

A COMPARATIVE STUDY OF WATER QUALITY IN SELECTED LAKES OF THE
WOODEN'S RIVER WATERSHED¹

by

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ABSTRACT

In 2000, we initiated a study of water chemistry (temperature, dissolved oxygen, pH, phosphate, chlorophyll a and color) in selected lakes in the Wooden's River Watershed. Samples were collected in the spring, the summer and the fall from at least two sampling stations in each of the lakes studied. Although the data is not complete for each of the lakes, we have now examined eight lakes (Cranberry, Black Point, Frederick, Five Island, Hubley Big, Long, Sheldrake and Birch Hill). Although there are many similarities, there are significant differences not only between the lakes, but between some of the sampling stations on the same lake. In the fall, when they are mixed, all the lakes are quite acidic (4.4-4.9), but the values vary with the time of year and the sample depth, and in some cases with the location of the sampling station. The lakes are also highly colored (39-120 in late fall). The Secchi depths, which provide a rough estimate of the photic zone where photosynthesis takes place, ranges from 1.2 m. in Sheldrake

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1. A report submitted to the board of the Woodens River Watershed Environmental Organization (WRWEO), May 2008. Posted at wrweo.ca on July 22, 2010 with permission of R.W. Chambers.

Lake to 4.6 m. in Cranberry Lake. Five of the lakes studied stratify at stations that are over 5 m. deep. Anoxia develops at all but one of these stratified stations. The phosphate concentrations of most of the lakes fall between 0.32 and 0.45 μM (10-14 $\mu\text{g P/l}$). In the late fall, Sheldrake Lake shows a significantly higher phosphate (0.61 μM , 19 $\mu\text{g P/l}$) than any of the other lakes. Cranberry Lake shows a significantly lower phosphate (0.20 μM , 6.1 $\mu\text{g P/l}$). When anoxia develops (in the summer), the phosphate levels and color increase and vary with depth. In Sheldrake Lake the phosphate concentration reached 6.26 μM at 7 m., which is 10-fold higher than the value obtained at 1 m. (0.77 μM). When Sheldrake is stratified and anoxic, the relationship between phosphate and color satisfies the equation:

$$\log [\text{phosphate}, \mu\text{M}] = 0.0053 \times \text{color (in Pt units)} - 0.4543$$

There is also a correlation between pH and [phosphate]:

$$\text{pH} = 0.10 [\text{phosphate}] + 5.083.$$

More data is required to see if similar relationships hold and different times of year and on different lakes. Statistical analysis of both summer and fall samples, indicates the phosphate concentration in Sheldrake Lake did not change significantly between 1991 and 2002. The phosphate concentrations of Hubley Big Lake and at sampling stations 2 and 3 on Five Island Lake did not change significantly between 2000 and 2002. In 2002, Station 1 on Five Island Lake showed a small, but significant, increase compared to the value obtained in 2000. This station bears watching.

INTRODUCTION

The Wooden's River watershed arises from Pot Lake, Lizard Lizard, Upper Sheldrake Lake, and Birch Hill Lake. The chain of lakes from Pot Lake is Cranberry, Black Point, Frederick, Five Island Hubley Big, the Mink Holes, Long, Croucher, Gates, Millyard, Albert Bridge, Old Mill Pond, Dolly's Pond and thence into St. Margaret's

Bay. Upper Sheldrake feeds Sheldrake, which empties into the northeast corner of Five Island. Lizard empties into Black Point ¹. Birch Hill empties into the northern tip of Hubley Big Lake.

In the past, there have been scattered camps on many of the lakes, but extensive, year-round housing development has occurred in the last 25 years. Sheldrake Lake is extensively developed. One side of Black Point is developed. More recently, part of Hubley Big Lake and additional parts of Five Island have been developed. Development of Birch Hill Lake began in 2002.

Since 1991 there have been several, sporadic, water surveys in which a number of parameters, (total "phosphorus", total "nitrogen", chlorophyll a, dissolved O₂, conductivity, color and turbidity) have been measured in selected lakes of the Wooden's River Watershed. In November, 2000, the Water Quality Committee of the Wooden's River Watershed Environmental Organization (WRWEO) asked the author to undertake a study of several lakes in the watershed to provide a base line for future reference and, where possible, to compare the results with earlier data. This report deals primarily with 2001 and 2002 data obtained from eight lakes in the watershed, and where possible compares the results with those obtained in earlier studies.

The experimental design addresses three questions: 1. Is there any statistically significant difference between the lakes? 2. Is there any statistically significant

¹The topographical maps show a stream connecting Lizard Lake to Five Island Lake. Actually, that stream drains a swamp that is adjacent to, and higher than, Lizard Lake. The Lake seldom gets high enough to spill over into the swamp. The maps do not show the stream from Lizard Lake to Black Point Lake, but it exists; it empties into the lake between the second and third house on Silver Birch Drive.

difference between different sampling stations on the same lake? 3. Have there been any statistically significant changes in these lakes with time?

We have measured depth, Secchi depth, color, temperature, dissolved oxygen, oxygen/reduction potential, pH and, periodically, total phosphate and chlorophyll a².

EXPERIMENTAL

Sample collection: The sample stations on Sheldrake Lake, Five Island Lake and Hubley Big Lake were established in 1995 from bathometric maps of these lakes. The same stations were also used in the current study though there is some variation in the exact location. Sample stations on Craberry Lake, which we studied for the first time 2002, were also established with aid from a bathometric map. Stations on other lakes were established by exploration using a sonic depth depth finder (Eagler Fish Finder). All the stations were marked with either a Garmin 45 GPS, which is accurate to within 15 m., or more recently, with a Garmin e-trek Venture GPS, which is accurate to 5 m. Fig. 1 shows a map with the approximate location of the sampling stations.

²In 2002, spring, summer and fall samples were collected from Five Island and Sheldrake Lakes. Summer samples were obtained from Frederick and Long Lake. Summer and fall samples were obtained from Birch Hill, Black Point, Cranberry, and Hubley Big Lakes.

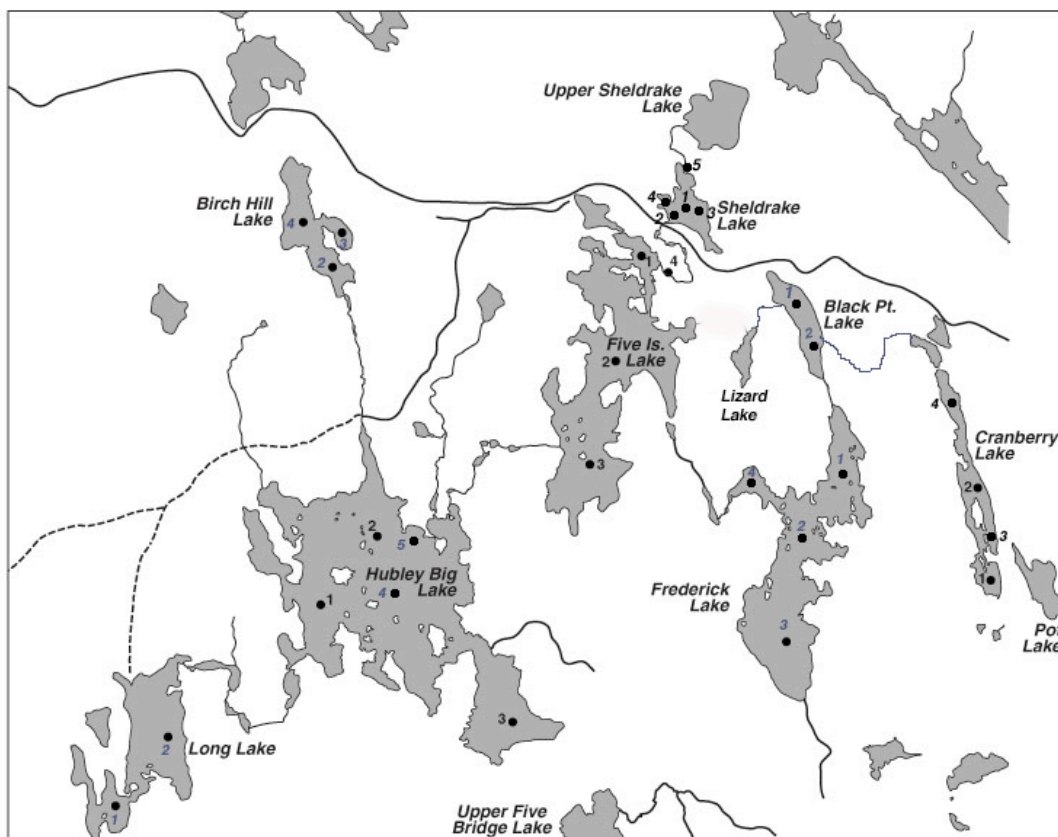


Fig. 1. Location of Sampling Stations.

Table 1 gives the actual coordinates of the stations currently in use Table 1.

Table 1. Location of Sampling Stations. The topological maps used were drawn in Universal Transverse Mercator Projection. The quadrangle is 20 T. The GPS was set to NAD 27 Canada in agreement with the maps used.

Lake	Station	Depth . m.	Lat. N. 44° nn.nnn'	Lon. W. 63° nn.nnn'	UTM 20T 043nnnn W	UTM 20 T 494nnnn N
Black Point	B-1	1.7	40.202	47.270'	7489	6384
	B-2	2.0	40.986	47.075'	7742	5985
Birch Hill	BH-1	4.0	40.478	50.561	3339	6935
	BH-2	4.0	40.37	50.262	3603	6711
	BH-3	5.3	40.468	50.136	3764	6961
	BH-4	9.1	40.513	50.360	3457	7001
Cranberry	C-1	8.0	38.924	45.929'	9275	3961
	C-2	2.5	39.100	45.966	9214	4325
	C-3	4.2	39.285	45.992'	9222	4667
	C-4	3.2	39.619	46.153	9014	5287

	C-5	6.3	39.365	46.016	9194	5032
Frederick	F-0	2.5	39.350	47.557	7155	4808
	F-1	4.5	39.550	46.826	7992	5170
	F-2	6.9	39.177	47.173	7659	4483
	F-3	5.0	38.585	47.257	7538	3388
	F-4	9.6	39.037	47.200	7621	4224
Five Island	FI-1	3.0	40.425	48.104	6285	6809
	FI-2	12.0	39.923	48.245	6196	5899
	FI-3	9.0	39.388	48.551	5781	4894
	FI-4 (inlet)					
Hubley Big	H-1	7.4	38.633	50.242'	3533	3519
	H-2	8.0	39.255	49.908'	3986	4666
	H-3	12.9	38.221	48.948	5235	2738
	H-4	3.6	38.869	49.812	4165	3946
	H-5	1.1	39.076	49.658	4373	4329
Long	L-1	2.1	37.823	51.520	1888	2033
	L-2	4.2	38.191	51.216	2297	2710
Sheldrake	S-0 (outlet)					
	S-1	8.2	40.529	47.864'	6769	7078
	S-2	5.5	40.587	47.868	6766	7102
	S-3	6.3	40.585	47.867	6768	7097
	S-4	2.6	40.611	48.045'	6533	7149
	S-5 (Inlet)	1.3				

Temperature, dissolved oxygen and pH were measured on site with a YSI 556 multiprobe meter. Often, when submersed, the probe gave abnormally low pH readings so samples were taken for measurement in the laboratory with a Radiometer pH meter using Beckman electrodes.

In the spring and summer, samples were taken at various depths using a Kemmerer Sampler. In the fall, when the lakes are mixed, 5 grab samples were taken randomly at 1 m. within a 50 meter radius of established sampling stations using a 2.5 meter telescopic sampling device designed and manufactured by CWRS staff³.

³Centre for Water Resource Studies, Dalhousie University, Halifax, Nova Scotia.

The samples were collected in 200 ml, high density polyethelene bottles that were rinsed 3 times with lake water before collecting the sample.

The water samples were placed immediately in a chilled cooler for storage and subsequent transport to the laboratory. Upon arrival at the laboratory, the pH of the 5 samples collected at each station was measured. An aliquot for phosphate analysis was frozen. The remaining sample was refrigerated until it could be analyzed further. All 5 samples from each station were tested for colour, and total phosphate within 5 days of collection.

Phosphate analysis was performed by the method of Murphy and Riley^{4,5}. This method measures the sum of inorganic and organic phosphate. Briefly, each sample was digested with persulfuric acid to lyse cells and convert organic phosphate to inorganic. The "molybdenum blue" color was developed by reduction with ascorbic acid and measured spectrophotometrically at 880 nm in a 10 cm. cell. Each sample was analyzed in duplicate and the absorbance values averaged. The absorbance was converted to $\mu\text{g P/l}$ using a standard curve prepared with known amounts of KH_2PO_4 . Even though the method measures phosphate, the data is expressed in $\mu\text{g P/l}$ so that it can be compared with earlier data. These data can be converted to the more useful unit, μM , by dividing $\mu\text{g P/l}$ by 31.

Color. Unfiltered samples were examined spectrophotometrically for color at 400 nm. in a 10 cm light path cell calibrated against a solution containing 2.492 g. K_2PtCl_6 + 2 g. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ + 200 ml conc. HCl made up to 1 liter with distilled water. This

⁴Phosphate and color analysis was done at the Centre for Water Resource Studies at Dalhousie University. We are indebted to Mr. Richard Scott for these analyses.

⁵Murphy, J. and Riley, J (1962). *Anal. Chim. Acta*, **27**, 31.

solution contains 1 mg Pt/ml and is 0.005M in Pt. A "total color unit" (TCU) has been defined⁶ as 1 mg Pt.

Statistical analyses (calculation of means and standard deviations, two sample t-tests, and box plots) were carried out with the computer program DataDesk. The various plots including curve fitting were done with the computer program, Kleidagraph, which uses the least squares method for curve fitting.

RESULTS

Do the Lakes Stratify and If They Do, Do They Become Anoxic? If a lake stratifies, this usually becomes most apparent in late summer. Table 2 shows the results of temperature and dissolved oxygen measurements taken in 2001 and 2002.

⁶Hongave, D. and Akesson, G. (1996). *Wat. Res.*, **30**, 2771-2775. The authors show that 410 nm is a more appropriate than 400 nm if one wishes to compare the results with older data obtained with a visual color comparator. Our spectrophotometric data, however, is internally consistent.

Table 2. Temperature Stratification and Anoxia in Selected Lakes of the Woolen's River Watershed.

The data is from late summer samples. BP, Black Point Lake; BH, Birch Hill Lake; C, Cranberry Lake; FI, Five Island Lake; F, Frederick Lake; H, Hubley Big Lake; L, Long Lake; S, Sheldrake. The numbers following the lake designation refer to different sampling stations. The Secchi depth can be used to estimate the depth to which sunlight penetrates.

	<u>Depth</u>	<u>Secchi Depth</u>	<u>Stratifies? 2001</u>	<u>Stratifies 2002</u>	<u>Anoxic 2001</u>	<u>Anoxic 2002</u>
BH-2	4.0	2.1	-	no	-	no
BH-3	5.3	1.8	-	yes	-	Yes (4.5 m.)
BH-4	9.1	2.8	-	yes		no
BP-1	2.0	bottom	no	no	no	no
BP-2	2.0	bottom	-	no	no	no
C-1	7.4	4.6	-	yes	-	yes (6.0 m.)
C-4	2.5	bottom	-	no	-	no
5I-1	2.5	bottom	no	no	no	no
5I-2	10.6	3.2	yes	yes	yes (7.0 m.)	yes (9.5 m.)
5I-3	8.0	4.2	yes	no	yes (8.0 m.)	no
F-0	2.6	bottom	no	no	no	no
F-1	2.6	bottom	no	no	no	no
F-2	6.7	0.4	no	no	no	no
F-3	4.7	3.9	no	no	no	no
F-5	9.6	3.7	no	no	no	no
H-1	8.0	3.4	yes	no	yes (7.0 m.)	no
H-2	7.2	3.7	no	no	no	no
H-3	13.7	2.6	yes	yes	no	no
L-2*	2.1	bottom	no	no	no	no
L-3*	4.5	2.9	no	no	no	no
S-1	8.2	1.2	yes	yes	yes (4 m.)	yes (3 m.)
S-2*	5.5	2.0	yes	yes	yes (4 m.)	yes (4 m.)
S-3*	5.5	2.0	yes	yes	yes (4 m.)	yes (4 m.)

Temperature Profiles. One can follow the development of stratification through the spring and summer. The results for Sheldrake Lake are shown in Fig. 27.

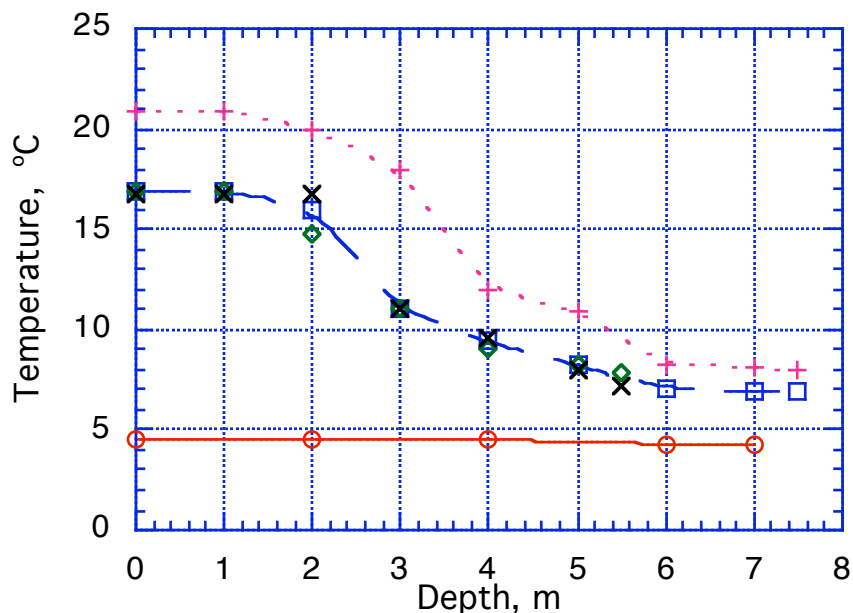


Fig. 2A. Spring, Summer and Fall Temperature Profiles for Sheldrake Lake in 2001. Measurements were taken at three different sampling stations (S1, S2 and S3). o S1, 11/22/2000; □ S1, 5/31/2001; ◇ S2, 5/31/2001; x S3, 5/31/2001; + S1, 8/29/2001

As shown in Fig. 2A, the temperature was constant from top to bottom in the fall of 2001 indicating the lake is mixed at this sampling station. As the upper layer lake began warming up in the spring, a temperature gradient (thermocline) formed between the upper and lower layers (epi- and hypolimnion). By June 31, a "textbook"

⁷In the limnology literature temperature profiles are usually plotted with depth (the independent variable) on the y-axis. Mathematically, it is customary to plot the dependent variable (temperature in this case) on the y-axis. Since we do want to analyze some of our data mathematically, we have adhered to the mathematical convention throughout, for the sake of consistency.

temperature profile had developed with a well defined epilimnion, middle layer (metalimnion) and hypolimnion. Also notice there was no difference between the profiles at 3 different sampling stations. This indicates that stratification occurs at most of the deeper (>5 m.) portions of the lake. As the lake warmed further, the curve shifted, but maintained its shape.

The temperature profiles were not always "ideal". Fig 2B shows an example.

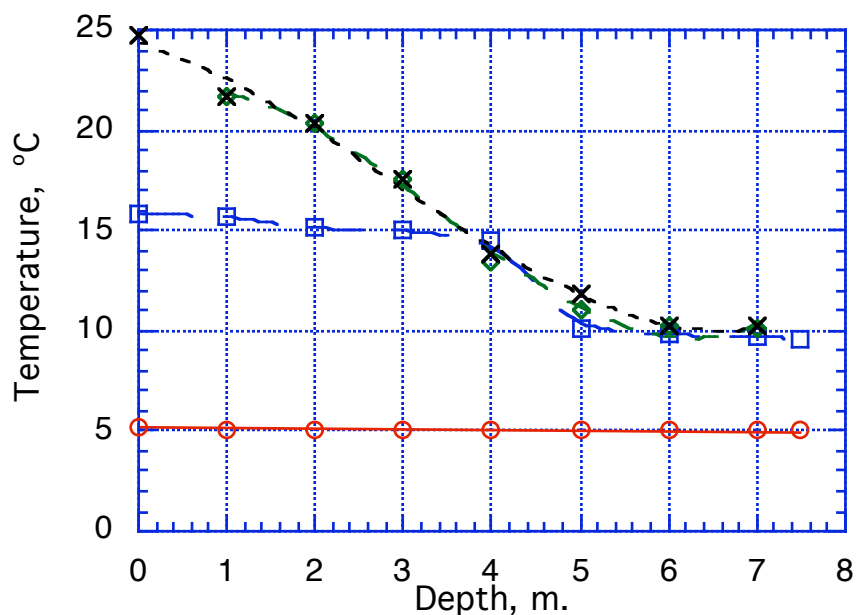


Fig. 2B. Summer Temperature Profiles for Sheldrake Lake in 2001-2002. o S1 11/15/2001; □ S1. 6/11/2002; ◇ S1, 7/23/2002; x S1, 7/31/2002.

In November, the lake was well mixed at station 1. By June 11, a typical stratification profile had developed. As the lake warmed further, however, the clearly defined epilimnion was replaced by a thermocline that extended from the surface to the hypolimnion at 5 m.

Most of the other lakes that stratify show patterns similar to those shown in Fig 2A or 2B. However, the shapes vary and a well defined layers are not always observed. Fig 2C shows an extreme example where there is a thermocline, but no clearly defined layers.

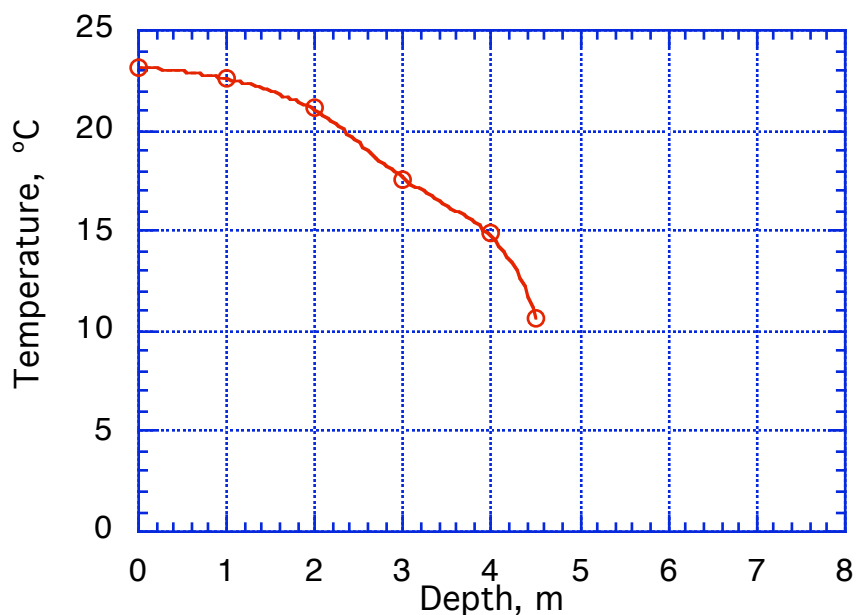


Fig. 2C. Birch Hill Lake, Station 3, August 8, 2002.

A smooth curve can be drawn (by computer) through the data points; this is shown in the figure. However, the data also fit an exponential curve quite well.

Three of the lakes we have studied, Black Point, Frederick and Long, do not stratify in the summer. Black Point Lake is only 1.5- 2 m deep so failure to stratify is not surprising. In fact, we have never seen stratification at sampling stations less than 5 m. deep. However, station 5 of Frederick Lake is 9.6 m. deep yet it does not stratify.

Oxygen Profiles. A lake receives oxygen from two sources, the air and photosynthesis. When a lake is well mixed, the oxygen concentration is essentially

constant from top to bottom. As shown in Table 1, this is the case for Black Point, Frederick and Long Lakes. It is also the case in other lakes where the sampling station is less than 5 m deep.

Since the thermal layers are quite stable and diffusion is a slow process, most of the oxygen in stratified lakes comes from photosynthesis. The Secchi Depth gives a rough estimate of the photic zone. Below this there is not enough light to support photosynthesis. However, a variety of organisms living in lakes (bacteria, phytoplankton and zooplankton, fish and higher plants) carry out respiration. Respiration uses oxygen, instead of sunlight, as an energy source. Respiration and photosynthesis are competitive processes. The amount of oxygen in a lake often depends on the balance between these two processes. Beyond the photic zone only respiration can occur. If this uses up oxygen faster than it can be delivered by mixing and/or diffusion (either from the surface/air interface or photosynthesis), then the lake may become anoxic.

Table 1 shows the stations where anoxia occurred and the depth at which it occurred. Fig. 3 shows the development of anoxia in Sheldrake Lake.

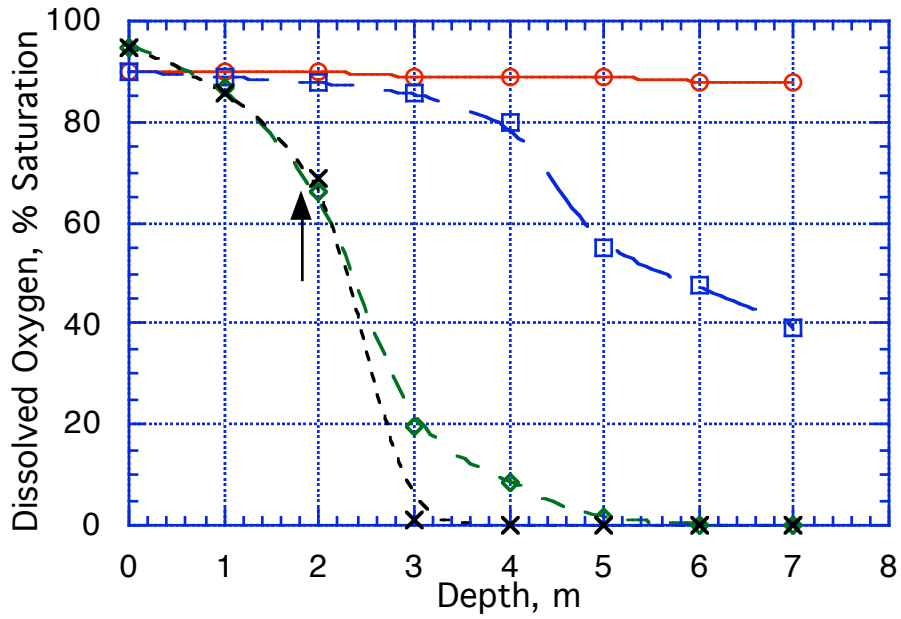


Fig. 3. Dissolved Oxygen Profiles for Sheldrake Lake in 2002.

○ June 11, □ July 23, ◇ July 31, x November, 1

The arrow indicates the depth at which dissolved oxygen is 0.19mM (6 mg/l) on July 31.

Among other things, the amount of oxygen that can dissolve in water is dependent upon temperature. Plotting the data as a percentage of the saturation value corrects for this. In the fall, Sheldrake Lake is well mixed (Fig. 2), and the DO is close to the saturation level at all depths (Fig. 3). As the lake warms up, it begins to stratify, and DO begins to drop below the saturation level, indicating that oxygen is being used up faster than it can be delivered. The lake continues to stratify (Fig. 2), and by mid-summer, the lake becomes anoxic at 3 m. (Fig 3).

It is generally accepted that trout require an oxygen concentration of about 0.19 mM (6 mg O₂/l)⁸. The depth at which this occurs is shown by the arrows in Fig. 4. Trout also seek cold water. In summer, the lake becomes anoxic at 3 m. where the water temperature is about 18°. The fish cannot seek out the colder water (10°C at 6 m.) because there is no oxygen for them to breathe. As expected, fish were detectable with a Sonic Fish Finder down to 3 m., but not below.

It does not follow, however, that stratification always leads to anoxia. Paradise Cove in Hubley Big Lake (H3) is a good example. It contains the deepest sampling station we encountered on any lake. It is isolated from the rest of the lake by a narrow neck that contains several huge boulders. It is undeveloped.

Fig. 4 shows as double Y plot of temperature and dissolved oxygen.

⁸Gibson and Fry (1954). More recent data (Evans, D.O. *abstr.*, Canadian Conference for Fisheries Research, 2003) suggest that a value of 7 mg/l.

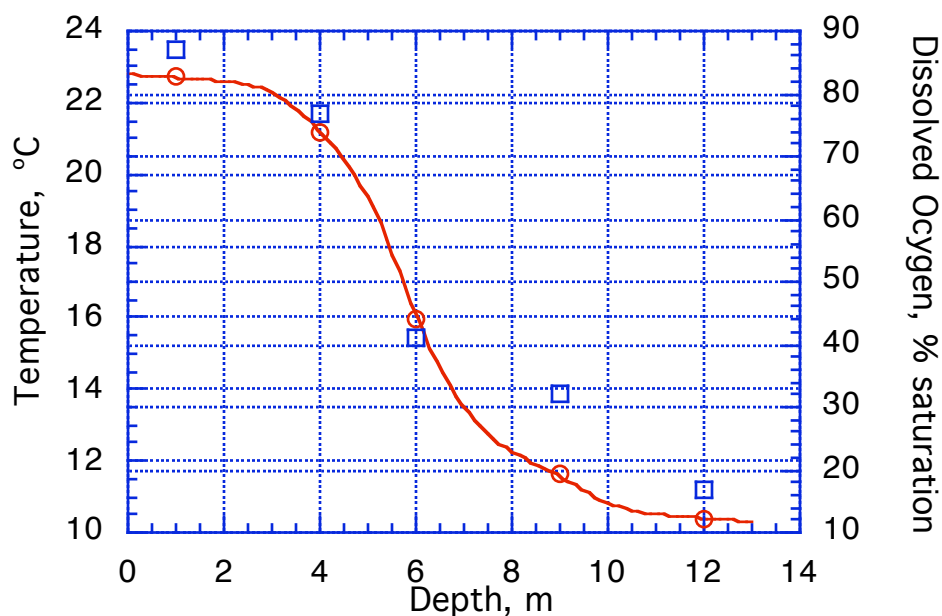


Fig 4 . Temperature/ Dissolved Oxygen Profiles for Paradise Cove on Hubley Big Lake. The data was collected on August 11, 2002. The smooth curve was drawn through the temperature points. ○ Temperature; □ Dissolved Oxygen.

The temperature profile shows stratification with clearly defined layers. Oxygen is being used up faster than it can be delivered to lower depths yet , unlike Sheldrake Lake, there is oxygen all the way to the bottom though the concentration is only $0.05 \mu\text{M}$ (1.7 mg/l , 15% of saturation) at 13 m. Fish were detected at 4, 5, 11 and 12 m., yet below 5 m. the dissolved oxygen is $< 0.19 \text{ mM}$. In several lakes, we have observed fish below the accepted cut off point of dissolved oxygen, but we have never seen them at depths where the lake is anoxic.

Compare the results obtained in Paradise Cove with those from Cranberry Lake. Like Paradise Cove, Cranberry lake has never been developed. It is a relatively clear lake having a lower color value and a greater Secchi depth than the other lakes (see

Table 1). Most of the lake is shallow (2-3 m.). However, there is a relatively deep hole (7-8 m.) at the southern end. Stratification occurs at this sampling station, but not at the other stations in the lake. Fig. 5 shows the temperature and oxygen profile in August, 2002.

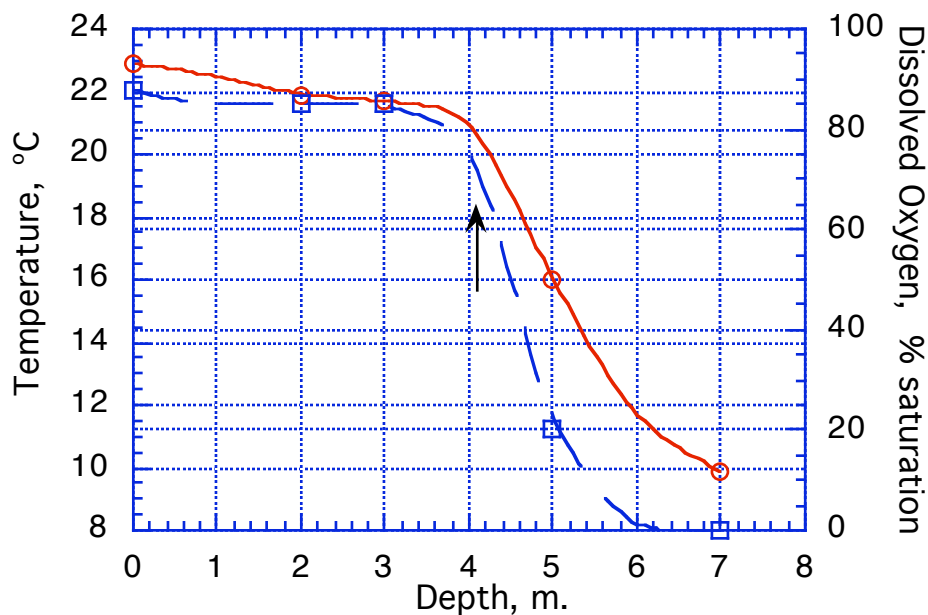


Fig.5. Dissolved Oxygen and Temperature Profiles at Sampling Station 1 of Cranberry Lake, August 22, 2002. See legend to Fig. 4 for other details.

Note the precipitous drop in dissolved oxygen. Anoxia occurred at about 6 m. A strong odor of hydrogen sulfide gas was detectable in a bottom (7 m.) sample. This indicates the presence of anaerobic sulfur bacteria that use sulfate as an energy source reducing SO_4 to H_2S the process.

These examples demonstrate clear differences between lakes and between sampling stations on the same lake. One cannot predict whether a lake will stratify, or if it does, whether it will become anoxic from its location in the watershed or the

development around it. One expects stratification at deep sampling stations, but this is not always the case. As Table 1 shows, there are several monitoring stations (S2, S3 and BH3) that stratify and become anoxic even though they are not very deep. There are other stations (BH4, F5, H1) that neither stratify nor become anoxic even though they are relatively deep for lakes in this watershed.

Phosphate Levels. In many cases, inorganic ortho phosphate⁹ limits the growth of algae. However, Total Phosphate (organic + inorganic) is usually measured and used as an indicator of trophic status. The spring and fall, when temperature profiles indicate the lakes are well mixed are the best times for sampling in order to compare averages in different lakes. However, as we show later, phosphate concentrations may vary with depth even though the temperature profile indicates the lake is mixed. Fig. 6 shows the results obtained in November, 2002.

⁹Limnologists report "phosphorus" concentrations as $\mu\text{g/l}$ or some variation of this (e.g. mg/m^3). This is a convenient way of normalizing the data (i.e. dividing the formula weight of the actual compound by 31, the atomic weight of phosphorus, for those compounds containing a single phosphorus atom). However, this can give the wrong impression, particularly to those not trained in limnology. The element, phosphorus, combines instantly with air and/or water and is converted to phosphate, PO_4^{3-} . Phosphate ions combine with hydrogen ions and/or various metal ions to form salts. There is never any free phosphorus in our lakes. Furthermore, μg is a weight measure. Lake samples are never analyzed for phosphate by weight. We will use the unit $\mu\text{g/l}$ simply because of its wide spread use in the literature. However, we will also report the far more useful unit μM phosphate (micromoles/l). A micromole corresponds to 6.02×10^{17} molecules regardless of the chemical species involved. [Phosphate] in $\mu\text{mol/l}$ (μM) is obtained by dividing [P] in $\mu\text{g/l}$ by the atomic weight of phosphorus (31).

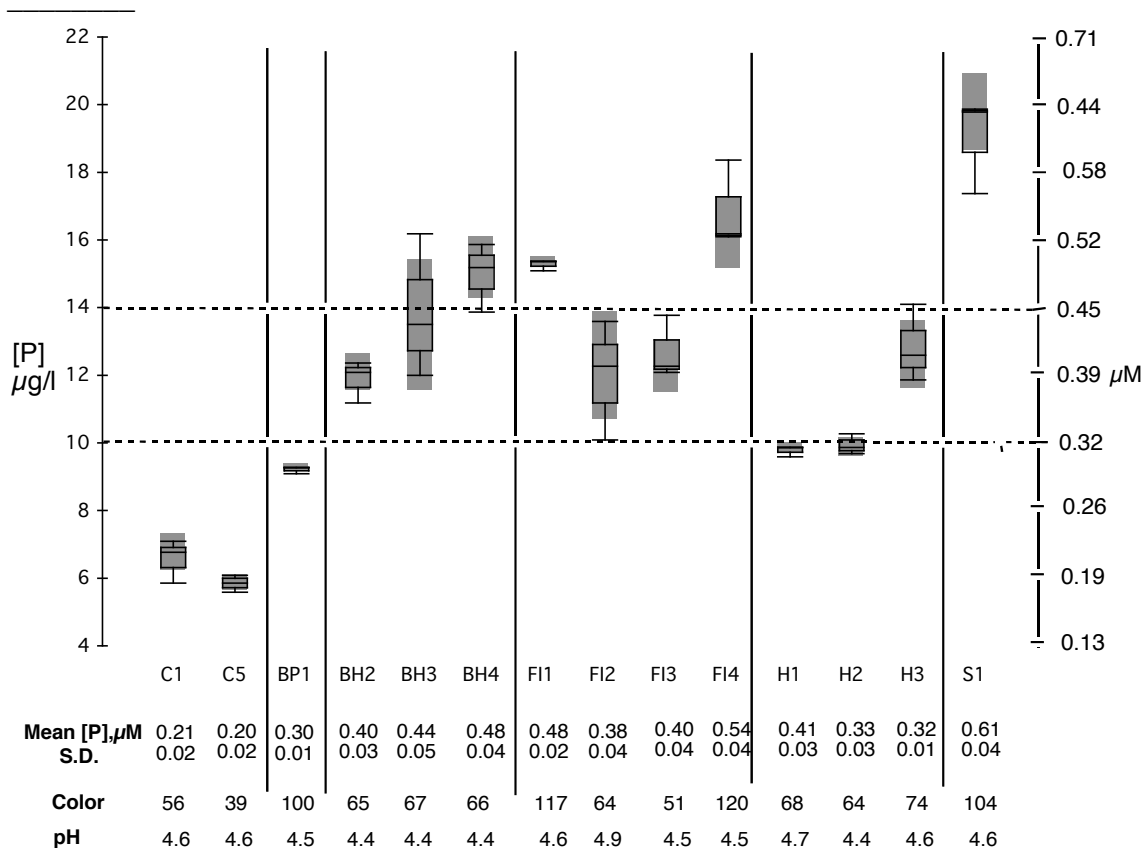


Fig. 6. Phosphate, Color and pH data obtained in November 2002 from Cranberry (C), Black Point (BP), Birch Hill (BH), Five Island (FI), Hubley Big (H) and Sheldrake (S) Lakes. Five random 1m grab samples were taken at each sampling station for analysis. There was no difference between the temperature or dissolved O_2 at the surface and at 1 m. Color is in Hazen Units. The box plots were calculated using the computer program Data Desk. If the shaded areas overlap, there is no significant difference between the median phosphate concentrations at the 95% confidence level. Student's t-tests with the means (data not shown) gave similar results. The upper and lower “hinges” of the box are at approximately the 25th and 75 percentiles. The median is indicated by a horizontal bar in the box. The “whiskers” indicate the bounds of the main body of the data, which is defined as from the high hinge of the box to highest data point that is not above the quantity $[high\ hinge + 1.5(high\ hinge - low\ hinge)]$ and from

the low hinge of the box to the lowest data point that is not below the quantity [$low\ hinge - 1.5(high\ hinge - low\ hinge)$]. Any data beyond these limits are plotted as a circle unless the data exceeds either $high\ hinge + 3.0(high\ hinge - low\ hinge)$ or the $low\ hinge - 3.0(high\ hinge - low\ hinge)$; data beyond these extremes is plotted as a starburst. The shaded intervals for comparing medians are placed symmetrically around the median at $median \pm 1.58(high\ hinge - low\ hinge)/n^{1/2}$.

Fig. 6 shows that there are statistically significant differences between the lakes and between certain sampling stations on the same lake. Though the selected range is arbitrary, the phosphate concentration in most of the lakes seems to be 0.32-0.45 μM (10-14 $\mu\text{g/l}$). We did not sample Frederick or Long Lakes in November 2002, but data from 2000 gave values in this range. There are, however, several stations outside this middle range.

Phosphate concentrations in Cranberry Lake, Sheldrake Lake and the inlet from Sheldrake to Five Island Lake (FI4) are clearly outside the middle range and represent special cases.

Phosphate concentrations in Black Point Lake (0.30 μM) is slightly below the middle range. This is surprising considering its very high color, which often indicates high productivity and a correspondingly high phosphate concentration.

Phosphate concentrations at station 4 of Birch Hill (0.48 μM) is above the middle range and significantly higher than station 2. There is a great deal of scatter in the data from station 3 of Birch Hill Lake, which is in the cove where development has started.

The 2002 data, as well as data from 2000 and 2001, indicate that the phosphate concentration at station 1 in Five Island Lake is consistently higher than at the other 2 sampling stations. Station 1 is near North Bay close to the houses on Sam's Lane. There are also camps on the nearby islands. Sir John A. MacDonald High School is in the

general area. The water is only about 2.5 m deep at this station. We have also observed high values at this station in the spring.

Station 3 in Hubley Big Lake is in Paradise Cove. The phosphate concentration is consistently higher than in the rest of the lake though it still lies within the middle range. Watershed soil samples taken by Michalski Nielson Associates for the Three Brooks Development Corporation Ltd. indicate Phosphate Absorption Ratios for station A and B, both of which are on the eastern shore of Paradise Cove, are much lower (25 and 313 respectively) than for stations C (1,514) and D (2,161), which are opposite the neck that connects Paradise Cove to the main lake, or E (2,158), which is opposite the main lake. It is possible that the high phosphate concentration seen consistently in Paradise Cove is due to runoff from soil with low phosphate retention, but there is no direct evidence to support this. It is also true that this sampling station is the deepest we have observed. Because of this and the location of Paradise Cove, its flushing rate may be considerably lower than the rest of the lake¹⁰. This might contribute to the higher phosphate concentration.

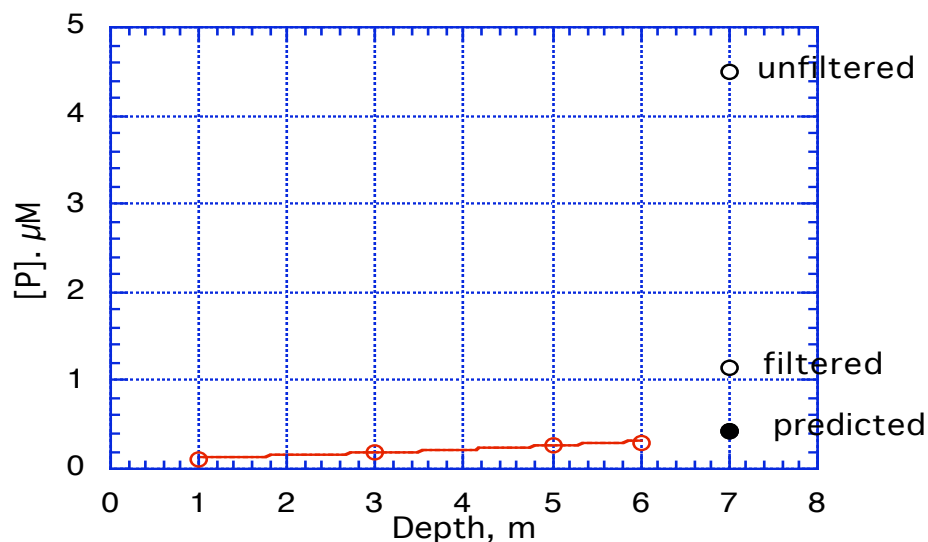
Since Cranberry Lake and Sheldrake are obviously special cases, it is interesting to compare them in more detail. The high phosphate concentrations of Sheldrake Lake were detected in 1992 and have been the cause of considerable concern. Sheldrake Lake is heavily developed around its perimeter, and most of this development has been in place for at least 20 years. The lake is fed by the headwater lake, Upper Sheldrake, for which we have no data. Highway 103 almost touches Sheldrake's northern tip and then crosses the feeder stream. It is tempting to blame the high phosphate levels on the development, but one cannot reach that conclusion from the kind of data presented here.

¹⁰Calculations made at the Centre for Water Resources Management give a flushing rate of 1.59 times/year for Paradise Cove compared to 5.91 for the rest of Hubley Big Lake. Richard Scott, Personal Communication.

Cranberry Lake, on the other hand, is a pristine, undeveloped lake. It is a long, narrow lake. Highway 103 runs alongside, but the lake is separated from the highway by a high ridge until the highway crosses the lake at its northern end.

As shown in Table 2, the deeper portions of both Cranberry and Sheldrake Lakes stratify and become anoxic in the summer. However, the photic zone (estimated from the Secchi Depth) is much greater in Cranberry Lake than in Sheldrake. In fact, it extends to the bottom over most of Cranberry. Because of this and the clarity of the lake, one sees a carpet of plant growth on the bottom. Fish Finder measurements indicate a higher density of fish in Cranberry than in the other lakes. The Fish Finder also gives us the relative size of the fish (small, medium or large), but there is no frame of reference for a more accurate assessment of size. The fish Finder does it tell us what kind of fish we are seeing.

Station 1 of Cranberry Lake stratifies and becomes anoxic (see Fig. 5). The phosphate profile is shown in Fig. 7.



**Fig 7. Phosphate Concentrations at Station 1 of Cranberry Lake
August 22, 2002.**

The 7 m. sample included some bottom sediment. The water was allowed to run out of the Kemmerer Sampler until it appeared clear by eye; then the sample was collected for analysis. On standing several days at 4° C a small amount of sediment had settled out in the sample bottle. Before analysis, the sediment was redistributed by shaking and total phosphate was measured. A value of 4.65 μM (144 $\mu\text{g/l}$) was obtained; this is shown in Fig. 7. Then the sample was filtered through a 1 μ filter and the filtrate was analyzed for total phosphate. A value of 1.03 μM (32 $\mu\text{g/l}$) was obtained; this is also shown in Fig. 7. Unfortunately, analysis was not done on filtered samples from other depths.

Using an exponential curve fit¹¹ to the 1,3,5 and 6 m. data, we predicted what the phosphate concentration would have been in the filtered 7 m. sample if we had not picked up sediment in the sample; the value is 0.38 μM , which is less than half the value actually obtained from the filtered sample (1.03 μM). Regardless of the exact value, it is clear that most of the phosphate resides in the sediment and its water interface, as expected.

The results from Sheldrake lake were even more dramatic. Fig. 8 shows the phosphate data for 2002, but the data for 2000 and 2001 is very similar.

¹¹These data fit a linear curve slightly better, but analysis of other data of this kind indicate the increase in phosphate with depth follows an exponential equation. The equation for the data in Fig. 7 is $[\text{P}] \text{ (in } \mu\text{M)} = 0.106 e^{0.183 d \text{ (in m)}}$, $R = 0.98$.

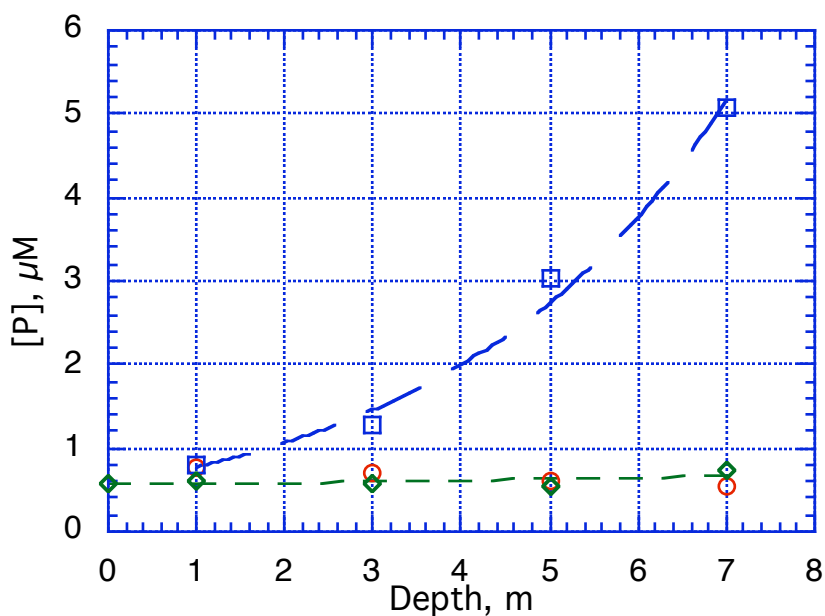


Fig. 8. Phosphate Concentration at Station 1 of Sheldrake Lake in the Summer of 2002. ○ November 11, 2001; ◇ June 6, 2002; □ July 31, 2002. The summer data fit the equation: $[P]$ (in μM) = $0.56182 e^{0.31715 d}$, $R = 0.99$, where d = depth in meters.

Note that the data for both Cranberry and Sheldrake Lake fit exponential equations quite well, but the equations themselves are quite different.

Correlation Between Color and Summer Phosphate Concentrations in Sheldrake Lake. At the same time that phosphate concentration increases exponentially with depth in Sheldrake Lake (Fig. 8), color increases linearly. Therefore, if there is a correlation between color and phosphate concentration, a plot of color vs. $\log [P]$ should be linear. This is shown in Fig.9.

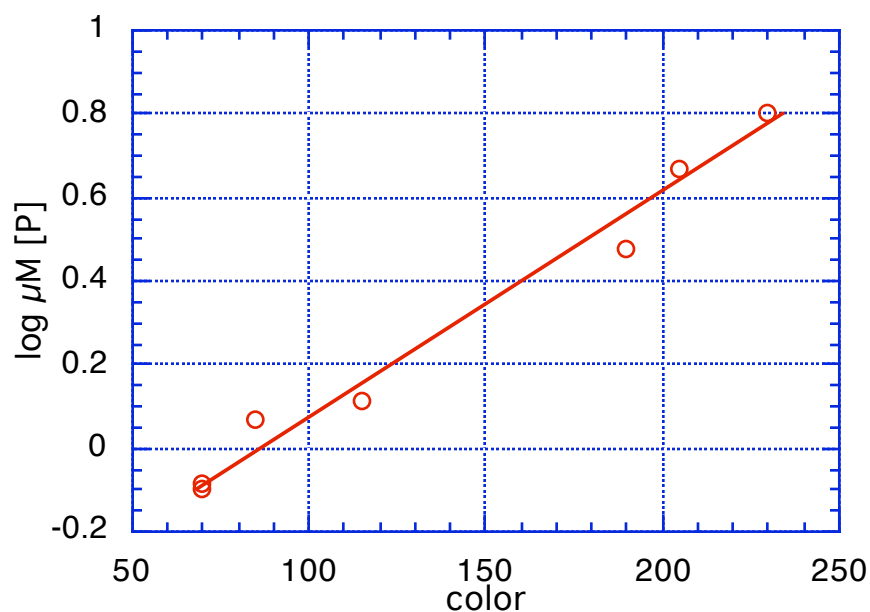


Fig 9. The Correlation Between Phosphate and Color in Sheldrake Lake. The data are from samples collected in the summers of 2001 and 2002.

The data fit the equation: $\log [P] = 0.0053 (\text{color}) - 0.45$ ($R = 0.99$). This suggests that the summer phosphate concentration at any depth can be estimated from color measurements using the equation:

$$[\mu\text{M Phosphate}] = 10(0.0053 \times \text{color}) - 0.45.$$

This is extremely important if it can be confirmed since it would markedly decrease the cost of sample analysis. We emphasize, however, that the equation cannot be used for other times of year or for other lakes. For example, it seems to overestimate the spring or fall phosphate levels of Sheldrake Lake. It grossly overestimates the phosphate concentration of Black Point Lake. Never-the-less, this surprising result

needs to be investigated further since different equations may hold for different lakes and for different times of year when the lakes are mixed rather than stratified.

Correlation Between pH and Summer Phosphate Concentrations in Sheldrake Lake. Like color and phosphate, pH may vary with depth in the summer when a lake is stratified and anoxic. Sheldrake Lake provides a particularly interesting example of this. Fig. 10 shows the correlation between pH and phosphate concentration.

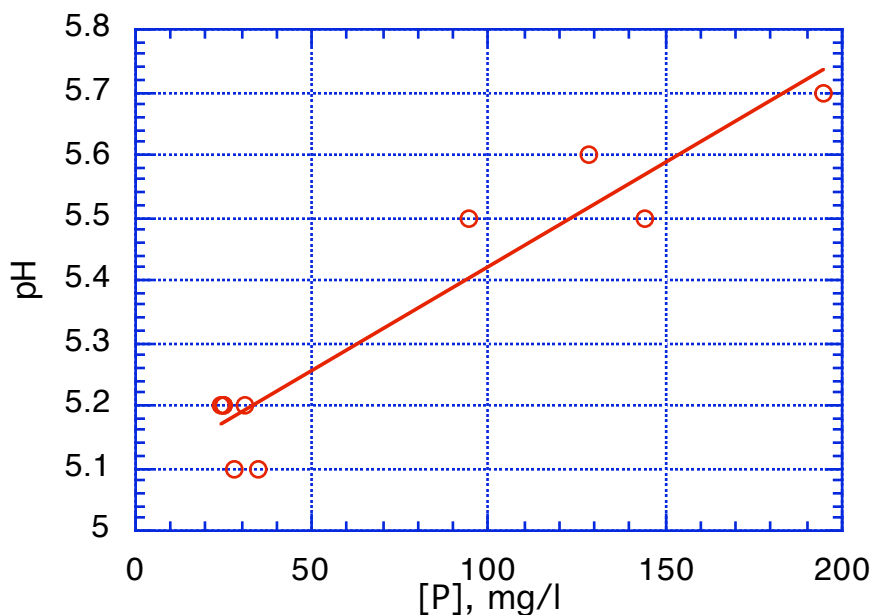


Fig 10. The Correlation Between pH and Phosphate Concentration at Three Different Stations in Sheldrake Lake on August 23, 2001.

The line in Fig. 10 fits the equation: $\text{pH} = 0.10 [\text{phosphate}] + 5.083$ where [phosphate] is in $\mu\text{mol/l}$; the correlation coefficient is 0.95. This interesting correlation needs to be investigated further. However, it should be noted that the pH at 1 m. in the fall was 4.6 compared to 5.2 at 1 m. in the summer. This is a six-fold difference in hydronium ion concentration. In general, we do not see any depth

dependent variation in pH in the spring or fall. Nor do we see it at non-stratified stations in the summer. However, we always see it at stations that have become anoxic.

Chlorophyll a Levels. Excessive algae blooms are often indicate degradation of water quality. Chlorophyll a concentration is widely used as a measure of algae proliferation. This parameter is measured by filtering the water sample from a measured volume to concentrate the algae. The cells are lysed mechanically and extracted with acetone. The extract is analyzed for chlorophyll a by fluorimetry. This procedure measures *intracellular* chlorophyll a, and is, therefore, a rough measure of intact, though not necessarily viable, algal cells. Since proliferation of algae requires light for photosynthesis, we would expect the mass of cells, and hence the chlorophyll a, to fall off with depth. Fig. 11 illustrates this for 3 lakes.

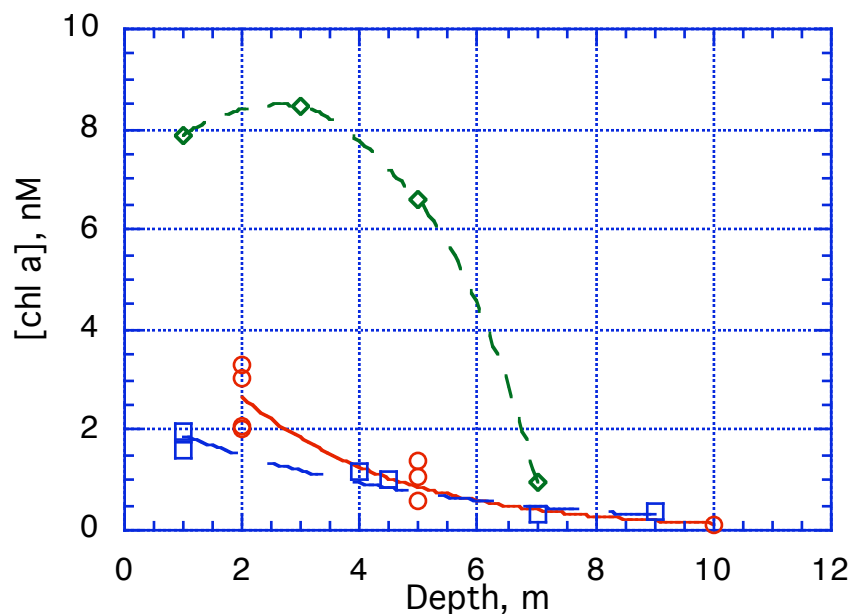


Fig. 11. Chlorophyll a Concentrations in Samples Taken from Sheldrake Lake, Five Island Lake and Hubley Big Lake in the summer of 1995¹². The samples taken

¹²These data were obtained by Richard Scott, Senior Research Scientist at the Centre for Water Resource Studies at Dalhousie University and are used with permission.

a three different depths.. ○ Hubley Big Lake; □ Five Island Lakes; ◇ Sheldrake Lake. The data for Hubley and Five Island Lakes fit both exponential and linear equations. The exponential fits are shown. The equations are: Hubley = $[chl\ a] = 5.6 e^{-37 d}$, $R = 0.90$; Five Island = $[chl\ a] = 2.4 e^{-0.23 d}$, $R = 0.96$, where d = depth in meters.

Fig. 11 shows that Hubley Big and Five Island Lakes have similar chlorophyll a profiles. Sheldrake Lake have a much higher chlorophyll a concentration than either Five Island or Hubley Big Lake, and the shape of the profile is very different. . Furthermore, Sheldrake Lake is more highly colored than either Hubley or Five Island and has an average Secchi depth of only 1.6 m. in the summer. Therefore, we expect the chlorophyll a to fall off rapidly below about 3 m. in Sheldrake Lake. The data shown in Fig. 11 are consistentd wtih this.

Phosphate concentration is widley used as a measure of algal mass. There is voluminous data showing the correlation of [P] and [chl a]. However, most of the data is from clearwater lakes. Since the lakes in our watershed are highly colored, it is important to examine the correlation between chlorophyll a and phosphate by direct measurements. A scatter plot of all our data is shown in Fig. 12.

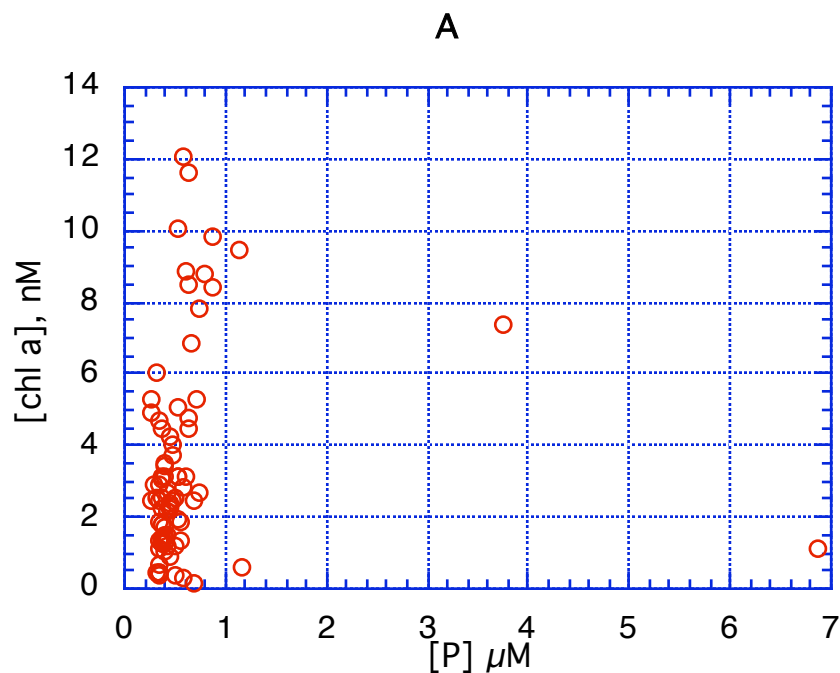


Fig 12A. Correlation Between Chlorophyll a and Phosphate Concentrations on Several Lakes in the Woodens River Watershed from 1995-2001. A. Data gathered at different depths from Black Point, Frederick, Five Island, Hubley Big and Sheldrake lakes.

It appears from Fig. 12A that most of the data fit a linear regression. There are, however, four points where the $[P]$ is greater than $1 \mu\text{M}$; two of these points are clearly aberrant. These four points are from measurements taken below 3 m. Fig. 12B shows the result when points where $[P]>1$ are removed and the scale is expanded. Now the scatter that is actually present in samples taken between 1 and 3 m. is clear.

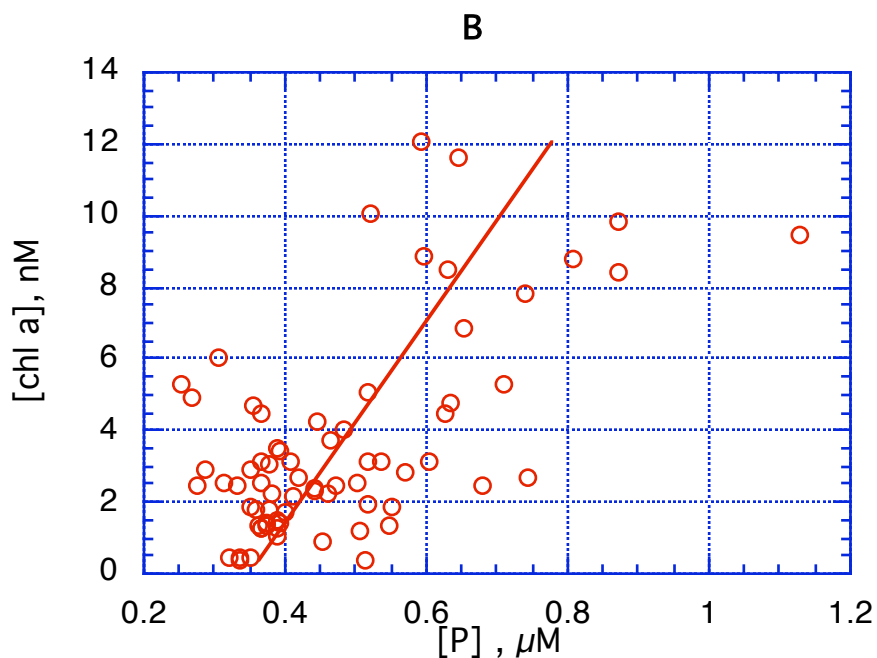


Fig 12B. B. The data were gathered at 1-3 m. The linear regression is:

$$[\text{chl a}] = 0.36 [\text{P}] + 0.35. R = 0.68.$$

While there is a clear correlation between [chl a] and [phosphate], there is so much scatter in the data (even within the same lake) that predictions of algal mass from total phosphate measurements can be very misleading. Part of the problem stems from the methodology that is widely used. Total phosphate includes both intra- and extracellular phosphate, but chlorophyll a measurements give only intracellular concentrations. Furthermore, the time of year and location of sampling station influence the data. We do not have enough data to analyze these variables adequately. Therefore, we urge extreme caution in using TP to estimate the trophic status of lakes in the Woodens River Watershed. If the November [P] is greater than $0.45 \mu\text{M}$ ($14 \mu\text{g/l}$), as it is in Sheldrake Lake and at Station 1 in Five Island Lake, then a detailed study should be initiated.

Color Gradients. The data in Fig. 6 show large differences in the color values not only between different lakes, but between different sampling stations on the same lake. Black Point Lake, which feeds Frederick Lake, has a very high color value. This allows us to do a "natural" dye tracking experiment. We have measured the change in color in Frederick Lake as a function of distance from a potential color source, station 2 on Black Point Lake. The results are shown in Fig. 13A.

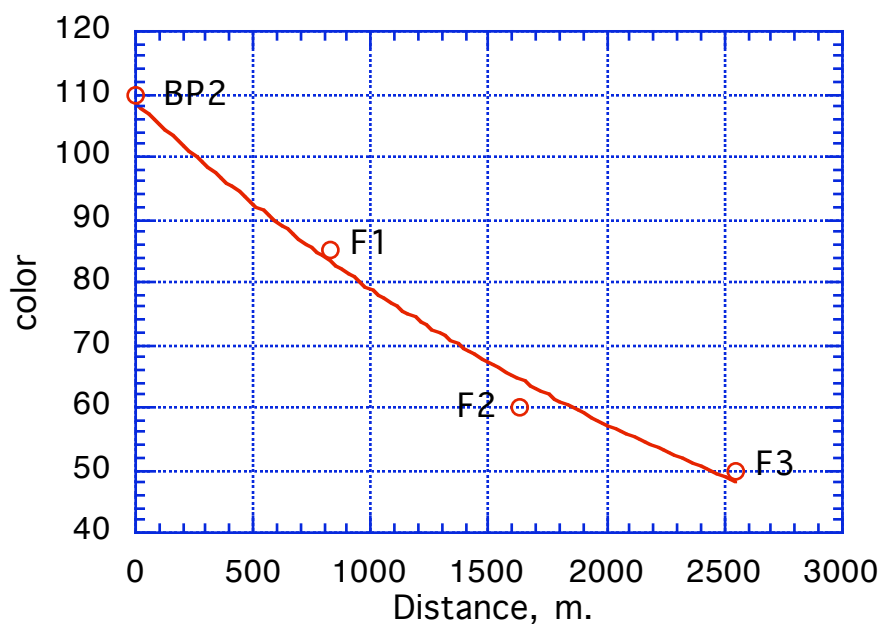


Fig. 13A. The Black Point Lake-Frederick Lake Color Gradient. BP2 = station 2 of Black Point Lake, which is near the outlet that feeds Frederick Lake. F1, F2 and F3 = sampling stations on Frederick Lake. The data was obtained from 1 m. grab samples taken at each of the stations indicated in the figure. These stations lie on a water course arc that approximates a straight line. Color is in "Pt color units" = TCU = Hazen units. The distances were obtained from 1:10,000 scale maps by measuring the water courses between the stations as straight lines. The data fit the equation:

$$\text{color} = 108.53 e^{(-00031 d)}, d \text{ in m.}, R = 0.994$$

The results suggest that surface currents exist. These currents may contribute to mixing and explain, in part, why Frederick Lake does not stratify in the summer.

The data for Sheldrake and Five Island Lake are shown in Fig.13B.

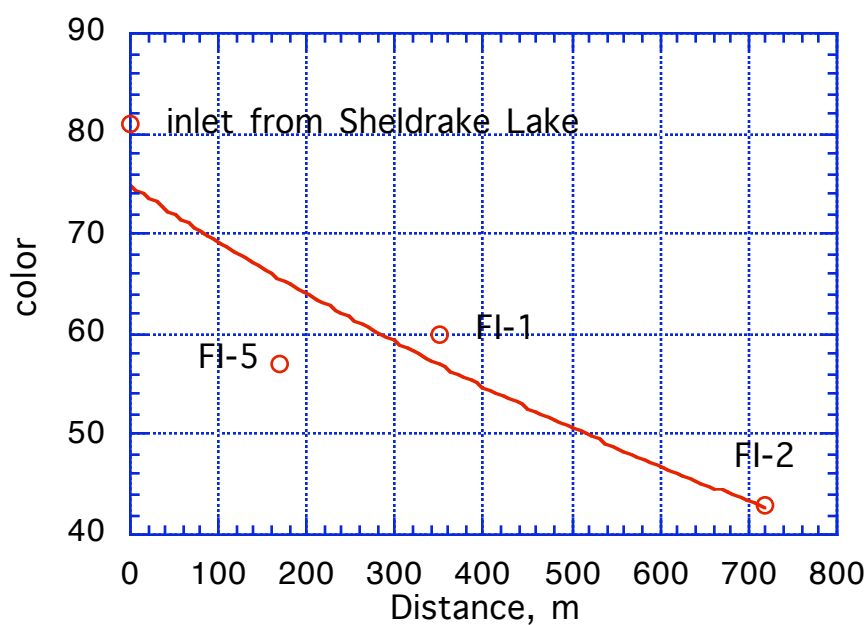


Fig 13.B. The Sheldrake-Five Island Color Gradient. The Sheldrake sample was taken near the outlet that feeds the stream connecting Sheldrake and Five Island Lakes.

Although the curve fit is not as good as for Frederick Lake, the data fit the equation, $\text{color} = 74.8 e^{-0.00078 d}$, $R = 0.92$, reasonably well. From the map (Fig. 1), it appears that the inflow is on a direct line to Station 1; stations 2 and 5 are at essentially right angles to this inflow line. Clearly, more data is necessary to assess these color gradients more accurately.

Have the Phosphate Concentrations of the Lakes Changed With Time? Fig. 14 shows the data for Sheldrake Lake.

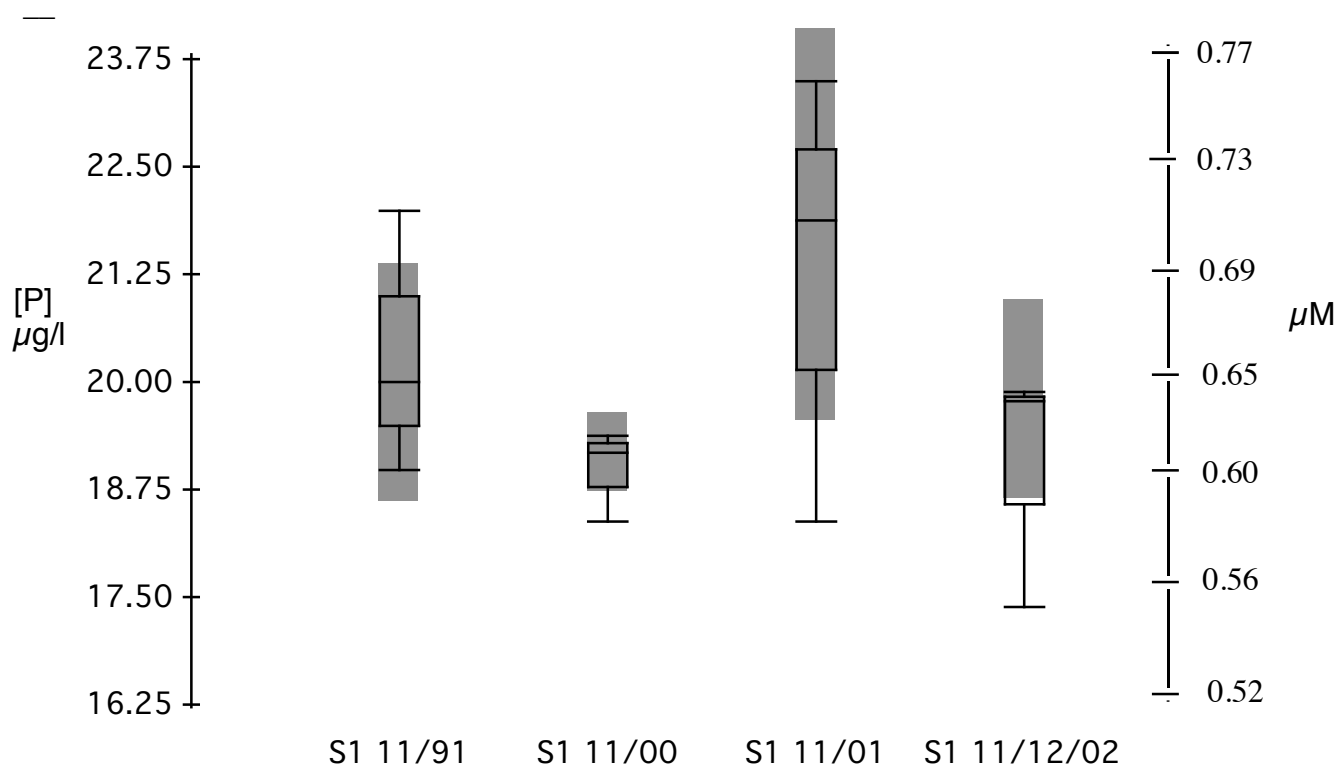


Fig. 14. Comparison of Fall Phosphate Concentrations in Sheldrake. Lake for Different Years. The data collected in 1991 was taken at various depths by The Center for Soil and Water Conservation and is posted on their web site. The remaining data was from 5 random, 1 m. samples. S1 is sampling station 1; the other numbers indicate the data when the samples were taken.

There is no significant difference between either the medians or the means (data not shown) for samples collected in November of 1991, 2000, 2001 or 2002. This suggests that Sheldrake Lake is at steady state with respect to its phosphate level. Further support for this conclusion comes from analysis of the summer data when the lake has stratified and become anoxic (Fig 15).

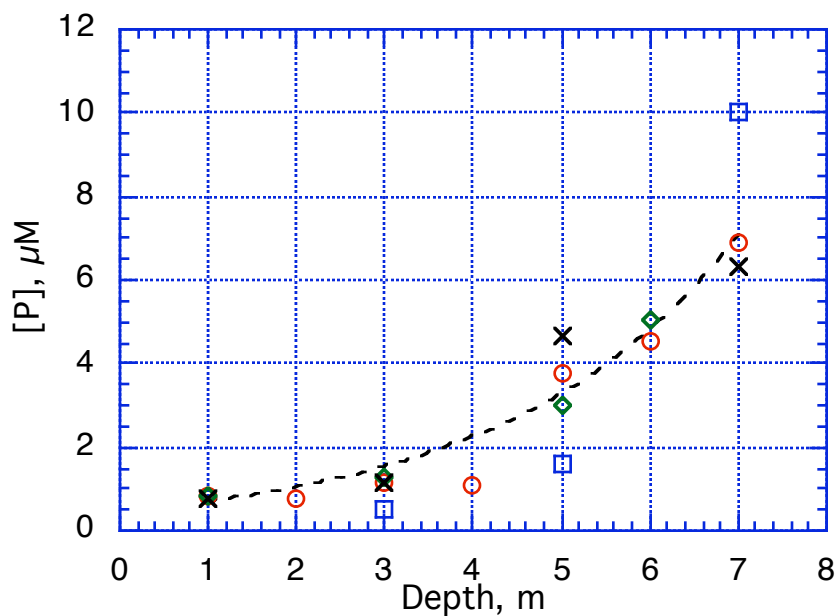


Fig. 15. Comparison of Summer Phosphate Concentrations in Sheldrake Lake from 1991 to 2001. In all cases, single samples were taken at different depths. The 1991 data is from the Soil and Water Conservation Society; the remaining data are ours. An exponential curve fit of the 2001 data gave: $[P] = 0.49e^{0.38}$, $R=0.94$.

With the possible exception of the 7 m. sample obtained in 1991, all the data fit a single exponential curve reasonably well. Clearly, there has not been any significant increase in the phosphate concentration in the last 10 years.

Fig. 16 shows the data for Hubley Big Lake.

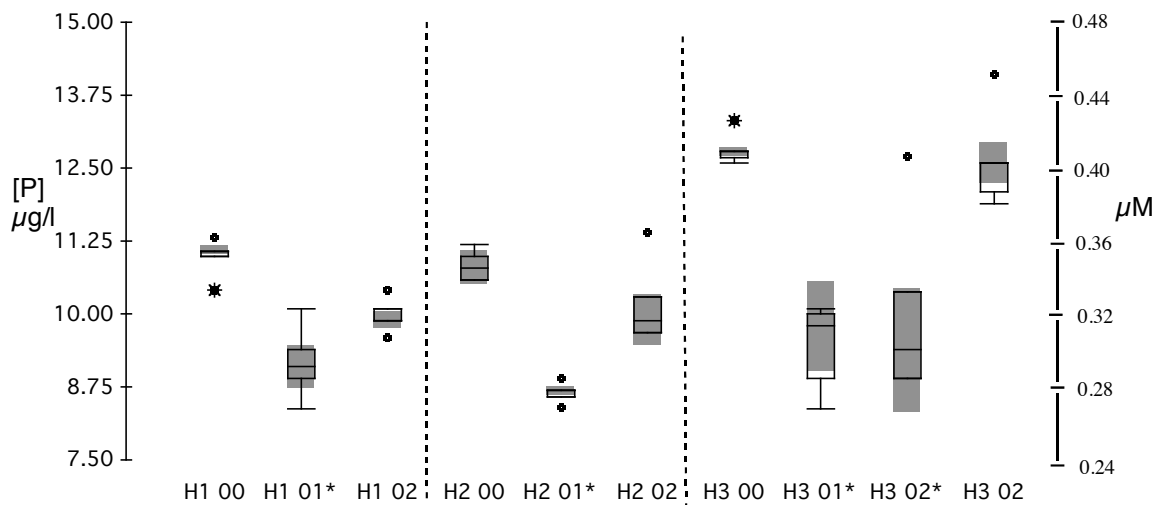


Fig. 16. Comparison of November Phosphate Concentrations at Three Sampling Stations in Hubley Big Lake in 2000, 2001 and 2002. Station 1 is near the outlet; station 2 is on the opposite side of the lake near housing development; station 3 is in Paradise Cove. Five, random, 1 m. samples were taken at each station except for data marked with * (e.g. H1 01*) where single samples were taken at 3,6,9 and 12 m. Note that both these sampling techniques were used at the same time at H3 in 2002.

The data in Fig. 16 confirm that the phosphate concentration of samples taken at 1 m. in November in Paradise Cove (H3) are higher than the mean values at the other stations in the lake (compare H1 00, H1 02, H2 00 and H2 02 with H3 00 and H3 02). The data make two additional points.

Even though the temperature profile indicated that Paradise Cove was mixed, the mean (or median) value obtained depended upon the sampling technique. Taking single samples at different depths gave a lower mean value than taking the same number of samples at 1 m. (e.g. compare H3 02 and H3 02*). The outlier in the H3 02* data is the mean value from the five 1 m. samples. This also indicates there is a real difference between the 1 m. samples and those taken at 3, 6, 9 and 12 m.

Second, there has been little, if any, change in the phosphate concentrations since 2000; if anything there has been a slight decrease (e.g. compare H1 00 and H1 02; H2 00 and H2 02; H3 00 and H3 02). This is somewhat surprising since the 2002 data was obtained after very heavy rainfall that produced exceptionally high water. One might think that runoff from the watershed would elevate the concentrations compared to other years, but the data do not support this.

Fig. 17 shows the phosphite data for Five Island Lake.

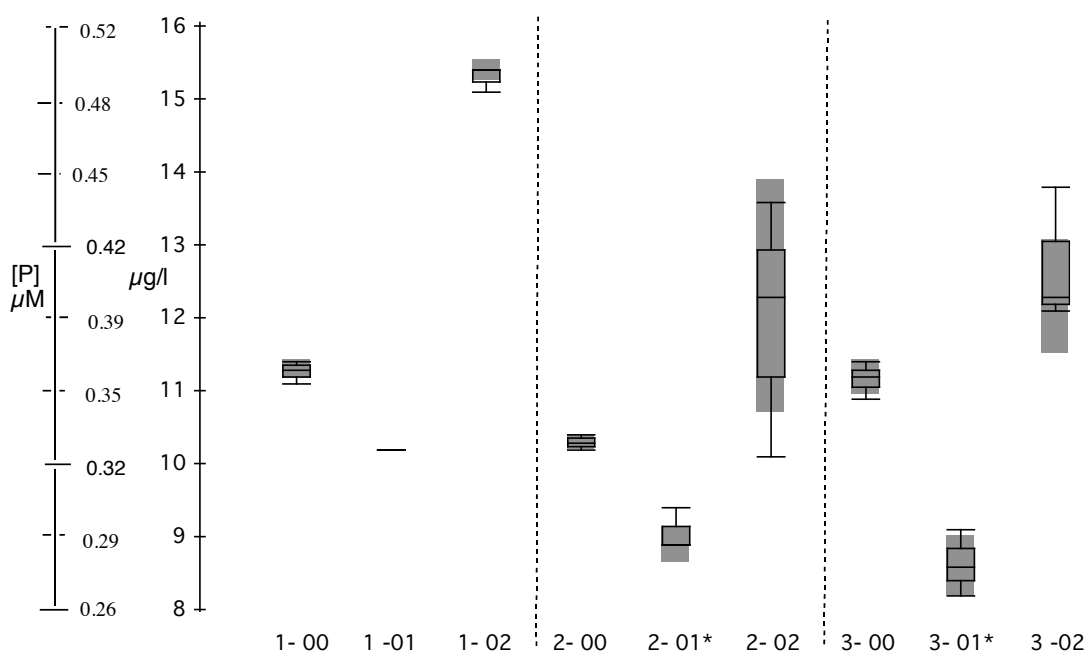


Fig 17. Comparison of November Phosphate Concentrations at Three Sampling Stations in Five Island Lake. The sampling procedures are as described in Fig. 12. The first number corresponds to the sampling station; the second to the year.

Again we see evidence that the sampling procedure makes a difference. Samples taken at different depths give lower mean values than samples taken at 1 m. With this in mind, we can compare the mean phosphate values at stations 2 and 3 for 2000 and 2002 when the sampling procedures were the same.. There seems to be a slight increase

in the phosphate concentrations (i.e. the gray areas of the box plots do not overlap), but these differences are marginal. There is no doubt that there has been a significant increase at station 1 in 2002 compared to 2000. However, there appears to have been a decrease in 2001. It is interesting that we routinely observed higher phosphate values in the spring at station 1 than at stations 2 or 3.

Phosphate Concentration Gradients. As we have shown it is possible to detect color concentration gradients. This suggested that if housing is contributing significant amounts of phosphate continuously, then it might be possible to detect a concentration gradient between stations located close to the houses and compared to those far removed. We have not been able to detect any such gradient on Sheldrake Lake or Hubley Big Lake¹³. There is some evidence for a gradient on Five Island Lake. Station 1 is a shallow portion of Five Island Lake near North Bay (See Fig. 1). There are houses nearby both on Sam's Lane as well as on the Islands and the northwestern peninsulas; Sir John A. MacDonald High School is also in the general area. We consistently see higher phosphate levels here than at stations 2 or 3, which are on the main lake. Of course, this does not prove cause and effect, but it does suggest that additional experiments that attempt to measure phosphate input directly might be informative.

DISCUSSION

There are clear differences in the water chemistry in the 8 lakes of the Woodens River Watershed that we have studied. Cranberry and Sheldrake lakes represent the extremes. There are also clear differences between individual sampling stations on many of the lakes.

Cranberry is undeveloped. It has the lowest color and phosphate of the lakes. Most of the lake is shallow (3-4 m) and its photic zone (as measured by the Secchi

¹³Paradise Cove in Hubley Big Lake should be regarded as a separate lake both from the standpoint of water chemistry and geological formations.

Depth), extends to the bottom . Most of the bottom is visible, and it is covered with a "carpet of green" .

Sheldrake Lake is almost completely developed. It has the highest color and phosphate of the lakes studied. Its color is 2-4 times higher than that of Cranberry Lake. Its Secchi Depth is only 1-2 m. In the fall, when the lake is well mixed, Its phosphate concentration is 3 times that of Cranberry Lakes. In the summer, much of the lake stratifies and becomes anoxic at 3-4 m. This is accompanied by a 10-fold, depth dependent, increase in phosphate.

Most of Cranberry Lake does not stratify. However, at one end of this long, slim lake, there is 8 m. hole (station 1) which stratifies and becomes anoxic in the summer. A bottom sample revealed "black mud", and the odor of H₂S was detected. This indicates the presence of anaerobic sulfur bacteria. which are probably using sulfates as an energy source. During this period, the phosphate levels, which were depth dependent, were quite high (6.7 μ M). In the fall, when station 1 was well mixed, the phosphate concentration dropped to 0.21 μ M, which is significantly lower than that in the other lakes. We did not distinguish between inorganic and organic phosphate, but it seems clear that phosphates are being released by cell lysis during the anoxic period.

Obviously, additional studies need to be done in this interesting lake, particularly in view of the twinning of Highway 103 runs alongside Cranberry Lake. While the current highway is separated from the lake by a ridge of land, the highway crosses the lake at one point. The planned widening of the highway will impinge on this area of the lake at a point very close to Cranberry Run, which passes through Cranberry Bog, the largest peat bog in the Woodens River Watershed, on its way to Black Point Lake. The effect of this construction on Cranberry Lake, Cranberry Run, Cranberry Bog, Black Point Lake and the rest of the watershed needs to be monitored carefully.

Sheldrake is extensively developed, and has been for many years. It has the highest color of the lakes studied (104 Hazen units in the fall compared to 56 at station

1 and 39 in the rest of Cranberry Lake). Only Black Point Lake has such a high color. This is typical of bog fed lakes. Sheldrake has the highest phosphate throughout the year of the lakes studied. The deeper portions of the lake stratify and become anoxic in the summer. When this occurs, the phosphate concentration increases 8-fold and is depth dependent.

CONCLUSIONS

- A. All the lakes are quite acidic (pH 4.4-4.9 in the late fall). However, in summer the pH may vary considerably with depth. For example, in August, the pH in Sheldrake Lake was 5.2 at 1. and 5.7 at 7 m. This represents a 3 fold decrease in $[H_3O]$. This change $[P]$ correlates with changes in phosphate concentration with depth (Fig. 10)
- B. All the lakes are highly colored (39-120 in late fall).
- C. There are differences between the lakes and between sampling stations on the same lake.
 - 1. With the exception of Cranberry Lake, the lakes in the Wooden's River Watershed that have been studied are highly colored.
 - 2. Neither Black Point Lake, nor Frederick Lake nor Long Lake stratify during the summer.
 - 3. Stratification usually occurs on other lakes at sampling stations over 5 m deep, but this varies from year to year.
 - 4. Sample station 3 on Birch Hill Lake, station 1 on Cranberry Lake, station 2 on Five Island Lake and 1,2 and 3 on Sheldrake Lake become anoxic in the summer.
 - 5. Stratification usually, but not always, occurs at the deepest sampling station.

6. When the lakes are well mixed, most of the phosphate concentrations fall between 0.32 and $0.45 \mu\text{M}$ (10 - $12 \mu\text{g P/l}$), but there are significant differences between the concentrations at different sampling stations on the same lake.
 7. The phosphate concentrations at station 4 on Birch Hill, station 1 on Five Island and all 3 stations in the main part of Sheldrake Lake have high phosphate concentrations.
 8. Black Point and Cranberry Lakes have low phosphates concentrations.
 9. The phosphate levels at station 1 of Cranberry is much lower ($0.19\mu\text{M}$) than in the other lakes. However, the concentration rises markedly at 1 station when it becomes anoxic in the summer. Furthermore, most of this phosphate is particulate and comes from the sediment.
 10. The phosphate level in all 3 stations in the main part of Sheldrake are much higher ($0.65 \mu\text{M}$) than the other lakes.
- B. There are no detectable increases in phosphate concentrations in Sheldrake Lake between 1995 and 2002. There appears to have been an increase at station 1 of Five Island Lake.
1. Neither the fall nor the summer phosphate concentrations of Sheldrake Lake show any significant change between 1995 (and probably 1991) and 2002.
 2. If anything, there has been a slight decrease in phosphate concentrations in Hubley Big Lake between 2000 and 2002.
 3. Both spring and fall measurements indicate that phosphate levels at station 1 in Five Island Lake are increasing. This may be a normal variation, but this station bears watching.