Lake Machado
Nutrient Flux Study

Presented to:
The Southern California Coastal Water Research Project

August 2007

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Executive Summary

Machado Lake is a shallow urban lake located in the Ken Malloy Harbor Regional Park (KMHRP), which is a 231 acre Los Angeles City Park serving the Wilmington and Harbor City areas. Machado Lake is subject to nutrient related water quality problems such as algal blooms and eutrophic conditions and it has been placed on EPA's list of impaired waterbodies. Now subject to a Total Maximum Daily Load (TMDL), environmental managers are attempting to quantify sources of nutrients to Machado Lake. The objective of this study was to estimate the potential maximum flux rate of ammonia, nitrate and phosphate from the sediments of Lake Machado to the water column during both warm and cold weather. This experiment represents an initial range-finding test to determine if sediment flux was a potential nutrient source of concern. Depending on the outcome of this study it may be determined that a more detailed equilibrium study could be warranted.

The experimental design consisted of laboratory incubations of sediment cores collected from the center of Lake Machado, CA. In order to make conservative estimates of potential flux, reconstituted laboratory water was adjusted to the hardness and alkalinity of Lake Machado water and tested at winter (15 °C) and summer (25 °C) ambient temperatures. The nutrient flux test was started when a total of 600 mL of reconstituted laboratory water was added to each of 42 cores. For each temperature regime, triplicate core samples were sacrificed at the beginning of the test (T_o), 4 (T_4), 8 (T_8), 12 (T_{12}), 24 (T_{24}), 48 (T_{48}) and 96 (T_{96}) hours. At each time period, overlying water samples were analyzed for ammonia, nitrate, dissolved and total phosphate.

Overlying water nutrient concentrations were at least an order of magnitude greater at T_0 compared to each of the following time exposure periods. This was a function of two factors; resuspension from the sediment surface when the laboratory water was added to the cores and steep concentration gradients from sediment to clean overlying water. Within 4 hours of the beginning of the study, water column nutrient concentrations had decreased, presumably due to settling. Since some bias was introduced by the resuspension of surface sediments at the beginning of the experiment, the T_0 data were removed from the flux calculations.

To estimate flux rates for each nutrient, the results for the T_4 to T_{96} were averaged (± 95% CI) together for both the 15 °C and 25 °C test groups. The results were:

		Flux (mg/m^2/hr)			
Temp	Sample Size	NH_3-N	NO_3-N	Dissolved PO_4-P	Total PO_4-P
15°C	24	11.7 ± 6.4	1.9 ± 0.9	3.4 ± 1.6	4.9 ± 2.3
25°C	21	7.9 ± 4.7	1.8 ± 0.9	3.6 ± 1.4	5.2 ± 2.0

These nutrient flux rates were similar to, or less than, flux rates from sediments in Malibu Lagoon or Upper Newport Bay.

The results of this study provide an approximate range of nutrient flux from the sediments of Lake Machado to clean surface waters. Laboratory incubations are only one method of estimating flux. If the range-finding results provided herein appear large relative to other nutrient sources, then additional methods should be pursued to better quantify sediment nutrient flux. These methods include potential diffusive flux or *in-situ* experimental designs. Even for laboratory incubations, additional experimental design factors might include altering overlying water concentrations, using ambient waters, and assessing other important biogeochemical mechanisms such as grain size, total organic carbon, total nitrogen, and total phosphorus, amongst others.

1.0 Introduction

Machado Lake is a shallow urban lake located in the Ken Malloy Harbor Regional Park (KMHRP), which is a 231 acre Los Angeles City Park serving the Wilmington and Harbor City areas. Machado Lake is subject to nutrient related water quality problems such as algal blooms and eutrophic conditions. Machado Lake provides numerous beneficial uses, including wildlife habitat, aquatic habitat and recreation. Ken Malloy Harbor Regional Park and Machado Lake provide an important and well visited public recreational site.

The Los Angeles Regional Water Quality Control Board is charged with implementing the provisions of both the State of California Porter-Cologne Water Quality Control Act and the federal Clean Water Act in the Los Angeles Region. Section 303(d)(A)(1) of the Federal Clean Water Act requires the Regional Board to identify water quality limited segments within the Region. This includes water bodies not attaining water quality standards. Once these water bodies are identified, TMDLs are to be established for pollutants causing the impairments. The US EPA approved listing Machado Lake on the 2006 303(d) list of impaired water bodies in California for algae, ammonia, and eutrophic conditions. The developing TMDL will include a strategy to reduce nutrient related impairments at Machado Lake in order to protect beneficial uses and achieve water quality objectives set to protect those uses.

1.1 Project Objective

The objective of this study was to estimate the flux rate of nitrogen and phosphate based nutrients from the sediments of Lake Machado to the water column during both warm and cold weather. This is the first study of its kind on Lake Machado sediments and was designed to provide gross sediment flux estimates. The findings of this study should provide valuable information for future, more detailed studies. Appendix B contains responses to several questions posed by the Lake Machado Stakeholder group after their review of the document.

1.2 Site Description

Ken Malloy Harbor Regional Park is a 231-acre park administered by the City of Los Angeles Department of Recreation and Parks and located west of the Harbor (I-110) Freeway (Figure 1). The park houses Lake Machado (40 acres) and associated wetlands (64 acres), which is one of the last surviving remnants of extensive wetlands system that once covered much of the area between Wilmington and Redondo Beach. The lake and wetlands serve as flood retention basins for approximately 20 square miles of the Dominguez Watershed. Discharges from the lake and wetlands enter the West Basin of the Los Angeles Harbor through the Harbor Outflow structure. The riparian woodland, seasonal wetland, and scrub

Figure 1. Ken Malloy Harbor Regional Park & Lake Machado

upland that surrounds the lake supports hundreds of birds including sensitive, threatened and endangered species such as brown pelican, California least tern, western least bittern, American peregrine falcon, coastal California gnatcatcher, western snowy plover, white-tailed kite, yellow warbler, and tri-colored blackbird.

Wilmington Drain delivers 65% of the runoff entering Machado Lake. It extends north from the lake for 1.8 miles. The channel is soft bottom with natural banks from where it passes under the Harbor Freeway until it joins with Machado Lake. The Los Angeles County Flood Control District has designated this section the Wilmington Drain Waterway and Wildlife Area. Mature riparian woodland lines both sides of the channel and localized areas support freshwater marsh.

2. Methods

2.1 Sediment Core Sampling

On April 16th, 2007 between 0900 and 1200 hrs, bottom sediment samples were collected by LARWQCB staff from a pontoon boat at the center of Lake Machado using an Ekman dredge (Figure 2). Once on board, sediments were sub-sampled by carefully inserting a 30 cm length of Lexan tubing (6.5 cm ID) approximately 5 to 10 cm into the sediment. The bottom, then the top, of each core was then sealed using plastic caps (Figure 3). Subsampling was repeated until a total of 42 cores were collected. Each core sample was placed in an ice chest on wet ice (4 °C) for storage and transport to the Aquatic Bioassay and Consulting Laboratories in Ventura, CA.

Figure 2. Ekman dredge sampler

During sampling, water quality measurements for temperature, dissolved oxygen, conductivity, pH and chlorophyll a were collected using a pre-calibrated YSI multi parameter probe. Grab samples of water were also collected for nutrient analysis.

2.2 Study Design & Analyses

The 42 core samples were divided into two groups of 21 cores each which were placed in separate rooms at temperatures mimicking winter (15 °C) and summer (25 °C) conditions. The 21 cores were divided into seven groups of three cores each. Excess water was carefully removed from each of the core samples so that the disturbance to surface sediments was minimized. Reconstituted laboratory water was adjusted to a hardness of 300 mg/L and alkalinity of 160 mg/L, similar to Lake Machado water (alkalinity – 185 mg/L; hardness – 310 mg/L). The cores and water were left over night to temperature equilibrate.

Figure 3. Sediment core container.

The nutrient flux test was started the next morning when a total of 600 mL of reconstituted laboratory water was added to each of the 42 core samples. After the addition of the water, the samples were allowed to sit for 20 minutes to allow particulate matter to settle. This represented time zero (T_o). At T_o water samples were drawn from three core samples from both the 15 °C and 25 °C test groups, using pre-cleaned plastic syringes. Water samples were placed in a refrigerator at 4 °C. This process was repeated following 4 (T_4), 8 (T_8), 12 (T_{12}), 24 (T_{24}), 48 (T_{48}) and 96 (T_{96}) hours, with three cores sampled from each temperature regime. Water samples were shipped to CRG Laboratories in Torrance, CA as necessary to meet holding time requirements.

Water samples were analyzed for the following nutrients (as mg/L):

Analyte	Method	MDL	MRL
Ammonia-N	SM 4500-NH3	0.01	0.05
Nitrate-N	EPA 300.0	0.01	0.05
Nitrite-N	EPA 300.0	0.01	0.05
Dissolved Orthophosphate as P	EPA 300.0	0.008	0.01
Total Orthophosphate as P	SM 4500-P E	0.01	0.01

The reconstituted laboratory was nondetectable for all nutrient constituents measured.

2.3 Flux Rate Calculations

Flux rates were calculated in mg / m^2 / hr by multiplying each nutrient concentration (mg/L) by the volume of the core water (600 mL), dividing by the surface area of the core sample (0.0031 m^2), and then dividing by the total exposure time in hours.

3.0 Results & Discussion

3.1 Sediment Nutrient Flux Rates

Nutrient concentrations and flux rates from the sediments of Lake Machado are presented in Table 1 and Figures 4 through 7. Detailed fluxes for each time exposure are presented in the Appendix, Table A1. Nutrient concentrations and flux rates for each constituent were at least an order of magnitude greater at T_0 compared to each of the following time exposure periods. This is most likely indicative of resuspended nutrients from the sediment surface when the laboratory water was added to the cores (Table A1). Within 4 hours of the beginning of the study, water column nutrient concentrations had decreased, most likely due to settling. As a result, the T_0 flux rates were not included in the data analysis.

After T_0, the concentration of surface water ammonia and nitrate decreased, and dissolved and total orthophosphate increased during the course of the 96 hour exposure period in cores held at both 15 °C and 25 °C (Figures 4 thru 7). The decrease in ammonia may have been due to biogeochemical reactions, including transformations to nitrite and nitrate. The decrease in nitrate could have been the result of nitrification and subsequent volatilization of N_2. The majority of phosphate appeared to be in the dissolved form (Figures 6 and 7). For example, total PO_4-P at T_4 was approximately 29 mg/L, while the dissolved PO_4-P was approximately 27 mg/L. By difference, particulate PO_4-P was approximately 2 mg/L (< 8%) of the total PO_4-P. In contrast to nitrogen compounds, however, phosphorus increased over time indicating that the sediment was continuing to flux PO_4-P.

Average ammonia and nitrate concentrations were greatest in cores held at 15 °C, while average dissolved and total orthophosphate concentrations were somewhat greater in cores held at 25 °C (Figures 4-7). Similarly, the sediment flux rates for ammonia and nitrate were greatest in cores held at 15 °C, while average flux rates for dissolved and total orthophosphate were somewhat greater in cores held at 25 °C (Table 1).

It is clear that resuspension of sediments in overlying waters at T_0 played a key role in the flux rates measured in this experiment. As a result, the combined average flux rate measured in the T_4 to T_{96} cores may be the best estimate of nutrient flux rates from the sediments (Table 1). Alternatively, T_{12} approximates a median flux with T_4 and T_{96} representing a minimum and maximum flux rate, respectively. When considering the Lake Machado T_{96} sediment cores only, there was a negative flux of ammonia (NH_3-N) to the sediments in both the 15 °C and 25 °C exposures. This probably represented some uptake of ammonia by the sediments, coupled with the oxidation of ammonia to nitrite and nitrate. There was a slight positive flux of nitrate (NO_3-N) that was nearly the same at both temperatures. Both dissolved and total orthophosphate were greatest in the cores held at 25 °C. When considering the combined average flux rate of each nutrient (T_4 to T_{96}), ammonia flux was greatest, followed by both dissolved and total orthophosphate. Fluxes were very similar between temperature regimes.

Nutrient flux rates from Lake Machado sediments were compared two studies conducted on sediments in Malibu Lagoon (ML) and the Upper Newport Bay (UNB) (Sutula et al 2004, Sutula et al 2006) (Table 2). Maximum ammonia flux rates in Machado Lake were similar to maximum flux rates in ML and less than in UNB. Lake Machado nitrate, and dissolved and total orthophosphate were greater than ML and far less than the maximum flux rates in UNB. Sutula (et al 2004 and 2006) found that the remobilization of nitrogen and phosphate from the sediments to the surface waters of ML and UNB was an important source of these nutrients during the dry season.

The results of this study provide an estimated range of nutrient flux from the sediments of Lake Machado to clean surface waters. If the results from this simplistic range-finding experiment indicate that sediment flux is a potentially large source of nutrients to Machado Lake, then additional methods to better quantify sediment flux should be explored. For example, Sutula et. al. (2006) measured pore water to estimate potential diffusive flux and a benthic flux chamber to measure sediment flux *in situ.* In addition, laboratory incubations like the kind used in the present experiment can be modified and adapted to better represent the variables that influence flux. For example, varying the concentration of nutrients in overlying waters may reduce, or even reverse, sediment flux by modifying the sediment:water concentration gradient. Sediment redox potential could play a large role in the release of nutrients from the sediment interface. Another important component would be to evaluate the influence of important geochemical factors that affect sediment flux such as grain size, organic carbon and organic nitrogen. Finally, validating sediment flux estimates for Machado Lake will require the evaluation of biological components, especially algae, since algal nutrient uptake will help drive concentration gradients and modify the geochemical environment.

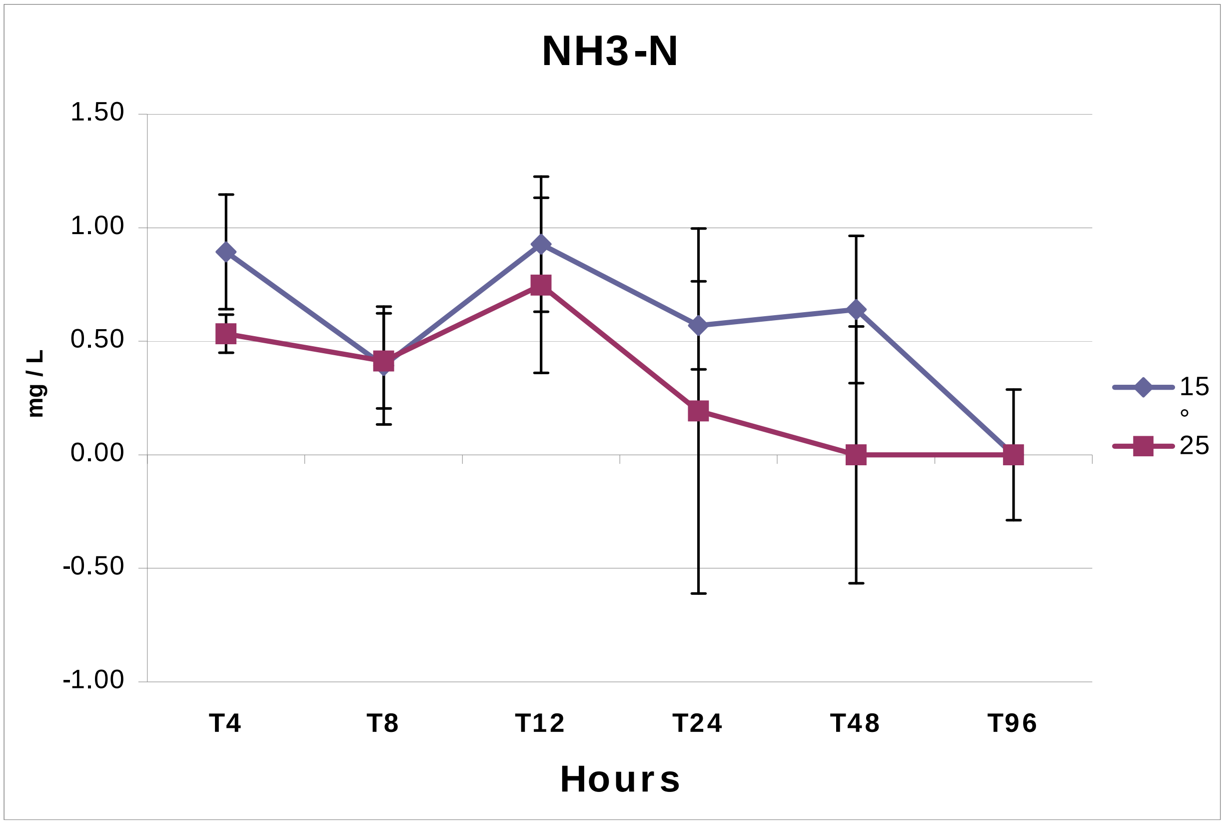

Figure 4. Ammonia (NH_3-N) concentrations (mg/L) (± 95% CI) in core surface water over 96 hours at both 15 and 25 °C.

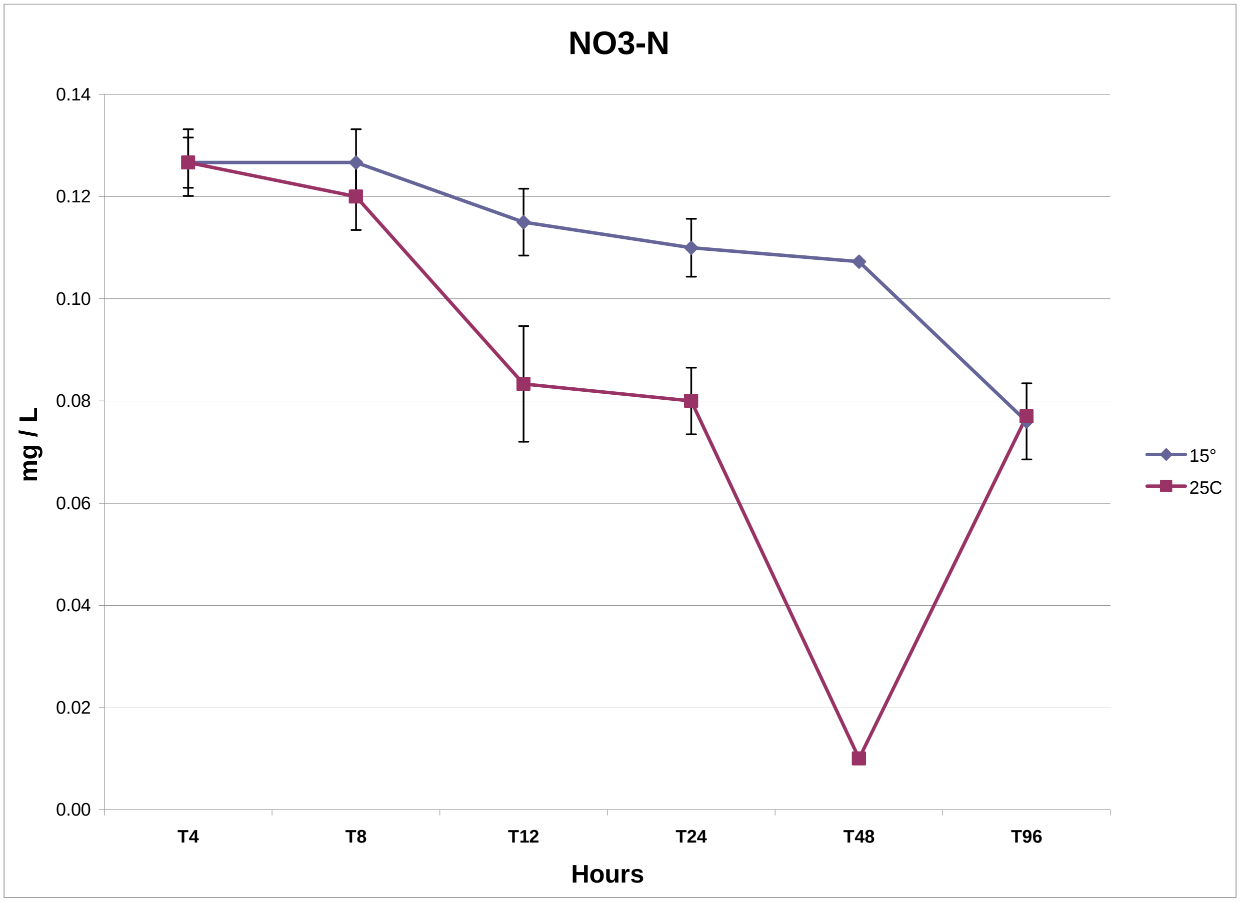

Figure 5. Nitrate (NO_3-N) concentrations (mg/L) (± 95% CI) in core surface water over 96 hours at both 15 and 25 °C.

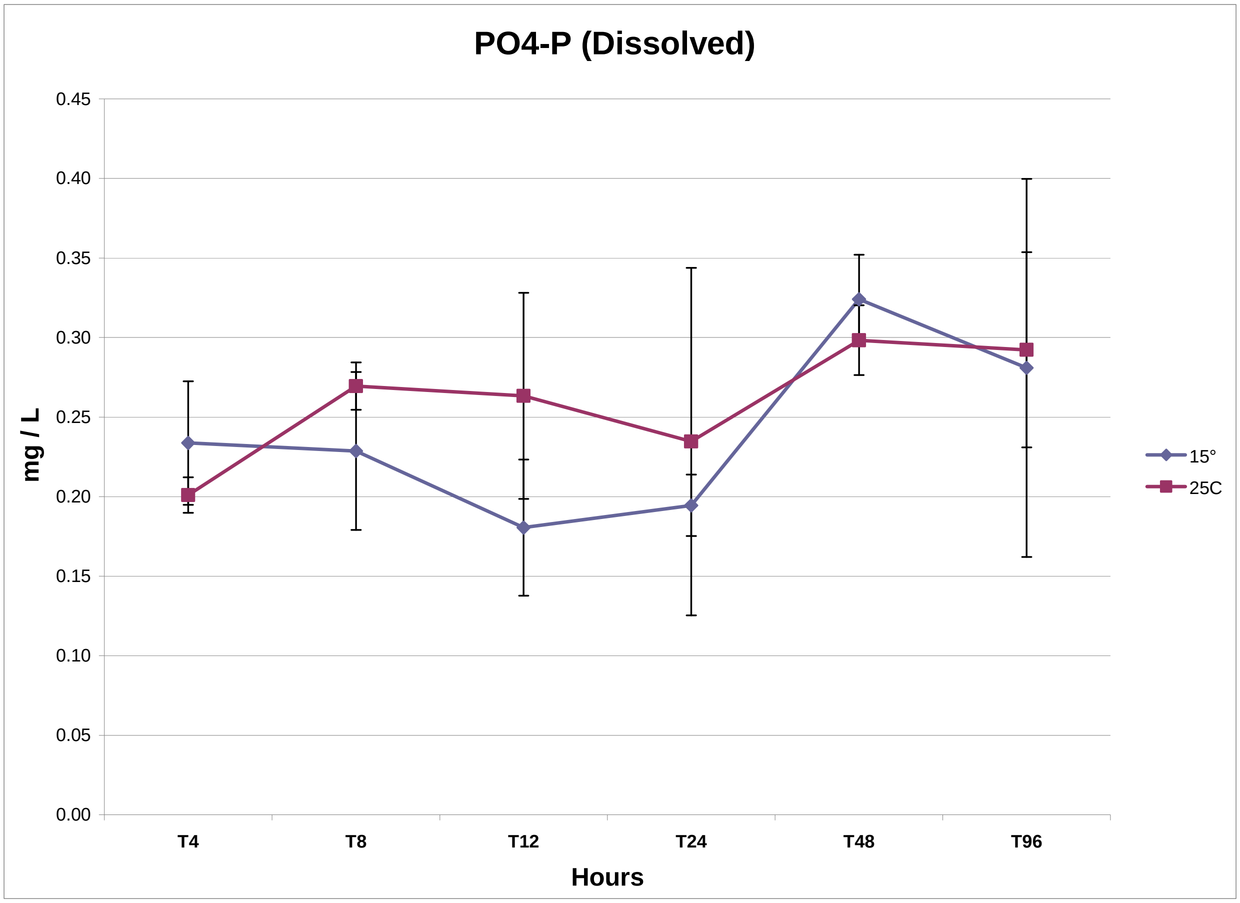

Figure 6. Dissolved phosphate (PO_4-P) concentrations (mg/L) (± 95% CI) in core surface water over 96 hours at both 15 and 25 °C.

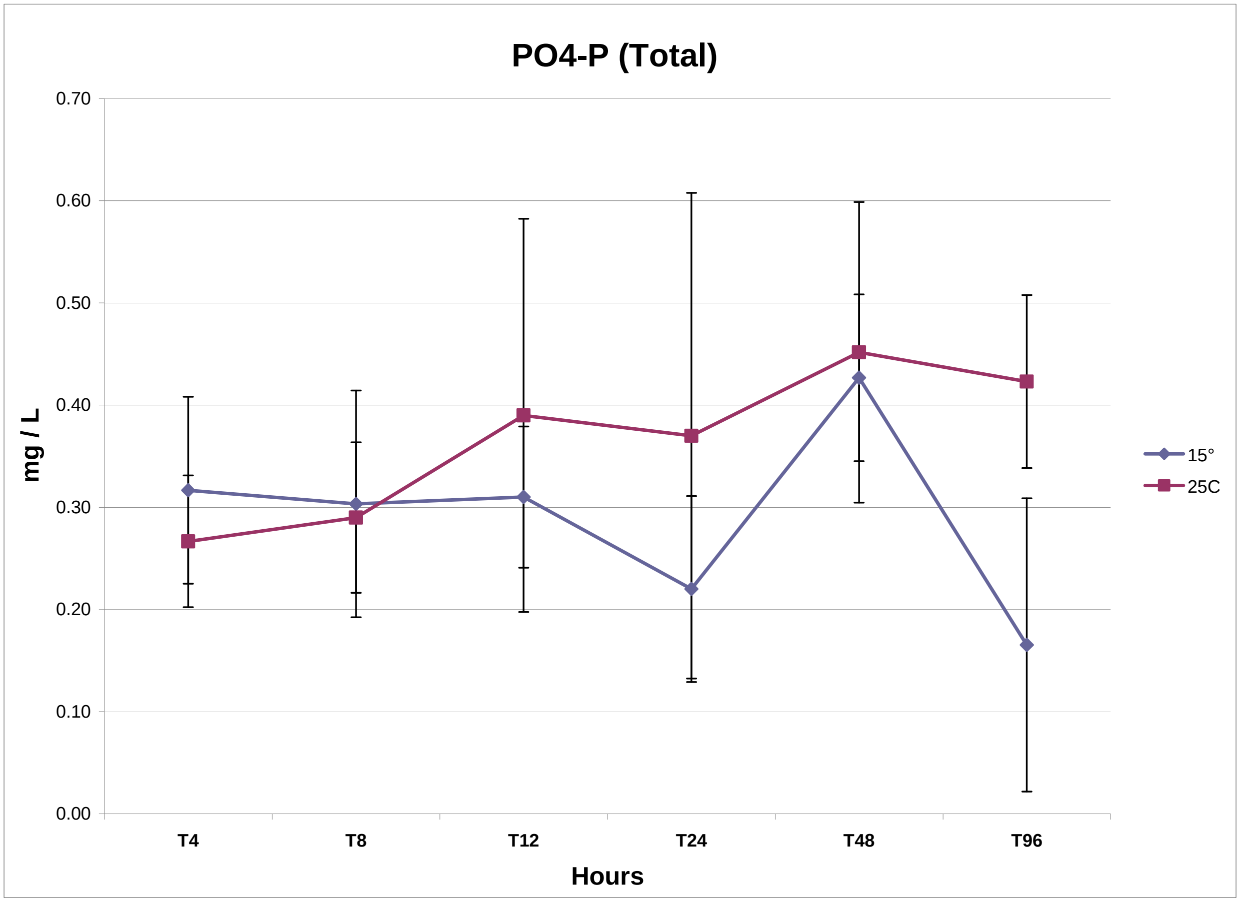

Figure 7. Total phosphate (PO_4-P) concentrations (mg/L) (± 95% CI) in core surface water over 96 hours at both 15 and 25 °C.

Table 1. Sediment nutrient flux rates (mg/m^2/hr ± 95% CI) for each temperature (15 and 25 °C) for each constituent exposed for 96, 12 and 4 hour time periods. The average 4 to 96 hour flux for all time exposures combined includes T_4, T_8, T_{12}, T_{24}, T_{48} and T_{96}.

	15 °C (n = 24)			
	NH_3-N	NO_3-N	PO_4-P (Dissolved)	PO_4-P (Total)
4 hour exposure	41.88 ± 12.17	5.94 ± 0.31	10.95 ± 2.33	14.84 ± 5.21
12 hour exposure	14.49 ± 3.02	1.80 ± 0.09	2.82 ± 0.30	4.84 ± 1.42
96 hour exposure	-0.04 ± 0.42	0.10 ± 0.10	0.18 ± 0.36	0.32 ± 0.46
Avg 4 to 96 hour exposure	11.72 ± 6.39	1.92 ± 0.87	3.44 ± 1.63	4.90 ± 2.25
	25 °C (n = 21)			
	NH_3-N	NO_3-N	PO_4-P (Dissolved)	PO_4-P (Total)
4 hour exposure	25.00 ± 9.81	0.27 ± 0.31	0.61 ± 0.70	3.05 ± 3.45
12 hour exposure	11.67 ± 12.56	1.30 ± 0.10	6.86 ± 1.71	6.09 ± 3.71
96 hour exposure	-0.17 ± 0.07	0.09 ± 0.10	0.04 ± 0.05	0.15 ± 0.17
Avg 4 to 96 hour exposure	7.89 ± 4.65	1.75 ± 0.93	3.55 ± 1.44	5.15 ± 1.95

Table 2. Sediment nutrient flux rate (g/m^2/yr) comparisons for Machado Lake (averaged T_4 to T_{96} exposures, ± 95% CI), Malibu Lagoon (± 95% CI) (Sutula 2004) and Upper Newport Bay (± SD) (Sutula 2006).

		n	NH_3-N g/m2/yr	NO_3-N g/m2/yr	PO_4-P (Dissolved) g/m2/yr	PO_4-P (Total) g/m2/yr
Lake Machado - 15 °C		3	99.05 ± 53.99	16.24 ± 7.32	29.09 ± 13.78	41.41 ± 19.01
Lake Machado - 25 °C		3	66.66 ± 39.25	14.81 ± 7.85	30.01 ± 12.15	43.47 ± 16.46
Malibu Lagoon	Min	4	0.01 ± 0.01	-19.00 ± 3.90	-0.04 ± 0.04	-0.03 ± 0.02
	Max	4	52.00 ± 52.00	0.12 ± 0.19	8.80 ± 5.20	8.80 ± 5.20
Newport Bay	Min	6	33.79 ± 1833.22	-5290.14 ± 2.62	158.82 ± 4526.44	238.23 ± 4605.85
	Max	6	506.88 ± 3151.10	3928.32 ± 18.33	317.64 ± 6035.25	277.94 ± 6035.25

References

Sutula, M., K. Kamer, J. Cable. 2004. Sediments as a non-point source of nutrients to Malibu Lagoon, California (USA). *Southern California Coastal Water Research Project, Technical Report 441.* Costa Mesa, CA.

Sutula, M., K. Kamer, J. Cable, H. Collis, W. Berelson, J. Mendez. 2006. Sediments as an internal source of nutrients to upper Newport Bay, California. *Southern California Coastal Water Research Project, Technical Report 482.* Costa Mesa, CA.

Appendix A

Table A1. Average sediment nutrient flux rates ($mg/m^2/hr$) for each time exposure at both 15 and 25 °C.

	15 °C							
	NH_3-N		NO_3-N		PO_4-P (Dissolved)		PO_4-P (Total)	
Time	mg/m2/hr	(±95% CI)	mg/m2/hr	(±95% CI)	mg/m2/hr	(±95% CI)	mg/m2/hr	(±95% CI)
T0	468.750	236.503	124.219	4.594	188.438	36.450	501.563	85.694
T4	41.875	12.169	5.938	0.306	10.953	2.327	14.844	5.206
T8	9.219	6.968	2.969	0.153	5.359	1.004	7.109	1.620
T12	14.492	3.025	1.797	0.088	2.820	0.301	4.844	1.420
T24	4.453	2.536	0.859	0.000	1.013	1.005	1.719	0.637
T48	2.500	1.123	0.419	0.029	1.266	0.464	1.667	0.560
T96	-0.039	0.422	0.099	0.097	0.183	0.359	0.323	0.460
	25 °C							
	NH_3-N		NO_3-N		PO_4-P (Dissolved)		PO_4-P (Total)	
Time	mg/m2/hr	(±95% CI)	mg/m2/hr	(±95% CI)	mg/m2/hr	(±95% CI)	mg/m2/hr	(±95% CI)
T0	69.104	78.197	5.413	6.125	94.409	106.831	53.309	60.323
T4	8.673	9.814	0.271	0.306	0.615	0.696	3.050	3.451
T8	7.987	9.038	0.234	0.265	3.768	4.264	3.984	4.509
T12	11.100	12.560	0.090	0.102	1.508	1.707	3.281	3.713
T24	3.902	4.415	0.361	0.408	0.151	0.171	1.016	1.149
T48	0.039	0.044	0.000	0.000	0.212	0.240	0.292	0.331
T96	0.063	0.071	0.087	0.098	0.041	0.046	0.151	0.171

Appendix B – Comment Letter

COMMENT LETTER: MACHADO LAKE NUTRIENT FLUX STUDY – DRAFT REPORT
CONTRACT 04-395-140-1, TASK 3
Letter Dated July 23. 2007

1. Please clearly describe the appropriateness of this laboratory experimental design to estimate gross nutrient flux rates in Machado Lake.

   This study was designed to estimate the maximum range of nutrients that could flux from Machado Lake sediments (See Section 1.1). If the flux rates in this experiment approached loads that could be considered a problem, then further investigations would be warranted (See Section 3.1, para 6). Further investigations should include more detailed techniques (Section 3.1, para 6).

2. How is the design of a flux rate experiment different from the design of an equilibrium experiment?

   The present study was not designed to provide equilibrium or ambient steady state flux estimates. It was designed to estimate potential maximum flux, hence, the use of nutrient-limited overlying water. There are a number of approaches to quantify ambient steady state flux including pore water potential flux or *in situ* benthic chambers (See Section 3.1, para 6). If additional laboratory experiments are desired to estimate ambient steady state flux, then more detailed experimental design factors should be incorporated including, but not limited to, use of ambient overlying waters, spatial characterization of sediment nutrient content, spatial characterization of water column nutrient content, sediment redox control, atmospheric control, flux from bedded and re-suspended sediments, water column particulate settling, sediment uptake and loss by algae, algal growth and decay, amongst others.

3. Will the experimental design provide steady state flux rate information?

   This study was designed as a range-finding experiment to assess potential maximum flux rate of selected nutrients from lake sediments after 96 hours.

4. Please discuss the advantages and disadvantages of adding 600 mL reconstituted laboratory water to each sediment core as opposed to using ambient lake water.

   The experimental design assumes sediment flux is a function of concentration gradient and the goal is to estimate potential maximum flux. The advantage of using reconstituted laboratory water is that this water source is nutrient poor. Thus, a strong concentration gradient between sediment and water is established maximizing nutrient flux. The disadvantage of using ambient lake water with varying levels of nutrient content is that a weaker concentration gradient is established. Thus, estimates of potential maximum flux would be biased low.

5. Please describe the importance of the redox conditions in relationship to sediment nutrient flux (oxic vs. anoxic conditions).

   Sediment redox conditions can have a large effect on nutrient flux. Amongst other effects, anoxic conditions can reduce NH_3 to N_2 resulting in volatilization (See additions to Section 3.1 para 6).

6. Please provide information on the oxic state of the sediments cores in this experiment, if available.

   No sediment redox measurements were taken.

7. Please address the wide range of flux rates estimated at the different time sets (T4 –T96). How does this wide range of flux rates affect the overall quality of the experiment and the results? Is it typical of flux rate experiments, similar in design to the Machado Lake experiment, to demonstrate a wide range of flux rates between the time sets?

   Variation is a problem inherent in both laboratory and in-situ experiments and large error within and between time series are common. The goal is to minimize this variation so that differences can be statistically modeled. In the case of the current study, variation was exacerbated by re-suspended surficial sediments (See Section 3.1 para 4).

8. The flux rates estimated in this experiment at Machado Lake are compared to two studies conducted on sediments in the Malibu Lagoon and Upper Newport Bay (Sutula 2004, 2006). Are the experimental designs similar among these three studies?

   The experimental designs were not similar. The cited studies provided more detailed estimates of the nutrient fluxes in these systems, such as those described in comment 2.

9. In figures 4 through 7 the unit for nutrient concentration on the graph and the unit identified in the figure caption are not the same units. Please confirm the units for nutrient concentration.

   Units confirmed as requested

10. In table 2 please confirm that all data presented are in the same unit. The units identified in the table caption and those in the table are not the same units (mg/m2/yr vs. g/m2/yr).

    Units confirmed as requested