
**SEDIMENT NUTRIENT FLUX AND OXYGEN DEMAND STUDY FOR CANYON LAKE WITH
NUTRIENT MONITORING AND ASSESSMENT OF IN-LAKE ALTERNATIVES:
JULY – SEPTEMBER, 2006**

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Introduction

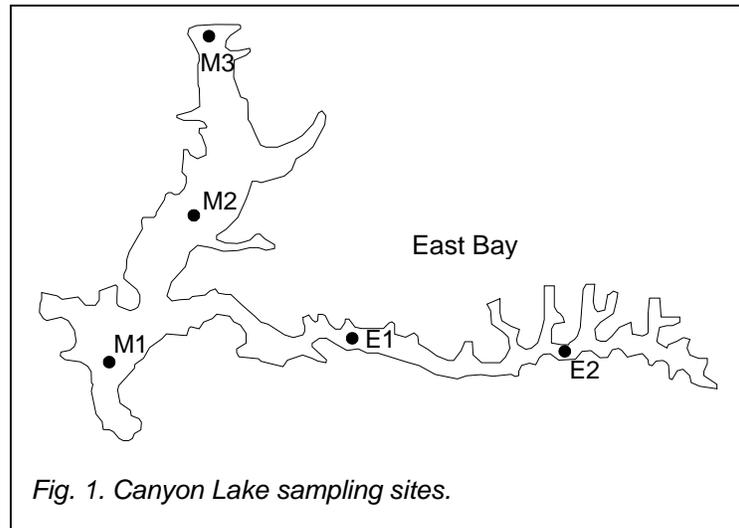
This report summarizes the results from water column and sediment sampling conducted during the summer quarter 2006 to assess water quality and evaluate potential in-lake treatments to improve water quality in Canyon Lake.

Approach

Nutrient Monitoring

Water column sampling was conducted biweekly over this reporting period. Field measurements included Hydrolab casts and water column sampling for a large number of constituents at 5 sites (M1, M2, M3, E1, and E2) on Canyon Lake (Fig. 1). These sites approximately correspond to sites 2, 9, 13, 17 and 23 from our earlier sediment characterization of the lake (Anderson and Oza, 2003).

A Hydrolab DataSonde4a multiparameter water quality monitoring probe was used to make *in situ* field measurements. The immersible probe is fitted with a pressure transducer, thermister, DO probe, turbidity sensor, and pH, electrical conductance (EC) and oxidation-reduction (ORP) electrodes connected to a Surveyor 4 data display/controller via a 15 m waterproof cable. The DataSonde4a was calibrated each morning before leaving for the lake; results were recorded in a calibration log. The DO probe was calibrated against an O₂-saturated water sample prepared by sparging with lab air, the pH electrode was calibrated against pH 7 and 10 buffers, EC was calibrated against a standard KCl solution, ORP was calibrated against quinhydrone, and turbidity calibrated against a turbidimetric standard (Fisher Scientific). The temperature sensor and pressure transducer were not calibrated, although they were confirmed as working properly and within specification by the factory in an instrument check-up earlier this spring. The transparency of the lake at these 5 sites was measured using a Secchi disk. Field data was recorded at the time of sampling in field logs that were then transferred to an Excel spreadsheet in the lab.



Water samples were collected as depth-integrated samples, down to the sediments at sites E1 and E2 in East Bay (Fig. 1) or to the bottom of the epilimnion in the main body of the lake using a flexible tube sampler; discrete samples were collected using a van Dorn sampler at the thermocline, which was found to have shifted downward throughout the course of the quarter, and at the upper, middle and bottom depths of the hypolimnion at the 3 main lake sites (M1, M2 and M3). Hypolimnetic samples were then composited to yield a depth-averaged hypolimnetic sample for each of these sites. Thus, 11 water samples were collected each sampling day through the summer. Samples were stored on ice until returned to the lab.

The samples returned to the lab were then analyzed for a number of constituents (Table 1). Water samples were filtered and acidified with sulfuric acid to $\text{pH} < 2$ for dissolved nutrient analyses (SRP, $\text{NO}_3 + \text{NO}_2\text{-N}$, and $\text{NH}_4\text{-N}$) following Standard Methods (APHA, 1998) using a Technicon autoanalyzer. Separate unfiltered subsamples were digested and analyzed for total N and total P following methods 4500-N and 4500-P (APHA, 1998). Organic N was calculated from the difference between total N and TIN (sum of $\text{NO}_3 + \text{NO}_2\text{-N}$ and $\text{NH}_4\text{-N}$) concentrations. Organic P concentrations were calculated from total P and SRP concentrations. Chlorophyll samples were analyzed according to standard method 10200 H.3 (APHA, 1998) that involves a six-hour acetone extraction procedure, with samples read on Perkin-Elmer LS1000 fluorescence spectrophotometer with an excitation 430 nm wavelength and emission wavelength of 663 nm. Dissolved Ca and Mg (for total hardness), and Fe and Mn concentrations were quantified on filtered samples acidified with metals-grade HNO_3 using the inductively

coupled plasma method (3120 B) on a Perkin-Elmer Optima 3000 DV. Total dissolved solids (TDS) and total suspended solids (TSS) concentrations were determined using standard methods 2540 C and 2540 D (APHA, 1998). Samples were also collected and analyzed for biological oxygen demand (BOD) and chemical oxygen demand (COD) following standard methods 5210 B and 5220 D, respectively.

Field	Laboratory	Calculated
Temperature	Chlorophyll a	TIN
DO	Total N	Organic N
Specific Conductance	Total P	Organic P
pH	NO ₃ -N+NO ₂ -N	
Turbidity	NH ₄ -N	
Redox Potential	SRP	
Secchi depth	Total Hardness	
	Dissolved Fe and Mn	
	TSS	
	TDS	
	BOD	
	COD	

Sediment Nutrient Flux and Oxygen Demand

Measurements of sediment nutrient release were conducted in July and September. In addition, sediment oxygen demand and water oxygen demand measurements were taken in July. Measurements were made on triplicated intact sediment cores collected from the 5 sites also sampled for water quality (Fig. 1).

Cores were collected following Beutel (2000) and Anderson (2001). An Ekman dredge was used to collect a grab sample, which was then subsampled by carefully inserting a 30.5 cm by 6.3 cm diameter Lucite tube approximately 10 cm into the sediment. The bottom of the core was sealed using a rubber stopper. The core was then carefully topped off with bottom water sampled using a van Dorn sampler, stoppered with zero headspace and transported back to the lab.

Cores were then incubated in the dark at the temperature and DO levels measured at the time of sampling. Approximately 10 mL of water was removed daily, filtered and analyzed for soluble NH₄-N, NO₃-N, and SRP using a Technicon autoanalyzer following standard methods (APHA, 1989). Dissolved oxygen was measured using a YSI Model 55 DO meter, with the water briefly sparged with N₂ or lab air necessary to maintain DO and to very gently mix the water column within the core.

The measured change in concentration was used in conjunction with water volume and sediment-water interfacial area to calculate a mass flux rate.

Following the end of the nutrient flux measurements (6-7 days), cores were sparged with air to approach saturation DO levels, sealed and monitored for loss of DO over time. Separately, water oxygen demand (WOD) was measured on water samples held at appropriate temperatures and analyzed for loss of DO over time. Sediment oxygen demand was calculated from known volumes, sediment surface areas, and rate of DO loss.

Results

Temperature and Dissolved Oxygen

The main body of Canyon Lake has been strongly stratified since the start of the monitoring campaign in June, with anoxic conditions present throughout the hypolimnion (e.g., Fig. 2). The epilimnion warmed from 26 °C in June to about 28 °C later in July and August, and deepened somewhat over the summer as a result of entrainment of hypolimnetic water. The temperature of the bottom waters were largely unchanged however, and remained near 14 °C from June through September (Fig. 2a). Temperature and DO measurements at site E2 in East Bay yielded quite different results (Fig. 3). At this much shallower site, (<4 m), the water column was nearly isothermal, with low DO concentrations present only just above the sediments. Supersaturated conditions were, in fact, present often 0-2 m below the water surface (Fig. 3a). As with site M1 (and the other sites, data not shown), the surface waters at site E2 increased in temperature somewhat from the June sampling and were generally slightly above 28 °C. The temperatures in East Bay were thus slightly warmer than in the main body of the lake at an equivalent depth.

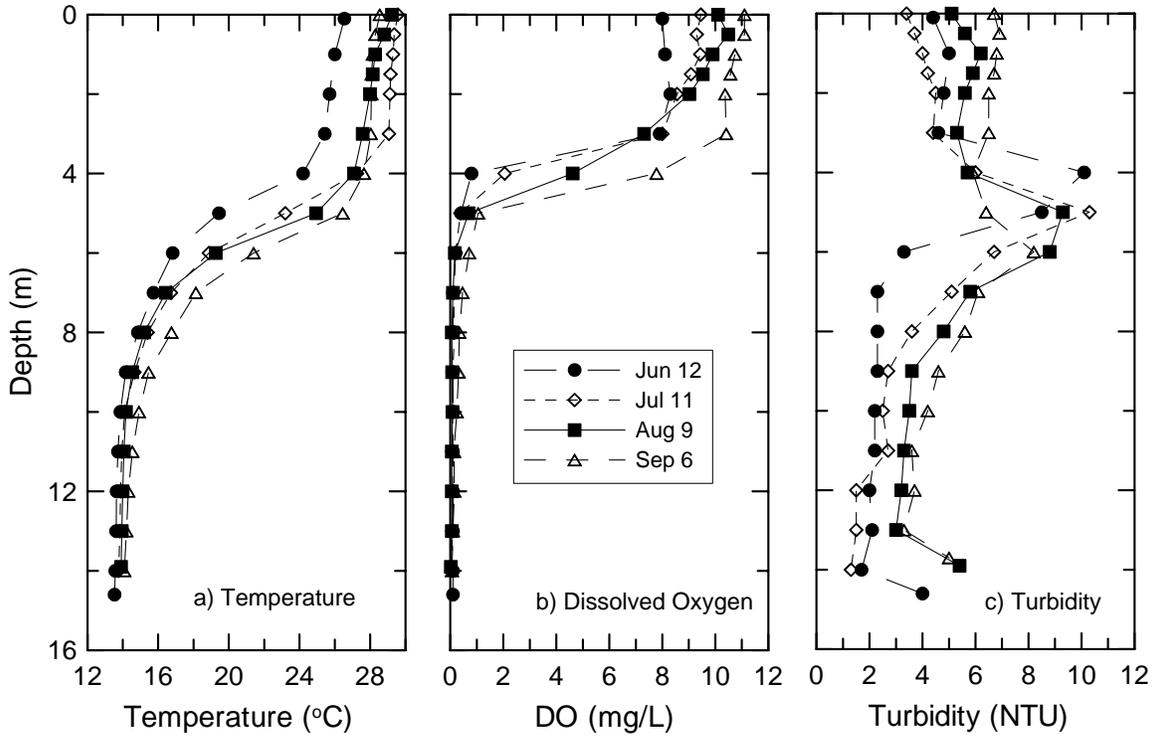


Fig. 2. Selected profiles from site M1: a) temperature, b) DO and c) turbidity.

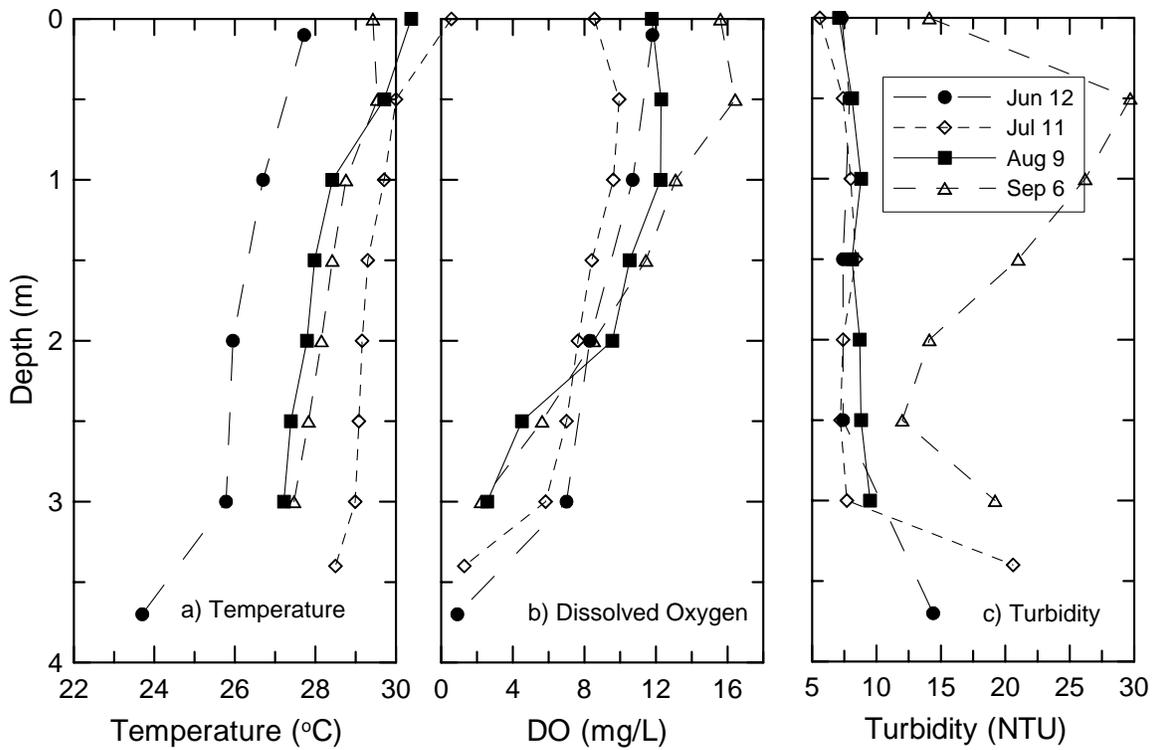


Fig. 3. Selected profiles from site E2: a) temperature, b) DO and c) turbidity.

Transparency and Chlorophyll Concentrations

Transparency, as measured with a Secchi disk, was found to differ between the sites and decrease through the summer (Fig. 4). Transparencies were 120-150 cm at the start of sampling in June, with greater Secchi depth values generally found in the main body of the lake relative to East Bay (Fig. 4). Secchi depths declined by about 50% over the ensuing 3 months, to e.g., approximately 50 cm at site E2 and 75 cm at M1. Transparencies are typically a sensitive function of phytoplankton concentrations in the water column, so these data imply higher chlorophyll concentrations and increased algal production through the summer.

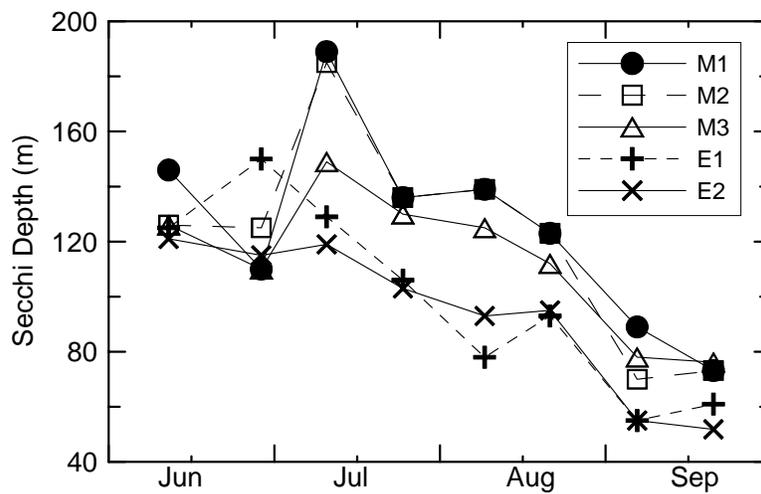


Fig. 4. Secchi depth transparencies over time.

Measured chlorophyll concentrations at sites E2 and especially E1 were, in fact, substantially elevated relative to concentrations found in the main body (Fig. 5). The much higher concentration at site E1 is in part a result of the sampling technique there. Specifically, the site was in fact stratified at the very bottom of the water column, although because of the small volume of hypolimnion, was sampled using the depth-integrated tube sampler. Site E1 thus exhibited differences in a number of properties relative to the other surface sites. Notwithstanding, the high chlorophyll levels in East Bay are consistent with prior observations (Anderson and Oza, 2003), and attributed to more intimate association of warm surface waters with sediments in the shallow East Bay relative to the much deeper and stratified main body. That is, nutrients released from bottom sediments can be directly taken up and used by phytoplankton in the photic zone. Moreover, chlorophyll concentrations were also found to increase over the time

period from mid-July to September, although relatively high chlorophyll concentrations were also found in June. It may be that the algal populations in the lake changed and thus altered chlorophyll-transparency relations.

In situ measurements of turbidity reveal strong vertical gradients present at stratified sites (e.g., Fig. 2c). Highest turbidity levels (and highest phytoplankton populations and chlorophyll concentrations) were found at the base of the epilimnion; this was previously observed in Canyon Lake (Anderson and Oza, 2003) and arises from increased nutrient availability with sufficient light at this depth to increase algal production there.

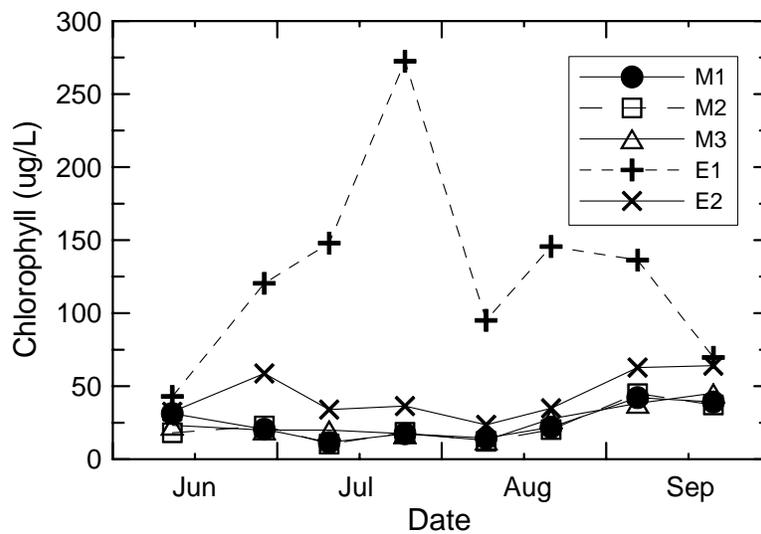


Fig. 5. Chlorophyll concentrations over time.

Nutrient Concentrations

Nutrient concentrations exhibited interesting differences between depths and over time. Total P and total N concentrations were markedly higher in the hypolimnion of the main body than thermocline or epilimnion samples there, or in depth-integrated samples from East Bay (Figs. 6 and 7; note difference in scale). Total P concentrations averaged about 0.12-0.16 mg/L in the depth-integrated surface samples from the main lake sites and at site E2, with gradual increases over time at most sites (Fig. 6a). Site E1, with depth-integrated total P concentrations closer to 0.4 mg/L resulted from the presence of stratification just above the sediments as previously discussed; thus sampling of some of this hypolimnetic water with elevated nutrient concentrations into the depth-integrated sample resulted in higher concentrations than found elsewhere.

Concentrations of total P at the thermocline of the three main sites (about 0.2 - 0.3 mg/L) were slightly higher than their concentrations in the epilimnion without a clear trend over time (Fig. 6b). Total P levels in the hypolimnetic samples were consistently much higher than samples from either the epilimnion or thermocline (Fig. 6). Concentrations increased over time at site M1, but were largely unchanged at the other sites.

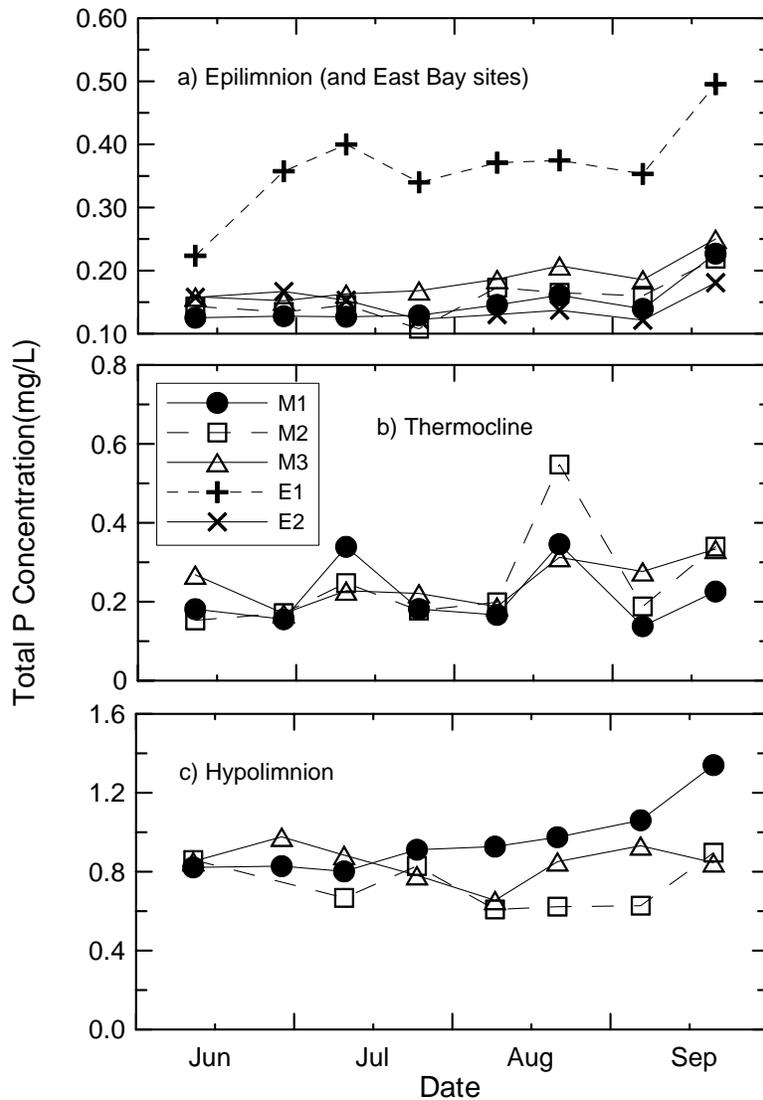


Fig. 6. Total P concentrations over time: a) epilimnion and East Bay sites, b) thermocline and c) hypolimnion. Thermocline and hypolimnion samples from the main lake sites only.

Concentrations of soluble-reactive P (SRP) followed very closely observed trends in total P. That is, with the exception of the depth-integrated sample from site E1, which included some hypolimnetic water, SRP concentrations were low in the surface samples,

slightly higher at the thermocline, and quite high in the hypolimnion (Fig. 7). SRP concentrations were lower than TP however, and SRP averaged 62.4% and 78.4% of total P in the epilimnion and thermocline samples, respectively, while effectively all of the phosphorus in the hypolimnion was in a soluble reactive form (98.4%). Thus essentially all of the P in the hypolimnion is in a soluble and readily bioavailable inorganic form (Table 2). The relative fraction of P in organic forms thus decreased with depth.

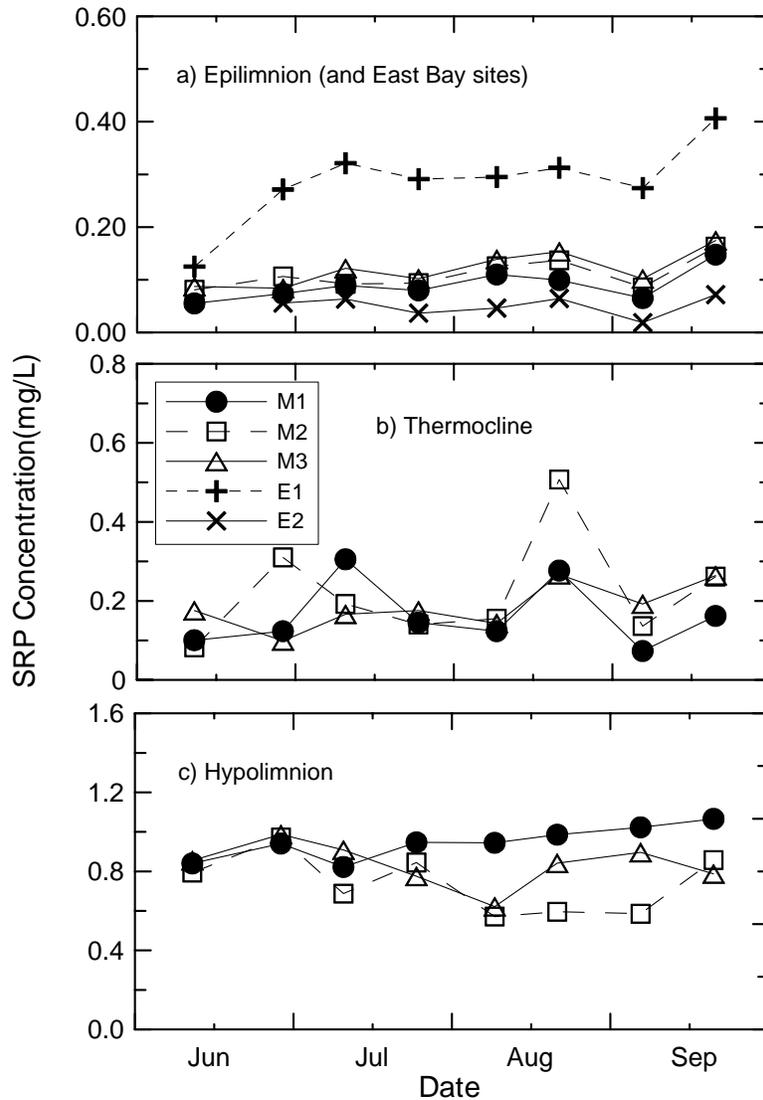


Fig. 7. SRP concentrations over time: a) epilimnion and East Bay sites, b) thermocline and c) hypolimnion. Thermocline and hypolimnion samples from the main lake sites only.

Total N concentrations varied less strongly with depth than total P, and averaged about 1.2 mg/L in the surface and thermocline samples with no substantial change over time (Fig. 8). The concentrations in the hypolimnion were higher than the other depths,

with levels at M1 rising over time, although trends were less clear for sites M2 or M3.

Depth	Inorganic P	Organic P	TIN	Organic N
Epilimnion	62.4	37.6	9.5	90.5
Thermocline	78.4	21.3	6.5	93.5
Hypolimnion	98.4	1.6	52.5	47.5

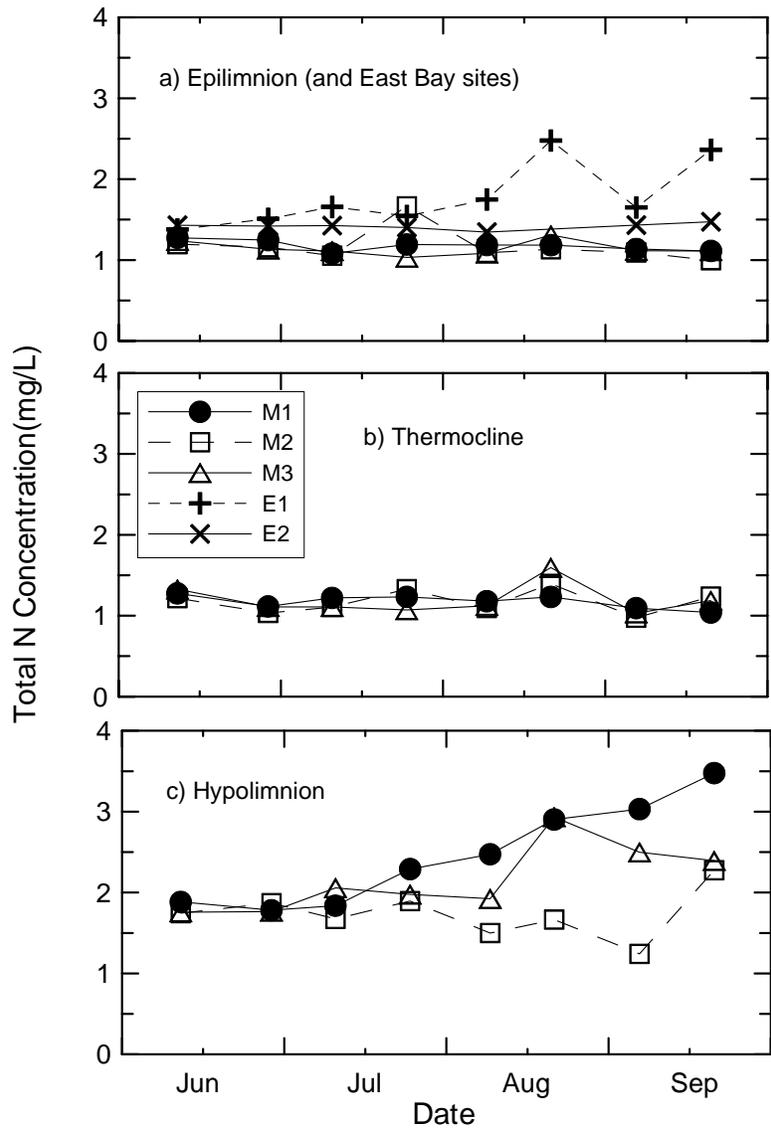


Fig. 8. Total N concentrations over time: a) epilimnion and East Bay sites, b) thermocline and c) hypolimnion. Thermocline and hypolimnion samples from the main lake sites only.

Ammonium-N levels were (with the exception of E1) quite low in the surface samples, often near 0.05 mg/L, while concentrations in the thermocline were slightly higher (0.05 - 0.2 mg/L), especially on the 2nd sampling in August (Fig. 9). Since there is a sharp gradient in dissolved nutrient concentrations near the thermocline, some of the variation is thought to result simply from sampling a bit further into the water column (i.e., closer to the hypolimnion) resulting in higher measured concentrations. NH₄-N concentrations were an order of magnitude or more greater in the hypolimnion than in the overlying waters (Fig. 9; note scale).

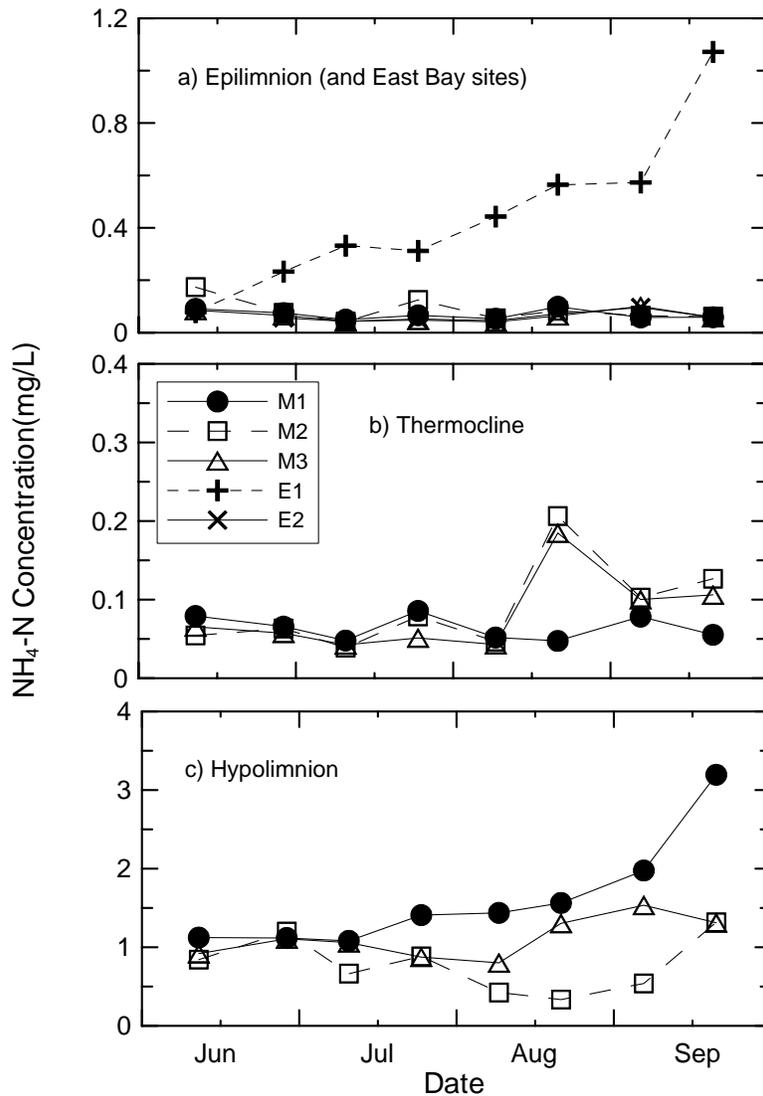


Fig. 9. Ammonium-N concentrations over time: a) epilimnion and East Bay sites, b) thermocline and c) hypolimnion. Thermocline and hypolimnion samples from the main lake sites only.

As with SRP, $\text{NH}_4\text{-N}$ concentrations increased quite substantially over time in the hypolimnion at site M1, although trends were less clear at the other sites. Most of the N was in an organic form in the surface and thermocline samples (on average >90%), although slightly more than one-half of the N was in an inorganic form in the hypolimnion (Table 2). Effectively all of the TIN was as $\text{NH}_4\text{-N}$, as $\text{NO}_3\text{+NO}_2\text{-N}$ concentrations were below detection for all samples

Ratios of total N to total P thus varied within the water column, with an average TN:TP ratio of 14.9 ± 3.8 in the surface samples, implying neither strong N nor P limitations. The TN:TP ratio in the thermocline samples were slightly higher and averaged 20.2 ± 6.6 .

Oxygen Demand

Chemical oxygen demand (COD) of the waters in Canyon Lake was determined using a colorimetric dichromate oxidation method. The COD concentrations were generally 25 – 35 mg/L in the epilimnion and East Bay samples, with generally slightly higher concentrations in East Bay (Fig. 10a). The COD levels in the thermocline and hypolimnion samples were initially lower than those present in the epilimnion (20-25 vs. 25-35 mg/L, respectively), but tended to increase over time, reaching or exceeding levels found in the overlying surface waters (Fig. 10).

Part of the chemical oxygen demand of the hypolimnetic samples is known to include sulfide, as these samples routinely smelled of sulfur. This was confirmed in September, when field measurements of sulfide were made using a colorimetric methylene blue method. The hypolimnion sample from site M1 was found to have a sulfide concentration of 10.0 mg/L, while a lower concentration was found in a hypolimnetic sample from site M3 (4.5 mg/L).

COD and BOD analyses were originally to be conducted by a outside contract lab; while we were able to set up for COD measurements relatively quickly, BOD measurements required a bit more time before we could perform the analyses. As a result, BOD analyses have been conducted monthly, on August 9 and September 6 samples (Table 3).

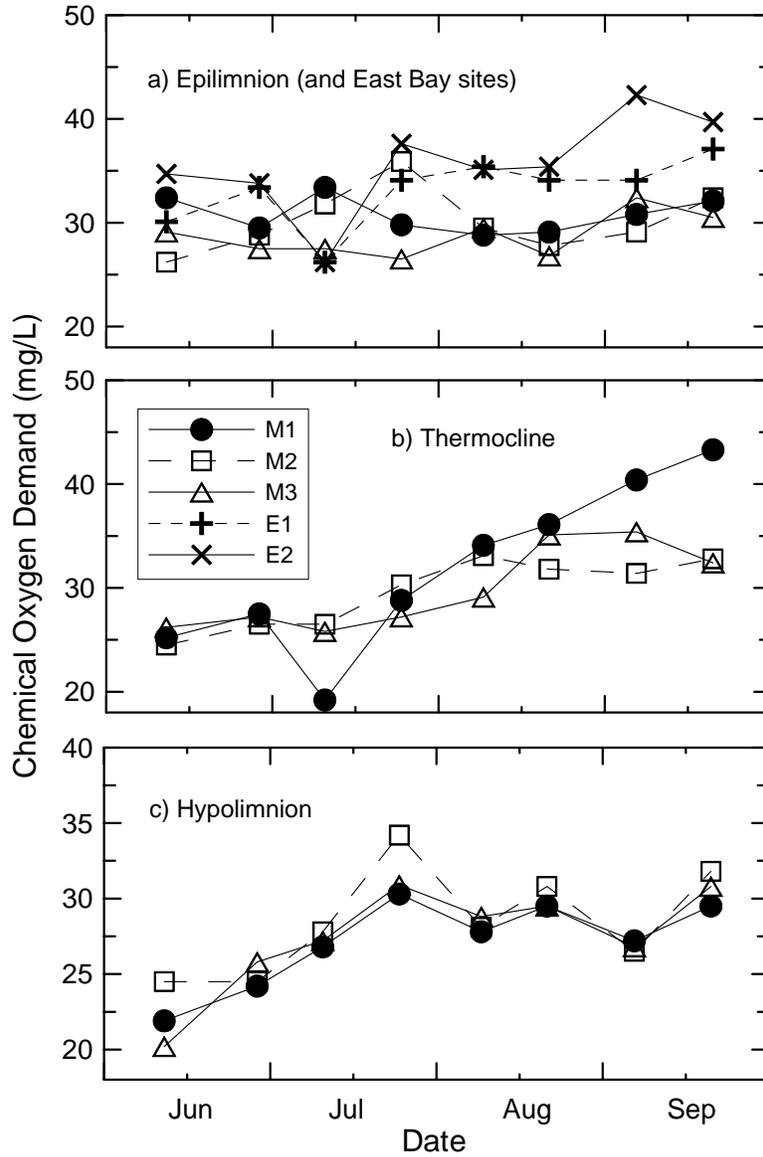


Fig. 10. Chemical oxygen demand (COD) concentrations over time: a) epilimnion and East Bay sites, b) thermocline and c) hypolimnion. Thermocline and hypolimnion samples from the main lake sites only.

BOD concentrations were generally greatest in the hypolimnion and lowest in the thermocline. The vertical gradient in BOD was more evident in the September 6 samples, with low BOD concentrations measured in the epilimnion and thermocline, typically 3- 5 mg/L, while much higher values were present in the hypolimnion (approximately 8-18 mg/L) (Table 3).

Table 3. BOD concentrations in samples collected on August 9 and September 6, 2006. Concentrations in units of mg/L.

Site	Sample Type	9-Aug	6-Sep
M1	Epilimnion	6.4	4.9
	Thermocline	5.0	3.9
	Hypolimnion	9.7	18.5
M2	Epilimnion	6.6	3.9
	Thermocline	7.4	4.7
	Hypolimnion	9.1	7.7
M3	Epilimnion	7.8	4.0
	Thermocline	7.0	3.2
	Hypolimnion	10.8	14.8
E1	Depth-Integrated	10.3	6.0
E2	Depth-Integrated	8.8	4.4

Other Chemical Properties

A suite of other chemical and physical properties were also determined, including total suspended solids, total dissolved solids, and hardness. With the exception of TDS, these parameters exhibited no clear spatial or temporal trends (Appendix), so mean values were calculated using all sites, depths and dates. Total suspended solids concentrations averaged 6.2 ± 8.8 mg/L, while TDS concentrations averaged 701 ± 84 mg/L. TDS levels were higher in the East Bay samples than in the main body, however (757 ± 73 vs. 687 ± 80 mg/L, respectively) and is thought to reflect greater evapoconcentration effects that result from evaporation from a smaller depth/volume of water. There thus exists a modest temperature (Figs. 2 and 3) and salinity gradient across East Bay and into the main body of the lake. Total hardness averaged 112.4 ± 3.4 mg/L and was relatively uniform across the lake. Dissolved Fe concentrations were very low in the epilimnion, East Bay and thermocline samples (averaging 0.004 mg/L across these samples), while the average hypolimnetic concentration was higher (0.020 mg/L), although one would expect much higher concentrations for such a strongly reduced environment in contact with sediments derived in part from soil particles eroded off the watershed.

Dissolved Mn concentrations were substantially higher in the hypolimnion and moreover increased with time (Fig. 11). As with the dissolved nutrients, the higher concentrations of dissolved Mn from the depth-integrated samples at site E1 result from inclusion of some hypolimnetic water into the sample that yields much larger

concentrations than found in the other surface samples. Dissolved Mn levels declined in the surface samples to concentrations that were below detection (<0.001 mg/L), while hypolimnetic concentrations were 1000x greater (about 1 mg/L) (Fig. 11).

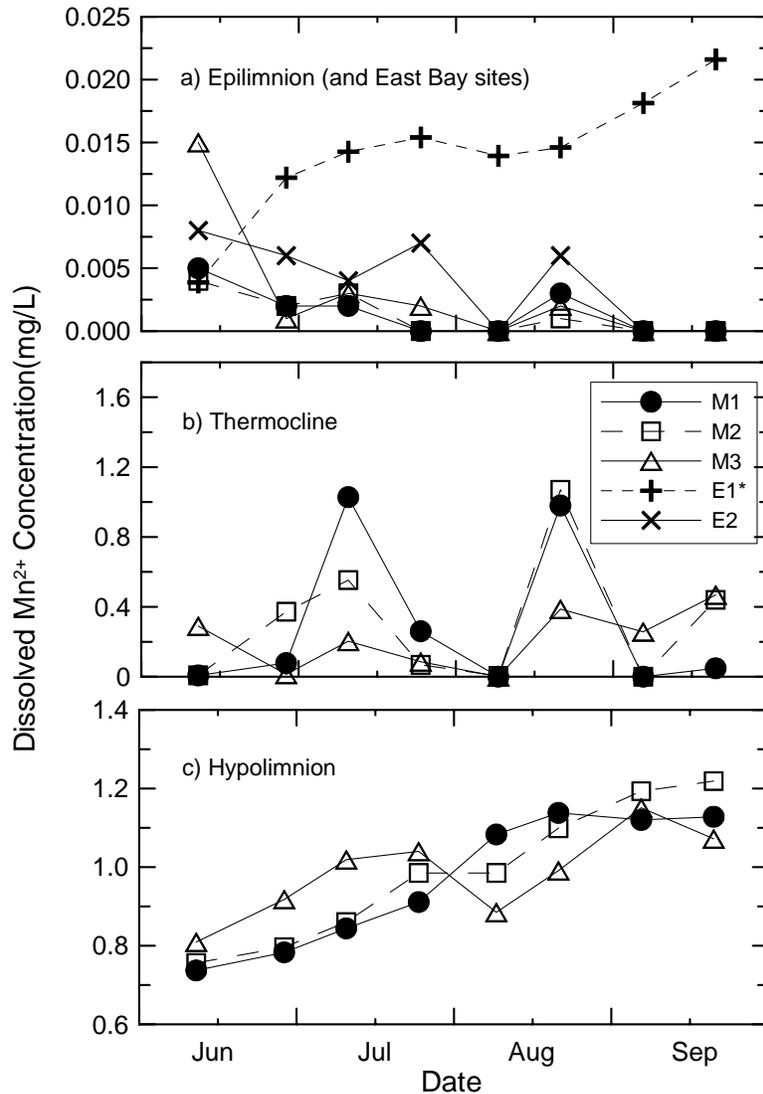


Fig. 11. Dissolved Mn concentrations over time: a) epilimnion and East Bay sites, b) thermocline and c) hypolimnion. Thermocline and hypolimnion samples from the main lake sites only. * Mn²⁺ concentration at site E1 scaled to fit on graph; actual concentration 15x greater (0.058 – 0.324 mg/L) and described further in text.

Thus, isolation of the lower portion of the water column from the atmosphere through thermal stratification results in depletion of DO (Fig. 2b), and increased levels of SRP (Fig. 7c), NH₄-N (Fig. 9c) and Mn (Fig. 11c). Since Fe and Mn are both redox-sensitive elements that are widely distributed in surface soils, the high concentrations of

Mn but low levels of Fe are somewhat surprising. It appears that sufficient sulfide has accumulated in the hypolimnion to precipitate most Fe as FeS or FeS₂ solid phases, and thus limit Fe²⁺ solubility. Dissolved Mn (as Mn²⁺), along with sulfide and Fe²⁺, would also contribute to the chemical oxygen demand of the hypolimnion, and these inorganic species (especially sulfide) probably constitute the majority of the COD in these bottom waters.

Sediment Nutrient Release and Sediment Oxygen Demand

While the accumulation of NH₄-N and SRP in the hypolimnion provides support for nutrient release from the sediments, nutrient release was explicitly evaluated through core-flux measurements made on cores collected on July 11th and September 6th (Table 4). The flux of SRP and NH₄-N from the sediments was large, and in all instances greater for cores collected in September than for those collected in July. Ammonium flux was approximately 3-4x higher than that of SRP. Release of nutrients was greatest at site E2, due in large measure to the higher water temperatures there than at the other sites (e.g., Figs. 2a and 3a).

Site	11-Jul		6-Sep	
	SRP flux (mg/m ² /day)	NH ₄ -N flux (mg/m ² /day)	SRP flux (mg/m ² /day)	NH ₄ -N flux (mg/m ² /day)
M1	10.1 ± 0.7	31.9 ± 9.3	20.2 ± 3.8	66.2 ± 5.6
M2	6.4 ± 3.1	19.2 ± 7.2	14.0 ± 3.1	56.6 ± 6.7
M3	9.8 ± 5.4	17.8 ± 7.2	13.3 ± 5.6	35.6 ± 16.2
E1	5.5 ± 2.6	25.5 ± 5.5	7.7 ± 4.4	49.8 ± 3.5
E2	20.3 ± 4.5	59.1 ± 4.5	24.0 ± 0.8	70.2 ± 0.9

The presence of respiring organisms and reduced chemical substances results in depletion of DO within the water column. While BOD and COD values provide a measure of the total demand for oxygen, it provides little information about the actual rate at which DO is removed from the water column. To assess the rate at which DO is depleted, water oxygen demand (WOD) measurements were made on samples collected on September 21, 2006 from the surface and bottom at site M2 and from the thermocline at site M1. The rate of DO depletion was 1.6 mg/L/d in the surface sample, 1.0 mg/L/d at the thermocline, and 1.8 mg/L/d in the bottom waters. Based upon these

rates, then, anoxia in the subsurface is expected to occur quickly following the onset of thermal stratification, potentially in as little as 4-8 days. These WOD values are comparable to those previously measured for Lake Elsinore (unpublished data).

The sediments can also exert, in some instances, a strong effect on DO levels in bottom waters; this was quantified through sediment oxygen demand measurements made on cores following nutrient flux measurements collected on July 11th (Fig. 11). Mean SOD values were quite similar across the 5 sites and averaged slightly less than 300 mg/m²/d, a rate lower than previously found for Lake Elsinore (~1000 mg/m²/d).

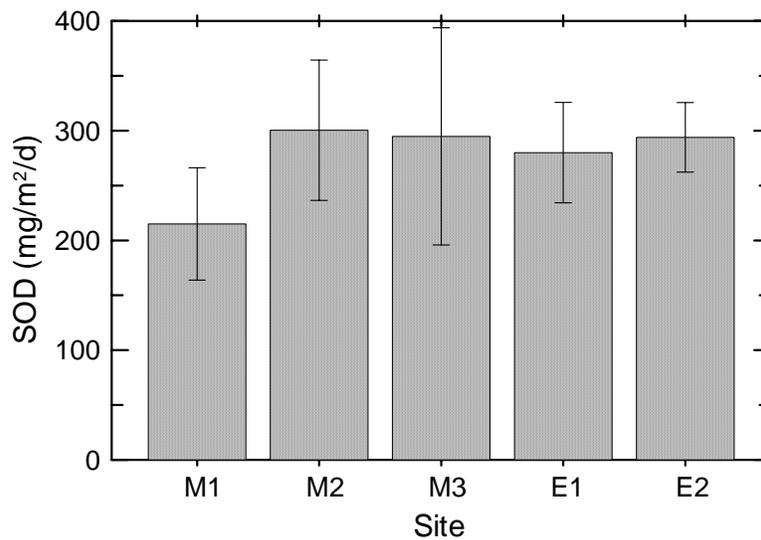


Fig. 12. Sediment oxygen demand measured on cores collected on July 11th.

Conclusions

During the summer quarter, Canyon Lake was found to be strongly stratified, with a warm (~27-28°C), well-aerated epilimnion extending 4-5 m below the water surface that deepened somewhat over time. A relatively sharp thermocline separated the epilimnion from a hypolimnion that was much cooler (about 14 °C) and strongly anoxic (DO <0.2 mg/L). Stratified conditions were present at the 3 main lake sites (M1, M2 and M3), with some stratification also found at the bottom of the water column at site E1. Site E2 was warm and essentially isothermal throughout the water column at this shallow (~4 m depth) site. Transparencies decreased through the summer, with greater transparencies in the main lake relative to the East Bay sites. High concentrations of total N, total P, SRP, NH₄-N and Mn²⁺ were present in the hypolimnion, with concentrations often increasing over time, especially at site M1. The greatest level of

algal production was found 4-5 m below the water surface, at the base of the epilimnion; this microenvironment provided adequate light for photosynthesis while also affording access to higher levels of nutrients present near the thermocline as a result of some diffusive exchange from the nutrient-rich hypolimnetic waters into the epilimnion. High levels of nutrients in the hypolimnion resulted in part from rapid rates of internal nutrient recycling from the bottom sediments. Biogeochemical processes in the sediments and lower water column also quickly deplete DO levels in the hypolimnion and have resulted in accumulation of sulfide and Mn^{2+} in the bottom waters of Canyon Lake.

References

- Anderson, M.A. and H. Oza. 2003. *Internal Loading and Nutrient Cycling in Canyon Lake*. Final Report. Santa Ana Regional Water Quality Control Board. 57 pp.
- APHA. 1998. *Standard Methods for the Examination of Water and Wastewater*. 20th Edition. American Public Health Association, Washington, DC.

Appendix

Field logs and laboratory results of all data collected during this quarter are provided in electronic form and submitted with this quarterly report.