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An evaluation of the importance of sulfate reduction and temperature to P fluxes from aerobic-surfaced, lacustrine sediments

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Abstract. We examined the influence of temperature and sulfate reduction rates on P-release from aerobic-surfaced, littoral sediments in a cooling reservoir. Annually, significant differences in P release from sediments at two sites (thermal effluent and non-effluent) were related to different temperature regimes, with higher rates of P release and decomposition at higher temperatures. Site-specific differences in solute fluxes were most pronounced in late summer, when water temperatures reached 40°C at the effluent site and solute fluxes increased dramatically. The thermal effluent site retained 65% of its annual P load, while the non-effluent site retained 92%. Relative P release (P-release normalized to inorganic carbon fluxes; RPR) data indicated that lake sediments retained P selectively (relative to C) throughout the year, except at the effluent site during late summer when stored P was released in excess of supply rates. Sulfate reduction rates were often typical of those measured in other freshwater lakes, but unusually high rates were measured at the thermal-effluent site especially in early fall and suggested higher DIC fluxes than we measured. These high rates suggest that sulfate reduction rates were overestimated and/or that most sulfide was recycled within the sediments. In any case, the highest sulfate reduction rates did not coincide with the highest P release rates. Furthermore, the total reduced inorganic sulfur content of surficial sediments did not significantly correlate to RPR, although concentrations varied widely throughout the year. Temperature was the only variable examined that significantly correlated to RPR (R^2 = 0.53, P-value = 0.017). Coupling between temperature and sediment P release was likely mediated through temperature effects on bioturbation and microbial metabolic rates.

Introduction

In many northern-temperate freshwater lakes, phosphorus (P) is the nutrient most limiting phytoplankton productivity (Schindler 1977). P inputs to lake water come from external sources such as streams and runoff (Cole 1983), or from internal sources such as water column regeneration and lake sediments (Riley and Prepas 1984; Cotner and Wetzel 1992; Brooks and Edgington 1994). In some lakes, the internal loading of P from sediments can be as high as external sources (Nürnberg 1984; Brooks and Edgington 1994). P accumulates in lake sediments to a greater extent than in the water column (Holdren et al. 1977), and large amounts can be released from sediments when bottom waters become anoxic (Mortimer 1941; Riley and Prepas 1984; Nürnberg 1984). While sediment P release into anoxic bottom waters is clearly an important internal P source, most lacustrine and oceanic surficial sediments are aerobic. Consequently, sediment P fluxes into oxic water columns may be of equal or greater importance than anaerobic fluxes (Jensen and Anderson 1992; Brooks and Edgington 1994). However, the mechanisms that govern P release/retention from sediments overlain by oxic bottom waters are not completely understood.

Various mechanisms have been proposed in the literature to explain P release from aerobic sediments. It was suggested over 50 years ago that sediment P fluxes may be influenced by lake sulfate concentrations (Hasler and Einsele 1948). P release could be influenced by sulfate through anion exchange processes in lakes of very high sulfate concentration (3–30 mM). In sediments of these lakes, sulfate may compete directly with phosphate for anion sorption sites (Caraco et al. 1989). Another mechanism ("sulfate reduction hypothesis") posits that at low sulfate concentrations (10–300 μM), sediment P release may be directly related to bacterial sulfate reduction rates (Caraco et al. 1989). Sulfide, one of the products of sulfate reduction, reacts readily with iron to form insoluble iron sulfides, preventing the re-supply of iron oxides at the sediment-water interface (Carignan and Tessier 1988; Caraco et al. 1989) and inhibits sediment P retention by sequestering available iron. Consequently, P is released into the water column.

There is evidence supporting the sulfate reduction hypothesis in marine sediments. In continental margin sediments, there was a positive correlation between the carbon to phosphorus ratio (C:P) and the degree of sediment pyritization (r^2 = 0.77; Mays (1987)). The role of sulfate reduction in anaerobic carbon degradation has generally been considered of limited importance in freshwater systems, largely due to low (50–500 μM) sulfate concentrations (Capone and Kiene 1988). However, high sulfate reduction rates have recently been measured in freshwater systems. A depth-integrated sulfate reduction rate of 143 mmol SO_4^{2-} m^{-2} day^{-1} was measured in a bog where the porewater sulfate concentration was approximately 150 μM (Wieder et al. 1990). In Lake Kinneret, Israel, an integrated rate of 29 mmol SO_4^{2-} m^{-2} day^{-1} was measured in sediments where porewater sulfate was 385 μM (Hadas and Pinkas 1995). These rates are in the same range as salt marshes, where the highest sulfate reduction rates have been measured in natural systems (25–425 mmol SO_4^{2-} m^{-2} day^{-1}; Howarth (1993)). The factors that maintain such high rates in freshwater are as yet not clearly understood.

Temperature is known to affect microbial sulfate reduction rates in temperate salt marshes (Nedwell and Abram 1979). Furthermore, increased temperature is known to increase fluxes of dissolved P from sediments in marine sediments (Jensen et al. 1995). However, the interactions of temperature, sulfate reduction and P fluxes from aerobic-surfaced sediments have not been well-studied in freshwater systems.

In this study, we took advantage of a temperature gradient in a Texas cooling reservoir to examine these interactions. We discuss the annual patterns of P fluxes and relate them to decomposition and sulfate reduction rates in these sediments.

Our approach to studying these poorly understood mechanisms has been the use of a dimensionless ratio termed relative P release (RPR; Caraco et al. (1989)). RPR is an *in situ* geochemical measurement whereby P release is related to a release rate expected based on the C:P ratio of decomposing organic matter and organic carbon remineralization rates. When measured sediment C:P flux ratios are higher than the theoretical ratio, it indicates that sediment processes (adsorption, mineral formation, bacterial uptake, etc.) are retaining P. Lower ratios indicate a net loss of inorganic P from the sediments. This technique can distinguish between low sediment P flux due to low availability of organic matter, and low P flux due to sediment retention (Caraco et al. 1989).

Methods and materials

Site description

This study was performed in a eutrophic reservoir, Fairfield Lake (836 ha), in Freestone County, Texas, USA (31° 45′N; 96 °W). The lake was built in 1969 and is used by Texas Utilities Generating Company as a source of cooling water for a 1,150 megawatt coal-burning power plant. Cooling water enters the plant condensers via a 1-km intake canal from the main reservoir, after which the heated water travels 0.7 km and enters a sub-reservoir. This thermally influenced sub-reservoir has a surface area of approximately 30 ha. Upon leaving the sub-reservoir, the heated effluent passes through a 2 km-long canal and returns to the main reservoir (Bowling 1980).

Site selection and sampling frequency

Study sites were chosen that demonstrated large differences in water temperature, but were otherwise similar for several key variables. We chose sites at two littoral locations in the lake that demonstrated a mean annual temperature difference of approximately 6 °C (Table 1). Elemental analyses of sediments were carried out by Soil Analytical Services (College Station, TX). Total metals were determined by sulfuric/perchloric digestion followed by ICP analysis of the digest, and total sulfur (S) was determined with a LECO high temperature induction furnace and an IR detector (American Public Health Association 1992). Organic C and total nitrogen (N) in the sediments were determinied by CHN analysis. Percent sand was measured by sieve (63 μm), and percent silt and clay via the pipette method (Folk 1980). Based on benthic grab-sample analyses, two sites were chosen in the thermal effluent influenced sub-reservoir and two in the main reservoir, and all were permanently marked with bottom-attached buoys. The two sites (thermal effluent and non-thermal effluent) consisted of two sub-sites and were sampled every six weeks for a period of one year, resulting in nine sampling periods between August 31, 1996 and September 3, 1997.

Table 1. Water column and sediment characteristics of the thermal and non-thermal effluent sites. Values in parentheses represent one standard error of the mean. Water column data were collected from either the non-effluent site number 1 (Sep 96 – Apr 97) or site number 2 (Jun 97 – Sep 97).

Parameter	Thermal Effluent Site	Non-Effluent Site 1	Non-Effluent Site 2
Sand (%)	92.5 (2.3)	94.3 (1.3)	91.5 (2.1)
Silt (%)	6.6 (2.2)	3.9 (1.1)	4.9 (1.0)
Clay (%)	0.9 (0.17)	2.0 (0.39)	3.6 (1.1)
Organic C (μmol C {g} dw^{-1})	254 (19.4)	175 (12.5)	179 (8.4)
Total N (μmol N {g} dw^{-1})	27.9 (1.7)	16.4 (1.1)	19.7 (0.0)
C:N (mol:mol)	9.1	10.7	9.1
Total Al (μmol {g} dw^{-1})	700 (85.2)	600 (66.7)	
Ca (μmol {g} dw^{-1})	57.0 (10.3)	40.6 (3.6)	
Fe (μmol {g} dw^{-1})	108 (10.4)	124 (0)	
Mg (μmol {g} dw^{-1})	26.8 (3.7)	21.0 (1.6)	
Na (μmol {g} dw^{-1})	288 (34.5)	275 (50.5)	
S (μmol {g} dw^{-1})	16.8 (1.6)	4.1 (0)	
P (μmol {g} dw^{-1})	3.4 (0.53)	2.0 (0.13)	
Water depth (m)	3.9 (0.16)	5.5 (0.28)	
Secchi depth (m)*	1.2 (0.1)	1.1 (0.1)	
Temperature (°C)*	29.4 (2.4)	23.7 (2.75)	
pH*	8.4 (0.1)	8.4 (0.11)	
D.O. (μM)	210 (17.5)	252 (16.4)	
Conductivity (μmhos cm^{-1})*	841 (37.1)	832 (35.4)	
SRP (μM)*	0.16 (0.09)	0.15 (0.07)	
SO_4^{2-} (μM)*	888 (18.0)	899 (20.7)	
Chl a (μg L^{-1})*	21.4 (3.03)	21.0 (3.19)	

* Values for these parameters were means from both non-effluent sites.

Water column sampling and measurements

For each sampling period, a Hydrolab H2O sonde was used to measure water-column depth profiles of dissolved oxygen, conductivity, temperature, redox, pH, and turbidity. Secchi depth was also measured at each site. Chlorophyll *a* was collected at the surface above each site and measured by filtering samples onto Whatman GF/F filters and extracting them in 90% acetone at room temperature for 2 to 24 h (Wetzel and Likens 1991), followed by measurement on a Turner model 10-AU fluorometer.

Seston samples were collected 0.5 m from the lake bottom by SCUBA divers using a sample bottle, and were analyzed in triplicate for particulate C, N, and P. Filters were dried, and analyzed for total C and N on a Carlo Erba elemental analyzer. Particulate P samples were analyzed in triplicate using the method of Solorzano and Sharp (1980) at 885 nm on a Perkin Elmer model C6180437 spectrophotometer with a 1-cm pathlength. Dissolved sulfate was measured using the turbidimetric technique (American Public Health Association 1992) at 420 nm on a Turner model 390 spectrophotometer.

In situ chemical fluxes

Fluxes of oxygen, dissolved inorganic carbon (DIC), pH, and soluble reactive phosphate (SRP) from the sediments were measured using dark benthic chambers. The chambers were similar to those described by Suplee and Cotner (1996), with some minor improvements. A 12-volt power supply, two YSI oxygen meters and a data logger were placed inside a submersible housing. Electrical power to the chamber pumps was controlled by an external switch on the housing. Prior to chamber deployment, the two YSI meters were air-calibrated, the data logger turned on, and the housing sealed. The two chambers and the housing were then deployed to the lake bottom by SCUBA divers. After placement on the sediments, the chambers were purged by exchanging water between the chamber interior and the water column with the pumps. The chambers were sealed and the pumps continually circulated water within the chambers. Samples were collected from a sampling port using 60 cm^3 plastic syringes, after a valve was opened to allow replacement water to enter. All syringe samples were placed on ice in the dark until they were returned to the lab. Real-time oxygen-concentration data were stored in the data logger. Two incubations were performed at each sub-site, providing four measurements per site for each period.

At the laboratory, pH changes that occurred during each chamber incubation were measured with a portable pH meter (calibrated daily) from syringe sub-samples. SRP samples (for both chamber syringe-samples *and* water-column flux experiments, below) were filtered through distilled-water soaked 0.45 μm filters at low vacuum (< 200 mm Hg) and frozen. Duplicate or triplicate samples were later analyzed via the ascorbic-acid molybdate method (Wetzel and Likens 1991) with a 5 cm pathlength.

DIC samples from the syringes were over-flowed into 30 ml Pyrex bottles, preserved with $HgCl_2$ (1% final conc.), and capped without air with Teflon-lined caps. DIC samples were analyzed via acidification with phosphoric acid, followed by measurement of the liberated CO_2 with an infrared detector (Shimadzu TOC 5000). All glassware was acid-washed.

Chemical fluxes from the sediments were calculated using the equation of Dollar et al. (1991). We corrected benthic chamber fluxes for water column changes in DIC, SRP and dissolved oxygen measured in 300 ml BOD bottles at ambient temperature in the dark. Fluxes were subtracted from the total chamber flux for each solute, giving sediment-only fluxes. Relative P release was calculated as the $SRP_{\text{sediment flux}}$: $DIC_{\text{sediment flux}}$ ratio, where the SRP flux is given in μmol P m^{-2} day^{-1} and the DIC flux as mmol C m^{-2} day^{-1} (Caraco et al. 1993).

Sulfate reduction rates and total reduced inorganic sulfur

Bacterial sulfate reduction rates in sediments were determined in cores as described by Suplee and Cotner (1996). In the present study, four sediment cores were collected from each site for each sampling period. Sulfate reduction rates were determined at five different depth intervals (0.5, 2.5, 4.5, 6.5 and 8.5 cm) below the sediment-water interface using the $^{35}SO_4^{2-}$ core injection technique (Jørgensen 1977). $^{35}SO_4^{2-}$ injections (1μCi in 80 μl water) were made at each depth interval and each injection had a maximum sulfate concentration of 22.5 μM. The cores were incubated in the dark for 10 min to 1.5 h (Hadas and Pinkas 1995) with the longer incubations in the winter when rates were lowest. Incubations were terminated by extruding the sediment from the core-tube, slicing out the appropriate depth intervals, preserving them in 2N zinc acetate, and freezing. The radiolabelled samples were processed using a single-step chromium reduction technique (Fossing and Jørgensen 1989). Killed controls (3.4% final concentration of formalin) were periodically run in parallel with live cores. For each site and each sampling period, porosity at each injection depth-interval was determined in quadruplicate core samples collected with the sulfate reduction cores.

Sediment total reduced inorganic sulfur (TRS) concentrations were determined from ZnS subsamples collected from the zinc acetate traps of the distillation apparatus (Fossing and Jørgensen 1989). Samples were analyzed using the methylene blue spectrophotometric method, or the iodometric titration technique (American Public Health Association 1992).

Volumetric TRS concentrations in μmol S cm^{-3} were calculated as: TRS $*$ sediment bulk density; where TRS is given in μmol S g^{-1}(dw), and sediment bulk density as g(dw) cm^{-3}. Areal concentrations (mol S m^{-2}) were calculated by depth integration.

Porewater collection and analysis

Porewater samplers were constructed following a design similar to Hesslein (1976). Each sampler was made of PVC plastic and housed six glass tubes at six depths. The samplers were 16.0 cm long, 15.5 cm wide, and 2.5 cm thick, and the tubes were 12.5 cm long with a diameter of 1.5 cm. The tube interval spacing and placement corresponded to the depth intervals of the $^{35}SO_4^{2-}$ injection points used for the sulfate reduction experiments. Each tube contained a horizontal slot for porewater exchange was filled with de-ionized water, and was individually wrapped with Supor 450® 0.45 μm pore-size filters (Gelman). The polyethersulfone filter was selected for its strength and inert qualities, as cellulose dialysis membranes have been shown to alter porewater concentrations of some chemical solutes (Carignan 1984). The six tubes were held in place by a frame across which was stretched a 0.63 μm nylon screen, which was itself secured to the sampler by two nylon screws. After assembly, no air bubbles remained within the housing.

Four samplers were deployed at each site. Prior to deployment by SCUBA, the samplers were placed into a cleaned plastic container filled with de-oxygenated, distilled water. The porewater samplers were pressed into the sediments and allowed to equilibrate for 7 to 11 days (Carignan 1984). The pH in each sampler was checked in one tube (10-cm depth) with a portable pH meter. The contents of each tube were immediately transferred to two sample bottles and preserved in the field for sulfate and SRP. Sulfate samples were preserved with 1% (final concentration) zinc acetate to precipitate any sulfides present, and the SRP samples were frozen. New membranes, caps, and nylon line were used for each sampling period.

To estimate net yearly sulfate reduction rates, integrated sulfate reduction at each site was determined by examining the drawdown in porewater sulfate concentration relative to the overlaying water column. The mean porewater sulfate concentration (μM) and porosity at each corresponding depth (ml cm^{-3}) were determined from replicate porewater samplers as described above. For each depth, the product of porosity and concentration (in nmol SO_4^{2-} cm^{-3}) was calculated, and the resulting depth profiles (between 0 and 9 cm) were integrated.

To estimate net sulfate reduction in the porewater, we subtracted the integrated porewater sulfate concentrations from that which we calculated assuming that the porewater sulfate concentration was the same as the overlaying water column. Integrating temporal data at each site over a 1 year period resulted in an estimate of net yearly sulfate reduction for each site.

Statistical approaches

Comparisons between the thermal effluent and non-effluent sites' annual fluxes of oxygen, DIC, and P, as well as sulfate reduction rates, were made by integration and a 'bootstrap' statistical approach. At each site there were four replicates, in units of mass m^{-2} day^{-1} for each sampling period (n = 9). For each parameter (i.e., DIC flux), the four replicates of each sampling period were randomized. The annual flux (mass m^{-2} $year^{-1}$) resulting from the integration of the nine randomly selected replicates was estimated. The ten randomly generated annual integrations from each site were considered random samples from a population, and a t-test for two population means was applied after checking that the data were normally distributed (Ott 1993). Differences between the thermal effluent and non-effluent sites were considered significant at $\alpha = 0.05$. A 90% confidence interval was also calculated for each annual integration.

Effluent and non-effluent site comparisons of seston P, seston C, and sediment TRS concentrations were made using repeated measures ANOVA (SAS Institute Inc 1994). The technique accounts for serial correlation, which can be a problem in time-series data. Differences between the effluent and non-effluent sites were considered significant at $\alpha = 0.05$. To analyze the relationship between RPR and various potential causal mechanisms, we employed linear and multiple regressions, coupled with the Durbin-Watson statistic (to check for serial correlation problems) and the Bonferonni adjustment (to compensate for a single hypothesis being tested more than once; Neter et al. (1983)). In general, Durbin-Watson values less than 1.4 indicates that serial correlation is a significant problem (Neter et al. 1983).

Results

Research sites

The relative amounts of major elements in the sediments were quite similar between the effluent and non-effluent sites with the exception of total S, which was approximately four times higher at the thermal-effluent site (Table 1). Mean total iron in the effluent and non-effluent site sediments was 108.3 and 124.1 μmol g(dw)$^{-1}$ respectively, with no significant difference between the sites. The C:N ratios of the effluent and non-effluent sites were similar, however, both organic C and total N concentrations were higher at the thermal-effluent site.

In spite of efforts to position the non-effluent site above the hypolimnion, the lake stratified in late May 1997 and anaerobic waters impacted the site. Therefore, in June 1997 a shallower nearby site above the hypolimnion was used as part of the routine sampling. The site had originally been considered during the initial survey, as it had similar sand, silt, and clay ratios, depth, and C:N ratio as the thermal-effluent site (Table 1). Water depth at the thermal-effluent site was generally shallower than the original non-effluent site, however it was almost the same as the second non-effluent site. There was no significant difference ($p < 0.05$) between the effluent and non-effluent sites ($n = 4$) in the percentage of sand, silt, or clay in the top 10 cm of sediment. Data presented herein, whether collected at the first or second non-effluent site, was only collected when the overlaying water column was aerobic.

The water column at the effluent and non-effluent sites

The mean annual difference in temperature between the thermal-effluent and non-effluent sites was 5.7 °C (Table 1). Conductivity, pH, and chlorophyll *a* were similar between the two sites on a month to month basis, but conductivity tended to be slightly higher at the thermal-effluent site, perhaps due to warmer water temperatures and higher evaporation rates. Aerobic conditions were consistently maintained at the thermal-effluent site throughout the study, and the June 1997 move to a shallower location at the non-effluent site assured the same conditions there (Table 1). Sulfate concentrations over the year ranged from 831 μM to 1,028 μM, and were essentially the same at both sites.

Nutrient ratios of the seston ranged from a minimum of 109 C:11 N:1 P (thermal-effluent site, July 1997) to a maximum of 253:20:1 (non-effluent site, June 1997; Table 2). In general, C:N:P ratios were higher at the non-effluent site than the thermal-effluent site. Annually, there was no significant difference between the seston C concentrations at the two sites (repeated measures ANOVA; $p > 0.05$). However, there was a significantly higher concentration of seston P at the thermal-effluent site ($p < 0.001$). As an annual mean, the thermal-effluent site had a C:P ratio of 135:1, and the non-effluent site was 155:1 (Table 2).

Table 2. Particulate carbon, nitrogen and phosphorus at the effluent and non-effluent sites. EF = Effluent Site; NEF = Non-effluent Site.

Date	Site	C (μM)	N (μM)	P (μM)	C:P	N:P
Sep 96	EF	205.9	27.18	1.37	150	20
	NEF	188.3	24.50	1.29	146	19
Oct 96	EF	268.2	35.92	1.76	152	20
	NEF	303.3	45.22	1.67	182	27
Dec 96	EF	172.7	22.2	1.43	121	15
	NEF	164.5	20.43	1.27	129	16
Jan 97	EF	189.3	24.41	1.26	150	19
	NEF	151.87	18.65	1.08	141	17
Mar 97	EF	160.4	21.64	1.32	121	16
	NEF	157.2	20.60	1.17	135	18
Apr 97	EF	160.6	21.13	1.30	123	16
	NEF	156.9	14.5	1.18	133	12
Jun 97	EF	209.3	21.66	1.37	153	16
	NEF	295.0	23.81	1.17	253	20
Jul 97	EF	94.91	9.16	0.87	109	11
	NEF	138.7	13.06	1.16	120	11

Benthic fluxes

A total of sixty-five chamber incubations were performed during the study, with incubation lengths ranging from 1.6 to 6.5 h. During the winter months, the chamber incubation lengths were increased in order to detect measurable changes, decreasing the number of incubations performed. In no case did the oxygen level within a chamber fall below 60 μM. Oxygen fluxes in the chambers were consistently linear, as were the DIC and P fluxes.

On an annual basis, there was a significantly higher ($p < 0.001$) sediment oxygen demand at the thermal-effluent site than the non-effluent site (Figure 1). The integrated annual oxygen flux at the thermal-effluent site was -19.9 ± 0.9 mol O_2 m^{-2} $year^{-1}$, and -11.6 ± 0.4 mol O_2 m^{-2} $year^{-1}$ at the non-effluent site. During the nine sampling periods, the mean daily fluxes at the thermal-effluent site ranged from -167.4 to -19.6 mmol O_2 m^{-2} day^{-1}, with the highest oxygen demands occurring in the late summer and fall (Figure 1). Daily oxygen fluxes at the non-effluent site showed much less variability than the thermal-effluent site, ranging from -60.4 to -16.2 mmol O_2 m^{-2} day^{-1}.

There was a significantly higher ($p < 0.001$) annual DIC flux at the thermal-effluent site than the non-effluent site (Figure 1). The annual integrated DIC flux at the thermal-effluent site was 22.6 ± 2.7 mol C m^{-2} $year^{-1}$, and 9.0 ± 1.4 mol C m^{-2} $year^{-1}$ at the non-effluent site. Mean daily DIC fluxes over the nine sampling periods at the thermal-effluent site ranged from 2.0 to 209.1 mmol C m^{-2} day^{-1}, and -68.8 to 80.9 mmol C m^{-2} day^{-1} at the non-effluent site. There was much more variability between repeat chamber incubations for DIC than

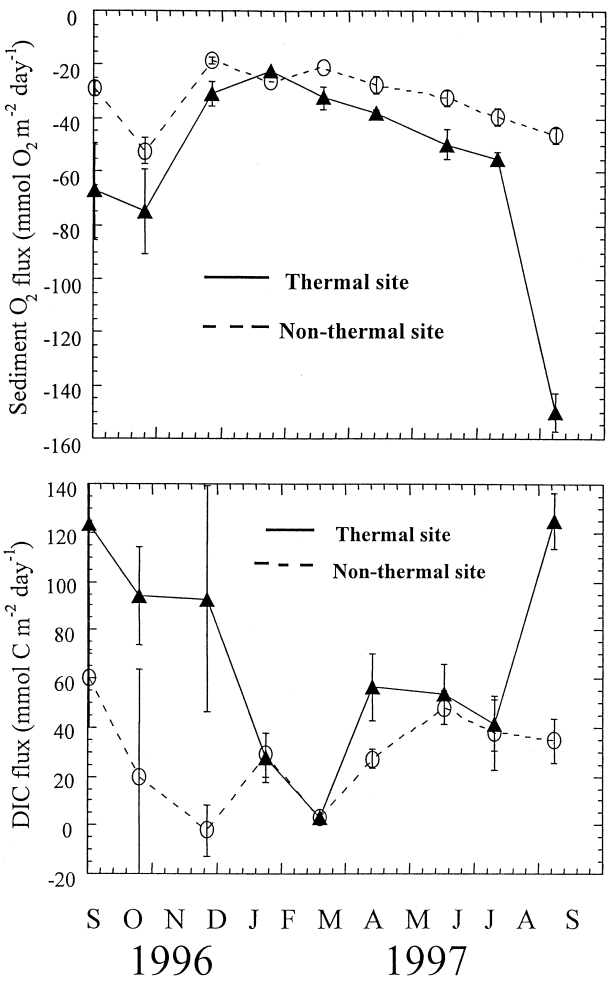

Figure 1. Annual sediment oxygen and dissolved inorganic carbon (DIC) fluxes

SRP, as shown by the error bars in Figures 1 and 2. Similar to the SRP flux, the greatest DIC release occurred in late summer at the thermal-effluent site.

Annually, there was a significantly higher ($p < 0.001$) release of SRP at the thermal-effluent site than the non-effluent site (Figure 2). The annual integrated SRP flux at the thermal-effluent site was 59.3 ± 5.5 mmol P m^{-2} $year^{-1}$, and 4.4 ± 2.5 mmol P m^{-2} $year^{-1}$ at the non-effluent site. Mean daily SRP fluxes over the nine sampling periods at the thermal-effluent site ranged from −8.5 to 1,353 μmol P m^{-2} day^{-1}, and −9.7 to 64.6 μmol P m^{-2} day^{-1} at the non-effluent site. From December through June, the SRP fluxes from the effluent and non-effluent sites were very similar. However, during the late summer the release rates of SRP at the thermal-effluent site increased rapidly, whereas at the non-effluent site, fluxes remained near their yearly average (Figure 2). Together, the SRP fluxes measured

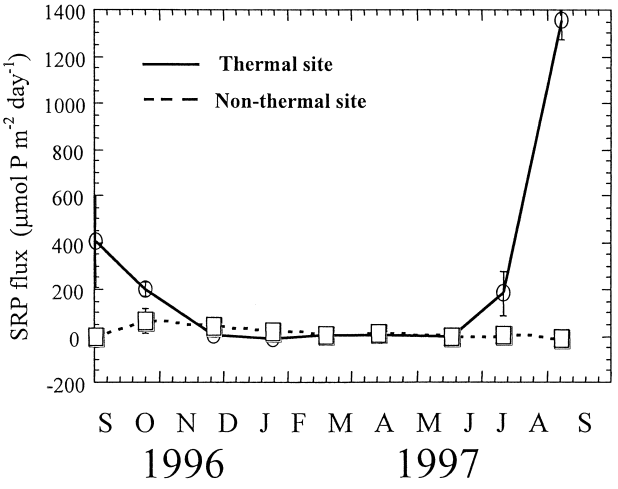

Figure 2. Annual soluble reactive phosphate (SRP) flux from Fairfield Lake.

during September 1996 and September 1997 contributed 58% to the total annual SRP flux measured at the thermal effluent site. The fact that the same phenomenon was observed twice, at the same site during the same month, lends weight to its significance.

Relative P release and pH

The pH changes within the chambers during incubations were very consistent throughout the study at both sites, consistently dropping between 0.0 and 0.3 units. The pH in the chambers at the initiation of incubations ranged from 8.9 (late summer and fall) to 7.9 (early spring).

At the thermal-effluent site, the RPR ranged from −0.35 to 0.63 during the winter and spring, and was below the P:C ratio of the seston supply (Figure 3). However, in late summer the RPR matched or exceeded the seston supply ratio, reaching values of 11.5 and 10.5 in September 1996 and 1997, respectively. In contrast, the mean non-effluent site RPR was well below the seston P:C ratio throughout the year, ranging from −2.73 to 1.49 (Figure 3).

Sulfate reduction rates and total reduced inorganic S

On an annual basis, there was significantly higher ($p < 0.001$) integrated gross sulfate reduction at the thermal-effluent site than the non-effluent site (Figure 4). The annual integrated sulfate reduction rate at the thermal-effluent site was 28.0 ± 4.2 mol S m^{-2} $year^{-1}$, and 14.6 ± 1.3 mol S m^{-2} $year^{-1}$ at the non-effluent site. Integrated sulfate reduction rates (0–9 cm) over the nine sampling periods at the thermal-effluent site ranged from 17.3 to 243.7 mmol SO_4^{2-} m^{-2} day^{-1}, and 3.4 to 110.1 mmol SO_4^{2-} m^{-2} day^{-1} at the non-effluent site. Note that the error bars for each

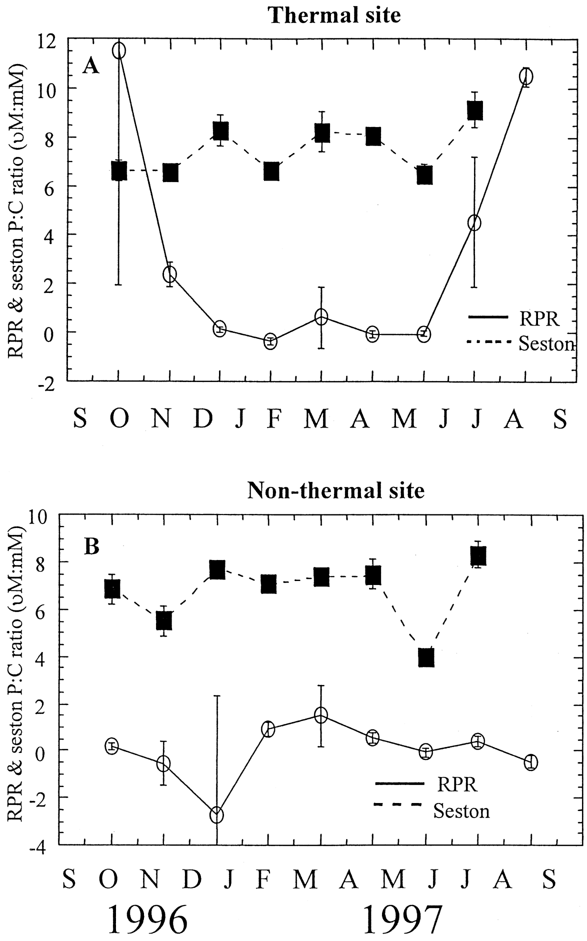

Figure 3. Relative P release (RPR) and seston P:C ratios of Fairfield Lake.

period were propagated by integrating the area under the curve of one standard error (n = 4) of the sulfate reduction rate for each of the five depths measured.

At both sites, the position of the peak sulfate reduction rate (nmol SO_4^{2-} cm^3 day^{-1}) in sediment profiles changed according to season (Figure 5). Generally, the highest rates were in the upper 2–5 cm in summer and fall, and in winter and early spring the peak was usually located at the 5–9 cm depth. This was corroborated by direct observation of sediment cores, in which a distinct black band (presumably iron sulfides) was located at the same depth intervals where the highest sulfate reduction rates were measured. The injected concentration of $^{35}SO_4^{2-}$ (22.5 μM) was 4–43 times lower than the ambient sediment porewater sulfate concentrations (see below), and should not have stimulated sulfate reduction. The mean recovery of injected ^{35}S label was 40.5% (n = 185) and 41.4% (n = 201) for the thermal effluent and non-effluent sites, respectively. Losses could be partly explained by advec-

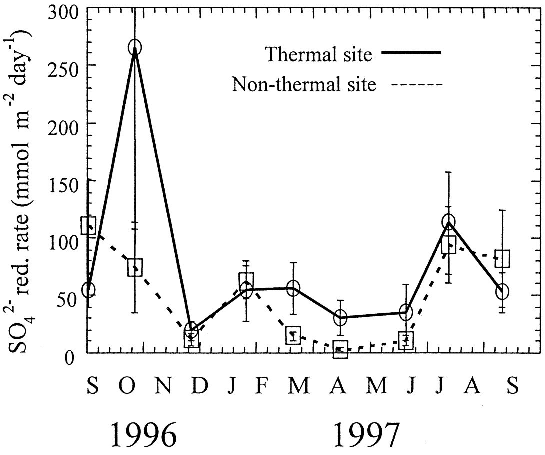

Figure 4. Integrated sulfate reduction rates (0–9 cm) in Fairfield Lake.

tion resulting from the injection process, as both $^{35}SO_4^{2-}$ and reduced ^{35}S compounds were found in the sediment segments that were between the 5 segments collected for analysis. There was little correlation ($r^2 = 0.07$) between percent recovery and measured sulfate reduction rates. In the killed controls, there was no reduced ^{35}S above background in any of the 6 tested cores.

There was a significantly higher (repeated measures ANOVA; $p = 0.02$) concentration of sediment total reduced inorganic S (TRS) at the thermal-effluent site than the non-effluent site for the 0–1 cm integration, as well as the 0–9 cm integration ($p = 0.001$; Figure 6). On a dry weight basis, TRS concentrations ranged from 1.4 to 42.8 μmol μmol S (g dw)$^{-1}$ at the thermal-effluent site, and from 0.0 to 34.2 μmol S (g dw)$^{-1}$ at the non-effluent site.

Porewater profiles

Mean sulfate concentrations ($n = 4$) in the thermal-effluent site porewater ranged from a high of 667 μM (0.5 cm, October 1996) to a low of 85 μM (2.5 cm, September, 1997). At the non-effluent site, sulfate ranged from 977 μM (1 cm, January 1997) to 92.1 μM (3 cm, September 1996; Table 3). Overall, porewater sulfate concentrations were higher in the winter and lower in summer and fall. At the non-effluent site, mid-winter sulfate concentrations in the upper centimeter of sediment were nearly identical to the water column concentration. The pH in the porewater (10 cm depth) at both sites ranged from 6.9 to 7.6 (mean = 7.1) for the entire study.

Net sulfate reduction rates calculated from the drawdown of sulfate in porewater (relative to the water column) resulted in yearly estimates lower than those determined by the $^{35}SO_4^{2-}$ injection method. Annually, the thermal-effluent site net sulfate reduction rate estimated from SO_4^{2-} drawdown was 987 mmol SO_4^{2-} m^{-2} year^{-1}, and the non-effluent site was 781 mmol SO_4^{2-} m^{-2} year^{-1}.

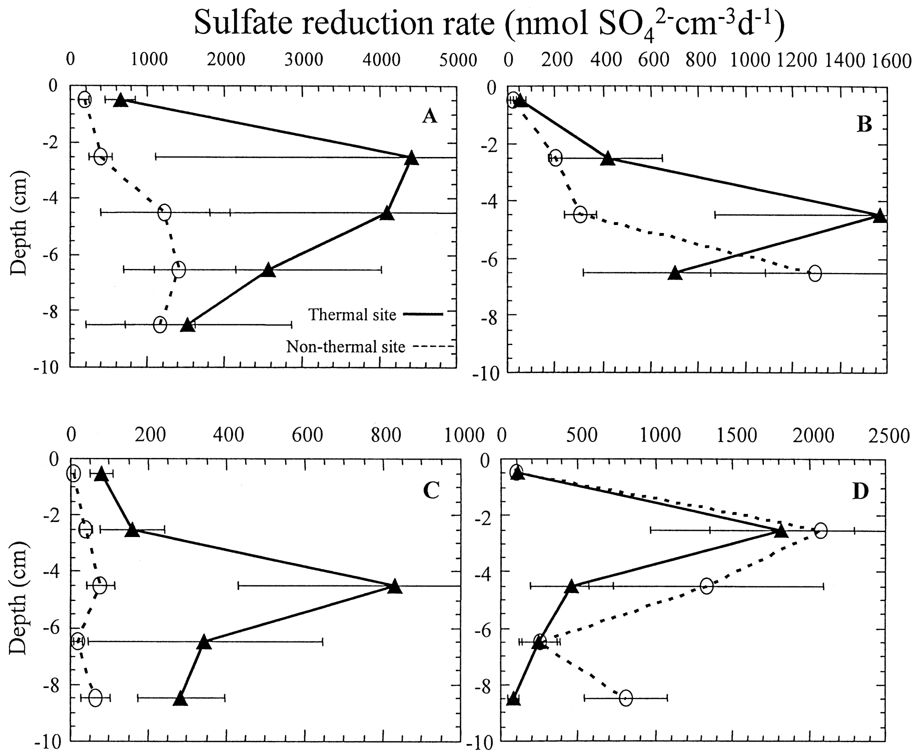

Figure 5. Sediment profiles of sulfate reduction rates during four seasons at the thermal and non-thermal sites. A. Fall (October 1996). B. Winter (January 1997). C. Spring (April 1997). D. Summer (September 1997).

Porewater SRP concentrations were consistently higher at the thermal-effluent site than the non-effluent site throughout the year (Figure 7), generally by one order of magnitude. The highest thermal-effluent site porewater SRP concentration was measured in the upper 1 cm of sediment in September 1996 (23.7 μM). The lowest values were found in early spring 1997, after which they began to rise. In September 1997, SRP concentrations in the upper 1-cm of the thermal-effluent site sediments again increased to values found the prior year (Figure 7). At the non-effluent site, the highest concentration was measured in October 1996 in the upper 1 cm (6.4 μM). The lowest concentrations were found in the early spring, after which they began to increase through the spring and into summer.

Regression analyses

Site-specific and grouped data were both examined to determine what factors influenced RPR most. After Bonferroni adjustment for a family of three tests (three for simple linear and three for polynomial regressions), the level of significance was set to $\leqslant 0.017$. Water-column temperature was the only independent variable

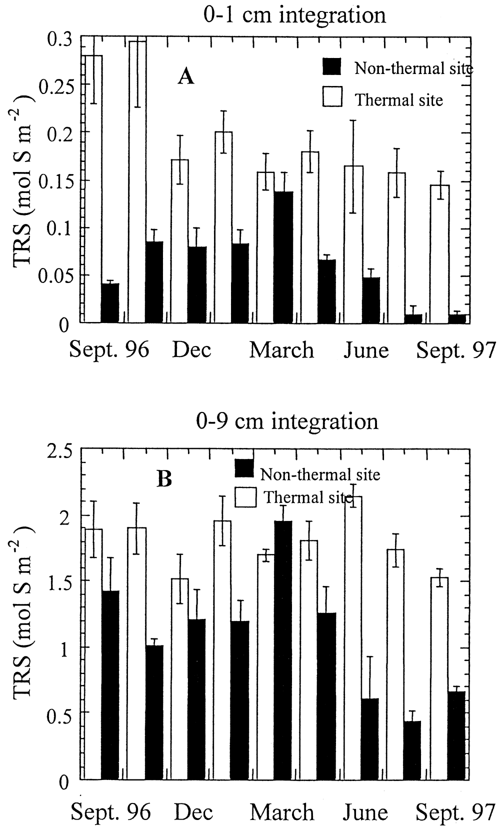

Figure 6. Total reduced inorganic sulfur (TRS) in Fairfield Lake sediments. A. 0–1 cm integration. B. 0–9 cm integration. Error bars are one standard error of the mean.

significantly correlated to RPR (Figure 8, Table 4). The relationship between water temperature and RPR was best described by a second-order polynomial model, with an R^2 of 0.53. The regression (grouped data) between water temperature and RPR also demonstrated a significant p-value using a first order model, however the Durbin-Watson value was too low (Table 4). TRS showed no significant relationships to RPR, nor did sulfate reduction rates (0–1 cm) demonstrate significant correlations for either first or second order models. Furthermore, regressions between the dependent variables and deeper integrations of TRS and sulfate reduction rates (i.e., integrations of 0–3 cm, 0–5 cm, and 0–9 cm) demonstrated progressively poorer coefficients of determination or multiple determination. Therefore, the results presented in Table 4 represent the most significant results for these data.

Table 3. Sulfate concentrations (μM) in Fairfield Lake sediment porewater during four seasons, at the thermal and non-thermal sites. Values in parenthesis represent one standard error of the mean (n = 4).

Date	Site	Depth (cm)				
		0.5	2.5	4.5	6.5	8.5
October 1996	Thermal	667 (237)	528 (175)	538 (153)	492 (127)	422 (134)
October 1996	Non-thermal	446 (83)	335 (30)	251 (5)	261 (26)	269 (17)
January 1997	Thermal	481 (51)	423 (40)	408 (65)	356 (40)	427 (65)
January 1997	Non-thermal	977 (171)	942 (213)	733 (247)	692 (182)	601 (106)
April 1997	Thermal	278 (67)	161 (13)	142 (9)	136 (4)	149 (18)
April 1997	Non-thermal	552 (75)	358 (75)	318 (81)	287 (93)	254 (77)
September 1997	Thermal	103 (27)	85 (17)	85 (8)	95 (8)	97 (3)
September 1997	Non-thermal	217 (61)	142 (31)	107 (9)	108 (13)	107 (7)

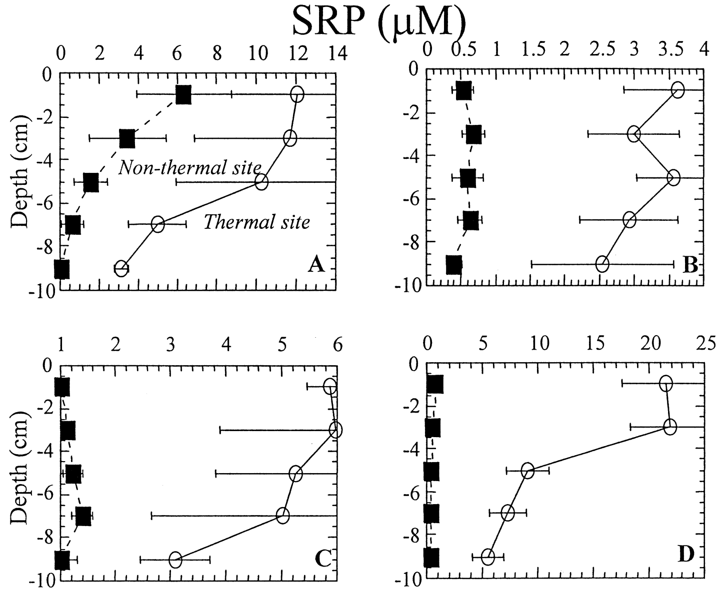

Figure 7. Soluble reactive phosphate (SRP) profiles in the thermal and non-thermal site sediments. A. October 1996. B. January 1997. C. April 1997. D. September 1997. Error bars are one standard error of the mean.

Discussion

Potential influence of benthic chambers on solute fluxes

In this study, benthic chamber incubation lengths were kept as short as possible in order to maintain aerobic conditions and assure that solute fluxes were linear. Excessive incubation length and/or high fluxes can result in non-linear concentration

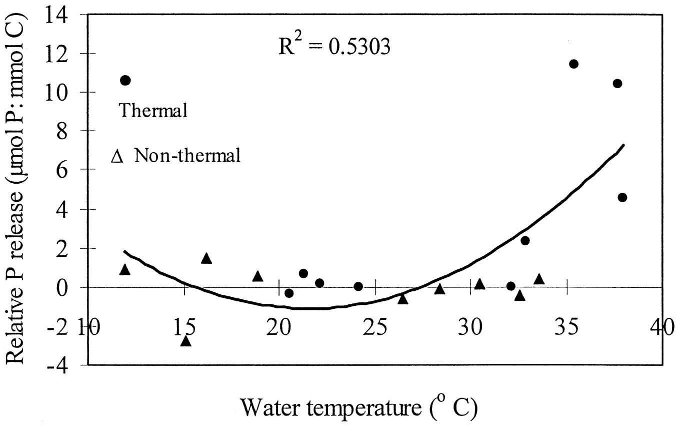

Figure 8. Relationship between relative P release and water temperature in Fairfield Lake. Thermal and non-thermal site data are differentiated by symbol.

changes over time within chambers (Forja and Gómez-Parra 1998). The use of dark benthic chambers may also have an influence on some solute fluxes. Dark chambers have the advantage of minimizing uptake of nutrients by water column and sediment autotrophs during the incubation, but also have the potential to diminish the oxidized microzone at the sediment water interface. Epipelic algal oxygen production inhibits P release to the overlaying water by contributing to the oxidized microzone, whereas in the dark this microzone can be diminished and increase the P flux from the sediments (Carlton and Wetzel 1988). Andersen (1997) found a weak ($r^2 = -0.21$) but significant negative correlation between sediment oxygen flux and SRP flux, suggesting that if dark chambers reduced O_2 production by periphyton, increased SRP release may result. In Fairfield Lake, this phenomenon was probably only important in the late summer, when porewater SRP concentrations were very high near the sediment-water interface. No light chamber experiments were undertaken in this study, and therefore the magnitude of this impact is unknown. The fluxes measured in this study are, therefore, equivalent to nighttime fluxes and should be considered as highest daily potentials.

P loading to the sediments and relative P release (RPR)

To estimate the percent P retained in the sediments at the two sites, we estimated annual C and P loading. Bowling (1980) measured primary productivity as 96.3 and 76.5 mol C m^{-2} year^{-1} at the effluent and non-effluent sites, respectively, and the mean DIC flux (this study) from the effluent and non-effluent sites was 22.6 and 9.0 mol C m^{-2} year^{-1}, respectively. Carbon dioxide release is a better estimate of organic matter decay than O_2 decline, as it accounts for anaerobic metabolism (Wetzel 1983), and in any case the annual DIC and O_2 fluxes we measured were in close agreement (Figure 1). The DIC fluxes represented from one quarter to one

Table 4. Simple linear and polynomial regressions between relative P release (RPR) and various independent variables. Significant relationships after Bonferroni adjustment ($P < 0.017$) are shown in bold.

Independent Variable (X)[1]	Dependent Variable (Y)[2]	Data set(s)[3]	Model Order	r^2	R^2	P-value	Durbin-Watson Value
Water temperature (°C) at bottom	RPR	EF	First	0.553		0.022	1.61
Water temperature (°C) at bottom	RPR	NEF	First	0.001		0.94	2.99
Water temperature (°C) at bottom	**RPR**	**EF + NEF**	**First**	**0.310**		**0.017**	**1.28**
Water temperature (°C) at bottom	RPR	EF	Second		0.630	0.310	1.74
Water temperature (°C) at bottom	RPR	NEF	Second		0.010	0.798	2.92
Water temperature (°C) at bottom	**RPR**	**EF + NEF**	**Second**		**0.530**	**0.017**	**1.68**
TRS (0–1 cm)	RPR	EF	First	0.069		0.493	1.50
TRS (0–1 cm)	RPR	NEF	First	0.035		0.630	2.80
TRS (0–1 cm)	RPR	EF + NEF	First	0.240		0.039	1.98
TRS (0–1 cm)	RPR	EF	Second		0.425	0.103	1.81
TRS (0–1 cm)	RPR	NEF	Second		0.200	0.309	3.10
TRS (0–1 cm)	RPR	EF + NEF	Second		0.260	0.503	1.93
Sulfate reduction rate (0–1 cm)	RPR	EF	First	0.036		0.623	1.10
Sulfate reduction rate (0–1 cm)	RPR	NEF	First	0.015		0.757	1.19
Sulfate reduction rate (0–1 cm)	RPR	EF + NEF	First	0.089		0.229	2.57
Sulfate reduction rate (0–1 cm)	RPR	EF	Second		0.541	0.043	2.24
Sulfate reduction rate (0–1 cm)	RPR	NEF	Second		0.106	0.463	1.42
Sulfate reduction rate (0–1 cm)	RPR	EF + NEF	Second		0.250	0.098	3.14

[1] Sulfate reduction rate and TRS values used in regressions were the means of the four replicates for a given sampling period.

[2] RPR values used in regressions were the means of the repeat measures of a given sampling period.

[3] EF = Thermal effluent site; NEF = Non-thermal effluent site.

eighth of primary productivity, similar to values measured in other shallow aquatic ecosystems (Nowicki and Nixon 1985; Alongi 1994).

For simplicity, we assumed that the DIC fluxes represented the total annual C loading, i.e, all carbon deposited was respired. The mean annual seston C:P ratio at the effluent and non-effluent sites was 135 and 155, respectively, giving a P load to the thermal-effluent site of 167 mmol P m^{-2} $year^{-1}$, and 58 mmol P m^{-2} $year^{-1}$ to the non-effluent site. When compared to the annual SRP fluxes from the sediments, these calculations indicated that the thermal-effluent site retained 65%, and the non-effluent site retained 92% of the sedimented P.

RPR data were consistent with the idea that these aerobic littoral sediments were a large sink for P in Fairfield Lake. With the exception of late summer at the thermal-effluent site, the RPR of Fairfield Lake sediments was well below the P:C ratio of the seston (presumed P and C supply to the sediments), indicating that there was net storage of P in the sediments throughout the year (Figure 3). The non-effluent site RPR values (−2.73 to 1.49) were similar to other freshwater lakes, most of which ranged from 0.4 to 2.0 (Caraco et al. 1993). In the winter and spring, thermal-effluent site RPR values were also in this general range. However, in early September 1996 and 1997 the thermal-effluent site RPR values reached 11.5 and 10.5, respectively, values that have only been reported in one freshwater lake (Green Lake, WI; Caraco et al. (1993)). These thermal-effluent site RPR values were higher than the seston P:C ratio which had an annual mean of 7.5, indicating that there was a net loss of P from these sediments in late summer.

These results indicate that the littoral sediments were an important sink for P in Fairfield Lake. More than half of the entire lake sediments (55%) are littoral, therefore, the processes that occur there have important impacts on nutrient availability in this lake and other similar systems. In small Canadian lakes, littoral decomposition rates were three times higher than in sediments outside of the littoral zone and more than half of the final decomposition products (CO_2 and CH_4) was produced there (den Heyer and Kalff 1998). Just as it has been shown that oxidized Fe at the sediment-water interface is a “P-trap”, on a whole-lake basis, the littoral sediments behave as a P-trap to the rest of the lake. Consistent with this observation, the littoral sediment POC:PP ratios were 74:1 and 89:1 at the effluent and non-effluent sites, respectively, while the seston POC:PP ratios were always greater than 100:1.

In our study, two different phenomena resulted in net P release from the littoral sediments. At the thermal effluent site, high summer temperatures (near 40 °C) coincided with net P loss from sediments. Also, anaerobic conditions in the hypolimnion had the same result (data not presented here). In both cases, net P release was likely a consequence of lowered redox conditions. In lakes where redox in the sediments remains relatively high at the sediment water interface, very little P fluxes from the sediments. Bioturbation is likely an important mechanism that introduces oxidized substrates from the water column to the surface sediments and helps maintain high redox conditions in littoral sediments (Kristensen and Blackburn (1987); see below).

Sulfate reduction and TRS

Most of the integrated sulfate reduction rates measured in this study were at the upper range of values for freshwater lakes (Dornblaser et al. 1994; Hadas and

Pinkas 1995). In October 1996, the thermal-effluent site sulfate reduction rate (243.7 mmol SO_4 m^{-2} day^{-1}) was extremely high, as high as those measured in salt marshes (Howarth and Teal 1979; King 1988). At the thermal-effluent site, sulfate reduction rates decreased in the late summer (Figure 4). Other studies have shown that sulfate reduction rates reach an optimum at 34 °C, and then decline rapidly above 41 °C (Arnosti et al. 1998). Although thermal-effluent site late-summer temperatures in the high 30's were recorded on the actual sampling dates of this study, we have frequently observed August temperatures in excess of 40 °C at the thermal-effluent site.

Sulfate reduction is typically considered unimportant in freshwater decomposition (Capone and Kiene 1988), although we measured very high gross rates in our study (Figure 4). These rates may have been overestimated, as the annual DIC fluxes measured at the thermal and non-thermal sites (22.6 and 9 mol C m^{-2} $year^{-1}$, respectively) were 2–3 times lower than what would be expected from our gross sulfate reduction rate measurements. Based on a 2:1 ratio of carbon oxidized to sulfate reduced, the annual integrated SRR at the thermal and non-thermal sites should have produced 56 and 29 mol C m^{-2} $year^{-1}$, respectively. Furthermore, dissolved oxygen fluxes were also 2–3 times lower than they should have been if sulfide was oxidized by oxygen. In a similar study, it was suggested that a "biologically unavailable sulfate pool" exists in freshwater, one that may be associated with dissolved organic matter (Roden and Wetzel 1996). Because determination of the sulfate reduction rate is dependent upon the porewater sulfate concentration, this would result in an overestimation of gross rates.

Estimates of net sulfate reduction in the sediments was also consistent with the idea that our sulfate reduction rates were overestimated. This approach resulted in rates of 987 and 781 mmol SO_4^{2-} m^{-2} $year^{-1}$ for the effluent and non-effluent sites, respectively. These values were much lower than the $^{35}SO_4^{2-}$ method estimates (28.0 and 14.6 mol SO_4^{2-} m^{-2} $year^{-1}$, effluent and non-effluent sites, respectively), and if correct, it suggests a rapid recycling of available sulfate, 96% and 95% annually at the thermal effluent and non-effluent sites, respectively. The mechanism(s) that allows porewater sulfate to be rapidly re-oxidized has intrigued other researchers working with freshwater sulfate reduction as well (Urban and Brezonik 1993). However, the fact that both DIC and dissolved oxygen fluxes were insufficient to account for the high sulfate reduction rates suggests that some of the discrepancy was due to an overestimation of the sulfate reduction rates. Rapid recycling may have occurred in Fairfield Lake sediments, but probably not to the extent that our data suggest.

Sulfur storage is the result of a balance between gross sulfate reduction and sulfide oxidation (Dornblaser et al. 1994). Over a one year period, net sulfate reduction (0–9 cm, porewater sulfate method) contributed 987 and 781 mmol S m^{-2} (effluent and non-effluent sites, respectively) to the reduced S pool of each site. The mean TRS concentration (0–9 cm) was 1,800 and 1,090 mmol S m^{-2} for the effluent and non-effluent sites, respectively (Figure 6), which means that 55–72% of the TRS accumulated in a single year. Because TRS presumably has been accumulating in the sediments since the time the reservoir was filled (> 25 years), these data suggest that net sulfate reduction was lower than our estimate or that S is being shunted into storage pools other than TRS, for example the organic S pool (Urban and Brezonik 1993). Thermal-effluent site sediments have both higher net and gross sulfate reduction, as well as 4 times more total S (Table 1). Perhaps much of this total S is organic, because the yearly mean sediment TRS concentration at the thermal-effluent site was only 1.7 times higher than the non-effluent site (see Figure 6).

Although it is intuitive that high sulfate reduction rates would coincide with increased short-term sulfur storage, this was not the case in Fairfield Lake. At the non-effluent site, the period of highest TRS concentrations in the sediments (winter and early spring) were the periods of lowest sulfate reduction rates (Figure 9). As much as 99% of the sulfide formed due to sulfate reduction is ultimately oxidized or lost from the sediments (Howarth and Teal 1979), and our results suggest that maximum reduced S oxidation rates coincided with maximum sulfate reduction rates. A relationship of this nature has also been observed in salt marshes (Howarth and Teal 1979). In their study of a New England salt marsh, the highest pyrite (FeS_2) concentrations were observed in May, when sulfate reduction rates were near their seasonal low. This relationship was attributed to the growth of *Spartina alterniflora* root tips, which introduce oxygen into microzones around the roots. Lack of root growth in winter and spring prevented pyrite oxidation, and there was a slow accumulation of pyrite in spite of the seasonally low sulfate reduction rates (Howarth and Teal 1979).

There were no macrophytes at our study sites. However, bioturbation (primarily from fish and invertebrates in Fairfield Lake) could have a similar effect and also varies seasonally, with minimal bioturbation occurring in winter and at high temperatures. When water temperatures reached their maximum in summer, we observed no fish in the water column or live invertebrates in the sediments at the thermal effluent site, coupled with a large fish die-off in June (discussed below).

Sediment oxygen demand, organic C, and the respiratory quotient (RQ)

SOD measured at the non-effluent site was within the range of values reported in the literature. Rates in other freshwater, aerobic, surface sediments ranged from −13 to −81 mmol O_2 m^{-2} day^{-1} (Edberg and Hofsten 1973; Jensen and Anderson 1992; Boon and Mitchell 1995; Erickson and Auer 1998). However, the mean late-summer thermal-effluent site flux of-150.0 mmol O_2 m^{-2} day^{-1} was outside this range, and was closer to values measured in aquaculture or eutrophic marine systems (Madenjian et al. 1987; Suplee and Cotner 1996; Morrisey 2000). The thermal-effluent site had nearly twice the yearly SOD of the non-effluent site, yet the sediment organic C concentration was 1.5 times higher than that of the non-effluent site (Table 1) and both sites had similar seston C concentrations (Figure 1, Table 2). Water column primary productivity was measured at the effluent and non-effluent sites as 96.3 and 76.5 mol C m^{-2} $year^{-1}$, respectively, in a previous study (Bowling 1980). Assuming productivity and biomass are proportional, and that the sedimentation rate was similar at both sites, one would expect lower organic C in the thermal-effluent site sediments due to higher sediment respiration. Because this was

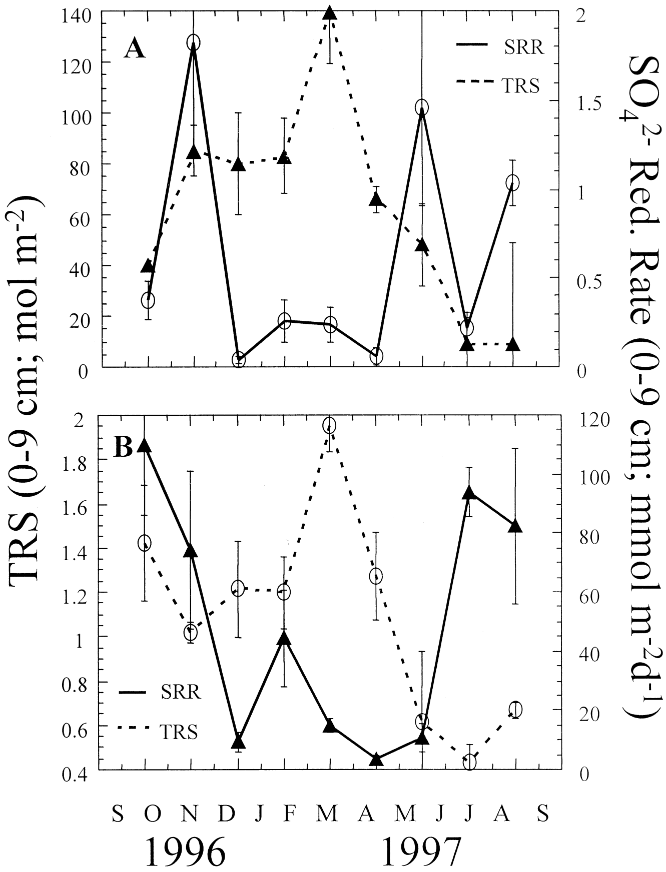

Figure 9. Integrated total reduced inorganic S (TRS) and sulfate reduction rates (SRR) in the non-thermal site sediments. A. 0–1 cm integration. B. 0–9 cm integration. Error bars are one standard error of the mean.

not the case, these data suggest that the thermal-effluent site sediments may have originally been enriched in C relative to the non-effluent site, or had higher benthic primary production rates. We have no measurements of benthic primary production, however it was probably contributing to the sediment organic-C load as algal growth was observed on the sediments of both sites in late summer.

Based on annual integrated DIC and O_2 fluxes from Fairfield Lake sediments, the RQ (CO_2/O_2 ratio) was 1.14 ± 0.2 for the thermal-effluent site and 0.78 ± 0.2 for the non-effluent site. Inorganic C fluxes can be generated by anaerobic processes such as sulfate reduction, denitrification, acetoclastic methanogenesis, and fermentation (Fenchel et al. 1998), and these processes increase the measured RQ, but only if the reduced products are not subsequently oxidized. Nonetheless, because the thermal-effluent site sediments were warmer, more reduced, and had higher sulfate reduction rates, it follows that the RQ was higher than the non-effluent site.

Decaying organic material contains a mixture of lipids, proteins, and carbohydrates, and a RQ of 0.85 is a reasonable average value for the mineralization of heterogeneous organic material (Wetzel 1983). The non-effluent site RQ (0.78) was close to this value, and suggests that the majority of sedimented organic material was respired aerobically at this site. A value considerably less than one would indicate oxygen consumption without CO_2 release, such as would occur during nitrification or sulfide oxidation in the sediments.

C, N, and P in seston and chamber fluxes

The molar ratio of C, N, and P in marine plankton, or Redfield ratio, is 106:16:1 (Redfield 1958). In this study the seston C:P ratio was consistently higher than this value. In contrast, the seston N:P ratio was usually close to Redfield ratio (Table 2). Systematic deviation from Redfield ratio is common in lake seston (Gächter and Bloesch 1985; Uehlinger and Bloesch 1987; Hecky et al. 1993). In their study of Swiss lakes, Gächter and Bloesch (1985) found that the C:P ratio of seston in near-bottom waters ranged from 64:1 to 668:1. Fairfield Lake seston was less variable annually, with a C:P ratio of 109:1 to 253:1. The mean seston C:P ratio for the effluent and non-effluent sites was 135 and 155 respectively, indicating that the seston supply ratios to the effluent and non-effluent sites were similar.

The SRP fluxes from the non-effluent site aerobic-surface sediments (maximum 64.6 μmol P m^{-2} day^{-1}) were all within the range of fluxes that have been reported for lakes (Burns and Ross 1971; Kamp-Nielsen 1975; Holdren and Armstrong 1980; Enell and Löfgren 1988; Søndergaard 1989; Jensen and Anderson 1992; Brooks and Edgington 1994; Andersen 1997). The thermal-effluent site aerobic-surface sediment P fluxes were similar to other lakes in the winter and spring. However in late summer the fluxes increased dramatically (Figure 2). In September 1997, the thermal-effluent site sediment P flux of 1.4 mmol P m^{-2} day^{-1} was as high as aerobic fluxes found in eutrophic lakes Klvind and Væng (Denmark), both of which demonstrated their peak release rates in summer or fall (Jensen and Anderson 1992).

Porewater solute concentrations and fluxes

Previous studies suggest that below 40 μM SO_4^{2-}, methanogenic bacteria are thermodynamically favored (Cook and Kelly 1992). However, the lowest concentration measured in Fairfield Lake sediments was 84.7 μM, and it was typically many times greater than this. At the non-effluent site in winter, porewater sulfate concentrations in surface sediments (0–1 cm) were nearly identical to water column concentrations. Low demand for sulfate would allow surface sediments to equilibrate with the water column, a supposition supported by the low winter sulfate reduction rates measured in the $^{35}SO_4^{2-}$-injected cores.

Overall, SRP concentrations in the porewater were similar to other eutrophic lakes, and tended to fall near the lower values (Enell and Löfgren 1988). The maximum porewater SRP concentration in Fairfield Lake (23.7 μM) was considerably lower than eutrophic lakes Trekanten, Öresjö, and Wingra, which had maximum concentrations of > 60 μM (Enell and Löfgren 1988). Solute oxidation due to insufficient removal of O_2 from the porewater equilibrators can be a problem in oligotrophic lakes (Enell and Löfgren 1988; Carignan et al. 1994), and some researchers retain their samplers in an N_2 environment for as long as 15 days prior to deployment (Warren et al. 1998). However, this problem is much less pronounced in eutrophic lakes (Carignan 1984) due to increased microbial activity and more reducing conditions, and was not likely to have been a serious problem in Fairfield Lake.

The seasonal patterns of SRP in the Fairfield Lake porewater were similar to other lakes, where the highest concentrations were observed in late summer and early fall, and the lowest concentrations in winter and early spring (Carignan 1985). Microbial activity is largely responsible for changes in surface-sediment porewater chemistry (Enell and Löfgren 1988), but variations in bioturbation may also play an important role (Shormann and Cotner 1997; Matisoff and Wang 1998). Similar to the spatial patterns observed for sulfate reduction, peak porewater SRP concentrations occurred in the upper sediments in the summer and fall, and in deeper sediments in the winter and early spring.

Temperature and SRP flux in Fairfield Lake

Overall, these data indicate that temperature was the most important factor controlling SRP flux over the range of conditions found in this study. Six regressions were run for each of the independent variables (water temperature, total reduced inorganic sulfur, and sulfate reduction rate) and water temperature produced the only significant relationships (bestfit $R^2 = 0.53$, $p = 0.017$) (Table 4). Water column pH was also examined as an independent variable, but no significant relationships were found (data not shown). Using RPR enhanced the robustness of these tests, as it helped to normalize site-specific differences associated with the magnitude of carbon loading to and rates of decomposition in the sediments. There was no correlative improvement using a multiple-regressions using the independent-variable combinations 'water temperature + sulfate reduction rate' and 'water temperature + TRS' had very low R^2 values ($\leqslant 0.25$) and were not significant ($p > 0.12$). In their examination of aerobic-surface sediment P fluxes of four Danish lakes, Jensen and Anderson (1992) found that water temperature alone explained 73% of the seasonal variability in sediment P flux. Søndergaard (1989); Kamp-Nielsen (1975) both found that sediment P fluxes (from anaerobic and aerobic surface sediments) were temperature dependent and further, that the relationship was non-linear as in this study.

Clues as to the nature of the temperature-SRP flux relationship may be found in the September thermal effluent site data. At that time, conditions were conducive for very high SRP fluxes and, based on the RPR values, it is clear that stored P was released from the sediments (Figure 3). Late summer is the peak of overall microbial metabolism, based on SOD and the DIC fluxes (Figure 1). Prior to this, in late June 1997, a massive fish die-off at the thermal effluent site occurred, an event that has been noted in past summers. Thermal effluent site waters have a fairly short residence time of nine hours when the power plant is pumping at its maximum rate of 2,800 m^3 min^{-1} (Bowling 1980), and are well mixed due to the mechanical action of the pumps. DO was never less than 144 μM (Oliphint 1977). The fish die-off was, therefore, probably a result of heat stress as water temperatures reached 40–43°C. Furthermore, thermal effluent site macroinvertebrate productivity, standing crop, and diversity, which were already low relative to cooler parts of the lake, were reduced to their seasonal lows in August and September (Oliphint 1977). Bioturbation can prevent the formation of a steep SRP gradient in the porewater of near-surface sediments by allowing oxidation of surface sediments (Fisher 1982). Oxidation of soluble ferrous compounds to insoluble ferric forms is tightly coupled to the adsorption of phosphate, and this typically occurs at or near the sediment-water interface where a redox boundary exists. This leads to the development of what has been termed an "iron curtain" (Chambers and Odum 1990). This ferric-iron layer forms a boundary to sediment P release and is more "impenetrable" when more iron is available, that is, the Fe:P ratio is high. Because microbial metabolism was at a seasonal high and bioturbation was at a seasonal low at the thermal effluent site during late summer, they may have interacted synergistically and resulted in the large sediment P-flux observed at that time.

There was likely an interaction between bioturbation, microbial metabolic rates and the Fe:P ratio of Fairfield Lake sediments. Jensen and Anderson (1992) suggested that when the sediment total Fe:P ratio (molar) is greater than 8.3 and the sediment surface is oxidized, P release is unlikely. However, other studies have revealed that lake-sediment P release was positively correlated to increasing total Fe:P ratios, and that peak P fluxes were usually noted in August and September (Phillips et al. 1994). Fairfield Lake's total Fe:P ratios (molar) were 32:1 and 61:1 for the thermal effluent and non-thermal effluent sites, respectively, and were considerably higher than those reported in the Phillips et al. (1994) study (maximum molar ratio 12:1). At the thermal effluent site during early summer (when temperatures had already reached 32 °C) bioturbation may have provided sufficient sediment mixing to maintain an oxidized or partially oxidized layer in the upper 0–4 cm, a layer which effectively adsorbed P. The layer's P-adsorbing ability was likely a function of iron oxyhydroxide formation (Morel and Herring 1993), the reactivity of the iron oxide species (Postma 1993; Mitchell and Baldwin 1998), or bacterial uptake (Gächter and Meyer 1993). As late summer approached and bioturbation had diminished, distinct, high-concentration layers of SRP formed near the sediment-water interface (Figure 7D), as has been found in other studies (Andersen 1997). Therefore, a significant deterioration of the iron curtain required only that redox should drop sufficiently to reduce the iron (Eckerrot and Pettersson 1993), which would occur around an Eh of 100 mV at Fairfield Lake's pH (Pankow 1991). High SOD driven by microbial metabolism likely provided the means for the redox drop that reduced the near-surface ferric iron, resulting in the large releases of SRP observed. This would also tend to corroborate the findings of Phillips et al. (1994), as high releases of SRP would be expected from sediments with a high total Fe:P ratio once conditions developed that could reduce the iron curtain.

The role of sulfate reduction in SRP flux

The total Fe:S ratio (molar) in Fairfield lake surface sediments was 6.4:1 and 30:1 at the thermal effluent and non-thermal effluent sites, respectively (Table 1). Carignan and Tessier (1988) found total Fe:S ratios (molar) ranged from 0.8:1 to 8:1 in a number of Canadian Shield lakes, and all of these lakes had a subsurface total S and Fe maximum between 2 and 8 cm below the sediment-water interface. They explained this as a result of H_2S from sulfate reduction sequestering iron and producing the FeS and FeS_2 subsurface peak. As the thermal effluent site total Fe:S ratio was also in this range, this suggests that S was sufficiently available to influence iron availability. This may not be as true at the non-thermal effluent site, where the Fe:S ratio was higher and more labile iron was probably available to react with P. If the sulfate reduction hypothesis were operating as expected, iron would be sequestered into TRS due to increased sulfide production, diminishing iron otherwise available for P binding. As a result, a positive correlation would be anticipated between TRS concentration (independent variable) and SRP flux (Hasler and Einsele 1948; Caraco et al. 1989). During the course of this study, a wide variation in TRS in near-surface sediments was observed; at the thermal effluent site, this variation was nearly 100% over the course of the year (Figure 6). There appears to have been sufficient variability in TRS to affect changes in SRP flux had TRS been a major factor in regulating it. However, no significant relationship between TRS and SRP flux was found. As the Fe:S ratio was fairly low at the thermal effluent site, S had a greater potential to regulate Fe availability there than at the non-thermal site, and one might have had a higher expectation that a significant relationship would be found between SRP flux and TRS. However, this again was not the case (Table 4). It would appear that there are other more significant factors controlling SRP flux such as microbial metabolism and bioturbation, both of which are influenced by temperature.

A poor relationship between sediment P flux and FeS formation was also found by Caraco et al. (1993). In an evaluation of the sulfate reduction hypothesis, the authors found that sulfate reduction was not correlated to Fe accumulation in lake hypolimnetic waters, contradicting the notion that FeS precipitation would sequester Fe and decrease its concentration. They indicated that the relationship between sulfate reduction and Fe concentration is complex and could result in either increased or decreased Fe accumulation. They did find that sulfate reduction was moderately correlated ($r^2 = 0.40$) to P accumulation in hypolimnetic waters, and weakly correlated ($r^2 = 0.18$) to RPR. P release *was* correlated to sulfate reduction, but apparently not for the reason (FeS formation) originally suggested by Hasler and Einsele (1948). Caraco et al. (1993) suggested that P may be less efficiently bound to sediments in low sulfate systems not because of FeS formation but rather due to elevated pH, bacterial Fe(III) reduction, or release of bacterial P from polyphosphate pools; the later two explanations certainly lend support to the correlation between temperature and RPR of this study.

Overall, we observed significantly greater P release from sediments that had a high mean annual temperature. Differences were most pronounced in late summer to early fall when the water temperatures at the thermal effluent site were greater than 32 °C. The high summer P-fluxes at the thermal effluent site occurred even though the water column remained aerobic, and it may have been a consequence of lowered redox potential in the near-surface sediments. This conjecture was supported by higher RQs at the effluent site, indicative of anaerobic metabolism. Higher P release rates at the thermal effluent site than the non-effluent site were also associated with increased porewater SOD and DIC fluxes than at the non-effluent site. Despite higher inorganic P fluxes at the thermal effluent site, the littoral sediments at both sites were a net sink for P throughout the year except during a period of extremely high temperatures at the thermal effluent site. On an annual basis, the thermal effluent site retained 65%, and the non-effluent site retained 92% of its annual P load.

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