Field and Laboratory Analysis of Controls on Groundwater Iron Concentration in Marsh and Forested Wetland Sediments

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GEOL 394

April 30th, 2004

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ABSTRACT:

This aim of this research project was to determine what controls iron (Fe) concentrations in an urban, shallow groundwater system as the groundwater table and other parameters change. Specifically, this study addresses the effect of microbial activity, and seasonal and topographical changes on the reduction-oxidation (redox) processes that occur in soils. This was done by the analysis of field data sets, one that I collected, and the other an existing data set put together by Nancy Katyl, a University of Maryland alumna, over the period 1993 to 1995 for her graduate thesis.

The preliminary part of the study was carried out at the Paint Branch tributary located in the North-eastern outskirt of the University of Maryland, College Park campus, and final part at the site in Annapolis MD where Katyl worked. The field and laboratory study commenced in September 2003 and culminated in April 2004. Fieldwork for this project included the collection of core sediment samples from both the Paint Branch site and the Annapolis site, and the set-up of laboratory experiments under controlled conditions to determine the relative amount, and rate of redox changes that occur as the position of the water table changes. These laboratory analysis results along with the graphical/mathematical analysis of Katyl's data allowed for an understanding of what the various controls on groundwater iron concentrations in marsh and forested wetland sediments are, and how significant a role each control plays in this ongoing process.

The results of the analyses and experiments have discredited one of the hypotheses formulated in this study, namely, the hypothesis that says that as temperature increases (during the warmer months) the amount of iron reduction occurring in sediment will increase. A second hypothesis, which says that marsh sediment at greater depths will be characterized by greater amounts of iron reduction, was neither supported not discredited. The third and final hypothesis, which says that the presence of microbes is essential for the fast reduction of Fe^{3+} in subsurface environments, was supported by the experiments carried out.

In general, the results of my laboratory experiments coupled with the data analysis suggest that most iron reduction does take place near the iron redoxcline and that the iron that moves into more anaerobic regions of the soil remains in solution and accumulates in deeper wells.

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INTRODUCTION:

Statement Of The Problem

Reduction and oxidation (redox) reactions, although they are known to be beneficial in many geological processes, such as the formation of economic metal ore deposits, can cause undesirable processes in the geologic environment. The influence that redox reactions have on the transport of contaminants in groundwater systems is one example of an undesirable process controlled by redox reactions. Redox processes occurring in groundwater include the complexing of Iron oxy-hydroxides that can release associated contaminants such as Arsenic, As, and Cadmium, Cd. These elements are released into the environment as ferric Fe is reduced. This Fe^{3+} can be in a variety of phases and the half-reaction below is usually paired with carbon oxidation:

$(Fe^{3+} + e^{-} = Fe^{2+}(aq))$

The result of such redox processes is seen in the illustration in figure 1 where an iron seepage film is easily visible in the orange / brownish areas of the water surface. It is the zone where these reactions most frequently occur (redoxcline) that can and should be monitored by measuring the amount of Fe^{2+} in solution. This issue of evaluating the redox conditions in groundwater (particularly those characterized by having pollution plumes) is as such important for the interpretation of the behavior of pollutants in groundwater, and further, for the development of appropriate remediation techniques (Christensen et al., 2000). The aim of this project was to interpret results generated by current field and laboratory work along with data previously collected to determine what are the main controls on ground water iron concentrations in marsh and wetland areas.

Fig 1 Seepage of Reduced Fe at Paint Branch Tributary

The results generated suggested that these controls include: 1) the site location, whether marsh or forested, these being influenced by sediment chemistry, microbial activity, iron (hydro) oxide availability and water table position, the depth of the piezometer, 2) the position of the water table as the area around the water table provides the appropriate environment for iron reduction, and 3) The depth of the sample, which can be influenced by the residence time of the water, the sediment chemistry or sulfide precipitation, among other things. The hypotheses I have created address the varying effects of the previously mentioned possible controls.

Previous Research

For the paint Branch site there is significant evidence from past work (UMD graduate student Karen Phemister did considerable testing for both Fe^{2+} and Fe^{3+} at this site for her senior thesis in 2002 and 2003) that there is a considerable amount of iron present (both ferrous and ferric), with concentrations changing seasonally in coherence with stream discharge. This finding formed the basis of my initial interest in this project. The following plots (figures 2 and 3) were created using Phemister's data to show the observed changes in Total Iron concentration and discharge at the Paint Branch site as the season changed from winter to spring.

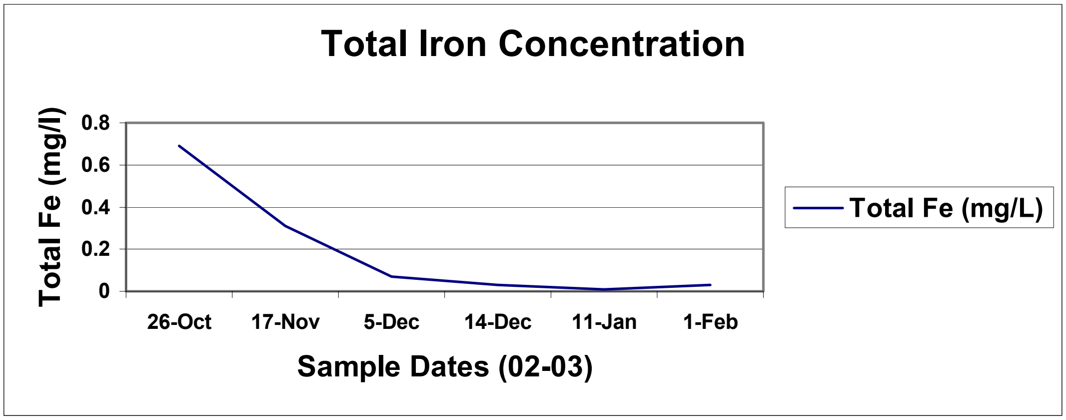


Fig. 2 Plot of changes in Total Fe concentration over time at Paint Branch Tributary using Phemister's data.

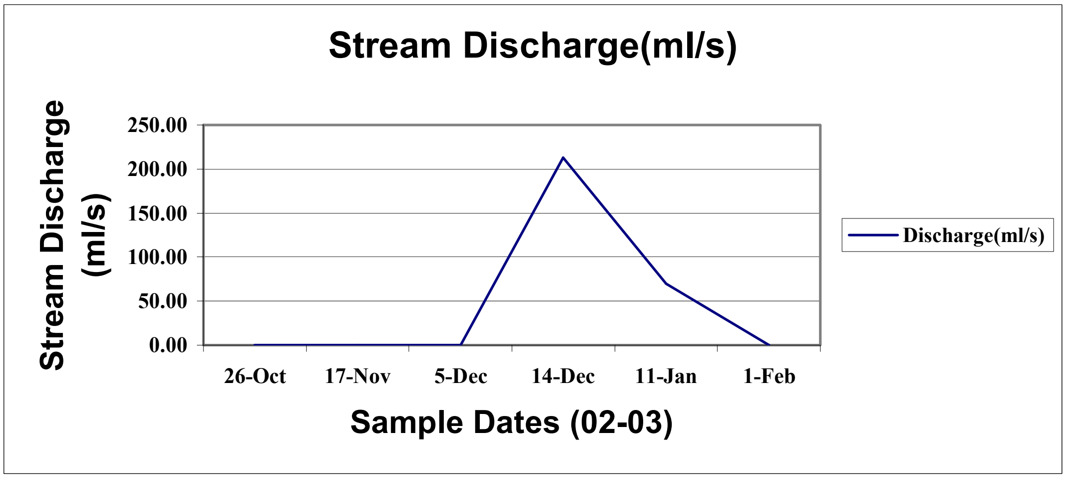


Fig. 3 Plot of changes in stream discharge over time at Paint Branch Tributary using Phemister's data.

Data also collected by Nancy Katyl over the period of 1993 to 1995 when carrying out her Graduate research also gave good indications of the relationship between Fe fluxes and a number of other variables such as depth, water elevation, time, and temperature. The general trends, illustrated in figures 4, 5 and 6, along with more detailed ones raised quite a few questions that my hypotheses will attempt to answer. The more detailed plots made using her data I have included in the results section of this paper. The general trends observed here are the constant pH of the samples even with changing temperature, the obvious higher groundwater heads during the wetter months and the notable increase in iron total concentrations with depth along with the separateness of the curve for the warmest of the months plotted (February) from the other months in figure 6.

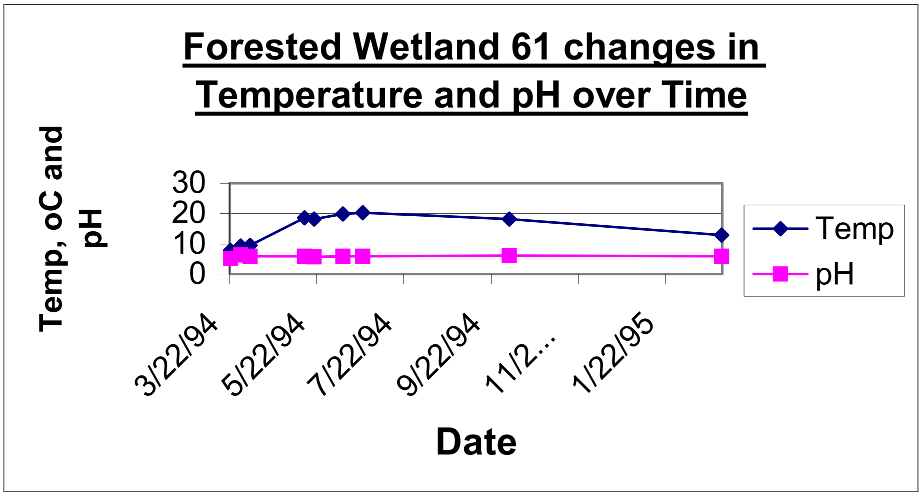


Fig 4 Plot showing the change in Temperature and pH over time at the Annapolis Forested Wetland site.

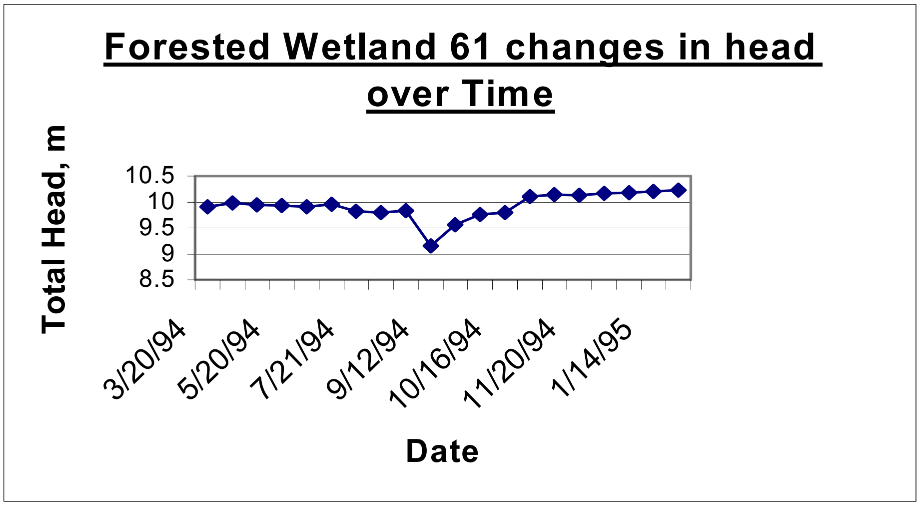


Fig. 5 Plot showing the change in Total Head over time at the Forested Wetland.

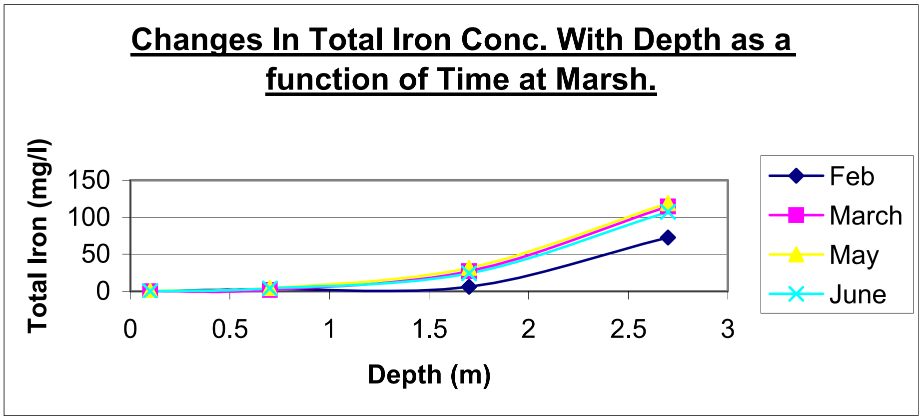
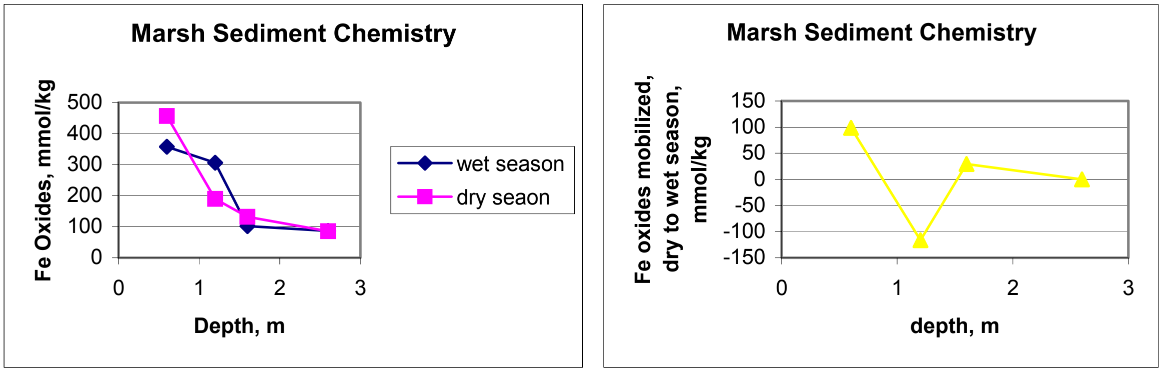
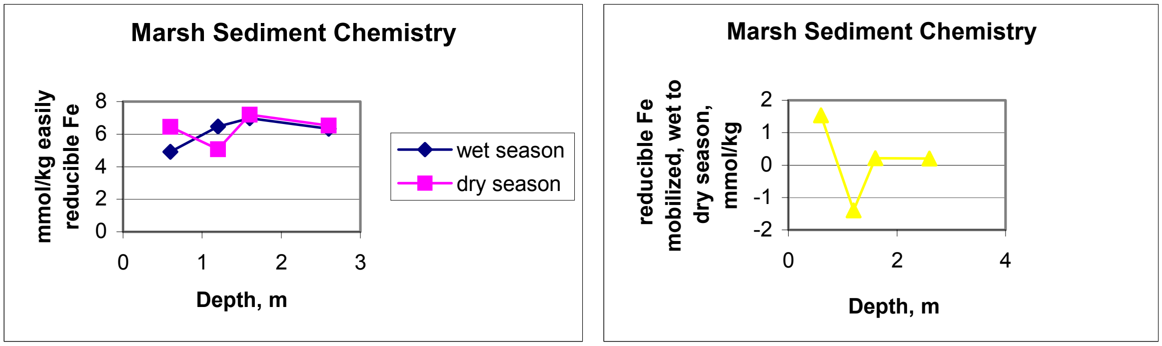


Fig. 6 Plot showing changes in Fe Total concentration with depth at the Marsh site.

Further general insight about the nature of the redox processes was gained fro another study done at the Annapolis wetland site. A chemical analysis of the sediment at the this site done by another UMD alumna, Lori Keith, in 1998 who did extractions with various acids to determine how much iron was on the surface of the wetland sediments that could be reduced. Two main types of iron were measured, easily reducible iron and iron oxides. It was found that most of the iron present was in the form of iron oxides and that the amounts of Iron varied move at the shallower depths but not at deeper depths. This is seen in the plots of the changes in Fe oxides and reducible Fe following (Figs.7a-8b).



Figs. 7a & 7b Plots showing changes in Fe Oxides with depth



Figs. 8a & 8b Plots showing changes in reducible Fe with depth

Similar studies involving the analyses of the means of Fe (III) reduction done by K. P. Nevin and D. R. Lovely in their article "Mechanisms for accessing Insoluble Fe (III) Oxide during Dissimilatory Fe (III) Reduction by Geothrix Fermentans", published in Applied and Environmental Microbiology, May 2002, provided another area of possible investigation, viz. the contribution that microbes make to the Fe reduction process. According to their article, microorganisms within the redox zone release electron shuttling compounds that can stimulate the reduction of Fe^{3+} without there being any physical contact with the organism; this significantly adds to the dynamic process being investigated in this study.

The laboratory study method adapted for this project (sediment incubation technique) was similar to the method used by Eric E. Roden and Robert G. Wetzel in their study entitled "Organic carbon oxidation and suppression of methane production by microbial Fe (III) oxide reduction in vegetated and unvegetated freshwater wetland sediments", Limnology and Oceanography, (Dec., 1996).

Hypotheses

1. As temperature increases the amount of iron reduction occurring in the sediment will increase.
2. Marsh sediment at greater depths will be characterized by greater amounts of iron reduction.

This addresses the possible controls of the residence time and velocities of the pore water in the sediments and the position on the iron redoxcline.

3. The presence of microbes is essential for the fast reduction of Fe^{3+} in subsurface environments.

STUDY SITES AND METHODS OF ANALYSIS:

Study Sites:

Initial work began at the UMD Paint Branch tributary site where sediment was collected and used for preliminary laboratory experiments. Upon observing the trends displayed Katyl's data and noting the similarity between the Paint Branch site and Katyl's Annapolis site (having both a forested wetland area of higher topography, and a marsh area of lower topography), the decision was made to not only process and interpret her raw data with greater detail, but to also collect sediment samples from her sites and to run the same laboratory incubation experiments using those samples. This experimental analysis using sediment from Katyl's site constituted the final part of the laboratory work that was done.

Fig. 9a Photograph of Marsh Site.

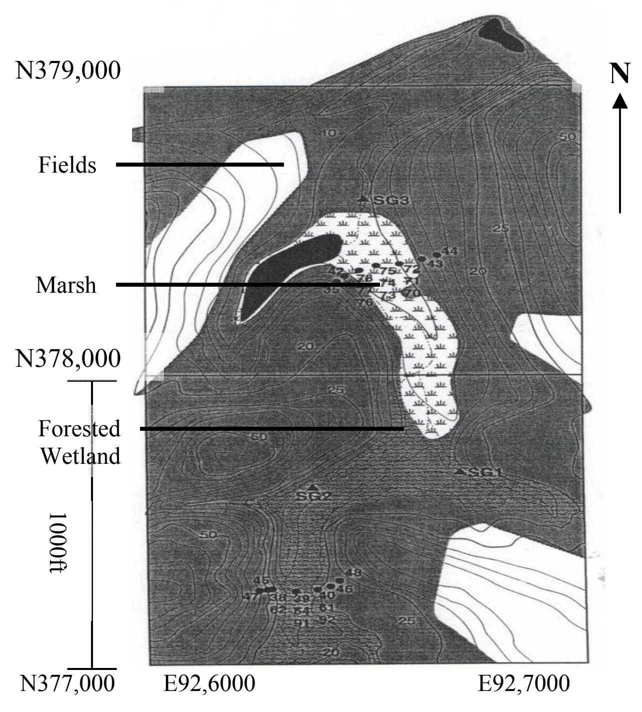


Fig. 9b Map showing Marsh and Wetland Sites modified after Winston, 1994.

FIELD AND LABORATORY METHODS

Collection and analyses of sediment core samples:

Preliminary experiments done to examine the rate of occurrence and reproducibility of the field iron reduction processes proved quite feasible. In this experiment sediment from the Paint Branch site was collected manually by simply digging up portions of the soil along the hill slope (from top to bottom). The particular type of sediment that was extracted was sediment that is orange-ish in color, indicating that the sediment was oxidized. To ensure homogeneity, all of the sediment collected was mixed together before separation into portions to be tested. The sediment was then transported to the laboratory where it was separated into portions and placed into beakers, and then waters of differing chemical contents added to the samples to mimic the influx of water into the soil in the natural setting. The types of water that were added were distilled water (creating an analog for precipitation), and two sets of water having a dissolved organic carbon content – one being filtered and the other not being filtered. The latter two types of water was prepared in the laboratory by simply adding leaf litter to tap water and leaving it to sit for approx 4-7 days. The waters were added to the sediment samples by pouring it into the top of the beaker. One set of sediment was placed in aluminum foil pans and oven dried for 35 minutes to kill the bacteria in the sediment. Beakers containing sediment having all of the varieties of water were covered and placed to sit in a darkened cupboard in the laboratory at a room temperature of approx 70 Fahrenheit (to minimize the occurrence of the processes of photo-reduction and evaporation). These sediment samples were later observed (after approx 1 week) for changes in color from the original orangish color to darker colors indicative of Fe reduction.

Photographs of the sediment samples in the beakers were taken using a digital camera, both at the inception and at the end of these experiments. In an effort to account for uncertainties in the analyses, each type of sediment – water combination was set up in triplicate in both settings.

At the end of the experiment, the water was centrifuged out of the samples and tested for Fe^{2+} in mg/l using the HACH DR/2000 Direct Reading Spectrophotometer and the ferrous iron test (Phenanthroline method, program # 255) using powder pillows. The detailed method of testing for Fe^{2+} can be found in the HACH Methods Manual. The general test procedures included the filtering of the water samples, and the placement of two portions of the sample (1 to be used as a blank and the other for actual testing) in 25-ml glass containers suitable for the spectrophotometer. The contents of the powder pillow are added to the test sample and the blank is then placed in the spectrophotometer for zeroing. After zeroing the machine, the test sample is placed in the machine, and by a process involving the determination of the specific wavelength of light passing through the sample relative to the blank, the machine is provides a digital read-out of the amount of Fe^{2+} present in the sample.

Following the successful completion of prototype experiments, the final experiments were conducted using sediment from the marsh site and following the exact procedure outlined above. The only changes made were the elimination of one of the types of water being added to the sediment, and the sediment collection method. The unfiltered leaf litter water was omitted; this omission was made based on the judgment of which experiments showed the most interesting results. Unlike in the preliminary experiments, the sediment was collected from varying depths using a soil auger. Thus the sediment collected for the final experiments was already significantly reduced (rather than oxidized as was the case in the preliminary experiments). In addition, it was originally planned that experiments were to be carried out at two temperatures, at room temperature and in the refrigerator, but analysis of Katyl's data indicated that this was not a necessity (as shall be later discussed in the results and discussion sections of this paper).

Experimental Analyses:

The independent variable in the analysis of the core samples was the position of the water table. The dependent variable was the amount of iron reduction determined by the color of the sediment sample columns after they are infiltrated with the various types of waters and made to sit for a period of time under controlled laboratory conditions. The control variables were water input chemistry, variation induced here by using the different types of water; bacterial /biological influences, tested also by using the two types of sediment viz. oven dried and regular sediment; and for the final experiment using sediment from the marsh, another control variable, depth, was introduced by analyzing samples from two depths at this site.

Analysis of Previous Data collected from Wetland:

Data collected by Nancy Katyl for her 1995 Masters thesis, entitled "Processes that influence Iron and Sulfur fluxes into and out of a freshwater wetland", included measurements of elevation to the water table, temperature, pH, dissolved oxygen, Fe – Total and Fe^{2+} for a site at a freshwater wetland area and one at a marsh in Annapolis, MD. The data was collected on a weekly basis between 1993 and 1995. For my study, her raw data was used to create plots of changes in head/ water elevation, temperature, pH, Fe-Total, and Fe^{2+} concentrations, versus time and with respect to changes in depth. These plots were used to observe trends, which may or may not aid in supporting my hypotheses.

RESULTS

Data Analysis Results

Using Katyl's raw data diagrams were created to show the relationship between various parameters and controls at the two sites. The most striking comparison is the notable difference between the amounts of iron present in samples taken from the two sites. There was an order of magnitude difference between the values obtained for the two sites, viz.: a maximum Fe Total concentration of 131 mg/l for the marsh, a maximum Fe Total concentration 4.84 mg/l for the forested wetland. Average Fe Total concentrations for the two sites were 41.60 mg/l and 1.74 mg/l, respectively (See Fig 10).

In addition, analyses of the data for the two sites showed a definite relationship between the depth from which the sample was taken and the amount of iron reduction occurring. For both the marsh and the forested wetland, samples taken from greater depths had a significantly larger concentration of iron than samples taken from shallower depths. This relationship is illustrated in figures 11 and 12. This observation influenced the design of the final laboratory experiments, which were set up to assess depth as a major control on the amount of reduction occurring in shallow ground water environments. These final laboratory experiments were set up using sediment samples extracted from two depths at the Marsh site.

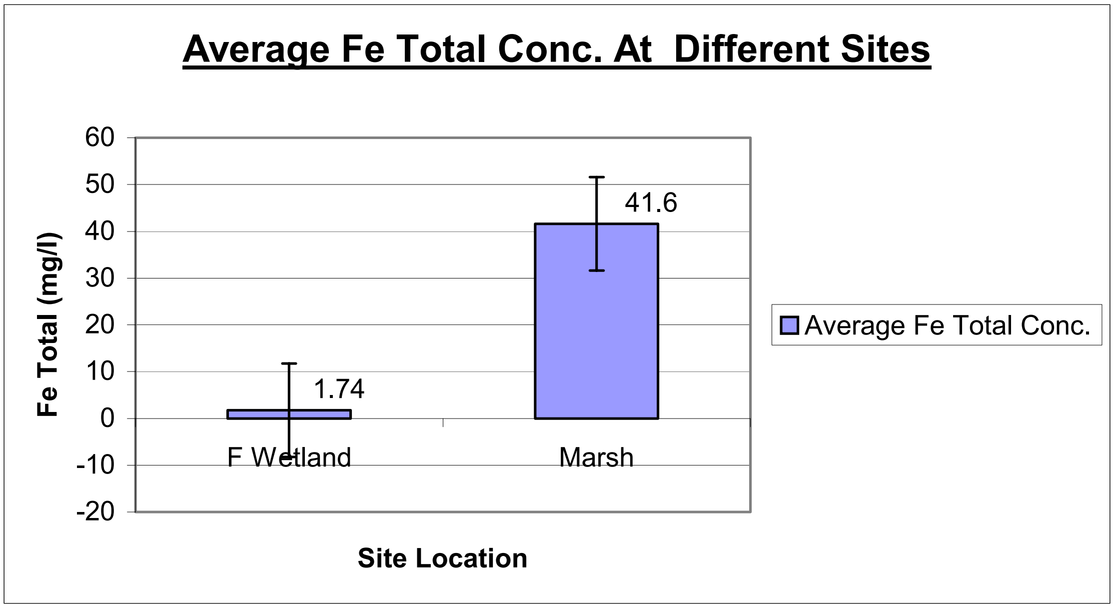


Fig. 10 Plot showing the average Fe Total concentration (mg/l) at the two sites with y-error bars to, 1 standard deviation

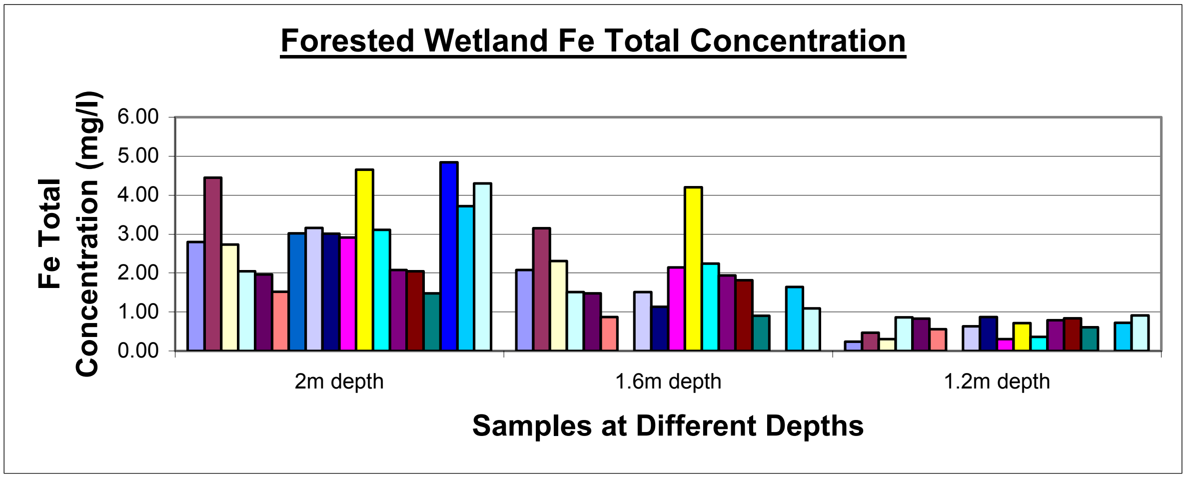


Fig. 11 Plot showing the relationship between Depth and Fe Total Concentration in Forested Wetland.

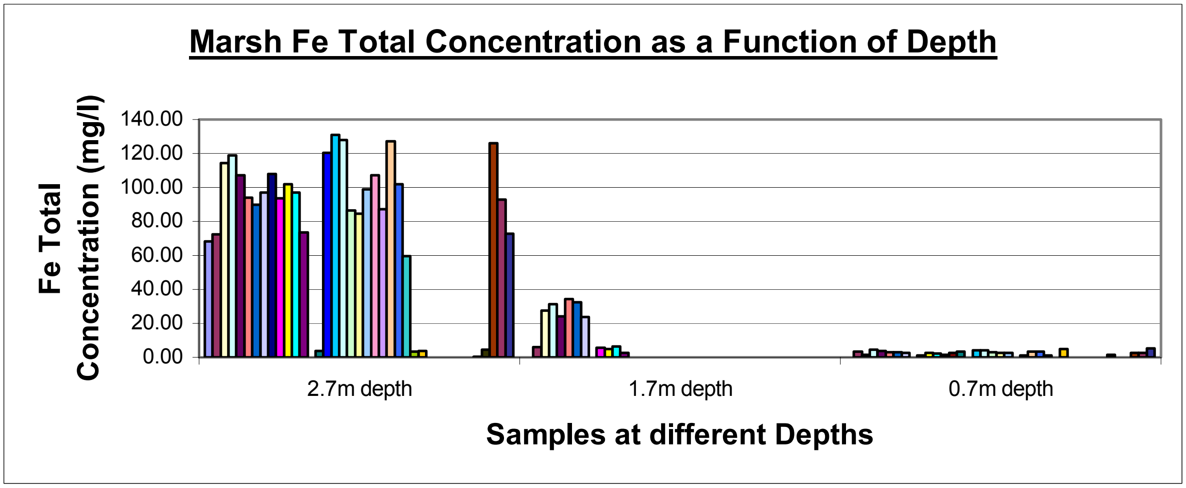


Fig. 12 Plot showing the relationship between Depth and Fe Total Concentration in Forested Wetland.

	Depth (m)	**Fe Total Concentration (mg/l)**	**Standard deviation (mg/l)**
Marsh	All Samples	1.74	1.30
Forested Wetland	All Samples	41.60	47.02
Marsh	2.70	68.62	48.24
Marsh	1.70	15.35	13.52
Marsh	0.70	1.99	1.61
Forested Wetland	2.00	2.99	1.02
Forested Wetland	1.60	1.67	0.98
Forested Wetland	1.20	0.56	0.29

Table 1: Mean and Standard Deviation of values obtained for Fe Total Concentration at the sites.

Other insight gained about the redox processes through the analysis of Katyl's data included the lack of influence that temperature had on the amount of Fe present in the samples. As depicted in the figures 13a and 13b below, for increasing temperatures the change in the amount of Fe total present is minimal or non-existent.

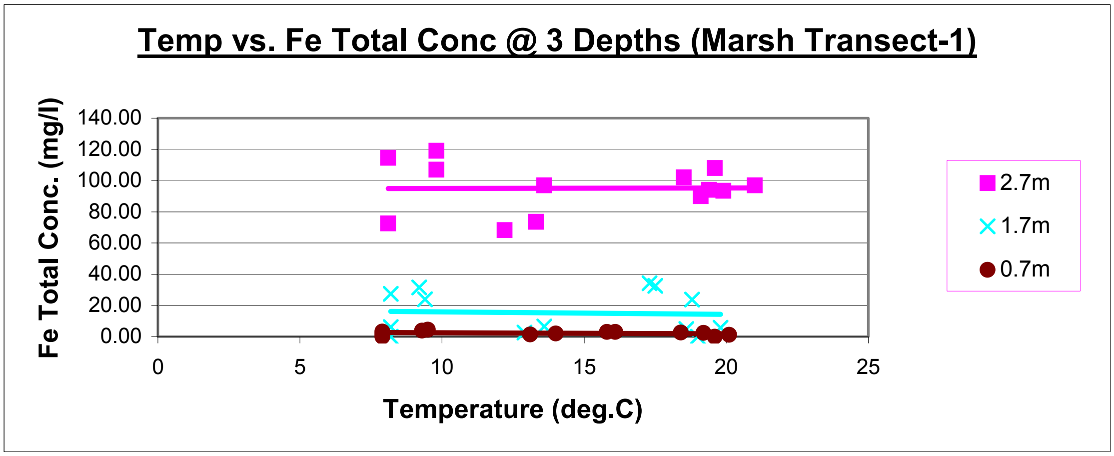


Fig. 13a Plot showing the relationship between Temperature and Fe Total Concentration as a function of depth in the Marsh

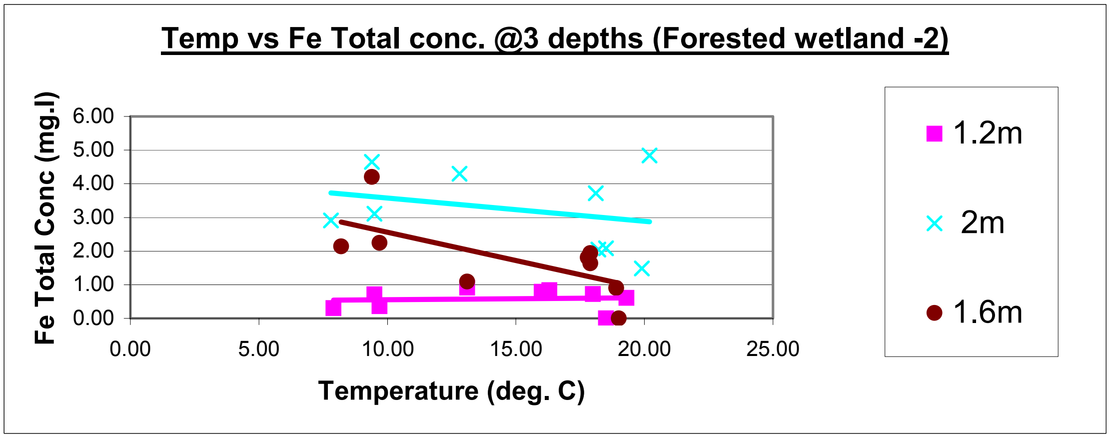


Fig. 13b Plot showing the relationship between Temperature and Fe Total Concentration as a function of depth in the Forested Wetland

The small decline seen in the Fe concentration with increased temperature for the forested wetland can be attributed to the drying out of the soil through evapo-transpiration as temperature increases and the uptake of water by vegetation. Altogether, temperature does not appear to be one f the major controls on the redox processes. This observation allowed for further adjustment of the design of the final laboratory experiments. Initially, the experiment design included the set-up and observation of soil samples at room temperature as well as at a lower temperature (in the refrigerator. However, since the plots made using Katyl's data allowed for the temperature control to be ruled out, the final experiments were conducted only at room temperature.

Assessments of the changes in bulk parameters showed that there was hardly any differences between the general at the two sites (see figs. 14a - 15b). These parameters include groundwater elevation, pH, temperature and dissolved oxygen. Samples tested from both sites showed virtually no change in pH, negligible change in dissolved oxygen content and similar changes in temperature from season to season. Also, for both sites water elevation dropped during the warmer months and rose during the colder, wetter months. However, the variation in head seen at the marsh site was smaller than that seen in the forested wetland. It must be noted that the portion of plots from June 1993 to December 1993, was characterized by a major oxidizing event; it was after this period that sampling for chemical testing began at these sites.

Figures 16a and 16b offered insight that influenced the set up of the final experiments. The notable higher concentrations in iron concentrations for greater depths led to the final laboratory experiments being designed to assess the sediment taken from different depths in the marsh.

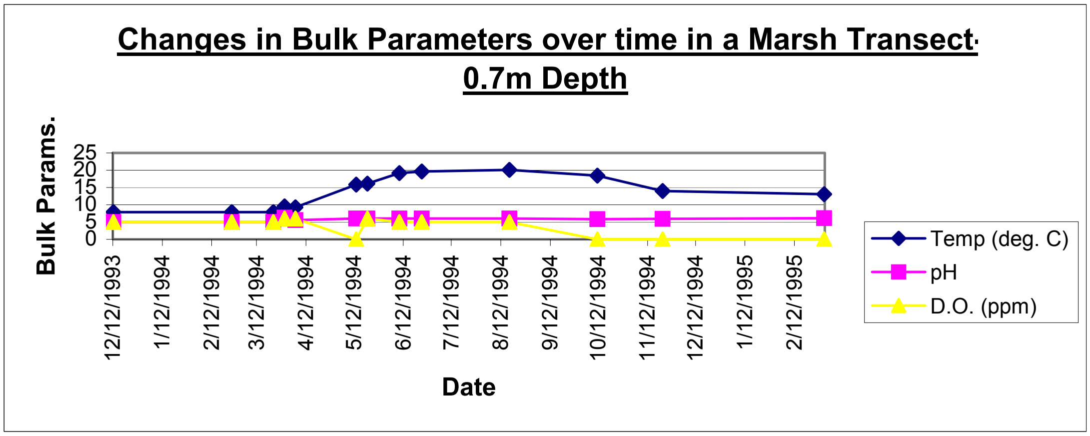


Fig. 14a Plot showing the change in bulk parameters over time at the Marsh

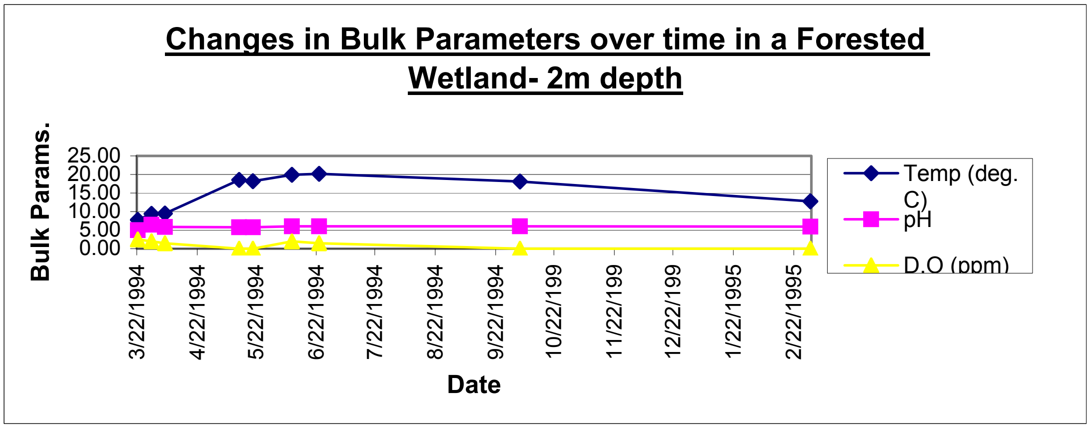


Fig. 14b Plot showing the changes in bulk parameters over time at the forested wetland

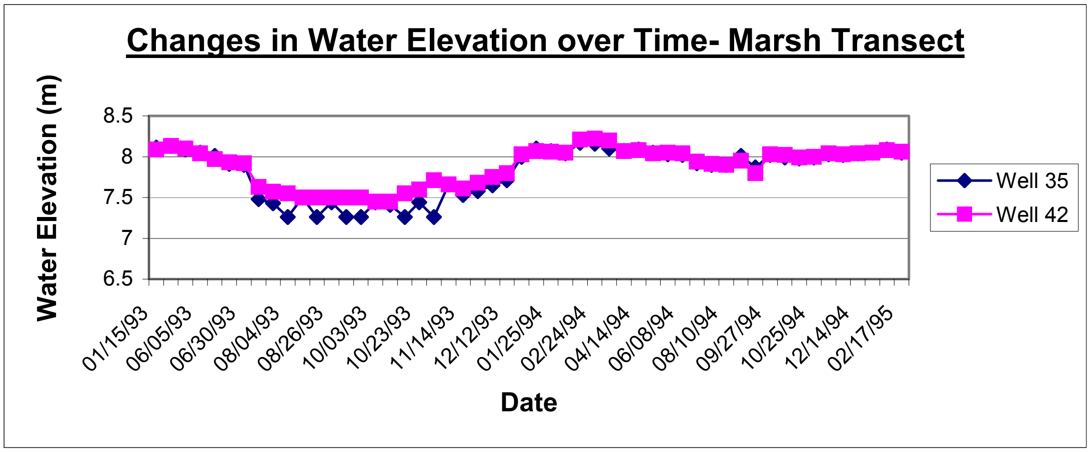


Fig. 15a Plot showing changes in Water Table Elevation in the Marsh

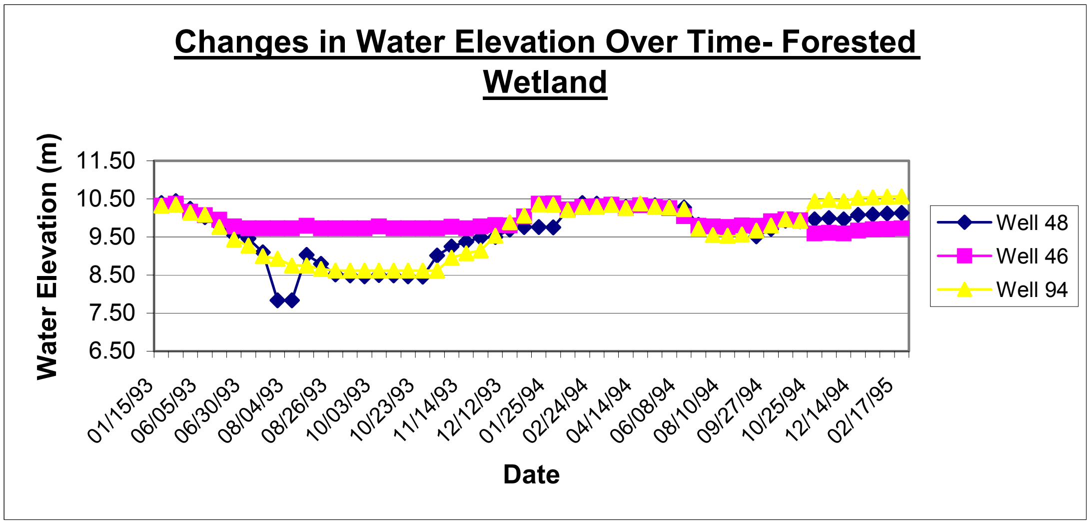


Fig. 15b Plot showing changes in water table elevation in the Forested Wetland

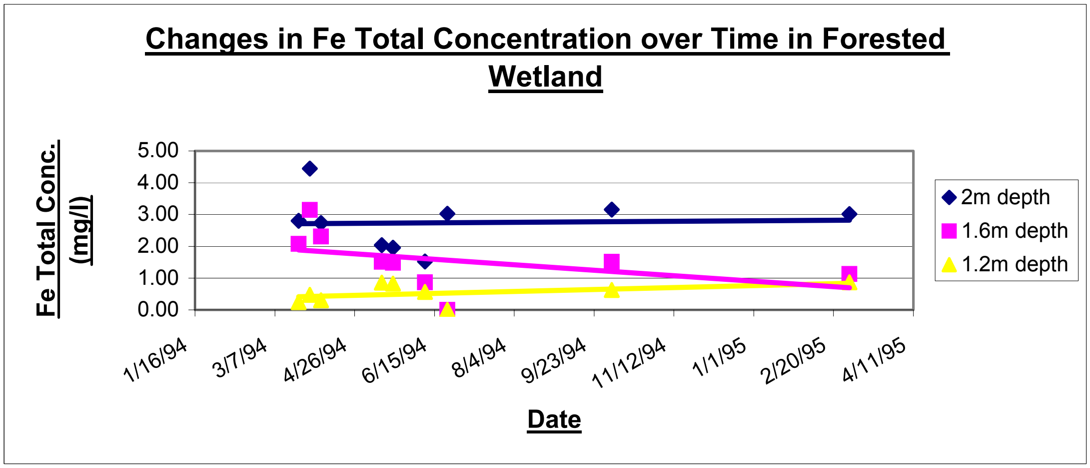


Fig. 16a Plot showing changes in Fe concentration over time in the Forested Wetland

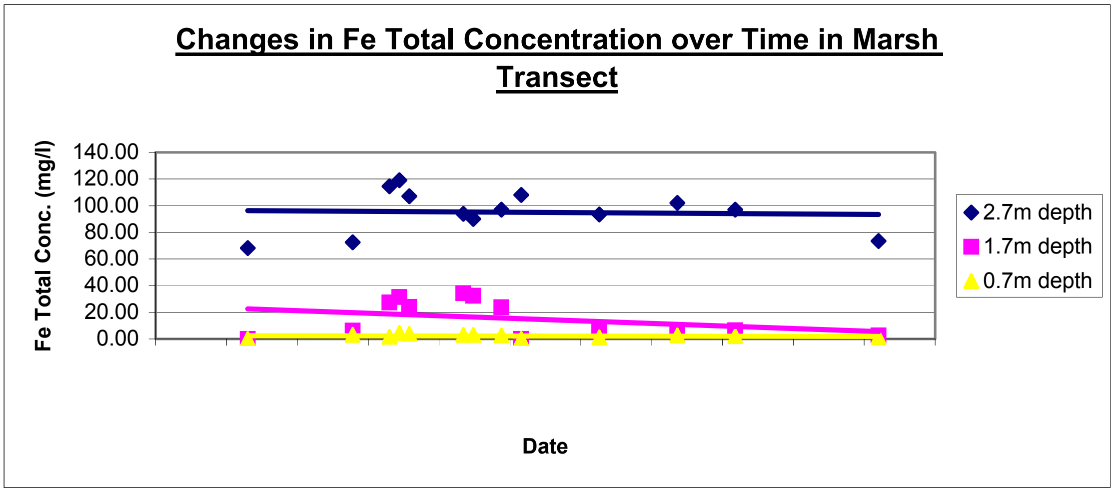


Fig. 16b Plot showing changes in Fe concentration over time in the Marsh

Preliminary Laboratory Analysis Results:

The laboratory analysis of sediment showed the rapid rate at which the redox processes occur groundwater systems. Over the 13-day period the following observations were made:

1. The oven-dried samples containing distilled water demonstrated no change in color, as would have been the case if redox processes had occurred therein.
2. All other samples, i.e. those containing leaf litter water (both filtered and unfiltered) and the distilled water showed significant color changes with the Fe^{2+} produced being easily visible.
3. The amount of reduction seen in the samples containing unfiltered leaf litter water and filtered leaf litter water was approximately the same. For this reason, the unfiltered leaf litter water was omitted from the final set of experiments.
4. The first set of water samples centrifuged out of the sediment from the Paint Brach Tributary showed amounts of Fe^{2+} present that were similar to the values obtained by Katyl at her forested wetland site, ranging from 3.30 mg/l (max.) to 0.28 mg/l (min) in 25ml samples. These water samples were taken from the filtered and unfiltered organic sediment samples; the oven dried and distilled water sediment samples did not have enough water remaining in them at the end of the study period to carry out the testing.

Final laboratory Analysis Results (using marsh sediments taken from two different depths

The final experiments were carried out using sediments from two depths at he marsh, namely:1.2 and 0.4m. Just like the preliminary experiments, there was easily visible evidence of reduced iron being produced after a two-week period. However, the fact that the sediment was extracted from depth may have influenced the amount of ferrous iron present in the samples at the end of the study since unlike the first experiments, the sediment was already reduced rather than oxidized. The ferrous iron concentrations determined by centrifuging the water out of the samples on the last day of the experiments and testing these water samples using the spectrophotometer are given in table 2 following. Also, photographs are given to show the visible changes the samples underwent over the study period. Just as was observed in the preliminary experiments, all samples except the sample that was oven dried showed the production of an orange colored ferrous iron film at some places on the surface of the sample. It was also noted that he samples containing distilled water contained the highest concentrations of ferrous iron.

	Sample Type		
	Filtered Organic	Distilled Water	Oven Dried+ Distilled Water
Ferrous Fe Content (mg/l) 1.2m Depth ± 2%	0.00	0.02	0.00
	0.00	0.02	0.00
	0.25	0.21	0.00
	0.32	0.70	0.00
	0.14 **Average**	**0.24** **Average**	**0.00** **Average**
Ferrous Fe Content (mg/l) 0.4m Depth ± 2%	0.10	0.46	0.00
	0.13	0.33	0.00
	0.13	0.45	0.00
	0.02	0.14	0.00
	0.10 **Average**	**0.35** **Average**	**0.00** **Average**

Table 2: Ferrous Fe Concentrations in Marsh sediments taken from 2 depths after 2-week period.

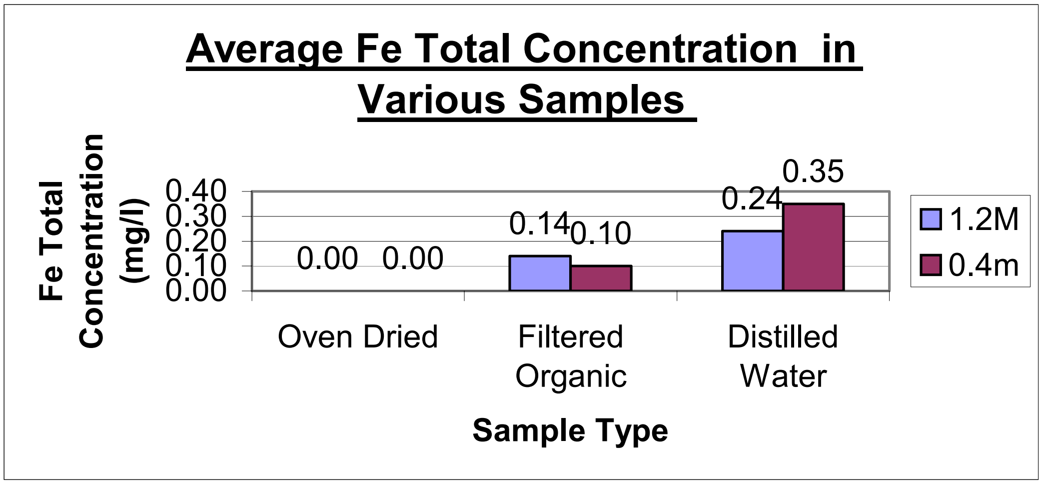


Fig. 17 Plot showing the Fe Total concentrations in the waters extracted from various sediments at the end of the laboratory analysis period.

Illustration of Laboratory Experiments and Results

Fig 18a: Filtered Org. Day 1

Fig 18b: Filtered Org. Day 14

Fig 19a: Distilled Water Day 1

Fig 19b: Distilled Water. Day 14

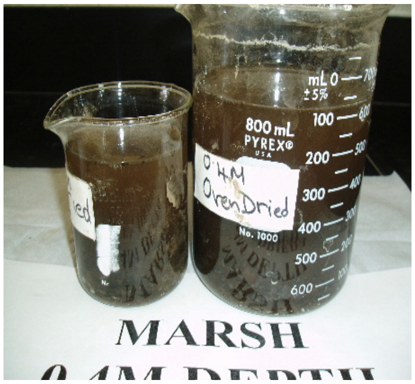


Fig 20a: Oven Dried Day 1

Fig 20b: Oven Dried Day 13

DISCUSSION/ CONCLUSION

The field and laboratory analyses suggest that the site location whether marsh or forested wetland is the most important control on the redox processes taking place in the shallow groundwater environment. This is evident from vast difference seen in the concentrations of iron in the marsh and forested wetland samples. This difference could be attributed to many factors including the rooting depth of the vegetation in the marsh versus the rooting depth of vegetation in the forested wetland. The density and depth of vegetation roots in the sediment may affect the balance between oxidation and reduction and ultimately the iron concentration. Also, iron reduction is favored over iron oxidation at depths below the rooting depths of the vegetation. Further, in trying to determine whether this difference is due to other factors such as sediment chemistry, the presence of microbial activity, iron hydroxide availability or the position of the water table other interesting trends were noticed.

One such trend was the relationship between the depth of the sediment sample and the amount of ferrous iron present. Considering this, the depth of the sediment was taken to be the next most important control. Specifically, in the marsh wetland, the data plots showed that the iron concentration was a power function of the depth of the sediment. This relationship could be attributed to factors such as residence time of the water in the sediment (considering variances in soil particle packing with depth), sediment chemistry or sulfide precipitation. However, the final laboratory experiments showed no distinct relationship between the depth of the sample and the amount of reduced iron present, as the average concentrations obtained were fairly similar for all samples. In addition, the values obtained were quite small especially for the filtered organic samples. This result could be due to the fact that the sediment used for these last experiments were already reduced in the natural setting. As such, in the laboratory, it was a matter of further reducing the sediments. A possible explanation for the small amount of reduced iron produced in the organic samples could be that the bacteria introduced into the system by adding the leaf litter water were somehow counterproductive to the reduction process.

Another interesting finding was that of all the samples analyzed in the laboratory, the samples containing distilled water (the analog for rain water) had the highest concentrations of reduced iron at the end of the testing period. Further, a comparison between the sediment with distilled water taken from 1.2m and 0.4m depths showed that the sediment at greater depth didn't produce as much reduced iron. A point to note is that the initial dark color of the sediment did indeed suggest that it was already fairly reduced.

Altogether, of the three hypotheses formulated for this study, the only one that was supported was the one that says that microbial activity is essential for the fast reduction in subsurface environments. This support was seen in the laboratory experiments where the samples that lacked bacterial content (the ones that were oven dried) failed to have any ferrous iron content at the end of the experiments. This is in keeping with the findings of previous studies; Fe (III) reduction in groundwater has recently been connected to several microorganisms: Geobacter metallireducens (Lovely and Phillips, 1998).

SUGGESTIONS FOR FUTURE WORK

Future work, which assesses the residence time of the ground water in forested wetland and marsh sediments may provide an explanation for the difference in iron concentrations seen in these two environments. This can be done using groundwater K and head values to determine flux rates and finally to establish a relationship between pore water velocity and iron concentrations.

Acknowledgements

I extend special thanks to Dr. Prestegaard, my advisor on this project; I truly appreciate your patience and willingness to offer sound guidance to me. I would also like to thank Karen Phemister for spending time with me in the laboratory and field to teach me how to use the pieces of equipment that I used in my study.

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Appendix

Honor Code

I pledge on my honor that I have not given or received any unauthorized assistance on this assignment; this includes plagiarizing.

Juanita Stevens
04/30/04