Investigation of Internal Phosphorus Loading in the Watervliet Reservoir, New York, August 2004

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Watervliet Reservoir, Spring 2003. Photo by Brian Tomasik.

Abstract

This study examined internal phosphorus release in a thermally stratified fresh water body in upstate New York. Temperature, dissolved oxygen, and total dissolved phosphorus were measured at regular intervals to the bottom of a shallow site and a deep site on the Watervliet Reservoir in mid-August 2004. Both temperature and dissolved-oxygen readings at the deeper sampling location closely matched the general pattern of a thermally stratified lake. Beneath the surface of the reservoir's epilimnion, which extended from 0.0 m to 5.0 m, dissolved oxygen was consistently between 4 and 6 mg O_2/L. However, beginning at the metalimnion—which lay between 5.0 m and 6.0 m—and continuing throughout the hypolimnion—which ranged from 6.0 m to the bottom—dissolved-oxygen concentrations fell close to zero. The water at the shallower sampling location, which was not significantly stratified, did not exhibit a similar plunge in dissolved oxygen. Even though metalimnetic and hypolimnetic dissolved-oxygen concentrations at the deeper sampling location were well below the 1-mg O_2/L threshold at which sediment-bound phosphorus typically begins to dissolve in earnest, no significant phosphorus mobilization was detected.

Introduction

Thermal stratification is a natural process generally found in temperate water bodies that are at least 5 m to 7 m in depth. It usually develops during the late spring and early summer, when direct exposure to sunlight and contact with warm air raise the temperature of water at the surface; meanwhile, bottom water receives little of this incoming heat. Because the density of liquid water decreases with increasing temperature, the warm water remains at the top and the cold water remains at the bottom. Thus, the reservoir stratifies into two distinct layers: the warmer epilimnion near the surface, which typically ranges between 20°C and 25°C, and the cooler hypolimnion near the bottom, which is usually between 4°C and 15°C. In between the two layers is the metalimnion, a zone of rapid transition in which water temperature changes by more than one degree Celsius per meter of depth; this section is generally in the temperature range of 15°C to 20°C. The thermocline is the specific depth within the metalimnion of maximum water-temperature change.

The mixing of water layers of different densities requires energy (usually wind energy), and a greater difference in density requires more energy. Since the epilimnion is directly exposed to the wind, it is thoroughly mixed and well oxygenated. However, when this mixing energy reaches the metalimnion, it is effectively stopped by that layer’s sharp density gradients. Because the hypolimnion is consequently unable to mix with the epilimnion, reoxygenation of the former is largely precluded.

The impact of this condition upon hypolimnetic dissolved-oxygen levels is relatively small in reservoirs that are oligotrophic, meaning that they have high water clarity and low algal and plant productivity by virtue of poor nutrient content. The virtual absence of dead organic matter in such waters translates into minimal oxygen consumption by decomposers of plant and animal detritus. However, in eutrophic reservoirs—those with low water clarity and high algal and plant productivity owing to rich nutrient content—the abundance of organic waste rapidly depletes dissolved oxygen. Because it is unable to replenish its oxygen supply by contact with air and because it is often too deep for sunlight to permit oxygen generation by photosynthesis, the hypolimnion of a eutrophic reservoir soon becomes anoxic, meaning that dissolved oxygen approaches 0.0 mg O_2/L.

Hypolimnetic anoxia generally triggers the release of nutrients—especially phosphorus—into the water column. Under oxic conditions, most of the PO_4^{3-} in a water body is bound to sediment by metal cations, particularly Fe^{3+}. But when concentrations of dissolved oxygen in the hypolimnion drop below 1 mg O_2/L, some of this Fe^{3+} is reduced to Fe^{2+}, and PO_4^{3-} is thereby released into the surrounding water.

Phosphorus is a macronutrient that plants must have in order to carry out a multiplicity of cellular processes: genetic coding, cell division and growth, photosynthesis, respiration, and energy storage. Because of its relative scarcity, phosphorus is the limiting nutrient in most fresh water bodies. In other words, phosphorus availability is typically the sole factor restricting, or permitting, further plant growth. Thence, when humans unnaturally augment levels of phosphorus in a reservoir—such as by pulp and paper production, urban storm runoff, road deicers, poorly sited and maintained septic systems, wastewater-treatment effluent, agricultural and lawn fertilization, logging, and virtually any other form of land development—the result is cultural eutrophication, the anthropogenic acceleration of the natural process of eutrophication by which the productivity of water bodies increases over time. This occurs not only because phosphorus is generally the growth-limiting factor in reservoirs; it also occurs because plants are able to utilize more efficiently other types of nutrients when phosphorus is present. In view of the close relationship between phosphorus and plant growth, Vollenweider (1975) proposed that the general dividing line between mesotrophy and eutrophy is a mean total-phosphorus concentration of 20 μg P/L for the epilimnion during the summer. The New York State Department of Environmental Conservation uses this same number as its guidance value for lakes and reservoirs in New York (Effler and Bader 1998, p. 129).

Because phosphorus is usually the limiting nutrient in a fresh water body, the mobilization of iron-bound phosphorus by low levels of dissolved oxygen accelerates the growth of algae and plants. Such growth creates more dead organic matter that must be decomposed, and thus further depletes the remaining supply of dissolved oxygen. This, in turn, triggers the release of even more phosphorus from the sediment. In this way, hypolimnetic oxygen depletion is often a self-exacerbating phenomenon.

But excessive plant growth, spurred by elevated levels of phosphorus, results in other harmful impacts, as well. The increased accumulation of dead organic matter accelerates the decline of a reservoir's water-retention capacity—the amount of water a reservoir can hold. Heightened plant productivity may give drinking water undesirable tastes and smells that remain even after treatment. It also creates higher levels of disinfection byproducts—chemicals that are formed by the reaction of organic matter in source water with disinfectants added thereto. Two of the most important groups of disinfection byproducts, trihalomethanes and haloacetic acids, are created by the process of chlorination with either chlorine gas or hypochlorous acid. Prolonged exposure to concentrations of trihalomethanes and haloacetic acids exceeding EPA's maximum-contaminant levels for those chemicals in drinking water may increase the risk of cancer, as well as the possibility of damage to the liver, kidneys, and central nervous system.

These potential effects of disinfection byproducts have aroused concern among some residents of the town of Guilderland, Albany County, New York, inasmuch as Guilderland drinking water, disinfected with chlorine gas, regularly contains annual-average concentrations of trihalomethanes and haloacetic acids that are close to, and sometimes above, EPA limits (Guilderland Study Circles 2003, p. 18-19). Most of this drinking water comes from the Watervliet Reservoir, which lies within the western section of Guilderland. The 2.55-squarekilometer water body has a capacity of 5.3 billion liters and a safe yield of 45 million liters per day. A previous study by this researcher found that the Watervliet Reservoir's epilimnetic total-phosphorus concentrations in August 2003 averaged 19 μg P/L, putting the reservoir at the upper end of mesotrophy according to the Vollenweider (1975) classification.

Hypotheses and Experimental Design

The first hypothesis was that the Watervliet Reservoir, with a maximum depth of approximately 9 m, would be thermally stratified during the late summer at depths of at least 5 m to 7 m, the range at which thermal stratification generally begins to occur in temperate water bodies. This was tested by observing trends of water temperature with depth to see how well they matched the typical patterns of a thermally stratified temperate water body.

The second hypothesis was that the anticipated thermal stratification would have caused hypolimnetic anoxia. This was evaluated by correlating trends in dissolved oxygen with apparent thermal layers.

The final hypothesis was that sediment-bound phosphorus would have been discharged into hypolimnetic waters by consequence of the expected anoxia. This was tested by measuring concentrations of total dissolved phosphorus throughout the water column. The reason for measuring total phosphorus was that all three of the differentiable phosphorus forms—inorganic orthophosphate, inorganic polyphosphates, and organic phosphorus—have the potential to dissolve. The water samples were filtered because only concentrations of dissolved phosphorus can reveal whether or not more phosphorus is dissolving into the water; levels of suspended phosphorus will not increase in the absence of oxygen and are hence unnecessary and potentially misleading for this purpose.

Materials and Procedure

On 17 August 2004, measurement and sample collection were performed from a rowboat at two sites on the Watervliet Reservoir, both of which were at its southeast end (Figure 1). The purpose of Location 1 was to discover whether or not thermal stratification occurred in the Watervliet Reservoir and, if so, how it affected concentrations of dissolved oxygen and dissolved phosphorus; wherefore, Location 1 was chosen to be the deepest spot that could be found. In order to make sure that any trends observed with increasing depth at Location 1 were in fact results of thermal stratification and were not merely inherent properties of water closer to bottom sediment, Location 2 was selected as a control site that appeared too shallow to stratify. The proximity of the two sites was intended to maximize the likelihood that the ambient conditions of each would be relatively similar.

Figure 1: Measurement and sample-collection sites on the Watervliet Reservoir.

First, the depth to the bottom of each site and water clarity at each site (Table 1) were measured with a 20-cm-diameter, black-and-white-quadrant Secchi disc (Lawrence Enterprises, http://www.watermonitoringequip.com/pages/home.html). Next, readings of temperature and dissolved oxygen were taken by lowering a Dissolved Oxygen Meter (YSI Model 58, http://www.ysi.com/index.html) at one-meter intervals to the bottom of both sites four separate times; during each lowering of the probe, readings were also taken at the depth of 5.5 m at Location 1, after a rapid drop in both temperature and dissolved oxygen was observed between 5 m and 6 m. Then, a Van-Dorn Water Sampler (Wildco, http://www.wildco.com/) was employed at both locations for scooping up some surface sediment, so that its general characteristics could be informally noted. The Van-Dorn bottle was also used to take water samples at one-meter intervals at both sites; three separate samples were collected from each depth, for a total of 33 samples. The glass sampling bottles had previously been rinsed, once with 10% HCl and thrice with deionized water. In the boat, the bottles were rinsed three times with sample water before the actual sample was poured in. The bottles were then refrigerated until testing the next day.

Table 1: Physical Characteristics of the Two Sampling Locations

	Location 1	Location 2
Depth (m)	8.82	3.82
Mean Secchi-Disc Transparency (m)	1.53	1.49
Observations on Water Clarity	Sampling was performed one day after a large rainstorm, and the water itself appeared slightly more brown than usual. Therefore, recorded Secchi-disc-transparency depths probably underrepresent the typical water clarity of the reservoir.	
Mean Air Temperature at the Time of Measurement (°C)	21.6	20.6
Weather Characteristics at the Time of Measurement	Sunny. Little wind.	Sunny. Little wind.
Surface-Sediment Characteristics	Very dark brown. Clay and organic matter. Less sand. Slimy.	Dark brown. Clay and organic matter. More sand. Rough.

The water samples were analyzed for total dissolved phosphorus at the Keck Water Quality Research Laboratory at Rensselaer Polytechnic Institute. First, they were filtered through a 0.4-µm Polycarbonate filter (Osmonics, Inc., http://www.gewater.com/index.jsp) using a Vacuum Pump (Welch, http://www.welchvacuum.com/) set to 15 in. Hg. These filtered samples were refrigerated overnight. The samples were then analyzed according to USEPA Method 365.2. Two 8.65-µg P/L quality-control standards were made from Spex Nut-2 (Table 5), and duplicates were made from three separate samples (Table 6).

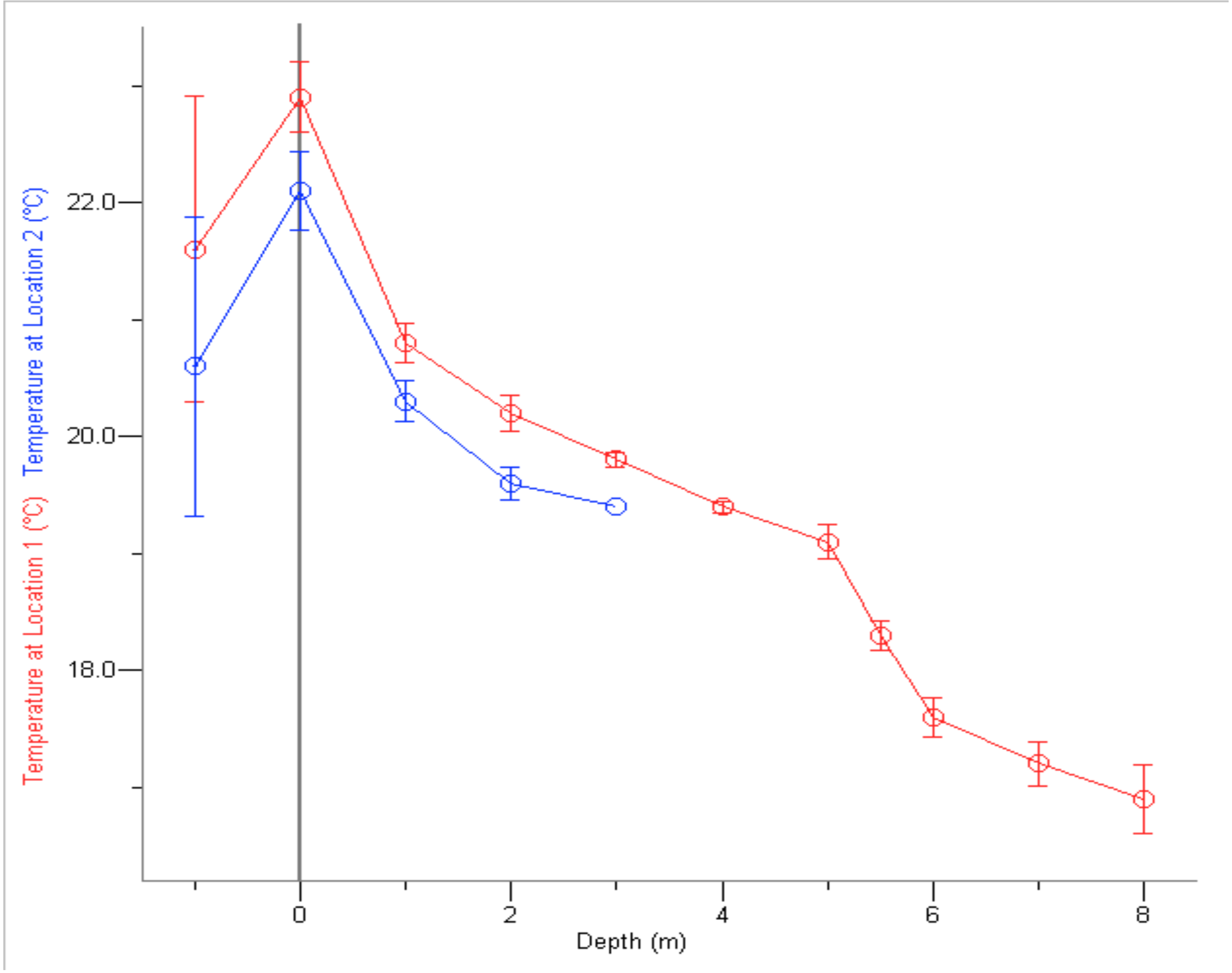
Results and Discussion

Results were analyzed with a program called JMP IN. It was used to determine whether or not the apparent differences of the measurements at various depths could actually be considered statistically significant according to a 0.05-probability F-test ANOVA.

A. Temperature

Both locations exhibited a general decrease in temperature with depth (Figure 2).

Figure 2: Temperature with Depth. (Vertical bars represent ± 1 standard deviation from the mean.)



Coefficient of variation is a measure of the variability of a set of data, and a coefficient of variation below 5 percent indicates good precision. Temperature measurements at all depths except for the air were very precise, as coefficients of variation were consistently below 2 percent (Table 2).

Table 2: Temperature with Depth

Location Number	Depth in the Water (m)	Trial 1 (°C)	Trial 2 (°C)	Trial 3 (°C)	Trial 4 (°C)	Mean (°C)	Standard Deviation (°C)	Coefficient of Variation (%)
1	(Air)	*Omitted*	22.0	22.6	20.1	21.6	1.31	6.05
	0.0	23.3	22.6	22.8	22.8	22.9	0.299	1.31
	1.0	20.8	20.9	21.0	20.6	20.8	0.171	0.820
	2.0	20.3	20.1	20.4	20.1	20.2	0.150	0.742
	3.0	19.8	19.7	19.8	19.7	19.8	0.0577	0.292
	4.0	19.4	19.4	19.3	19.4	19.4	0.0500	0.258
	5.0	19.2	19.2	19.2	18.9	19.1	0.150	0.784
	5.5	18.3	18.2	18.4	18.1	18.3	0.129	0.707
	6.0	17.7	17.6	17.8	17.4	17.6	0.171	0.969
	7.0	17.1	17.0	17.4	17.3	17.2	0.183	1.06
	8.0	16.8	16.5	17.0	17.2	16.9	0.299	1.77
2	(Air)	22.5	19.9	20.0	19.9	20.6	1.28	6.24
	0.0	22.5	22.1	22.0	21.7	22.1	0.330	1.50
	1.0	20.5	20.4	20.3	20.1	20.3	0.171	0.840
	2.0	19.8	19.6	19.5	19.5	19.6	0.141	0.722
	3.0	19.4	19.4	19.4	19.4	19.4	0	0

Table 3 utilizes changes in temperature per meter of depth to classify each interval between measurement depths into an apparent thermal layer. Location 1 seems to be fully stratified, with an epilimnion from 0.0 m to 5.0 m, a metalimnion between 5.0 m and 6.0 m, and a hypolimnion from 6.0 m to the bottom; the thermocline lies between 5.0 m and 5.5 m. Location 2 shows no signs of significant stratification.

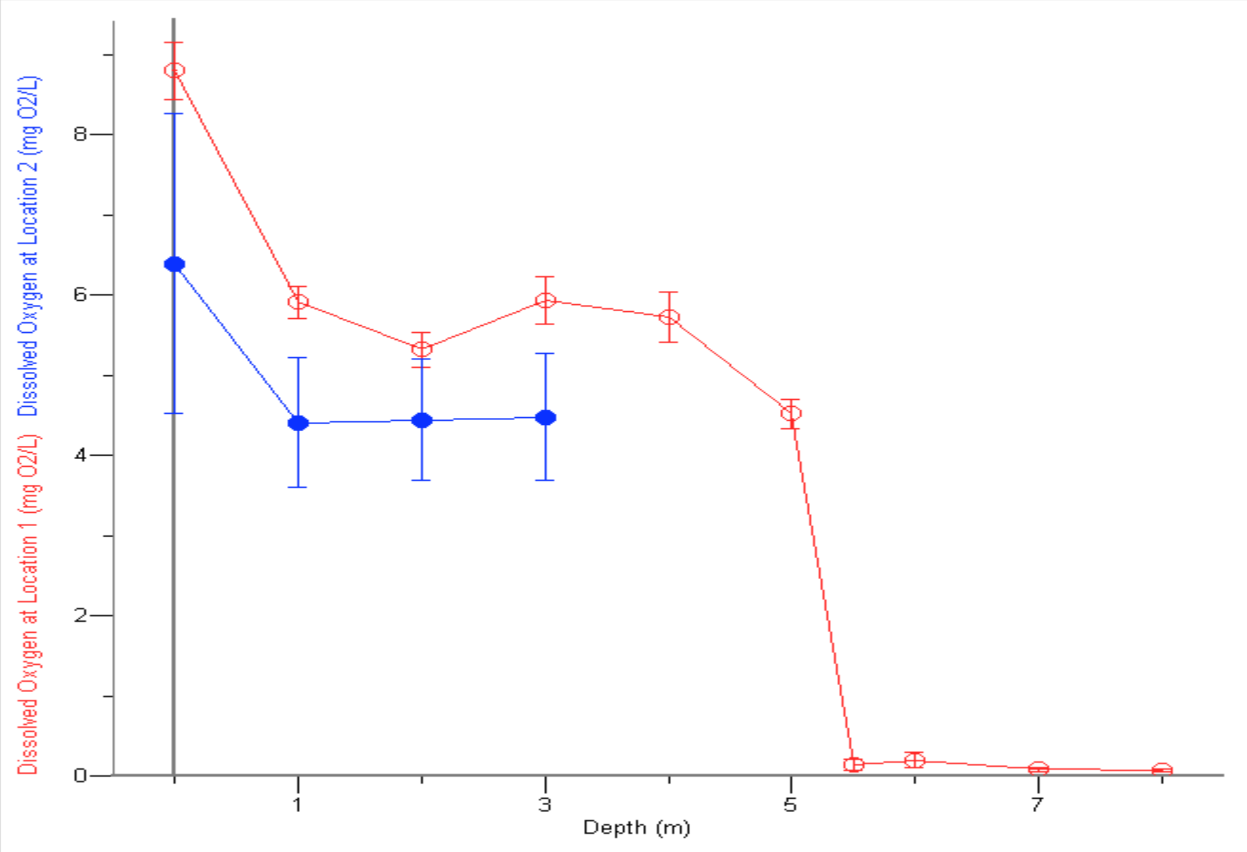
Table 3: Intervallic Changes in Temperature

Location Number	Interval	Change in Mean Temperature per Change in Depth (°C/m)	Corresponding Water Layer
1	0.0 m to 1.0 m	-2.1	Epilimnion
	1.0 m to 2.0 m	-0.6	Epilimnion
	2.0 m to 3.0 m	-0.4	Epilimnion
	3.0 m to 4.0 m	-0.4	Epilimnion
	4.0 m to 5.0 m	-0.3	Epilimnion
	5.0 m to 5.5 m	-1.6	Metalimnion (Thermocline)
	5.5 m to 6.0 m	-1.4	Metalimnion
	6.0 m to 7.0 m	-0.4	Hypolimnion
	7.0 m to 8.0 m	-0.3	Hypolimnion
2	0.0 m to 1.0 m	-1.8	Not stratified
	1.0 m to 2.0 m	-0.7	Not stratified
	2.0 m to 3.0 m	-0.2	Not stratified

B. Dissolved Oxygen

Location 1's dissolved-oxygen levels correlate very closely to its apparent thermal layers. Dissolved oxygen was relatively stable throughout the epilimnion—discounting the surface water, which was in nearly direct contact with the air—and concentrations consistently remained between 4 and 6 mg O_2/L (Figure 3). However, beginning at the metalimnion and continuing through the hypolimnion, concentrations of dissolved oxygen fell close to zero (even far below the 1-mg O_2/L threshold at which sediment-bound phosphorus typically begins to dissolve in earnest). The relationship between thermal stratification and dissolved-oxygen depletion is reinforced by the fact that Location 2, which did not seem to stratify, did not experience a statistically significant drop in dissolved-oxygen concentrations with depth, nor was the water above the sediment anoxic as it was at Location 1.

Figure 3: Dissolved Oxygen with Depth. (Vertical bars represent ± 1 standard deviation from the mean.)



Precision throughout the epilimnion of Location 1 was fairly good, with coefficients of variation consistently below 6 percent (Table 4). However, it worsened enormously at and beyond the metalimnion, where dissolved-oxygen concentrations were too low for precise readings by the electronic meter. Curiously, precision remained very poor at Location 2 even though the measured dissolved-oxygen concentrations were close to those observed in the epilimnion of Location 1. It should be noted that dissolved-oxygen concentrations of the water below the surface at Location 2 seemed generally to decrease more from one trial to the next than from one depth to the next. These measurements were taken just as the sun was setting, and it appears plausible that the rapid decline in sunlight could have substantially slowed photosynthesis and the attendant production of oxygen. Substantial machine drift is another possible explanation.

Table 4: Dissolved Oxygen with Depth

Location Number	Depth in the Water (m)	Trial 1 (mg O_2/L)	Trial 2 (mg O_2/L)	Trial 3 (mg O_2/L)	Trial 4 (mg O_2/L)	Mean (mg O_2/L)	Standard Deviation (mg O_2/L)	Coefficient of Variation (%)
1	0.0	8.4	8.82	8.72	9.27	8.80	0.359	4.08
	1.0	5.8	6.20	5.75	5.90	5.91	0.202	3.41
	2.0	5.6	5.25	5.07	5.35	5.32	0.221	4.16
	3.0	6.2	6.13	5.85	5.55	5.93	0.296	5.00
	4.0	6.1	5.78	5.64	5.35	5.72	0.312	5.45
	5.0	4.6	4.71	4.29	4.46	4.52	0.182	4.02
	5.5	0.1	0.22	*Omitted*	0.11	0.14	0.067	47
	6.0	0.2	0.10	0.29	0.08	0.2	0.1	60
	7.0	0.09	0.09	0.09	0.06	0.08	0.02	20
	8.0	0.08	0.08	0.07	0.06	0.07	0.01	10
2	0.0	8.75	6.98	5.28	4.55	6.39	1.87	29.3
	1.0	5.47	4.40	4.26	3.49	4.41	0.815	18.5
	2.0	5.30	4.60	4.40	3.46	4.44	0.759	17.1
	3.0	5.39	4.65	4.42	3.47	4.48	0.792	17.7

C. Phosphorus

Throughout the entire measurement process for the phosphorus samples, the absorbance of deionized water changed only from 0.000 to –0.001, indicating that spectrophotometer drift was negligible. The standard-curve equation—Concentration (μg P/L) = 166.426(Absorbance – Blank) – 2.0656—had a coefficient of determination (r^2 value) of 0.998197. Both my laboratory accuracy, as measured by two equally concentrated quality-control standards made from Spex Nut-2 (Table 5), and my laboratory precision, as measured by my duplicates (Table 6), were quite good, with percents error and coefficients of variation all below 4 percent.

Table 5: Percent Error with Quality-Control Standards Made from Spex Nut-2

	Measured Concentration (µg P/L)	Actual Concentration (µg P/L)	Percent Error (%)
Quality-Control Standard 1	8.4	8.65	-2.7
Quality-Control Standard 2	8.4	8.65	-2.7

Table 6: Precision of Laboratory Duplicates

Location, Depth, and Trial Number of Sample	Absorbance of Trial 1 at 885 nm	Absorbance of Trial 2 at 885 nm	Standard Deviation	Coefficient of Variation (%)
Location 1, Depth of 1 m, Trial 3	0.107	0.113	0.00424	3.86
Location 1, Depth of 5 m, Trial 3	0.161	0.169	0.00566	3.43
Location 2, Depth of 1 m, Trial 3	0.077	0.078	0.00071	0.91

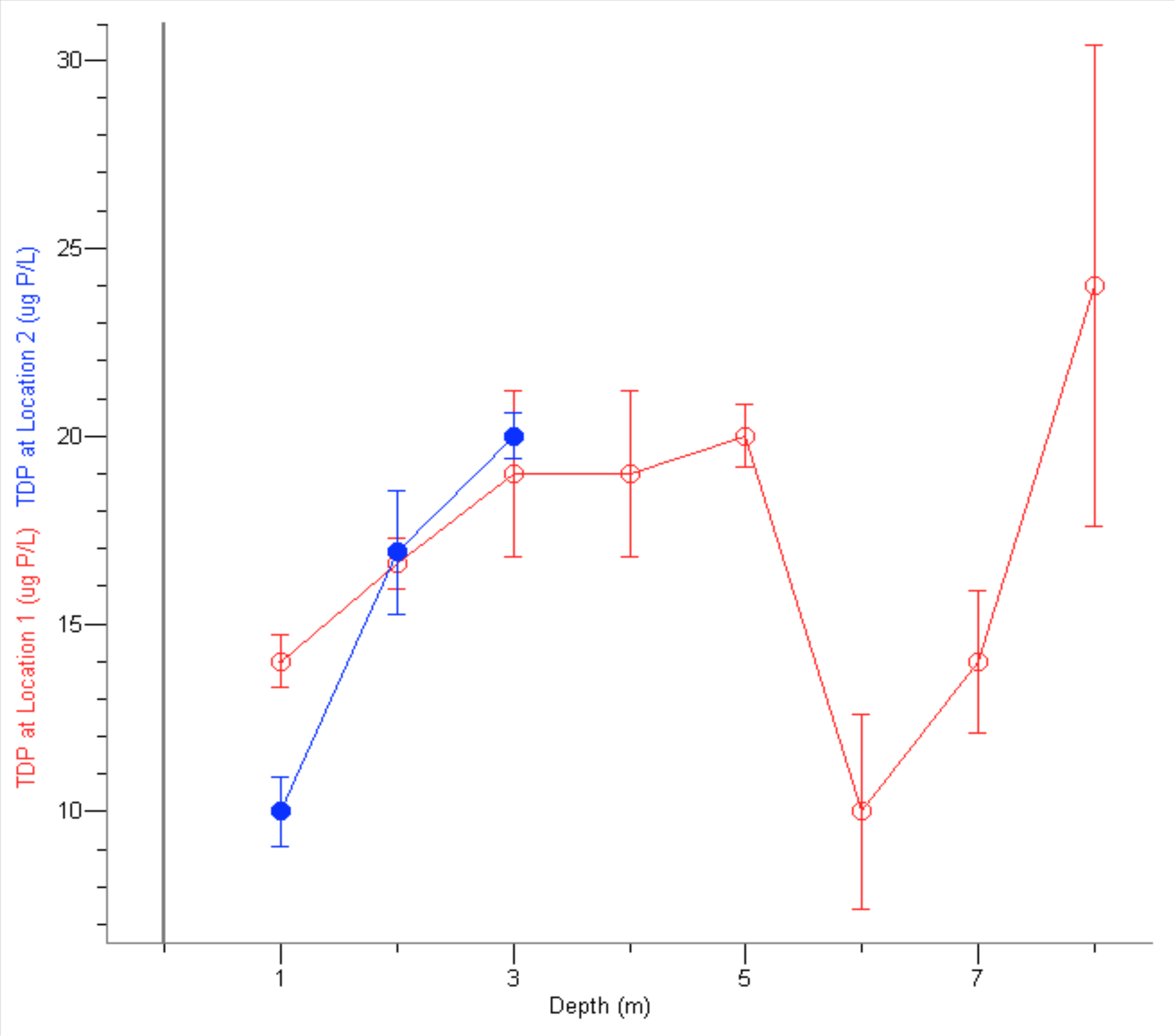
The precision of the three samples taken separately from each depth (Table 7) was generally much worse than the precision of duplicates made from a single sample (Table 6), in part because the former included field imprecision and laboratory imprecision while the latter measured only laboratory imprecision.

Table 7: Total Dissolved Phosphorus with Depth

Location Number	Depth in the Water (m)	Sample 1 (µg P/L)	Sample 2 (µg P/L)	Sample 3 (µg P/L)	Mean (µg P/L)	Standard Deviation (µg P/L)	Coefficient of Variation (%)
1	1.0	13	13.9	14.2	14	0.69	5.1
	2.0	16.6	17.2	15.9	16.6	0.666	4.02
	3.0	21	16.9	17.7	19	2.2	12
	4.0	18	22	18	19	2.2	11
	5.0	20.	21	20.	20.	0.84	4.1
	6.0	13.1	9.1	8.1	10.	2.6	26
	7.0	16.2	13.7	13	14	1.9	13
	8.0	25	30.3	18	24	6.4	26
2	1.0	10.	11	9.3	10.	0.93	9.0
	2.0	15.7	16.1	18.7	16.9	1.64	9.74
	3.0	21	20.	19.6	20.	0.61	3.0

Location 1 showed a statistically significant increase in total dissolved phosphorus from the top (1 m) to the bottom (5 m) of its epilimnion; similarly, total dissolved phosphorus at Location 2 was statistically higher at 2 m and 3 m than at 1 m. Secchi-disc transparency (Table 1) revealed that sunlight penetrates at least 1.49 m into the water, so the reservoir's photic zone is probably just a few meters deep. Thence, it is possible that some dissolved phosphorus in the upper epilimnion was consumed by photosynthetic organisms that were incapable of surviving in the lower epilimnion.

Figure 4: Total Dissolved Phosphorus with Depth. (Vertical bars represent ± 1 standard deviation from the mean.)



Even though dissolved-oxygen concentrations in the hypolimnion were well below 1 mg O_2/L, significant internal phosphorus mobilization does not appear to have occurred. Although there was a statistically significant increase in total dissolved phosphorus from 1 m and 2 m to 8 m, this increase did not even approach the jump of at least five times, and often more than ten times, that is typically observed when phosphorus is released from the sediment (Kishbaugh 2004). Moreover, the other three depths in the epilimnion—3 m, 4 m, and 5 m—could not be considered statistically different from the 8-m depth in total dissolved phosphorus (though the conclusiveness of this fact is diminished by fairly poor precision at most depths).

The lack of significant phosphorus release during anoxia, while perhaps atypical, is not unprecedented. Effler and Bader (1998) reported similar findings for New York's eutrophic Cannonsville Reservoir: despite the existence of deep-water anoxia through most of August and early September 1995 (p. 131), total-dissolved-phosphorus concentrations measured on 29 August 1995 were virtually uniform throughout the water column (p. 136), and no major discharge of phosphorus from the sediments was observed during that period (p. 134). To explain this, the authors cited the findings of Froelich et al. (1979) and Kelly et al. (1988): during anoxia, thermodynamic properties cause such electron acceptors as Mn^{4+} and NO_3^- to be reduced before Fe^{3+}. Since it is the reduction of Fe^{3+} that mobilizes iron-bound phosphate, internal phosphorus loading should not be expected so long as the more thermodynamically favored electron acceptors remain. This was indeed the case for the Cannonsville Reservoir, whose hypolimnetic NO_x supply was never fully depleted throughout the entire period of anoxia in 1995 (Effler and Bader 1998, p. 134). Whether or not this explanation applies to the Watervliet Reservoir, however, cannot be determined, inasmuch as its hypolimnetic Mn^{4+} and NO_x were not measured.

While no significant phosphorus release was detected in mid-August 2004, it is still possible that internal phosphorus loading occurred later in the summer, after sampling was completed, or will occur at some point in the future. For example, if the Cannonsville-Reservoir conditions do in fact apply to the Watervliet Reservoir, phosphorus release could be triggered if electron acceptors like NO_3^- decline in future years (Erickson and Auer 1998, p. 275).

In spite of these limited conclusions, it is hoped that this study will provide at least tentative limnological information for citizens and local governments seeking to manage excessive plant growth on and improve the water quality of the Watervliet Reservoir.

Conclusions

Measurements taken on the Watervliet Reservoir in August 2004 indicated the existence of thermal stratification at depths of at least 5.0 m and the virtual absence of dissolved oxygen in the hypolimnion, yet it did not appear that this anoxia triggered any significant liberation of sediment-bound phosphorus. Unless a more extensive, long-term study is conducted, however, the possibility that internal phosphorus loading might occur at some point in the future should not be ruled out.

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