Abstract
The objective of this analysis is to focus on phosphate and summarize and integrate the data on inputs into the southern end and the transition of the stream water into lake water.

Estimates of inputs of streams into the south end of the lake combined with inputs from WWTP and lake source cooling on a daily basis were prepared and compared with measured values of samples from the southern shelf region of the lake. Approximately the concentration of the inputs decreased by 50% and 80% within 100 m and 1000 meters, respectively, of the input stream.

Two conclusions are evident to me: lake source cooling has had no measurable influences on the lake; the LSC inputs are on the order of 10% of total P inputs and a substantial portion of this is immobilized or dispersed and b) the shelf region of the lake appears to ameliorate the stream inputs and rapidly transforms the stream inputs into something approaching the composition of the main body of the lake; until these reactions are understood DO NOT even think about “cleaning up the shelf area”.
Transition from stream water to lake water

INTRODUCTION

The objective is to follow the inputs of phosphate from streams, effluent from waste water treatment and effluent from lake source cooling into the southern part of Cayuga Lake as the water moves along the shelf from 1.5 meter to 6 meter depth. This portion of Cayuga Lake is an excellent place to study the transition of stream water to lake water.

Fall Creek drains about 18% of the total drainage area. Periodically since 1972 samples of the stream water have been analyzed for inorganic nutrients. Flow records are available from 1926 to the present. The remainder of the drainage into the southern end of the lake is comprised of several steams which coalesce into a short “inlet” stream just before entering the lake. Together with Fall Creek these streams furnish about 40% of inflow into the lake. These streams have been sampled and monitored over the last 50 years. Together the above data has been assembled and it furnishes a reasonable way to estimate the inputs of water, phosphate fractions, nitrate and other inorganic elements using Fall Creek as a “master” stream.

This is the 4th in a series of summaries of Fall Creek, Cayuga Lake and its watersheds, and this is a summary of interactions between stream inputs and the “shelf area of southern Cayuga Lake.
In the late 1990s Cornell University established a project to use the deep, cold lake water as a coolant. The south end of the lake is about 1.5 meters deep and the depth increases gradually over a distance of about 2000 meters to more than 6 meters and then drops off very rapidly. A subsequent slide (Figure 1a) is a map of the southern end. Since 1998 the project has sampled 10 locations in the lake, most concentrated in the 1 to 6 meter depth.

Briefly the above were reacted as follows. The inputs of phosphate from lake source cooling, the wwtp and the streams are used as inputs together with the inflow of stream water in a “plug flow” model to follow the inputs of phosphate to the 6 meter level.

The next page contains excerpts from the EIS for the lake source cooling. It describes the phosphate fractions and hypotheses about the biological significance of the fractions.
Excerpts from 2.3.3.1.2 Tributary Phosphorus

Two major tributaries, Fall Creek and Cayuga Inlet, flow into southern Cayuga Lake. As discussed in Section 2.3.1.3, these two tributaries account for approximately 40 percent of the direct drainage into Cayuga Lake. A comprehensive evaluation of the Fall Creek watershed was conducted in the early 1970s as part of an investigation of nutrient flux in agricultural watersheds (Bouldin 1975). This research effort was designed to quantify loading of four phosphorus fractions (MRP [equivalent to SRP], TSP, total particulate phosphorus, and labile particulate phosphorus and one form of nitrogen). Additional sampling of Fall Creek and the other southern tributaries (Cayuga Inlet, Cascadilla Creek, and Six Mile Creek) was conducted between March 1987 and February 1989. These data indicate that the flow-weighted TSP concentration in Fall Creek had not significantly changed since the field monitoring program conducted in the 1970s. Based on these results, the Fall Creek and Cayuga Inlet TSP concentrations were assigned values of 26 µg/l.

Bouldin (1975) defined the four phosphorus fractions he measured in the Fall Creek samples based on operational procedures. MRP (Equivalent to SRP). MRP was defined as the fraction reacting colorimetrically with molybdate without persulfate digestion. The second fraction, TSP, was measured by the colorimetric molybdate reaction after the sample aliquot underwent persulfate digestion. TSP presumably includes all of the soluble and low-density particulate organic phosphorus that is oxidized by persulfate. Total Particulate Phosphorus. Total phosphorus was measured on the particulate material as the third fraction. Labile Particulate Phosphorus. The amount of labile or sorbed phosphorus on the particulate material was measured by a sorption isotherm.

Bouldin (1975) presented the following hypotheses: all MRP is available, most TSP is available, labile or sorbed phosphorus is of limited importance (and present in very small amounts), and total particulate phosphorus is of no consequence to Cayuga Lake ecology. We have therefore chosen the Fall Creek TSP data set as the basis for estimating tributary phosphorus input in this southern Cayuga Lake phosphorus budget.
Relevant aspects of southern part of Cayuga Lake. Numbered circles are locations of Lake source cooling monitoring sites, Intake and discharge of lake source cooling, stream inputs of Fall Creek and Inlet as well as discharge of wwtp are identified.
A preview of things to come

This slide is a map of the shelf area of the lake with average concentrations of MRP and chlorophyll over the season. Note the large decrease in concentration of MRP relative to concentration of input from streams, and its decrease with distance from stream inputs and constant concentration of chlorophyll in the surface. The next 6 slides provide the data which went into preparation of this slide.

<table>
<thead>
<tr>
<th>2002</th>
<th>MRP</th>
<th>CHL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.7</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5: Sampling sites, setting, approximate bathymetry, for LSC monitoring program, southern end of Cayuga Lake. Sites sampled during the SPP 1996 study (27, 74 and 311). Locations and Inlets (1997) are included for reference. Locations of sampling sites and outlets are approximate.
Consolidated loading of MRP for Fall Creek, 1972-2008. The important conclusion is that the data from the different periods is so similar that there is no reason to conclude that there has been an important change in MRP concentration - flow relationship over 47 years. The next slide summarizes the data as concentration.
Box boundary, 25th and 75th percentile and "whiskers" 10th and 90th percentile

714 SAMPLES, 1972-2006
C:\caylk\mrpxflowxls.xls page regression
average MRP on average flow
10.89 + 0.0127*cfs - 1.7e-6*cfs^2 \[ r^2=0.96 \]

median mrp on median flow
8.76 + 0.0136*cfs - 1.9e-6*cfs^2 \[ r^2=0.97 \]
Plot of TDP minus MRP, 544 samples, average of mean = 13, average of median = 10.7

TDP-MRP $\sim$ soluble organic phosphate

The general lack of change in median with flow is interpreted to mean that TDP –MRP is a constant as described above.
BEST APPROXIMATION to total stream flow into southern shelf is:

<table>
<thead>
<tr>
<th>Fall Creek flow*2.22</th>
</tr>
</thead>
</table>

Some Justification:
C:\Users\user\Documents\FcP11\flow\fc_flow_1_1_95to2_21_08.xlsx
---Enfield/FC--- ---six mile/FC---
area ratio* 0.279 area ratio* 0.312
--------------flow ratio--------------
1/1/1995 to 2/21/08 10/1/98-2/21/08
Mean 0.243 Mean 0.321
Median 0.224 Median 0.301
Minimum 0.029 Minimum 0.034
Maximum 2.371 Maximum 1.510
Sum 1153 Sum 1082
Count 4741 Count 3372
ci 95% 0.004 ci 95% 0.004

area ratio*= area above USGS gauge
The above data illustrates that the drainage area ratios are reasonable approximations of flow ratios:

BEST APPROXIMATION to total stream flow into southern shelf is:
Total = ratio of Fall Creek flow * total drainage area/ Fall Creek flow
TOTAL inflow=Fall Creek Flow * 2.23
Best approximation of loading of phosphate fractions from stream water inputs into south shelf: \( \text{LOADING FOR SHELF} = \text{LOADING FOR Fall Creek} \times 2.2 \)

**Justification:**
From March 1987 to February 1989, 57 sets of samples were taken from 4 streams tributary to the shelf. Results for TDP(=TSP) are given below.
The average concentration for each is multiplied by area (area is a stand in for flow)

<table>
<thead>
<tr>
<th>location</th>
<th>avg</th>
<th>TDP</th>
<th>area+</th>
<th>TDP*area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fall Creek at Forest Home</td>
<td>33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fall Creek at Lake Street</td>
<td>31</td>
<td>331</td>
<td>10592</td>
<td></td>
</tr>
<tr>
<td>Six mile Creek at Burns Road</td>
<td>31</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Six Mile Creek at Albany street</td>
<td>36</td>
<td>128</td>
<td>4608</td>
<td></td>
</tr>
<tr>
<td>Cascadilla at Fish Res Station</td>
<td>49</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cascadilla at Franklin Street</td>
<td>44</td>
<td>36</td>
<td>1584</td>
<td></td>
</tr>
<tr>
<td>Cayuga inlet at Rt !3 Bridge</td>
<td>22</td>
<td>91</td>
<td>2002</td>
<td></td>
</tr>
<tr>
<td>Unmonitored++</td>
<td></td>
<td>154</td>
<td>4928</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>740</td>
<td>23714</td>
<td></td>
</tr>
</tbody>
</table>

Area based average \((23714/740)\) 32
Area+(Oglesby1978 in Bloomfield ed Lakes of NY State)
unmonitored++ TDP set equal to Fall Creek
Comparison of volume of segments of southern end of Cayuga Lake relative to volume of daily stream inflow, Fall Creek + inlet

<table>
<thead>
<tr>
<th>Depth (meter)</th>
<th>Volume, m³</th>
<th>Inflow CFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5-3.0</td>
<td>1.5e6 m³</td>
<td>100</td>
</tr>
<tr>
<td>3.0-4.0</td>
<td>3.6e6 m³</td>
<td>0.53e6 m³</td>
</tr>
</tbody>
</table>

100 to 200 cfs are common flow regimes; residence time of inflow is on the order of less than 1 to more than 7 days
Note the large decrease in MRP from stream inputs to main lake and no change in chlorophyll (chl). “Deep intake” is intake for LSC.
The graph of phosphate fractions vs log of distance from input of streams shows that the concentration decreases rapidly with distance from stream input, 2002. Data for 2006 is similar. A plug flow model predicted a uniform concentration of ~ 15 ppb P, the flow weighted concentration. The plug flow model was modified to remove P so that the predicted concentrations and observed were about the same as illustrated in the next slides.
Diagrammatic representation of shelf area of lake.

One “plug flow” model imagines that the stream input over one day accumulates and mixes with water in segment 1. Then a volume of segment 1 equal to the inflow is moved and mixed with segment 2 etc. The inputs of phosphate from streams (Fall Creek plus inputs into “inlet”), wwtp, and lsc are input into segment 1 and assumed mixed with water already there.

The program accumulates the daily results and they are compared with the measured LSC (usually biweekly) data. The average lsc data from locations 2 and 7 are averaged and compared with calculated results for segment 1; likewise lsc data for locations 1,3,4 are averaged and compared with calculated data for segment 2. The model also allows for removal of phosphate from both segments as a result of dispersal and in situ immobilization by biological fixation and precipitation. Result for MRP in 2006 are shown in the next slide.
Results of model for 2006 MRP data, segment 1, where segment 1 is the average concentration of MRP(=SRP) in locations 2 and 7.

The green symbols are with no loss and hence as expected follow the flow weighted concentration of inputs. The black symbols are the measured LSC data; clearly reflect a large loss by dispersion/immobilization (DI). The red symbols represent model result with a daily loss of 7 kg. Annual summary is presented in next slide.
The MRP balance for 2006 documents losses of well over 50% of inputs by some combination of dispersal and immobilization

The stream flow was characterized by mostly 50 to 300 cfs except storm June 26 through June 30. when about 12% of total flow and 19% of total MRP was accumulated. For this reason the balance was segmented into periods.

<table>
<thead>
<tr>
<th>Source</th>
<th>apr1-june</th>
<th>oct26</th>
<th>apr-oct26</th>
</tr>
</thead>
<tbody>
<tr>
<td>stream</td>
<td>701</td>
<td>994</td>
<td>3530</td>
</tr>
<tr>
<td>wwtp</td>
<td>160</td>
<td>130</td>
<td>415</td>
</tr>
<tr>
<td>lsc</td>
<td>36</td>
<td>72</td>
<td>176</td>
</tr>
<tr>
<td>total in</td>
<td>896</td>
<td>1197</td>
<td>4121</td>
</tr>
<tr>
<td>*model lost</td>
<td>700</td>
<td>820</td>
<td>2130</td>
</tr>
<tr>
<td>**Model out</td>
<td>196</td>
<td>377</td>
<td>1991</td>
</tr>
</tbody>
</table>

out as % in 21.9 31.5 48.3  
*model lost as illustrated in previous slide, loss of MRP by dispersal and immobilization was 10 Kg per day for segments 1 and 2 combined

**Model out= input minus loss

Another balance model is to consider the amount of MRP leaving the shelf through a line defined by locations 1,3,4. The flow through that line would be equal to total inputs of water from streams, wwtp, and lsc. This was 244 million m3

Average concentration 1,3,4 was 3 PPB P

Total P out=732 kg or 18 % of total P in
Similar to the MRP balance for 2006, the balance for 2002 documents losses of well over 50% of inputs by some combination of dispersal and immobilization in the following table.

<table>
<thead>
<tr>
<th>Source</th>
<th>Whole Season</th>
<th>Apr 1-June 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kg Inflow Streams</td>
<td>3427</td>
<td>1996</td>
</tr>
<tr>
<td>Kg Total In</td>
<td>3923</td>
<td>2142</td>
</tr>
<tr>
<td>Lost</td>
<td>2840</td>
<td>1526</td>
</tr>
<tr>
<td>Out Seg2</td>
<td>1140</td>
<td>690</td>
</tr>
<tr>
<td>Out/In</td>
<td>0.29</td>
<td>0.32</td>
</tr>
</tbody>
</table>

The precipitation during 2002 was similar to 2006 during first part of season but in 2002 August and September were very dry. Thus considering the flow patterns for years 2002 and 2006, 2006 contained a very large flow episode while 2002 contained a very dry period but the in/out ratio was not very different. Casual examination of other years indicated similar losses. In the next slide we discuss hypotheses related to these losses.
The preceding slides illustrate large differences (losses?) between inputs from streams, wwtp, and LSC and the measured concentrations in the shelf locations. There are several hypotheses that are consistent with these differences (losses) either alone or in combination: 

a) incompatibility between methods of analysis between stream and LSC.
b) algal proliferation/immobilization 
c) precipitation as calcium phosphate and/or coprecipitation with calcium carbonate 
d) loss of inorganic carbon thru air water interface 
e) reaction with sediments. Recall that the water is between ~ 1 to 6 meters so the latter 2 reactions may be important but would be unimportant for water deeper than 6 m.

These hypotheses will be examined in the following.

There is a companion discussion of the chemistry which is central to some of these hypotheses entitled “Descriptions of calculations of chemistry of stream and lake samples”.

S18, version feb25
S19, version of feb25

One obvious hypothesis for the loss calculated above is that the analytical procedures for stream vs lake are incompatible and hence losses are fictional. The excerpts from the EIS in a previous slide describe the conceptual framework for phosphate analytical. The operational procedures described there were followed in my laboratory since then. In my opinion the procedures followed by the analysis for the lake source cooling samples are consistent with the stream samples.
Over the last several years I have developed a computer program which essentially creates a framework for comparison of data from stream and lake with expectations based on inorganic chemistry and biological activity. This is described in detail in “Description of calculations of chemistry of stream and lake samples”.

Essential features of the program: a) electrical neutrality b) ion activities of all phosphate and carbonate ions, Ca, and H c) ion activity products of selected solid phases. Many conclusions are shown here which follow from this but details are described there so you may follow this by referring to it.
Next let us consider the total inorganic carbon (TIC) balance as a means to evaluate algal immobilization. The pH of the solutions usually ranges from about 8.0 to 9.0. Recall that the pH is expressed as the negative logarithm of the H ion; at pH 8 the concentration is $1.0 \times 10^{-8}$ moles per liter and at pH 9.0 is a factor of 10 less. These concentrations are about a factor of 100 less than phosphate. The pH of solutions is buffered to some extent by the TIC. Recall that TIC is the sum of CO$_2$, H$_2$CO$_3$, HCO$_3$ and CO$_3$ in solution. Within the pH ranges given above, most of the TIC will be in the HCO$_3$ form, but the ratio of HCO$_3$ to CO$_3$ changes with pH. Suppose we have solution at pH 8.28, Ca = $1.0 \times 10^{-3}$ m/l (=to $2.0 \times 10^{-3}$ eq/), alk = $2.0 \times 10^{-3}$ eq/l and tic = $2.0 \times 10^{-3}$ m/l of tic by algal proliferation but keep Ca and alk constant; the pH will increase to 8.58!
Seasonal data, 2006; Illustrated are the concentrations of MRP in stream inputs, the average MRP in the LSC locations 1 to 8, chlorophyll concentration and pH.

The results are not entirely consistent with the hypothesis that the difference between input concentrations of P and LSC are result of P immobilization by algal proliferation as evidenced by chlorophyll concentrations and pH. The peak in input and LSC concentration (day 70-100) is result of major rainfall; the increase in LSC concentrations at beginning and end of season is consequence of low temperature.

This latter discrepancy is hypothesized to be a consequence of immobilization as a suspended inorganic solid phase and/or with bottom sediments.
The biological activity is restricted by the low concentrations of phosphate so that the removal of other ions is relatively unimportant as illustrated below. There is great variability in ionic ratios of P:N:C in biomass in Cayuga lake (thesis of Bruce Jon Peterson, Cornell University, 1971) and over 2000 lakes in Europe and USA (Science 326:835-837. 2009). I have chosen as best for the following discussion: atomic ratios of P:N:C = 1:36:240 and for P:chl ratios (microgp:microgchl) =1.5. The inputs of stream data is on the order of 15 ppb and by loc 5 the P concentration is about 2. If we use this disappearance of MRP as a measure of phytoplankton proliferation, and use the above ratios as estimates of likely changes in inorganic nitrogen and inorganic carbon (tic) we see the following: For changes of mrm from 15 to 5 ppb MRP =loss of 0.3e-6 mole P/l; thus ratio of loss In above ratio is 0.3:11:72 micromoles per liter of MRP:inorganic N:tic. The estimated initial concentration is: 15:100:2000 and after reaction is 5:99:1930. Now we keep alkalinity and Ca constant since the phytoplankton has not changed this ratio and adjust the pH from 8.1 to 8.6 so that tic has changed from 2000 to 1927. These effects are on the border of detecting by changes in concentration of nox and TIC but the pH has changed by 0.5 pH units. This is a fair representation of effects when the population is just beginning to proliferate in the warming spring weather.
Chlorophyll- phosphate data. Once phytoplankton are established, the biomass P is conserved by phytoplankton/zooplankton interchange so that NET biomass P content tends to constant as illustrated by following: During the 1968-1970 seasons, J B Peterson estimated the balance between phytoplankton requirements and excretion by zooplankton with the results shown below. In general the excretion supplies more or less of the requirements.

This is further illustrated by the constantly changing mixture of phytoplankton species found in bi weekly samples – same amount of biomass but different individuals.
Let us revisit the slide below. Ignoring the blip from about 90 to 120 days from storm inputs, the pH and chl data are parallel; the difference in stream inputs minus average LSC MRP is about 0.3 micromoles/liter and this was shown above to cause a pH increase of about 0.5 units which is consistent with a decrease in ~ tic of about 90 micromoles per liter. However, the persistence of the low concentration in LSC is not entirely consistent with proliferation and decline of phytoplankton.

During the decline of chl, the zooplankton should continue to release P but this is not observed. Is this due to precipitation reactions of some sort? The 2002 data are very similar to the above.
The figure below compares the MRP/SRP of LSC lake samples in the shelf region (open red circles) with Fall Creek samples (large blue triangles). The black dots are the expected concentration in equilibrium with carbonate apatite \((Ca^{10})*(PO4^{6})*(CO3)\). The hypothesis is that there are enough seed crystals in the lake but not in the creek samples to promote precipitation of some form of carbonate substitution into the apatite crystal.
The preceding slides illustrate a) that, based on a plug flow model, the concentration of P in the LSC sites should be equal to the flow weighted concentration of the stream inputs; this is clearly not true b) removal of P from plug flow model which make the model consistent with the observed LSC yields loss of well over 50% of inputs, which presumably is a consequence of immobilization and/or dispersion. Finally a previous slide illustrates that it is unlikely that photosynthetic activity is sufficient to explain all of the “losses”. Another slide illustrates that an apatitic form of calcium phosphate may be an important actor. The important issue is that some of the losses are a consequence of precipitation, either as calcium phosphates and co-precipitates with calcium carbonates, or sorption on inorganic “soil particles” or even sorption on the bottom-sediment. All of the fine particulates in the water may furnish templates for rapid precipitation.

Two conclusions are evident to me: lake source cooling has had no measurable influences on the lake; the LSC inputs are on the order of 10% of total P inputs and a substantial portion of this is immobilized or dispersed and b) the shelf region of the lake appears to ameliorate the stream inputs and rapidly transforms the stream inputs into something approaching the composition of the main body of the lake; until these reactions are understood DO NOT even think about “cleaning up the shelf area”.