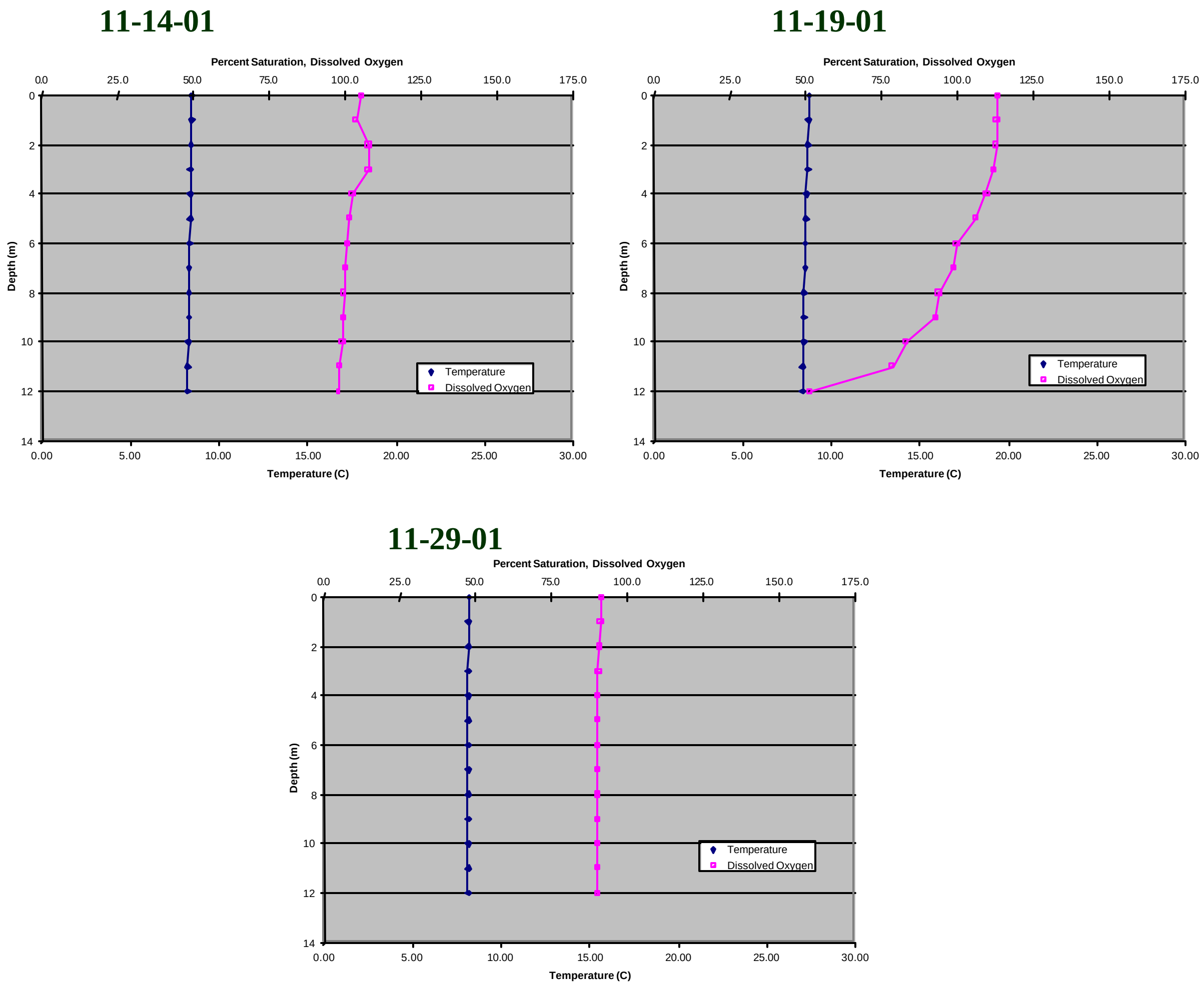


11-14-01

11-19-01

11-29-01

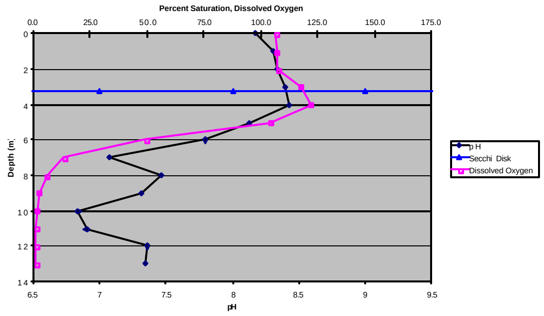
Figure 15. Percent dissolved oxygen and temperature profiles for Lake Pleasant during fall turnover, center sampling point

Dissolved Oxygen in the Metalimnion

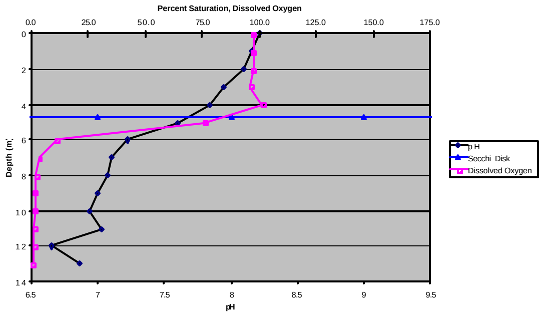
From 6-05-02 through 8-19-02, a spiked increase in % DO saturation occurred in the top of the metalimnion in comparison to percentages in the epilimnion and hypolimnion (Figure 16). The DO% spike was not apparent in the 9-06-02 reading because the lake had started to turnover, causing the upper 4m of water to mix, distributing DO. The metalimnion extends from about 2 to 7m. When DO% and pH profiles were plotted, the pH levels corresponded with the changing DO levels.

It is proposed that a phytoplankton population adapted to lower light conditions experienced a population surge in the metalimnion at a depth of about 2 to 4 meters. This is consistent with Secchi disk measurements taken at that time of about 2.7 to 4.7 m. The Secchi disk depths over this time period had a mean of 3.13 m, and a mode of 3.0 m (the middle value once the values were sorted from min to max). Generally, the Secchi disk depth is equal to one half the photic zone depth: here, the photic zone (the depth to which light can travel into the lake) would extend to about 6m, well within the area of the DO% spike. Also, Secchi disk measurements during this time period generally correspond to the depth just above the DO% spike, suggesting that the source of this marked increase in DO% is also decreasing the clarity of the lake at that level.

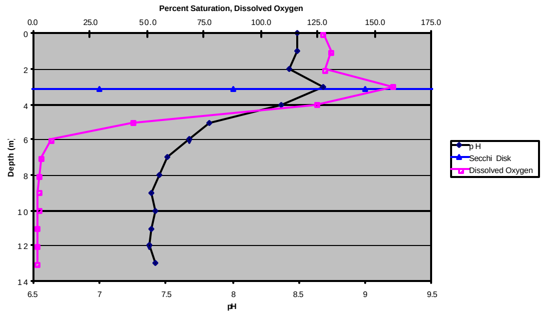
**6-05-02**



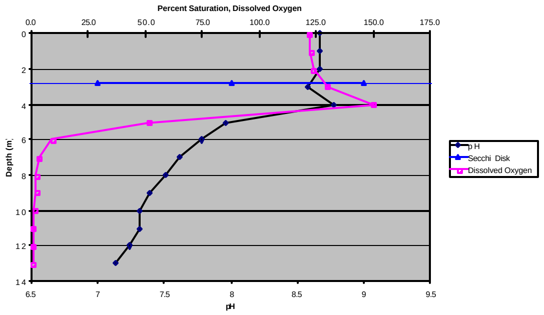
**6-13-02**



**7-02-02**



**7-08-02**



7-16-02

7-22-02

7-31-02

8-15-02

8-19-02

9-06-02

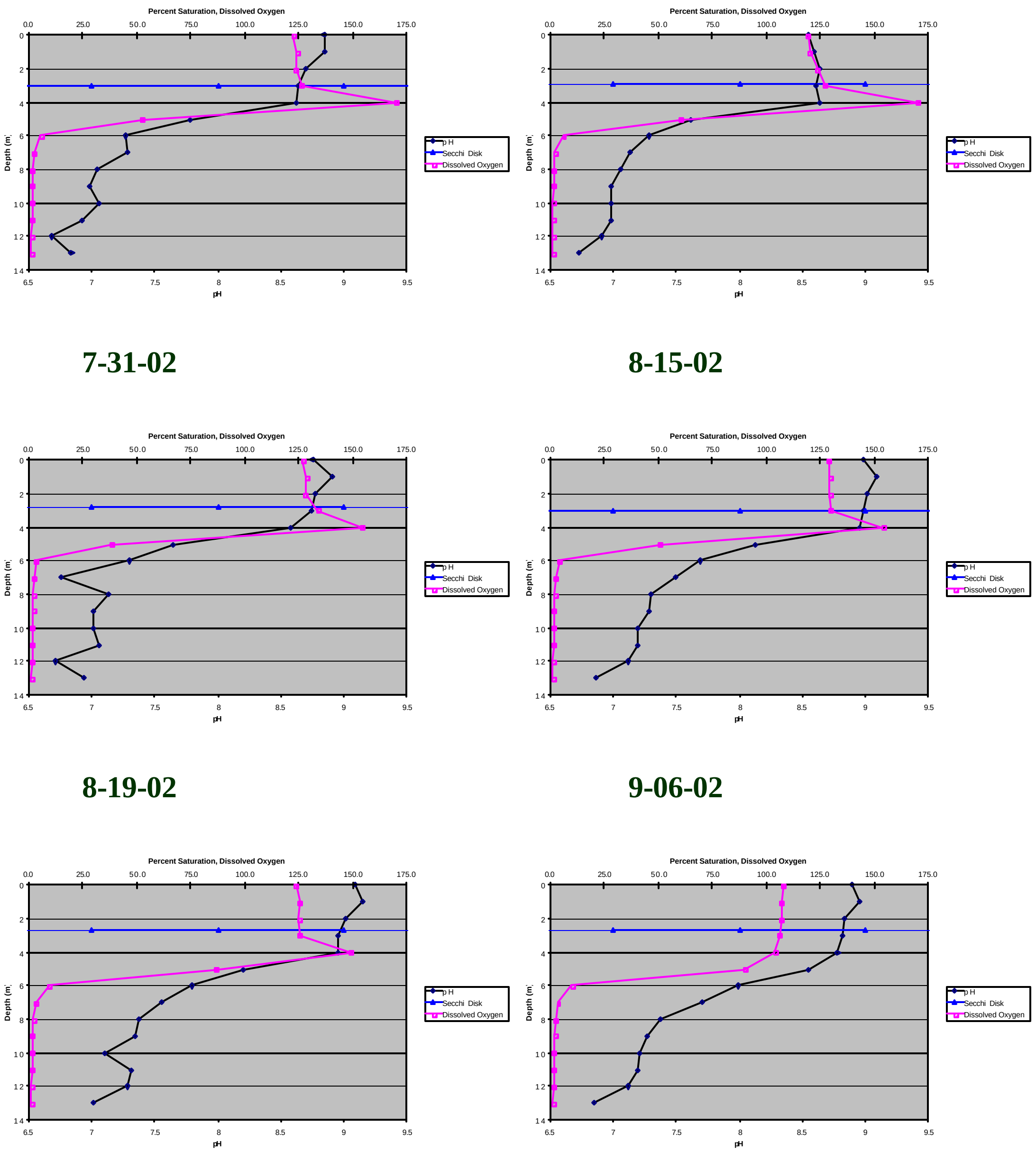


**Figure 16. Lake Pleasant % DO, pH, and secchi disk (m) depth profiles 6/5/02 through 9/6/02, center sampling point**

Increased production of $O_2$ in photosynthesis is coupled with increased $CO_2$ consumption in the reaction:

$$6CO_2 + 6H_2O \text{ ? } \quad 6O_2 + C_6H_{12}O_6$$

Because the metalimnion is isolated from the air column above the lake, diffusion of $O_2$ from the air is not available directly. Waves and mixing in of DO from the atmosphere in the epilimnion are thermally isolated from the metalimnion.

The increase in pH at about 4m, is likely due to the increased consumption of $CO_2$ by the photosynthetic population. This relationship is influenced by the carbonate chemistry of the lake in relation to the following reactions:

$$CO_2 + H_2O \text{ ? } H_2CO_3$$

$$H_2CO_3 \text{ ? } H^+ + HCO_3^-$$

$$HCO_3^- \text{ ? } H^+ + CO_3^{2-}$$

As the $CO_2$ is consumed, the entire system is driven to the left to replace the $CO_2$. In this process, the number of dissociated $H^+$ ions is reduced. Since pH is the negative log of the number of $H^+$ ions, a reduction in $H^+$ signifies an increase in pH.

In the bottom part of the epilimnion (or thermocline), a steep drop in pH is observed until the top of the hypolimnion with values hovering around 7. Decreasing pH would result in the carbonate reaction shifting to the right (increased $H^+$ ions). Bacteria and fungi (decomposers) in the hypolimnion help with the decomposition of dead organic matter that has settled to the bottom of the lake. In the process of respiration, they consume $O_2$ and release $CO_2$. This excess of $CO_2$ drives the carbonate reaction to the right, resulting in a greater concentration of $H^+$ ions and therefore, a decrease in pH.

$$6O_2 + C_6H_{12}O_6 \text{ ? } 6CO_2 + 6H_2O$$

### *5.1.2.2 Diurnal Variation*

Even during stratification, when the lake and its associated constituents are well mixed, diurnal variation in DO levels can occur because $O_2$ is a product of photosynthesis, a process which requires light and generally occurs during the daytime hours. Levels of $O_2$ should be lowest in the morning hours, gradually increasing throughout the day. During the night, continual $O_2$ consumption by animals, plants and some bacteria decreases the $O_2$ levels that accumulated during the day, back to levels characteristic of morning hours. This pattern, evident in Lake Pleasant, is shown in Figure 17.

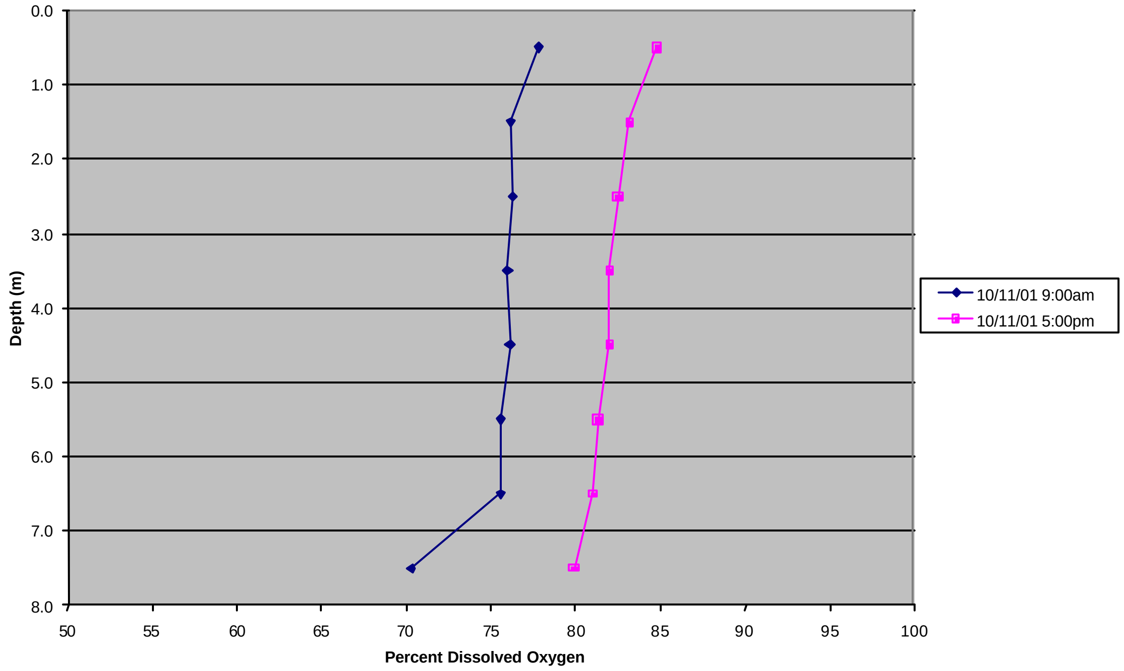


**Figure 17. Diurnal variation in %DO in Lake Pleasant, 10-11-01**

### *5.1.2.3 Aquatic Life Thresholds and Effects*

Aquatic animals need DO for respiration and efficient energy production. Below certain limits, animal life cannot survive. In the absence of dissolved oxygen, a cell would have to switch from oxidative phosphorylation to glycolysis for energy production, resulting in a net loss of 34 ATP per mol of glucose (Nilsson, 2001). It is an inefficient method of energy production, causing ATP stores in the brain to deplete within minutes (Nilsson, 2001). The brain has a high demand for ATP, needed for the operation of $Na^+$-$Ca^+$ ion pumps. Without the proper ionic gradients and associated electrical activity, the brain will swell and neuronal death will occur mainly due to a rapid influx of $Ca^+$ into cells (Nilsson, 2001). The fish would also suffer from acidosis due to the build-up of lactic acid in the tissues – a byproduct of glycolysis (Nilsson, 2001).

General threshold limits exist that describe concentrations of DO and DO% in terms of the fitness of aquatic organisms. These values are described in Tables 5 (http://lakeaccess.org/russ/oxygen.htm) and 6 (www.gvsu.edu/wri/education/manual/oxygen.htm).

**Table 5. DO threshold values for aquatic organisms in non-salmonid waters**

| ORGANISM | EFFECTS OF DO CONCENTRATION | DO (mg/L) |
|---|---|---|
| **FISH** | | |
| Early life stages | No production impairment | 6.5 |
| | Slight production impairment | 5.5 |
| | Moderate production impairment | 5 |
| | Severe production impairment | 4.5 |
| | Limit to avoid acute mortality | 4 |
| | | |
| Other life stages | No production impairment | 6 |
| | Slight production impairment | 5 |
| | Moderate production impairment | 4 |
| | Severe production impairment | 3.5 |
| | Limit to avoid acute mortality | 3 |
| | | |
| **INVERTEBRATES** | No production impairment | 8 |
| | Moderate production impairment | 5 |
| | Limit to avoid acute mortality | 4 |
| | | |

**Table 6. %DO threshold values for aquatic organisms**

| Percent Dissolved Oxygen Saturation | Interpretation |
|---|---|
| Below 60% | Poor, water too warm or bacteria using DO for decomposition |
| 60-79% | Acceptable for most aquatic organisms |
| 80-125% | Ideal conditions for most aquatic organisms |
| >125% | Too high, could cause gas bubbles in blood |

In 2002, DO% values fell below 60% saturation (the level below which is unfavorable for aquatic organisms) on:

- 2-18-02, 7m below surface to12.5m.
- Mid-March through late April, 11m below surface to12.5m.
- Late April through late May, about 8m below surface to 12.5m.
- Late-May, 7m below surface to 12.5m.
- Late May through Late June, 6m below surface to 12.5m.
- July through August, 5m to bottom.
- September through early October, 6m to bottom.

The lake was completely mixed by 11-6-02, replenishing the entire water column with acceptable levels of DO to support aquatic life.

Levels of DO below 4mg/L are known to cause acute mortality for early-life stage fishes and most benthic invertebrates. For other fish, the acute mortality threshold is 3mg/L. Therefore, where DO falls below 4mg/L, Lake Pleasant would be considered uninhabitable by most fish and benthic invertebrates.

From late May through early October, the period of summer stratification, about 70% of the volume of Lake Pleasant contained >4mg/L DO and would be considered suitable aquatic animal habitat in terms of dissolved oxygen.

The Pennsylvania Department of Conservation and Natural Resources (DCNR) lists fish species of special concern that have been known to live in Lake Pleasant. *Etheostoma exile* (Iowa darter) and *Notropis heterodon* (blackchin shiner) are benthopelagic freshwater fish species: they can feed at the bottom, middle, or surface of the water, and they prefer vegetated lakes (Froese and Pauly, 2001). Because these fish are not strict bottom feeders, they can likely survive the low levels of DO in the summer hypolimnion.

*Lepomis gulosus* (warmouth), another species of special concern historically recorded from Lake Pleasant, are dimersal freshwater fish, which feed primarily at the bottom of the lake. Ideally, they prefer a pH range of 7-7.5, temperatures ranging from 10-20 ºC, and they tend to live in well-vegetated lakes (Froese and Pauly, 2001).

The area within Lake Pleasant available for these fish to live is severely restricted by summer temperatures and low DO levels. As the lake began to stratify in April 2002, temperatures were ideal in the upper 3 to 4 meters of water, extending through the upper 7m of water by May 16, 2002. However, by mid-June 2002, the upper 3m of water warmed to temperatures above 20°C. By early June the low DO levels below 6m make these waters uninhabitable by fish and most invertebrates. Therefore, by mid-July, ideal conditions for this species would exist only in the lower metalimnion – from about 4 to 6 meters below the surface, leaving about 20% of the water volume of the lake available for habitat.

### 5.1.3 Conductivity/Specific Conductance

Conductivity is a measure of water's ability to convey an electric current. It provides an estimate of the amount of dissolved solids in the water. As the concentration of dissolved, ionized particles increases, the conductivity of the water increases due to decreased resistance of the solution. Conductivity of water is measured in terms of resistance, expressed as milliSiemens per meter ($mS\ m^{-1}$), and is dependent on temperature and characteristics of the cell being measured (Stednick, 1991). When the conductivity measurement is standardized for temperature and distance between electrodes (i.e. characteristics of the cell being measured), the measurement is expressed as specific conductance and allows comparisons between different water bodies. Specific conductance is the reciprocal of the amount of resistance the solution has to an electric current.

Specific conductance profiles can help to estimate the amounts of dissolved constituents in a water body (EPA, 1990b). It is expected that the greater the specific conductance value, the greater the concentration of dissolved constituents. Specific conductance was measured in the field using the YSI 600R sonde and reported as microSiemens per centimeter ($\mu S\ cm^{-1}$). The average specific conductance for the water column during fall turnover in 2001 was 259 $\mu S\ cm^{-1}$ and in 2002 was 221 $\mu S\ cm^{-1}$. It was evident during winter stratification that anoxic conditions in the hypolimnion caused reducing conditions that liberated ionic constituents from the lake sediments. During the winter months, sampling showed an average specific conductance of 260 $\mu S\ cm^{-1}$ in the oxygen-rich upper six meters. The average specific conductance in the oxygen-depleted bottom 6.5 meters was 315 $\mu S\ cm^{-1}$ with a specific conductance of 395 $\mu S\ cm^{-1}$ at the sediment-water interface. The average specific conductance for the water column during spring turnover in 2002 was 265 $\mu S\ cm^{-1}$. Summer stratification showed similar results as winter with anoxic conditions liberating ionic constituents from the lake sediments and a resultant increase in specific conductance (Figure 18).

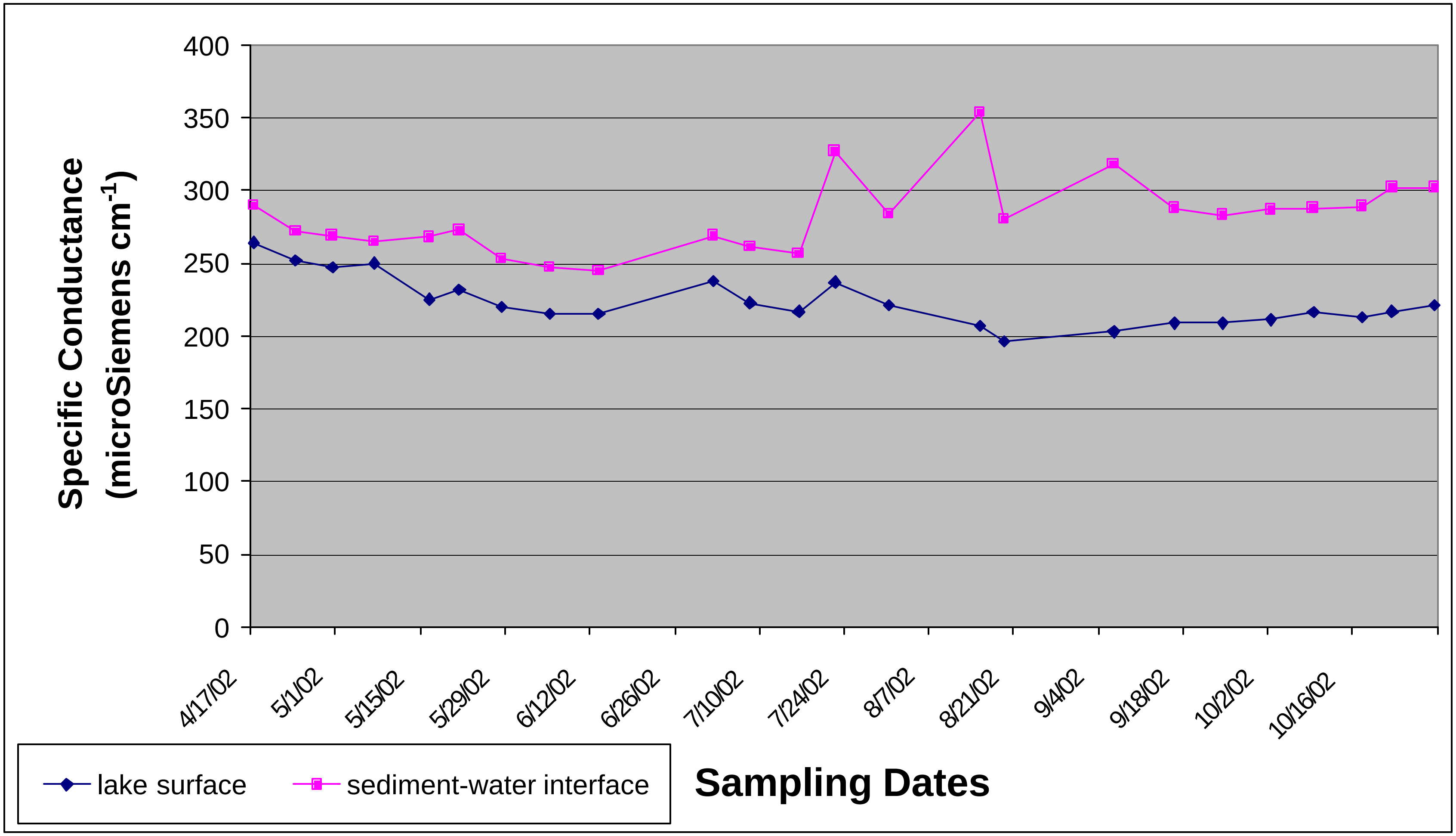


**Figure 18. Specific conductance in Lake Pleasant during summer stratification**

### 5.1.4 pH

pH is an estimation of hydrogen ion concentration in a solution and as such, is a measure of the acidity of the lake water. The pH scale is logarithmic ($pH = -\log[H^+]$), meaning that the $H^+$ ion concentration of a solution with a pH of 7 is ten times higher than one with a pH of 8, or a pH of 7 is 100 times higher than a pH of 9, etc. Because of this, small pH variations can be considered significant. pH is represented on a scale from 0 to 14 with pure water having a pH of 7.0. The earth's freshwater typically falls between 2 and 12, where pH levels naturally below 4 usually occur in volcanic regions due to high levels of mineral acids (Wetzel, 2001). pH values below 7.0 are considered acidic and above 7.0 are basic. pH is closely associated with acidity and alkalinity concentrations in water, however it cannot be used interchangeably. Alkalinity is a measure of water's ability to buffer acid inputs (increased hydrogen ion concentrations), which would result in a decrease of pH. Alkalinity is expressed in mg/L $CaCO_3$ (calcium carbonate). Water can have a circumneutral or slightly basic pH but may have low alkalinity, which would result in a reduction in pH with only minimal acidic inputs. Alkalinity is an important aspect in Lake Pleasant and will be discussed later in this section.

pH is impacted by a variety of processes within the lake ecosystem and it in turn helps to drive many of the processes. The speciation of metals, for example, is often pH dependant. pH is also a major parameter important in the functioning of fish gill respiration.

pH can vary vertically within the water column as respiration and photosynthesis increases or decreases $CO_2$ levels, as organic material is broken down by bacteria, and with metal speciation at the water-sediment interface. Increases in pH in the epilimnion during summer 2002 were described earlier as a result of photosynthesis by algae and consumption of $CO_2$. pH decreases are also evident in the hypolimnion due to bacterial decomposition of organic matter and release of $CO_2$. pH is further depressed near the sediment-water interface due to metal speciation and release of hydrogen ions (see Figure 16).

pH in Lake Pleasant is characteristic of the region; circumneutral to slightly basic due to the significant fractions of highly alkaline calcium carbonate and dolomite material in the subsurface geology. This is a direct result of the glacial history of the region and causes marked differences in the groundwater and surface water chemistry of northwest Pennsylvania when compared to other areas in the state. Due to its downwind position from major industrial areas along the Great Lakes, Pennsylvania receives some of the highest amounts of acid rain in the country. As a result of this and combined with acid mine drainage from a legacy of coal mining, Pennsylvania's freshwater resources are often acidified with depressed pH levels. The lack of coal in the geologic strata of northwest Pennsylvania, and subsequent lack of mining, combined with the capacity of the subsurface geology to buffer acid deposition, results in circumneutral pH levels for most of the streams and lakes in the region.

Ironically, the highly alkaline glacial material that protects Lake Pleasant's water quality and buffers it against the acid deposition plaguing the region is the same material that is extracted by sand and gravel mining operations. The extraction of this material in this relatively small watershed threatens the lake's ability to buffer inputs from acid deposition. Past and current mining operations have left the water table exposed to the atmosphere in many places throughout the watershed where gravel extraction was deep enough to reach the groundwater. This results in alterations to the water chemistry and increased evaporation rates.

pH readings from the gravel pit ponds ranged from 7.41 to 9.89. Fluctuations in pH values in the ponds, especially near the sediment-water interface, are attributable to the respiration, photosynthesis and decomposition processes occurring as a result of bacteria, phytoplankton, algae, and macrophytes that have begun to colonize.

Similar trends in pH were seen in the lake itself where fluctuations throughout the water column and seasonally were attributable to bacterial decomposition and the processes of photosynthesis (Figure 19).

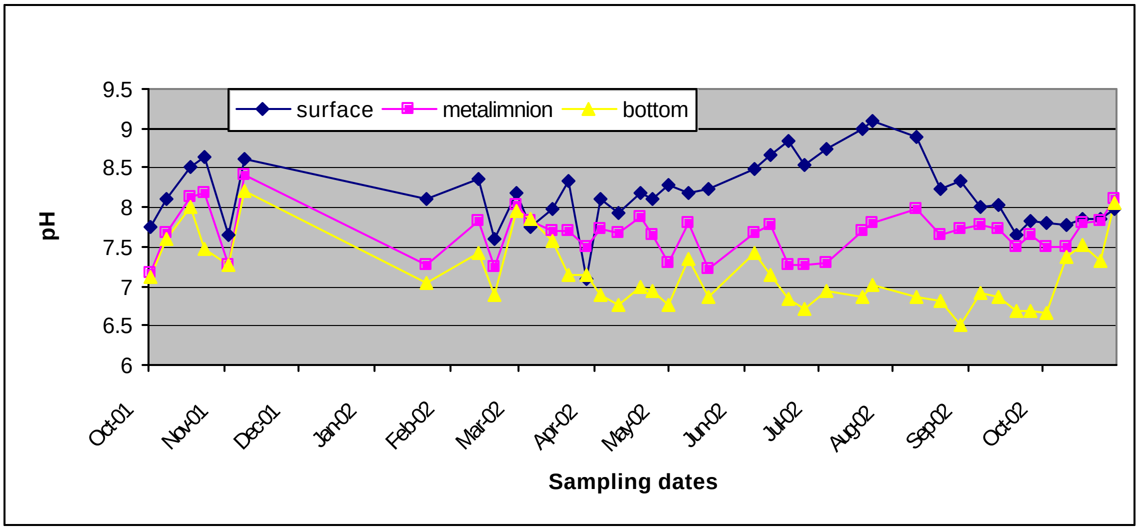


**Figure 19. pH values throughout the water column at sampling point, center**

pH values decreased in the lower levels of the water column as a result of depleted oxygen and increased carbon dioxide levels. Bacterial decomposition near the sediment-water interface further suppressed pH levels as carbon dioxide levels increased. During the warmer summer months, as macrophytes and phytoplankton increased, diurnal pH values increased in the photic zone as carbon dioxide was utilized during photosynthesis.

Groundwater pH levels, measured in all wells, ranged from 6.72 to 8.21. Inputs from UNT 1 and UNT 2 (stream) had pH ranges between 6.98 and 8.12.

### 5.1.5 Oxidation Reduction Potential

Negative ORP readings were recorded in the hypolimnion from 5-28-02 through 10-29-02 and correlate directly with the amount of DO present in the water. At both spring and fall turnovers, when $O_2$ was replenished in the hypolimnion, ORP became positive throughout the lake. Phosphorus released from the sediments gets mixed throughout the lake and leads to algal blooms seen following turnover.

The oxidation-reduction potential (ORP) is an estimate of whether a medium is in an oxidizing or reducing state. A positive ORP value is indicative of oxidizing conditions while a negative ORP is indicative of reducing conditions.

This can affect the valence state of major redox sensitive parameters: O2, NO3-/N2/NH4+, SO4+2/HS-, Mn(II)(IV), Fe(II)/(III). Some trace elements that are redox sensitive include As(III)/(IV), Se(IV)/(VI), and Cr(III)/(IV). The effects of these parameters vary depending upon whether conditions favoring reduction or oxidation are present – Cr III is not as toxic to humans or organisms as Cr IV for example (Schuring *et al*, 2000). Reducing conditions in the anoxic hypolimnion can cause these metals, as well as large amounts of oxidatively bound phosphorus, to be released from the sediments and reintroduced to the water column. If periods of anoxia are prolonged, excessive amounts of phosphorus can be released causing over production and excessive algal blooms.

### 5.1.6 Sulfide/Sulfate

Sulfur is a necessary constituent of most living organisms. It can however, have detrimental impacts to freshwater systems through affects to nutrient cycling, ecosystem productivity, and distribution of biota if anthropogenic sources cause high levels of sulfur compounds (Wetzel, 2001). Sulfur exists in an oxidized form as sulfate ($SO_4^{2-}$) and in the presence of water forms sulfuric acid ($H_2SO_4$). The primary source of sulfates is industrial emission of sulfur dioxides, which react with oxygen and water in the atmosphere. Sulfates can be deposited several hundred miles from the industrial point of origin. In hard water lakes, $SO_4^{2-}$ can be abundant from the dissolution of carbonate-rich rocks (USGS, 2001).

In aerobic conditions in the water column, sulfur exists almost entirely as sulfate, $SO_4^{2-}$. However, in the anoxic hypolimnion, sulfur released from decomposing organic matter exists largely as hydrogen sulfide gas, $H_2S$ (g). Hydrogen sulfide gas, $H_2S$ (g), is toxic to aquatic life. Under reducing conditions, hydrogen sulfide reacts with metal ions to form metal sulfides such as iron sulfide, FeS, as well as metal sulfides with Cu, Zn, and lead (Pb) (Wetzel 2001). As these metal ions are liberated from the sediments, there is a decrease in phosphorus binding, which allows it to be reintroduced to the water column. This can lead to an increase in primary productivity but it can also increase the lake's ability to allow phosphorus to exit the system.

Sulfide levels in this study were below detection limits (<0.06 mg/L) at all sample sites. Sulfate levels varied between sample sites; non-gravel pit wells had a mean sulfate level of 12.4 mg/L (8-17), while well gravel M1D had a sulfate level of 33 mg/L; sampling site north had a mean sulfate level of 10.5 mg/L (8-14); sampling site center had a mean sulfate level of 7.8 mg/L (<5-9); the lake outlet had a mean sulfate level of 9.5 mg/L (8-11); and the gravel pit ponds had a mean sulfate level of 15 mg/L (8-22).

## 5.1.7 Major Cations and Anions

### *5.1.7.1 Salinity*

Salinity is the sum concentration of all of the dissolved ionic constituents in inland waters (Wetzel, 2001). The major cations and anions that occur in lakes, especially those considered to have hard water, are $Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, $K^{+}$, $HCO_3^{-}$, $CO_3^{-}$, $SO_4^{-}$, and $Cl^{-}$: together, they constitute the total ionic salinity of the water (Wetzel 2001).

As groundwater moves through the substrata, the amounts of anions and cations (i.e. $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$, $HCO_3^{-}$, and $SiO_2$) added to the water from the weathering of rock is dependant on regional geology and mineralogy (Hounslow 1995). In the groundwater, the dominant ionic constituents are $HCO_3^{-}$ and $Ca^{2+}$, reflective of the calcium carbonate rich limestone and dolomite present. The concentrations of these two ions are higher in the groundwater than in the lake suggesting that the groundwater is responsible for their recharge within the lake.

#### Hardness (Ca and Mg)

Calcium and Magnesium ions dissolved in a body of water, together, define the general hardness of that system. Both metals are macronutrients (Chang and Cockerham 1994) and are necessary for metabolic processes and cell maintenance in plants: calcium is used for the maintenance of cell membranes and metabolism, and magnesium is required for enzymatic activity and for the utilization of chlorophyll. Lake Pleasant contains plant species that are characteristic of calcium rich waters. As concentrations of calcium in the water table decrease, so can the numbers of these plants. Although magnesium is a nutritional requirement , the occurrence of low magnesium levels is generally rare (Wetzel 2001).

- $Ca^{2+}$ and $Mg^{2+}$ were sampled in the lake on 7-2-02 at the sampling points north, 0.5, 4.5 and 7.0 meters; center, 0.5, 5.5, and 6.0 meters; outlet, 0.5 meters; and bridge, 0.5 meters. UNT 1, UNT 3, and stream were dry on 7-2-02.
- On 7-3-02 pond a, 2.0; pond b, 1.0; pond c, 0.5; pond d, 1.0; pond f, 0.5; pond g, 0.5; and pond h, 1.0.
- On 9-16-02, north, 0.5, 6.5; center, 0.5, 7.0, 12.0; outlet, 0.5; pond a, 0.5; pond b, 0.5m; pond d, 0.5m; pond e, 0.5m; pond f, 0.5m; pond g, 0.0m; and pond h, 0.5m.

Calcium levels appear to remain steady in the lake due to recharge from calcium carbonate rich groundwater. The dissolution of calcium carbonate rich rocks by groundwater likely drives the consistently high calcium levels in the lake. High levels of calcium contribute to the proliferation of calcium loving plants, some of which are of special concern in Pennsylvania.

### Chloride, Sodium, and Potassium

Runoff from Lake Pleasant Road (SR 1001), which runs along side the lake, is channeled to the lake via drainage culverts and enters the lake as direct runoff. Concentrations of chloride may increase significantly due to runoff from road salting (Wetzel, 2001). Na+ and Cl- plumes from road salt, and the use of septic systems that discharge effluent have been shown to enter open wetlands via ground water. These plumes are often found to be consistent with the growth of dense areas of non-native, invasive wetland species like cattails. Lake Pleasant's degraded shoreline along Lake Pleasant Road, is a site of extensive colonization by non-native cattails, reed canary grass, and Phragmites.

An indirect result of increased NaCl from road deicing may be the increased mobilization of heavy metals from roadside soils and introduction to the lake via runoff. A study done by Allegheny College, in conjunction with this assessment, showed that levels of Cu, Ni and Pb in the soils along Lake Pleasant Road were at least two times higher than the national average (Fidorra, 2003). These heavy metals are commonly associated with vehicle use, tire and brake wear, etc. In laboratory experiments, the study provided evidence that the application of NaCl solution to soils increased mobilization of these heavy metals and increased their concentrations in the resultant runoff (Fidorra, 2003).

Sodium and potassium are important due to their role in ion transport and exchange (Wetzel, 2001). Sodium, although it may not be crucial in the growth of most plants, can influence the growth of blue-green algae, and there is usually little variation in the distribution of these cations (Wetzel, 2001). Increased sodium from anthropogenic sources like road deicing agents and septic systems are a threat to Lake Pleasant.

### *5.1.7.2 Carbonate/Bicarbonate and Alkalinity*

A distinctive characteristic of Lake Pleasant is its carbonate system. Lake Pleasant's valley contains a glacial outwash possessing significant amounts of limestone ($CaCO_3$) and dolomite ($CaMgCO_3$). Since the lake is groundwater fed, this carbonate containing outwash contributes to the carbonate-enriched groundwater entering the lake and wetlands. Lithified beds surrounding the lake range from a few centimeters to a meter in thickness. These deposits react vigorously with acid indicating their basic, carbonate composition and suggest supersaturation in the sediments surrounding Lake Pleasant. In addition, carbonate species can enter the lake as dissolved carbon dioxide from the atmosphere. Carbon dioxide makes up 0.0355% of the atmosphere and is very soluble in water (200 times more than oxygen). Carbon dioxide diffuses across the air-water interface based on Henry's Law ($CO_2 = P_{CO2} X K_H$). Dissolved carbon dioxide reacts with water to form carbonic acid ($H_2CO_3$). Carbonic acid is a weak, diproctic acid, which dissociates to form bicarbonate ions ($HCO_3^-$) with the loss of one proton and carbonate ions ($CO_3^{2-}$) with the loss of another. The equilibrium constants for these reactions are temperature and pH dependent.

$$CO_2 + H_2O \ ? \ \ H_2CO_3^*$$

($H_2CO_3^*$ = sum of aqueous carbon dioxide and carbonic acid since the concentration of carbonic acid is too small to measure alone)

$$H_2CO_3^* \ ? \ \ H^+ + HCO_3^-$$

$$HCO_3^- \ ? \quad H^+ + CO_3^{2-}$$

Bicarbonate and carbonate ions also react with water:

$$HCO_3^- + H_20 \ ? \quad H_2CO_3 + OH^-$$
$$CO_3^{2-} + H_20 + \ ? \quad HCO_3^- + OH^-$$

When protons are added to the system, they react with the hydroxyl anions to produce water. More bicarbonate and carbonate ions are then formed based on Le Chatilier's principle that a system in equilibrium will resist changes. In this manner, the pH of the system is able to remain relatively stable, varying from 6.7 below six meters in depth to 8.2 in the top six meters, until all of the bicarbonate and carbonate ions are exhausted. The buffering ability of Lake Pleasant allows it to neutralize acids and lessen the harmful effects of acid rain. The proportion of free carbon dioxide, carbonic acid, bicarbonate and carbonate in solution is a function of pH.

Carbonate, bicarbonate and total alkalinity were measured weekly in Lake Pleasant from 11/12/01 through 5/7/02 and in the ponds on 9/16/02. As is normally the case in moderately hard freshwater systems, virtually all of the total alkalinity in the lake was attributable to bicarbonate alkalinity, therefore subsequent analyses only reported total alkalinity. Total alkalinity was measured in Lake Pleasant weekly 9/16/02 through 10/17/02 while the lake was stratified and again on 11/5/02 while the lake was mixed and isothermal (Figure 20). While the lake was stratified, total alkalinity increased as depth increased due to increased $CO_2$ production in the hypolimnion. This pattern was evident during summer and winter stratification. During spring and fall turnover, total alkalinity values were constant throughout the water column.

Total alkalinity was measured in the ponds on 9/16/02 (Figure 21) (Pond C was excluded because it was not formed from a gravel mining operation) and in the wells on 10/9/02 (Figure 22) (Oprendek W1 was not sampled due to lack of accessibility at time of sampling). Total alkalinity was measured in UNT 2 (stream) weekly from 11/12/01 through 5/7/02 and in UNT 1 weekly from 4/24/02 through 5/7/02 (Table 7). Total alkalinity values for UNT 2 during 2001 are approximately equal to the total alkalinity of the lake surface. Because UNT 2 flows through wetlands before its confluence with the lake, under normal conditions discharge is minimal and the lake tends to back up into the channel for UNT 2. During increased spring flows like those seen between 3/27/02 and 5/7/02, the discharge in UNT 2 increases beyond the capacity of the wetlands and surface flow increases to the lake. During this time period, both UNT 2 and UNT 1 are significant sources of depressed alkalinity (acidity) to Lake Pleasant.

Mean total alkalinity in the groundwater as measured in the wells is 141 mg/L $CaCO_3$, which is significantly higher than that seen in the lake. Therefore, groundwater recharge probably accounts for all the alkalinity in Lake Pleasant. In the gravel pit ponds, the mean total alkalinity is 54 mg/L $CaCO_3$. This is significantly lower than the groundwater responsible for recharging these ponds. There are several reasons why this may be including acid inputs from atmospheric deposition or waterfowl. Directly or indirectly, the chemistry of groundwater in the Lake Pleasant watershed is altered once it is exposed to the atmosphere in these ponds. This is further supported by lowered alkalinity values seen in the tributary streams as a result of precipitation runoff.