Metal-Base Cation Exchange in Cape Cod Freshwater Ecosystems

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Abstract

Increased acid deposition causes deterioration in the quality of soils and freshwater ecosystems, as well as decreasing their ability to buffer acidity. Aluminum in soils increases acidity and is toxic to the biota of freshwater systems. This survey is meant to monitor ability of soils to buffer pH and observe the role of aluminum in acidity in and around three freshwater ponds on Cape Cod. The organic and mineral layers of the soil around Flax Pond, Miles Pond, and Mares Pond were sampled and tested for acidity, base cations and aluminum content, then leached with acid to see if aluminum would be released with increased acid deposition. The groundwater and pond water was also sampled and tested for acidity and alkalinity. In every soil sampled, sufficient amounts of base cations were found to be able to buffer acidity from reaching the ponds in the near future, aluminum was found to contribute significantly to acidity, and a large increase in acidity was not found to release any aluminum from the soils.

Key Phrases: Cape Cod, Flax Pond, Miles Pond, Mares Pond, acid deposition, soil base cations, soil aluminum, base saturation, cation exchange capacity, exchangeable acidity, exchangeable bases

Key Words: alkalinity, pH, aluminum, acidity, buffering, cations, freshwater, soil

Introduction

Acid deposition presents a major threat to aquatic freshwater ecosystems. Likens and Borman (1974) found the average pH of freshwater streams in the Northeast United States have decreased significantly since the Industrial Revolution due to nitrous oxides and sulfur dioxide emissions. They describe how these compounds form nitric and sulfuric acid respectively and are created by the combustion of fossil fuels. However, acidity can be buffered by base cations (Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, NH$_4^+$) which are replaced by H$^+$ in soils, which neutralizes the free H$^+$ (McFee et al. 1976). In contrast, the Al$^{3+}$ cation reacts with water to create additional acidity in the form of H$^+$. Aluminum thus provides a positive feedback mechanism, in addition to being naturally toxic to fish (De Vries et al. 1989). Alkalinity (often measured as [HCO$_3^-$]) can buffer acidity once it enters a body of water by reacting with H$^+$ to create relatively inert compounds. However, as a result of increased acidity, base cation concentrations in soils are decreasing, as are alkalinity concentrations in freshwater (Schindler 1988).

Cape Cod soils are naturally low in pH, alkalinity and mineral content due to their parent material (Mattson et al. 1992). Thus, they are naturally poorly equipped to deal with acid deposition. The ponds on Cape Cod tend to be glacial kettle ponds fed by groundwater, making their chemistry highly dependent on the surrounding soil composition (Ahrens and Siver 2000). Even though the ecosystems of Cape Cod seem highly susceptible to damaging acidity, they are naturally more acidic than pond systems elsewhere, and precipitation is more influence by the ocean than inland locations due to it being a peninsula, mitigating the damaging acid deposition seen in other locations in the Northeast.
The goal of my experiment was to assess the current state of soils and water in freshwater ponds on Cape Cod in terms of acidity. I wanted an overview of the differing conditions in ponds of different pHs, so the survey ponds were selected based on their pH. The focus of my survey was the role of aluminum in acidity on Cape Cod and the amount of acidity the soils can absorb before aluminum leaching begins. This is ecologically important because aluminum is only leached once other soil nutrients (e.g. base cations) have been depleted, and aluminum has a positive feedback loop with acidity. Therefore, assessing the likelihood of this occurring is crucial to maintaining the health of the ecosystems on the cape.

Methods

Field Sites
The three freshwater ponds I sampled were Flax Pond, Miles Pond, and Mares Pond. The ponds were sampled from early November 2011 to mid-November 2011. Flax Pond is located in Dennis, MA, while both Miles Pond and Mares Pond are located in Falmouth, MA. I chose these sites based on their water pH values from previous studies, which describe Flax Pond as having a lower pH (≈4.4), Mares Pond as having a higher pH (≈6.8), and Miles Pond as having a pH within the range of these two (≈5.3) (Ahrens and Siver 2000) (Giblin et al. 1990). Each pond is fed by groundwater and located within a suburban development as well.

Field Collection
At each site, I took five soil samples, each with a mass of ≈100 grams, from the organic topsoil layer at a distance of 3-5 metres from the pond surface at random locations around the ponds. I took an additional five samples of ≈100 grams of mineral soil from depths ranging from 5-10 cm at the same location as the organic soils. I used a well point and pump to obtain five samples of 250 mL of groundwater from five sites around each pond in locations where the groundwater was flowing into the pond. I also took five samples of 250 mL of surface water from the same locations as the groundwater.

Laboratory Analysis
I incubated all the soil samples in plastic dishes at 60°C for three days to completely remove any moisture. After the samples were sufficiently desiccated, I homogenized them by hand, and measured their pH by weighing out five grams of each organic soil and 10 grams of each mineral soil and placing them in separate plastic cups, then adding 50 mL of deionized to each sample. The samples were stirred and a pH meter was used to measure the pH, which was then recorded.

After allowing the water samples to reach equilibrium with the air, I analyzed the groundwater and pond water samples for alkalinity by measuring out 25 mL of each sample into a small beaker. Each sample was stirred using a magnetic stirrer, and the initial conductivity of each sample was measured in mV using a pH meter. The conductivity and the temperature were both recorded. I then titrated the samples with .16 N sulfuric acid using a dropper that
dispensed the sulfuric acid in units of 1/800 mL until the conductivity reached 195 mV. I recorded the amount of sulfuric acid needed to reach this conductivity, then added 20 more units of acid nine more times, recording the conductivity and total acid added after each addition.

In order to free base cations from the soils, I placed two grams of each mineral soil sample in a falcon tube and leached them with 20 mL of 1 M ammonium acetate. The organic soil was treated in a similar fashion, but 30 mL of 1 M ammonium acetate was used to allow easier separation of the solution and soil. I then placed the tubes on a shaker table which shook them for two hours. Once this was finished, I used a centrifuge to spin each sample at 4100 rpm for 10 minutes, to help separate the soil from the liquid. I proceeded to remove 15 mL of the ammonium acetate solution from each sample and transferred the samples into separate scintillation vials. After the liquid was removed, I disposed of the remaining soil, and measured the concentrations of sodium, calcium, potassium, and magnesium using an flame atomic absorption spectrophotometer. Due to the standards used having low concentrations of the metals I wished to analyze, all the samples analyzed for sodium and potassium were diluted to 20:1 with deionized water, while several of the organic soil samples analyzed for magnesium were diluted 200:1 with deionized water. The measured concentrations were all recorded in mg/L (Modified from Van Reeuwijk 2002).

To measure the aluminum content of each soil sample, I placed five grams of each soil sample in plastic cups and added 50 mL of 1 N potassium chloride. I then shook the samples for an hour on a shaker table and filtered out the potassium chloride using an electric pump and filter paper. An additional 100 mL of 1 N potassium chloride was added in 25 mL pulses as the samples were filtered. I disposed of the filters and transferred the extract to 125 mL polyethylene bottles. I removed 25 mL of the extract with a pipette and transferred it to a beaker. A magnetic stirrer stirred the sample while a pH meter measured the initial pH of each sample. I added four drops of a phenolphthalein solution to each sample as it was stirred. After I had recorded the pH of the sample, I titrated it with a .07 M sodium hydroxide solution until the pH reached 8.15. I recorded the amount of sodium hydroxide added, then added 2.5 mL of 1 M potassium fluoride to the sample. I allowed half an hour to go by to assure the fluoride had fully reacted with the solution, and then titrated the sample with .07 M hydrochloric acid until the pH returned to 8.15, and recorded the volume of acid used.

The final laboratory procedure I used was leaching the base cations with a 1.581 mM hydrochloric acid solution, which is the equivalent of 50x the acidity of normal Cape Cod rainfall. To 10 grams of two soil samples from each site and depth, I added 90 mL of this solution and shook the samples in plastic cups on a shaker table for 12 hours. The acid was removed and the leached base cations were then analyzed with an flame atomic absorption spectrophotometer and recorded in mg/L.

**Calculations**

I entered the alkalinity data I gathered into a spreadsheet given to me by Ann, which calculated the total alkalinity in mEq in each sample by calculating the slope of the line created by the conductivity, which then indicates the alkalinity as the y intercept of the line.
In order to analyze the aluminum titration data, I multiplied the molarity of the sodium hydroxide used by the volume of sodium hydroxide used then multiplied the resulting product by the total potassium chloride volume. This gave me the total amount of hydrogen protons in mEq in each sample. The aluminum concentration in mEq was found through the same equation, but using the hydrochloric acid molarity and volume rather than the sodium hydroxide normality and volume. I calculated the percent of acidity from aluminum by dividing the aluminum concentration by the proton concentration and multiplied this by 100.

For the ammonium acetate extractions and hydrochloric acid extractions I converted the data from mg/L to mEq by correcting for any dilution then multiplied the true concentration by the charge of each cation measured and divided by the atomic weight of each cation. The cation exchange capacity per sample was derived by adding the cation values for each sample together and multiplying this number the total volume of ammonium acetate used in L. This number was then added to the total acidity data, which gives the total cation exchange capacity. Finally, the percent base saturation of each sample was calculated by dividing the cation exchange capacity per sample by the total cation exchange capacity and the result was multiplied by 100.

Results

The average measured pH of pond water from Flax Pond was 4.66, while the average pH of groundwater from this pond was 5.40. The pond water from Miles Pond had an average pH of 6.11 with a groundwater average of 5.11. Mares Pond had an average pond water pH of 5.91 and an average groundwater pH of 5.07. The average measured organic soil pH values from Flax Pond, Miles Pond, and Mares Pond were 3.85, 4.27, and 4.08 respectively, while the average mineral soil pH values were 3.96, 3.99, and 3.77 respectively (figure 1).

Potassium was the most prevalent base cation in the mineral soils of Flax Pond, Miles Pond, and Mares Pond, with averages of 0.250 mEq, 0.314 mEq, and 0.191 mEq respectively. Sodium, calcium, and magnesium values in the mineral soil of Flax Pond were 0.129 mEq, 0.062 mEq, and 0.022 mEq respectively. In Miles Pond the average sodium value was 0.097 mEq, the average calcium value was 0.037 mEq, and the average magnesium value was 0.121 mEq, while in Mares Pond the averages for sodium, calcium, and magnesium were 0.050 mEq, 0.070 mEq, and 0.006 mEq respectively (figure 2).

Magnesium was the most prevalent base cation in the organic soils of each pond, with an average value of 4.739 mEq in Flax Pond, an average value of 2.773 mEq in Miles Pond, and an average value of 3.324 mEq in Mares Pond. The average sodium, calcium, and potassium organic soil values in Flax Pond were 0.740 mEq, 0.776 mEq, and 1.072 mEq respectively. In Miles Pond and Mares Pond the average organic soil sodium values were 0.369 mEq and 0.540 mEq respectively, the average organic soil calcium values were 0.321 mEq and 0.588 mEq respectively, and the average organic soil potassium values were 1.348 mEq and 1.504 mEq respectively (figure 3).

The average total cation exchange capacity for the organic soils of Flax Pond, Miles Pond, and Mares Pond were 0.678 mEq, 0.449 mEq, and 0.632 mEq in corresponding order,
while the average total cation exchange capacity for the mineral soils of the ponds was 0.137 mEq, 0.201 mEq, and 0.182 mEq respectively (figure 4). The calculated percent base saturations for the organic layer of each pond, in the same order as above, were 32.9%, 32.7%, and 28.5%, while the calculated percent base saturations for the mineral layers, in the same order, were 7.57%, 6.12%, and 3.68% (figure 5).

Flax Pond and Mares Pond pond water samples both had negative average alkalinity measurements, indicating high acidity, with values of -390 and -15.1 µEq/L respectively. Miles Pond pond water had an average alkalinity of 141 µEq/L. The ground water average alkalinity values for Flax Pond, Mares Pond, and Miles Pond were 213 µEq/L, 102 µEq/L, and 76.6 µEq/L respectively (figure 6).

The average percent of acidity from aluminum in organic soils ranged from 10.2% in Mares Pond to 24.8% in Miles Pond, with Flax Pond having an average value of 17.8%. In mineral soils, the average percent of acidity from aluminum ranged from 32.4% in Flax Pond to 56.3% in Miles Pond with an average value 52.0% in Mares Pond (figure 7).

There is a slight trend ($r^2=0.347$) between the pH of organic soils vs. the percent of cations leached and a stronger trend ($r^2=0.737$) between the pH of mineral soils vs. the percent of cations leached (figure 8). When leached with hydrochloric acid, the acidity took up 29.8%, 34.1%, and 27.3% of the total cation exchange capacity in the organic soils of Flax Pond, Miles Pond, and Mares Pond respectively. Acidity took up 28.9%, 12.2%, and 38.3% of the total cation exchange capacity in the mineral soils of these ponds, in their respective order (figure 9).

**Discussion**

The pond water pH values I measured were different than those recorded in previous studies (Ahrens and Siver 2000) (Giblin et al. 1990). Contrary to what was expected, Miles Pond was slightly less acidic than Mares Pond, although their pH values were comparable. The difference in values is likely a result of a number of factors, such as the pH of recent rainfall, temperature, atmospheric pressure, and surface wind changing the equilibrium of the ponds and atmosphere. It is also interesting to note that the groundwater of Flax Pond, which had the lowest pond water pH, is actually the least acidic. This implies that surface runoff may play a large role in providing water to this pond or that the sediment the ground water seeps through is especially acidic. Pollution may also be affecting the pH of this pond, as large amounts of garbage (e.g. aluminum cans, plastic waste etc.) were found on the banks of the pond. The organic soil of Flax pond is more acidic than that of the other ponds as well, which indicates the sediment may be more acidic. Mares Pond and Miles Pond were comparable across all pH measurements, although the soils of Mares Pond were slightly more acidic (figure 1).

Few significant trends were found in the mineral soil base cation measurements, with the exception of potassium being the most prevalent cation across all sites, and magnesium being much more concentrated in Miles Pond than in the other sites. The reason for the absence of trends is probably due to slightly different parent material and weathering rates for these soils (figure 2). The organic soils had several interesting pieces of base cation data. The magnesium levels were especially high across sites, which contradicts the values expected for
magnesium deposition through sea spray (Barnes 1954). According to Barnes (1954), sodium should be the highest concentration in sea water, followed by magnesium, calcium, and potassium. With the exception of magnesium, the observed trend is actually the opposite of what would be expected. This indicates that sea spray is not the predominant source of cations in organic soil at these ponds, although it likely still contributes. It’s possible that anthropogenic sources, such as lawn care products and road salt are contributing to the cation concentrations in conjunction with decaying organic matter to create the concentrations measured (figure 3).

The organic soil in Miles Pond had a significantly lower cation exchange capacity than either of the other organic soils. This may just be due to statistical fluctuations. The Flax Pond and Mares Pond organic soil had similar cation exchange capacities, as did the mineral soil layer for all three ponds, probably because of similar soil composition (figure 4). The percent base cation saturation in the organic layer was lowest in Mares Pond, but not significantly so. The percent base cations were all similar for the mineral layers as well. Once again this is likely due to similar soil compositions (figure 5).

The absence of alkalinity in the pond water of Mares Pond and Flax Pond is explained by the acidity of these two bodies of water, as well as the calcium poor nature of the soils which prevents alkalinity buildup (figure 2 and figure 3). Free protons react with alkalinity, which eliminates it from the water. Miles Pond, being less acidic, still has alkalinity present within it. The high alkalinity in Flax Pond groundwater once again indicates some mechanism which is either acidifying the groundwater as it enters the pond, or that groundwater is not as important a source of water in the pond as was supposed. The high level of error in the Miles Pond groundwater data is likely due to the marshy nature of some of the sampling sites, which allows more organic acids to react with alkalinity, as compared to the less marshy sampling sites at the same pond. The groundwater at Mares Pond probably has slightly more alkalinity than the pond water through the same mechanism, i.e. organic acids in the sediment (figure 6).

The acidity from aluminum was significantly lower in the organic soils, possibly due to organic acids forming the bulk of the acidity. It is also likely that there is less aluminum in the organic layer due to the lessened role of mineral weathering in the formation of these soils. Variations between sites are likely due to the nature of the decaying organic matter at each site. Aluminum acidity is higher in the mineral soils for the opposite reason, i.e. the mineral soil is formed more from weathering of parent material which contains more aluminum than the organic compounds that form the organic layer. Variations between sites in the aluminum acidity of the mineral layer are not statistically significant, and no correlation was found between average pH and average acidity from aluminum (figure 7).

The percent of the total cation exchange capacity taken up by hydrogen through removal of base cations was fairly consistent across sites, with the exception of the Miles Pond mineral soil (figure 9). This could be due to the relatively higher pH of this soil as compared to that of the other mineral soils, as seen by the trend in figure 8. The organic soil values may also be correlated to the pH of the soils, but there is not an especially large trend and there are not enough data points for a clear picture of why the cation leached data is as it is. This data indicates that Cape Cod soils are not in immediate danger from aluminum being leached out of the soils, especially considering that the cations will be replaced as time goes on. A radical
increase of acidity in a short period of time would be necessary to deplete the soils of their base cations, despite the naturally impoverished nature of the soils.
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Citation


Figure 1: Comparison of pH values across sites and samples

- Organic Soil Layer
- Mineral Soil Layer
- Ground Water
- Pond Water
Figure 2: Comparison of base cation concentrations across sites in mineral soils
Figure 3: Comparison of base cation concentrations across sites in organic soils
Figure 4: Comparison of total cation exchange capacity across sites and soils
Figure 5: Comparison of percent base saturation across sites and soil
Figure 6: Comparison of total alkalinity across sites and water samples
Figure 7: Comparison of percent acidity from aluminum across sites and soils

- Flax Organic: 17.8%
- Miles Organic: 24.8%
- Mares Organic: 10.2%
- Flax Mineral: 32.4%
- Miles Mineral: 56.3%
- Mares Mineral: 52.0%
Figure 8: Percent base cation saturation versus pH

R² = 0.3471

R² = 0.7372

Percent of Base Cations Leached Compared to Total CEC

pH

Organic Soils
Mineral Soils
Figure 9: A comparison of percent of total base cations leached with hydrochloric acid compared to total CEC

- Flax Organic: 29.8%
- Miles Organic: 34.1%
- Mares Organic: 27.3%
- Flax Mineral: 28.9%
- Miles Mineral: 12.2%
- Mares Mineral: 38.3%

Legend:
- Red: Total CEC
- Blue: Base Cations Leached