

Historical and Short-Term Controls on Sulfate Reduction and Alkalinity Generation in Three Aquatic Ecosystems of Cape Cod, Massachusetts

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Abstract

Alkalinity generation by way of sulfate reduction was measured using sediment core incubations from three different sites in the Cape Cod region of Massachusetts. Cores were manipulated with respect to sulfate concentrations in the overlying water, oxygen availability, and iron availability and measured for changes in sulfate and alkalinity over time. We also examined sediment profiles for total sulfur, iron-bound sulfur in the form of pyrite, carbon, and lead.

We found that oxygen availability was the most important factor controlling short-term alkalinity generation in aerobic cores. Sulfate concentrations were found to be more important controls under anaerobic conditions and iron was not found to be limiting to alkalinity generation under any of the experimental conditions created in this study.

In the sediments, we found that historical peaks in sulfur storage were probably due to periods of increased sulfate reduction and consequent burial of ferrous sulfides and not to increased sedimentation rates. We found rates of sulfur burial since 1930 to range from 3.59 to 6.73 mmol m⁻² y⁻² and rates of alkalinity generation to range from 7.19 to 13.47 mEq m⁻² y⁻¹ in freshwater sediments.

Keywords: Sulfate reduction, alkalinity, acid precipitation, pyrite, sediments

Introduction

First described as acid rain in 1852 by Scottish chemist Angus Smith, all forms of atmospheric acid deposition continue to be an environmental problem faced by industrial nations and geologically susceptible regions today. The acid precipitation phenomenon became publicized in the early 1970's when scientists in Sweden and the Northeastern United States noted declines in fish populations in certain lakes (Morris). Low pH precipitation strips aluminum, calcium, and magnesium cations preferentially from the soil matrix, replacing them with hydrogen ions as it runs overland. The fish kills were due to increased aluminum concentrations in the water, which are toxic to fish because they interfere with oxygen flow over the gills.

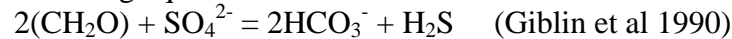
At first only a matter of concern to fishermen, acid deposition from fossil fuel burning has been shown to have far-reaching ecological consequences in aquatic systems. In regions not susceptible to aluminum toxicity, the main concern for affected systems is decreased pH. Many juvenile fish and lower trophic level organisms are intolerant of low pH. The disappearance of these intolerant species can stress higher trophic levels, leading to starvation and changes in species composition throughout all trophic levels (Schindler).

Acid precipitation, with a pH ranging from 4.3 to 4.7, falls on the Cape Cod region (USGS). Due to clean-up efforts in the 1980's and 90's sulfate concentrations in rainwater, a product of coal burning, have decreased, accompanied by a rise in rainwater pH, but acid precipitation remains a problem in many regions with poorly buffered soils. Scrubbers on power plant smokestacks reduce gaseous emissions as well as particulate matter. Reduced particulate matter decreases the amount of acid-neutralizing cations that are released into the atmosphere and deposited on the land (The Green Lane). Meanwhile, watersheds have been depleted of their alkalinity stores by decades of acid precipitation, and current rates of acid deposition, decreased as they may be, are unable to be buffered by the soil. Other sources of acidity to aquatic systems may be acid mine drainage or increased surface runoff due to deforestation or agriculture.

Two sources of alkalinity to any aquatic system are terrestrial inputs and in-situ biogeochemical processes. Drainage basins contribute alkalinity to aquatic systems by adding cations that runoff the soil. If the residence time of water in a system is less than a year, terrestrial sources are likely to be the greatest contribution to alkalinity budgets (Schlesinger). Human-induced land changes may increase the amount of alkalinity contributed by the watershed. Agriculture, deforestation, and forest fires intensify the mobilization of soil cations. In addition to inorganic ions, organic matter, in the form of humic and organic acids, may also contribute to the alkalinity budget of a system (Schlesinger).

In-situ processes that consume sulfate and nitrate also contribute alkalinity to a system. Sulfate reductions has been determined to be the more important process in previous studies because of the tendency of watersheds to retain nitrate (Giblin et al 1990), but denitrifying processes and the adsorption of sulfate or nitrate molecules to sediments and minerals also contribute alkalinity (Schlesinger). Assimilatory sulfate reduction is a process by which plants take up sulfate, reduce it, and incorporate the sulfur into amino acids that make up essential proteins. Dissimilatory sulfate reduction is used by specialized bacteria, such as *Desulfovibrio* and *Desulfotomaculum*, to make

energy in anoxic waters (Kelly et al 1982). These bacteria use sulfate as a terminal electron acceptor during the oxidation of organic matter, producing sulfide end products according to the following equation:



According to this equation, each unit of sulfate reduced generates an equivalent unit of alkalinity. The products of sulfate reduction must be bound with iron or organic matter and to prevent reoxidation, which generates acidity, thereby depleting alkalinity stores. Burial of sulfide minerals generates permanent alkalinity. It is these processes that are responsible for any natural buffering capacity in lakes in regions with poorly buffered soils.

Currently there is much debate over controls on these acid-neutralizing microbial processes. Previous studies have shown controls on alkalinity generation by dissimilatory sulfate reduction to be strongly correlated to the sulfate concentrations in the overlying water and the amount of sulfur able to be stored in sediments (Giblin et al 1990, Siver et al 2003). Because sulfides often bind with iron or organic material to be buried and generate permanent alkalinity, it has been suggested that iron inputs from the watershed may limit ferrous sulfide burial (Cook 1981). In shallow lakes, where epilimnetic sediments dominate, organic sulfide burial has been found to be more important in the long term than ferrous sulfide burial (Rudd et al 1986). This finding suggests that alkalinity generation may be limited by the delivery of carbon to sediments. Furthermore, the trophic status of a system may play a role in determining the amount of organic sulfide burial. More productive systems will probably have greater amounts of carbon sinking to the sediments from the overlying water than an unproductive system. Another set of controls on sulfate reduction is related to basin morphology and oxygen availability. Net rates of oxidation, which are related to oxygen content of bottom waters, can affect rates of alkalinity generation, and anoxic sediments, where the reoxidation of sulfide compounds is negligible, have been shown to be more important than aerobic sediments in terms of sulfur storage (Giblin et al 1990, Kling et al 1991). Furthermore, basins that have lower surface area to volume ratios will have more regions of anoxia compared to basins with high surface area relative to total volume. Controls on assimilatory sulfate reduction are phytoplankton and bacterial abundance and productivity.

The intricacies of sulfur storage and alkalinity generation have been shown to differ between individual ecosystems. It is important to understand the importance of different acid neutralizing processes, such as sulfate or nitrate reduction, and the magnitude of in-situ alkalinity generation that different types of aquatic systems are capable of. This will allow scientists to construct lake acidification models that will predict how individual aquatic systems will respond to further acid deposition. The main purpose of this study is to examine alkalinity dynamics, as they are related to sulfate reduction, in two freshwater ponds on Cape Cod and one marine site in Massachusetts Bay. During the course of this research we manipulated a total of 16 sediment cores to represent different environments. We were interested in how each treatment responded in terms of sulfate disappearance or production, sulfide production, and alkalinity generation. These sediment core incubations would help explain short-term controls on alkalinity generation. We also looked at total amounts of sulfur and carbon buried in the sediments to see how sulfur storage has changed throughout recent history. Analyzing

sediment profiles offer insight into long-term processes that control in-situ sulfate reduction and alkalinity generation. Incubating marine cores along with freshwater cores offers an interesting comparison between the alkalinity dynamics of two different types of ecosystems. The Massachusetts Bay cores represent a system that is completely saturated and reducing sulfate at maximal rates. The amount of alkalinity generated by these high rates of sulfate reduction represents the theoretical maximum amount of acid neutralizing capacity able to be contributed to an aquatic system by in-situ processes.

Methods

Site Description

Sediment cores were taken from Mares pond and John's pond on Cape Cod, Massachusetts and one site in Massachusetts Bay. Both ponds are freshwater kettle ponds that have developed shorelines with permanent homes and public boat landings. They differ in size, depth, pH, sulfate concentration, and trophic status. Mares Pond is 5 km inland, covers 28 acres, and reaches a maximum depth of 55 feet. John's Pond is ~8.5 km inland, covers 243 acres, and has a maximum depth of 65 feet. Both ponds receive acid precipitation with pH ranging from 4.3- 4.7 (USGS). Marine cores were collected at a site 9 miles outside of Boston Harbor in Massachusetts Bay. Overlying seawater had a salinity of 34 ppm.

Sampling and Incubation Procedure

SCUBA divers collected a total of 22 cores at a depth of approximately 35 feet at freshwater sites shortly after fall turnover. A total of six cores were collected by box carry at the marine site. Two cores from each site were sectioned in 1 cm intervals down to 10 cm, 2 cm intervals from 10 to 20 cm, and 4 cm intervals below 20 cm. Sections were dried at 60° Celsius for two days, ground, and stored in airtight containers for solid phase chemical analysis.

Remaining cores were incubated in the dark in water baths at approximately 15° Celsius. Two marine cores received sulfate free seawater and two were left untreated as controls. Two freshwater cores from both John's and Mares Pond were left as controls, two received sulfate additions, and two were made anaerobic. All cores, except anaerobic treatments, were bubbled using air stones and aquarium pumps. Initial ambient water was siphoned off the cores and replaced with filtered water from respective sites. The water in the sulfate free marine cores was replaced with a sulfate free artificial seawater mix. Water was collected in 20-liter carboys at each site, GFF filtered, and stored in a cool, dark place until time of use. Anaerobic cores received water that was bubbled with nitrogen to remove oxygen and immediately capped to prevent remixing with ambient atmosphere. Sulfate additions, in the form of Na₂SO₄, to four freshwater cores raised ambient concentrations to 2mM. After 20 days of incubation, iron was added to one John's Pond replicate core for each treatment and both marine control cores. Iron additions were prepared by adding approximately 3 ml of highly concentrated NaOH solution to 2 ml of a one molar ferrous chloride solution to raise the pH of the solution and precipitate out iron oxide. The solution was then centrifuged and the supernatant decanted off. Approximately 15 ml of water from the appropriate core was mixed with the precipitate and the entire mixture was poured back into the core.

Cores were sampled a total of 6 times over a four week period. Anaerobic cores were gently stirred before sampling to ensure a representative sample. Water samples were taken with a syringe and passed through 25mm Gelman or Swinnex GFF filters.

Alkalinity samples were stored in 60 ml Nalgene or glass BOD bottles. Sulfate samples were stored in 20 ml scintillation vials. Samples that smelled of sulfide were bubbled with nitrogen until the odor became undetectable. Sulfide was sampled in anaerobic treated cores using zinc acetate sulfide traps. All samples were refrigerated until time of analysis. Overlying water was replaced in anaerobic cores after each sampling. All other cores received water additions only once throughout the entire incubation.

Analysis

Dried and ground sediments were analyzed for total sulfur, carbon, total iron, inorganic iron, and lead. Total sulfur was measured using a LECO SC32 Sulfur Analyzer. Carbon was measured on a Perkin-Elmer CHN elemental analyzer. Iron and lead were extracted with HCl and measured on a Perkin Elmer 2380 Atomic Absorption Spectrophotometer as described in detail by Crosby 2003 (unpublished data).

Water samples included alkalinity, sulfate, and sulfide. Alkalinity was determined by titration with H₂SO₄ using an Accumet pH meter and Gelman digital titrator. Sulfate was measured on a Dionex ion chromatograph. Sulfide was determined by calorimetric analysis using a Shimadzu UV-1601 spectrophotometer.

Results

Sediment Profiles

Total sulfur in John's Pond sediments ranged from 11.07 umol/g to 207.7 umol/g (figure 1). Sulfur peaked between 5 and 10 cm of depth and then decreased. Replicate cores showed the same general patterns. Mares Pond sediments had total amounts of sulfur that ranged from 22 to 165 umol/g (figure 2). Two peaks of equal magnitude were found at 3 cm and 17 cm deep separated by a region with small, but variable amounts of sulfur. Massachusetts Bay cores had sulfur that ranged from 35 to 80 umol/g (figure 3). Core 2B had higher amounts of sulfur at all depths but both cores followed the same general trend of increasing S with depth.

Concentrations of FeS₂ in John's Pond sediments ranged from 3.22 umol/g to 105.7 umol/g (figure 1). Both replicates showed the same trends, with a large peak in pyrite burial around 9 cm. In Mares Pond, pyrite concentrations ranged from 3.8 to 118.8 umol/g (figure 2). In both replicate cores concentrations peaked around 3 cm and then decreased with depth. Pyrite in marine sediments did not replicate very well between sites. Concentrations ranged from 39 to 123 umol/g and were generally highest in more recent sediments (figure 3).

Percent carbon in John's Pond sediments ranged from 1 to 11% and was greatest in the top 4 centimeters. Below 4 cm %C decreased quickly with depth (figure 4). Percent carbon in Mares Pond sediments mirrored the John's Pond profile to a depth of 10 cm. Below this point, %C increased with depth. In Mares Pond %C ranged from 6 to 15%. Marine sediments had relatively consistent amounts of carbon throughout the sediment profile, with a range of 0.94 to 1.79 % C.

C: S ratios in John's Pond sediments decreased from surface sediments to 10 cm, and then began to increase with depth (figure 5). Ratios were greatest at 24 cm and ranged from 11.2 to 30.7. In Mares Pond C:S ratios decreased from the surface to 4 cm and then began to increase with depth. Ratios were greatest at the surface and ranged from 15.8 to 35.2. Marine sediment C:S ratios, ranging from 12.5 to 5.7, were highest in surface sediments and generally decreased with depth.

Lead concentrations in John's Pond were higher in surface sediments and began to increase around 20 centimeters of depth (figure 6). The point in time at which lead concentrations began to rise rapidly was assumed to be the year 1930. Under this assumption, the calculated sedimentation rate for John's Pond is 2.857 mm/yr. In Mares Pond sediments, lead concentrations began to increase at 12 cm and the sedimentation rate was calculated to be 1.714 mm/yr (figure 7). In marine cores lead concentrations fluctuated slightly throughout the sediment profile but generally remained constant (figure 8). Because there was no distinct drop-off in lead at any point in the profile, a sedimentation rate could not be calculated.

Using sedimentation rates from lead profiles and the total sulfur content of the sediments, historical rates of sulfate burial and alkalinity were calculated for freshwater sites (Table 1). In John's Pond, the mean rate sulfate burial since 1930 was 6.73 mmol m⁻² y⁻¹ and the mean rate of alkalinity generation was 13.47 mEq m⁻² y⁻¹. In Mares Pond, the mean rate of sulfate burial was 3.59 mmol m⁻² y⁻¹ and the mean rate of alkalinity generation was 7.19 mEq m⁻² y⁻¹.

Sulfate

Initial sulfate concentrations were higher in John's Pond than in Mares Pond. In both ponds, sulfate was released from the control cores over time (figure 9). When sulfate was added to freshwater cores, both ponds followed the same general trend, ending with a slight overall disappearance of sulfate from overlying water (figure 10). Anoxic sediments from both ponds steadily took up sulfur until iron was added on the eighteenth day of incubation (figure 11). In all time course figures, the broken vertical line marks the time of iron addition. Marine cores 31 and 34 had high initial concentrations of sulfate, which were taken up quickly over time (figure 12). Cores 30 and 32 were overlain with sulfate free seawater. Over time sulfate concentrations in these cores increased.

Sulfide

Sulfide production was measured in all anoxic cores. All cores produced sulfide until the eleventh day of incubation, after which point sulfide concentrations dropped and remained mostly steady throughout the rest of the incubation (figure 13). One exception is the John's pond anoxic replicate that received an iron addition on day 18. Over the next 6 days, sulfide concentrations dropped to near zero.

Alkalinity

John's Pond control cores produced alkalinity throughout the first half of the incubation (figure 14). During the second half, the cores lost alkalinity, resulting in a net loss over the 25-day period. Mares Pond control cores steadily lost alkalinity throughout the entire incubation. John's Pond cores that received sulfate additions gained alkalinity until iron was added (figure 15). Mares Pond cores responded to sulfate additions with a slow loss of alkalinity over time. Anoxic cores in both ponds produced alkalinity (figure 16). Cores from John's Pond that received iron lost alkalinity after the addition. Alkalinity increased in all marine core treatments. Again, after cores 31 and 34 received iron additions, there was a slight loss in alkalinity (figure 17).

Mass Balance

Before iron additions were made, there was a net loss of sulfate from all John's Pond cores. Mares Pond control and sulfate cores experienced a net gain in sulfate, and in anoxic cores sulfate disappeared from the water column over time (figure 18). Despite

slight losses of sulfate from John's Pond control cores, there were also slight losses of alkalinity. However, sulfate and anoxic John's Pond cores experienced a net gain in alkalinity over time (figure 19). Mares Pond lost alkalinity in the control and sulfate treatments but gained alkalinity in the anoxic treatments.

Cores 30 and 32, whose overlying water initially contained little or no sulfate, experienced net gains in sulfate over time (figure 20). Cores 31 and 34, which had high initial concentrations of sulfate saw high rates of sulfate disappearance before iron additions. All four marine cores produced alkalinity (figure 21). Rates of alkalinity generation were similar but the high sulfate cores, 31 and 34, produced alkalinity slightly faster than low sulfate cores 30 and 32.

Iron was added to one control, one sulfate, and one anoxic replicate from John's Pond as well as cores 31 and 34. In all freshwater cores that received iron additions there was a net gain in sulfate from the time of the iron addition to the end of the incubation (figure 22). The corresponding replicates that didn't receive iron also produced sulfate in the water column from day 18 to day 25 of the incubation. All John's Pond cores, with and without iron additions, saw declines in alkalinity production during the second half of the incubation (figure 23). The largest losses of alkalinity occurred in the anoxic replicate that did not receive iron. Cores 31 and 34 also experienced net gains of sulfate after addition of iron (figure 24). With the appearance of more sulfate in the overlying water, core 31 lost alkalinity (figure 25). Core 34 continued to produce alkalinity, although at a slower rate than pre-iron addition conditions.

Discussion

Sediment Profiles

In order to contribute alkalinity to an aquatic system reduced sulfur compounds, which are the end products of dissimilatory sulfate reduction, must avoid reoxidation. The most common method by which sulfides are isolated is by burial in sediments. The total sulfur content of sediments represents both organic and inorganic sulfur compounds. Organic sulfur in the sediments may come from two sources. Assimilatory sulfate reduction in the water column incorporates sulfur into live organic matter, which will senesce and rain down on the sediments (Schlesinger). The other source is products of dissimilatory sulfate reduction that bind with organic material in the sediments. Inorganic reduced sulfur takes the form of FeS, FeS₂, and elemental S in sediments. These compounds are end products of dissimilatory sulfate reduction that bind with iron (Giblin et al 1990). Looking at the sediment profile of a system with respect to sulfur, carbon, iron, and lead can show historical trends in sulfate storage and alkalinity generation.

The dissimilatory sulfate reduction contributions to total sulfur can be assumed to generate alkalinity. Assimilatory sulfate reduction also contributes alkalinity. However, because sulfur is not limiting to organisms, assimilatory sulfate reduction is assumed to remain constant despite changing sulfate concentrations. Therefore, all changes in total sulfur storage in sediments cannot be due solely to increased sulfate concentrations in the water from acid precipitation. Increased deposition of seston and sediment from the overlying water due to eutrophication or watershed disturbances may greatly increase the amount of organic sulfur and carbon reaching sediments, but such events would not increase the amount of reduced inorganic sulfur stored in the sediments (Giblin et al

1990). Therefore, it is important to compare the amount of organic carbon to sulfur in the sediments to determine if changes in sulfur storage are related to increased sediment loads or increased reduced burial of reduced sulfur species. The presence of pyrite, a common product of sulfide binding with iron, in the sediments also indicates when dissimilatory sulfate reduction was occurring.

In John's Pond, total sulfur storage seems to have decreased in the top few centimeters of most recently deposited sediments. This decrease is not due to lower rates of sulfate reduction in recent years but to the diffusion of oxygen into the top few centimeters of sediment. There is a peak in sulfur storage between 4 and 12 cm of depth that is most likely due to dissimilatory sulfate reduction (figure 1). It is evident that this peak is not due to increased delivery of organic sulfur to the sediments because the C: S ratio is low in this region of the profile (figure 5). A peak in pyrite in the sediments in this same region also indicates a period of increased sulfate reduction. Earlier in history sulfate reduction probably did not play a large role in alkalinity generation. This assumption is supported by low total sulfur content and a high C: S ratio in the sediments and decreased pyrite concentrations. A peak in sulfur storage in Mares Pond can be similarly explained by high total sulfur and a low C:S ratio (figures 2 and 5). A second, deeper peak in sulfate storage, as indicated by a high corresponding C:S ratio, may be due to a watershed disturbance instead of increased sulfate reduction. The shape of the pyrite profile for Mares Pond also supports this idea.

Lead profiles were examined in order to determine approximate rates of sedimentation throughout recent history (figures 6 and 7). Previous studies using ^{210}Pb dating of sediments have identified the point at which rapid increases in lead concentrations occur to be the year 1930 in New England lake sediments. Historical increases in sediment lead are a reflection of increased atmospheric concentrations of lead from the use of leaded gasoline. Because of deep mixing in marine sediments, a sedimentation rate for the marine sediments could not be calculated (figure 8). The rate calculated for John's Pond was higher than that of Mares Pond. The difference between the two rates may indicate that John's Pond is a more productive system than Mares Pond.

After sedimentation rates were established, we used the % sulfur content of the sediments to determine historical rates of sulfur storage in both systems. According to the equation for sulfate reduction, one mole of sulfate reduction yields an equivalent mole of alkalinity (Giblin et al 1990). Therefore, the rate of sulfur storage could also be used to obtain historical rates of alkalinity generation (Table 1). When these calculated rates are compared with rates of sulfate disappearance and alkalinity generation in our short-term incubations, the historical rates are much lower in cores that produced alkalinity. However, between the two freshwater sites, rates from the incubations followed the same trends displayed by the rates determined from the sediment profiles. In both parts of the experiment, John's Pond generally saw more sulfur disappearance and alkalinity production than Mares Pond. Cores from both ponds were both taken in regions that are generally anoxic during periods of stratification and that experience turnover twice a year. Since sediments from both ponds are subject to similar oxygen regimes throughout the year, these results suggest that higher ambient sulfate concentrations in John's Pond facilitate greater sulfate reduction and alkalinity generation (Giblin et al 1990). One explanation for the differences between the magnitudes of historical versus incubation

rates is that incubation rates are calculated from sulfate disappearance from the water column while historical rates are calculated from actual sulfur storage in the sediments. Differences between the magnitudes of alkalinity rates may be due to different processes that control long term versus short term alkalinity stores.

In marine sediments the total amount of sulfur stored seems to have decreased over time (figure 3). Smaller percentages in shallow sediments are accompanied by increased C:S ratios from historical values (figure 5). This indicates that sedimentation rates may be increasing over time. However, the total carbon concentration of the sediments was not shown to increase in recent history in our analysis (figure 4). Furthermore, seawater has naturally high concentrations of sulfate, and sulfate reduction should constantly proceed at maximum rates. High rates of sulfate reduction do not guarantee maximum rates of sulfur burial however as reflected in the low amounts of sulfur stored in marine sediments versus freshwater sediments (figure 3). Assimilatory sulfate reduction by organisms in the water column should not vary much with changes in atmospheric sulfate concentrations either. The distribution of pyrite throughout the sediments also showed no clear trends and seemed to be well mixed. An alternate explanation for the shapes of the marine sediment profiles is mixing. The site at which our marine cores were collected is aerobic and sediments may frequently mix to a depth of 10 or 12 centimeters, reincorporating oxygen for a short time. Buried sulfide compounds will reoxidize when oxygen is present and be lost to the overlying water, which accounts for low concentrations of total sulfur and iron-bound sulfur in surface sediments. Deep sediment mixing is also facilitated by burrowing animals, which bring up material from deeper in the sediments. These mixing forces cause marine sediments to be a relatively homogenous mixture of carbon and sulfur in most cases.

In John's Pond the carbon content of the sediments have been increasing over time (figure 4). This trend may reflect the slow but steady eutrophication of the pond throughout recent history. As the shoreline becomes more developed, nutrient loads to the pond may increase primary production in the lake and increased organic carbon deposition on the sediments. Mare's Pond shows the same potential pattern of steady eutrophication with increased human impacts on the land. However, below 10 cm in the sediments there is a large peak in % C. This may be due to a historical disturbance in the watershed, such as a flood or fire, or any other even that might have greatly increased sediment loads to the pond.

Sediment Incubations

After analyzing historical trends as displayed by sediment profiles of all sites studied, results from the core incubations show how systems respond to environmental changes on a short-time scale. The two freshwater sites had different initial concentrations of sulfate in their water. Aerobic control cores from both ponds initially maintained their natural sulfate concentrations but released sulfate into the water column over time (figure 9). This is most likely due to the oxidation of reduced sulfide compounds in surface sediments. Increased sulfate in freshwater controls was accompanied by alkalinity loss over time for both sites (figure 14). Although John's Pond did produce alkalinity for a short time, the final result was a slight net loss of alkalinity throughout the incubation (figure 19). The loss in alkalinity occurs when sulfide compounds are oxidized. The process contributes acidifying hydrogen ions to the water when sulfide is separated from the iron or organic matter that it was previously

bound to. Under aerobic conditions it is possible that sulfide oxidation was hastened by carbon limitation in the sediments (Rudd et al 1986). Over short time scales, the products of sulfate reduction have been found to bind more readily with organic material than iron.

Two freshwater cores from each site received sulfate additions to bring concentrations to approximately 2mM. This concentration was chosen because it is thought to be the saturation point for dissimilatory sulfate reduction. Seawater typically has sulfate concentrations ranging from 28 to 30 mM. We expected this treatment to cause the cores to take up sulfate and produce alkalinity, testing the hypothesis that sulfate reduction is controlled by sulfate concentrations in the overlying water (Giblin et al 1990). Replicates from both ponds did take up sulfate during the incubation (figure 10 and 18), but sulfate loss was not accompanied by large gains in alkalinity (figure 15). Mares Pond cores actually experienced a net loss in alkalinity and John's Pond cores produced only a small amount of alkalinity (figure 19). If all sulfate disappearance was due to sulfate reduction, the amount of alkalinity produced should have been equivalent to the amount of sulfur reduced according to equation for sulfate reduction (Giblin et al 1990). A more likely explanation for large amounts of sulfate disappearance is that sulfate from the water diffused into the sediment pore water. On such a short time scale, sulfate-reducing processes were not able to respond to produce equivalent amounts of alkalinity. Furthermore, short term sulfur storage is often carbon limited and any sulfate that was reduced may have been reoxidized quickly because the core water was aerobic. It is also possible that the form of the sulfate additions, Na SO_4 , could have produced acidity through cation exchange processes between sodium and hydrogen ions.

Freshwater anoxic cores from both ponds began with sulfate concentrations similar to the control cores. Throughout the incubation, anoxic cores experienced decreasing sulfate concentrations (figure 11). Decreasing sulfate was accompanied by dramatic increases in alkalinity (figure 16). Alkalinity generation was expected because, under anaerobic conditions, the end products of sulfate reduction are not threatened by reoxidation. The magnitude of sulfate disappearance in anoxic cores was less than that of freshwater cores that received sulfate additions (figure 18). However, more alkalinity was produced on a per square meter basis in the anoxic cores (figure 19). These results support the idea that oxygen concentrations in the overlying water are a major control on alkalinity generation by sulfate reduction.

Closely tied to the presence of alkalinity is sulfide concentration. Sulfide is an end product of dissimilatory sulfate reduction. It commonly binds with either iron or organic matter and then is buried to generate permanent alkalinity. However, as long as sulfide avoids reoxidation it does not have to be buried to contribute alkalinity. Therefore, increased sulfide concentrations indicate the occurrence of sulfate reduction. Additionally, decreased sulfide concentrations do not necessarily indicate decreased alkalinity generation because sulfide may be bound with iron and precipitated out of the water. In the freshwater anoxic cores an initial increase in sulfide during the first half of the incubation (figure 13) corresponds with sulfate disappearance and alkalinity production in John's Pond (figures 18 and 19).

Patterns of sulfate disappearance and alkalinity generation in freshwater anoxic cores were similar to those expressed by control marine cores. In cores 31 and 34 that were covered with seawater with relatively high concentrations of sulfate, sulfate disappeared rapidly and alkalinity was produced (figures 12 and 17). Conversely, cores

30 and 32 that received sulfate free seawater experienced a net gain in sulfate over the course of the incubation (figure 20). The appearance of sulfate is due the diffusion of sulfate from the sediments. The site at which the marine cores were collected was subject to full seawater with sulfate concentrations of approximately 26mM, and sediments from this site would have been saturated with sulfate. When subject to overlying water with little or no sulfate, the sediments release sulfate in attempt to reach equilibrium. Although cores 30 and 32 produced sulfate, they still were able to generate alkalinity at rates similar to the control cores (figure 21). It seems that the amount of sulfate added to the artificial seawater from the sediments alone was enough to fuel high rates sulfate reduction and alkalinity generation in the experimental cores. It is possible that bicarbonate, which is the main source of alkalinity in seawater, was also diffusing out of the sediments and contributing to alkalinity in the cores.

Post Iron Additions

In an attempt to test the hypothesis of iron limitations on alkalinity generation, iron was added to three John's Pond cores and two marine cores. Sulfide end products are commonly buried with iron in sediments as FeS and FeS₂ (Giblin et al 1990). Burial of sulfide as iron sulfide minerals has been shown to be particularly important under anaerobic conditions while burial of sulfides in organic matter may be more important in oxic epilimnetic sediments (Rudd et al 1986). It has been hypothesized that, in systems where inorganic sulfide burial dominates, iron inputs to a system may not match rates of sulfide burial. In this situation, iron would become a limiting factor to alkalinity generation (Giblin et al 1990). In our incubation, we expected to see increased rates sulfate disappearance and alkalinity generation as well as sulfide disappearance with iron additions.

In all freshwater cores that received iron, sulfate was produced (figure 22). It is worth noting that replicate cores that did not receive iron were also producing sulfate at this time, but the magnitude of sulfate production was greater in cores with iron for all three treatments. The appearance of sulfate in cores that were previously consuming sulfate is unexpected and difficult to explain. A possible explanation for this turn-around is simply that the cores were becoming less active at this point in the incubation. As sulfate appeared in the cores, alkalinity was also consumed. Again, in John's Pond control and sulfate treatments, replicate cores that received iron consumed alkalinity at a greater rate than replicates without iron (figure 23). However, in the anoxic treated cores, alkalinity consumption was greater in the replicate core without iron. Considering that both anoxic replicates were consuming alkalinity at this time in the incubation, the lower rate of alkalinity consumption by the iron replicate could be due to the presence of iron. If sulfides produced by sulfate reduction were binding with readily available iron, alkalinity consumption may have decreased. Sulfide concentrations after the iron addition support this conclusion. Sulfide in the anoxic iron core (JP anoxic 1) dropped significantly after iron was added on day eighteen while sulfide remained steady in the replicate without iron (figure 13). The decrease of sulfide in John's Pond anoxic 1 can be assumed to be due to the increased binding of sulfide with iron.

Of the marine cores, controls 31 and 34 both received iron additions. During the days after the addition, sulfate started to be produced by both cores (figure 24). This change is dramatic when compared to rates of pre-iron sulfate disappearance (figure 20). With the increases in sulfate production, core 31 began to consume alkalinity while core

34 continued to generate alkalinity (figure 25). It is important to note that the rate of alkalinity generation after the iron addition was lower than the rate of alkalinity generation before iron addition, implicating an actual decrease in the amount of alkalinity generated. These results obviously do not support the hypothesis of iron limitation. However, there are a number of reasons why the iron additions appeared to cause the cores to react oppositely of expected results. One possible reason for the strange results is that the incubations were not continued long enough to see the true effects of the iron additions. The five-day period between the time of addition and the next time of sampling may not have been long enough for the system to equilibrate and react. Additionally, iron has generally been shown to be limiting in systems where anaerobic conditions prevail. If organic sulfide burial truly dominates in aerobic environments then iron additions would not be expected to affect rates of sulfide burial and alkalinity generation in most of the cores that received iron. According to the aforementioned hypothesis, the only core that should have been expected to increase rates alkalinity production and sulfate disappearance should have been the anoxic core.

Conclusions

The results of our study have shown that the most important short-term control on sulfate reduction and alkalinity generation in freshwater systems is oxygen availability in water overlying sediments. Aerobic control cores in both ponds generally lost alkalinity over time. Aerobic cores that received sulfate additions either produced very little alkalinity or consumed alkalinity. These cores saw high rates of sulfate disappearance due to increased concentrations in the overlying water but sulfate reduction was not able to contribute significant amounts of alkalinity. These results imply that increased sulfate concentrations in the overlying water will not necessarily increase alkalinity generation because it is difficult for the end products to escape reoxidation.

Sulfate concentrations also proved to be an important limiting factor in the anoxic cores. When the reoxidation of ferrous sulfides is not a threat to alkalinity generation, higher concentrations of sulfate resulted in more alkalinity production. In our study this conclusion is supported by greater rates of alkalinity generation in anoxic John's Pond cores as compared to Mares Pond cores (figure 16). As mentioned previously, John's Pond naturally has higher concentrations of sulfate in the pond water than Mares Pond. These results, along with those of John's Pond sulfate cores, imply that sulfate concentrations do limit dissimilatory sulfate reduction under oxic and anoxic conditions. Its importance as a control, however, is much greater under anoxic conditions.

Furthermore, iron was not shown to be limiting by the results of this study. Although there are possible sources of error in this portion of the experiment, iron additions did not increase the disappearance of sulfate or the generation of alkalinity in any of the cores. The only evidence for iron limitation was shown by decreased concentrations of sulfide in the anoxic core with iron. After iron was added, sulfide in the water column dropped significantly, indicating that iron sulfide minerals can be an important end product of sulfate reduction that contributes alkalinity to a system. Our systems did not seem to be limited by iron, and our results concur with those of Rudd et al 1986 in concluding that iron limitation is unlikely to occur in systems that bury products of sulfate reduction primarily in organic forms.

The majority of the cores in our experiment are representative of alkalinity dynamics in epilimnetic sediments. The aerobic quality of the overlying water also

represents times of turnover in seasonally stratified systems. Shallow systems that are dominated by aerobic sediments may not be able to rely on dissimilatory sulfate reduction as a method of buffering acid precipitation as heavily as deep systems dominated by anoxic sediments. Even if there are high rates of alkalinity production in anoxic sediments during periods of stratification, significant amounts of alkalinity may be consumed during periods of turnover. Results from the anoxic incubations indicate a steadier source of alkalinity to aquatic systems, but also one that is subject to frequent perturbations and controlled by interactions between multiple limiting factors. While in-situ reduction processes have been shown to generate alkalinity on both short and long term basis, sulfate-alkalinity interactions in individual systems may differ in response to changing environmental conditions, and cannot always be relied on to be a steady and significant supply of alkalinity to aquatic systems.

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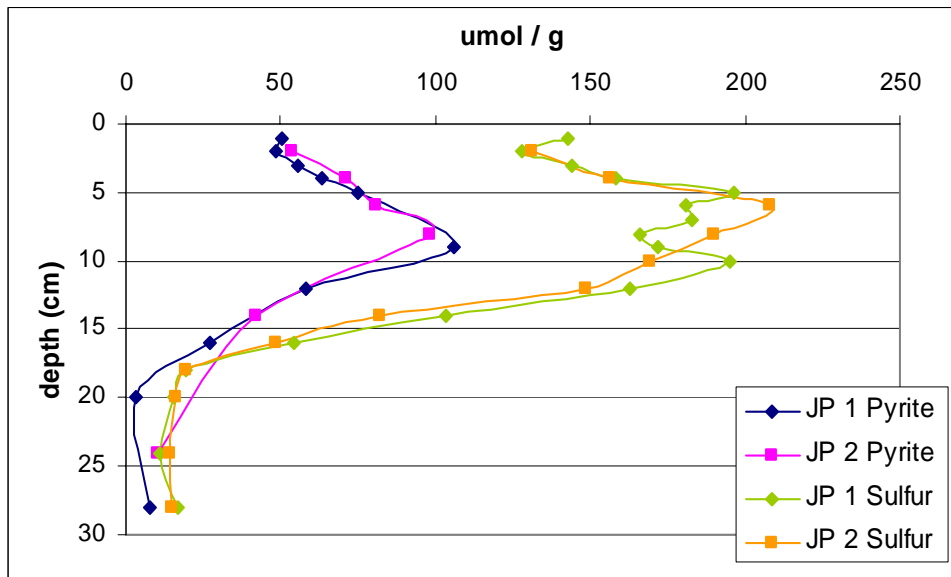


Figure 1. Total sulfur and iron burial in the form of pyrite in two replicate sediment cores from John's Pond.

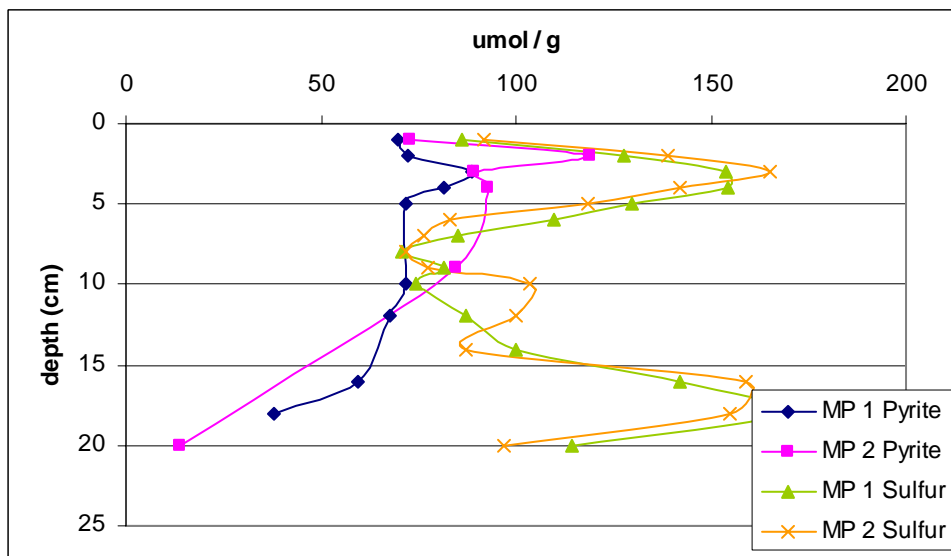


Figure 2. Total sulfur and iron burial in the form of pyrite in two replicate sediment cores from Mares Pond.

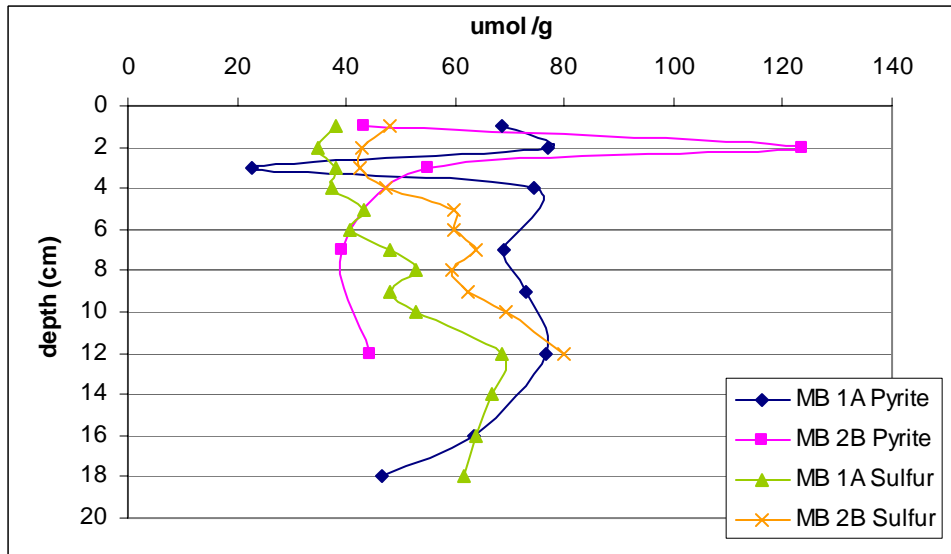


Figure 3. Total sulfur and iron burial in the form of pyrite in two replicate sediment cores from Massachusetts Bay.

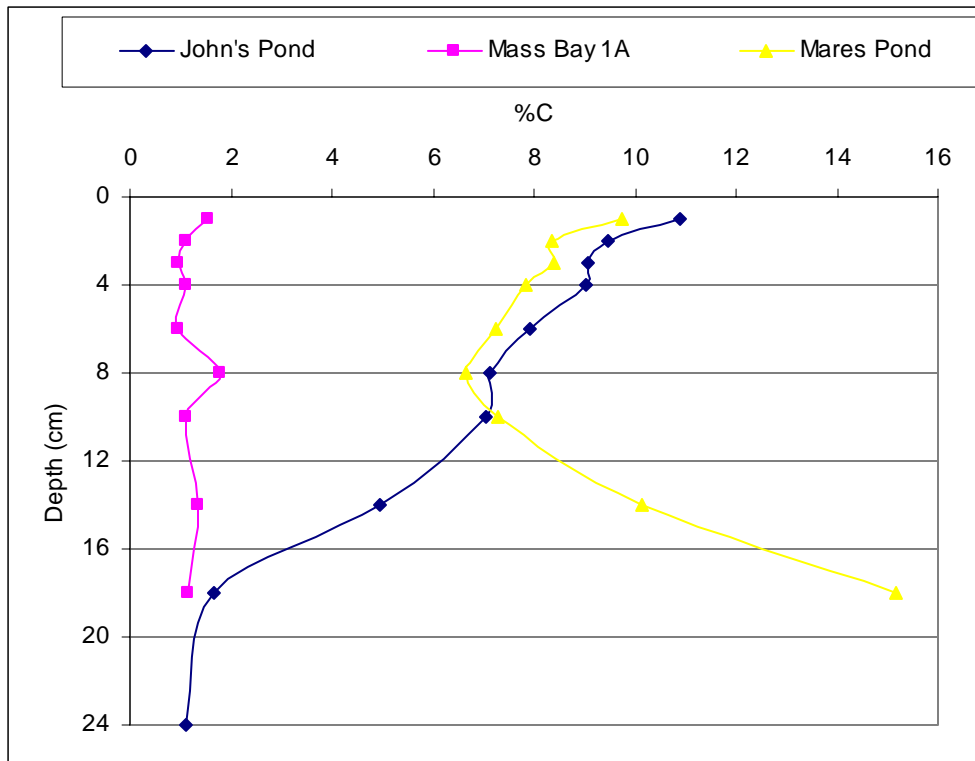


Figure 4. % Carbon profiles in three aquatic systems.

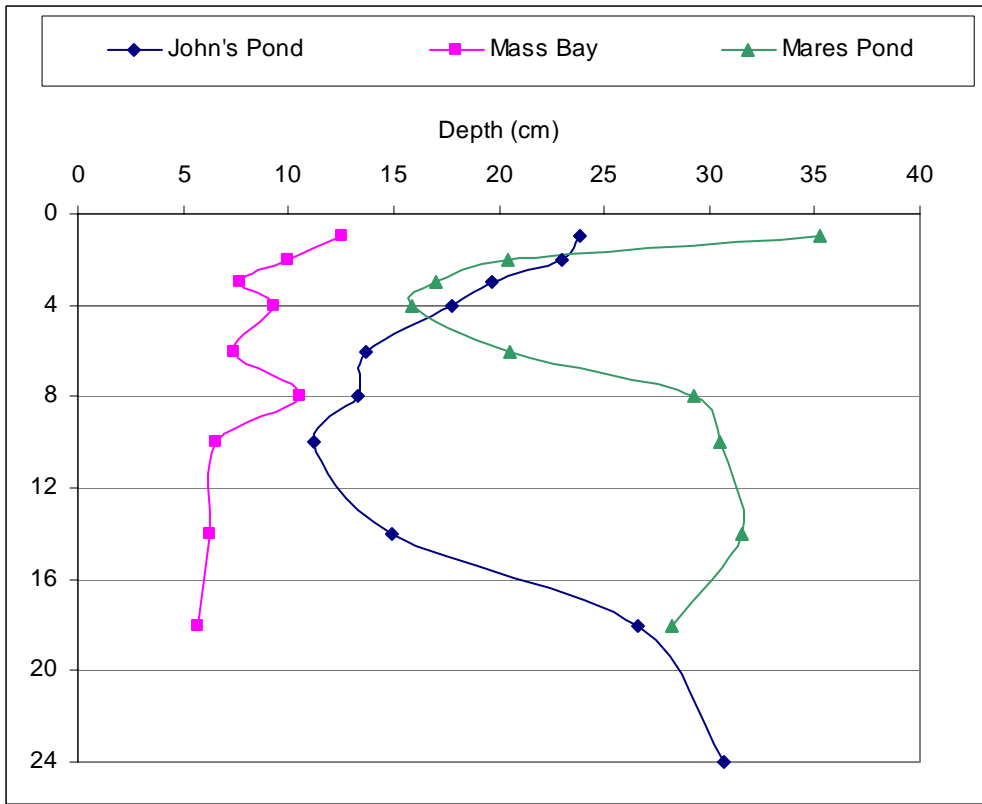


Figure 5. Carbon to sulfur ratios throughout the sediments of three aquatic systems.

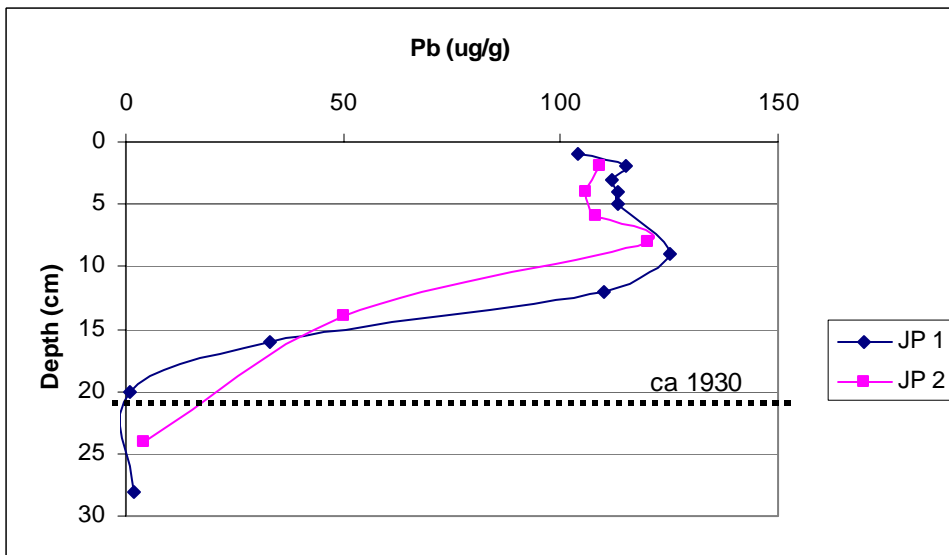


Figure 6. Lead profiles for two replicate John's Pond sediment cores.

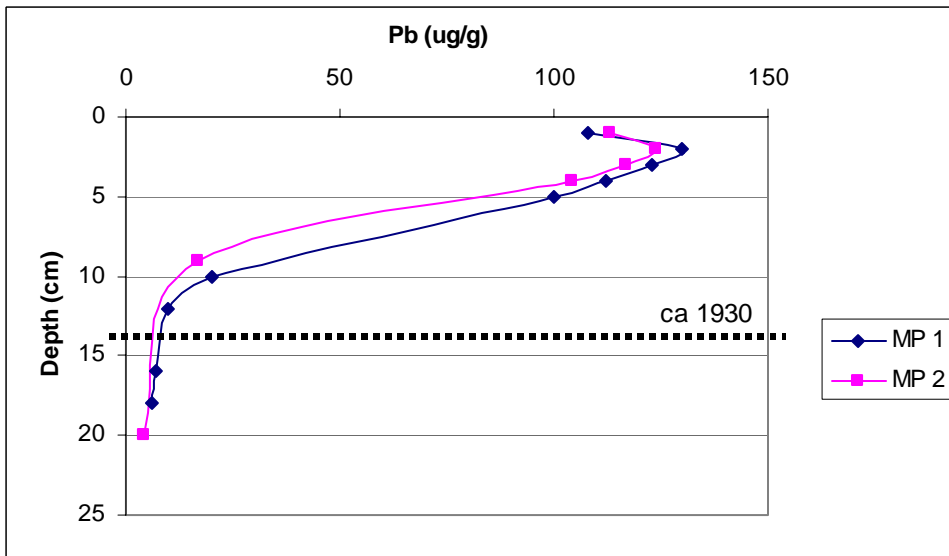


Figure 7. Lead profiles for two replicate Mares Pond sediment cores.

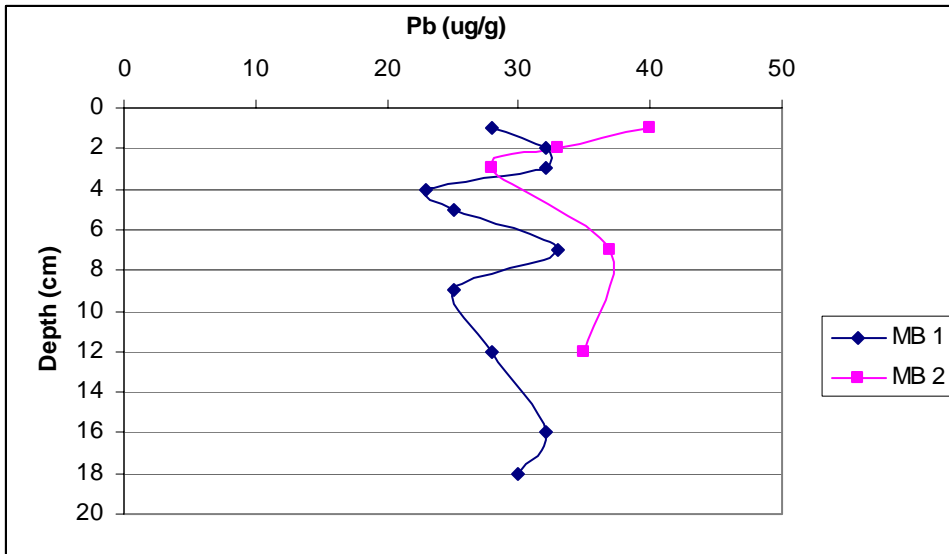


Figure 8. Lead profiles for two replicate marine sediment cores.

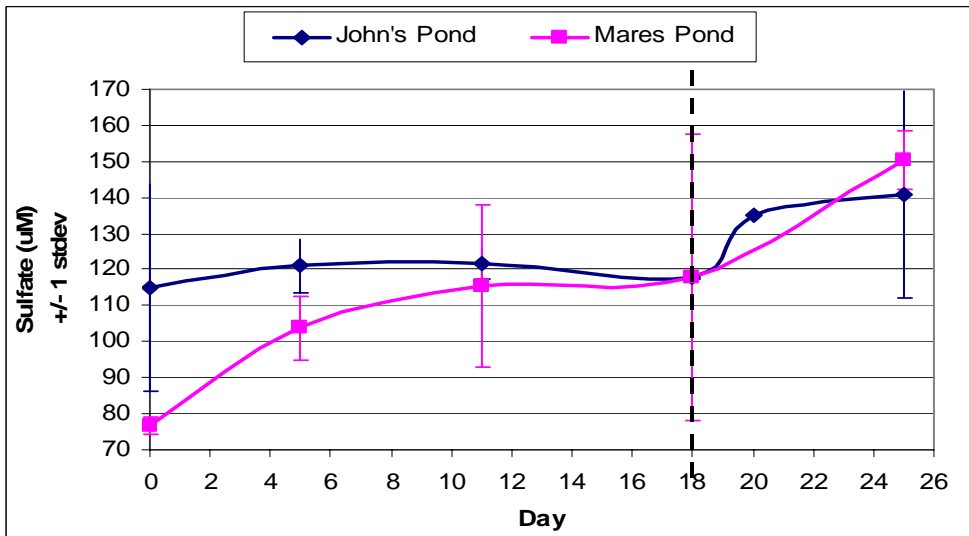


Figure 9. Mean sulfate concentration (+/- 1 sd) versus time for freshwater control cores.

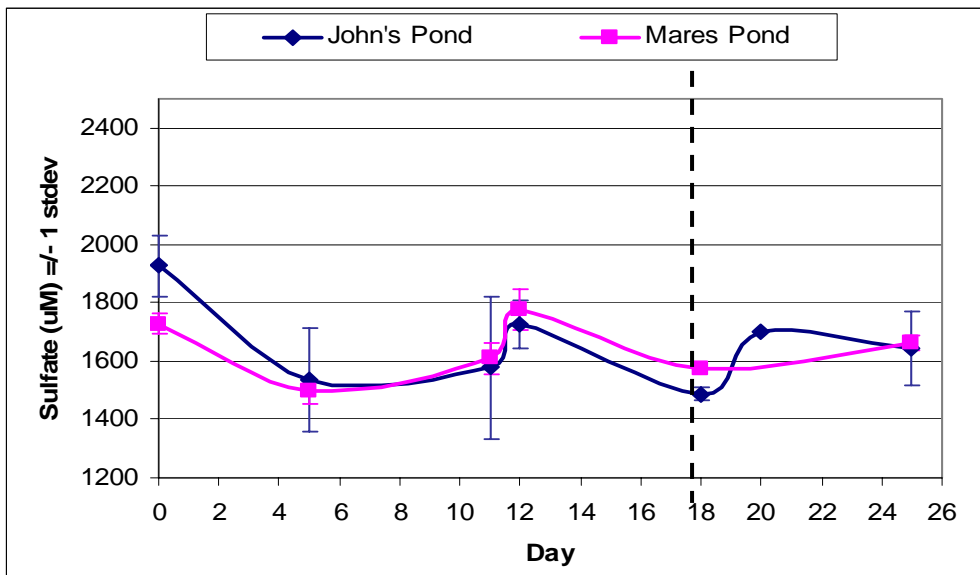


Figure 10. Mean sulfate concentration (± 1 sd) versus time for freshwater sulfate cores.

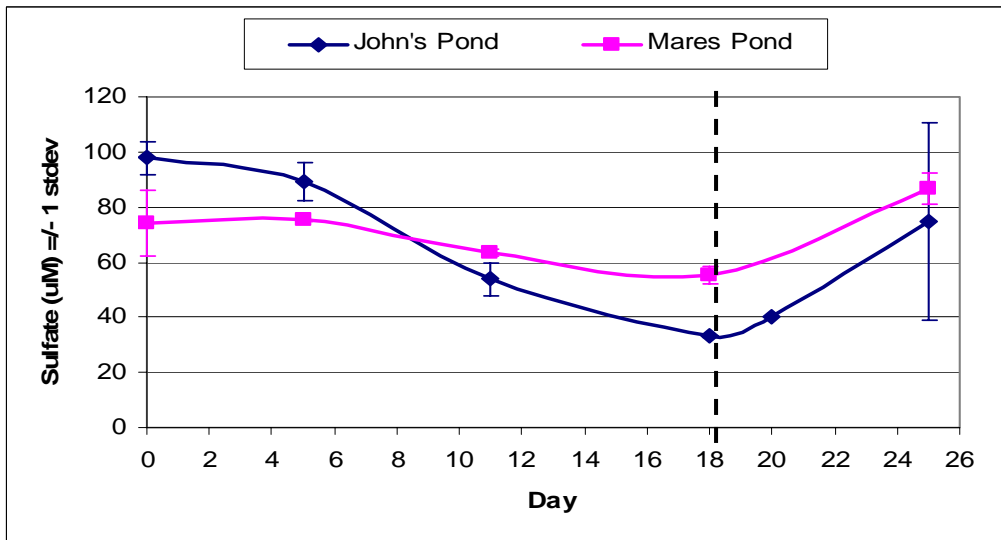


Figure 11. Mean sulfate concentration (± 1 sd) versus time for freshwater sulfate cores.

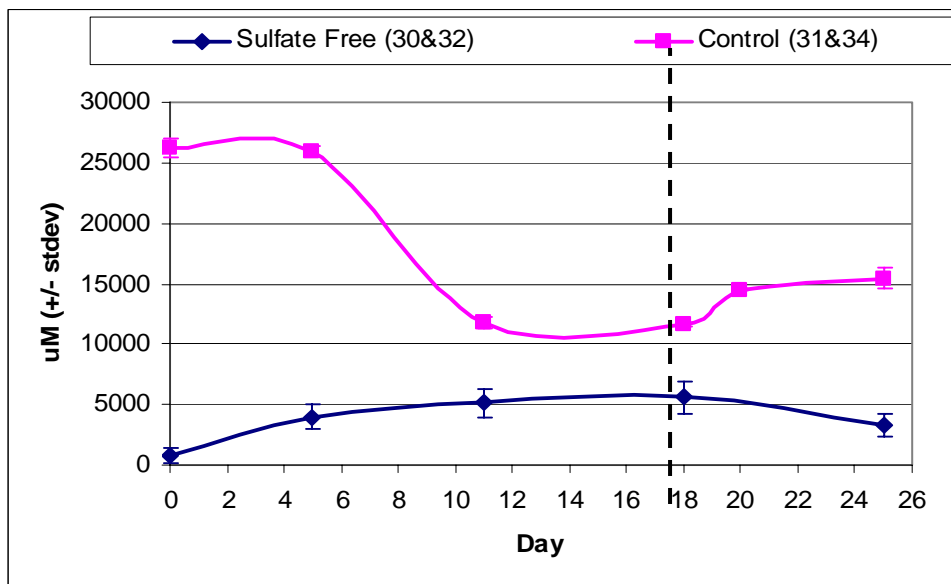


Figure 12. Mean sulfate concentrations (± 1 sd) versus time for all marine cores.

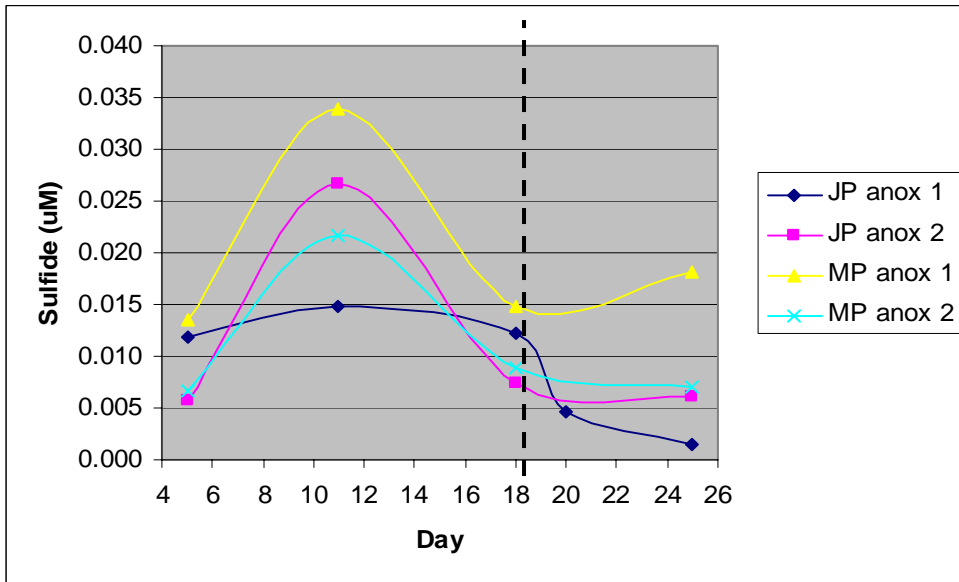


Figure 13. Sulfide concentrations versus time in freshwater anoxic cores.

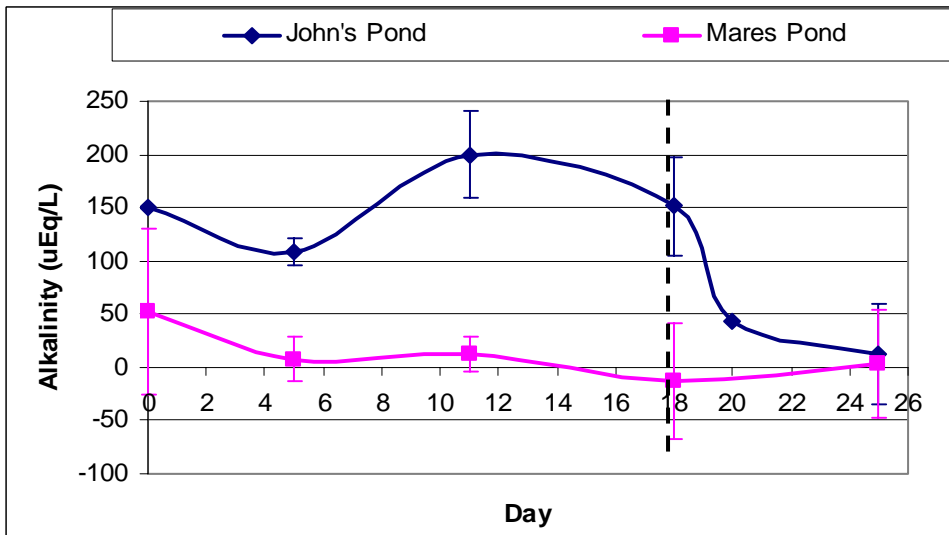


Figure 14. Mean alkalinity (+/- 1 sd) versus time in freshwater control cores.

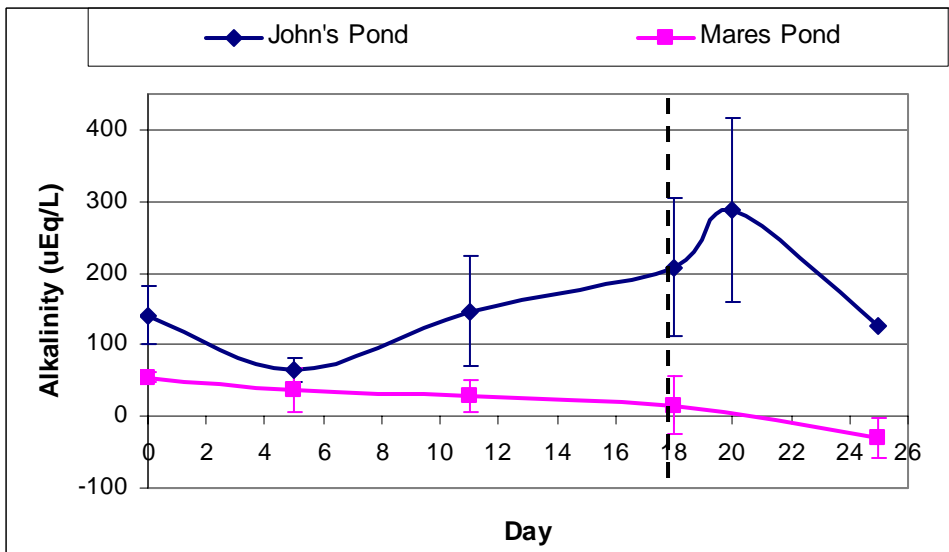


Figure 15. Mean alkalinity (+/- 1 sd) versus time in freshwater sulfate cores.

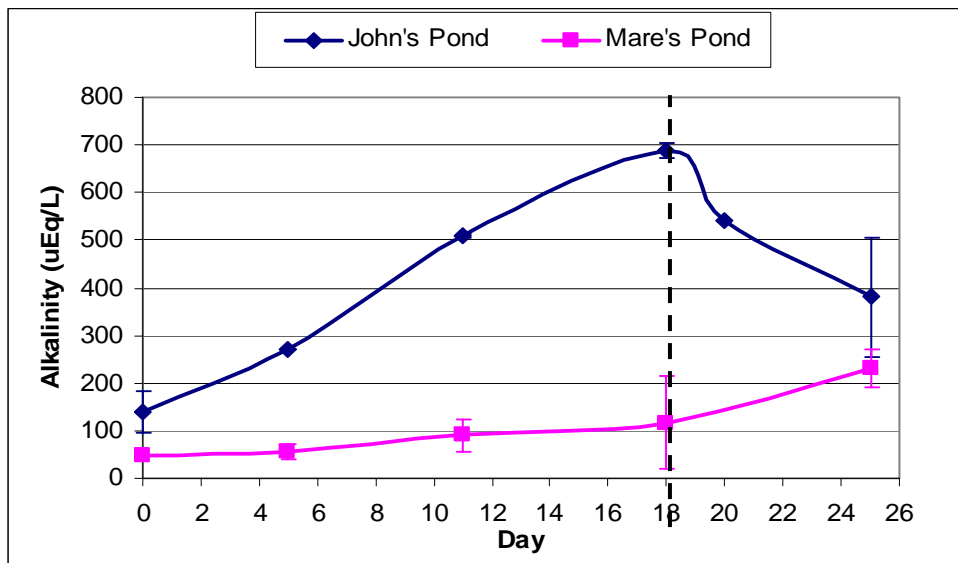


Figure 16. Mean alkalinity (± 1 sd) versus time in freshwater anoxic cores.

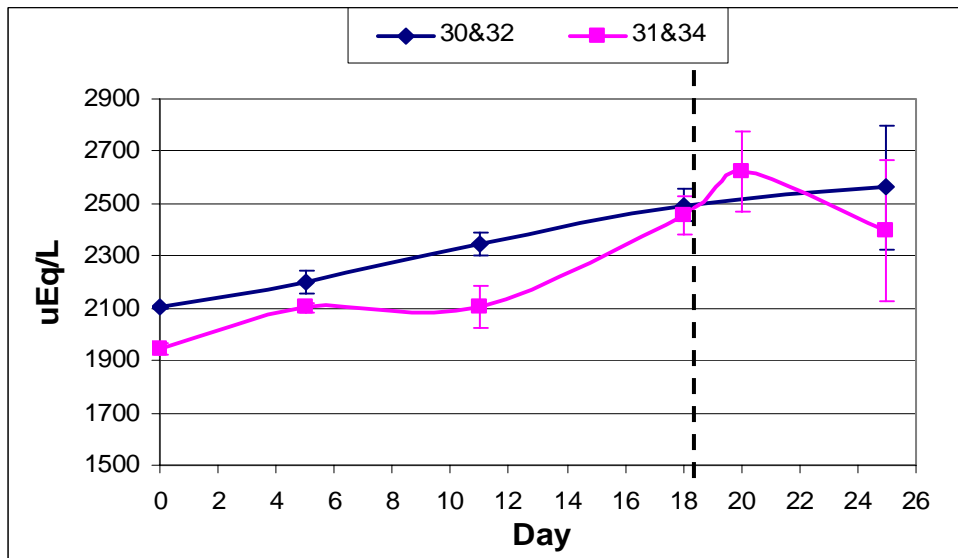


Figure 17. Mean alkalinity (± 1 sd) versus time in marine sediments.

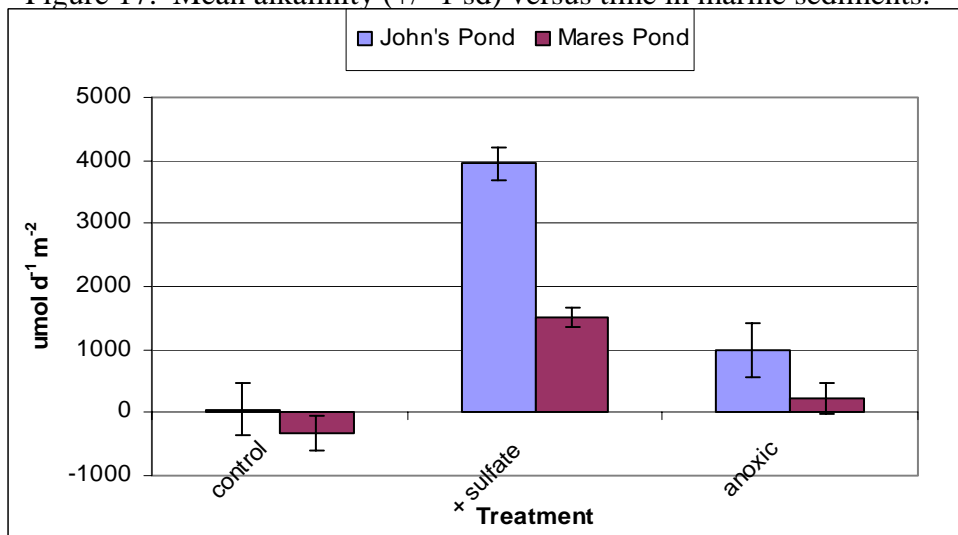


Figure 18. Mean rates of sulfate disappearance (± 1 sd) in all freshwater cores before iron additions.

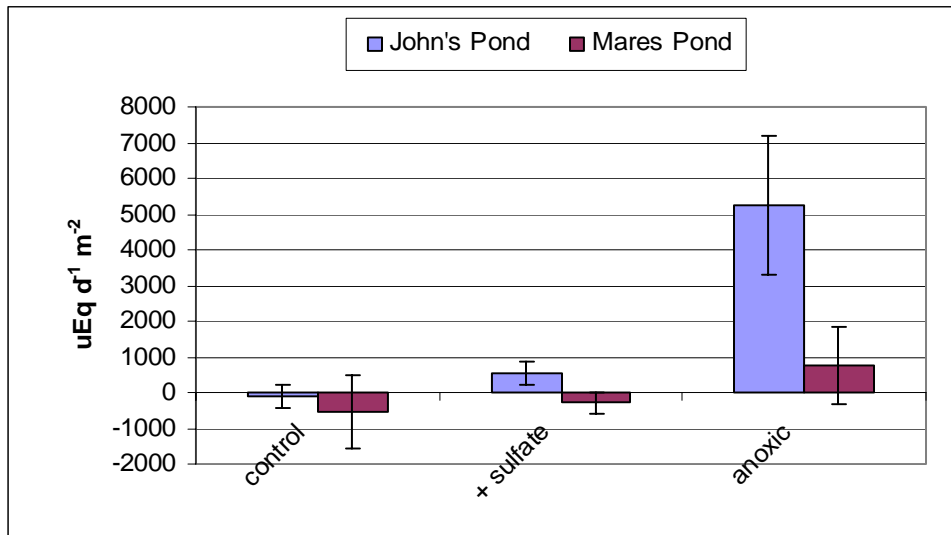


Figure 19. Mean rates of alkalinity generation (+/- 1 sd) in all freshwater cores before iron additions.

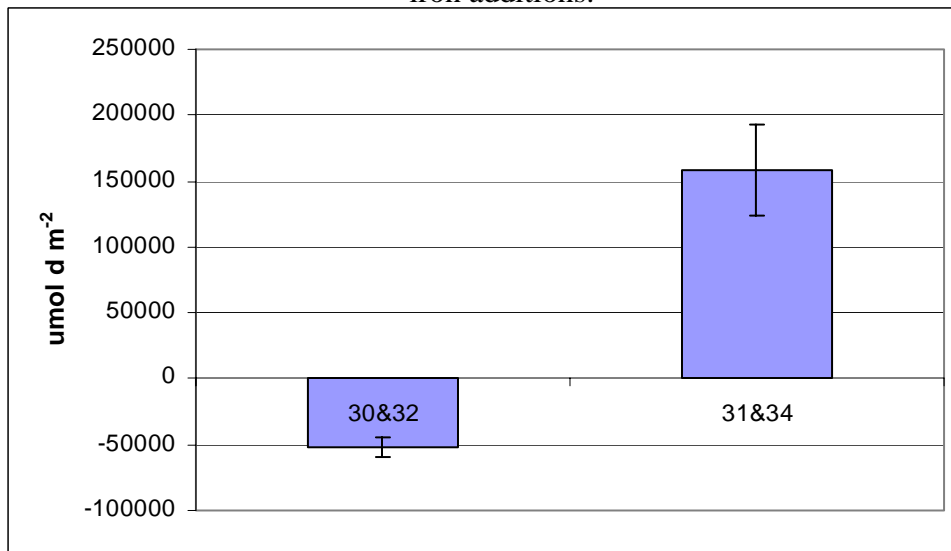


Figure 20. Mean rates of sulfate disappearance (+/- 1 sd) in all marine cores before iron additions.

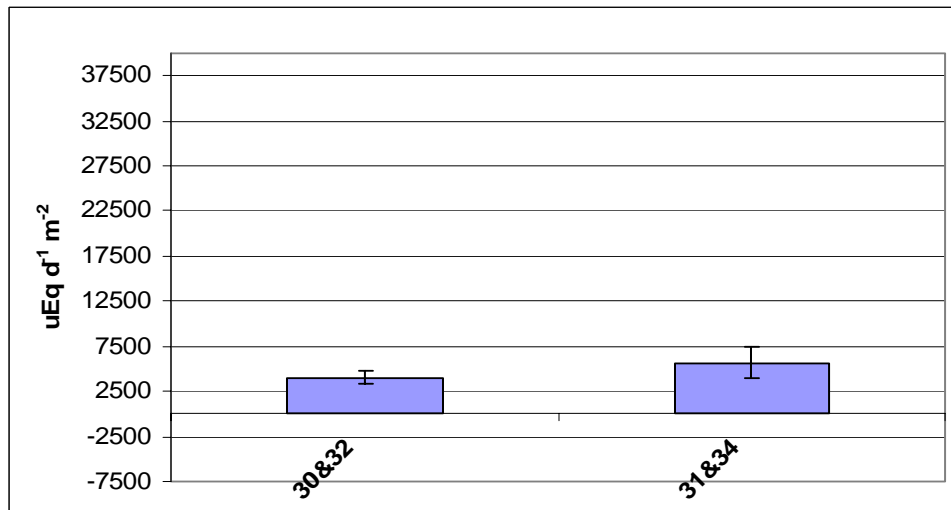


Figure 21. Mean rates of alkalinity generation (+/- 1 sd) in all marine cores before iron additions.

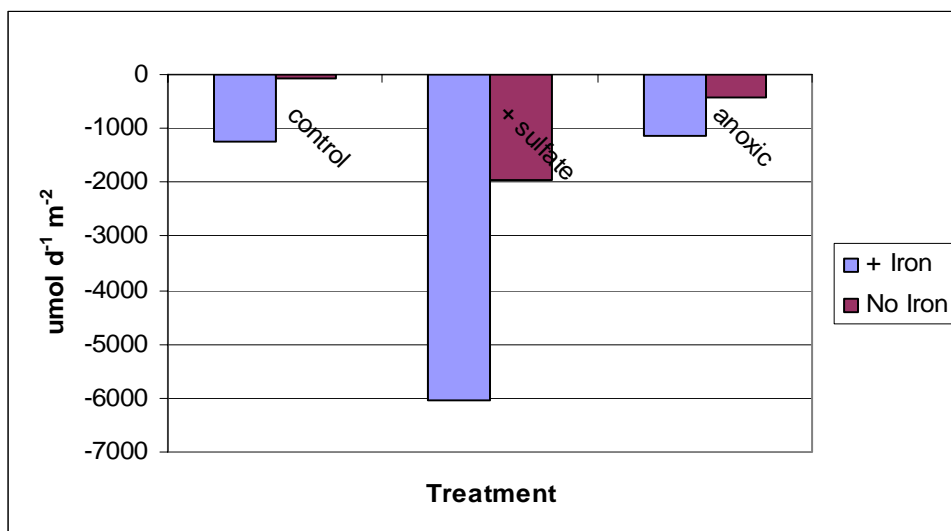


Figure 22. Rates of sulfate disappearance in all John's Pond cores after iron additions

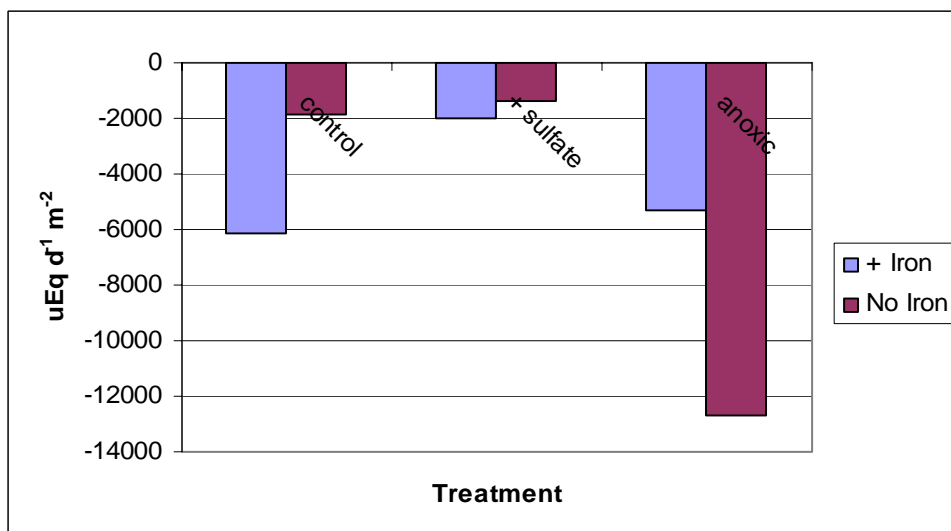


Figure 23. Rates of alkalinity generation in all John's Pond cores after iron additions.

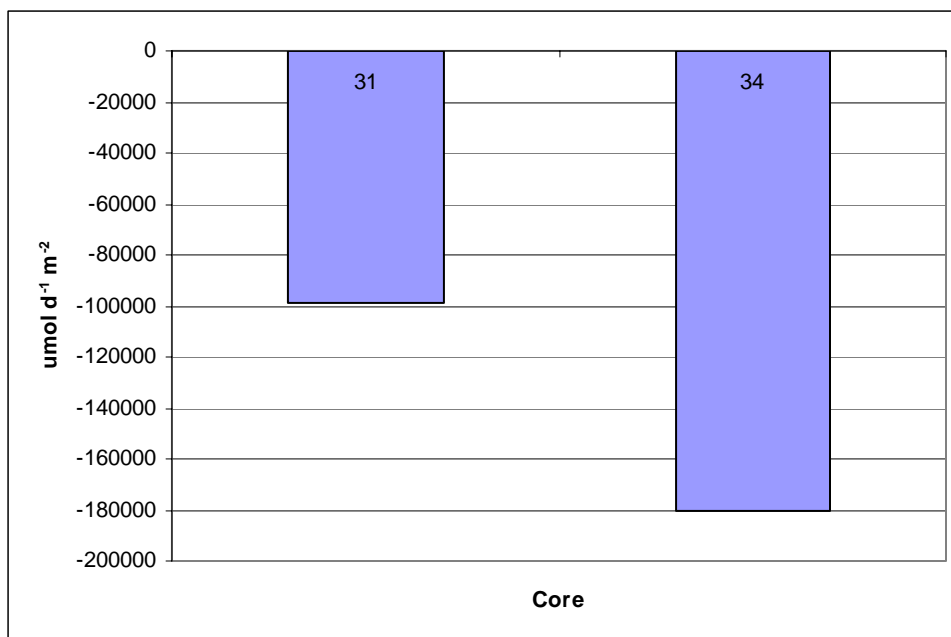


Figure 24. Rates of sulfate disappearance in marine cores that received iron additions.

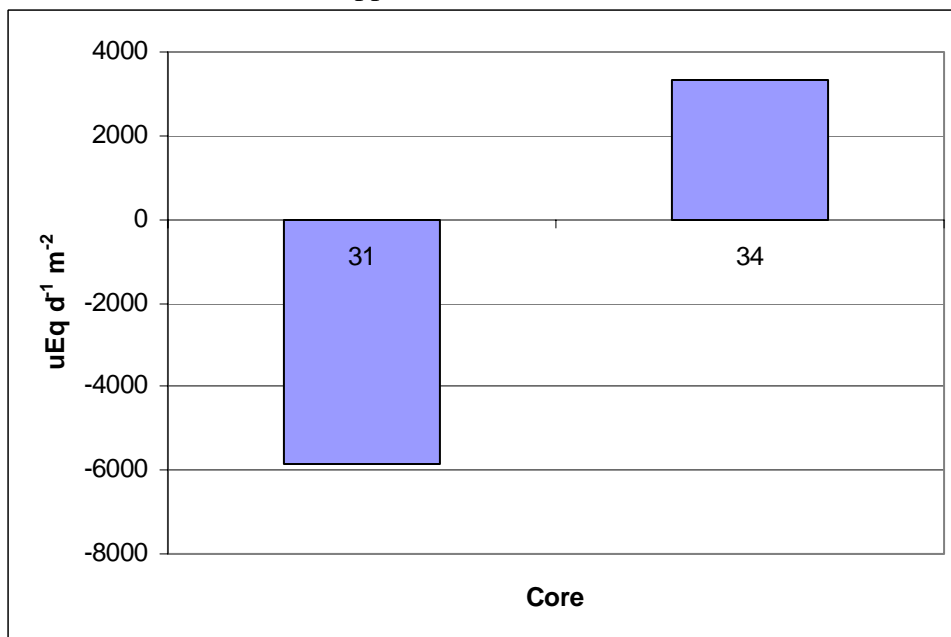


Figure 25. Rates of alkalinity generation in marine cores that received iron additions.

Site	Mean Rate of Sulfur Burial (mmolS m ⁻² y ⁻¹)	Mean Rate of Alkalinity Generation (mEq m ⁻² y ⁻¹)
John's Pond	6.73	13.47
Mares Pond	3.59	7.19

Table 1. Mean rates of historical sulfur burial and alkalinity generation as calculated from freshwater sediments.