

Table 15. Copper concentrations in groundwater wells that exceeded published CCC and CMC values

Well ID	Total Copper (µg/L)	Hardness (mg/L as CaCO ₃)	Unfiltered and Hardness Adjusted Values	
			CMC	CCC
Lyons M1D	21	237	31.56365	19.50084
Lyons M1S	11	230	30.68452	19.0076
Lyons M2D	42	173	23.46316	14.90188
Lyons M2S	25	167	22.69566	14.45913
JOHNSONW2 (Well 2)	148	209	28.03762	17.51442
JOHNSONW1 (Well 3)	150	140	19.22123	12.43647

Data were collected on August 28, 2002 (Lyons M1S, M1D, M2S, M2D, and Gravel M1D) and October 9, 2002 (well 2 and 3). Hardness values for well 2 and 3 were calculated from Ca²⁺ and Mg²⁺ concentrations measured on October 9, 2002. The hardness adjusted values were calculated using measured hardness concentrations and the equations in Table 13. Unfiltered values were calculated by dividing the hardness adjusted values by the conversion factors in Table 14. Bolded values indicate copper concentrations that exceed hardness adjusted unfiltered CCC and/or CMC values.

Zinc was detectable in all wells except LYONSW1. However, only JOHNSONW2 exceeded threshold values for zinc upon calculation of hardness-specific, total recoverable thresholds (Table 16).

Table 16. Zinc concentration in JohnsonW2 that exceeded published CCC and CMC values

Well	Total Zinc (µg/L)	Hardness (mg/L as CaCO ₃)	Unfiltered and Hardness Adjusted Values	
			CMC	CCC
JOHNSONW2 (Well 2)	743	209	223.7568	223.7568

Data were collected on October 9, 2002. The hardness value for well 2 was calculated from Ca²⁺ and Mg²⁺ concentrations measured on October 9, 2002. The hardness-adjusted values were calculated using measured hardness concentrations and the equations in Table 13. Unfiltered values were calculated by dividing the hardness-adjusted values by the conversion factors in Table 14. Bolded values indicate zinc concentrations that exceed hardness adjusted unfiltered CCC and/or CMC values.

6.3 Analysis of Metals in Surface Water

6.3.1 Methods

Surface water samples were collected and analyzed using EPA test method 200.7, Inductively Coupled Plasma for the analytes Chromium, Copper, Nickel, Silver, and Zinc.

All detection limit values are from Microbac Laboratories in Erie, Pa. Detection limits (instrument sensitivity) and threshold values (CMC's and CCC's) vary from analyte to analyte (see Table 12).

Samples were collected in glass jars provided by Microbac. All sample containers were pre-filled with acid and other preservation materials for the maintenance and fixation of any sample materials placed in the jar. The samples were kept in a cooler on ice until their delivery to Microbac, not more than 24 hours later.

Water samples included in the initial screening for metals were taken from the sampling points: center, north, outlet, and ponds a, b, c, d, e, f, g, and h. Samples were taken using a Kemmerer sampler from a canoe.

6.3.2 Results

All samples contained nondetectable levels of constituent. Notably, copper and zinc, both measured as elevated in groundwater samples, were not present in detectable concentrations in lake samples.

6.4 Discussion of Metal Constituents in Water

Uncertainty is an inherent component of the use of screening ecological values. While useful, there are many assumptions that must be made in their use.

Hardness is the only variable acknowledged for the waterbody-specific derivation of CCC and CMC values. Factors other than hardness have been found to contribute to the bioavailability, and therefore toxicity of a metal. For example, copper toxicity has been shown to decrease with increasing alkalinity, hardness (Schamphelaere and Janssen, 2002) (Pagenkopf, 1983), and total organic carbon values (EPA, 1986) (Erickson *et al.*, 1996). Speciation of the metal is also a factor in toxicity. Dissolved inorganic forms such as Cu^{2+} , are significantly more toxic than those dissolved forms that are complexed to organic matter (EPA, 1992a). Even water hardness itself can vary toxicological effects: water samples that have different Ca:Mg ratios, but share the same hardness value, have been shown to differ in toxicity results for different species (Naddy *et al.*, 2002).

Using surface water values in the screening of groundwater is a technique designed to be overprotective. The groundwater entering Lake Pleasant has a higher concentration of constituents than the water stored in the lake basin due to natural weathering of rock in the substrata. The groundwater entering the lake gets diluted with precipitation and

surface water inputs, this is why the groundwater can exceed CCC and CMC values (for copper and zinc) while the surface water remains below threshold limits. A very low risk likely exists for wildlife due to excessive copper or zinc inputs.

Copper is classified as a priority pollutant because of its adverse health effects on aquatic animals. There is evidence that copper can be toxic to fishes in the forms Cu^{2+} and CuCO_3 . The binding of the Cu^{2+} ions onto carbonate compounds is pH dependant. Based on existing data, the toxicity of Cu has been shown to decrease as alkalinity, total organic carbon, and hardness increase (EPA, 1986).

Copper can replace calcium on the gills, causing epithelial damage and inhibition of transport enzymes (Taylor 1995). Lethal levels of copper can affect respiratory gas exchange resulting in death. Sublethal concentrations will reduce swimming performance. Both sublethal and lethal concentrations of copper have been shown to cause an increase in ammonia in tissues and plasma.

Cu^{2+} is also known to compete with Ca^{2+} ion pumps at the gill-water interface, inhibiting their action. If the Ca^{2+} concentration is low, the Cu^{2+} ion has less competition for binding sites. This idea is the basis of the Biotic Ligand Model (BLM).

The BLM was developed to account for the effects on metal toxicity by natural variations in pH, hardness, total organic carbon, alkalinity, etc. The BLM assumes that the basis of metal toxicity is the interaction of free metal ions with metal-specific receptor sites at the water-organism interface (Schamphelaere and Janssen, 2002). At the water-organism-interface (i.e. gills in fish), the metal ion may interact with a receptor and cause a direct physiological response, or the ion may interact with a cell transport site, causing a different physiological response in the cell (Schamphelaere and Janssen, 2002). With any receptor-ligand interaction, the amount of receptors available will limit reaction/response time with excess ligand available for binding. With limited ligand, the response depends on the amount of ligand that is available for interaction with the receptors. For example, if a small concentration of an ion is present and is distributed throughout the water, the ligand receptor interaction can be dependent upon the chances that the ligand will encounter the receptor. Schamphelaere and Janssen showed that increasing concentrations of Ca^{2+} , Mg^{2+} , and Na^{2+} increased the 48-hour EC50 in copper toxicity tests (decreased toxicity of copper) (Schamphelaere and Janssen, 2002). These results suggest that the Ca^{2+} , Mg^{2+} , and Na^{2+} ions may be competitive ligands for the Cu^{2+} binding sites (Schamphelaere and Janssen, 2002). Therefore, traditional toxicity tests, and threshold values may be over protective in waters with high concentrations of these ions, such as the calcareous waters of Lake Pleasant.

The calcium carbonate sediments of Lake Pleasant are likely to be beneficial to fish species because free Ca^{2+} ions help to reduce toxicity of metals already present in the lake, and will mitigate potential increases in levels of other metals.

6.5 Analysis of Metals in Sediment

Monitoring the metals content in sediments of the lake and wetlands will serve to establish the general toxicity of the area, as well as to identify possible sources of contamination. In order to gain an understanding of the existing levels of metals in the

sediments of the lake, analytical data will be presented from Wellington, 2001, a related, unpublished study.

Most metals detected in the sediments are expected to represent normal background concentrations for the area. Metals are naturally occurring components of rocks and soils and cycle through geologic weathering processes. Background concentrations are constituent levels that would occur in a parent material such as, rock or soil, without contributions from anthropogenic sources. Fish, plants, and other aquatic communities in the system are assumed to have adapted to these conditions.

The effects of high levels of chemicals on the environment and the organisms that live in it are often reported as effects values. Threshold Effects Levels (TELs) are used to screen conservatively; and although they do not predict toxicity, they are the values below which any contamination can be considered, with a high degree of confidence, to pose no threat (NOAA, 1999). Probable Effects Levels (PELs) are used to describe concentrations of compounds that are more likely to be at toxic levels (NOAA, 1999). When an effects level is lower than that of a detection limit, it may not be possible to determine if the chemical is problematic or not. Antimony and Cadmium have the potential for uncertainty based on effects levels falling below detection limits.

Samples were taken from the center of the lake on June 28, 2001. Future sediment sampling is recommended every five to ten years, minimum, at the center and outlet of the lake.

The following metals exceeded their associated threshold values (Table 17):

- Copper (over TEL only)
- Nickel (over TEL only)
- Arsenic (over both)
- Zinc (over TEL only)
- Mercury (over both)

Table 17. Sediment concentrations and associated effects levels of metals in Lake Pleasant from Wellington 2001 (unpublished data)

Analyte	Sample Concentration (mg/kg)	Threshold Effects Level (mg/kg)	Probable Effects Level (mg/kg)
Aluminum	14889		58030
Antimony	<30.5	2	25
Arsenic	25.1	5.9	17.0
Barium			
Beryllium	<5.1		
Boron	<203		
Cadmium	<5.1	0.596	3.53
Calcium	9554		
Chromium	21.9	37.3	90.0
Cobalt		50	
Copper	43.7	35.7	197.0
Iron	44516		
Lead		35	91.3
Magnesium	4380	460	1100
Manganese	1128		
Mercury	1.25	0.174	0.486
Molybdenum			
Nickel	26.4	18.0	35.9
Potassium			
Selenium	<35.6		
Silver	<5.1		
Sodium			
Thallium			
Tin	<203		
Vanadium	58.9		
Zinc	191	123	315.0

6.5.1 Discussion

Arsenic was detected in the sediment of Lake Pleasant in a concentration of 25.1 mg/kg in June/July of 2001. (Wellington, 2001) In some forms, arsenic is highly toxic, carcinogenic, and can bioaccumulate (Drum, 2001). It has several exposure routes including ingestion and dermal contact, which not only have the potential to harm wildlife, but also humans who consume fish with elevated levels of arsenic.

Arsenic was reported to have a value of 25.1, over both the TEL and PEL. Arsenic has been detected at a level deemed unsafe for aquatic biota but it is unknown as to whether

these levels represent natural background conditions or elevated levels from human activities. Potential anthropogenic sources of arsenic include fossil fuel combustion and industrial emissions.

An elevated sediment concentration, 1.25 mg/kg of mercury, was measured in Lake Pleasant in 2001 at the center sampling point by Wellington. Mercury is of primary interest to the stakeholders of this watershed because of its ability to bioaccumulate in the tissues of organisms. Mercury exceeded both the PEL and TEL for Lake Pleasant sediments. Anthropogenic sources of mercury in dry deposition and precipitation are expected to be the cause.

Wildlife species with high bioaccumulation factors are at increased risk of mercury effects in systems impacted by high levels of mercury in dry deposition and acid rain (EPAM, 2000).

Release of methylmercury from sediment has not been well documented. However, correlations between high mercury sediment concentrations and elevated fish tissue concentrations have been observed (EPAM, 2000).

One third (~52 tons) of anthropogenic mercury emissions in the US are deposited as dry and wet deposition within the contiguous United States (EPAM, 2000). Another 34 tons are deposited from anthropogenic global sources. (EPAM, 2000).

Toxicity of mercury compounds can be extensive. Inorganic mercury itself generally does not cross the blood brain barrier (BBB) and tends to cause kidney damage by necrosis in the renal proximal tubules (Chang and Cockerham, 1994). However, methylmercury (CH_3Hg), mercury in its organic form, can enter the central nervous system (CNS) effectively and is a potent neurotoxin (Chang and Cockerham, 1994). CH_3Hg has an affinity for sulfhydryl ($-\text{SH}$) ligands. Cysteine, a sulfur containing amino acid contains $-\text{SH}$ groups that are able to complex with CH_3Hg and enter the CNS (Chang and Cockerham 1994). Once within the BBB, CH_3Hg can bind to organelles within cells disrupting energy production; it can mimic methionine, the amino acid start codon for protein synthesis, inhibiting protein synthesis; and it can demethylate generating cytotoxic CH_3 free radicals (Chang and Cockerham 1994).

Fish tissue samples (data available from EPA Storet) from Lake Pleasant taken in the 1990s show that despite sediment concentrations of mercury that exceed threshold values, little mercury has worked its way up through the food chain. Continued monitoring of this metal and its pathways into the lake are recommended.

Iron and Manganese Chemistry

Between pH 4 and 12, and in the presence of atmospheric CO_2 , three solid iron compounds control the speciation of Fe in solution (Evangelou, 1998). $\text{Fe}(\text{OH})_3$ controls the release of Fe^{3+} and $\text{Fe}(\text{OH})_2$ and FeCO_3 controls the release of Fe^{2+} . pH and Eh control the stability and speciation of these forms. When oxidizing conditions are present, Fe^{3+} is most stable, while at reducing conditions, Fe^{2+} is most stable as a carbonate solid (Evangelou, 1998).

Between pH 4 and 12, and in the presence of atmospheric CO₂, several solids control speciation of Mn: MnO₂, MnO₂H, Mn₃O₄, MnCO₃, and Mn(OH)₂. Under reducing conditions, MnCO₃, and Mn(OH)₂, control Mn²⁺ release. Mn-carbonate is the most stable species in the pH range of 7.5 to 11.2. However, at a circumneutral pH, Mn-oxides are the most stable.

Manganese and iron release and uptake in the sediment are interrelated. The release of Mn from sediment precedes that of iron (Wetzel, 2001). Manganese can be used as an indicator of the removal of heavy metals from water (Evangelou, 1998).

Elevated levels of iron and manganese were detected in the water of the hypolimnion of Lake Pleasant (Wellington, 1991). Release of sediment bound constituents is dependent upon the reduction-oxidation status at the sediment-water interface. "If the mud surface is oxidized, the iron is present in the ferric state precipitated in a complex colloidal structure which prevents phosphate exchange. If the mud surface becomes anaerobic however, ferric is reduced to ferrous, the complexes break down and phosphate moves from the sediments into the overlying water." (Harper, 1992) This may explain the elevated levels of constituents in the lower waters of the lake, as well as have contributed to the dispersion of phosphorus upon turnover, resulting in an observed, fall algae bloom.

Available iron content expected in a hard water calcareous lake is extremely low. Wetzel (2001) notes that the reactive iron in a documented lake rarely exceeded 5ug/L over a period of a year. In lakes where low levels were observed, Fe was said to limit high primary productivity. An increase in Fe, in its complexed form, "resulted in immediate increases in photosynthetic rates" (Wetzel, 2001). Total Fe levels in Lake Pleasant were measured at 2660.0 µg/L one m above bottom, and 57ug/L one m below surface. These levels are higher than expected for a typical calcareous lake. Higher Fe levels may contribute to increased primary production in the lake.

Conversely to the expected effect of iron, high concentrations of manganese (>1mg/L) can inhibit algal growth. (Wetzel, 2001) The total manganese concentration in water 1 meter below the surface was 14.1ug/L (.0141mg/L), and dissolved manganese was 1.33ug/L (.00133mg/L). However, a total manganese concentration of 2640ug/L (2.640mg/L) and a dissolved manganese concentration of 2590ug/L (2.590mg/L) were detected in samples from water in the bottom one meter of the lake. The elevated levels near the bottom are likely a result of sediment release due to anoxic, reducing conditions in the hypolimnion. Manganese could be expected to have an inhibitory effect on algal growth if the measured concentration within the photic zone upon mixing and distribution throughout the water column reached levels >1mg/L.

However, increasing calcium concentrations can reduce the inhibitory effects of high manganese, therefore the calcareous nature of the lake may have reduced any inhibitory effects of the Mn on algae growth. Levels of manganese should be monitored to evaluate and establish its relationship with other constituents such as chlorophyll a and calcium in this system.

Iron and Manganese oxides can also be protective because they coprecipitate cobalt, zinc, and copper inhibiting the absorption of the soluble forms of these metals (Cockerham and Shane, 1994).

7. PHOSPHORUS BUDGET

7.1 Background

Phosphorus is an extremely important nutrient for biological productivity in lakes and is considered the first limiting nutrient for primary production because it is often found in much lower concentrations than other nutrients, particularly nitrogen (Wetzel 2001). Sources of phosphorus to freshwater systems include atmospheric deposition from anthropogenic pollution sources (typically burning fossil fuels), agricultural practices (fertilizers), detergents and sewage.

Phosphorus has been shown to be the limiting nutrient for biological processes in Lake Pleasant (Section 5.1.8.3). Other important biological components, including carbon, hydrogen, nitrogen, oxygen and sulfur, are found in relatively higher natural supply. Therefore, management of phosphorus inputs to the lake system becomes extremely important in regulating productivity of the system and trophic conditions in the lake.

Phosphorus may be present in a variety of forms in freshwater. It may be found in both inorganic and organic form depending on its source. The most important inorganic form of phosphorus is soluble orthophosphate. Typically organic forms of phosphorus comprise greater than 90% of the total phosphorus in freshwater (Wetzel 2001). When sampling began on Lake Pleasant in November 2001, both total phosphorus and orthophosphate were sampled for. In weekly sampling through 12/26/01 and then again on 2/18/02 and 3/11/02, orthophosphate was undetected in the lake water. In order to conserve resources, orthophosphate sampling was discontinued.

Total phosphorus was sampled weekly from the lake, inlet streams, outlet and groundwater wells. Total phosphorus concentration was also sampled in rain and snow as well as dry deposition falling on the surface of Lake Pleasant. Dr. Milt Ostrofsky, Allegheny College, supplied internal loading data for phosphorus released from lake sediments. Ostrofsky's sampling had been done during summer 2000 and allowed us to apply funding elsewhere and avoid duplication of data collection.

A phosphorus budget attempts to show all inputs and outflows of phosphorus to the lake ecosystem. Sources of phosphorus to Lake Pleasant include precipitation, dry depositions, stream runoff, groundwater, internal loading from sediment release, and point and nonpoint sources such as septic systems and direct surface runoff. Phosphorus leaves the lake water either by outflow or sedimentation. The amount of phosphorus inputs should equal the amount of phosphorus leaving the lake and can be shown with the following equation:

$$P_{\text{ppt}} + P_{\text{dep}} + P_{\text{swi}} + P_{\text{gwi}} + P_{\text{sr}} = P_{\text{out}} + P_{\text{sed}}$$

Where:

P_{ppt} = total phosphorus in wet precipitation to the lake

P_{dep} = total phosphorus in dry deposition to the lake

P_{swi} = total phosphorus in surface water inflow

P_{gwi} = total phosphorus in groundwater inflow

P_{sr} = total phosphorus from sediment release

P_{out} = total phosphorus flowing out outlet

P_{sed} = total phosphorus trapped in sediments

7.2 Phosphorus Inputs

7.2.1 Groundwater

The phosphorus content of groundwater is normally low; average concentrations are about 20 $\mu\text{g/L}$ (Wetzel 2001). Phosphate-containing minerals are generally relatively insoluble and most phosphorus landing on the ground surface is utilized by plants or adheres to soil particles (Wetzel 2001). Areas in the Lake Pleasant watershed that have been stripped of vegetation, such as cultivated fields, or stripped of vegetation and topsoil, such as gravel-mined areas, increase the rate at which water infiltrates the groundwater. This rapid infiltration decreases the uptake of phosphorus by plants and may increase the amount of phosphorus in groundwater. This is further exacerbated by the addition of fertilizers to agricultural fields and lawns as well as septic system influences on groundwater.

7.2.1.1 Sampling and Analytical Methods for Groundwater

Monitoring wells and drinking water wells were sampled for total phosphorus during summer/fall 2002. The wells were sampled again on September 5, 2003. Prior to 2002 sampling, monitoring wells were purged using a hand bailer until a minimum of three well volumes had been removed. The wells were allowed to recharge before the sample was taken. Drinking water wells were sampled from a faucet nearest the well. The faucet was allowed to run for a minimum of five minutes prior to the sample being taken. All samples were placed in acid-fixed glass bottles, iced and delivered to Microbac Laboratories within two hours of collection.

During the 2003 sampling, above protocols were followed except a battery-operated pump was used to purge the monitoring wells for ten minutes prior to sampling. Microbac Laboratories used EPA test 365.1 for total phosphorus analysis.

Ponds in the gravel pits were sampled for total phosphorus monthly 7/2/02 through 9/16/02. Results from these ponds may not represent a direct impact to Lake Pleasant but may be indicative of impacts to groundwater by exposure to the atmosphere. These ponds may represent a threat to Lake Pleasant if they become a sink for excess phosphorus, possibly contaminating groundwater and promoting the growth of nuisance algae and invasive species in the watershed.

7.2.1.2 Results

Results from the pond samples ranged from 30 µg/L to 420 µg/L with a mean of 132 µg/L (Table 18). A phosphorus concentration of 12,000 µg/L in pond C was not included in the analysis due to contamination of the sample by algae. It is important to note however that pond C is the oldest pond, hand-dug approximately 50 years ago, and is significantly eutrophied as evidenced by thick blooms of filamentous green algae and excessive duckweed growth. Levels of total phosphorus in the newly formed gravel pit ponds are slightly higher than those seen in surrounding groundwater, which may be attributable to algae and plankton communities, inputs from waterfowl excreta, and atmospheric deposition. If pond C is an accurate indication, the gravel pit ponds' phosphorus levels will continue to increase and the ponds will become highly eutrophied in a short time period without proper restoration and management.

Table 18. Summer phosphorus concentrations in gravel pit ponds of the Lake Pleasant watershed

Pond	Total Phosphorus (mg/L)			
	7/2/02	8/15/02	9/16/02	Average
A	60	190	70	107
B	80	170	420	223
C	180	12,000*	--	--
D	70	190	140	133
E	80	120	150	117
F	90	260	130	160
G	70	140	30	80
H	60	150	50	87
Average	86	174	141	132

*disregarded in data analysis due to sample contamination by algae

Table 19 shows the results for groundwater phosphorus concentrations. Phosphorus concentrations were higher during the 2002 sampling possibly due to contamination of the wells by clay particles that had settled in the bottom as a result of drilling the wells. Phosphorus adheres readily to clay due to a difference in ionic charge. The wells had been purged repeatedly between the 2002 sampling and the 2003 sampling for other sampling events. This may have lead to a “cleaning out” of any material that had been in the bottom of the wells during the 2002 sampling.

We calculated groundwater phosphorus contribution using the average flow rate of 2 cfs of groundwater to the lake. This allowed us to estimate total groundwater flowing to the lake of 1.78×10^9 L/year. Given an average concentration of 113.75 µg/L P in the

monitoring wells, we estimate the groundwater contributed 2.03×10^{11} $\mu\text{g P}$ during the budget year.

Table 19. Phosphorus concentrations measured in groundwater in the Lake Pleasant watershed

Sampling Location	Total Phosphorus (mg/L)	
	8/28/02	9/5/03
Lyons W1	180	80
Johnson W1	110	120
Johnson W2	100	100
Lyons M1S	210	70
Lyons M1D	430	110
Lyons M2S	250	130
Lyons M2D	290	80
Gravel M1D	380	220
Average Total Phosphorus (mg/L)	244	114

7.2.1.3 Discussion

Groundwater Point Sources

The only groundwater point sources of phosphorus in the Lake Pleasant watershed are on-lot septic systems associated with the houses and cottages surrounding the lake. Septic systems may be difficult to classify as point sources because of their tendency to diffuse nutrients and organic wastes over a broad area as the plume travels outward from the source. However, because the source can be traced back to a discharge pipe through proper testing, they are considered in this report a point source of pollution.

Impacts to the lake from nutrient loading associated with septic systems is obvious in some cases. One property in particular near the northwest corner of Lake Pleasant has an on-lot septic system located very close to the lake. It is suspected that this system is too close to the lake to provide adequate filtration of nutrients. This is supported by a dense algae bloom and excessive duckweed growth each year that is only evident adjacent to this particular property. Other septic systems around the lake may also be too close to the lake for adequate filtration of nutrients to occur. This unfiltered wastewater may be entering Lake Pleasant from diffuse sources along the shoreline and contributing to the overall nutrient load in Lake Pleasant.

Groundwater Background Source

Phosphorus concentrations were typically higher than what is considered normal for an unpolluted area (~20 µg/L). This may be partly attributable to the high percentage of limestone material in glacially derived soils and geology of the region. Limestone typically contains higher levels of phosphorus (1.3%) than many other forms of parent rock material (Wetzel, 2001). Also, the higher pH levels in soils as a result of the high levels of calcium carbonate in the parent material, promote greater amounts of phosphorus in association as apatites and calcium phosphates (Wetzel, 2001).

7.2.2 Atmospheric Sources

Phosphorus is introduced directly to Lake Pleasant from the atmosphere through rain, snow and dry deposition that falls on the lake surface. Phosphorus also reaches the lake from the atmosphere indirectly by way of stream runoff from precipitation that falls in the watershed. Sources of phosphorus in the atmosphere include natural sources such as fine particles of soil and rocks that have been weathered and transported by wind, as compounds released by plants and natural fires, as well as living and dead organisms (Wetzel, 2001). More importantly, phosphorus is also loaded into the atmosphere through the burning of fossil fuels in automobiles, homes, and industries.

7.2.2.1 Sampling and Analytical Methods for Atmospheric Sources

Rainfall was analyzed for total phosphorus on two separate occasions. A sample was collected at Lake Pleasant on April 14, 2002 and again on September 15, 2002. These samples were collected in a clean, acid-washed plastic bucket and transferred to a glass acid-fixed sample bottle for immediate delivery to Microbac Laboratories.

Snowfall was also analyzed for total phosphorus. A snow sample was taken from the frozen lake surface on February 27, 2003. The sample was a composite core sample from the snow surface down to the ice surface and represented snowfall on the lake surface over several weeks of the winter 2002-2003. The snow was collected in a large, clean glass jar and taken immediately to Microbac Laboratories for analysis.

Dry deposition was the remaining source of atmospheric deposition analyzed for total phosphorus. Dry deposition to Lake Pleasant was captured between April 12 and April 15, 2003 in a clean, acid-washed plastic tray containing distilled water. At the end of the collection period, the water was transferred to an acid-fixed glass bottle for immediate delivery to Microbac Laboratories. By measuring the surface area of the water in the collection tray, the concentration of total phosphorus in the sample delivered to the tray over a specific time period, could be extrapolated to calculate the total phosphorus added to the lake annually through dry deposition to the lake surface. All total phosphorus samples were analyzed using EPA test 365.1 at Microbac Laboratories.

In order to calculate the amount of phosphorus added to the lake, the total phosphorus concentration for each atmospheric constituent was multiplied by the annual amount of that constituent hitting the surface area of Lake Pleasant.

7.2.2.2 Results

The concentration of total phosphorus in the spring rain sample (April 14, 2002) was 50 µg/L and in the summer rain sample (September 15, 2002) was 60 µg/L (Table 20). The concentration of total phosphorus in the snow sample was 60 µg/L. And the concentration of total phosphorus in the dry deposition sample was 110 µg/L. It is assumed that these concentrations are representative of seasonal precipitation and annual dry deposition concentrations.

By measuring total precipitation at Lake Pleasant for the budget year and comparing to long-term averages (40 in/yr), we estimate precipitation contributed 1.495×10^{10} µg P directly to the surface of the lake for the budget year. Dry deposition loading of P to the lake surface was estimated at 6.4×10^9 µg P for the budget year.

Table 20. Phosphorus concentrations introduced to Lake Pleasant from atmospheric sources

Total Phosphorus (mg/L)	Atmospheric Source			
	Spring rain	Summer rain	Snow	Dry deposition
	50	60	60	110

7.2.3 Surface Inflow

In general, phosphorus concentrations in surface water are closely related to phosphorus concentrations in the surrounding soil (Wetzel, 2001). Surface flow phosphorus levels may be increased as a result of atmospheric deposition, agriculture and lawn fertilizers, sewage, and other pollution sources. Lake Pleasant receives stream inflow from two small tributaries that flow only during wetter periods throughout the year. One of these streams, UNT 2, flows through wetlands in the riparian area before entering the southwest corner of the lake. Both UNT 1 and UNT 2 flow into Lake Pleasant from the west where the littoral zone is up to 20-30m wide. Plants and soils in the riparian wetlands and littoral zone are capable of up taking nearly all nutrients entering the lake by way of these tributaries (Wetzel, 2001). Of course, much of the nutrient loading by these streams probably occurs during the early spring runoff, prior to the growing season, when agricultural fields and other areas are denuded of vegetation, laden with fertilizer and under significant snow cover.

7.2.3.1 Sampling and Analytical Methods for Surface Inflow

Total phosphorus was sampled weekly at sampling points center, outlet, bridge and UNT 2 from 11/4/01 through 5/7/02. Weekly sampling resumed 7/2/02 through 11/5/02. Total phosphorus was not sampled 5/7/02 through 7/2/02 because total phosphorus data for that

time period was contributed by Dr. Milt Ostrofsky, Allegheny College. Utilizing previously collected data allowed us to focus funding elsewhere and conserve resources.

Water samples were collected for the entire water column at 1-meter intervals from sampling point, center, using a Kemmerer sampler from 11/4/01 through 5/7/02. Later sampling was reduced to three samples at sampling point, center, to represent the epilimnion, metalimnion, and hypolimnion and reduce sampling costs. A single sample was taken weekly from sampling points, outlet and bridge, mid-depth in the water column using the Kemmerer sampler. The mouth of UNT 2 was accessed via kayak and sampled weekly when flows were sufficient to avoid back-up of lake water into the channel.

UNT 1 was sampled weekly 4/24/02 through 5/7/02 and 7/2/02 through 11/5/02 when the stream was flowing. Sampling point, north, was sampled weekly 7/2/02 through 11/5/02 at two depths, just below the surface and just above the lake bottom. This site was added to detect differences in total phosphorus that may be attributable to inputs from the north end of the lake. Discharge was calculated for UNT 1 during each sampling event. Discharge measurements for UNT 2 were not possible due to access issues from a private landowner. For the purposes of this study, we monitored discharges at UNT 3 and used those to estimate discharge of UNT 2. While admittedly this procedure lacks certainty, UNT 3 drains a smaller watershed than UNT 2 and was consistently lower in discharge than UNT 2. As a result, our estimate of discharge and subsequent P loading for UNT 2 is conservative.

7.2.3.2 Results

Total phosphorus concentrations at surface inflow and outflow sites are listed in Table 21 for the budget year. Phosphorus concentrations leaving the lake by way of the outlet increased following fall and spring turnover, shown in yellow. This is a result of phosphorus being released from the anoxic sediments during the summer and winter stratified periods and getting mixed throughout the water column during turnover. Increases in phosphorus at surface flow points on 4/30/02 and 5/7/02 coincided with a major rain event and are shown in green. Fall and winter phosphorus concentrations in UNT 2 also appear to be high and are shown in blue. Land use in the tributary watershed includes a small dairy farm and rowcrops. Barnyard runoff, livestock access to the stream, and fertilizers applied to crop fields are probably contributing to the nutrient load in UNT 2.

We estimate total P loading by UNT 1 and UNT 2 to be 1.183×10^{10} $\mu\text{g P}$ for the budget year.

Table 21. Total phosphorus concentrations at surface flow sampling points in the Lake Pleasant watershed for the budget year

Date	Total Phosphorus (mg/L)			
	Outlet	Bridge	UNT 1	UNT 2
11/4/01	30	110	nd	180
11/12/01	160	220	nd	150
11/19/01	60	80	nd	170
11/28/01	160	50	nd	90
12/6/01	230	90	nd	260
12/11/01	240	150	nd	250
12/20/01	80	110	nd	80
12/26/01	140	80	nd	Ice
2/18/02	ice	90	nd	Ice
3/11/02	90	110	nd	160
3/27/02	40	60	nd	80
4/1/02	40	100	nd	40
4/10/02	430	410	nd	30
4/17/02	220	40	nd	230
4/24/02	40	30	140	50
4/30/02	170	210	90	40
5/7/02	180	170	280	140
7/2/02	110	110	dry	dry
8/15/02	180	170	dry	dry
9/16/02	30	nd	90	dry
9/24/02	nd	90	dry	dry
10/2/02	nd	130	100	dry
10/9/02	nd	120	dry	dry
11/6/02	80	nd	dry	dry

7.2.4 Internal Loading

Phosphorus trapped in the sediments can be reintroduced to the water column under reducing conditions that occur in the anoxic hypolimnion during periods of summer and winter stratification (Figure 24). This process, known as internal loading, can be a significant source of phosphorus for lakes and must be considered when determining a phosphorus budget. Internal loading rates for Lake Pleasant were calculated using summer 2000 data provided by Dr. Milt Ostrofsky, Allegheny College. Partnering with Dr. Ostrofsky allowed us to better utilize limited funding and avoid duplication of efforts. We assumed internal loading rates were consistent between summer 2000 and the budget year, summer 2002. The severity of winter hypolimnetic oxygen deficit varies annually with duration of ice cover. Sampling through the ice in late winter 2001-2002 did not indicate substantial phosphorus accumulation in the hypolimnion. Moreover, phosphorus levels throughout the water column were much lower in the winter than the spring and summer periods when sources of phosphorus would be more prevalent in the watershed.

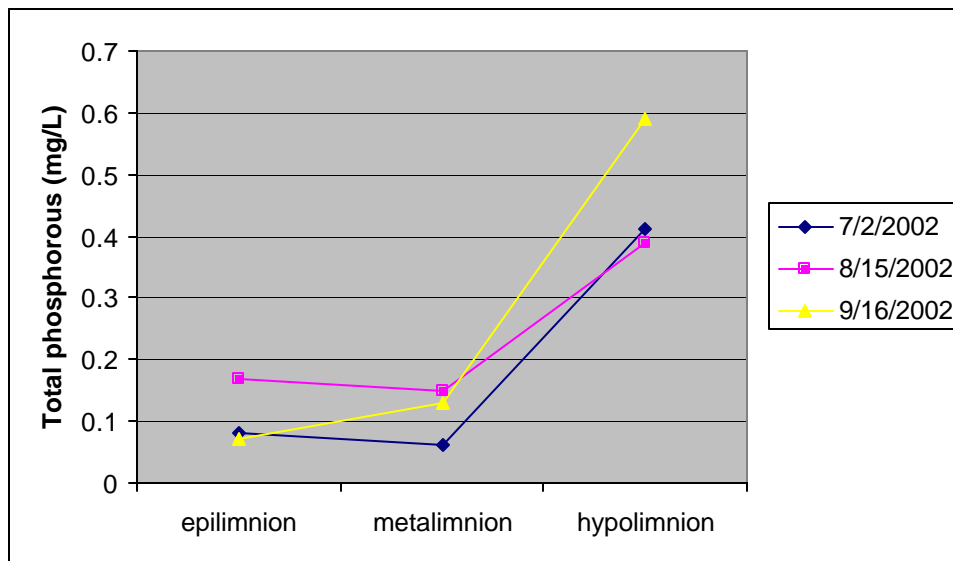


Figure 24. Increase in total phosphorus in the hypolimnion during anoxic summer conditions

7.2.4.1 Calculation of Internal Loading

Internal loading of phosphorus from sediment release was estimated by calculating the mass of phosphorus in the hypolimnion as the sum of the products of the volume of water in each meter of the hypolimnion (Table 22) and the concentration of phosphorus measured in that meter. Figure 25 shows the mass of phosphorus in the hypolimnion as a function of time. These calculations were based on methods used by Ostrofsky and Owen in a similar study on Conneaut Lake (1989). Estimations of water volume per stratum in the hypolimnion were made by Ostrofsky and contributed to this study.