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Making Green Water Clear: Using Alternative Technology to Treat Eutrophic Freshwater

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research article

Making Green Water Clear: Using Alternative Technology to Treat Eutrophic Freshwater

—Hethre Larivee (Edited by Alex Miklos)

It's a beautiful, sunny day, perfect for a quick swim in the local pond. Once you and the family arrive, however, you see that the water is an unsightly green color, thick with slimy algae. The water is not very inviting after all. Disgusted, you turn away and begin to wonder what is wrong with the pond. This is the case of a pond in the small town of Phillips, Maine. Over the years, residents living on Toothaker Pond have seen the condition of the pond severely decline. (Fig. 1)



Fig. 1. Toothaker Pond Eutrophication in summer. (cr. A. Rollo)

What *is* wrong with the pond? After years of increased nutrient input, the pond has become eutrophic, which means there is an excess growth of algae in the water. This algae bloom can degrade water quality to the point of its being toxic to aquatic and, possibly, human life. When freshwater is eutrophic, older algae die and microorganisms feed on the organic matter. During microbial decomposition, the amount of dissolved oxygen (DO) in the water is reduced and the biological oxygen demand (BOD) increases. (BOD is the amount of dissolved oxygen used by microorganisms during decomposition of organic matter.) Insufficient levels of DO

can suffocate aquatic life and cause fish kills, which further reduces DO and increases BOD. When microbes break down the organic matter, they also release phosphorus back into the water that now feeds new algae blooms; and thus the cycle is perpetuated. (Fig. 2)

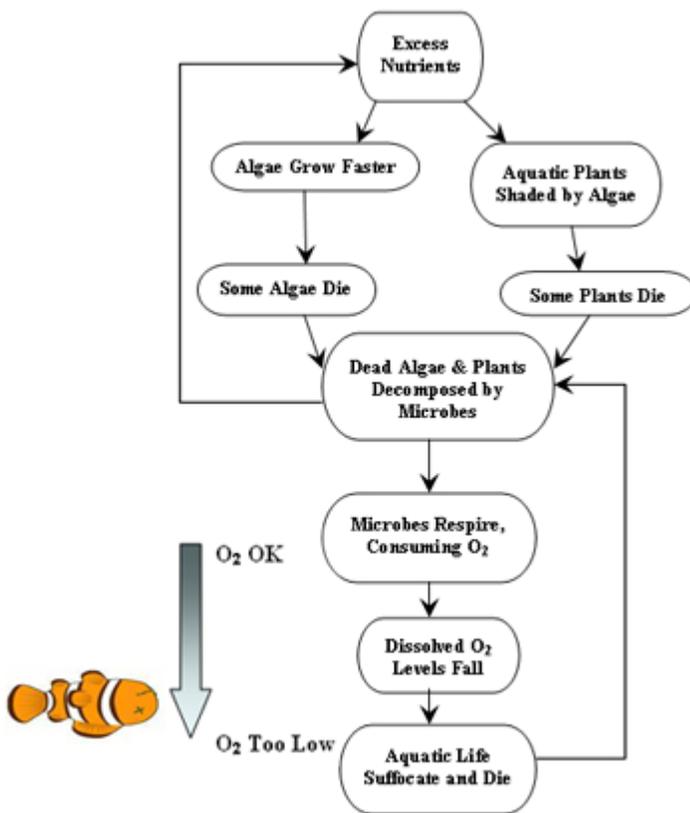


Fig. 2. Eutrophication process (adapted from the BBC)

A limiting nutrient is one that controls a process such as algae growth. In a freshwater system such as Toothaker Pond, phosphorus (P) is the limiting nutrient. P is essential to aquatic, vegetative, animal, and human life. However, excess P input causes eutrophication. Excess P can enter freshwater systems from aquaculture, agriculture, and septic systems as well as from household use of fertilizers and detergents.

Late in 2006, the residents of Toothaker Pond in Phillips, Maine, contacted Dr. Kevin Gardner, Director of the Environmental Research Group (ERG) at the University of New Hampshire. They explained to Dr. Gardner that Toothaker Pond has experienced severe eutrophication for about the past twenty years. A nearby fish hatchery, built upstream in the 1960s by the Maine Department of Environmental Protection (MDEP), emptied into Toothaker Pond, depositing hundreds of gallons of phosphorus-rich effluent. The fish hatchery effluent was eventually diverted away from Toothaker Pond; however, the problem persisted. In fact, the water quality is so bad that this pond is listed on the United States Environmental Protection Agency's 303(d) List of Impaired Waters

(MDEP, 2004). The residents were looking for a student-designed solution to their problem, so in spring 2007 Dr. Gardner encouraged me to work with them using apatite phosphate rock as a possible treatment for their pond.

Why Me and Why Apatite Phosphate Rock?

While I was an environmental science undergraduate, I worked as a laboratory assistant for research scientist Bradley Crannell in the Environmental Research Group (ERG). At the time, he was researching how apatite phosphate rock could be used as a reactive barrier to remediate estuaries contaminated by heavy metals. During his research in Great Bay, a saltwater estuary, Crannell observed that this material could remove phosphorus from the water. This was the springboard to my undergraduate research. I wanted to take his observation further and determine if apatite phosphate rock could also remove P from freshwater, thereby preventing the eutrophication cycle.



Fig. 3. The author outside her lab building, Gregg Hall, on her way to a test site.

Currently, commonly used treatments to control phosphorus in eutrophic bodies of water include applications of lime (calcium carbonate), aluminum, oxygen, or iron; however, these materials and methods can be expensive to produce and apply. The calcium content of apatite phosphate rock is important in determining its effectiveness in P removal: increased calcium concentration will elevate the water's pH value which results in increased P precipitation. Experiments have been performed using apatite phosphate rock, with varying calcium concentrations, to remove P from wastewater with acceptable results. The results verified that apatite phosphate rock with higher calcium carbonate concentrations increases the amount of P removed (Bellier, et al. 2006).

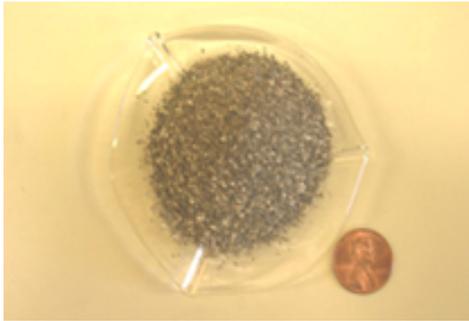


Fig. 4. Apatite phosphate grains (penny for size reference)

Apatite is the most abundant of the phosphate minerals on earth, found in almost all types of rocks. It comes in a variety of colors, from grey to green to pink, and can be transparent or opaque. It is also an inorganic, non-metal compound found in teeth and bones. The apatite phosphate rock used in this study was obtained as a recycled material from a phosphate mining operation in the southeast United States. The apatite phosphate rock is a 5 on the Mohs hardness scale, which is relatively soft, a quality which made it easy for me to pulverize into sand-size particles using an electric grinder. (Fig. 4)

Lab Experiments and Results

During the chemical reaction, phosphorus molecules are attracted to various points in the crystalline structure of the apatite (Hughes and Rakovan, 2002). In this way, the P molecules cling to the multi-faceted surface of the rock and become immobilized. I designed the initial lab experiment to determine if, in fact, the P molecules would cling (adhere) to the apatite phosphate rock.

Enough phosphorous in liquid form was added to deionized water to make a solution containing 3.0 mg/L of phosphorous. (A minute amount of sodium was also added to the water to mimic an estuarine environment.) Sand-size ground apatite rock particles were added to half of this solution, and both solutions were mixed continually for twenty-four hours. The solutions were then filtered and samples (ranging in pH value from 5.0 to 9.0) analyzed on a spectrophotometer using the Malachite Green Method (Ohno and Zibilske, 1991). The Malachite Green Method produces shades of green relative to the concentration of P present in the sample. In this method, the greater the P concentration, the darker is the shade of green. I compared the results of the samples treated with apatite to those of the control (untreated) samples which did not contain apatite. Success!

There was a significant difference in the concentrations of P remaining in the water samples treated with apatite phosphate rock and the controls. (Fig. 5) Both the control group and treated samples had been initially mixed with 3.0 mg/L phosphorus. The final average P concentration of the samples treated with apatite was reduced to 0.1 mg/L, while the P concentration of the control samples remained virtually unchanged at 2.9 mg/L. The apatite phosphate rock, therefore, did remove P from the water. From this initial success, I was able to proceed with further experiments.

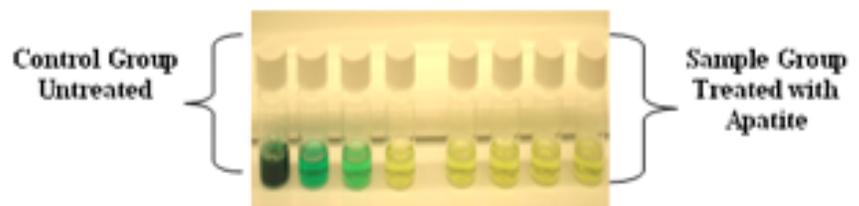


Fig. 5. Controls and samples using Malachite Green Method

The next experiment focused on the reaction rate, or sorption kinetics, of the apatite phosphate rock, that is, how fast the P was removed during the chemical reaction. Replicating the steps performed in the initial experiment, I sampled at specific time intervals during a 24-hour period. These treated and untreated samples, at pH 6 and 8, were again analyzed using the Malachite Green Method. Results of this analysis indicated that the bulk of the rapid reaction took place within the first four hours of the 24-hour period. (Fig. 6) This means that samples treated with apatite went from a concentration of 3.0 mg/L phosphorus to an average of 0.128 mg/L phosphorus in under four hours. That's pretty quick!

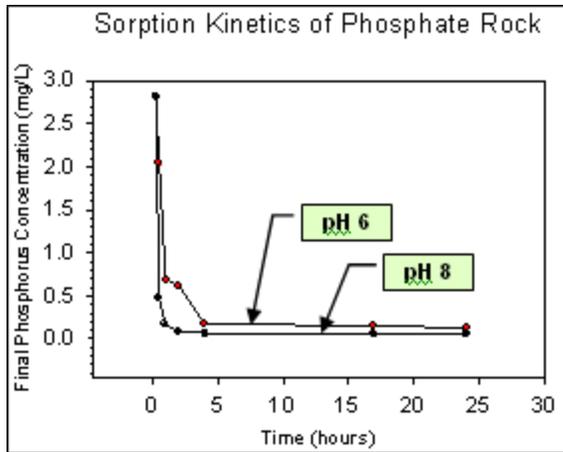


Fig. 6. Final phosphorus concentration vs. time

Other researchers have found that if apatite phosphate rock was subjected to extreme heat, its crystalline structure would change (Tonsuaadu, et al. 2003). This structural change increased the surface area of the rock for heavy metals to cling to. Therefore, I wanted to know how apatite phosphate rock would react with phosphorus if the rock was activated, that is, subjected to extreme heat.

I activated a small quantity of apatite phosphate rock in a high-temperature oven to 800°C (or 1498°F—that's hot!). I tested a batch of the activated rock in water samples containing phosphorus and compared the results against samples treated with non-activated apatite rock. The comparison indicated that the mean final P concentration in the solutions with activated apatite was 0.12 mg/L, while the mean final P concentration for the non-activated apatite was only 0.01 mg/L. Therefore, the activated apatite phosphate rock was not as effective at removing phosphorus as was the non-activated. Heating the apatite phosphate rock to such extreme temperatures likely altered the chemical structure and surface acceptor sites in such a way that phosphorus in solution could not cling to the activated apatite phosphate rock as well as it could to the non-activated apatite rock.

Toothaker Pond Field Experiment and Research

Before the end of the spring 2007 semester, I took the next step in my research experiments by using fresh water samples. Near the end of April, I drove through the cold, rainy, and sometimes snowy mountain roads to Phillips, Maine, to meet the residents of Toothaker Pond and obtain water samples. Phillips is located approximately one hour north of Mexico, Maine, and approximately two hours northeast of Berlin, New Hampshire. After a six-hour drive, I arrived at a pond that was half covered in ice and appeared to have a slight green hue although I could not actually see any algae. Two loons serenely floated past as I observed the initial site conditions. Meeting with some of the seasonal residents, I asked them about their experiences on the pond. They indicated that the eutrophication has become worse with each passing year. In recent summers the pond was as lime-green as a golf course.

When looking into the treatment history of Toothaker Pond, I had discovered that in May 2001 seventy-five barley straw bales were put into the pond for five months in an attempt to prevent new algae growth. The water quality during that summer improved only slightly, and the pond continued to have algae blooms. Treatments such as applications of aluminum, calcium-nitrate, iron and algaecides; aeration; sediment dredging; and drawdown (draining the pond) have been considered but have not yet been used due to expense, toxicity, and/or environmental concerns (MDEP, 2004). Historically, in the upper layer of water, total phosphorus concentration averaged a high 25 ppb and dissolved oxygen has been depleted in the deeper

(4 m mark) areas of the lake. The data for Toothaker Pond show a trend of declining conditions that currently violate Maine's water quality criteria, which allows a total phosphorus loading limit of 5 kg/yr, or 13 ppb (MDEP, 2004).

Finally, it was time to get down to business. One of the residents and I piled into a small, wobbly canoe and paddled around the ice sheets. Leaning carefully out of the canoe, I scooped up sediment samples and grabbed water samples from five different locations. Still in the canoe, I tested the temperature, acidity, electrical conductivity, and amount of dissolved oxygen in the water, using portable equipment borrowed from ERG.

When I returned to the lab the next day, I filtered the water samples and treated some samples with varying concentrations of apatite phosphate rock. Some water samples also received a small amount of pond sediment in an attempt to increase the phosphorus concentration. The samples were mixed for twenty-four hours, filtered, and analyzed using the Malachite Green Method (Ohno and Zibilske, 1991). Upon analyzing the samples, however, I found that the P concentrations of the samples were below my method detection limit, that is, they were too small to be detected by my analysis method. The results of the experiment, therefore, were inconclusive. The time of year may also have contributed to the low concentrations since phosphorus levels are typically lower in colder months. At this point, time and funds were running out; the spring semester was closing, and I had to gear up for finals and graduation.

What's Happened Since Then?

Post-graduation, I was asked by Dr. Jeffrey Melton, associate professor of civil engineering, to continue my apatite phosphate rock research. I designed a column study, a method I had not used previously. In the column study, natural freshwater samples obtained from North River Pond in Northwood, NH, were pumped through six glass columns. Three glass columns were filled with non-reactive sand and the remaining three glass columns were filled with sand-size apatite phosphate rock particles. To my frustration, the results from this experiment were also inconclusive, possibly due again to equipment and method detection limitations along with time of year samples were collected.

My experiments in the lab, where I could control variables such as salinity, acidity, phosphorus concentration, and apatite phosphate rock concentration had demonstrated that apatite phosphate rock could remove phosphorus from solution. Other research has shown that apatite phosphate rock can remove phosphorus from wastewater (Bellier, *et al.* 2006). Therefore, I feel that my research with apatite, even with inconclusive results, has promise for finding an alternative treatment method for removing excess phosphorus from eutrophic freshwater systems such as Toothaker Pond.

I would like to sincerely thank my faculty mentor, Bradley Crannell, and my faculty advisor, Kevin Gardner. I would also like to give thanks to the UNH Contaminated Sediments Center; the Hamel Center for Undergraduate Research staff and donors who funded my research; to Jeffrey Melton, William McDowell, Jeff Merriam, Amy Lindsay, Anna Bourakovsky, Taylor Eighmy, Serita Frey, and the residents of Toothaker Pond. Without your guidance, expertise, contributions, insight, and support, this study would not have been possible for me to conduct.

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Author Bio

Hethre Larivee of North Sutton, New Hampshire, graduated in 2007 with a B.S. in environmental science and has entered the University of New Hampshire’s graduate program in civil engineering. The research she describes in her article took place during spring semester, 2007, and became part of her senior thesis. Hethre became interested in the possible uses of apatite phosphate rock while a laboratory assistant for Bradley Crannell, one of her mentors. Despite inconclusive results, Hethre very much enjoyed her research and gained valuable real–world experience in important environmental issues, such as eutrophication, as well as practice in writing up her analyses. She also gained a firm understanding of the reality that research does not always pan out as planned. Hethre spends her free time as a glass artist and has work in the permanent collection of the Corning Museum of Glass in Corning, New York.

Mentor Bios

*Before the grant funding his research expired in October 2007 **Bradley Crannell** was a level II research scientist in the Environmental Research Group of the Department of Civil Engineering at the University of New Hampshire. Crannell had been with UNH for eleven years and specializes in environmental chemistry with a focus on remediating heavy metal pollution, often with phosphorus from apatite rock. In his first time as an official faculty mentor, he inspired Hethre to do further research on apatite rock for her senior thesis. He found working with Hethre on her research project to be very rewarding for both himself and Hethre.*

*Dr. **Kevin Gardner** is Director of the University of New Hampshire's Environmental Research Group as well as an associate professor in the Department of Civil Engineering. He has spent eight years at UNH specializing in environmental and sustainability engineering with particular interests in contaminated sediments, industrial ecology, and materials recycling. Gardner found Hethre's research project interesting and worthwhile even though some problems in the field interfered with obtaining conclusive field-scale results.*