

Figure 20. Average total alkalinity values for Lake Pleasant from 9/16/02 – 10/17/02 while the lake was stratified and total alkalinity on 11/5/02 when the lake was mixed

Lake Pleasant has been categorized as an alkaline lake. Alkalinity is a measure of the acid-neutralizing capacity of an aqueous system (Stumm and Morgan, 1981). The pH value at the titration equivalence points used in alkalinity and acidity determinations, 4.5 and 10.3 represent approximate thresholds below and above which, respectively, life would be impaired (Stumm and Morgan, 1981). In other words, alkalinity is a measure of the extent to which a water body will be able to naturally buffer against large fluctuations in pH (Stumm and Morgan, 1981).

Carbon Dioxide (CO₂) is about 200 times more soluble in water than oxygen (Wetzel, 2001). In water, CO₂ hydrates to form H₂CO₃. H₂CO₃ (carbonic acid) dissociates to form HCO₃⁻ (bicarbonate ion) and free H⁺ ions, which increases the pH of the system. The bicarbonate ion further dissociates to form CO₃²⁻ (carbonate ion) and another free H⁺. The bicarbonate ion and carbonate ion can each dissociate to form OH⁻ (hydroxyl ion). The increase in concentration of hydroxyl ions increases the overall pH of the system. The overall sets of equations are:



The lake becomes enriched with CO₂ as a byproduct of respiration.

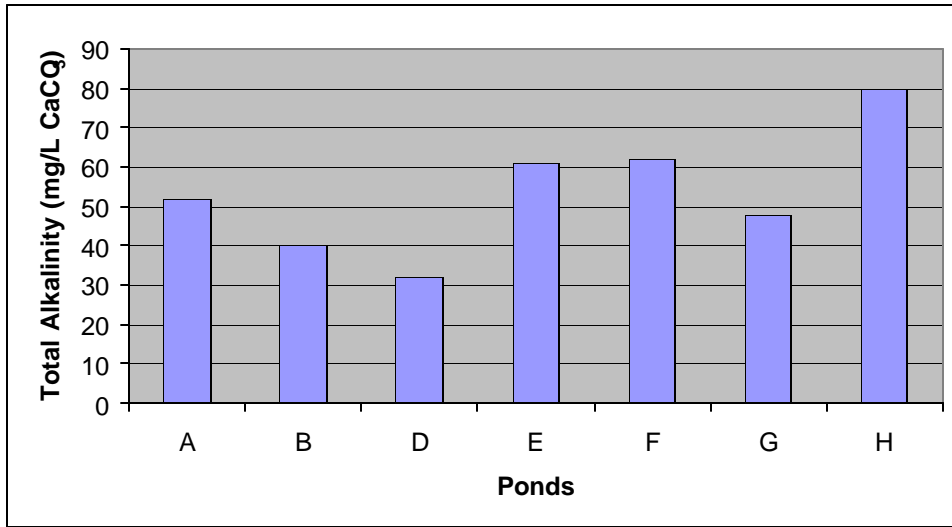


Figure 21. Total alkalinity measured in all gravel pit ponds, 9/16/02

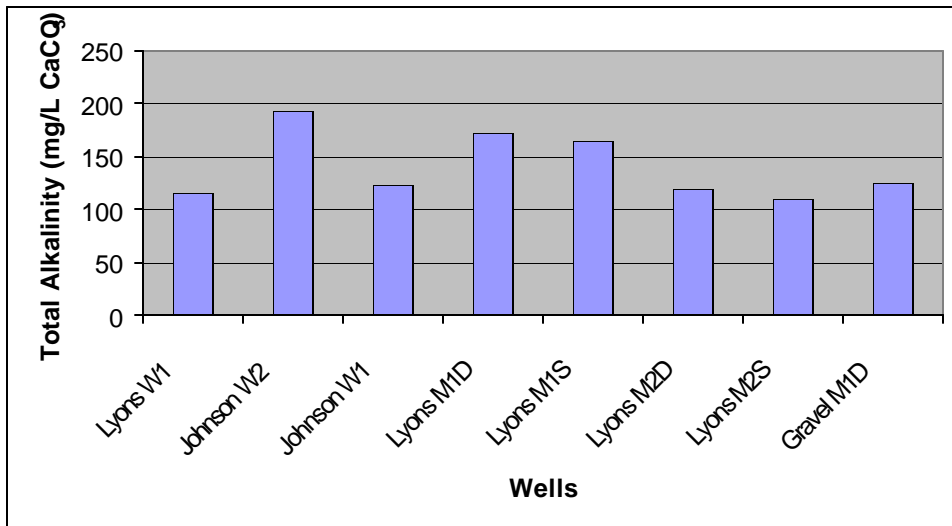


Figure 22. Total alkalinity measured in all monitoring wells, 10/9/02

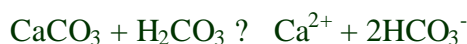
Table 7. Total alkalinity comparison between tributary streams and lake surface

Date	Total alkalinity (mg/L CaCO ₃)		
	UNT 1	UNT 2	Lake Surface
11/12/2001	--	110	100
11/19/2001	--	104	102
11/28/2001	--	96	90
12/6/2001	--	134	112
12/11/2001	--	128	110
12/20/2001	--	80	106
12/26/2001	--	ice	112
2/18/2002	--	ice	58*
3/11/2002	--	98	94
3/27/2002	--	26	86
4/1/2002	--	28	82
4/10/2002	--	28	82
4/17/2002	--	38	88
4/24/2002	28	42	88
4/30/2002	22	36	88
5/7/2002	26	44	84

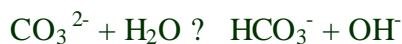
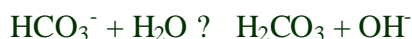
*lake surface frozen, sampled through ice

Lake Pleasant is situated in a limestone rich glacial till. Limestone (CaCO₃) is only slightly soluble in pure water; however, the presence of carbonic acid, increases its solubility, freeing calcium ions and sequestering H⁺ ions, reducing the pH (creating a more alkaline environment) and increasing the hardness of the water.

The CO₂ reacts and produces carbonic acid. Calcium bicarbonate dissociates, increasing both the concentrations of Ca²⁺ and HCO₃⁻ (Wetzel, 2001):



As mentioned previously, further dissociations occur, resulting in an alkaline system due to the addition of hydroxyl ions:



When H^+ ions are added to this type of system, they react with OH^- immediately, producing neutral water molecules. However, simultaneously, more hydroxyl ions are being produced. In this way, waters of carbonate lakes act as buffers, resisting change in the pH of the system despite any acidic inputs (acid rain, for example). This system remains intact as long as the limestone/carbonic acid interactions continue, replenishing the CO_3^{2-} supply (Wetzel, 2001). Added hydroxyl ions would react with bicarbonate to make carbonate and water.

“The ontogeny of an oligotrophic lake toward eutrophic conditions can be altered markedly by natural inputs of carbonates and associated cations from surrounding sedimentary bedrock and glacial till” (Wetzel, 2001). Often, oligotrophic states are maintained due to decreased nutrient availability affected by steady calcareous inputs to the system (Wetzel, 2001). The glacial till and sedimentary bedrock in the area naturally contain high concentrations of carbonates. In these regions, “high inputs of carbonates can be maintained over a long period of time (millennia)” (Wetzel, 2001).

Succession of a calcareous lake to a eutrophic lake can occur with decreased $CaCO_3$ inputs and/or increased dissolved organic matter. Phosphate, iron and manganese tend to form insoluble compounds with carbonates and precipitate out into the sediment (Wetzel, 1983).

Many of the plants of special concern that have been identified in the lake’s watershed are characteristic of glacial lakes and/or calcareous waters and are likely to be particular to specific water chemistry requirements for survival. These plants include *Aster borealis*, *Cardamine pratensis* Var *Palustris*, *Carex diandra*, *Carex prairea*, *Cladium mariscoides*, *Eleocharis olivacea*, *Epilobium strictum*, *Megalodonta beckii*, *Myriophyllum exallescens*, *Potamogeton friesii*, *Potamogeton illinoensis*, *Potamogeton friesii*, *Potamogeton richardsonii*, and *Rhamnus alnifolia*. Disruption of these communities may lead to elevated populations of exotic species. Exotics such as *Typha* spp. (cattail) and *Phragmites* spp. (common reed) can be considered opportunists in that they can thrive under conditions that are less than optimal for the rare species of plants. Once given the opportunity to establish their own community, they can replace the existing, more sensitive plant community because they are better competitors for light, CO_2 , space, etc and can survive under a wider range of environmental conditions.

“Hardly a group of freshwater animals exists in which the distribution of some species has not been related to calcium concentration. Like algae and certain macrophytes, in some groups, most of the species found in calcareous waters, and their numbers decrease as the concentration of calcium declines” (Wetzel, 1983).

5.1.8 Other Analytes

5.1.8.1 Total Solids: Dissolved and Suspended

Total solids is a measure of all material, organic and inorganic, that is in water and can be suspended or dissolved in solution. It is used as an indicator of how much material might be washing off roadways or parking lots, eroding from stream banks or fields, or being contributed by other sources. Water will naturally contain a certain amount of solids

from normal weathering of rock and soil. If the amount of solids suspended or dissolved in water becomes too high, it could limit the amount of light penetration and plant growth and may indicate high levels of nutrients or other pollutants. Runoff that enters the lake via streams or directly as surface flow tends to carry higher levels of suspended solids while groundwater typically has higher levels of dissolved solids from the surrounding geology.

Total, suspended and dissolved solids were measured weekly from 11/6/01 through 5/7/02. Suspended solids in Lake Pleasant were typically <5 mg/L, therefore only total dissolved solids were measured from the lake for the remainder of the study. Total dissolved solids (TDS) were measured from the lake, ponds, and streams through 11/5/02 and from the wells on 8/28/02 and 10/9/02. Total suspended solids (TSS) were measured from UNT 1 and UNT 2. Results are presented in Tables 8-10.

Table 8. Total dissolved solids (TDS) and total suspended solids (TSS) for sampling points center, bridge, UNT 1 and UNT 2

Date	Total Dissolved Solids (mg/L)				Total Suspended Solids (mg/L)	
	Center	Bridge	UNT 2	UNT 1	UNT 2	UNT 1
11/6/2001	170	164	174	nd	<5	nd
11/12/2001	164	150	165	nd	15	nd
11/19/2001	158	152	176	nd	44	nd
11/28/2001	153	130	150	nd	60	nd
12/6/2001	159	160	160	nd	10	nd
12/11/2001	181	160	200	nd	<5	nd
12/20/2001	148	120	110	nd	40	nd
12/26/2001	135	120	ice	nd	ice	nd
2/18/2002	156	120	ice	nd	ice	nd
3/11/2002*	200	130	150	nd	<5	nd
3/27/2002	154	110	80	nd	<5	nd
4/1/2002	141	100	65	nd	<5	nd
4/10/2002	161	130	78	nd	12	nd
4/17/2002	144	120	61	nd	19	nd
4/24/2002	158	140	79	67	19	17
4/30/2002	151	120	68	57	6	18
5/7/2002	149	160	94	80	<5	19
7/2/2002	153	nd	dry	dry	dry	dry
8/15/2002	nd	nd	dry	dry	dry	dry
9/16/2002	157	nd	dry	dry	dry	dry
9/24/2002	173	nd	dry	dry	dry	dry
10/2/2002	160	nd	dry	dry	dry	dry
10/9/2002	157	nd	dry	dry	dry	dry
10/17/2002	160	nd	dry	dry	dry	dry
11/5/2002	92	nd	dry	dry	dry	dry

*immediately following ice-off

Higher levels of suspended solids seen in UNT 1 and UNT 2 coincide with rain and snow events during winter and spring months. These streams drain a dairy farm and an area that has been gravel mined. Both of these land use activities could be sources for increased sediment and suspended solids.

Table 9. Total dissolved solids (TDS) in the gravel pit ponds

Date	Total Dissolved Solids (mg/L)							
	A	B	C	D	E	F	G	H
7/2/2002	170	110	230	67	150	130	140	110
9/16/2002	160	120	nd	98	110	160	99	150

Table 10. Total dissolved solids (TDS) in the wells

Date	Total Dissolved Solids (mg/L)			
	Lyons W1	Johnson W1	Johnson W2	Lyons M1D
8/28/2002	200	nd	nd	310
10/9/2002	200	170	270	280

Date	Lyons M1S	Lyons M2D	Lyons M2S	Gravel M1D
8/28/2002	250	210	200	260
10/9/2002	230	210	180	250

5.1.8.2 BOD, COD and TOC

The biochemical oxygen demand (BOD) of a sample is representative of the amount of oxygen (mg/L) required by microorganisms to completely oxidize any organic matter present. Chemical oxygen demand (COD) is a similar analysis to BOD, but uses a chemical oxidant in place of the microorganisms. Both of these methods provide an indirect estimate of the amount of organic material in a sample.

The total organic carbon of a sample is measured by the chemical oxidation of a sample followed by direct analysis for CO₂. The TOC is a more direct measure of the amount of organic waste present in a water body and that enters a water body by run off – including herbicides, pesticides, and detritus.

BOD, COD, and TOC were measured in Lake Pleasant on the following dates and sampling locations. Results are summarized in Table 11:

- 7/2/02 and 7/3/02: north; center; outlet; ponds a,b,c,d,e,f,g,h
- 9/16/02: north; center; outlet; ponds a,b,d,e,f,g,h
- 9/24/02: north; center; outlet
- 10/2/02: north; center; outlet
- 10/9/02: north; center; outlet
- 10/17/02: north; center; outlet

Table 11. Summary of BOD, COD, and TOC measurements in the Lake Pleasant watershed

Parameter	Location ID	Average (mg/L)	Min (mg/L)	Max (mg/L)	SD	Count (n)
BOD ₅	North	2	2	2	0	12
BOD ₅	Center	8	2	35	10.8	17
BOD ₅	Outlet	2	2	2	0	6
BOD ₅	All ponds	5.93	2	26	7.48	15

Parameter	Location ID	Average (mg/L)	Min (mg/L)	Max (mg/L)	SD	Count (n)
COD	North	11.25	15	19	3.82	12
COD	Center	15.6	3	64	14.6	17
COD	Outlet	12.3	5	18	5.99	6
COD	All ponds	30.1	7	94	23.1	14

Parameter	Location ID	Average (mg/L)	Min (mg/L)	Max (mg/L)	SD	Count (n)
TOC	North	3.57	3.1	4.9	0.485	12
TOC	Center	4.52	2.8	11.1	1.90	17
TOC	Outlet	3.72	3.4	4.3	0.33	6
TOC	All ponds	5.78	3.5	9.5	1.79	15

5.1.8.3 Nitrogen

Nitrogen is one of the most important nutrients for primary production in aquatic systems. Sources of nitrogen include atmospheric deposition from anthropogenic pollution sources, direct fixation from atmospheric molecular nitrogen, decomposition of nitrogenous organic compounds, agricultural activities, and sewage. Nitrogen cycles through freshwater systems in a complex cycle known as the nitrogen cycle. Much of the nitrogen cycling in freshwater systems is controlled by bacteria and to a lesser extent, algae and vascular plants.

Nitrogen levels in the epilimnion are normally very closely associated with atmospheric molecular nitrogen levels. As the epilimnion warms and solubility decreases, levels of nitrogen in the epilimnion may decrease (Wetzel, 2001). During periods of anoxia in the hypolimnion, nitrogen fixation by aerobic bacteria ceases and nitrogen levels increase in

the hypolimnion (Wetzel, 2001). Because of the availability of nitrogen from natural atmospheric sources as well as anthropogenic sources, nitrogen levels are typically more than sufficient to meet primary production needs in freshwater systems. Other nutrients important for primary production but existing in much lower concentrations become limiting. It has been proposed that the lower concentrations of phosphorus in area lakes in relation to nitrogen levels make phosphorus the limiting nutrient for primary production (Ostrofsky and Owen, 1989). In other words, with the abundance of nitrogen naturally occurring, if phosphorus inputs to a lake ecosystem are controlled, primary production (algae and plant biomass) and the eutrophication process can be controlled. It has been estimated that if the ratio of nitrogen to phosphorus is at least 12:1, then phosphorus will be the limiting nutrient (Ostrofsky and Owen, 1989).

Levels of total nitrogen and total phosphorus were measured during fall turnover in 2001. The average ratio of nitrogen to phosphorus in the water column was greater than 25:1. Based on this analysis, it was determined that phosphorus was the limiting nutrient driving primary production in the Lake Pleasant ecosystem. A determination was made to forego further nitrogen sampling in order to conserve funding. Instead, the study focused on phosphorus levels in the lake, as well as inputs and outflows of phosphorus in order to create a phosphorus budget for the lake. Results of phosphorus analysis and a detailed phosphorus budget are presented in section 7.

5.1.8.5 Total Phosphorus

Total phosphorus concentrations at sampling point, center, are shown in Figure 23. It is important to note that data collected November 4, 2001 through May 7, 2002 was analyzed at Microbac Laboratories. Data from May 12 through September 20 was collected in 2000 and analyzed by Dr. Milt Ostrofsky, Allegheny College. We made the assumption that phosphorus data did not vary significantly from year to year and utilized the existing data in order to minimize costs. While there are apparent differences in results between the two labs, it is important to note that phosphorus concentrations are not significantly different as a function of depth except when oxygen levels drop in the hypolimnion during periods of summer and winter stratification. The anoxic conditions in the hypolimnion allow phosphorus bound to the sediments to be reintroduced to the water column. This phenomena will be discussed in section 7.2.4.

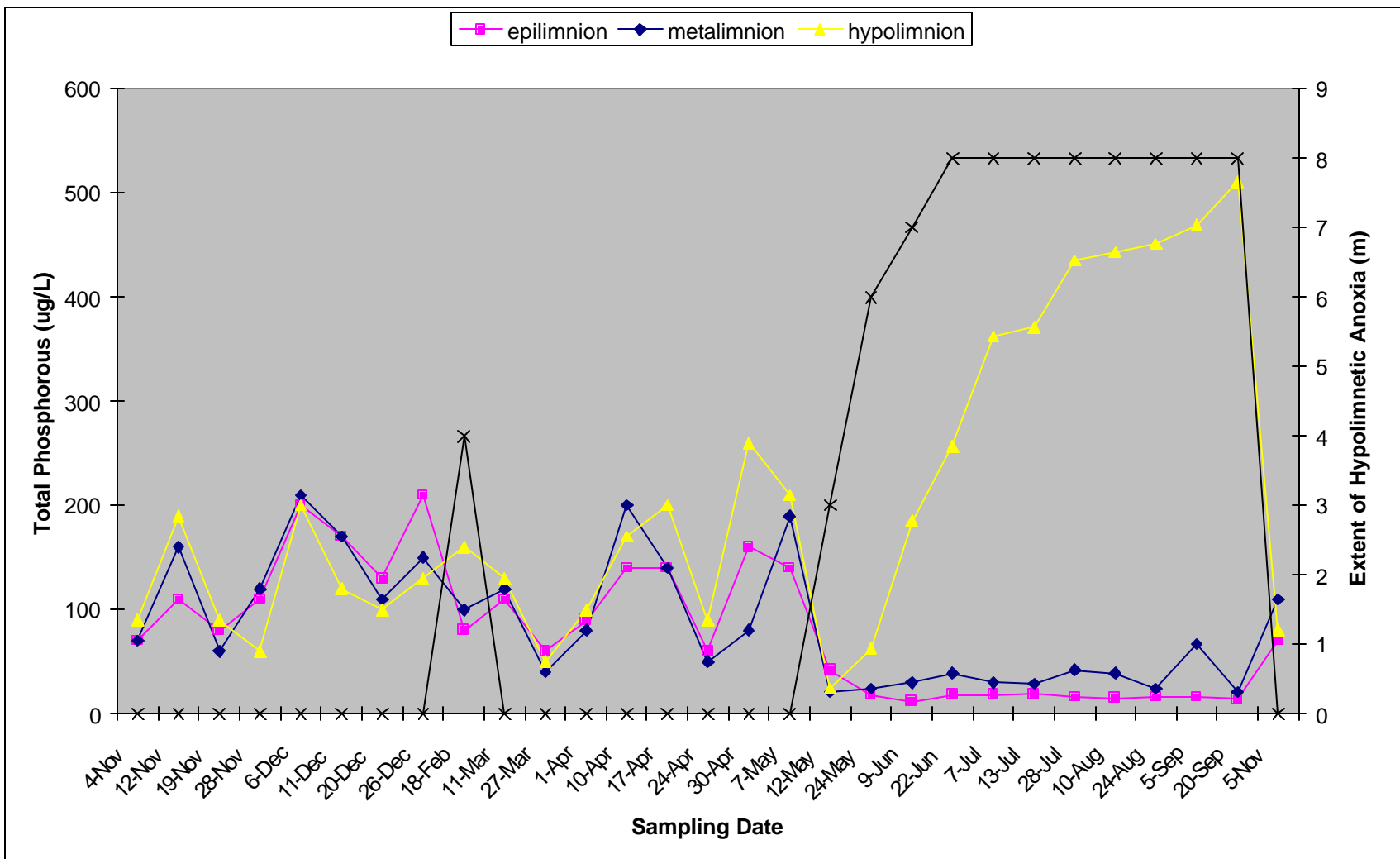


Figure 23. Total phosphorus concentrations in the epilimnion, metalimnion and hypolimnion throughout the budget year

6. METALS ANALYSIS

6.1 Background

Elemental metals are naturally occurring: they cycle within an ecosystem as different ionic species and compounds. Life could not be sustained without some metals, such as those considered to be macronutrients: calcium, magnesium, iron, potassium, and sodium (Chang and Cockerham, 1994). The trace elements – chromium, cobalt, copper, manganese, nickel, selenium, and zinc – serve as structural components of molecules and cofactors in metabolic processes but are required in much smaller amounts (Chang and Cockerham, 1994). Both macronutrients and trace elements can be toxic if present in excessive concentrations. Other metals can have negative effects on an organism in relatively small amounts and are not required for biological processes. These metals include lead, cadmium, and mercury (Chang and Cockerham, 1994).

Because the impacts of pollution on Lake Pleasant and its wetlands have been identified as one of the goals in the development of a management plan (Management Objective 1: Principal Study Components 1 and 2, Section 1.2.1), and because of its existing populations of species of special concern, Lake Pleasant was assessed relative to the risk that certain metals pose to the health of aquatic organisms – including fish, plants, arthropods, etc. A starting point for the selection of analytes was the EPA’s list of priority pollutants. Priority pollutants were defined in section 307 (a) of the Clean Water Act (CWA) as “the most persistent, prevalent, and toxic chemicals” that “could compromise or interfere with a waterbody’s designated use” when present in a great enough concentration (EPA, 1999). In the current literature, metals identified as priority pollutants include: Antimony, Arsenic, Beryllium, Cadmium, Chromium (III and VI), Copper, Lead, Mercury (elemental and Methylmercury), Nickel, Selenium, Silver, and Zinc (EPA, 2002). Cobalt, although not listed as a priority pollutant, was also included in this analysis because of its role as a trace element.

6.1.1 Threshold Values

Ecological risk assessments use data from previous toxicological studies in the form of threshold values to estimate the likelihood that undesirable effects (reduction in reproductive fitness, unfavorable genetic mutations, altered growth and development, untimely death, etc.) would occur, given a set of existing or projected conditions. Risk assessments are helpful in the process of determining the state of a waterbody; but it must be made clear that these analyses are estimates because they are based on many assumptions. Specific uncertainties will be addressed topic by topic.

Threshold values are screening tools used in making these estimations and are useful when determining if a considerable risk to the health of aquatic animals exists due to a particular constituent concentration in the water. Threshold values are readily available through government agencies such as the EPA and the National Oceanic and Atmospheric Administration (NOAA).

The threshold values used in this study are the Criterion Maximum Concentration (CMC) and the Criterion Continuous Concentration (CCC). The CMC is equal to one-half of the final value calculated for short-term toxicity tests for a given parameter in aquatic organisms (Final Acute Value) (EPA, 1986). CMC's are acute values, or values that have been shown to have observable short-term exposure effects – most commonly, death due to temporarily elevated concentrations of a constituent (NCDWQ, 2001). The Criterion Continuous Concentration (CCC) is equal to the lowest of the Final Chronic Value, the Final Plant Value, or the Final Residue Value (EPA, 1986). The CCC may also be obtained from one or a combination of the Final Chronic Equation, the Final Plant Value, and/or the Final Residue Value if the toxicity values are related to water quality (EPA, 1986). CCC values are chronic concentrations, or measures of the concentrations at which long term, repeated, or continuous exposure to a constituent will cause measurable adverse effects on an organism, such as a decrease in reproduction rates, or abnormal growth and development (NCDWQ, 2001).

Biological toxicity data must be available for at least one species in a minimum of eight different families for the derivation of acute and chronic aquatic health threshold values (EPA^A, 2002): the CCC and CMC values are rounded to two significant digits upon calculation (EPA, 1986).

The criterion is stated as: The procedures described in the Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses indicate that, except possibly where a locally important species is very sensitive, freshwater aquatic organisms and their uses should not be affected unacceptably if the 4-day average concentration of the constituent of interest does not exceed the CCC more than once every 3 years on the average and if the 1-hour average concentration does not exceed the CMC more than once every 3 years on the average (EPA, 1986).

CCC and CMC values from EPA's National Recommended Water Quality Criteria for Priority Toxic Pollutants (NRWQC) and from the NOAA Screening Quick Reference Tables (NOAA SQuiRTs) were compared to detection limits obtained by the laboratory chosen to run the samples, Microbac, Inc. in Erie, Pa., to ensure that the detection limits were below the threshold values. The detection limit is the lowest concentration that the lab can detect in a given sample and varies from analyte to analyte. For example, if the detection limit for copper was 200 mg/L, and the concentration in the lake was under that limit, the results would be reported as <200mg/L. If the threshold limit was 50mg/L, it would be unclear whether the concentration of copper in the sample was between 200 and 50mg/L (an unsafe value), or if the concentration fell below 50mg/L (a safe value). Again, safe is defined as the level at which no adverse effects will occur in aquatic organisms. Published CCC and CMC values along with Microbac laboratory detection limits and test methods for metals in groundwater and surface water are listed in Table 12.

Table 12. Microbac, Inc.’s method detection limits for priority metals relative to the associated ecological criteria for surface water and groundwater

Metal	Microbac Method Detection Limits (mg/l)	Surface and Groundwater Test Method	CMC (mg/L)	CCC (mg/L)
Antimony ^a	3	SM 183113B	88	30
Arsenic ^a	5	SM 18 3114B	340	150
Beryllium ^a	1	200.7	130	5.3
Cadmium ^{a,b}	3	200.7	2.0	0.25
Chromium (tot)	22	200.7		
Cobalt	10	200.7		
Copper ^{a, b}	10	200.7	13	9
Lead ^{a, b}	50	200.7	65	2.5
Mercury ^a	0.2	SM 18 3112B	1.4	0.77
Nickel ^{a, b}	14	200.7	470	52
Selenium ^a	2	SM 18 3114B	13-186 total	5.0
Silver ^{a, b}	20	200.7	3.2	
Zinc ^{a, b}	11	200.7	120	120

Criteria Maximum Concentrations (CMC) are acute dissolved threshold values. The Criteria Continuous Concentrations (CCC) are chronic dissolved threshold values. Selenium, however, is expressed as a total recoverable value. CMC and CCC values are calculated for 100mg/l hardness as CaCO₃. CMC and CCC values are from EPA 2002 with the exception of Antimony (proposed value), Beryllium (Lowest Observed Effects Level), and Selenium (CMC, only) both from NOAA 1999. ^a indicates metals that are Priority Pollutants. ^b indicates metals that have CCC and/or CMC values that are hardness dependant. The threshold values listed in the table are intended to be demonstrative and have been calculated assuming a hardness value of 100mg/L CaCO₃. Metals and their detection limits that are bolded indicate that the method detection limits are insufficient to meet threshold screening criterions. All analytes listed are included in the analysis of a single sample of groundwater or surface water.

Although groundwater samples are often held to drinking water standards, in this study groundwater will be held to CMC and CCC surface water standards. This will be done to assess the quality of groundwater in relation to the organisms of the ecosystem, not humans. Assuming that the groundwater entering the system is diluted, or is mixed with water from other sources, CMC and CCC values are likely to be overprotective.

For some threshold values, adjustments must be made to approach a more accurate representation of Lake Pleasant’s water chemistry. Hardness, or the sum of the Ca²⁺ and Mg²⁺ ions in a sample, can increase the threshold value, or decrease the toxicity of certain metals (EPA, 2002). These metals, Cadmium, Chromium ³⁺, Copper, Lead, Nickel, Silver, and Zinc, are referred to as hardness dependent. Published threshold values are calculated for 100mg/L hardness as CaCO₃ for illustrative purposes (EPA, 2002); however, most of the measured hardness values for Lake Pleasant are above 100mg/L. Due to the mathematical relationship established between the threshold values and the hardness expressed as CaCO₃ (Table 13), hardness values measured in Lake Pleasant will increase CCC and CMC thresholds above those published. Therefore, any concentrations

that did not exceed the CCC or CMC expressed in relation to 100mg/L hardness as CaCO₃ were excluded without further calculations. If a given metal concentration was above one or both of the threshold values, accurate hardness specific CCC and CMC values were determined by inserting the measured hardness at each applicable sampling point where an exceedance was observed into the formulas given in Table 13.

Table 13. Equations for the derivation of total recoverable Criteria Continuous Concentration (CCC) and Criteria Maximum Concentration (CMC) values for hardness dependent metals

Metal	Hardness Calculations	
	CMC	CCC
Cadmium	$CMC = e^{1.0166 [\ln(\text{hardness})] - 3.924}$	$CCC = e^{0.7409 [\ln(\text{hardness})] - 4.719}$
Chromium III	$CMC = e^{0.819 [\ln(\text{hardness})] + 3.7256}$	$CCC = e^{0.819 [\ln(\text{hardness})] + 0.6848}$
Copper	$CMC = e^{0.9422 [\ln(\text{hardness})] - 1.7}$	$CCC = e^{0.8545 [\ln(\text{hardness})] - 1.702}$
Lead	$CMC = e^{1.273 [\ln(\text{hardness})] - 1.46}$	$CCC = e^{1.273 [\ln(\text{hardness})] - 4.705}$
Nickel	$CMC = e^{0.846 [\ln(\text{hardness})] + 2.255}$	$CCC = e^{0.846 [\ln(\text{hardness})] + 0.0584}$
Silver	$CMC = e^{1.72 [\ln(\text{hardness})] - 6.59}$	CCC – no criteria
Zinc	$CMC = e^{0.8473 [\ln(\text{hardness})] + 0.884}$	$CCC = e^{0.8473 [\ln(\text{hardness})] + 0.884}$

For samples that exceeded the CCC and/or CMC values calculated at 100mg/L hardness expressed as CaCO₃ (Table), a hardness specific value was calculated by inputting the hardness value measured at the sampling point as closely as possible to the day that the specific metal concentration was measured. The hardness dependent equations were taken from EPA’s National Recommended Water Quality Criteria for Priority Toxic Pollutants (EPA 2002).

Copper, Lead, Selenium, and Silver had threshold values that were below detection limits. However, because Copper, Lead, and Silver are hardness dependant metals (EPA, 2002), the thresholds will increase due to measured hardness values above 100mg/L CaCO₃. Any detection limits that continued to fall above thresholds upon hardness specific calculations will be addressed later.

Furthermore, samples taken from Lake Pleasant are representative of total metals concentrations. An analysis expressed as the total metal concentration consists of the dissolved component plus the particulate component of a metal in a sample. The dissolved component consists of ionic or complexed (as carbonates, oxides, or organics) forms of the metal. When a sample is analyzed for the total or total recoverable metal concentration in a lab, acid is used to digest the particulate matter, allowing for detection. A total metals analysis uses a greater concentration of acid and a greater temperature in the analysis than total recoverable metals concentrations (EPA, 1992a); therefore, a total

metals analysis will generally allow for greater detection of constituent. Analysis of the total metals content in water samples from Lake Pleasant ensures that the criteria used will be protective to overprotective.

Dissolved values discount particulate metal and may be detrimental to aquatic life. Metals can enter an organism through phagocytosis or by uptake in their soluble (dissolved) form (Chang and Cockerham, 1994). Generally, metal toxicity increases with increasing acidity because the dissolved metal component increases with increasing acidity. Given this, the acidic environment present in the vicinity of a fish's gills, or within its stomach, may contribute locally to increased toxicity (EPA, 1992a), and may make particulate metals more biologically available.

Published CCC's and CMC's are expressed as dissolved metals, but can be converted to total recoverable values. The EPA's NRWQC calculated the dissolved metal CCC and CMC values for Cadmium, Chromium (III), Copper, Lead, Nickel, Silver, and Zinc using the total recoverable value obtained from the hardness dependent calculations in Table 13 multiplied by a dissolved metals conversion factor (CF) listed in Table 14 (EPA, 2002). To obtain a total recoverable value, the CF step was omitted. Published values that were not hardness dependent – Arsenic, Chromium (VI), and Mercury were already multiplied by the appropriate CF to obtain a published dissolved value (EPA, 2002). In those cases, dividing the published value by the CF is necessary to obtain the total recoverable value. The Selenium CCC is published as the total recoverable value, making alterations unnecessary. Antimony, Beryllium, and Selenium (CMC only) values were obtained from the NOAA SQUIRT's. The Antimony value is a proposed concentration and the Beryllium value is the Lowest Observable Effects Level (LOEL) (NOAA, 1999). A LOEL is the lowest dose given in a toxicity test that produces observable effects on the test organism (Page, 1994).

Because the dissolved metal concentration is a fraction of the total metal concentration in a sample, the dissolved value alone will always be less than or equal to the total value. Given this, if the total concentration of a given metal does not exceed dissolved threshold values, it will not exceed the larger threshold value calculated in terms of total recoverable metals. Therefore, calculation of the total recoverable threshold values in these cases is unnecessary.

Both groundwater and surface water were sampled for metals screening. Water sample results were compared to threshold values for each metal to determine if any of the selected parameters exceeded this calculated risk level derived from toxicological studies.

Table 14. Unfiltered (total) to filtered (dissolved) metals conversion factors

Metal	Unfiltered to Filtered Conversion Factors	
	CMC	CCC
Arsenic	CF = 1	CF = 1
Cadmium	CF = 1.136672 – [(ln hardness) (0.041838)]	CF = 1.136672 – [(ln hardness) (0.041838)]
Chromium ³⁺	CF = 0.316	CF = 0.860
Chromium ⁶⁺	CF = 0.982	CF = 0.962
Copper	CF = 0.960	CF = 0.960
Lead	CF = 1.46203 – [(ln hardness) (0.145712)]	CF = Same as CMC
Mercury	CF = 0.85	CF = 0.85
Nickel	CF = 0.998	CF = 0.997
Selenium	CF = The freshwater criteria are expressed as total recoverable: CF = 0.922	
Silver	CF = 0.85	CF =
Zinc	CF = 0.978	CF = 0.986

CMC and CCC values are published as dissolved values. To obtain a total recoverable metals CCC or CMC for those metals that are not hardness dependent, divide the dissolved value by the conversion factor (CF) appropriate to the metal of interest. To obtain a total recoverable CCC or CMC for hardness dependant metals, use the hardness dependant formulas in Table 13, and omit the CF step.

6.2 Analysis of Metals in Groundwater

6.2.1 Methods

Five groundwater monitoring wells, Lyons M1S, M1D, M2S, and M2D and Gravel M1D, were installed in July 2002 to provide potentiometric and groundwater chemistry data. Three of the wells (Gravel M1D, Lyons M1D and M2D) also provided information on the geologic strata adjacent to the western side of the lake and wetlands. LYONS W1, JOHNSONW1, JOHNSON W2, and OPRENDEKW1 are existing wells that were also used in this investigation.

Groundwater samples were collected on August 28, 2002 (Lyons M1S, M1D, M2S, M2D, and Gravel M1D) and October 9, 2002 (JOHNSONW2 and JOHNSONW1) and analyzed for the metals specified in Table 12, using EPA test method 200.7 Inductively Coupled Plasma. When threshold values were incompatible with detection limits (instrument sensitivity), other tests were substituted to lower detection limits. These alternate test methods used were: Antimony, SM 183113B, Arsenic, SM 18 3114B, Mercury, SM 18 3112B, and Selenium, SM 18 3114B. Microbac Laboratories in Erie, Pa. ran the samples and provided the detection limit values. Detection limits and threshold values (CMC's and CCC's) varied from analyte to analyte (see Table 12).

Prior to sampling, monitoring wells were purged with a battery-powered pump until purged water ran clear of sediment. The pump ran for a minimum of five minutes to insure a minimum of three well volumes were purged before samples were collected. Samples from residential wells were collected from a tap nearest the well. The faucet was allowed to run for 10 minutes prior to sample collection. Samples were collected in

glass jars provided by Microbac Laboratories, Erie, Pa. All sample containers were pre-filled with acid and other preservation materials by the lab for maintaining and fixing all 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.

All wells were sampled for a suite of metals, identified by the EPA as priority pollutants: Arsenic, Antimony, Beryllium, Cadmium, Chromium (III, VI), Copper, Lead, Mercury, Nickel, Selenium, Silver, and Zinc. Cobalt, a trace element that can be toxic in excessive quantities, was also included in the analysis. A full metals analysis was used as a screening device. Again, any metals that were non-detects were excluded from the study. Any metals that exceeded the CMC or CCC thresholds should be monitored more closely in further investigations.

6.2.2 Results

Concentrations of Antimony, Beryllium, Cadmium, Chromium (III, VI), Lead, Mercury, Nickel, Selenium, and Silver fell below the detection limits. Arsenic was detected in Lyons M1D, Lyons M1S, Lyons M2S, and Gravel M1D on August 28, 2002. However, the values fell below the threshold values for this constituent.

Copper and zinc were detected in groundwater samples at levels exceeding CCC and CMC values. Because copper and zinc are hardness dependent, further calculations were performed to determine the hardness-dependent, total recoverable thresholds. The hardness values used for JOHNSONW1 and JOHNSONW2 were calculated from Ca^{2+} and Mg^{2+} concentrations. After correction of values, copper levels exceeded the CCC value in well Lyons M1D and the CCC and CMC values in wells Lyons M2D, Lyons M2S, JOHNSONW2, and JOHNSONW1. Again, the samples from Lyons M2D and Lyons M2S were collected on August 28, 2002 and the samples from JOHNSONW2, and JOHNSONW1 were collected on October 9, 2002. These values are expressed in Table 15.