, n=3) in the bottles but only 0.65ng/L (+/- 0.65, n=3) in filtered water. This suggests that some of the inorganic mercury in DI water was adsorbed to the new Rhizon during filtration when no ligands were available to bind the mercury.

For *methyl mercury* in DI water, bottle blanks were below detection limits (0.03 ng/L) in two bottle samples and 0.15 ng/L in the third bottle. Filtered samples were below detection limits in one bottle and 0.03ng/L and 0.07 ng/L in the other bottles.

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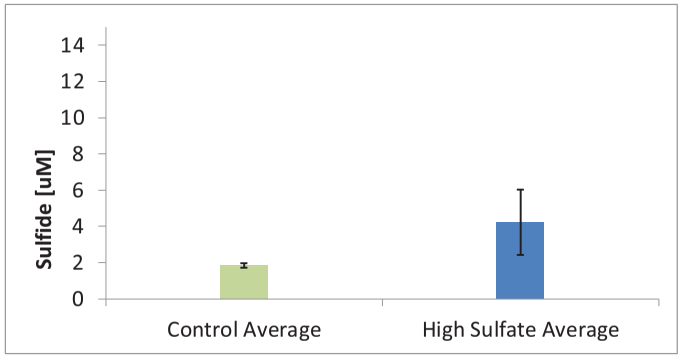
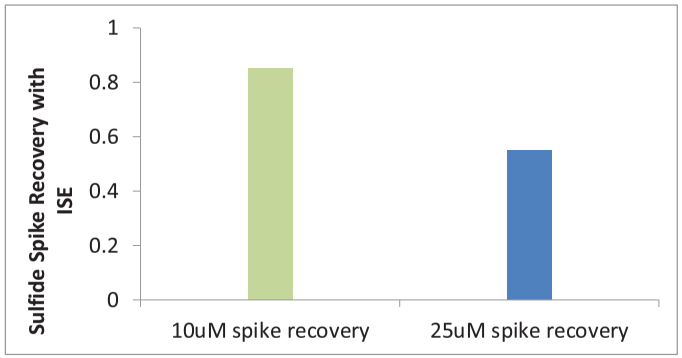
APPENDIX A: Sipper samples from UMD Microcosms

Pastor's microcosms: sippers, SULFIDE RESULTS

Bottle Label	Treatment	Sulfide (uM)	average	St. dev.	
SN2-1	High Sulfate Sample-1	3.342043248			
SN2-2	High Sulfate Sample-2	3.053137543			
SN2-4	High Sulfate Sample-3	6.306418737	4.233867		1.800686308
SN2-12	Control Sulfate Sample	1.95816198			
SN2-11	Control Sulfate Sample	1.826828979			
SN2-15	Control Sulfate Sample	1.716572003	1.833854		0.120948112
SN2-8	Spike 1	0.257336053			
SN2-9	Spike 2	0.70469084			
SN2-10	Spike 3	0.010506627			
Low 1 (10 uM)	Lab Spike	8.449773177			
Low 2 (10 uM)	Lab Spike	8.556305747	8.503039		0.075329903
High 1 (25 uM)	Lab Spike	14.00582061			
High 2 (25 uM)	Lab Spike	13.6022992	13.80406		0.285332726
SN_2-10	Lab Spike	0.889682149			

SULFIDE RESULT	Average	St. Dev
Control Average	1.83385432	0.120948112
High Sulfate Aver	4.23386651	1.800686308
10uM spike recov	8.503039462	0.850303946
25uM spike recove	13.80405991	0.552162396



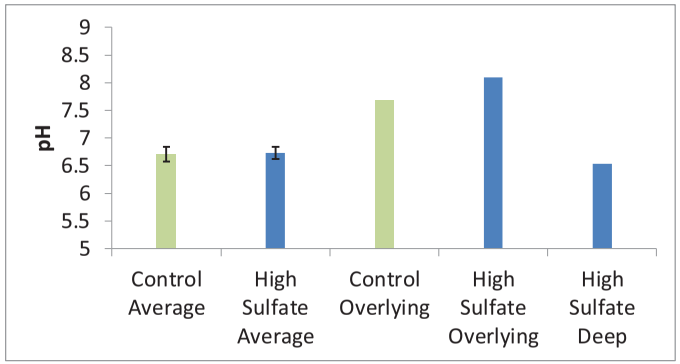


Pastor's microcosms: sippers, pH RESULTS

pH Results

Low Sulfate Overlying	7.69		
Control Sulfate Sample-1	6.77		
Control Sulfate Sample-2	6.55		
Control Sulfate Sample-3	6.8	6.706667	0.136503968
High Sulfate Overlying	8.09		
High Sulfate Sample-1	6.79		
High Sulfate Sample-2	6.8		
High Sulfate Sample-3	6.6	6.73	0.112694277
High Sulfate Sample-3 (deep	6.53		

Control Average	6.706666667	0.136504
High Sulfate Average	6.73	0.112694
Control Overlying	7.69	
High Sulfate Overlying	8.09	
High Sulfate Deep	6.53	



Pastor's microcosms: sippers, FERROUS IRON RESULTS

Initial Bottle mass 101.7 +/- 0.3 g

Final Bottle mass

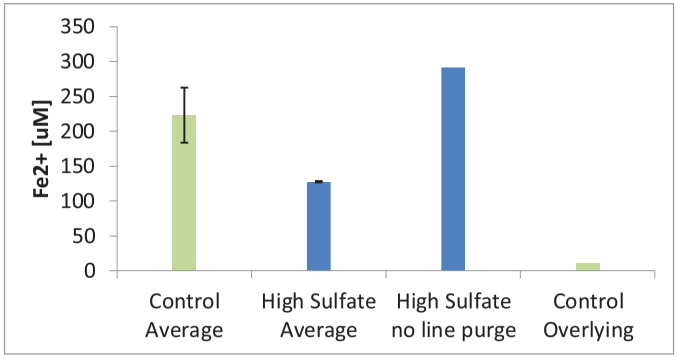
Bottle ID	Mass	mL added	Add'n adde	Dilution	Absorbanc	Raw Conc	Actual Con	ave	stdev	
1	108.5	6.8	3.2	0.85	0.6125	107.8656	126.9007			High Sulfate Sample-1
2	110.1	8.4	1.7	0.93	0.677	119.0955	128.0597			High Sulfate Sample-2
3	112.2	10.5	0	1.035	1.724	301.3858	291.194	127.4802	0.819531	High Sulfate Sample-3 (no line purge)
4	107.7	6	4	0.81	1.126	197.2697	243.5428			Control Sulfate Sample-1
5	108.3	6.6	3.4	0.84	1.188	208.0643	247.6956			Control Sulfate Sample-2
6	113	11.3	0	1.075	1.09	191.0018	177.6761	222.9715	39.28189	Control Sulfate Sample-3
15	124.7	23	0	1.66	0.089	16.72044	10.07255			Control Sulfate Overlying

Calibration

yesterday's

Conc [uM]	Abs				Fe2+ Conc Ave	Stdev	n
0	0			Control Average	222.9715	39.28189	3
10	0.06			High Sulfate Average	127.4802	0.819531	2
50	0.25			High Sulfate no line purge	291.194		
200	0.997			Control Overlying	10.07255		
400	1.987	corrected					
m	201.1270141	161.2998826		dilution from adding extra 1mL...			
b	0.487381579			0.801980198			
	0.999976512			1	deox h20	0	
today's				1	phen	1	
Conc [uM]	Abs			0.5	acet	0.5	
0	-0.001		ratio of slo	0.05	hcl	0.05	
50	0.273		1.15519	2.5	sample	2.5	
200	1.109			5.05		4.05	
600	3.46						
m	174.1072676						
b	1.224890706						
	0.999851537						

High Sulfate Sample-3 (deeper)



Pastor's microcosms: DATA ANALYSIS, FES SOLUBILITY

Solubility Calculat log Ksp (Morse et al. 1987)

mackinawite	-3.543633967	0.000286
amorphous	-2.943095149	0.00114
gregite	-12.82390874	1.5E-13
pyrite	-16.40011693	3.98E-17

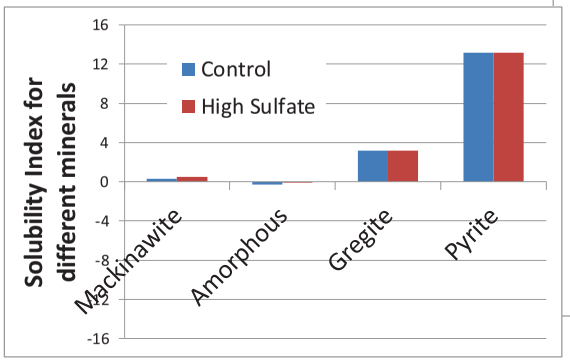
	Average HS- [uM]	Average Ferrous [uM]	Average pH	Mackinawite			Amorphous			Gregite			Pyrite		
				IAP: [Fe][HS]/[H]	SI = log(IAP	Appearant	IAP: [Fe][H	SI = log(IAP	Appearant	IAP: ([Fe][HS]/[I	SI = log(IAP	Appearant	IAP: [Fe][H	SI = log(IAP	Appearant
Control	0.527937207	222.9715122	6.706667	0.000599099	0.321132	-3.2225	0.000599	-0.27941	-3.2225	2.15028E-10	3.156404	-9.66751	0.000599	13.17762	-3.2225
High Sulfate	1.266021757	127.4801929	6.73	0.00086673	0.481518	-3.06212	0.000867	-0.11902	-3.06212	2.15028E-10	3.156404	-9.66751	0.000599	13.17762	-3.2225

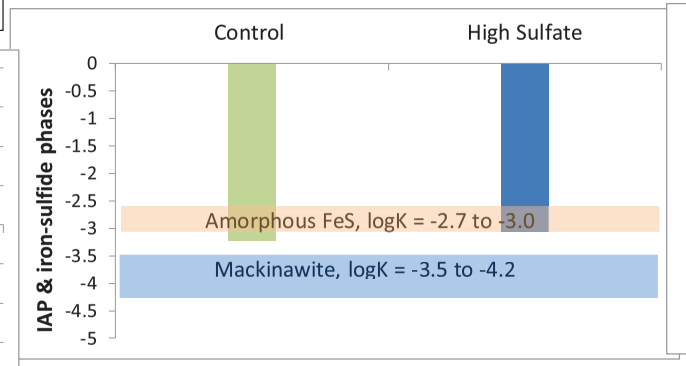
$$\Omega = \frac{\left\{\frac{[Fe^{2+}][HS^-]}{[H^+]}\right\}}{10^{-4.2}}$$

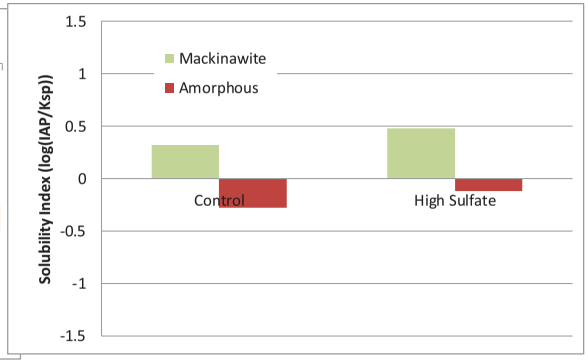
$$FeS_{(s)} + H^+ \Leftrightarrow Fe^{2+} + HS^-, \log K = -4.2$$

$$\frac{[Fe^{2+}][HS^-]}{[H^+]} = 10^{-4.2}$$

	Mackinawi	Amorphou	Gregite	Pyrite
Control	0.321132	-0.27941	3.156403691	13.17762
High Sulfat	0.481518	-0.11902	3.156403691	13.17762







APPENDIX B: Electrode measurements from UMD Microcosms

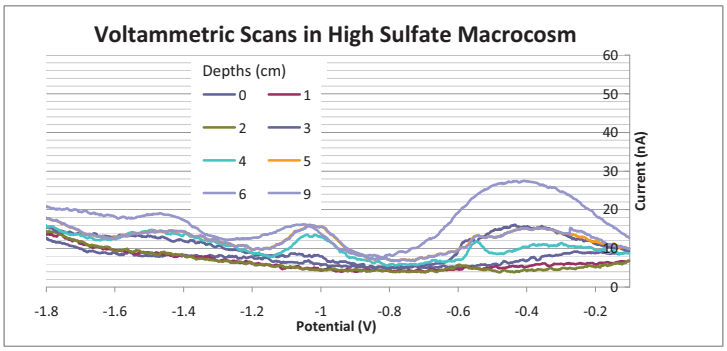
Pastor's microcosms: VOLTAMMETRY ELECTRODES PROFILE - AMENDED MICROCOSM

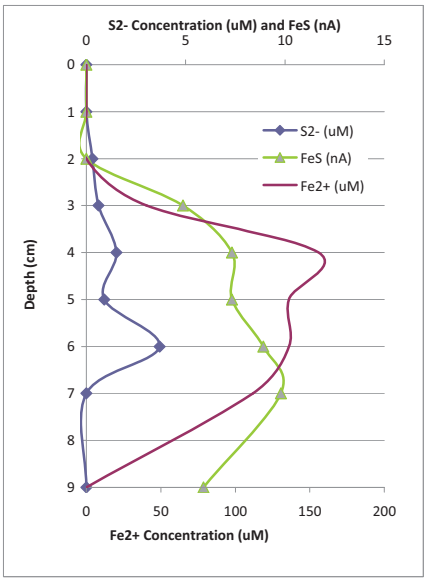
Measurements in nA

Depth	S2- (nA)	Fe2+ (nA)
0	0	0
1	0	0
2	0.8	0
3	1.6	1.01
4	4	3.9
5	2.383	3.4
6	9.7	3.4
7	0	2.8
9	0	0

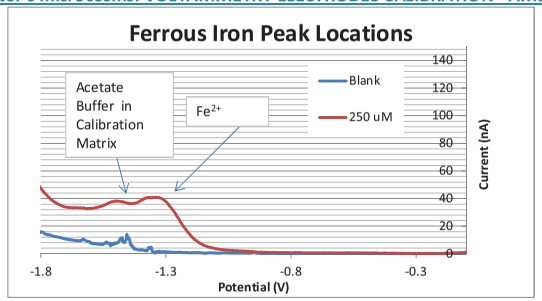
Concentration Calculations

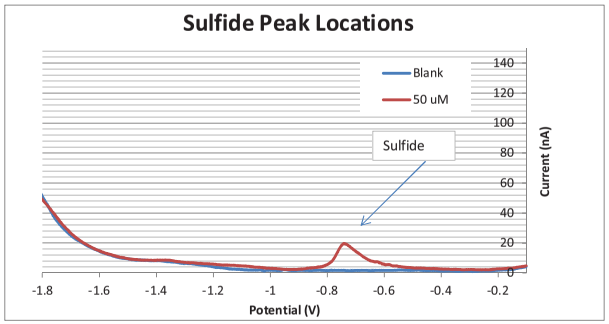
S2- (uM)	Fe2+ (uM)	FeS (nA)
0.00	0.00	0
0.00	0.00	0
0.30	0.00	0
0.61	40.40	4.863634
1.52	156.00	7.33741
0.91	136.00	7.33741
3.69	136.00	8.915993
0.00	112.00	9.799198
0.00	0.00	5.9





Pastor's microcosms: VOLTAMMETRY ELECTRODES CALIBRATION - AMENDED MICROCOSM





Calibrations Applied to nA measurements (Luther, 1995)

Analyte	Slope (uM/nA)
Fe^{2+}	40.00

Calibration Applied to nA Measurements from one point calibration

Analyte	Slope (uM/nA)
S^{2-}	0.38

Sulfide QA/QC

MDL	LOQ	S/N Ratio
2.23	7.11	5.26

Pastor's microcosms: VOLTAMMETRY ELECTRODES PROFILE - CONTROL MICROCOSM

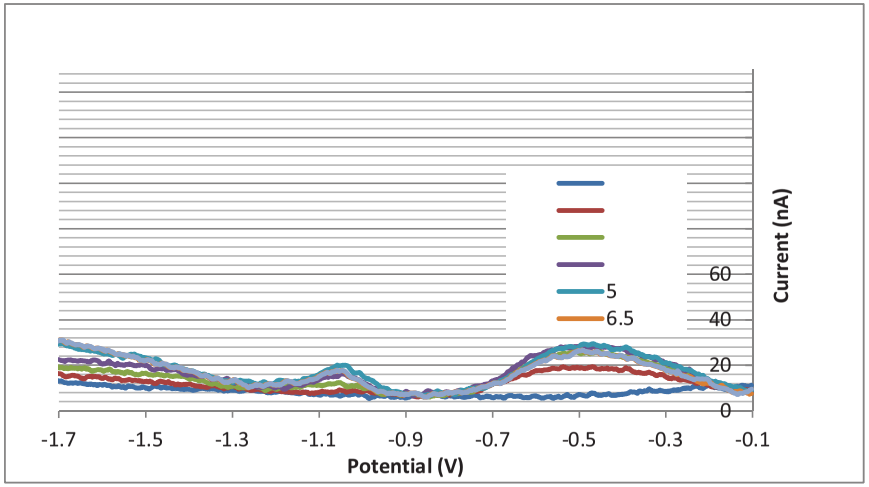
Note: electrode response had degraded by the time the control microcosm was sampled. Electrode results in this microcosm may have been compromised.

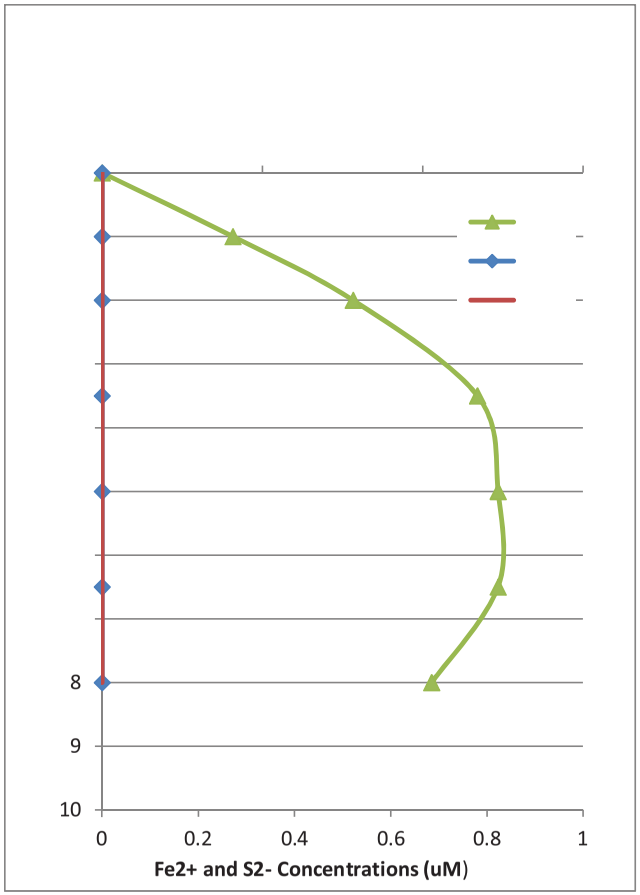
Measurements in nA

Depth	S2- (nA)	Fe2+ (nA)	FeS (nA)
0	0	0	0
1	0	0	4.076337
2	0	0	7.82497
3.5	0	0	11.70149
5	0	0	12.34491
6.5	0	0	12.34491
8	0	0	10.27078

Concentration Calculations

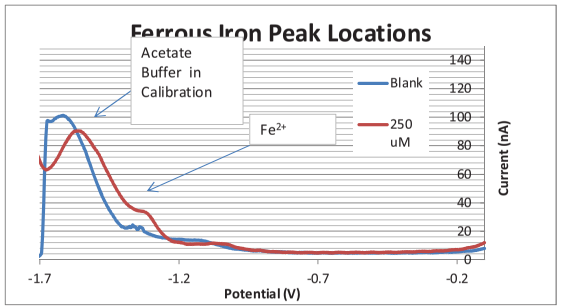
Depth	S2- (uM)	Fe2+ (uM)	FeS (nA)
0	0	0	0
1	0	0	4.076337
2	0	0	7.82497
3.5	0	0	11.70149
5	0	0	12.34491
6.5	0	0	12.34491
8	0	0	10.27078

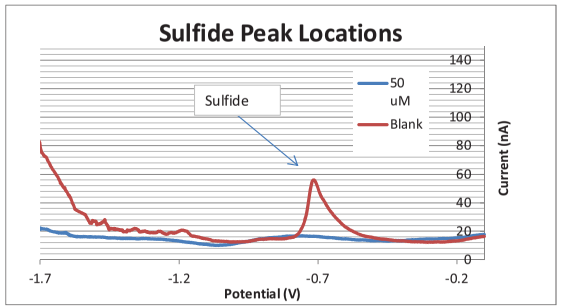




Pastor's microcosms: VOLTAMMETRY ELECTRODES CALIBRATION - CONTROL MICROCOSM

Note: electrode is clearly not as responsive to iron as it was in the amended microcosm. Iron results for this electrode should be inerpreted with caution.





Calibrations Applied to nA measurements (Luther, 1995)

Analyte	Slope (uM/nA)
Fe^{2+}	40.00

Calibration Applied to nA Measurements from one point calibration

Analyte	Slope (uM/nA)
S^{2-}	0.84

Sulfide QA/QC

MDL	LOQ	S/N Ratio
2.23	7.11	5.26

APPENDIX C: Peeper anion data from field site

Anions at field site: PROFILE RESULTS

Left Peeper

Depth	Well	F (mg/L)	Cl (mg/L)	SO4 (mg/L)	NO2 (mg/L)	Br (mg/L)	NO3 (mg/L)	PO4 (mg/L)
-43.00	L36	0.446	2.220	0.936	nd	nd	nd	nd
-38.05	L34L33	0.174	0.902	0.517	nd	nd	0.406	nd
-33.10	L30L31	0.109	0.585	0.662	0.050	nd	0.718	nd
-28.15	L28L27	0.108	0.353	0.457	nd	nd	0.138	nd
-23.20	L24L25	0.057	0.423	0.215	nd	nd	0.451	nd
-18.25	L22L21	0.155	0.508	0.567	nd	nd	0.496	nd
-13.30	L18L19	0.124	0.527	0.488	nd	nd	0.474	nd
-10.00	L17L16	0.103	0.706	0.627	nd	nd	0.550	nd
-6.70	L15L14	0.089	0.738	0.569	nd	nd	0.240	nd
-5.05	L13	0.093	0.931	0.646	nd	nd	0.377	nd
-3.40	L12	0.079	1.088	0.766	nd	nd	0.418	nd
-1.75	L11	0.112	1.207	0.960	nd	nd	0.515	nd
0.00	L10	0.119	1.521	0.694	nd	nd	0.975	nd
1.75	L9L8	0.141	1.915	0.640	nd	nd	1.063	nd
14.92	L3L2	0.200	2.020	2.766	nd	nd	0.172	nd

Center Peeper

Depth	Well	F (mg/L)	Cl (mg/L)	SO4 (mg/L)	NO2 (mg/L)	Br (mg/L)	NO3 (mg/L)	PO4 (mg/L)
-44.65	C36	0.135	0.974	0.640	nd	nd	0.200	nd
-39.7	C34C33	0.142	0.968	0.505	nd	nd	0.312	nd
-34.75	C31C30	0.134	1.025	0.672	nd	nd	0.742	nd
-29.8	C28C27	0.125	0.496	0.522	nd	nd	0.145	nd
-24.85	C25C24	0.130	0.537	0.749	nd	nd	0.215	nd
-19.9	C22C21	0.254	0.751	0.645	nd	nd	0.156	nd
-14.95	C18C19	0.278	0.561	0.514	nd	nd	0.392	nd
-11.65	C17C16	0.186	0.741	0.646	nd	nd	0.510	nd
-8.35	C14C15	0.184	0.788	0.622	nd	nd	0.132	nd
-6.7	C13	*	1.119	0.633	nd	nd	0.124	nd
-5.05	C12	*	0.995	0.711	nd	nd	0.220	nd
-1.75	C10	*	1.175	0.561	nd	nd	0.146	nd
0	C8	*	1.343	0.527	nd	nd	0.098	nd
		*						

Duplicates

Depth	Well	F (mg/L)	Cl (mg/L)	SO4 (mg/L)	NO2 (mg/L)	Br (mg/L)	NO3 (mg/L)	PO4 (mg/L)
-11.65	C17C16 ©	*	137.913	0.817	nd	nd	0.161	nd
-8.35	C15C14 ©	*	140.944	1.022	nd	nd	0.213	nd
0	C8 © Dup	*	128.537	0.892	nd	nd	0.183	nd
0	C8 Dup	*	1.376	0.543	nd	nd	0.061	nd
-39.56	R35R34 Dup	*	1.099	0.840	nd	nd	0.177	nd
-14.95	L18L19 Dup	0.176	0.653	0.512	nd	nd	0.455	nd
-11.65	L17L16 Dup	0.138	0.761	0.646	nd	nd	0.419	nd
-38.05	L34L33 Dup	0.248	0.973	0.571	nd	nd	0.377	nd
-38.05	C34C33 Dup	0.133	0.974	0.498	nd	nd	0.285	nd

Anions at field site: PROFILE RESULTS

Right Peeper

Depth	Well	F (mg/L)	Cl (mg/L)	SO4 (mg/L	NO2 (mg/L	Br (mg/L)	NO3 (mg/L	PO4 (mg/L)
-39.56	R35R34	*	1.065	0.725	nd	nd	0.401	nd
-29.24	R29R28 ©	*	122.860	0.952	nd	nd	0.127	nd
-34.4	R32R31 ©	*	122.478	1.105	nd	nd	0.071	nd
-30.00	R29R28 ©	*	132.662	1.287	nd	nd	nd	nd
-24.08	R26 ©	*	126.248	1.129	nd	nd	nd	nd
-18.92	R23R31 ©	*	115.681	1.010	nd	nd	0.071	nd
-15.48	R21R20 ©	*	140.293	0.819	nd	nd	0.902	nd
-12.04	R19R18 ©	*	141.765	0.996	nd	nd	0.199	nd
-8.6	R16	*	1.372	0.703	nd	nd	0.086	nd
-6.88	R15	*	1.311	0.705	nd	nd	0.154	nd
-3.44	R12 ©	*	122.694	0.817	nd	nd	0.998	nd
0	R11	*	1.677	0.553	nd	nd	0.214	nd
8	R7R6 ©	*	113.475	1.337	nd	nd	0.223	nd
12	R5R4 ©	*	135.507	2.501	nd	nd	0.213	nd

Sippers

Depth	Bottle	F (mg/L)	Cl (mg/L)	SO4 (mg/L	NO2 (mg/L	Br (mg/L)		
	5M#1	*	5.064	0.603	nd	nd	NO3 (mg/L	PO4 (mg/L)
	5M#3	*	0.676	0.338	nd	nd	0.117	nd
	5M#4	*	5.167	0.641	nd	nd	nd	nd
	10M#5	*	0.939	0.566	nd	nd	0.135	nd
	10M#7	*	1.397	0.315	nd	nd	0.102	nd
	10M#8	*	4.327	1.636	nd	nd	0.082	nd
	15M#1	*	1.718	1.111	nd	nd	0.086	nd
	15M#10	*	1.585	0.399	nd	nd	0.080	nd
	15M#11	*	2.058	1.699	nd	nd	0.165	nd
							0.131	nd

Note: © denotes a sample was taken from a cation vial that was preserved with concentrated HCl

Note: Depths were taken from Fe2+ analysis

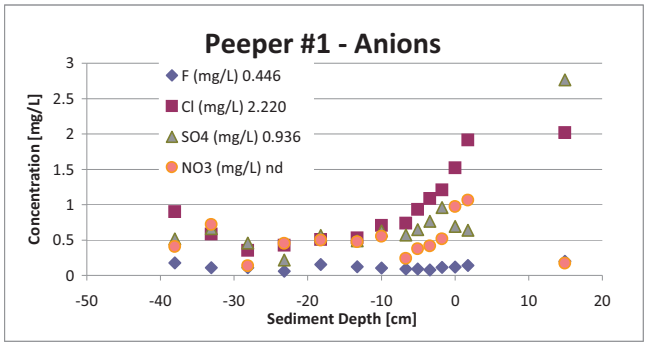
Note: The second run would not allow for the calculation of Fluoride even though the calibration wa acceptible.*

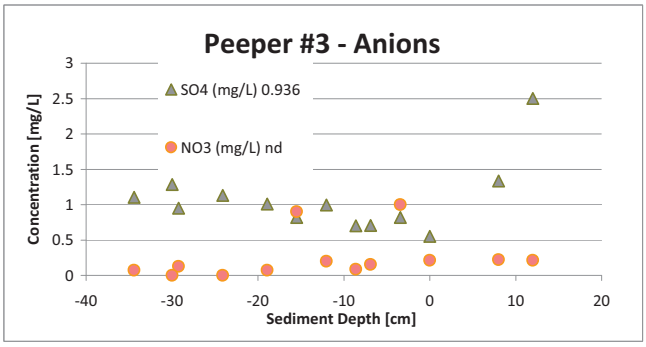
Note: nd = no detect

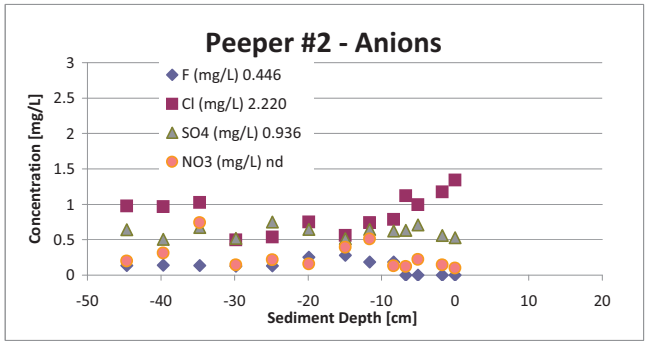
Note: MDLs and LOQ for the IC have yet to be deteriminec

perc diff					
F (mg/L)	Cl (mg/L)	SO4 (mg/L	NO2 (mg/L	Br (mg/L)	NO3 (mg/L)
		26.5%			-68.4%
		64.2%			61.6%
		69.1%			86.8%
	2.4%	3.1%			-37.7%
	3.2%	15.9%			-55.8%
41.3%	23.7%	4.9%			-3.9%
33.5%	7.8%	3.1%			-23.7%
42.4%	7.9%	10.6%			-7.3%
-23.7%	8.1%	-3.7%			-29.8%

Anions at field site: PROFILE RESULTS







APPENDIX D: Peeper iron and pH data from field site

Well #	Depth (cm)	Peeper [Fe] (uM) Left	Peeper [Fe] (uM) Center	pH Left	pH Center
36	-41.0	1022.2	560.3	6.95	6.81
33	-36.3	579.4	503.4	6.78	5.62
30	-31.5	527.0	500.1	6.84	6.85
27	-26.8	555.5	513.2	6.63	6.63
24	-22.0	483.7	499.0	6.76	6.7
21	-17.3	486.3	525.5	6.83	6.72
18	-12.6	475.0	507.2	6.71	6.67
16	-9.4	487.3	498.5	6.87	6.69
14	-6.2	457.6	488.6	6.9	6.71
13	-4.7	432.1	393.3	6.92	6.96
12	-3.1	485.1	528.9	6.85	6.85
11	-1.5	614.3	602.9	6.93	6.96
10	0.0	891.8	670.2	6.93	6.82
9	1.6	948.7	911.7	7.08	6.76
5	7.9	142.3	795.9		
2	12.6	9.5	288.6	7.47	6.96

Well #	Depth (cm)	Peeper [Fe] (uM) Right	pH Right
34	-33.1	726.0	6.86
31	-28.4	648.9	6.54
28	-23.6	508.6	6.55
25	-18.9	543.1	6.55
22	-14.1	544.3	6.56
20	-11.0	517.0	6.68
18	-7.8	795.5	6.66
16	-4.7	790.6	6.75
15	-3.1	705.5	6.81
13	0.0	729.5	6.71
11	3.2	1018.8	6.96
9	6.3	904.1	6.92
4	14.2	18.4	7.18

Sipper @5m from shore

Depth	[Fe] (uM)
-5	524.6494
-5	494.9833
-5	569.9000