Pewaukee Lake
Phosphorus Monitoring
2003-2004

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ABSTRACT

Phosphorus load and concentration:

Water and sediment samples were collected from Pewaukee Lake (Pewaukee, WI) and analyzed for total phosphorus (P) concentration. Water flow rates were measured to determine P loading from the inflowing streams. P loading calculations are available for the summer of 2004, while only P concentration data is available for the summer 2003.

Method analysis:

The sediment samples were digested with sulfuric acid and persulfate in an autoclave. The water samples were digested with persulfate in an autoclave. Phosphorus concentrations were determined using a uv-vis spectrometer and analyzing the 625 nm absorption peak based on the association of malachite green with phosphomolybdate under acidic conditions. Lower detection limit results from this complex having a molar absorptivity constant more than three times greater than the phosphoantimonylmolybdenum blue in the standard Murphy-Riley method. While the malachite green method does provide signal at lower concentrations, the Murphy-Riley method provided greater dynamic range and a more reliable standard curve.

INTRODUCTION

The most important nutrients in aquatic ecosystems are phophorus (P) and nitrogen (N). In Pewaukee Lake, plant and algae growth is limited by P as it is a body of fresh water.[1] In marine areas the opposite is true, and N is the most likely limiting nutrient.[2]

Elevated nutrient levels create a eutrophic environment with increased plant and algae growth. When the plants and algae die and decompose, dissolved oxygen levels in lakes and streams are depleted, which can lead to odors, death of fish, and a general degradation of the aesthetic and recreational value of the environment.[3] Pewaukee Lake has been classified as a eutrophic lake by Aqua Tech, Inc. in 1972 and by Southeastern Wisconsin Reagional Planning Commission (SEWRPC) in 1984.[4,5]

Phosphorus measurement background.

There are several spectrometric methods to determine phosphorus concentration in water and soil extracts. Methods based on the formation of phosphoantimonylmolybdenum blue with ascorbic acid as a reductant are commonly suggested for the determination of P in water and in soil-water extracts. These are based on the procedure of Murphy and Riley for orthophosphate analysis.[6] Alternatively, a method has been developed in which the molybdophosphate is reacted with the cationic dye, malachite green, to produce absorbance at 625 nm.[7]

In order to measure total P, the condensed and organic forms of phosphorus must be converted into orthophosphate for spectrometric analysis. Commonly, fusion or boiling acid digestion techniques are used to convert the phosphorus.[8] A more easily automated digestion by persulfate and autoclave was chosen for this step.[9]

Note: Acceptable units for reporting P concentration in sediment are in terms of parts per million (ppm), in water, it is common to use either ppb or µg/L. Some comparisons are made between the different unit systems, so it will be helpful to keep in mind: 1 ppm = 1 mg/L = 1 µg/mL = 1,000 ppb = 1,000 µg/L.

MATERIALS AND METHODS

Phosphorus concentration measurements were made at several central lake locations. Measurements of total P in water samples from several central lake locations and the outflow water in the Pewaukee River have been made. Measurement of P concentration and flow rates from the inlets Coco Creek, Meadowbrook, and Zion Creek provided the data in order to calculate total P loads. This is a portion of the P budget for the lake, and can indicate overall lake trends and clarify a picture of major P contributors. A comprehensive P budget would take into consideration estimates of inputs from direct drainage, precipitation, and dry fallout. The necessary outputs would include measurements of the outgoing river flow and estimates of the weed and fish harvests.

Flow Measurements

A rotating-cup Price AA current meter was used in a velocity-area method to measure inflow. The velocity-area method involves measuring the channel area and water velocities of a stream at a cross section that is perpendicular to the main flow of the channel. The channel is divided into a number of vertical "subsections." The area and mean velocity in each subsection is measured and the subsection discharge is computed. The total discharge within the stream is the sum of the individual subsection discharges.

Sample collection

Water samples from the lake were taken with an integrated sampler. This is a 2 meter PVC pipe (collection tube) with a PVC ball that acts as a water locking mechanism. The contents of the tube were transferred to 100 ml HDPE bottles. Water samples from the inlets were gathered by submerging the bottles just under the water surface.

The sediment samples were collected with an Eckman dredge. Most samples were taken in triplicate. All standard deviations in the tables or error bars represent the replicate measurements for water and sediment samples.

Persulfate Digestion and Malachite Green (Chemical Analysis Protocol)

Reagent 1: 28.4 mmol/L ammonium molybdate tetrahydrate in 3.15 Molar H_2SO_4

Reagent 2: 3.5 g/L polyvinyl alcohol (PVA) and 0.35g/L malachite green

Standard P solutions made by KH_2PO_4 and then successive dilutions

Persulfate solution for digestion: 5% $K_2S_2O_8$ (solubility is 5.2%)

Soil digestion: In 15 ml glass incubation tubes
- 50 mg of dried and ground sediment
- 2 ml persulfate solution
- 0.50 ml of concentrated sulfuric acid
- Autoclaved 1hr. at 121°C

Added 10 ml of DI and shake for 1 min.
Centrifuged and removed 10 ml of liquid for analysis

Water digestion: In 15 ml glass incubation tubes
10 ml of water sample (including all standards, and blank)
1.5 ml persulfate 5%
Autoclaved 30 min
Cooled to near room temp

Malachite green and spectrometric analysis:
Added 2 ml of reagent 1 to digested samples
Capped and mixed
Added 2 ml of reagent 2
Waited 30 min. before measuring absorbance at 625nm
with 1 cm pathlength

Ascorbic Acid (Murphy-Riley)
Modified Ascorbic Acid method from Dick and Tabatabai.[10]
Absorbance measured at 882 nm.