

**Sediment Nutrient Flux and Oxygen Demand Study for Canyon  
Lake with Assessment of In-Lake Alternatives**

*Final Report*

*Submitted to:*

San Jacinto River Watershed Council  
2160 Santa Anita Road  
Norco, CA 92860  
Attn: Pat Boldt

*Submitted by:*

Michael A. Anderson, Catrina Paez and Sotheary Men  
Dept. of Environmental Sciences  
Univ. of California  
Riverside, CA 92521

June 25, 2007

## Introduction

Canyon Lake is a warm monomictic lake that is impaired by nutrients and pathogens. The lake can be separated into a small north basin that receives San Jacinto River flow and two southern basins – the shallow East Bay, which has high algal turbidity and low transparency, and the larger deeper main basin with greater transparency (Anderson and Oza, 2003). The deeper main basin of the lake ( $Z_{\text{max}} = 13\text{-}15\text{ m}$ ) maintains thermal stratification with an anoxic hypolimnion that persists for approximately 8 months of the year, while shallow East Bay is mostly well-mixed and oxic.

Sediment properties were previously found to vary across the basin, with higher concentrations of C, N, P, S and  $\text{CaCO}_3$  in the finest sediments (>60% clay-sized particles) that were principally located in the deeper regions of the main basin of the lake and occupied 31% of the lake bottom (Anderson and Oza, 2003). Coarse-grained sandy sediments were generally found close to the shoreline and in shallow embayments and comprised about 21% of the lake bottom, while silty sediments were mostly concentrated in East Bay and occupied an estimated 48% of the total area in the lake. The silty sediments of East Bay and other shallow embayments had greater rates of nutrient release, based on core-flux measurements than either the shallow sandy sediments or the deeper (colder) profundal sediments (average value of  $15.1\text{ mg/m}^2/\text{d}$  vs.  $6.3$  and  $6.5\text{ mg/m}^2/\text{d}$ , respectively). Internal recycling of N proceeded at an annual average rate approximately 4x that of P ( $23 - 35\text{ mg/m}^2/\text{d}$ ). Accumulation of SRP and  $\text{NH}_4\text{-N}$  within the hypolimnion of the main basin of the lake was used to independently estimate nutrient flux from the sediments; good agreement was found between core-flux and hypolimnetic mass balance methods.

Given the limited watershed runoff of 2001-2002, internal processes (nutrient recycling and resuspension) were the dominant source of nutrients to the lake over the study period. More recently, Canyon Lake received substantial runoff inputs from the watershed in 2004-05. Under such hydrologic conditions, runoff is expected to be a more significant source of nutrients to the lake.

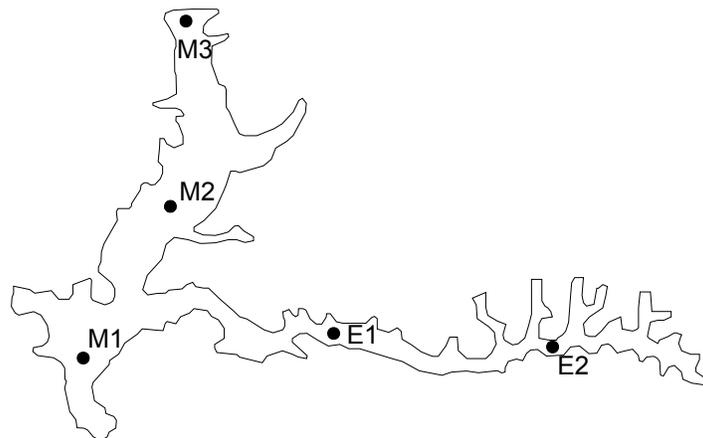
External loading can thus dominate water quality conditions during the cool rainy season and into the spring and summer, although these nutrients may be recycled a number of times, thus contributing to internal nutrient loading. Internal recycling of nutrients can thus dominate water quality through much of the year, especially during drought conditions. For example, external loading of phosphorus was estimated at only

about 4% of the loading due to internal recycling in 2001-2002 (Anderson and Oza, 2003). Similarly, external loading of N was only about 6% of the input from internal nutrient recycling from the sediments.

It is important, then, to understand internal recycling rates and the factors influencing those rates. Previous studies indicate that internal recycling is a complex function of temperature, local dissolved oxygen concentrations, sediment properties and overall lake water quality. This report summarizes results from a study conducted from June 2006 – April 2007 that (i) quantified nutrient release from sediments in the lake, (ii) determined sediment and water oxygen demand, and (iii) evaluated the suitability and effectiveness of different in-lake nutrient control strategies.

### Approach

Water column and sediment measurements were made at 5 sites in Canyon Lake (Fig. 1). Two of these sites were included in the assessment conducted in 2001-02, and thus allow direct comparison of internal recycling rates and other properties as found during a drought, 2001-02 (Anderson and Oza, 2003) with those in place following a high runoff year such as found in 2005 (this study). Measurements were also conducted to assess alternative in-lake treatment technologies for improving water quality in Canyon Lake. Based upon previous investigations, 3 alternatives were evaluated in lab studies: (i) aeration, (ii) hypolimnetic oxygenation and (iii) alum application.



*Fig. 1. Study site showing sampling sites in the main basin (M1, M2 and M3) and East Bay (E1 and E2).*

*(a) Sediment Nutrient Flux and Oxygen Demand*

Measurements of sediment nutrient release were conducted in July, September, November and April (2006-07). Sediment oxygen demand was determined on cores collected in the summer (July) and early spring (April). Measurements were made on triplicated intact sediment cores collected from 5 sites (also sampled for water quality) (Fig. 1). As previously noted, nutrient flux measurements were previously made for 2 of these sites, and sediment characterization was completed for all of them (Anderson and Oza, 2003). Moreover, sites M1 and M2 represent relatively deep locations with sediments below the thermocline, and so will remain cool and isolated from the atmosphere during much of the year, while the others are in warm shallow waters. This will provide a clear assessment of the two different environments present in the lake.

Cores were collected following Beutel (2000). 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 subsequently 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  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$  and SRP using an Alpkem autoanalyzer following standard methods (APHA, 1998). Dissolved oxygen was measured using a YSI Model 55 DO meter, with the water briefly sparged with  $\text{N}_2$  or lab air as needed 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 on cores collected in July 2006 and April 2007, 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.

### *(b) Evaluation of In-Lake Treatment Alternatives*

The above measurements provide information about the rates of nutrient release and oxygen demand under conditions present in the lake at the time of collection. Separate measurements were also made to assess the capacity of aeration, hypolimnetic oxygenation and alum application to slow the rate of internal loading. The efficacy of dredging at reducing internal loading is presently being evaluated under a separate agreement with Canyon Lake POA.

To evaluate the effectiveness of aeration and oxygenation at controlling nutrient release from sediments, two additional sets of triplicate cores were collected in August 2006 and April 2007 at the 2 deepwater sites (M1 and M2) on the main basin of the lake (Fig. 1). One set of these sediment cores from each site was aerated at the average epilimnetic temperature to simulate aeration achieved with destratification, while the 2<sup>nd</sup> set was aerated at the hypolimnetic temperature, as would be achieved with hypolimnetic oxygenation (i.e., without destratification). Sediment oxygen demand was also quantified for these cores under these temperature and oxygen conditions.

To assess the suitability of the lake for an alum treatment, jar tests were conducted to evaluate the pH, alkalinity and dissolved Al levels in Canyon Lake water collected on October 9, 2006 prior to and following after additions of 0 – 40 mg/L Al as the aluminum sulfate salt. Separately, alum floc was added to sets of replicate intact cores collected on November 27, 2006 from East Bay (site E2) and the main basin (site M1) to demonstrate control of SRP release from treated sediments. The forms of phosphorus within the sediments were determined using sequential extraction following Lewandowski et al (2003). The extraction results were also used to provide an estimate of the aluminum dose required to inactivate phosphate P within sediments from East Bay and the main basin of the lake (Rydin and Welch, 1999).

## **Results**

### *Forms of Phosphorus in the Sediments*

The sediment in Canyon Lake was found to be dominated by a reducible iron form (Fe-P) that accounted for about 1000 mg/kg or 60% of the average total P recovered by the extractions (Fig. 2). Aluminum-P was 2<sup>nd</sup> most abundant on average, accounting for 20-25% of the P in sediment from sites M1 and M2, although it constituted a smaller fraction (10.4-12.9%) of the total P recovered by extraction in the other sites. Calcium-P exhibited the largest spatial gradient, with over 400 mg/kg (27%)

of the extracted P from sediments at site E2, while the other, deeper sites ranged from 117-174 mg/kg (7.2-10.7%). The higher Ca-P at site E2 may be due in part to greater local inputs to this site of eroded calcareous soils from the Salt Creek watershed relative to the other sites due simply to proximity to the creek inlet. Labile-P includes SRP in porewater as well as readily-exchangeable forms of P in the sediments and accounted for only about 5% of the extracted P (Fig. 2). Organic-P was also a minor component of the P in the sediments, at concentrations of 39 – 147 mg/kg (2.1 – 7.0% of the P recovered by the extractants) (Fig. 2).

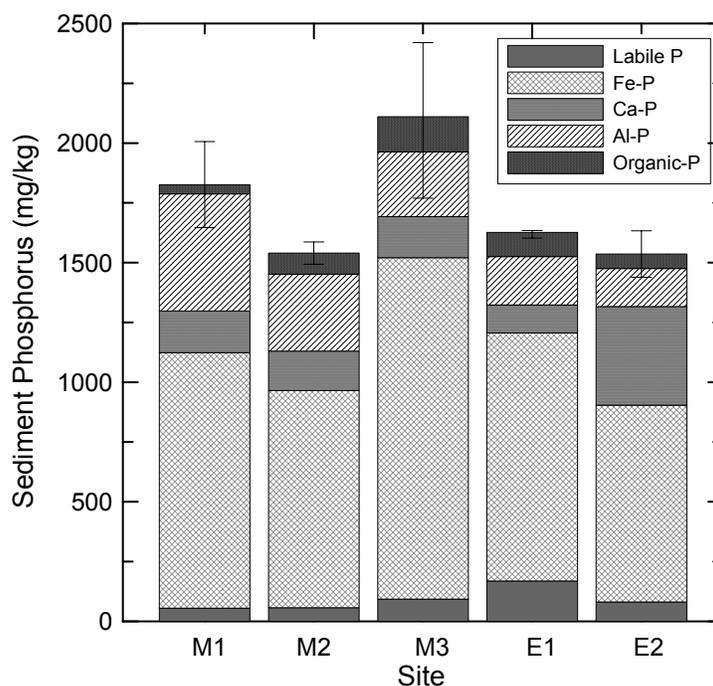


Fig. 2. Forms of phosphorus in sediments recovered using the sequential extraction technique of Lewandowski et al. (2003).

The porewater+exchangeable P (i.e., labile-P) is the most readily available for release to the water column, although Fe-P also serves as a readily available form when anoxic conditions in the hypolimnion and sediments reduce the iron(III) phases retaining the phosphate via specific adsorption and precipitation reactions. Organic-P is also potentially released through mineralization reactions, although it generally considered that such P would partition to Fe, Al or Ca phases upon release from organic matter. The Al-P and Ca-P forms are generally considered to be fixed against release since Al and Ca are not subject to reductive dissolution reactions (in contrast to Fe(III) phases). (The

quantity of P in labile+Fe-P forms is often used to estimate alum dose requirements. This will be addressed later in this report.)

The quantity of labile+Fe-P was highest at site M3 (1521 mg/kg) and lowest at site E2 (904 mg/kg); one might anticipate SRP flux to follow this trend, although nutrient flux is a complex function of sediment and water column properties.

#### *Nutrient Release from Sediments*

The release of  $\text{NH}_4\text{-N}$  and SRP from sediments varied seasonally as well as across the sites. SRP was released from site E2 at a very high rate through the year (19.6 – 25.7  $\text{mg/m}^2/\text{d}$ ) (Fig. 3). SRP flux was lower and varied more strongly over the year at site E1 (Fig. 3a). While both sites are within East Bay, site E2 is in shallow water (only about 3 m depth) that was well-mixed with generally high DO levels and high temperatures during the summer (e.g., Men and Anderson, 2007). In contrast, site E1 was located in deeper water (~6 m) and just below the thermocline that resulted in cooler summer temperatures with strong anoxia.

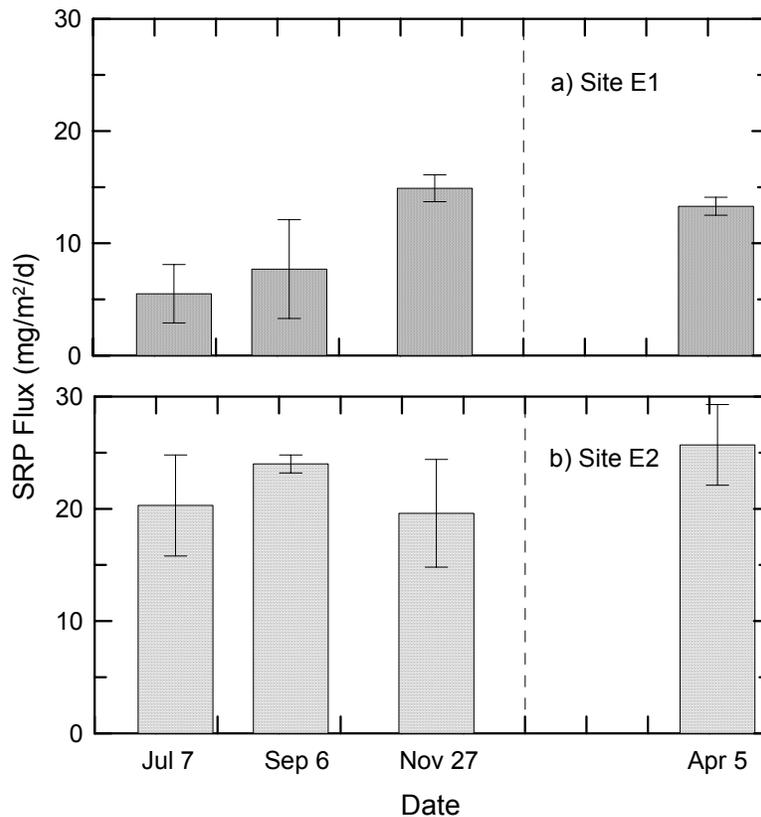


Fig. 3. SRP flux from East Bay sites: a) site E1 and b) site E2.

The rates of SRP flux from the 3 main sites followed the seasonal trends present at site E1, with generally lower rates during the summer and higher rates during winter and early spring (Fig. 4). The consistently highest rate of release occurred from cores collected on April 5<sup>th</sup>, 2007, with sites M1, M2 and M3 all releasing phosphate at rates exceeding 20 mg/m<sup>2</sup>/d (Fig. 4).

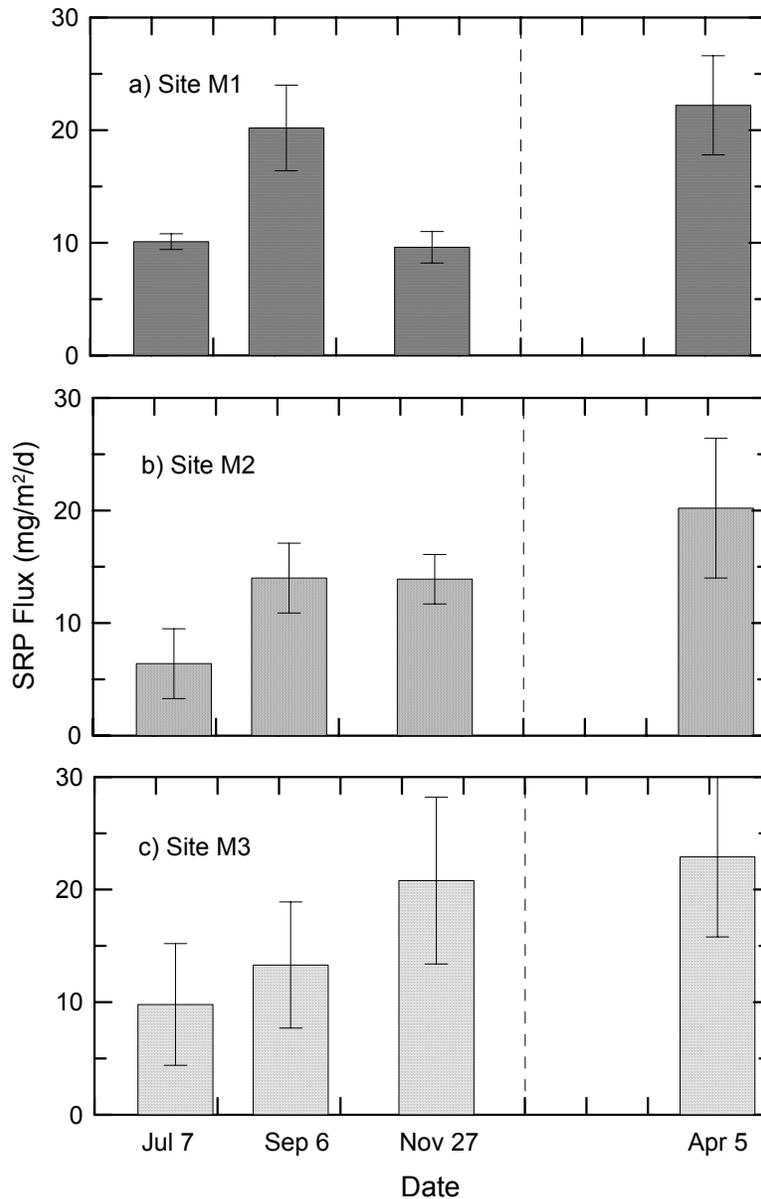


Fig. 4. SRP flux from main basin sites: a) site M1, b) site M2 and c) site M3.

The temperature and DO conditions varied rather little during sampling at sites M1-M3 and E1, however, and were consistently anoxic and cool (12-16 °C) (Table 1), so the seasonal variation in SRP flux appears to be due in more complex ways to the presence and duration of stratification, algal succession and other factors. In contrast, site E2 was consistently warmer on all 4 sampling dates with high levels of DO found in November and April (Table 2). The effects of DO and temperature on SRP flux were explicitly evaluated as part of the in-lake treatment assessment and will be discussed later.

Date	Sites M1-M3, E1		Site E2	
	Temperature (°C)	DO (mg/L)	Temperature (°C)	DO (mg/L)
Jul 7	14	<1	26	>1
Sep 6	14	<1	25	1
Nov 27	16	<2	16	>6
Apr 5	12	<1	12	>4

The flux of NH<sub>4</sub>-N from the sediments at site E2 was strongly correlated with temperature, with the lowest flux rate from cores collected in April and incubated at 12 °C, while much higher rates of NH<sub>4</sub>-N release were measured during the summer, with rates exceeding 60 mg/m<sup>2</sup>/d (Fig. 5). NH<sub>4</sub>-N flux rates at the main sites were generally highest following mixing in November and exceeded 80 mg/m<sup>2</sup>/d at site M3 (Fig. 6). The average ratio of NH<sub>4</sub>-N flux to SRP flux for all sites and dates was 3.2 and reflected the rather strong N-limitations present in Canyon Lake through much of the year (Paez and Anderson, 2007).

These flux rates are generally higher than those found in 2001-2002 (Oza and Anderson, 2003). Two sites from the 2001-2002 study were included in this evaluation (sites M1 and E2). The SRP flux from site M1 increased from an annually-averaged value of 3 mg/m<sup>2</sup>/d in 2001-02 to 15.5 mg/m<sup>2</sup>/d in 2006-07. Similarly, the rate of SRP release from East Bay sediments increased from 18.8 to 22.4 mg/m<sup>2</sup>/d. NH<sub>4</sub>-N flux at both sites also increased from values measured in 2001-02 (e.g., from average values of 26.4 and 35.4 mg/m<sup>2</sup>/d in 2001-02 to 49.8 and 44.9 mg/m<sup>2</sup>/d in 2006-07 at sites M1 and E2, respectively).

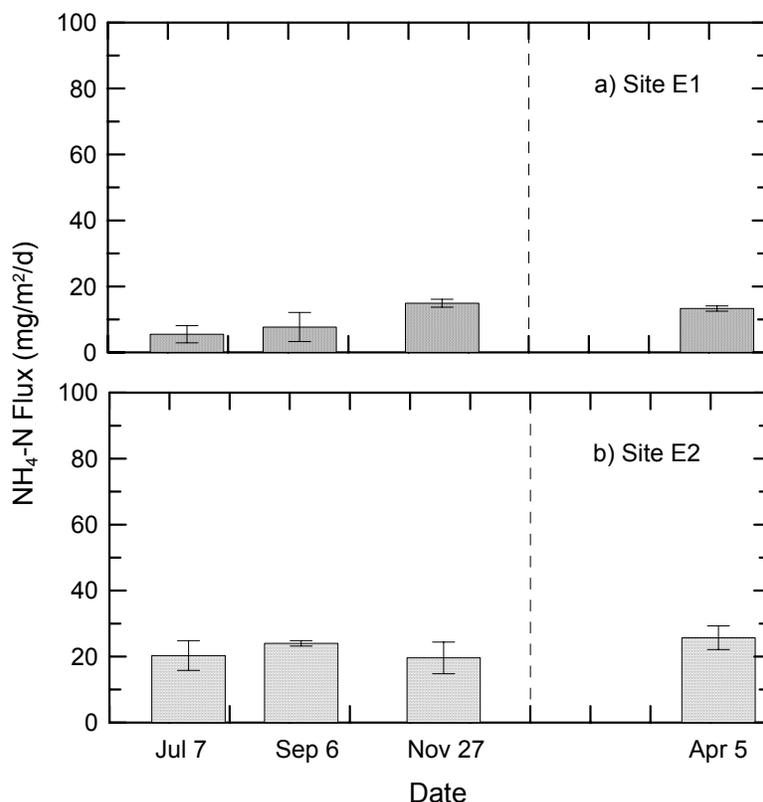


Fig. 5. NH<sub>4</sub>-N flux from East Bay sites: a) site E1 and b) site E2.

These findings demonstrate that the sediments act as a long-term source of nutrients in the lake, irrespective of drought conditions (2001-2002) or following a large runoff year (2006-2007), although these results indicate greater internal recycling following large external loading events. In the absence of continued, external loading, burial, conversion of labile forms to less reactive forms, and other reactions slowly reduce the rate of internal recycling.

The average nutrient release rates measured in this study can be compared with those determined for other lakes in the region (Table 2). The average rate of SRP flux from Canyon Lake this past year exceeded, as previously noted, rates measured in Canyon Lake in 2001-2002, as well as rates found in Lake Elsinore and, by a very large margin, the average rate of SRP flux recently determined for Lake Skinner (Table 2). Ammonium-N flux was also up from that measured in 2001-2002 and 5x higher than that determined for Lake Skinner, but below the rate measured in Lake Elsinore (Table 2).

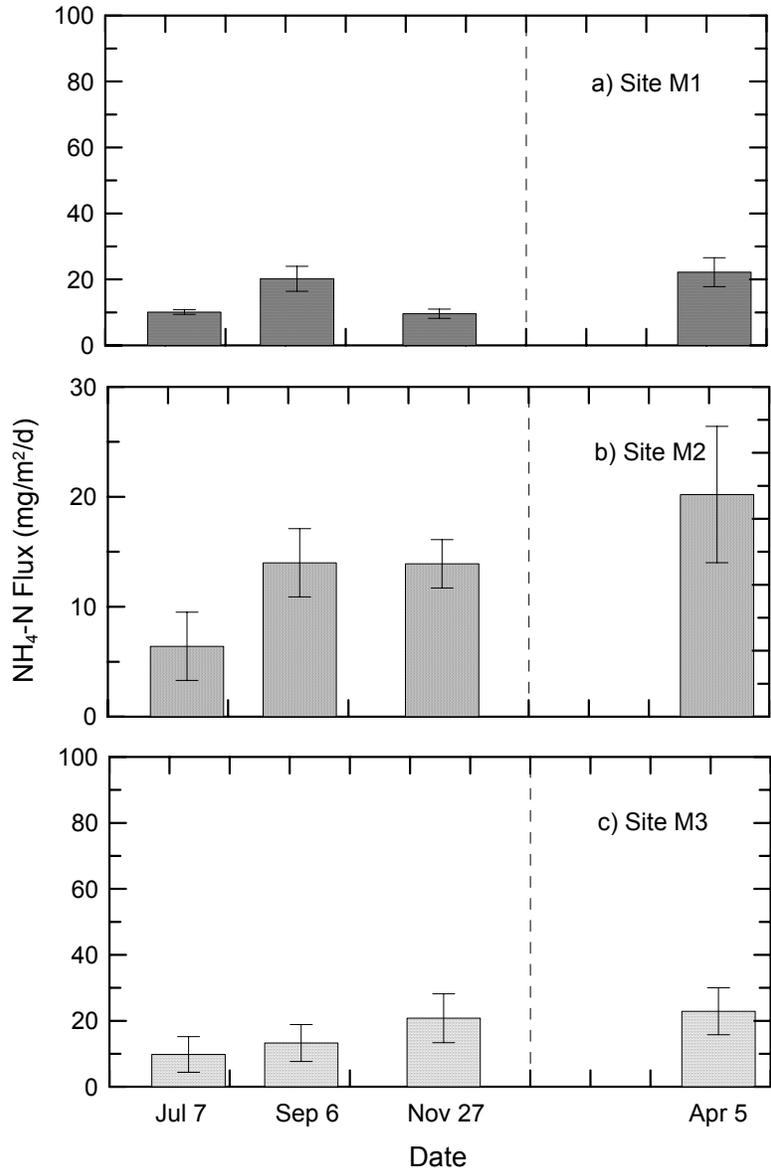


Fig. 6. NH<sub>4</sub>-N flux from main basin sites: a) site M1, b) site M2 and c) site M3.

Flux (mg m <sup>-2</sup> d <sup>-1</sup> )	Canyon L. (This Study)	Canyon L. (2001-02)	L. Elsinore (2001)	L. Skinner (2007)
SRP	15.7	9.4	9.4	0.5
NH <sub>4</sub> -N	44.1	28.5	72.2	8.6

This capacity for sediments to serve as a long-term source of nutrients, effectively functioning as a long-term buffer system that can supply nutrients and fuel algal growth for many years, has led to a number of control strategies to inhibit internal recycling. Particular emphasis has been placed on control of phosphorus, since it is the most common limiting nutrient in freshwater systems.

### *Assessment of In-Lake Treatment Alternatives*

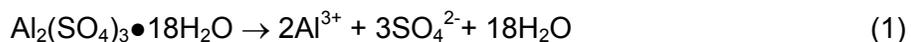
Three different approaches to inhibit nutrient release from Canyon Lake sediments were evaluated in this study: alum treatment, aeration and hypolimnetic oxygenation.

#### a) Alum Treatment

The goal of an alum treatment is to convert labile-P and Fe-P (forming so-called mobile-P) (Fig. 2) into irreversibly sorbed/precipitated Al-P forms. Since Al is not a redox-sensitive element, the  $\text{Al}(\text{OH})_3$  phase formed following alum addition is stable under both oxic and anoxic conditions; phosphorus is thus retained by Al irrespective of DO conditions near the sediments. This contrasts the Fe(III)-phases in sediments that, while possessing a high capacity for binding phosphate, readily dissolve under low redox conditions thereby releasing SRP back to the water column.

Naturally occurring Al-phases were present in the sediments Canyon Lake sediments and retained 159 – 490 mg/kg P (or 10.4 – 26.8 % of the total recovered by extractions) (Fig. 2). This compared with the 60 – 70% associated with labile+Fe-P forms. Addition of alum drives the conversion to Al-P forms and thus inhibits SRP release from the sediments.

The suitability of an alum treatment for Canyon Lake depends in part upon the chemistry of the lake. Addition of alum results in dissociation of the alum salt:



followed by hydrolysis of Al and production of acidity:



Thus 3 mols of  $\text{H}^+$  are produced for each mol of Al added. Care must be taken to avoid low pH following treatment however, as the solubility and toxicity of Al increases markedly at low pH values.

As a result, the first step in considering an alum treatment is to evaluate the acid-neutralizing capacity (alkalinity) of the lake. Alkalinity in the lake has been measured regularly as part of the monitoring component of our work on the lake. Alkalinity has averaged about 3.4 meq/L across all sites and depths. On that basis, the lake should be able to readily accept an alum dose up to 3 meq/L of Al or 1 mmol/L. Since the atomic weight of Al is 27 g, 1 mmol/L Al is equivalent to 27 mg/L, so an alum dose up to at least 27 mg/L could be added without greatly lowering the pH.

Jar tests were used to more carefully evaluate pH, alkalinity, and dissolved Al levels as a function of alum dose in lake water collected on October 9, 2006. Alkalinity and pH were determined approximately 1 h after alum addition and again 24 h later after vigorous sparging with air to hasten the approach to chemical equilibrium (Anderson, 2004). Samples were also filtered and analyzed for dissolved Al after 24 h.

The pH of the water declined significantly with increased alum dose immediately following treatment, although pH values returned to near pretreatment levels (7.6-8.4) after equilibration (Fig. 7a). This pH shift has been observed in prior laboratory studies and is due to the out-gassing of CO<sub>2</sub> formed from reaction of H<sup>+</sup> with bicarbonate alkalinity (Anderson, 2004).

Correspondingly, alkalinity declined linearly with increasing alum dose (Fig. 7b). Alkalinity was also unchanged over time, with equilibrium values that were generally within 0.05 meq/L of the concentrations determined shortly after alum addition (Fig. 7b). Dissolved Al concentrations after equilibration exhibited maximal concentrations at low alum doses that decreased nonlinearly with increasing dose (Fig 7c) and modestly reduced pH (Fig. 7a) following known pH-solubility relationships for amorphous Al phases (Anderson, 2004). These experimental results confirm that an alum dose up to 30 mg/L as Al will not dramatically alter the equilibrium pH or dissolved Al levels, and in fact a dose up to 40 mg/L may be possible. Higher doses would require use of buffered alum or aluminate.

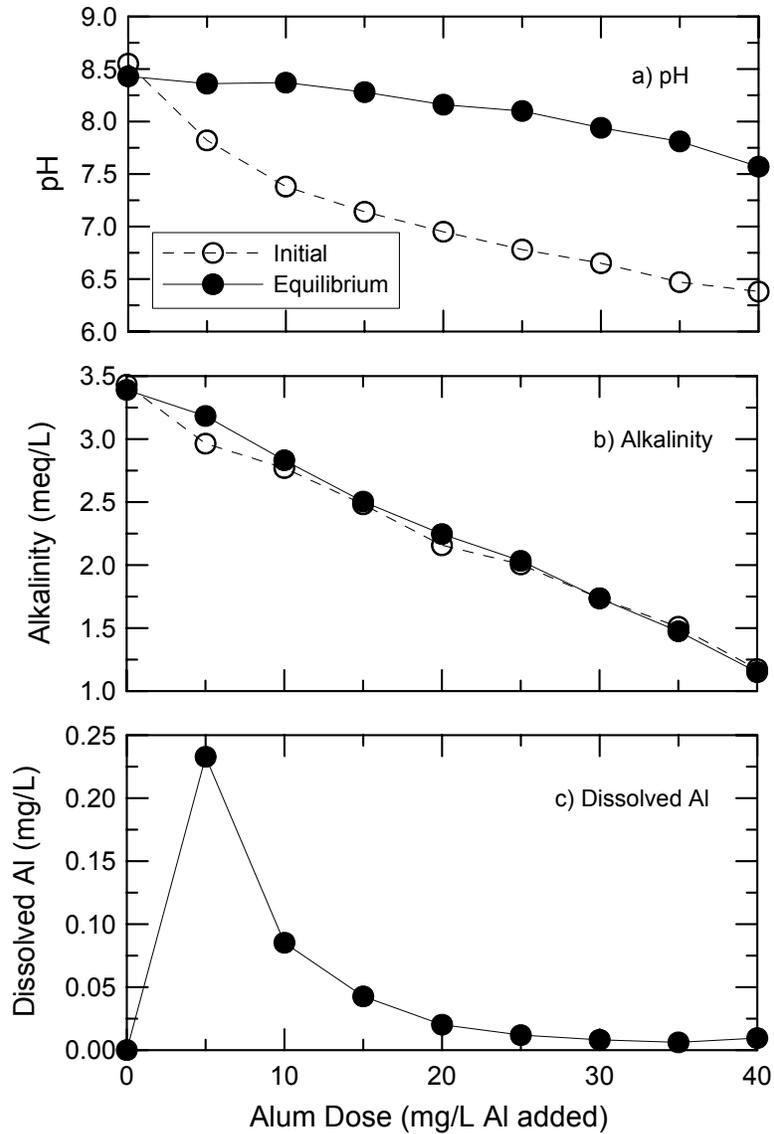


Fig. 7. Jar test results: a) pH, b) alkalinity and c) dissolved Al as function of alum dose.

Alum floc added to cores collected on November 27<sup>th</sup> at a rate of approximately 20 g Al/m<sup>2</sup> greatly reduced the rate of SRP flux when compared to rates measured from reference cores (i.e., without alum floc added) (Fig. 8). In fact, alum floc *removed* SRP from the water column overlying site M1 cores, resulting in a significant negative flux. While a higher rate of SRP flux from the sediments at site E2 was found, alum also very effectively controlled P release at this site as well, achieving an 85% reduction in SRP flux (Fig. 8). Alum floc added to cores also slowed by 20-70 % the release of NH<sub>4</sub>-N from sediments collected at these sites (data not shown). Although NH<sub>4</sub><sup>+</sup> is not thought to

interact strongly with alum floc, some additional cation exchange capacity, combined with greater impedance to diffusive flux, is thought to have altered the rate of ammonium flux in these cores.

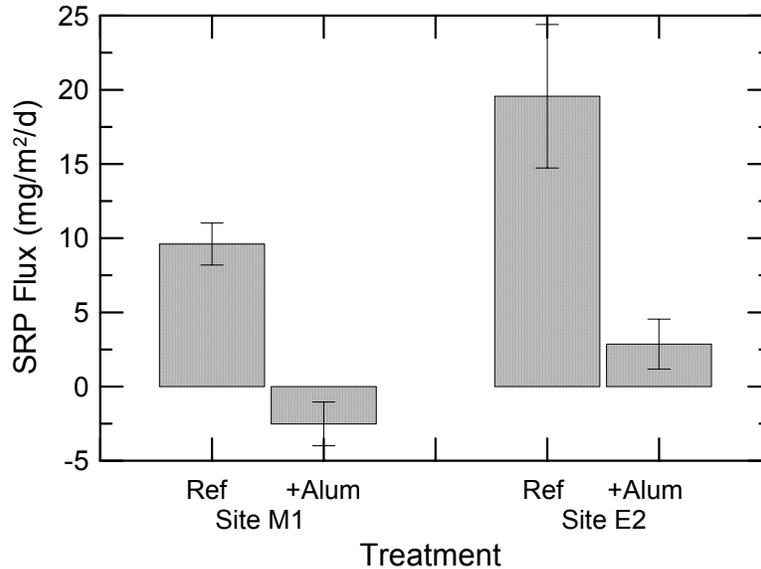


Fig. 8. Effect of alum floc on SRP flux from sediment cores.

The amount of alum needed to inactivate the potentially mobile P in the sediments can be estimated alternately from extraction results (Fig. 2) as well as measured SRP flux rates (Figs. 3-4).

As previously noted, mobile-P is generally taken as labile-P+Fe-P (Rydin and Welch, 1999). Mobile-P concentrations ranged from 904 – 1521 mg/kg and averaged 1144 mg/kg over the 5 sites (Fig. 2). For this calculation, we will ignore site to site differences and use the average mobile P concentration. The total amount of mobile-P to be inactivated is a function of the assumed depth of active exchange with the water column and the mass of sediment per unit volume of wet sediment (water+sediment). From prior work on sediments, approximately 90% of the wet sediment volume is typically present as water. The remaining 10% of the sediment volume exists as solids; the density of the sediment solids can vary from about 1.0 g/cm<sup>3</sup> for organic matter to 2.6 g/cm<sup>3</sup> for SiO<sub>2</sub>. For these calculations, it was assumed that the particle density was 2.0 g/cm<sup>3</sup> to reflect the modest organic matter contents in the sediments (Anderson and Oza, 2003). Further assuming a 10-cm reactive zone and using a target of 10:1 added Al

to mobile P (Rydin and Welch, 1999), the average alum dose to inactivate the mobile-P in the sediments is estimated at 229 g Al/m<sup>2</sup>.

For comparison, one can estimate the alum dose required to inactivate P based upon SRP flux measurements. The annual average SRP flux for the 5 sites varied from 10.4 – 22.4 mg/m<sup>2</sup>/d, with a mean value across the 5 sites of 15.7±4.4 mg/m<sup>2</sup>/d. The required alum dose is a function of the anticipated longevity of the treatment. While alum has been shown to be effective for 10-15 yrs, given the hydrology of the region and the potential for periodic large external loading events, we will assume a desired 5-yr treatment effectiveness. Thus, the product of the annual average internal loading rate, treatment duration, and a 10:1 added Al to mobile-P ratio, one calculates a required alum dose of 287 g Al/m<sup>2</sup>.

These two estimates are in reasonable accord and point to a very high alum application rate. For comparison, the Al dose applied to Big Bear Lake in 2004 was 29 g Al/m<sup>2</sup>.

To reach these dose rates will require adding a significant of alum that may yield quite high concentrations in the lake, especially in East Bay and other shallow areas of the lake if treated. The local concentration of Al in g/m<sup>3</sup> (or equivalently, mg/L) can be readily calculated from the Al dose rate (e.g., 229 g Al/m<sup>2</sup>) divided by the depth (m). Thus, treatment of much of East Bay with depths of about 3 m (e.g., near site E2) to the mobile-P based dose of 229 g Al/m<sup>2</sup> would require addition to an average concentration of 76 mg/L Al. Importantly, this far exceeds the water's alkalinity and natural capacity to neutralize the acidity generated from alum hydrolysis, and so would require use of buffered alum to maintain appropriate pH values there. The depth-averaged Al concentration would be lower in the main portion of the lake however (e.g., 18 mg/L at site M1 that has a depth of approximately 13 m). This lower treatment concentration is within the lake's natural capacity to buffer against strong reduction in pH, so regular liquid alum could be at the deep-water regions.

#### b) Aeration

The effects of aeration on nutrient release from sediments were evaluated by comparing flux rates from natural and aerated sediment cores collected on September 20, 2006 and April 5, 2007 from sites M1 and M2. Sites M1 and M2 represent the 2 deepest sites in this assessment and thus are subject strong summer stratification. One set of triplicate cores from each site was incubated at the temperature and DO

conditions present at the time of sampling (flux rates previously described), while a 2<sup>nd</sup> set of cores were vigorously sparged with air. Samples were filtered and analyzed for SRP and NH<sub>4</sub>-N as previously described.

The flux of SRP was reduced an average of 37% (excluding the apparent increase in flux at site M2 from the September 2006 assay) (Table 3). Since aeration would destratify the water column, the aerated cores were incubated at warmer temperatures (21-25 °C) than the reference cores, which were held at 12-15 °C. This, combined with potentially insufficient airflow, may account for the elevated SRP flux relative to the M2 reference cores. Since this feature was not found when repeated in April 2007, this observation was excluded from the calculation of the average % reduction in SRP flux. Careful inspection of the cores from April 2007 confirmed continual vigorous airflow and development of a light brown oxidized layer on the surface of the sediments. Despite strongly aerobic conditions, SRP flux was observed to continue, albeit at a slower pace. A reduction in SRP flux of 35-40% is consistent with results from similar measurements made on Lake Elsinore sediments.

	M1		M2		Average % Reduction
	Reference	+Aeration	Reference	+Aeration	
<i>SRP Flux</i>					
Sep 2006	14.0±1.4	9.3±3.1	8.7±1.2	12.7±1.5 <sup>a</sup>	37%
Apr 2007	22.2±4.4	13.9±4.8	20.2±6.2	12.1±6.4	
<i>NH<sub>4</sub>-N Flux</i>					
Sep 2006	71.3±4.1	98.3±46.4	27.0±4.6	71.3±34.7	Variable
Apr 2007	41.2±2.6	-36.6±0.1	21.2±0.8	-19.4±9.6	

The flux of NH<sub>4</sub>-N exhibited different behavior in cores collected in September 2006 with those collected in April 2007 (Table 3). The measurements from the fall indicated an increase in NH<sub>4</sub>-N flux, presumably due to the higher temperatures. Seasonal trends support the role that higher temperatures can play on rates of NH<sub>4</sub>-N flux. Measurements repeated in April 2007 found a net loss of NH<sub>4</sub>-N from the water column, however, indicating not only a reduction in NH<sub>4</sub>-N flux but also a reversal in the direction of flux. That is, under vigorous aeration at approximately 22 °C, NH<sub>4</sub>-N

concentrations in the water overlying the sediments actually declined. Specifically, the concentrations increased slightly over the 1<sup>st</sup> day, but declined rapidly after 1-2 days. Apparently 1-2 days were necessary to establish nitrifying conditions in the cores, although nitrate concentrations were not explicitly quantified in these samples.

### c) Hypolimnetic Oxygenation

The effect of hypolimnetic oxygenation on nutrient flux was simulated in laboratory studies by sparging water overlying replicate cores with air while maintaining the temperature at that of the hypolimnion present at the time of sampling. Thus, both the sets of reference cores as well as the sets of oxygenated cores were maintained at the same temperatures (15 and 12 °C for the September and April tests, respectively). DO concentrations remained >8 mg/L in the oxygenated cores while levels declined to <1 mg/L in the untreated (reference) cores.

A large variation in the effect of hypolimnetic oxygenation on SRP flux was found in the September 2006 tests, with essentially no SRP flux out of the sediments at site M2, while only a modest effect on flux from site M1 was found (Table 4). These tests were repeated in April and confirmed the very dramatic reduction in SRP flux at site M2. A more dramatic reduction was also found for site M1 as well (Table 4). It appears there may be sufficient geochemical differences present at the 2 sites to yield large spatial differences. Notwithstanding, averaged over both sites and dates, hypolimnetic oxygenation was found to lower SRP flux by 71%.

The flux of NH<sub>4</sub>-N was more variably affected than SRP, although flux rates were lowered by an average of 35% across all tests. The source of the variability remains unclear, but differences over time and space in the types and concentrations of algal/detrital organic matter, bacterial population dynamics, and other factors no doubt play some role. Unlike aeration, we did not find evidence for nitrification over the modest duration of the core-flux studies simulating hypolimnetic oxygenation, although that is probably a result of the cooler temperatures (12°C vs. 21 °C). The cooler temperatures presumably slowed the development of a robust community of nitrifying bacteria when compared with the warm conditions in the aerated cores; it is expected that such a community would develop in a relatively short period of time and reduce NH<sub>4</sub>-N flux to extents exceeding that in Table 4.

	M1		M2		Average % Reduction
	Control	+Oxygenation	Control	+Oxygenation	
<i>SRP Flux</i>					
Sep 2006	14.0±1.4	12.0±4.4	8.7±1.2	-0.1±2.2	71%
Apr 2007	22.2±4.4	5.4±5.0	20.2±6.2	1.1±1.6	
<i>NH<sub>4</sub>-N Flux</i>					
Sep 2006	71.3±4.1	60.3±11.8	27.0±4.6	3.7±13.7	35%
Apr 2007	41.2±2.6	17.5±1.8	21.2±0.8	25.2±6.0	

### *Sediment Oxygen Demand*

Both aeration and hypolimnetic oxygenation must supply DO at a rate sufficient to meet sediment oxygen demand (SOD). In the above tests, excess O<sub>2</sub> was provided to ensure that SOD was met and aerobic conditions were maintained at the sediment-water interface. Because of the electrical costs to operate compressors to drive a diffused aeration system, and the costs of oxygen in hypolimnetic oxygenation systems, it is prudent to have an estimate of the oxygen demand that must be met to maintain the sediment-water interface in an aerobic condition. Measurements were conducted on 2 dates to quantify the SOD in the lake.

In the initial assessment, SOD from all 5 sites was quantified on cores collected on July 11<sup>th</sup>, 2006. Mean SOD values from triplicate cores were quite similar across the 5 sites and averaged slightly less than 300 mg/m<sup>2</sup>/d (Fig. 9), a rate lower than previously found for Lake Elsinore (~1,000 mg/m<sup>2</sup>/d) and more recently for the Salton Sea (2,100-2,400 mg/m<sup>2</sup>/d) (Anderson, unpubl. data).

In follow-up measurements made on cores collected from sites M1 and M2 on April 5, 2007, both short-term and longer-term SOD rates were determined. Short-term SOD was specifically evaluated for cores held at 12 °C and not previously aerated to simulate the demand shortly after start-up of a hypolimnetic oxygenation system, while longer-term demand was measured on cores that had been continuously sparged at hypolimnetic temperatures (12 °C) for the preceding 6 days. Short-term SOD at the 2 deepest sampling sites was somewhat higher than found in the preceding summer, with SOD slightly lower at site M2 compared with site M1 (Table 5).

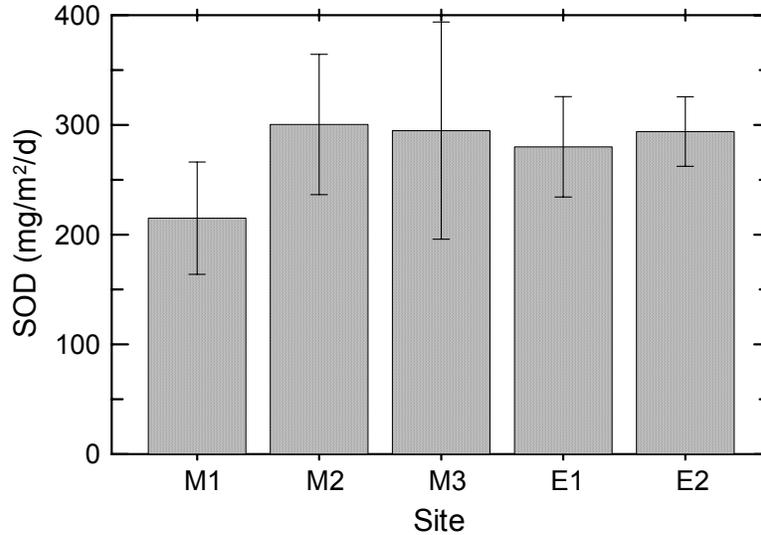


Fig. 9. Sediment oxygen demand measured on cores collected on July 11, 2006.

Prior sparging of the water column at hypolimnetic temperatures lowered the SOD rate by more than 1/3<sup>rd</sup> or 130-140 mg/m<sup>2</sup>/d at the 2 sites due to the oxidation of sulfide, Fe<sup>2+</sup> and Mn<sup>2+</sup> in the surface sediments. Further reductions in SOD may be witnessed under protracted oxygenation as reducing power of the sediments is offset by the diffusive flux of DO into the sediments.

Core Site	Hypolimnetic Oxygenation (12 °C)		Aeration ( 21°C)
	Short-term SOD (mg/m <sup>2</sup> /d)	Long-term SOD (mg/m <sup>2</sup> /d)	Long-term SOD (mg/m <sup>2</sup> /d)
M1	383 ± 23	251 ± 28	471 ± 14
M2	361 ± 17	221 ± 49	312 ± 20

Long-term demand under higher temperatures (21 °C in this experiment), as would be present during aeration that would destratify the main basin of the lake, was greater than SOD values measured at cooler temperatures present during hypolimnetic oxygenation (12 °C here). This is consistent with the increased rates of biological and chemical reactions with increasing temperature. The SOD was also greater at site M1 than M2, as found in the other SOD measurements, although the disparity was greater at 21 °C than 12 °C (Table 5).

With some assumptions about the area of sediments below the thermocline, one can make a provisional estimate the total O<sub>2</sub> needed to maintain oxic conditions near the sediments. Based upon lake bathymetry and water column profile measurements, we will assume about 140 acres of sediments lay below the thermocline and therefore will consume O<sub>2</sub> supplied by a hypolimnetic oxygenation system. Further assuming a long-term SOD rate of approximately 230 mg/m<sup>2</sup>/d, the daily O<sub>2</sub> requirement would be a modest 130 kg O<sub>2</sub>/d. Further assuming stratification is in place from March 15<sup>th</sup> – November 15<sup>th</sup> (245 days) and that the SOD rate remains unchanged with prolonged oxygenation, the total O<sub>2</sub> that must be supplied would be 31,850 kg. Additional O<sub>2</sub> would be needed to offset consumption due to biological respiration reactions in the water column. Water-oxygen demand (WOD) was measured at 1.8 mg/L/d in hypolimnetic water in the July experiment, although this included DO used to oxidize free sulfide, Fe<sup>2+</sup> and other reduced chemical species, and so does not represent a realistic long-term WOD in a well-oxygenated water. The BOD measured on March 22<sup>nd</sup>, shortly before sampling the cores in April, averaged 2.7 mg/L for the M1 and M2 sites, so using this value and the duration of the test (5-days), yields what is likely to be a more accurate WOD for the lake (about 0.5 mg/L/d). With an average hypolimnetic thickness somewhere near 5 m, the contribution of the water column is thought to be broadly comparable to the demand exerted by the sediments, so the total oxygen demand is expect to be closer to 250 kg O<sub>2</sub>/d.

#### *Cost Estimates for In-Lake Treatment Alternatives*

Cost estimates for the 3 in-lake treatment alternatives were taken from previous reports (Fast, 2002; Horne, 2001) or other documentation (BBMWD, 2004). Alum application to 200 acres of sediments (most of the main basin and East Bay) at the full recommended dose of 229 g Al/m<sup>2</sup> based upon the average mobile-P in the sediments is projected to cost \$ 1.1M assuming a cost of \$1.30/gal liquid alum (Table 6). The treatment would represent a one-time application and thus a one-time cost, so no annual operating costs are associated with such a treatment. The estimated capital costs for the diffused aeration and hypolimnetic oxygenation systems are both somewhere near \$250K and substantially lower than that for a full alum treatment (Table 6). Unlike alum, however, these systems would have significant annual operating costs, estimated to be on the order of \$20K-50K and associated with electrical costs (diffused aeration) and liquid oxygen (hypolimnetic oxygenation).

Table 6. Estimated costs for the 3 in-lake treatment alternatives. (Sources: <sup>a</sup> BBMWD; <sup>b</sup> Fast, 2002; <sup>c</sup> Horne, 2001).			
Costs	Alum <sup>a</sup>	Diffused Aeration <sup>b</sup>	Hypolimnetic Oxygenation <sup>c</sup>
Capital Costs	\$ 1.1 M	\$ 250K	\$ 200K - \$ 500K
Operating Costs (yr <sup>-1</sup> )	\$ 0	\$ 30K	\$ 20K - \$ 50K

These costs can also be normalized to unit mass of nutrient removed. For this analysis, we will focus on SRP flux, since it was previously noted that alum would be expected to have little long-term direct effect on nitrogen release. Assuming a nutrient source area of approximately 200 acres that releases an average of 15.7 mg SRP/m<sup>2</sup>/d, and a 10 yr project period, one estimates that 46,380 kg of SRP. Based upon SRP flux reductions determined in this study for alum, diffused aeration and hypolimnetic oxygenation (85, 37 and 71%, respectively), one can infer unit costs per kg SRP removal of \$27.9/kg SRP for alum, \$32.1/kg SRP for diffused aeration, and \$12.1-\$30.4/kg SRP for hypolimnetic oxygenation. While it is difficult to conduct a similar analysis for N, aeration and oxygenation are also expected to offer greater overall control for N than alum. Based upon this analysis then, hypolimnetic oxygenation offers the lowest cost for nutrient control.

### Recommendations and Conclusions

Internal recycling represents a substantial source of nutrients to the water column of Canyon Lake. A nutrient budget developed for 2001-02 indicated that >90% of the nitrogen and phosphorus loading to the lake was due to internal recycling. While a nutrient budget was not developed in this study, the very low precipitation and runoff this past winter, combined with high rates of internal loading (rates that were, in fact, higher than measured in 2001-02), certainly make internal processes once again the dominant source of nutrients to Canyon Lake. Moreover, the higher rates of N and P release from the sediments measured this year suggest that internal recycling rates increase following large external loading events (e.g., 2005).

Laboratory studies indicate that alum treatment, aeration and hypolimnetic oxygenation would all help slow the rate of nutrient release and improve water quality in the lake. Based upon our laboratory measurements, alum was the most effective at controlling internal loading of SRP, reducing by 85% or more SRP flux from the sediments. Hypolimnetic oxygenation was 2<sup>nd</sup> most effective, and achieved an average reduction in SRP flux of 71%, while aeration was the least effective, yielding an average

reduction in internal loading of SRP by 37%. The effect of these different in-lake treatments on  $\text{NH}_4\text{-N}$  release was more variable and thus makes it difficult to draw firm conclusions. On average, alum and hypolimnetic oxygenation had broadly similar effects on  $\text{NH}_4\text{-N}$  flux, achieving short-term average reductions of 35-45%. The effect of aeration varied dramatically, with comparatively weak aeration hastening the release of  $\text{NH}_4\text{-N}$ , although more intense aeration resulted in nitrification and strong removal of  $\text{NH}_4\text{-N}$  from the waters overlying the cores. Overall, however, sufficient evidence exists in the literature to indicate that maintenance of an adequate concentration of DO, either through hypolimnetic oxygenation or aeration, would limit  $\text{NH}_4\text{-N}$  release and promote active nitrification in the surficial sediments (Wetzel, 2001). The cooler temperatures associated with hypolimnetic oxygenation should slow the overall rate of N release compared with aeration, however.

Thus, while all 3 techniques have some merit, *hypolimnetic oxygenation* in our view offers the greatest overall potential for reliably and cost-effectively improving water quality in Canyon Lake. It was demonstrated to substantially lower the rate of internal recycling of SRP and also slow sediment release of  $\text{NH}_4\text{-N}$ , with the capacity to achieve even greater reductions in  $\text{NH}_4\text{-N}$  flux over a longer period of time than used in our studies. The conversion of  $\text{NH}_4\text{-N}$  to  $\text{NO}_3\text{-N}$  should also foster denitrification reactions and thus provide a mechanism for the net removal of N from the system. Alum is unlikely to achieve this. This is an important consideration since Canyon Lake often exhibits strong N-limitations. That is, simultaneous control of both P and N should have a greater beneficial effect on water quality than just P control likely to be achieved with alum. Concern also exists about watershed inputs overwhelming an alum treatment and rendering it ineffectual in controlling subsequent SRP flux. Finally, alum will not provide any control on the release and accumulation of  $\text{H}_2\text{S}$ ,  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  in the water column. These constituents make the hypolimnetic water unsuitable for routine use as a raw drinking water supply. Hypolimnetic oxygenation would dramatically improve water quality from this perspective as well. Aeration was found to be less effective than hypolimnetic oxygenation at controlling SRP flux and also necessarily destratifies the lake. Maintenance of stratification is viewed as highly desirable, since stratification limits the migration of any nutrients released from the deepwater sediments to the photic zone and, if adequately oxygenated, also provides a cool-water habitat that should provide for a richer and more diverse fishery as well as a daytime refuge for *Daphnia* and other zooplankton in the 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.
- Anderson, M.A. 2004. Impacts of metal salt addition on the chemistry of Lake Elsinore, California: 1. Alum. *Lake Reserv. Manage.* 20:249-258.
- APHA. 1998. *Standard Methods for the Examination of Water and Wastewater*. 20<sup>th</sup> Edition. American Public Health Association, Washington, DC.
- Beutel, M. 2000. *Lake Elsinore Sediment-Water Interface Study*. Final Report. 27 pp.
- Fast, A. 2002. *Lake Aeration System for Canyon Lake, California*. Report prepared for the Lake Elsinore-San Jacinto Watersheds Authority. 23 pp.
- Horne, A.J. 2001. *Restoration of Canyon Lake and Benefits to Lake Elsinore Downstream*. Report to the Santa Ana Watershed Project Authority. 24 pp.
- Lewandowski, J., I. Schauser, and M. Hupfer. 2003. Long term effects of phosphorus precipitations with alum in hypereutrophic Lake Süsser See (Germany). *Water Res.* 37:3194-3204.
- Rydin, E. and E.B. Welch. 1999. Dosing alum to Wisconsin lake sediments based on possible in vitro formation of aluminum bound phosphate. *Lake Reserv. Manage.* 15:324-331.
- Wetzel, R.G. 2001 *Limnology: Lake and River Ecosystems*. 3<sup>rd</sup> edition. Academic Press, San Diego, CA. 1006 pp.