Internal Nutrient Loads from Sediments in a Shallow, Subtropical Lake

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Abstract

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Fluxes of dissolved inorganic nitrogen, DIN, (as ammonia, NH_4-N) and phosphorus (as dissolved reactive phosphorus, DRP) from the sediments to the water column of Lake Okeechobee were determined from two separate techniques: increases in nutrient concentration in the water column above intact cores and concentration gradients determined with pore water equilibrators. These fluxes were estimated from different sediment types within the lake (sand, peat, mud) and at two major inflows (Kissimmee River and Taylor Creek). DRP release from peat sediments was highest. Measurements in other sediments were not significantly different from each other. DRP flux to the lake was estimated as 326 Mt·yr^{-1} in 1989 and had increased to 472 Mt·yr^{-1} in 1999. Because of measurement variation, this increase was not statistically different. These estimates of internal DRP loads are greater than estimated external surface DRP loads that averaged 316 Mt·yr^{-1} from 1979-1988 and 258 Mt·yr^{-1} from 1989-1999. DIN flux was highest near Taylor Creek. There was no consistent pattern between sediment type and DIN flux. Internal loads of DIN were estimated in 1999 as 4,500 Mt·yr^{-1}, which is greater than the external surface loads of DIN estimated for the period of 1989-1998, of 896 Mt·yr^{-1}. Sediment oxygen demand measured in the cores was strongly correlated to DRP and DIN flux, indicating that these fluxes are largely a result of mineralization of organic material. This study indicates that sediment diffusive fluxes are a significant source of DRP and DIN to the lake water column.

Key Words: Lake Okeechobee, sediments, nutrient flux, dissolved reactive phosphorus, dissolved inorganic nitrogen, nutrient loads, eutrophication

Internal nutrient loads can have significant influence on the water quality of shallow lakes that have experienced excessive external nutrient loads (*e.g.*, Jensen and Andersen 1992). These internal loads occur through diffusive fluxes from the sediment to the water column and resuspension of sediments (see Marsden 1989 for a summary). This source of nutrients is a major contributor to phosphorus concentration in the water column, as well as lake trophic status (Nürnberg 1988, Marsden 1989, Boström *et al.* 1982). The difference between external nutrient load reductions and expected declines in water column total phosphorus (TP) levels is, in some instances, due to supply of phosphorus from the sediments to the water column (Sas 1989, Rossi and Premazzi 1991). This source of phosphorus should be considered when constructing

whole-lake nutrient budgets in order to explain lake trop status trajectory following external nutrient load reducti or other lake restoration projects. These internal loads ca substantial; from equivalent to external loading (Moore e 1998) to four-fold greater (Ryding and Forsberg 1977).

Lake restoration through reduction of external loads may decades to succeed because of these substantial internal lo Also, changes in water quality at tributary inflows (and he external loads) may not change very rapidly in respons basin management practices due to years of accumulatio nutrients in surface soils (Nair and Graetz 2002). Thus, to in shallow lake recovery, in-lake restoration measures o are required (Moss *et al.* 1999). These measures can inc: dredging, flushing, biomanipulation and chemomanipula (Van Liere and Gulati 1992).

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Table 1.-Location of the sediment flux experiments performed in June of 1999 (Datum NAD83).

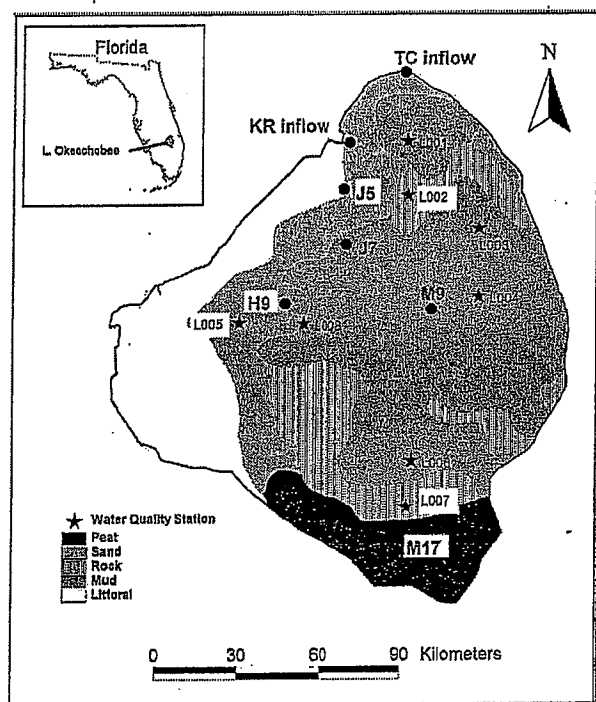| Station	Zone	Depth (m)	Latitude	Longitude
Taylor Cr.	Inflow	2.0	27° 11' 55"	80° 47' 40"
Kissimmee R.	Inflow	2.5	27° 08' 33"	80° 51' 01"
M9	Mud	4.0	26° 58' 17.6"	80° 45' 38.4"
J5	Littoral	1.5	27° 05' 28.1"	80° 51' 28.2"
J7	Sand	3.5	27° 02' 11.0"	80° 51' 19.8"
H9	Sand	3.5	26° 58'·40.6"	80° 55' 35.4"
M17	Peat	2.0	26° 45' 24.4"	80° 46' 36.8"

Figure 1.-Map of Lake Okeechobee, showing sediment distribution and location of sampling stations used in this study.

Lake Okeechobee is an example of a shallow lake experiencing large internal P loads. The internal load of this large (1730 km²), shallow (average depth 2.7 m), turbid lake in the peninsula of south Florida, is approximately equivalent to external loads (Moore et al. 1998). This internal load has resulted from decades of increased P loads to the lake (Havens et al. 1997). The lack of a response of water column TP to reductions in external P loads is in part attributed to this internal sediment P load (James et al. 1995a,b).

Because of excessive P loads to Lake Okeechobee, the lake has changed from a P limited system in the 1970s to an N limited system in the 1990s (Havens et al. 1997). Water quality model simulations indicate that diffusive ammonium

fluxes from sediments contribute a significant amount of N to the water column (James et al. 1997). However, the accuracy of the simulated N flux is unknown, since it has not been measured in the lake. Because N flux from the sediment ultimately could impact phytoplankton growth in the lake, accurate measurements are needed to determine their significance.

The objectives of this study were to determine diffusive fluxes of NH_4-N and DRP from various sediment types in Lake Okeechobee (sand, peat and mud) to the overlying water column. The goal of the study was to compare these measurements to external nutrient loads to determine the relative contribution of the sediments to the lake's nutrient budget. A secondary goal was to compare DRP fluxes in this study to flux measured 10 years prior in order to determine if flux has changed in response to lake and basin management practices.

Materials and Methods

Sediment Sampling Locations

The station selection was based on an attempt to replicate a similar study done from 1989-1990 (Moore et al. 1998) and to represent each of the major Lake Okeechobee sediment types and two of the major hydraulic and nutrient inflow sources; Kissimmee River and Taylor Creek (Table 1; Fig. 1). Two methods were used to estimate gross flux of N and P from the sediments to the overlying water column: porewater equilibrators and intact sediment cores. Equilibrators were deployed at stations M9 and M17 on June 19, 1999. On the same date, intact sediment cores were obtained from near the mouth of the Kissimmee River, near the mouth of Taylor Creek and at stations M9, J7, M17 and H9. Seasonal effects on nutrient exchange rates were not examined in this study. In a previous study, Moore et al. (1998) found no significant seasonal differences in sediment phosphorus release rates at any of the pelagic stations (M9, J7, M17). Their study demonstrated that release rates determined in June were generally within one standard deviation of the mean annual flux at respective stations. Both methods were performed in triplicate. Sediment characteristics were highly variable between stations (Table 2). Sediment at station M9 consisted of low bulk density mud, sand at stations J7, J5, and H9, low phosphorus peat at station M17, and silty sands at the two inflow stations. Even though the variability in sediment characteristics between sediment zones was high, the coefficient of variability within a sediment zone is typically low (approx. 30%) (Fisher et al. 2001). Therefore, results from a single station were used to represent a lake sediment zone when estimating whole-lake nutrient budgets.

Table 2.-Selected physico-chemical characteristics of sediments at Lake Okeechobee intact core and peeper stations.

Station	Description	Ash %	Bulk Density g cm⁻³	Porewater				Dry Sediment		
				DRP mg L⁻¹	NH₄-N mg L⁻¹	Fe mg L⁻¹	Ca mg L⁻¹	Total P mg kg⁻¹	TN g kg⁻¹	TOC g kg⁻¹
H9	Sand	96.1	0.75	0.045	3.06	0.04	57	178	1.5	17.5
KR	Muddy sand	97.7	0.98	0.058	1.56	0.06	38	146	1.0	12.3
J5	Sand	98.9	1.26	1.025	5.84	0.09	49	88	0.2	5.5
J7	Sand	98.8	1.03	0.561	4.13	0.14	57	103	0.1	5.4
TC	Sand	99.7	1.54	0.464	4.50	0.20	54	40	ND	1.2
M17	Peat	21.7	0.15	0.128	0.88	0.10	43	243	28.0	437.1
M9	Mud	77.4	0.26	0.614	1.36	0.06	46	958	6.8	104.5

NA = not available; ND = not detectable

Porewater Equilibrators

The porewater equilibrators (or "peepers") were similar to those described by Hesslein (1976). The equilibrators were 2-cm by 10-cm by 50-cm blocks of clear acrylic that consist of discrete 8-ml cells that are spaced at 1-cm vertical intervals. The cells were filled with deionized water, overlain with a 0.2-mm pore size polyethersulfone membrane, and a slotted, acrylic face plate was fastened to the device. The membrane and faceplate were held tightly to the equilibrator with stainless steel screws to ensure that there was no mixing between the vertical cells. They were then sealed in acrylic cases and purged of O_2 with N_2 gas. In the field, the equilibrators were removed from the case, pushed into the sediment and left for a period of two weeks, allowing time for dissolved constituents in the sediment porewater to equilibrate with the water inside the cells. Each device was then withdrawn from the sediment and the individual cells were immediately sampled by withdrawing their contents with a syringe. The samples were stored at 4°C until analyzed for DRP, NH_4-N, SO_4^{2-}-S, CO_2-C, CH_4 C, and pH as described below.

Dissolved reactive P and NH_4-N were analyzed with a Technicon AutoAnalyzer (Tarrytown, NY) using EPA methods 365.1 and 351.2 (U.S. EPA 1993). Sulfate was determined with a Dionex Series 4500i ion chromatograph (Sunnyvale, CA). Methane and dissolved inorganic carbon (DIC) were determined with a Shimadzu Model 8A gas chromatograph (GC) (Columbia, MD), equipped with a thermal conductivity detector and a Porpak N 80/100 column, with He carrier gas. DIC was determined by acidifying the sample to convert all inorganic carbon species to CO_2, followed by GC analysis of the CO_2 gas. Dissolved O_2 was determined with a YSI Model 58 dissolved O_2 meter (Yellow Springs, OH). The pH was determined with a Corning model 314 pH meter (Corning, NY) and temperature with a Campbell Scientific CR10 data logger (Logan, UT).

The concentration gradients of DRP and NH_4-N were determined from these equilibrators and used to determine the flux across the sediment-water interface using Fick's First Law of Diffusion. The concentration gradients were used to estimate the flux of P across the sediment-water interface using:

$$J_i = \phi D_s \frac{\partial C}{\partial Z} \, 8.64(10^5)$$

where:

J = diffusive flux of component i, mg m⁻² day⁻¹; ø = sediment porosity, cm³ cm⁻³; D_s = bulk sediment diffusion coefficient, cm² sec⁻¹; $\frac{\partial C}{\partial Z}$ = concentration gradient of component i with respect to depth, Z (cm); 8.64 10⁵ = units conversion.

The average pH in the upper 10 cm of sediment during the February 1996 equilibrator sampling at M9 and M17 was 7.75. This was used to determine the diffusion coefficient of P in water. Since the speciation of soluble P is pH dependent, an interpolated value of D_s was used. Li and Gregory (1974) reported the diffusion coefficients of HPO_4^{2-} and $H_2PO_4^-$ in pure water as 7.34 (10⁻⁶) and 8.46(10⁻⁶) cm² sec⁻¹, respectively. An average of these two values was used in the calculation of diffusive flux of P, 7.9 (10⁻⁶) cm² sec⁻¹. The diffusion coefficient for NH_4 in water is 1.98(10⁻⁵) cm² sec⁻¹ (Li and Gregory 1974). The diffusion coefficients were modified for the restrictive effect of sediment structure by dividing it by the square of the sediment tortuosity. Sediment tortuosity (Θ) was calculated from a relationship developed by Sweerts et al. (1991), or

$$\Theta^2 = -0.47\,\phi + 1.91$$

where ø is the sediment porosity. The resulting diffusion coefficients were 5.1(10⁻⁶) (P) and 1.29 (10⁻⁵) (N) cm² sec⁻¹ for stations M9 and M17.
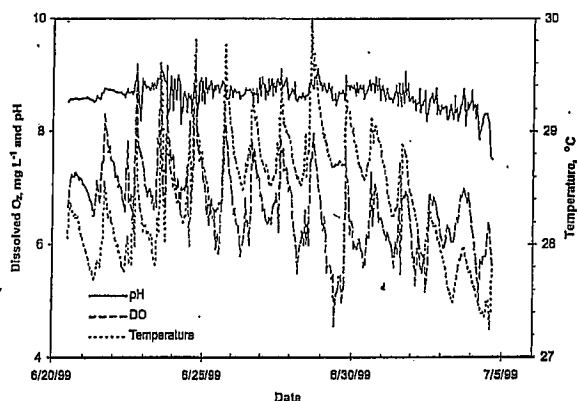
Figure 2.-In situ Lake Okeechobee conditions of dissolved oxygen, pH and temperature during the 14 day period that the intact core experiment was conducted. Data from mid-water column (1.5-m).

Intact Sediment Cores

Core tubes were made of clear polycarbonate, measuring 7-cm I.D. by approximately 50-cm in length. A SCUBA diver took three intact sediment cores at each sampling station by mallet-driving the core tubes into the sediment. The cores were sealed on the top and bottom and returned to the boat. The depth of sediment retrieved from each station varied from 10-cm (H9) to 25-cm (M9). The cores were then transported to the laboratory in a foil-covered box.

The cores were placed into a temperature-controlled water bath that was completely covered with foil to exclude light, thus diminishing photosynthesis and the algal uptake of nutrients. The experiment began on June 21, 1999 and was terminated after 14 days. The temperature of the water bath averaged 27.0 (±1.2 SD) °C, which is close to the in situ water column temperature (Fig. 2).

Prior to initiation of the core flux experiment, the overlying water was removed from each core, filtered through a 0.45-μm pore size polyethersulfone filter and gently replaced into the respective cores to a final water column depth of 15 cm, or 0.6 L. The water column was slowly bubbled with ambient air throughout the experimental period, both to ensure an aerobic water column, and to completely mix the water column. The water column was treated with the nitrification inhibitor, nitrapyrin (N-Serve™), to prevent the formation of nitrate and subsequent (unmeasured) denitrification losses. Nitrapyrin was added to obtain a water column concentration of 0.033 mg·L^{-1}, or 1/16 the rate recommended for standard biochemical oxygen demand (BOD) assays (McCarty and Bremner 1990). Nitrate levels were near the limit of detection throughout the experimental period (data not shown). A variety of live invertebrate organisms were noted throughout

the experimental period and this was taken as evidence that the application rate was not toxic to biota.

A 25-ml water column sample was taken at 0, 1, 2, 3, 4, 5, 7, 10, and 14 days and analyzed for NH_4-N and DRP as described above. All water samples were taken at mid-water column (7.5 cm) with a polyethylene syringe. A 25-ml volume of filtered, Nitrapyrin-spiked site water of known composition was added to each core after each sampling to replace the water column removed. This volume was accounted for in the flux determination.

A Hydrolab DataSonde 3 (Austin, TX) was installed in the lake near station J5 for the two-week period of the sediment core incubation to measure water temperature, pH, and dissolved O_2. These data were used to confirm that in situ conditions were maintained in the lab-incubated cores (Fig. 2).

Nitrogen and P fluxes were calculated from the sediment cores by determining the slope of the concentration vs. time curve, using linear regression, and applying the following formula (Gomez-Parra and Forja 1993, Fisher and Reddy 2001):

$$J_i = \frac{dC_i}{dt} \cdot \frac{V}{A} \qquad (1)$$

Where: J_i is flux of component i (mg·m^{-2}·day^{-1}), C_i is component i's concentration in water column (mg·L^{-1}), V is water column volume (L), A is sediment surface area (m^2) and t is time (days). Only the initial linear portion of the release curve was used to calculate sediment release rates.

Sediment Oxygen Demand

Sediment oxygen demand (SOD) was estimated from the intact sediment cores after the termination of the core flux study. The water column was aerated to approximately 6 mg O_2·L^{-1}. The initial dissolved O_2 content was determined for each core and the cores were sealed. The final dissolved O_2 was measured approximately 12-hrs later. Preliminary studies indicated that rate of oxygen consumption during the 12-hr period is linear (data not shown). The final dissolved O_2 content was generally in the range of 4 - 5 mg·L^{-1}. The SOD determination was conducted in a temperature-controlled water bath maintained at 25°C. Nitrapyrin was re-added to each of the intact cores at a rate of 0.033 g Nitrapyrin·L^{-1} to prevent nitrification-associated O_2 uptake.

Sediment Core Profiles

At the end of the experimental incubations, the sediment cores were sectioned into 0-2, 2-4, 4-10, 10-15, and 15-20 cm depth intervals. The sediment was extruded into pre-weighed polycarbonate centrifuge tubes inside an N_2-filled glove box. An inert atmosphere was used to prevent precipitation of

Table 3.-Dissolved reactive P and NH$_4$-N flux determined from porewater concentration gradients in Lake Okeechobee during July 1999. Values given represent the mean of three replications. Values in parentheses are one standard deviation.

Station	Gradient Interval cm	pH	Gradient mg·L^{-1}·cm^{-1}	Flux mg·m^{-2}·day^{-1}
Dissolved Reactive P				
M9	0-6 (1)	7.63	0.24 (0.03)	0.83 (0.11)
M17	0-4 (2)	7.90	0.11 (0.05)	0.38 (0.17)
Ammonium-N				
M9	0-6 (1)	7.63	0.35 (0.03)	3.1 (0.3)
M17	0-4 (2)	7.90	0.42 (0.42)	3.7 (3.7)
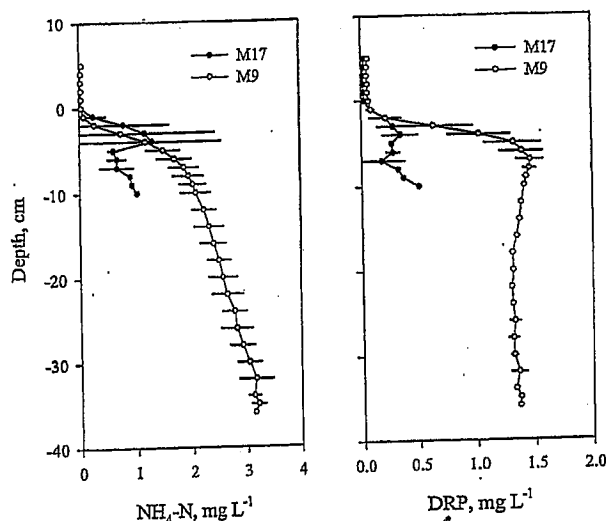
Figure 3.-Sediment porewater concentrations of DRP and NH$_4$-N at stations M9 and M17 in July 1999 (error bars indicate ±1 standard deviation).

DRP as ferric phosphates, as Fe is a principal regulator of P solubility in Lake Okeechobee sediments (Moore and Reddy 1994). Porewater was then removed by vacuum filtration under N$_2$ atmosphere, after centrifuging the sediment in a refrigerated centrifuge at 6000 rpm for 10 minutes.

Nutrient Budgets

For comparison to estimates from internal diffusive fluxes, nutrient budgets were developed for TP, DRP, TN and DIN using information from South Florida Water Management District Databases and procedures from James *et al.* (1995a) and the Surface Water Improvement and Management (SWIM) Plan update for Lake Okeechobee (SFWMD 2002). These loads were averaged for the 10 years preceding the flux measurements to give average annual estimates. The loads did not include estimates from atmospheric deposition. Sediment flux measurements were averaged by sediment type and multiplied by the estimated area for each type to produce an estimate of annual flux for the lake as a whole using procedures as described by Moore *et al.* (1998).

Statistical Analyses

All flux and SOD measurements were calculated separately and then averaged together to produce estimated nutrient flux or SOD for each sampling location. The ANOVA (Analysis of Variance) procedure of SAS (SAS Institute 1990b) was used to determine differences in fluxes and SOD among the stations. The GLM (General Linear Models) procedure of SAS (SAS Institute 1990c) was used to determine if DRP flux had changed over the past decade by comparing current

flux data and the results reported by Moore *et al.* (1998). The CORR and REG procedure (SAS Institute, 1990a 1990c respectively) were used to determine relationships between SOD and fluxes of DRP and DIN, and relationships among porewater concentrations of DRP, NH$_4$-N, SO$_4^{2-}$-S, CO$_2$-C, CH$_4$ C.

Results

Porewater Equilibrators

At station M9 (central mud region) the three equilibrators had good agreement for both DRP and NH$_4$-N concentration gradients (Fig. 3). Concentration of DRP increased from 0.02 mg·L^{-1} in the overlying lake water to 1.5 mg·L^{-1} in the sediment porewater at a depth of 5 cm below the sediment-water interface. The estimated P flux averaged 0.83 mg·m^{-2}·day^{-1} (Table 3). Data from a 1989 study by Moore *et al.* (1998) indicated a diffusive flux of 0.60 mg·m^{-2}·day^{-1} at this station. *In situ* NH$_4$-N concentration in the sediment-water column increased from 0.03 mg·L^{-1} in the water column to 2 mg·L^{-1} in the sediment porewater at a depth of 5 cm below the sediment-water interface (Fig. 3). The diffusive NH$_4$-N flux was estimated as 3.1 mg·m^{-2}·day^{-1} (Table 3).

The concentration gradients at station M17 (southern peat region) were more variable among the replicate equilibrators (Fig. 3). Uppermost equilibrator cells reflected lake water concentrations of DRP and NH$_4$-N, averaging 0.02 and 0.03 mg·L^{-1}, respectively. Porewater concentrations increased to approximately 0.5 mg·L^{-1} (DRP) and 1 mg·L^{-1} (NH$_4$-N) at a depth of 10 cm below the sediment-water interface. Phospho-

Table 4.-Selected physico-chemical parameters of the water column of intact sediment cores retrieved from Lake Okeechobee in June 1999 and the lake during the incubation period. The water column sample concentrations of DRP and NH_4-N represent the concentration of the filtered lake water used to reflood the cores; all other parameters summarize the entire experimental period. Lake Okeechobee values reflect the 1978 to 1988 and 1988 to 1998 periods of record for water quality samples taken from 1-m depth at stations L001 through L008 (Fig. 1).

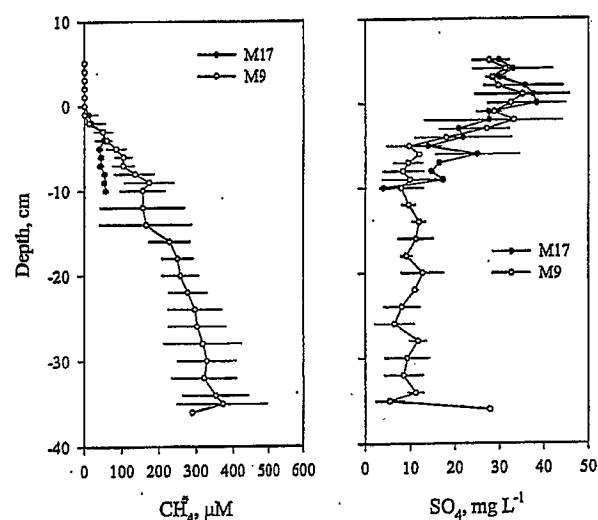| Data type		DRP mg·L⁻¹	NH_4-N mg·L⁻¹	pH s.u.	Dissolved O_2 mg·L⁻¹	Temperature °C
Water	Mean	0.011	0.043	7.88	6.01	27.0
Column	Std. Dev.	0.011	0.034	0.18	0.77	1.2
(cores)	Max.	.0.024	0.116	8.40	7.28	34.4
	Min.	ND	0.018	7.43	3.78	26.2
Lake	Mean	0.025	0.014	8.6	6.6	28.5
1978-	Std. Dev.	0.020	0.029	0.2	0.7	0.5
1998	Max.	0.185	0.427	9.1	9.3	30.0
	Min.	0.002	0.005	7.5	4.6	27.3
Lake	Mean	0.027	0.015	8.1	8.4	24.8
1988-	Std. Dev.	0.023	0.014	0.4	1.3	5.0
1998	Max.	0.134	0.150	9.6	16.0	36.6
	Min.	0.002	0.010	6.2	4.5	10.0

Figure 4.-Sediment porewater concentration of CH_4, and SO_4 at stations M9 and M17 in July 1999 (error bars indicate ±1 standard deviation).
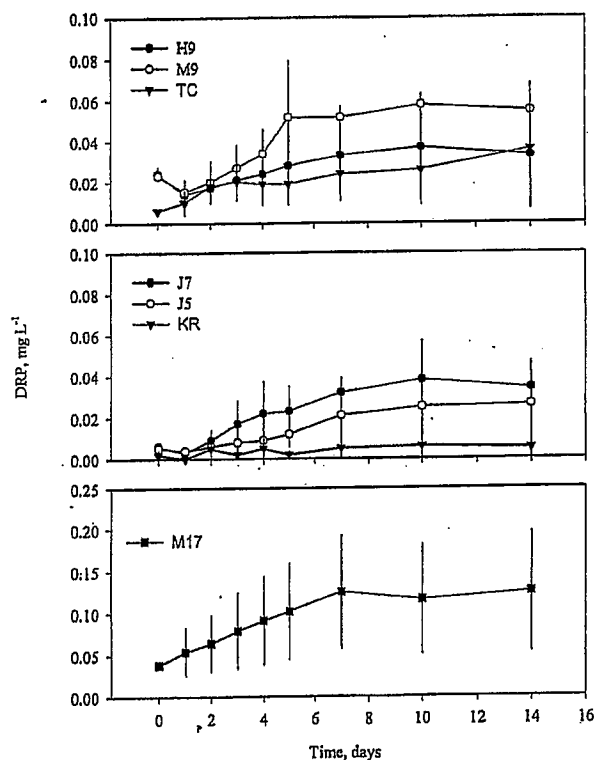

Figure 5.-Water column DRP concentrations from intact sediment core experiments (error bars indicate ±1 standard deviation).

rus release calculated from porewater concentration gradients averaged 0.38 $mg \cdot m^{-2} \cdot day^{-1}$ (Table 3). The average NH_4-N flux at station M17 was much greater than the other stations due to a high value from one of the replicate equilibrators. The flux estimated for this replicate was 7 $mg \cdot m^{-2} \cdot day^{-1}$, whereas the other two replicates averaged approximately 1.5 $mg \cdot m^{-2} \cdot day^{-1}$.

The pH at both stations was approximately 8 in the water column, decreased slightly in the porewater to an average between 7.5 and 7.9 (Table 3). Dissolved CO_2 concentrations were only slightly elevated relative to the overlying lake water concentration, averaging approximately 6 $mg \cdot L^{-1}$ at station M17 and 8 at station M9. Porewater methane concentrations were below detection in the water column and increased throughout the sediment profile (Fig. 4). Methane concentrations at station M17 were considerably lower than at station M9. Sulfate concentrations decreased sharply below the sediment-water interface, from 30 $mg \cdot L^{-1}$ in the water column to 10 $mg \cdot L^{-1}$ at a depth of 5 cm below the sediment-water interface and remained at that level throughout the sediment profile. Declining sulfate levels with respect to sediment depth suggest its use as a terminal electron acceptor in the oxidation of sediment organic matter.

At station M9, methane concentrations increased from near zero at the surface to over 300 µM at 30 cm (Fig. 4). This increase occurred despite the presence of SO_4-S at these depths, which is known to inhibit methanogenesis (Cappenberg 1974). It appears that methane diffuses upwards from strata deeper than those sampled with the porewater equilibrators (i.e., > 40 cm). Porewater concentration of NH_4-N and DRP were negatively correlated ($P < 0.005$) with sulfate and positively correlated with inorganic carbon, suggesting their production under anaerobic conditions from the mineralization of sediment organic matter.

Intact Sediment Cores

The range of DRP concentrations in the overlying water column at the initiation of the intact core flux experiment was 0.01 to 0.05 $mg \cdot L^{-1}$ (Table 4). The initial water column concentration reflects the ambient conditions at the time of collection of the sediment cores, since the cores were reflooded with water from respective sites. In general, the pelagic stations (M9, H9, M17) had higher initial DRP concentrations, averaging approximately 0.03 $mg \cdot L^{-1}$ (Fig. 5). In spite of their location proximal to sources of external nutrient loading, the inflow stations (Kissimmee River and Taylor Creek) had the lowest overall initial water column DRP concentrations; less than 0.01 $mg \cdot L^{-1}$.

Most of the cores had a gradual increase in DRP over the first week of the experimental period, with little increase thereafter (Fig. 5). The highest final DRP concentration was seen in the

Table 5.-Mean ambient Lake Okeechobee water column total phosphorus and dissolved reactive phosphorus concentration from 1990-2001 at long-term water quality monitoring stations (Fig. 1). Standard deviation in parentheses.

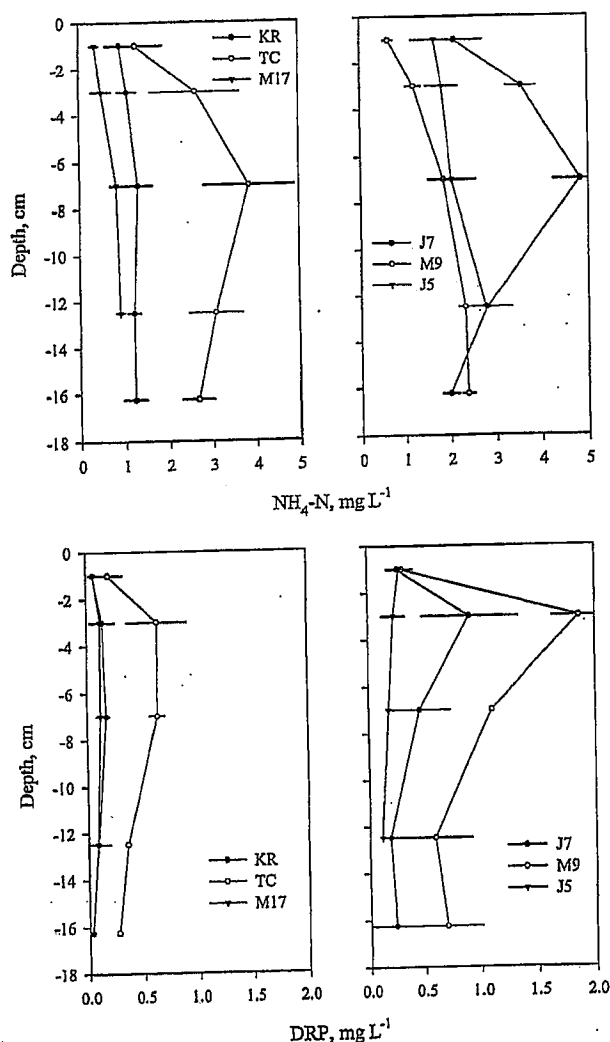| Station	TP mg L^{-1}	n	DRP mg L^{-1}	n
L001	0.093 (0.040)	189	0.022 (0.019)	187
L002	0.087 (0.040)	242	0.022 (0.022)	239
L003	0.115 (0.050)	192	0.030 (0.019)	189
L004	0.120 (0.047)	190	0.036 (0.017)	186
L005	0.069 (0.040)	236	0.014 (0.020)	237
L006	0.110 (0.044)	238	0.036 (0.017)	236
L007	0.090 (0.042)	191	0.028 (0.020)	188
L008	0.114 (0.057)	185	0.026 (0.019)	183

Figure 6.-Concentration gradients of NH_4-N and DRP from intact sediment cores (error bars indicate ±1 standard deviation).

Table 6.-Average sediment oxygen demand (SOD), phosphorus, and NH_4-N flux calculated from three intact sediment cores obtained from Lake Okeechobee at each station. Standard deviation in parenthesis. NH_4-N flux was determined only in the 1999 study. Values in a given column with the same superscript letters are not significantly different from one another based on the Duncan's Multiple Range Test. Standard deviations given for 1988 represent the variability of four seasonal measurements. ND = not determined.

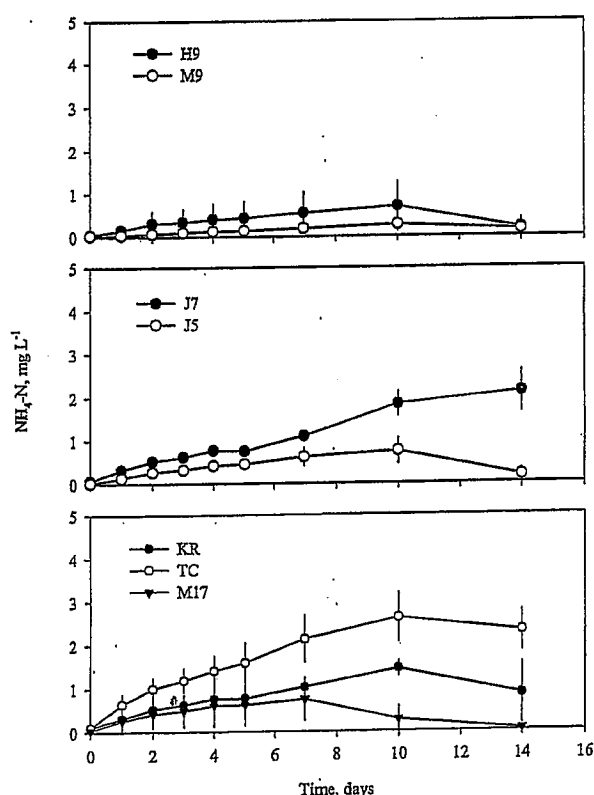| Station	Phosphorus 1999 mg m^{-2} d^{-1}	Phosphorus 1989-90 mg m^{-2} d^{-1}	NH$_4$-N mg m^{-2} d^{-1}	SOD mg m^{-2} d^{-1}
Taylor Creek	0.39 (±0.23)[b]	0.40 (±2.51)	40.1 (±5.7)[a]	863 (±202)[a]
Kissimmee River	0.58 (±0.05)[b]	0.34 (±1.77)	21.1 (±2.4)[b,c]	652 (±159)[a,b]
J5	0.37 (±0.36)[b]	1.09 (±0.45)	12.2 (±4.4)[c,d]	471 (±159)[b]
J7	0.62 (±0.29)[b]	0.26 (±0.17)	26.8 (±4.4)[b]	891 (±117)[a]
M9	1.01 (±0.03)[b]	1.69 (±0.69)	5.2 (±2.8)[d]	718 (±55)[a,b]
H9	0.51 (±0.39)[b]	ND	10.7 (±9.3)[c,d]	539 (±118)[b]
M17	2.12 (±1.16)[a]	2.22 (±0.91)	15.9 (±10.3)[b,c,d]	893 (±223)[a]
Average	0.78 (±0.58)	1.0 (±0.81)	18.8 (±11.7)	718 (±173)

Figure 7.-Water column NH_4-N concentrations from intact sediment core experiments (error bars indicate ±1 standard deviation).

pattern observed in the lake, with higher values in the central mud region, low values in the northern end of the lake, and intermediate values in the region of the lake underlain by sand (Table 5). An analysis of variance showed that DRP flux in 1999 was significantly different among stations (Table 6). This result is attributed to the peat sediment station M17, which had the highest DRP flux rates. DRP flux rates at all other stations were not significantly different from one another. Flux ranged from 0.37 mg·m^{-2}·day^{-1} at station J5 to 2.12 mg·m^{-2}·day^{-1} at station M17. Porewater concentration gradients of DRP at station M9 had porewater maxima of approximately 1.5 mg·L^{-1} at a depth of approximately 4 cm below the sediment-water interface, both in the sectioned cores and the porewater equilibrators (Figs. 3 and 6). This was the highest concentration of porewater DRP observed in either the equilibrators or the intact sediment cores.

An analysis of variance indicated that there was no significant difference between the 1999 flux rates and the 1989 flux rates obtained from Moore et al. (1998). However there was a significant interaction between station and date, which indicated that at some stations the flux value increased (Kissimmee River J7) while at others they declined (J5 and M9) (Table 6).

Ammonium-N increased in the water column of the intact cores, from an average 0.05 mg·L^{-1} to a maximum of approximately 3 mg·L^{-1} in the cores retrieved from Taylor Creek (Fig. 7). The ammonium fluxes among the stations were significantly different (Table 6). The cores from stations J7 and Taylor Creek had the greatest increase in water column NH_4-N, with calculated fluxes of 27 and 40 mg·m^{-2}·day^{-1} respectively. At station M9 the calculated flux was the lowest at 5 mg·m^{-2}·day^{-1}. There was no consistent pattern between NH_4-N flux and sediment type. Porewater profiles, determined from sectioned cores, clearly indicate that porewater concentrations of NH_4-N were greater at Taylor Creek and J7 than all other stations, thus indicating the importance

intact cores from station M17; approximately 0.1 mg·L^{-1}, a result consistent with the porewater equilibrators from this station. Cores from the inflow stations (Taylor Creek and Kissimmee River) had the lowest average increase in concentration. The final water column DRP concentrations for the inflow stations were 0.01 - 0.02 mg·L^{-1}. The maximum DRP concentration reached in the intact cores followed the

Table 7.-Estimate of the contribution of soluble nitrogen and phosphorus to the overall Lake Okeechobee nutrient budget. Calculation based on results obtained from intact sediment cores. (a- Recalculated from Reddy et al. 1995), b-from Moore et al. (1998)) External loads do not include estimates from atmospheric deposition and are calculated using methods from James et al. (1995a) and the Surface Water Improvement and Management Update (SFWMD, 2002). External loads are averages from periods 1979-1988 and 1989-1998. DIN = dissolved inorganic N.

Year	Source	Area km²	Internal DRP mg·m⁻²·day⁻¹	External DRP mg·m⁻²·day⁻¹	External Total P mg·m⁻²·day⁻¹	Internal DIN mg·m⁻²·day⁻¹	External DIN mg·m⁻²·day⁻¹	External Total N mg·m⁻²·day⁻¹
1988	Mud	716[a]	0.81[b]			NA		
	Sand	393[a]	0.30[b]			NA		
	Peat	214[a]	0.91[b]			NA		
	Mean		0.67	0.65	1.15	NA	2.57	11.30
1998	Mud	668	1.01			5.2		
	Sand	309	0.56			18.7		
	Peat	210	2.12			15.9		
	Mean		1.09	0.60	1.07	10.6	2.07	10.4

of porewater chemistry in regulating the magnitude of sediment-water nutrient exchanges. There was a large difference in NH₄-N flux between stations J5 and J7, even though both were located in a region of the lake dominated by sand sediments (Table 6). However, sectioning of sediments revealed that the core at station J7 contained approximately 3-cm of organic sediment, overlying sand. Station J5 sediments were comprised almost entirely of low organic matter sands.

The sediment oxygen demand (SOD) also was significantly different among the stations (Table 6). The values ranged from 539 mg·O₂·m⁻²·day⁻¹ at station J5 to 893 mg·O₂·m⁻²·day⁻¹ at station M17. Sediment oxygen demand was generally low and there was no clear trend, either with respect to physical sediment characteristics, or lake zone. This is counterintuitive, given the dramatic differences in sediment type across the lake. Both DIN and DRP flux observed in the core flux study were positively correlated with SOD (r = 0.52 and 0.47, respectively; P<0.025), suggesting the significance of mineralization of sediment organic matter to the supply of inorganic, bioavailable nutrients to the lake's water column.

Discussion

Porewater concentrations of both DRP and NH₄-N were approximately three-fold higher at station M9, compared to station M17 (Fig 3). This is probably due to the differences in the origins of the sediments and their related physical characteristics between the two locations (Table 2). The sediments that comprise the region around station M9 are very fine, somewhat cohesive muds, whereas the sediments in the southern region of Lake Okeechobee are peat (Fisher et al. 2001). In spite of this difference, flux from cores taken from station M9 was not significantly different from any other sediment type, with the exception of M17 (Table 6). A lack of significant differences in P release rates between

mud and sand sediments may reflect the aerobic conditions under which the intact core experiment was conducted. For instance, Moore et al. (1998) subjected Lake Okeechobee sediment cores to anaerobic conditions and observed dramatically increased release of P in both sand and mud sediments, though the increase was greater in the mud sediments. In Lake Okeechobee, the iron content of mud sediments (4.1 ± 1.8 SD mg·kg⁻¹) is approximately 5 times higher than in any of the other sediment type (Fisher et al. 2001), therefore redox conditions may play a larger role here in regulating P exchange dynamics. Anaerobic conditions could be significant because dissolved oxygen levels below 3 mg L⁻¹ occurred in approximately 5% of the samples taken on the lake from 1978 to 1998. For this reason, the aerobic release rates reported here may underestimate actual nutrient flux in the lake.

While flux from M9 was lower than expected, flux from M17 was approximately 5 times greater than that suggested by porewater concentration gradients alone (Table 3). This may reflect a comparatively active benthic invertebrate community at station M17, as benthic organisms can augment solute flux well in excess of that indicated by porewater concentration gradients alone. Sediments at station M17 are peat, and it is located in the shallow (z = 2m) southern region of the lake. This region is proximal to the littoral fringe of the lake and could be expected to harbor a comparatively active benthic community. Many researchers have demonstrated the effect of benthic organisms through comparisons of gradient-calculated flux and flux calculated using more direct methods, such as intact cores and benthic chambers (McCaffrey et al. 1980, Callender and Hammond 1982, Gomez-Parra and Forja 1993, Devol 1987, Hopkinson 1987). Van Rees et al. (1996) found that the diffusion rates varied as much as five-fold within a single sediment type. Therefore, the flux calculated from porewater concentration gradients probably represents a conservative estimate of sediment-water nutrient exchange.

The final water column concentrations observed at the termination of the intact core study reflects the "quasi" equilibrium P concentrations (EPC), or that concentration at which the sediments act neither as a significant source nor sink for P. A true equilibrium between porewater P and water column P would likely occur only over geological time scales and in the absence of any inputs of new P. However, for some limiting water column P (the EPC), flux slows to marginal levels; essentially zero. This concentration ranged from 0.01 to 0.02 mg L^{-1} for the inflow stations and 0.02 - 0.05 mg·L^{-1} for the remaining stations, suggesting somewhat higher EPC concentrations for the open water areas than for the inflow regions. Water quality sampling in the lake from 1990 to 2001 reveal that DRP averaged 0.022 mg·L^{-1} near the inflows (stations L001 and L002), from 0.030 to 0.036 mg·L^{-1} in the open water region (stations L003, L004, L006), and 0.028 in the region with peat sediments (L007) (Fig. 1; Table 5). Thus, under average conditions, regions near the inflow generally act as a sink for P, whereas the mud zone sediments and the peat on the southern side of the lake function as a source.

Water column concentration of DRP and NH$_4$ in the cores was lower than averaged lake data for the past decade, but still within the range of the ambient water quality data. Despite the increase of TP in the lake over the past few decades (Havens et $al.$ 1997), the averaged decadal values for DRP and NH$_4$ were nearly the same as the past decade (Table 4). However, the maximum and minimum values have changed. Comparing the two decades, there also was an increase in temperature, which has been observed previously (James et $al.$ 1995b) and a coincident reduction in dissolved oxygen.

Overall, there were only minor differences in P flux when comparing the 1988 to the 1999 measurements, indicating long-term steady state flux (Table 6). There were significant (P<0.02) declines in P flux in the 10 year period at some of the sampling stations as indicated by the ANOVA interaction term, STATION*DATE (Table 6). Only two stations had decreased P flux in the 11-year period; stations M9 and J5 (Table 6). Phosphorus flux from station J7 actually increased, possibly due to inclusion of a thin layer of organic-rich surface sediments in the 1999 cores. Phosphorus flux from stations adjacent to the lake inflows was, on average, lower than the rest of the lake stations for both the 1988 and the 1999 experimental periods, whereas the peat station (M17) had the highest P flux for both periods.

The tributary loads of total P and N averaged over ten years (1989-1998) were 464 and 4,505 Mt·yr^{-1}, respectively. Despite a reduction in external loads by 16 and 17 percent, respectively for TP and TN, between the two decades (1979-1998 and 1989-1998), the changes in external loads are not statistically significant. If the flux measurements determined in the intact core study can be assumed to be representative of an entire sediment zone, total internal NH$_4$-N and

DRP loads from each sediment zone can be determined and compared to external nutrient loads to get an estimate of the contribution of the sediments to the overall lake nutrient budget (Table 7). Internal loading estimates of inorganic P and N of 1.09 and 10.6 mg·m^{-2}·day^{-1} respectively are similar to total external P and N loads but are much greater than estimated external loadings of inorganic P and N (0.60 and 2.07 mg·m^{-2}·day^{-1}, respectively). The estimated internal loading is therefore a larger source of bioavailable nutrients than external loading.

The sediment release rates reported here should also be viewed in the context of release rates reported in other aquatic ecosystems, when contemplating lake restoration strategies. For instance, release of P from hypereutrophic Lake Apopka, Florida, sediments was 2.7 mg·m^{-2}·day^{-1} (Moore and Reddy 1991). In the northern Everglades, P release rates ranged from undetectable at pristine sites to 6.47 mg·m^{-2}·day^{-1} at a nutrient impacted site (Fisher and Reddy 2001). Nürnberg (1988) studied seven temperate North American Lakes of varying trophic status and found flux averaging 3.45 mg·m^{-2}·day^{-1}. Flux from the mud sediments in Lake Okeechobee of 0.83 mg·m^{-2}·day^{-1} is relatively low compared to these values. In fact, Nürnberg (1988) reports that flux of less than 1 mg·m^{-2}·day^{-1} is generally associated with oligotrophic lakes. However, because Lake Okeechobee is so shallow (average depth of 2.7 m), even the low flux observed in this experiment may be significant.

The fluxes determined in this study represent gross fluxes to the water column and therefore do not take into consideration the deposition of relatively non-labile sestonic material at the sediment surface. Based on whole-lake nutrient budgets, the net transfer of P and N is from the water column to the sediment, making the sediments a net sink for P and N (James et $al.$ 1995a, SFWMD 2002). Even though the overall flux of total P and N for most lakes is to the sediment, the biogeochemical processes that are unique to the sediment environment are capable of transforming relatively refractory P compounds that are deposited on the sediment surface to more bioavailable forms (Wetzel 1999). Bioavailable P is then released to the water column and this internal P source can become a major factor in regulating lake productivity. The rate of this internal loading source depends on many factors such as bioturbation, redox status, mineral equilibria, sediment resuspension, and other physico-chemical properties of the sediment. Thus, even though internal loading does not (usually) represent a net source of nutrients to the lake, it can be a significant source of labile P and is therefore an important regulator of lake trophic conditions. A reduction in external loads will eventually result in a decline in sediment release rates as a consequence of depletion of exchangeable and labile organic P pools, though this may take many years (Marsden 1989). Also, declines in external nutrient loading may lag improvements in basin management practices. For

instance, Nair and Graetz (2002) have shown that the soils underlying the dairy farms of the northern Lake Okeechobee drainage basin have a high degree of P saturation. Subsurface lateral transport of this P may take many years to decline to pre-settlement export levels. Lake managers need to inform stakeholders in lake restoration plans that lake responses (such as reduced algal biomass) to nutrient reduction strategies may not be immediately apparent, and that gradual improvement in water quality is the goal. This is especially the case for large, shallow lakes. Further research is needed to determine the fractional TP permanent burial rate of material delivered to the sediment surface and the long-term steady-state flux of nutrients from the sediments under an acceptable external nutrient loading regime.

Conclusion

Sediment flux of P to the water column measured in intact cores ranged from 0.37 $mg \cdot m^{-2} \cdot day^{-1}$ to 2.12 $mg \cdot m^{-2} \cdot day^{-1}$. Mud zone sediments (M9) showed a decrease in P flux from 1.7 in 1989 to 1.0 $mg \cdot m^{-2} \cdot day^{-1}$ in 1999 (not significant). There were no clear trends in P flux from any sediment type within the lake. NH_4-N flux ranged from 40 $mg \cdot m^{-2} \cdot day^{-1}$ to 5.2 $mg \cdot m^{-2} \cdot day^{-1}$. Lake-wide, the magnitude of P release observed in this study was similar to release rates measured in 1989. Estimated flux of P and N from the sediment to the water column is 472 $Mt \cdot P \cdot yr^{-1}$ and 4,500 $Mt \cdot N \cdot yr^{-1}$. Estimated flux of P from sediments in the previous decade was 326 $Mt \cdot P \cdot yr^{-1}$, which was lower but because of the variability of measurements, was not statistically different.

Results from the porewater equilibrators were generally lower than those determined with the intact sediment cores, which may be due to bioturbation from invertebrates in the intact cores. Sediment oxygen demand was positively correlated to N and P flux and averaged 718 (±205) $mg \cdot m^{-2} \cdot day^{-1}$. This correlation indicates that mineralization of organic material contributes to the fluxes of N and P. Internal nutrient loading from the sediments, though not generally a net source of total nutrients to the water column, can be a major source of highly labile P and N and thus may serve a major role in regulating lake productivity, even after reduction in external loads. The fluxes reported here are low compared to other aquatic ecosystems.

Acknowledgments

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