UNC-WRRI-93-275

SEDIMENT-WATER PHOSPHATE EXCHANGE IN THE NEUSE RIVER, NORTH CAROLINA

by
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The research on which this report is based was financed in part by the United States Department of the Interior, Geological Survey, through the N.C. Water Resources Research Institute.

Agreement No. 14-08-0001-G1580
USGS Project No. 03 (FY 89)
WRRI Project No. 70096

ACKNOWLEDGEMENTS

Successful completion of this work involved a large number of individuals. Thanks are due to B. King, N. Young, G. Lackey, R. Willis, S. Fin, A. Agbodjan, and D. Melton, for assistance in the field and laboratory, to J. Ledwin, M. Daniel, and K. Kinchloe for additional field assistance, to D. Daniel for the mapwork, and to M. Hollingsworth for assistance in preparation of the manuscript.

Special thanks are due to Dr. R. R. Christian for the many stimulating discussions which went into the formulation of this project, and for his review and valuable comments on the manuscript.

This work relied heavily in techniques developed through research funded by University of North Carolina Sea Grant Project NA86AA-D-SG046 to W. M. Rizzo and R. R. Christian. Also, the data presented in this report for Cowpen Landing was collected through funding provided by this project.

ABSTRACT

Experiments were conducted to determine the conditions under which sediments of a freshwater portion of the Neuse River (North Carolina) release phosphorous and the conditions under which they take up phosphorus; the extent to which benthic microalgae may mediate the uptake and release of filterable reactive phosphorous (FRP) by sediments; and if the mediating effects of benthic microalgae are influenced by the concentration of FRP in the water column. Exchanges of FRP and other materials between sediments and the water column were examined using sediment core incubation and microcosm techniques. Sediment cores with water columns containing ambient concentrations of FRP (1.98 to 9.65 μM) and sediment cores with water columns containing experimentally altered concentrations of FRP (2 μM, 5 μM, and 10 μM) were incubated under light and dark conditions, and material exchanges between sediment and water column were measured. Material exchanges over longer periods were measured in microcosms containing ambient and manipulated concentrations of FRP. Observations of incubated cores showed that under ambient concentrations, sediments were consistently sources of FRP to the water column in both light and dark. However, releases in light incubated cores were only 34-61% of releases in dark incubated cores. Examination of cores with manipulated FRP concentrations showed that as concentrations increased, release of FRP by sediments decreased and at the highest concentration, sediments took up FRP rather than releasing it. Results of microcosm experiments support the results of core experiments. Results indicate that benthic microalgae play a role in the source/sink function of sediments in this portion of the Neuse River; that at ambient FRP concentrations below 4 μM, sediments are sources of phosphorus to the water column; and that at ambient FRP concentrations above 6 μM, sediments become sinks for phosphorus. However, observations of hydrological and other physical conditions in this portion of the Neuse during the period when core samples and sediment samples for microcosms were taken indicate that the benthic microalgae community was not well developed. These observations suggest that this study may underestimate the influence of benthic microalgae on sediment uptake/release of FRP and that under more normal flow conditions, Neuse River sediments may function more frequently as FRP sinks.

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SUMMARY AND CONCLUSIONS

An earlier study (Rizzo and Christian, unpublished data) at a site on the lower Neuse River between March 1987 and July 1989 showed that river sediments consistently removed filterable reactive phosphorous during the summer when water column FRP concentration exceeded ≈ 5 μM but released FRP during winter when concentrations fell below 5 μM. These findings suggested that river sediments could become sources of internal FRP loading to the water column if management efforts are successful in reducing external loading to the Neuse and lowering FRP concentrations. One goal of this study was to determine the conditions, including FRP concentration, under which sediments act as source or sink for phosphorous.

Recent lake studies have established that microalgae present at the sediment-water interface can significantly mediate phosphorus dynamics through active uptake and an uptake/release mechanism that affects oxic/anoxic conditions. A second goal of this study was to determine the degree to which benthic microalgae may influence the uptake and release of FRP by Neuse River sediments and whether this influence is affected by concentrations of FRP in the water column.

Sediment core incubation experiments were conducted to establish short-term rates of both heterotrophically mediated and microalgae-mediated exchange (flux) of FRP between sediments and the water column under a range of FRP concentrations. Cores were taken from three sites on the lower Neuse River. As cores were taken, water and sediment samples were also taken for water column and sediment characterization, and hydrologic and other physical conditions were noted. One set of cores was incubated with water column concentrations of FRP corresponding to ambient FRP concentrations at sampling sites when samples were taken (1.98 to 9.65 μM). Another set of cores was incubated with manipulated FRP concentrations of 2, 5, and 10 μM. To study microalgal effects in sediments, some cores from each set were incubated under illumination. To study effects of heterotrophic metabolism sediments, some cores from each set were incubated in darkness.

Most cores with FRP concentrations corresponding to ambient concentrations released FRP under both light and dark conditions. However, light-incubated cores generally released FRP at lower rates than dark-incubated cores or took up FRP. Flux rates showed a concentration dependence, with FRP being either taken up or released at very low rates when FRP concentrations exceeded 6.50 μM and no uptake occurring at concentrations below 3.80 μM. Microcosm experiments were conducted to establish the effects of FRP concentration on uptake/release activity of sediments over a period of days. Two experiments involving four microcosms each were conducted. Each microcosm contained 6 cm of sandy sediment typical of the study sites which had been allowed to equilibrate with ambient river water in semi-darkness for 4 days.

In the first experiment, microcosms were drained, one was refilled with filtered river water and the other three were refilled with filtered river water plus solutions to achieve concentrations of 10 μM NH_4-N and 30 μM NO_3-NO_2-N and FRP concentrations of 2.42, 5.15 and 10.49 μM. Over a 14-day period, numerous parameters were measured, with FRP being measured daily and NH_4-N and NO_3-NO_2-N being measured at various intervals. In the three microcosms with manipulated concentrations of FRP, considerable day-to-day fluctuations in FRP concentration were noted, but at day 13 all had reached similar FRP concentrations (3.95 to 5.53 μM). This response indicated that at a water column concentration of about 4 - 5 μM sediments begin taking up rather than releasing FRP. On the 14th day of the experiment, FRP concentrations increased and oxygen decreased in these microcosms, suggesting a burst of heterotrophic activity which may have been caused by a hatch of gastropods. Initial and final FRP concentrations in the microcosm with an ambient FRP concentration were similar, but day-to-day concentrations fluctuated considerably. In this microcosm, total carbon (TC) concentration increased, oxygen decreased, and total nitrogen (TN) was unchanged, while in the microcosms with experimental FRP concentrations, TC and TN declined and oxygen changed little. These results suggest that the benthic communities in the microcosms with experimental FRP concentrations were greatly diminished, and, since the ambient microcosm received two river water replenishments rich in dissolved inorganic nitrogen (DIN), also suggest that nitrogen limitation may have caused the decline in benthic microalgae in the experimental microcosms.

In the second microcosm experiment lasting 11 days, changes in water column FRP were examined under initial conditions of low to undetectable concentrations of DIN. Nitrogen limitation reduced the daily fluctuations in FRP observed in the first experiment, allowing regression analysis to determine the FRP concentration at which the source-sink switch occurs. Results suggest a release/uptake switch at between 3.74 and 4.38 μM, in good agreement with core studies and the first microcosm experiment. Rates of release calculated from results of this experiment indicate that while Neuse River sediments may be a long-term internal source of phosphorus, the internal loading will not be high enough to obscure real gains in water quality.

During the study period, river flow was unusually high. The unusually high discharge produced conditions—such as greater depth, reduced nutrient concentrations, turbidity, and bottom scouring—not conducive to development of benthic microalgae communities. Indeed, chl. a concentrations were very low during most of the study. The reduction of benthic microalgal communities in sediment samples was problematic for interpretation of results of the light-dark incubation experiments. It is possible that during periods of normal flow benthic microalgae communities are better developed and their ability to mediate the dynamics of sediment-water column FRP exchange is greater. Under these conditions, it would be expected that the role of sediments as phosphorous sinks would be enhanced.

INTRODUCTION

The Phosphorus Cycle in Lake Sediments

Sediments are important in the phosphorus cycle of aquatic ecosystems because they can store phosphorus for a period of time, then release it to the water column, making it bioavailable. Most knowledge of how the sediment-water phosphorus exchange in fresh waters occurs has come from lake studies.

The classic model of the control of FRP exchange between sediments and the water column was elucidated fifty years ago (Einsele, 1936; Einsele and Vetter, 1938; Mortimer, 1941; 1942). In this model, much of the inorganic phosphate in oxic sediments is associated with iron (Fe^{+3}) in FeOOH-PO_4 complexes. With the onset of hypoxic/anoxic conditions and lower reduction potential (Eh), this solid phase is rapidly dissolved due to reduction of Fe^{+3} to Fe^{+2}, releasing ortho-phosphate (PO_4). PO_4 diffuses down its concentration gradient toward the sediment surface. At a higher Eh, either in surface sediments or the water column, the PO_4 may again form FeOOH-PO_4 complexes. However, if the PO_4 enters the water column it is also available for biological uptake. Deeper in the sediments (> 2 to ≈ 10 cm), phosphorus cycling may be geochemically controlled by iron/aluminum-PO_4 adsorption/desorption processes in response to changes in physical-chemical controls such as changes in interstitial concentrations of FRP, Eh, or pH (Sondergaard et al., 1990).

In the classic model, organisms contribute to the exchange only indirectly by consuming oxygen during decomposition of organic matter thereby creating conditions for reduction of Fe^{+3} (Einsele, 1936; Einsele and Vetter, 1938; Mortimer, 1941; 1942). However, the classic model for phosphorous exchange across the sediment-water interface has recently been undergoing revision, with evidence that microorganisms that respond to redox potential and nutrient concentrations play a direct and more significant role in the uptake and release of phosphorous (Gachter et al., 1988).

Thus, it now appears that net FRP exchanges can be dominated by largely biological events at or near the sediment-water interface (Raaphorst and Brinkman, 1984; Sondergaard et al., 1990) or by largely physical-chemical events at greater depths (Sondergaard, 1989). Both types of processes occur simultaneously, and may act either antagonistically or synergistically in affecting exchanges. An example of the difficulty in ascribing biological or physical-chemical mechanisms to observed sediment-water exchanges is demonstrated by a recent study of a Swiss lake (Gachter et al., 1988). Changes in bacterial metabolism resulted in high rates of FRP release with the onset of anoxic conditions. Thus, the well-known phenomenon of FRP release during anoxia could result either from a physiological mechanism (Gachter et al., 1988) and/or from the classical physical chemical mechanism (Einsele, 1936; Einsele and Vetter, 1938; Mortimer, 1941; 1942). In the Swiss study, restoration of oxic conditions induced rapid bacterial FRP uptake, in some cases depleting water column concentrations within 2 hours (Gachter et al., 1988), again paralleling the physical-chemical model.

In addition to heterotrophic metabolism, there are other biological influences on sediment-water FRP exchange. Benthic microalgae can reduce FRP release by taking up mineralized FRP before it can leave the sediments or remove FRP directly from the water column (Carlton and Wetzel, 1988; Vymazal, 1988; Forsberg, 1989). Burrowing and bioturbation can increase contact between overlying water and deeper nutrient-rich sediments enhancing diffusive releases to the water column (Aller, 1983). Sediment resuspension by bioturbation can also increase FRP release (Officer and Lynch, 1989). Lastly, aerobic respiration reduces the thickness of the surface oxic layer, indirectly lowering the adsorptive capacity of the sediments.

The Phosphorous Cycle in River Sediments

Phosphorus cycling in river ecosystems differs from cycling in lakes because in rivers, flow shortens water residence time, and limits sediment exchange with a given water mass. In addition, river sediments may be flushed much more quickly than lake sediments. During very high flows the entire benthic habitat can be removed by scouring. Scouring events occur with unpredictable frequency and severity, but are important mechanisms for periodic "resetting" of benthic communities by allowing secondary succession (Power et al., 1988). High flows are also accompanied by greater water depths and increased turbidity. The latter two factors can interact to greatly inhibit the development of benthic autotrophic communities by eliminating or reducing light penetration to the sediments. Water flow and benthic microalgae photosynthesis also favor maintenance of oxic conditions in the surficial sediments promoting FRP storage in the sediments compared to stratified lentic or estuarine ecosystems which are more prone to sediment and bottom water anoxia.

Nutrient Concentrations and Algal Bloom Formation in the Neuse River

The Neuse River watershed drains approximately 5,700 square miles or 12% of the land area of North Carolina and contains 14% of the state's population (Harned, 1980). Most of the basin's land use is forest or agriculture. Nutrient concentrations in the freshwater portion of the Neuse River have long been elevated and have been linked to nuisance blooms of the cyanobacterium *Microcystis aeruginosa* (Paerl, 1983; 1987; Christian et al., 1986; 1988). These blooms have had detrimental effects on the taste and odor of water and have been linked to more serious impacts such as low dissolved oxygen and fish kills (Christian et al., 1986; 1988). About 70% of the nutrient inputs are from non-point sources (Stanley, 1988). Of the remaining 30% of the external nutrient loading, approximately 88% comes from 16 municipal and industrial point sources (Harned, 1980).

The "seed" for algal blooms is ubiquitous in river sediments (Paerl, 1987). High nutrient concentrations and low flows are associated with bloom formation (Paerl, 1983; 1987; Christian et al., 1986). Thus, blooms tend to occur during seasons and in areas of lowest flow. In the Neuse River these conditions are most frequently met in late summer and fall and between New Bern and Goldsboro. Recently the North Carolina Division of Environmental Management (NRCD, 1987) recommended nutrient loading reductions of 30% for nitrogen and 50% for phosphorus in order to stem the formation of M. aeruginosa blooms. This goal is to be achieved through implementation of agricultural best management practices and reduction of point source effluents (NRCD, 1987). Part of the latter effort included implementation of a ban on phosphate detergents, which began in January 1988.

Paerl (1987) determined that blooms are more often nitrogen limited than phosphorus limited during summer. During his study, phosphate concentrations always exceeded M. aeruginosa growth requirements, while dissolved inorganic nitrogen (DIN), principally nitrate, concentrations were generally in excess of requirements during high flow periods. Despite the greater potential for DIN limitation, it is often easier to reduce FRP, primarily ortho-phosphate, loading than nitrogen loading. To this end, NRCD (1987) has set a target for effluents of $\leq$ 1mg P l^{-1} (64.5 μM). Numerous studies have reported that internal loading from sediments in lakes with a long history of eutrophication have maintained the eutrophic status of these lakes long after external loadings have been eliminated or reduced (Sondergaard, 1987; 1989; Connor and Martin, 1989;

Istanovics, 1988; Levine and Schindler, 1989; Uhlmann and Guderitz, 1988; Forsberg, 1989; Marsden, 1989; Redshaw et al., 1990). Thus, the question arose: Will internal phosphorous loading from Neuse River sediments prolong ecosystem recovery time and obscure real gains in external loading reductions?

Research Problem

Sediment-water nutrient exchanges were studied at Cowpen Landing in the lower Neuse River between March 1987 - July 1989 (Figure 1). The first year of data showed that these sediments consistently removed FRP during summer when water column concentrations exceeded ≈ 5 μM, and released FRP during winter when concentrations fell below 5 μM. The data from Cowpen Landing suggested that the river sediments would become sources of internal FRP loading to the water column if low water column concentrations were maintained.

The first goal of this study was to determine the conditions under which Neuse River sediments act as sources or sinks of FRP to the water column, taking into account exchanges controlled by both heterotrophic and autotrophic processes. The second goal was to determine the effect of differing FRP concentrations on the source/sink role of sediments and to assess any changes in the relative importance of autotrophic vs. heterotrophic controls of FRP exchange.

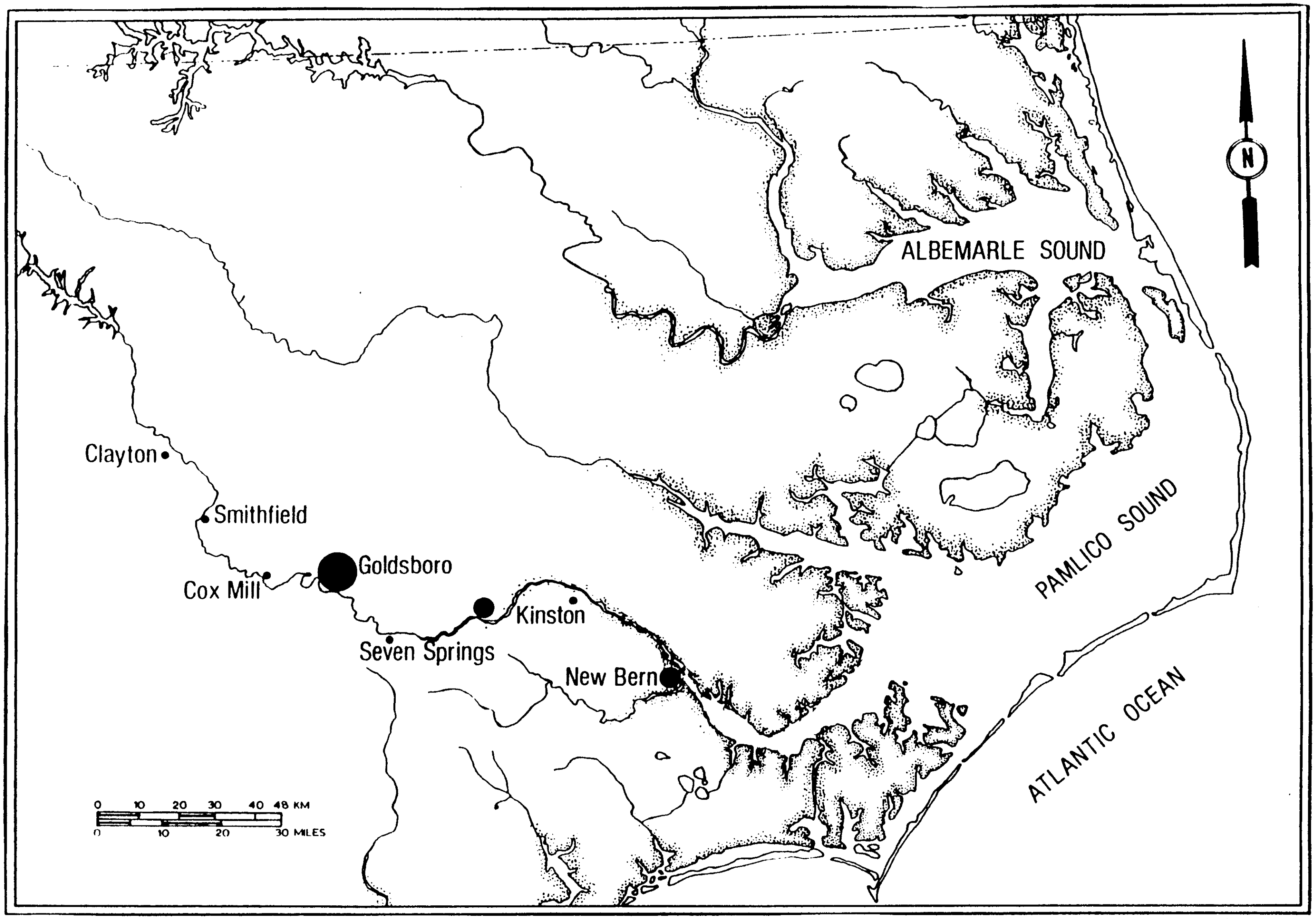

Figure 1. Location of study sites.

MATERIALS AND METHODS

Field Procedures

Study sites were chosen at Cox Mill (#1), approximately 15 km southeast of Smithfield); Seven Springs (#2) and Kinston (#3) (Figure 1). The sites historically represent a decreasing downstream gradient in FRP enrichment (Stanley, 1983). At each site, four to thirty-two sediment cores were collected for experiments. The experiments involved incubating the cores under light or dark conditions with either ambient or experimentally controlled concentrations of FRP in the overlying water, then analyzing the water for FRP concentration after 4 h.

Initially, clear plexiglass corers were used for collecting sediments for incubations in the light, and PVC corers were used for dark-incubations (both ≈ 3.5 cm I.D.). Later, clear plexiglass corers double-wrapped in aluminum foil were used for dark incubations. The clear core tubes allowed easier inspection of any potential disturbances during collection and aided the detection of macrofauna. Cores were either taken by hand or collected from a boat using a 1.25-meter (m) galvanized pipe threaded onto a brass fitting to achieve the appropriate connections to the pipe and to our core samplers. Water flowed through a one-way valve into the pipe as the apparatus was lowered into the water. As the device was raised, hydrostatic pressure against the now closed one-way valve provided the seal allowing the core to be removed from the sediment. The sediment cores with their overlying water were immediately stoppered at both ends before removing the core from the water.

Core samples were placed in coolers filled with water and maintained at ambient temperature. Ambient surface water was collected in Nalgene bottles and also placed in the coolers. The time between sampling and return to the laboratory was less than 3 hours. On each sampling date, profiles of photosynthetically active radiation (PAR) were determined at 0.2 m intervals (LiCor Model 185A with spherical sensor), and data on temperature, conductivity (YSI model 33) and dissolved oxygen (YSI model 57) were collected at surface and bottom depths.

General Laboratory Methods

In the laboratory, the ambient river water was filtered twice through 1.0-μm glass-fiber filters (Whatman 934-AH) and twice through 0.45-μm membrane filters (Gelman GN-6) to eliminate interference from water column metabolism. The water overlying the cores was quickly (< 1 minute) withdrawn by syringe and replaced with the filtered water.

Four to six cores were randomly assigned to dark or light treatments. The light treatment selected was sufficient to saturate photosynthesis of Neuse River Estuary benthic microalgae ($\approx$ 360 μE m^{-2} s^{-1}; G. Lackey, unpublished data). Light was supplied by eight General Electric cool-white (F40CW) fluorescent lights alternating with eight wide-spectrum (F40PL/AQ) lights. Light-incubated cores were covered with a layer of mineral oil about 5 mm thick to provide an airtight seal while allowing light to reach the sediment. All light-incubated cores were wrapped with black rubber at the level of the sediment-water interface to prevent light exposure to the sides of the cores.

Incubation intervals ranged from 4-6 h. At the end of the incubation period the overlying oil was carefully removed with a plastic syringe and all the overlying water was withdrawn using a second 60-cc plastic syringe. A 10-cc subsample was withdrawn with a glass syringe and fixed for oxygen determination using the azide modification of the Winkler dissolved oxygen method scaled to the appropriate sample volume (Rizzo and Wetzel, 1985). Two 12-ml subsamples were withdrawn immediately and fixed for determination of (NH_4) concentration (Solorzano, 1969), and two samples for FRP (Environmental Protection Agency, 1979). The remaining water was stored in a polypropylene bottle and frozen for later automated determination of NO_3 + NO_2 (Scientific Instruments Corporation, 1981). FRP exchange rates were calculated from changes between sample concentration taken just prior to filling the cores, and post-incubation concentration. Positive values denote an increase in FRP concentration in the incubation water, and therefore, FRP release from the sediments.

On the day following the experiment, the top centimeter of sediment was removed from each core. Sediment samples from the light-incubated cores were taken for chlorophyll _a_ (chl. _a_) determination following procedures given in Rizzo (1990). Chl. _a_ concentrations, corrected for pheophytin, were calculated using the equations of Lorenzen (1967). A 5-g subsample was taken from each dark-incubated core and frozen for later determination of grain size (U.S. Geological Survey, 1977). The remaining sediment was dried to a constant weight at 70°C. After drying, approximately 10 mg (fine sediments) or 20 mg (sandy sediments) subsamples were removed and stored in glass vials for later determinations of total carbon (TC) and total nitrogen (TN) (Model 440 CEC elemental analyzer) following procedures given by Leeman Labs (1990). The remaining sediment was weighed, combusted for 4 h at 500°C, then re-weighed for determination of ash-free total organic matter (TOM) content. The results are shown in Table 1.

Experimental Manipulations of FRP Concentrations

Cores used in experimental manipulations of FRP concentrations were handled as described above except for the composition of the incubation water. Cores were randomly assigned to light- and FRP-concentration treatments giving four light-incubated and four dark-incubated replicates for each concentration treatment. Most experiments used target concentrations of 2 μM, a FRP treatment typical of winter minimum concentrations; 5 μM, the concentrations at which Cowpen Landing sediments appeared to reverse their role as source/sink and the concentration generally closest to ambient; and a high FRP treatment $\geq$ 10 μM. Additional experiments were occasionally carried out using different FRP treatment concentrations.

Table 1. Edaphic variables determined for the study sites. Total organic matter (TOM) values are based on ash-free dry weight, total carbon (TC) and total nitrogen (TN) values on dry weight. Sites: K = Kinston, S = Seven Springs and C = Cox Mill. Mean ± standard deviation, for three or more replicates.

Date and Site	% Organics	% TC	% TN	Chl. a mg m^{-2}
16 Oct 88				
K	0.40 ± 0.20	0.03 ± 0.01	0.004 ± 0.005	
S	0.72 0.35	0.23 0.13	0.020 0.010	
C	0.55 0.32	0.07 0.05	0.006 0.004	
15 Nov 88				
K	2.08 ± 1.21	0.24 ± 0.11	0.030 ± 0.020	
S	1.33 2.69	0.16 0.12	0.010 0.006	
C	0.63 0.31	0.07 0.02	0.010 0.000	
27 Dec 88				
K	1.90 ± 0.93	1.27 ± 0.90	0.070 ± 0.050	1.97 ± 1.32
29 Dec 88				
C		0.04 ± 0.00	< 0.003	1.58 ± 2.74
03 Jan 89				
S	2.43 ± 1.43	3.38	0.23	36.7 ± 19.2
19 Jan 89				
K	2.01 ± 0.99	0.40 ± 0.18	0.030 ± 0.020	30.3 ± 8.91
24 Jan 89				
C	0.61 ± 0.42	0.13 ± 0.10	0.005 ± 0.006	11.1 ± 14.5
26 Jan 89				
S	0.42 ± 0.14	0.05 ± 0.01	0.005 ± 0.005	
25 May 89				
mud-S		1.95 ± 0.95	0.120 ± 0.060	19.1 ± 21.6
sand-S		0.23 0.08	0.008 0.009	
01 Jun 89				
K	2.57 ± 1.14	0.52 ± 0.36	0.040 ± 0.020	6.86 ± 10.3
15 Jun 89				
C		0.08 ± 0.04	0.003 ± 0.004	< 1.00
11 Jul 89				
C	0.54 ± 0.43			3.17 ± 7.21
13 Jul 89				
K	1.91 ± 0.56	0.38 ± 0.30	0.030 ± 0.020	2.50 ± 3.80

Table 1. Continued.

Date and Site		% Organics	% TC	% TN	Chl. a mg m^{-2}
01 Aug 89					
	K	0.50 ± 0.28			1.51 ± 3.22
08 Aug 89					
	C	0.30 ± 0.40	0.04 ± 0.01	0.003 ± 0.005	< 1.00
14 Sep 89					
	S	0.17			
	C	0.88 ± 0.72	0.07 ± 0.05	0.006 ± 0.003	
21 Sep 89					
	K	2.18 ± 1.04	0.96 ± 0.59	0.070 ± 0.040	
19 Oct 89					
	C	0.99 ± 0.86	0.13 ± 0.07	0.010 ± 0.005	
31 Oct 89					
	K	5.91 ± 7.58	1.48 ± 1.48	0.100 ± 0.040	
Mean	K	2.16 ± 1.59	0.66 ± 0.52	0.050 ± 0.030	8.64 ± 12.3
	S	1.01 0.90	1.16 1.47	0.080 0.100	
	C	0.66 0.21	0.08 0.03	< 0.010	< 5.29

To achieve the desired treatment concentrations, the FRP concentration of the ambient unfiltered water was first determined immediately after return to the laboratory. Based on this concentration, the appropriate volume of filtered river water was diluted with a major ion solution to yield 5 liters (l) of stock solution with a FRP concentration of 1 μM. The composition of the ion solution is that given by Paerl (1987): de-ionized water amended with micronutrients (Si, Ca, Mg, Na, K, Cl, and SO_4). The 1 μM stock solution was amended with NH_4Cl and KNO_3 to achieve typical river concentrations of 10 μM NH_4-N and 50 μM NO_3-N, respectively. The experimental FRP concentrations were prepared by adding appropriate amounts of KH_2PO_4.

Microcosm Studies

Microcosms were used to study the effects of FRP concentration on the source/sink role of sediments over longer periods (days). The microcosms were fabricated from pine and coated with white enamel paint. Partitions created four microcosms, each 20 x 120 x 12 cm. The seams were sealed with silicone-based aquarium sealer. Each section was individually filled with water to test for leakage before the experiments began. Four variable speed aquarium pumps constantly circulated the water in each section. Water was pumped from a 3-l reservoir through tubing which ran under the sediment for the length of each section. Water from the pump flowed over a baffle of aluminum foil to prevent disturbance of the sediment surface.

Sandy sediment typical of the study sites was collected at Cowpen Landing on 10 August 1989, from the surface 10 cm. This layer encompasses the approximate depth of sediment involved in sediment-water FRP exchanges (Sondergaard, 1989). The sediment was immediately taken to the laboratory and placed in the microcosms to a depth of 6 cm. While existing physico-chemical gradients were destroyed during collection, each microcosm contained typical ambient pools of phosphorus. After adding the sediment the microcosms were filled with ambient river water and allowed to equilibrate at room temperature (21 ± 2°C) for 4 days before beginning the experiments. The microcosms were covered with a plywood sheet except for about 1 hour each day during sampling. The cover did not provide a complete seal, allowing some room light to reach the sediments.

During the experiments, the pH and dissolved oxygen concentration of the water in each reservoir was monitored daily. Temperature was monitored daily in one microcosm. Water samples for nutrient analysis were collected at three locations in each microcosm (20, 60 and 100-cm from the pump). During the first experiment, cores were taken for analysis of chl. a, TC, and TN on 15 August and 28 August 1989. FRP was sampled daily while NH_4 and $NO_3 + NO_2$-N were sampled at various intervals of the experiment. Two experiments were conducted:

Experiment 1. August 14-28, 1989. On 14 August, one randomly chosen microcosm (microcosm A) was drained and re-filled with ambient, filtered river water (also collected August 10, 1989). The other three microcosms were drained and re-filled with filtered river water plus ion solution. These three microcosms were amended with KNO_3 and NH_4Cl to achieve initial concentrations of 10 μM NH_4-N and 30 μM $NO_3 + NO_2$-N. FRP treatments were achieved by addition of KH_2PO_4. NH_4 and $NO_3 + NO_2$-N determinations were made at 2-4 day intervals. On 18 August and 22 August, water was added to the microcosm reservoirs to replace evaporative losses. Filtered river water (containing ambient FRP and DIN) was added to microcosm A, and ion solution (with no additional DIN) to the other microcosms after adjusting the FRP concentrations to those determined for each microcosm in the morning sample.

Experiment 2. September 12-23, 1989. Experiment 2 examined water column FRP concentration changes under conditions of either high or low initial FRP concentration, but under initial conditions of low to undetectable concentrations of DIN (NH_4 = < 1-μM and undetectable NO_3 + NO_2). All microcosms were drained and re-filled with de-ionized water (no micronutrients). Microcosms A and D were amended with sufficient KH_2PO_4 to achieve an initial FRP concentration of 38-μM (reflecting historical high concentrations). Initial concentrations in microcosms B and C were < 3-μM (reflecting observed minimum concentrations).

Statistical Methods

Cores found to contain the bivalve (_Corbicula fluminea_) after conclusion of an experiment were excluded from data analysis. Data were heteroscedastic and not normally distributed. Treatment effects were examined using non-parametric tests. Mann-Whitney tests were used to compare light effects and Kruskal-Wallis tests for FRP concentration effects (Wilkinson, 1986). All results are considered significant at $P \leq 0.05$.

RESULTS AND DISCUSSION

Water Column Characteristics of the Study Sites

Virtually the entire study period was characterized by unusually high river flow. The high river flow affected other important factors such as water depth, turbidity, light penetration, grain size, and water column FRP concentrations (Tables 1, 2 and 3). Figure 2 shows the daily discharge at Kinston during the study period compared to the long-term average daily discharge by month for the period 1931-1988 (U.S. Geological Survey, 1931-1988). Discharge exceeded the long-term average in November 1988 and from late February through late August 1989 by 191-440% of the long-term mean. Mean discharges less than 50% of the long-term mean occurred from December 1988 through early February 1989. Severe flooding prevented sampling from late February 1989 to late May 1989.

River depth increases with increasing discharge, and the magnitude of the effect increases with distance upstream from Kinston where the river narrows and water velocities increase (Christian et al., 1986). Light attenuation through a deeper water column could have limited growth of benthic microalgae. For example, at Kinston water depth averaged 1.6 m during the high discharges (mean = 216% of the long-term mean) between June and August. During near normal discharges in September (16% below the long-term mean) the depth was 0.5 m. At 1.6 m, PAR is below levels saturating to benthic microalgae ($\approx$ 250 $\mu E\ m^{-2}\ s^{-1}$) in the Neuse River Estuary for the entire photoperiod. Although

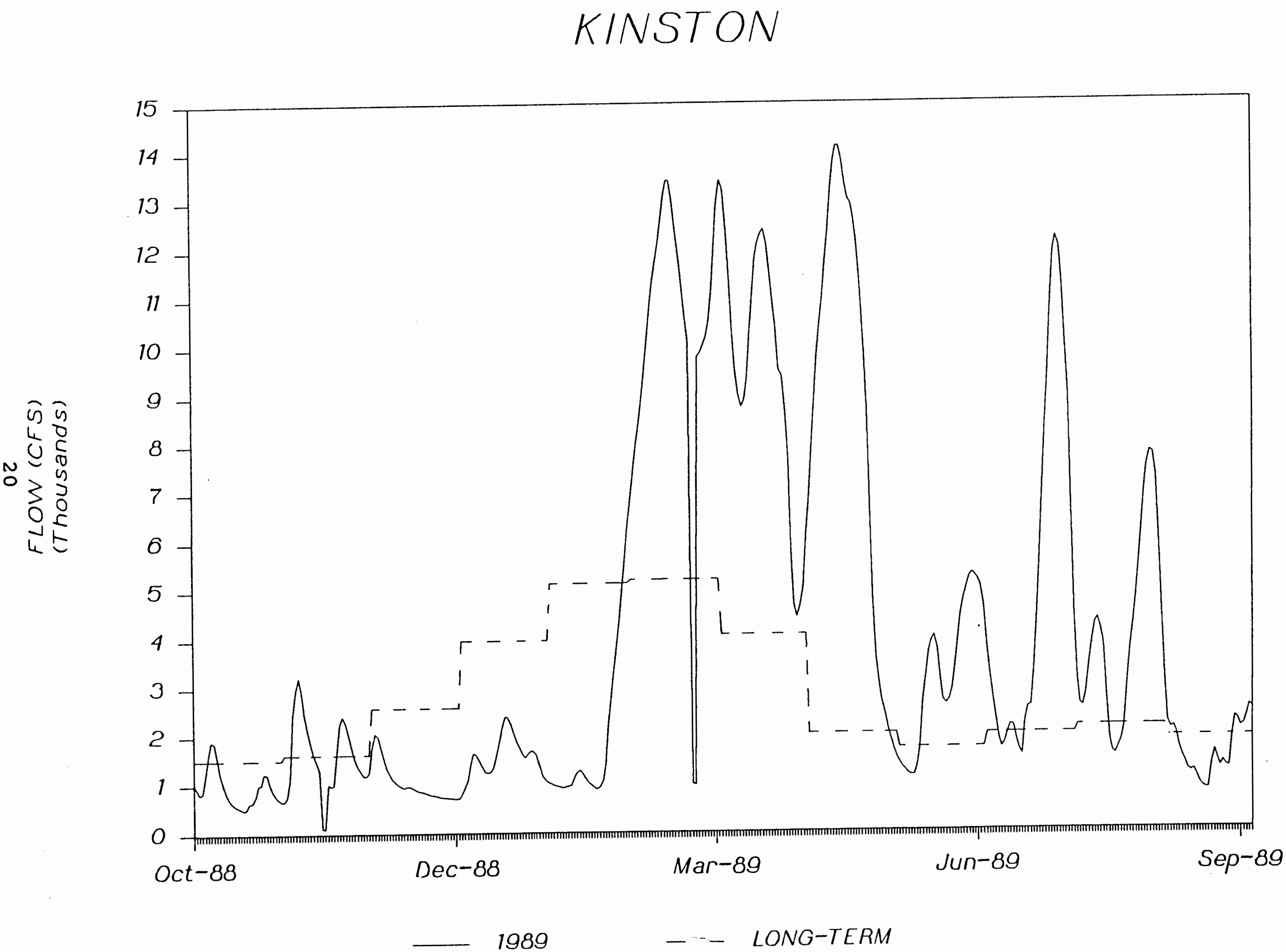

Figure 2. Discharge during the study period compared to long-term discharge.

measured water depths varied greatly among study dates (four-fold to eight-fold), actual variation in depth at the sites was much greater. At Seven Springs the difference in water depth between the spring flood stage and the late May sample was estimated to be over 5 m.

Poor light transmission to the benthos because of the increased water depth may have been exacerbated by the turbidity increases which accompany high discharges. Light penetration in the Neuse River is typically poor due to high concentrations of both particulates and highly-colored dissolved humic substances. The vertical PAR attenuation coefficients (Table 2) indicate rapid light reduction and are similar to values reported by Christian et al. (1986). Values generally exceeded 2.5 m^{-1} but were markedly improved during the low-flow September sample.

Large areas of the benthos are affected by fluctuating water depth since water depth varies little over the river cross-sections of the study sites. Cross-sectional depth profiles were determined at Cox Mill and Seven Springs by wading across the river during low flow periods and measuring depths at 1 m intervals. The depth variation at these stations was < 10 cm except for slightly deeper troughs (50 cm deeper) extending 1-2 m from the shoreline on both sides of the river. These deeper areas were estimated to constitute < 5% of the cross sectional area. The Kinston site also had a deeper trough (75 cm deeper) within 2 m of the south shoreline and also shoaled rapidly toward

Table 2. Physical and chemical characteristics of the water column at the study sites. NH_4 = ammonium, FRP = filterable reactive phosphorus, NO_3 + NO_2 = nitrate + nitrite.

Date	Depth (m)	Temp. (°C)	pH	Atten. Coeff. (m^{-1})	NH_4 (μM)	FRP (μM)	NO_3 + NO_2 (μM)
				KINSTON			
16 Oct 88	1.25	14.0			6.91	2.16	75.78
15 Nov 88	0.80	14.0		3.78	9.37	2.84	55.95
27 Dec 88	0.90	8.5			7.96	4.40	93.00
19 Jan 89	1.00	7.0			7.81	3.88	52.74
01 Jun 89	1.10	24.5	7.4	2.08	9.81	3.77	
13 Jul 89	0.80	29.0		3.96	6.11	9.21	56.07
01 Aug 89	3.00	26.0			7.29	5.21	50.70
17 Aug 89	1.50	26.0		2.35	6.40	3.72	
21 Sep 89	0.50	25.5	7.5	3.47	4.57	4.62	67.71
31 Oct 89	1.25	17.0	6.7		6.55	2.23	42.96
Mean	1.21		7.2	3.13	7.28	4.20	61.86
				Seven Springs			
16 Oct 88	0.50	14.0			9.30	4.87	88.58
15 Nov 88	0.75	13.0		3.50	14.02	9.65	40.61
03 Jan 89	0.65	7.5		3.07	15.76	4.58	78.94
26 Jan 89	1.50	7.5			19.67	6.19	61.45
25 May 89	2.00	22.5	7.0	3.20	12.95	5.37	49.12
03 Aug 89	1.80	22.0		4.30	8.23	4.21	52.51
14 Sep 89	0.50	27.0	7.6	1.25	8.88	3.55	78.75
Mean	1.10		7.3	3.06	12.69	5.49	64.28
				Cox Mill			
16 Oct 88	0.30	14.0			5.87	4.76	102.05
15 Nov 88	0.90	11.5		4.01	6.95	9.25	67.31
29 Dec 88	0.65	8.0		2.86	6.36	4.89	103.95
24 Jan 89	1.40	6.5			10.12	3.65	54.92

Table 2. Cox Mill Continued.

Date	Depth (m)	Temp. (°C)	pH	Atten. Coeff. (m^{-1})	NH_4 (μM)	FRP (μM)	NO_3+NO_2 (μM)y
15 Jun 89	1.75	24.2		6.95	4.74	7.14	50.75
11 Jul 89	1.00	27.5			7.72	4.28	61.32
08 Aug 89	2.40	28.0		3.90	5.68	1.98	18.42
14 Sep 89	1.20	27.0	7.2	0.98	8.48	6.48	95.94
19 Oct 89	1.00	20.5			6.58	5.51	67.84
Mean	1.18		7.2	3.74	6.94	5.33	69.17

midstream, but the entire cross-sectional profile was not determined.

While discharges were unusually high for most of the study period, winter flooding is common in the Neuse River watershed. However, such high water (e.g. August) during the summer is very unusual and usually occurs only during hurricane-associated rain events. Thus results from this study may therefore be least applicable to average summer and early fall conditions.

Nutrient concentrations decrease during high discharge periods (Harned, 1980; Stanley, 1983). Annual mean FRP and NO_3 + NO_2 concentrations in the high flow years of 1979 and 1982 were substantially lower than in the low flow years of 1980 and 1981 (Stanley, 1983), while NH_4 concentrations were slightly reduced. The discharge effect increases with distance upstream. The annual mean of FRP concentration near Kinston ranged from 10 μM in low discharge years to 4 μM in high discharge years. At Goldsboro the FRP concentration annual mean ranged from 30 μM in low discharge years to 10 μM in high discharge years (Stanley, 1983). During this study mean ambient water column FRP concentrations at Kinston, Seven Springs and Cox Mill were 4.20, 5.49 and 5.33 μM, respectively (Table 2). Thus the mean FRP concentration at Kinston was similar to other high flow years, but mean FRP concentrations at the other two sites were less than half the average for other high flow years. Consequently, ~~the~~ study results may have also been affected by unusually low to very low ambient water column FRP concentrations.

Sediment Characteristics of the Study Sites

The high discharges resulted in frequent and often severe scouring of the benthic community exacerbating the effects of light reduction on development of benthic microalgae. Chl. a concentrations were extremely low over most of the study (Table 1). Highest concentrations occurred in January just prior to the onset of severe flooding. In normal to low flow periods, the author observed growth of diatoms, green algae and cyanobacteria in sediments, especially in summer and fall. For instance, seventeen samples of both mud and sand were taken between March 1987 and April 1988 at Cowpen Landing. Mean water depth was 1.30 m and mean chl. a concentration was 56 mg chl. a m^{-2} (range 8-199 mg m^{-2}). This mean is nearly twice the concentration of any single sample from this study.

Chl. a concentrations may also have been underestimated in this study. Particularly when chl. a concentrations are low, degraded pigments of detrital origin may result in underestimation of chl. a concentrations (Whitney and Darley, 1979). Also, even though it is common practice to extract the top centimeter of sediment (Colijn and van Buurt, 1975; Cadee and Hegeman, 1977; Rizzo and Wetzel, 1985; Rizzo, 1990), benthic microalgae are photosynthetically-active only in the top few millimeters (Taylor, 1964; Fenchel and Staarup, 1971). Inclusion of deeper sediments in the analysis may thus further increase the relative concentration of degraded pigments. Therefore, the chl. a data should be used primarily as a qualitative indicator of biomass and not as an indicator of potential productivity. For instance, sediments at Cox Mill released oxygen on two occasions, indicating appreciable benthic microalgal photosynthesis, when chl. a concentrations were undetectable (< 1 mg m^{-2}).

Nevertheless the reduction or elimination of the benthic microalgal community from some samples, due to scouring or light limitation, was particularly problematic in the interpretation of the light-incubation experiments over the entire study.

Concentrations of TOM, TC, and TN (Table 1) and grain size distributions (Table 3) also underwent changes during the study, undoubtedly related to hydrologic events. Sediments at all sites were over 95% sand at the beginning of the study. The Kinston and Cox Mill sites remained sandy throughout the study although the amount of fine sediments (silts and clays) varied by 20% at the Kinston site. However, major fluctuations in grain size

Table 3. Edaphic variables determined for the study sites. Grain size percentages are based on wet weight, total carbon (TC) and total nitrogen (TN) on dry weight, and total organic matter (TOM) on ash-free dry weight. Sites: K = Kinston, S = Seven Springs and C = Cox Mill. Mean ± standard deviation, for three of more replicates.

Date	Site	% Sand	% Clay	% Silt
16 Oct 88	K	97.1 ± 3.1	0.3 ± 0.5	0.8 ± 1.2
	S	96.5 ± 7.2	1.3 ± 1.4	2.6 ± 2.4
	C	105.7	0.02	0.2
15 Nov 88	K	76.5 ± 14.3	7.6 ± 2.7	14.7 ± 8.0
29 Dec 88	C	98.8 ± 1.1	0.2 ± 1.1	0.3 ± 0.1
03 Jan 89	S	29.1	39.8	38.1
25 May 89	S	60.2	17.4	24.3
15 Jun 89	C	98.0 ± 2.4	0.4 ± 0.2	0.7 ± 0.2
Mean	K	86.8	4.0	7.8
	S	61.9 ± 33.7	19.5 ± 19.3	21.7 ± 17.9
	C	100.8 ± 4.2	0.2 ± 0.2	0.4 ± 0.3

occurred at Seven Springs. A 10-cm layer of fine sediment was deposited between the November 1988 sampling date and the January 3, 1989 date. These fine sediments were completely absent three weeks later (January 26), but were present again on the first post-flood sampling date (May 25). The site was again dominated by sandy sediments in September, 1989.

Sandy sediments were always low in TOM, TC and TN. The Cox Mill site was generally lowest in organic matter concentrations, but TN was often near detection limits at both Seven Springs (sandy sediments only) and Cox Mill. Deposition of fine sediments at Seven Springs was accompanied by substantial increases in TC and TN. While similar ephemeral episodes may have gone unobserved at the other sites, the sediments were typically very low in organic matter concentrations during the study.

Nutrient and Oxygen Exchanges Under Ambient Conditions

FRP Exchanges. Mean FRP fluxes of sediment cores under ambient conditions incubated in the light and dark are shown in Table 4. Mean flux rates and most individual samples (Appendix Table 1) show that the sediments were sources of FRP to the water column at all three sites, in both light and dark. Uptake occurred in only 12-33% of all experiments. Mean FRP release was similar for respective light treatments between Kinston and Cox Mill, but was much higher at Seven Springs. This probably reflects the infrequent sampling at Seven Springs, particularly at times when lower FRP releases occurred at the other sites. The maximum release at all three sites occurred between December 1988-January 1989 and suggests pulses resulting from rapid aerobic mineralization of post-bloom phytoplankton detritus (Sondergaard, 1989). At other times FRP exchanges were typically low, < 50 μmol P m^{-2} h^{-1}.

Except for July at Kinston and Cox Mill (Figure 3), FRP releases were much higher than those reported by Kuenzler et al. (1982) for the Chowan River (Table 4). The mean FRP exchanges in this study were very similar to the mean rates for the sandy sediments (TOM < 2%) at Cowpen Landing, but were much greater than the mean for muddy sediments (TOM > 6%; Table 4). However, for the latter sediments the low mean FRP exchange can be

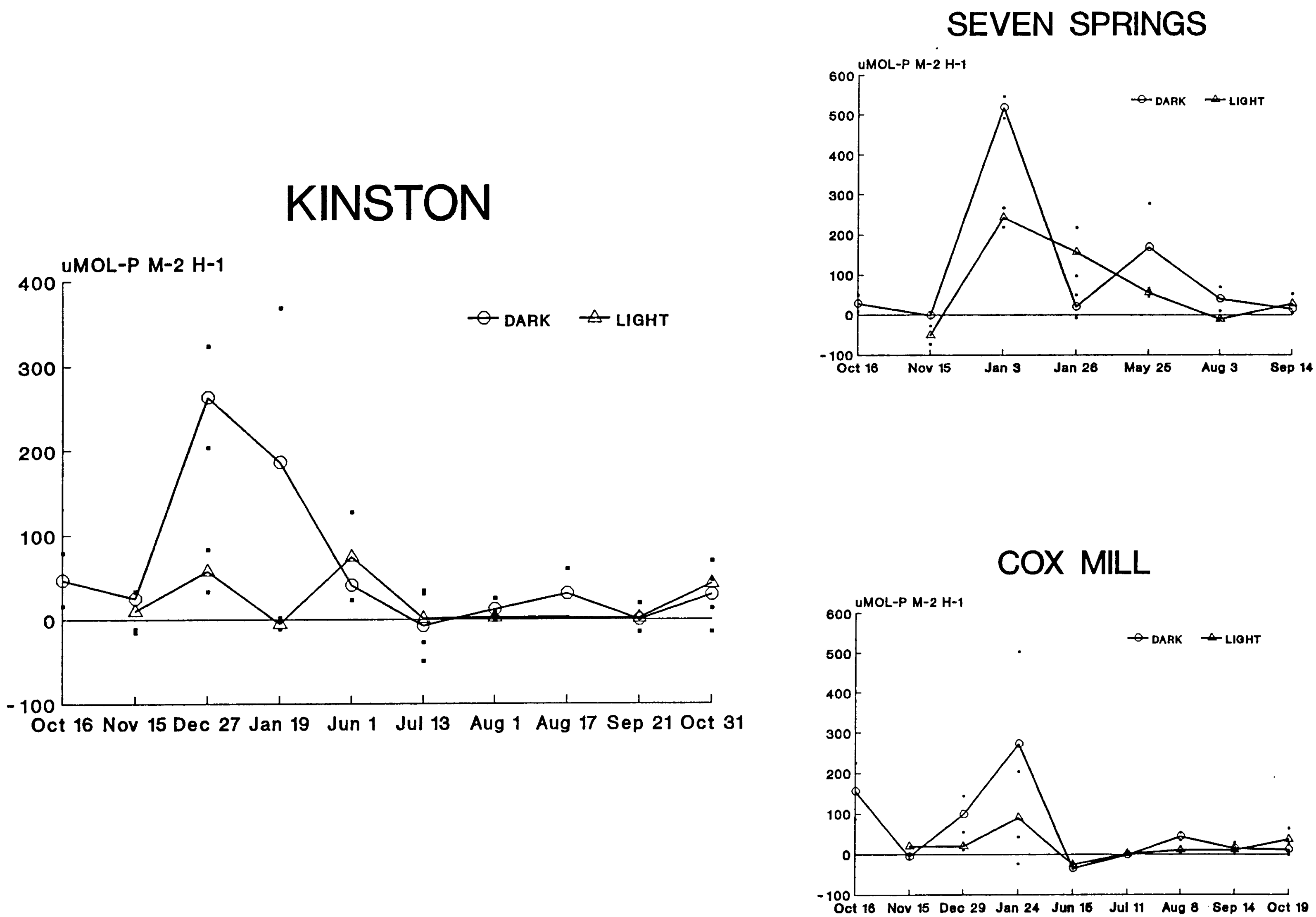

Figure 3. Means (+ standard deviations) of FRP fluxes.

Table 4. Average hourly rates (m^{-2}) of nutrient and oxygen exchange at the Neuse River study sites in light-incubated core and dark-incubated cores. Nutrient fluxes are in μmol-N or P, oxygen in mg O_2.

	Mean Flux Rate	S. D.	No. of Samples	Mean Flux Rate	S.D.	No. of Samples
	FRP			NH_4		
Kinston						
Light	22.9	± 30.5	9	25.2	± 77.8	9
Dark	62.3	89.0	10	40.4	48.4	10
Seven Springs						
Light	70.1	± 109.8	6	8.3	± 45.1	6
Dark	112.8	187.5	7	11.7	37.1	7
Cox Mill						
Light	10.8	± 19.4	8	3.3	± 39.8	8
Dark	65.2	102.7	9	-3.9	25.8	9
Cowpen Landing[1]						
Mud-Dark	4.4	± 62.2	36	311.6	± 307.7	36
Sand-Dark	91.7	161.3	7	129.9	91.2	7
Chowan River[2]						
Dark	4.1			91.4		
	$NO_3 + NO_2$			O_2		
Kinston						
Light	-4.9	± 77.8	9	-7.7	± 14.2	9
Dark	-19.9	79.8	10	-18.3	15.3	10
Seven Springs						
Light	16.5	± 102.6	6	-3.9	± 12.5	6
Dark	-2.2	62.5	7	-18.7	12.3	7
Cox Mill						
Light	-4.1	± 43.3	8	-2.0	± 9.3	8
Dark	6.6	30.4	9	-10.4	7.5	9
Cowpen Landing[1]						
Mud-Dark	-103.4	± 74.8	33	-25.5	± 16.0	37
Sand-Dark	-99.3	67.1	7	-21.5	14.1	7
Chowan River						
Dark	1.3			-5.6		

[1] Rizzo and Christian (unpublished)
[2] Kuenzler et al. (1982). Mean of 12 sites, June sampling only. Converted from daily rates by dividing by 24 hours.

attributed to the strong seasonal pattern of the exchanges from fine sediments. These sediments were FRP sources during winter when concentrations were low (mean = 4.00 μM) but became sinks during summer at higher concentrations (mean = 6.20 μM). Consequently, the net flux (mean flux) was near zero.

The ambient flux rates from this study also showed a concentration dependence similar to that for Cowpen Landing (Figure 4). When initial FRP concentrations exceeded 6.50 μM, FRP was either taken up or released at very low rates. Between 4-6 μM, FRP was taken up infrequently, and no uptake was observed at initial concentrations below 3.80 μM although FRP release was low at these concentrations.

NH_4 Exchanges. Even though mean NH_4 fluxes indicate that the sediments were sources to the water column (except for dark-incubated sediment at Cox Mill), sediments removed NH_4 from the water column in 61% of the core incubations (excluding mud sediments) for both light treatments. The mean flux values were greatly affected by the large fall releases, especially at Kinston (Figure 5). Thus, in contrast to FRP fluxes, sediments were NH_4 sinks most of the time. NH_4 fluxes decreased with distance upstream. Release of NH_4 from both types of sediments at Cowpen Landing (Table 4) was much greater than any upstream site. The Cowpen Landing rates were more similar to those measured in the lower Chowan River sediments. While the difference in NH_4 release between Cowpen Landing and other Neuse

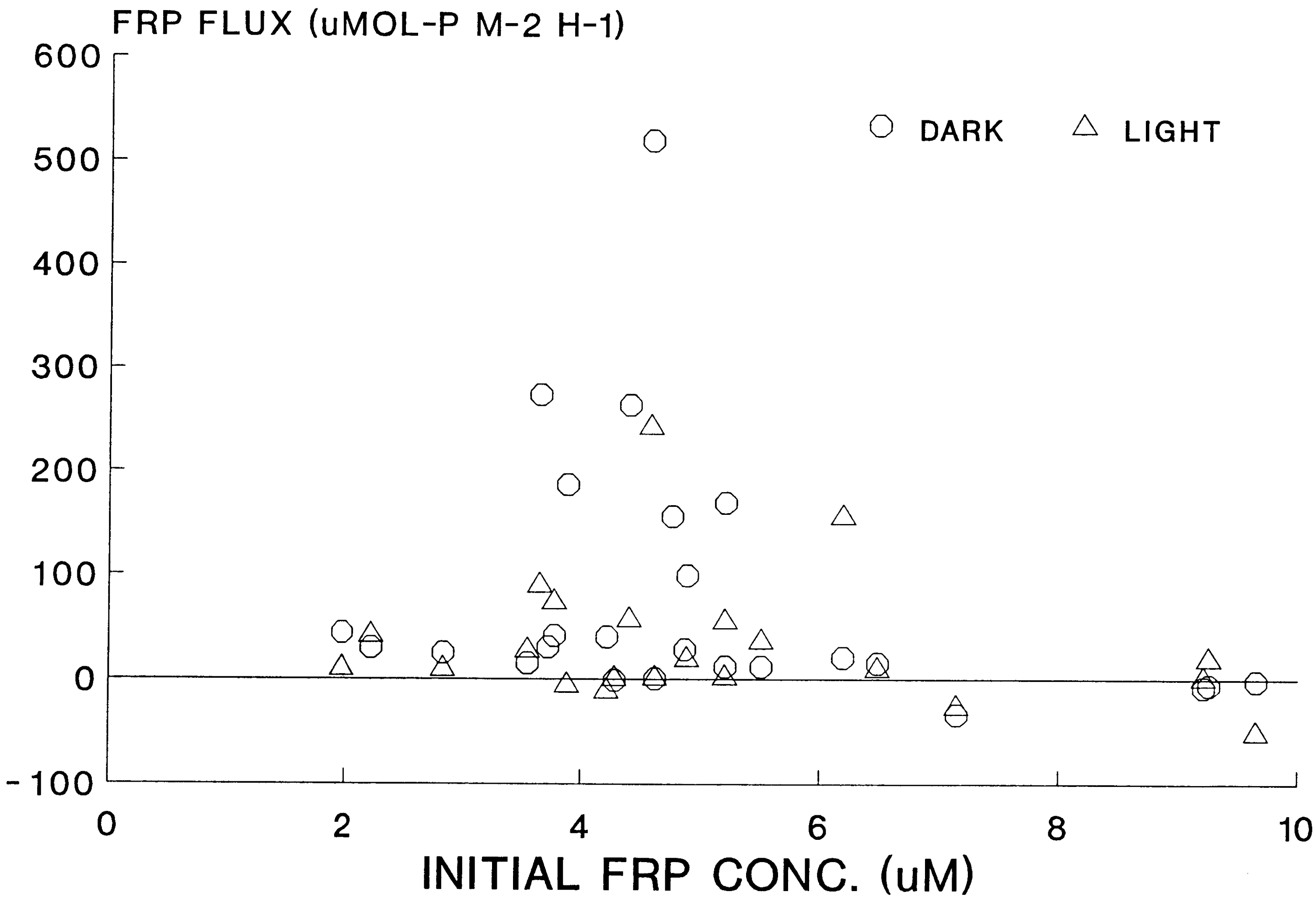

Figure 4. FRP flux at all sites vs. initial concentration.

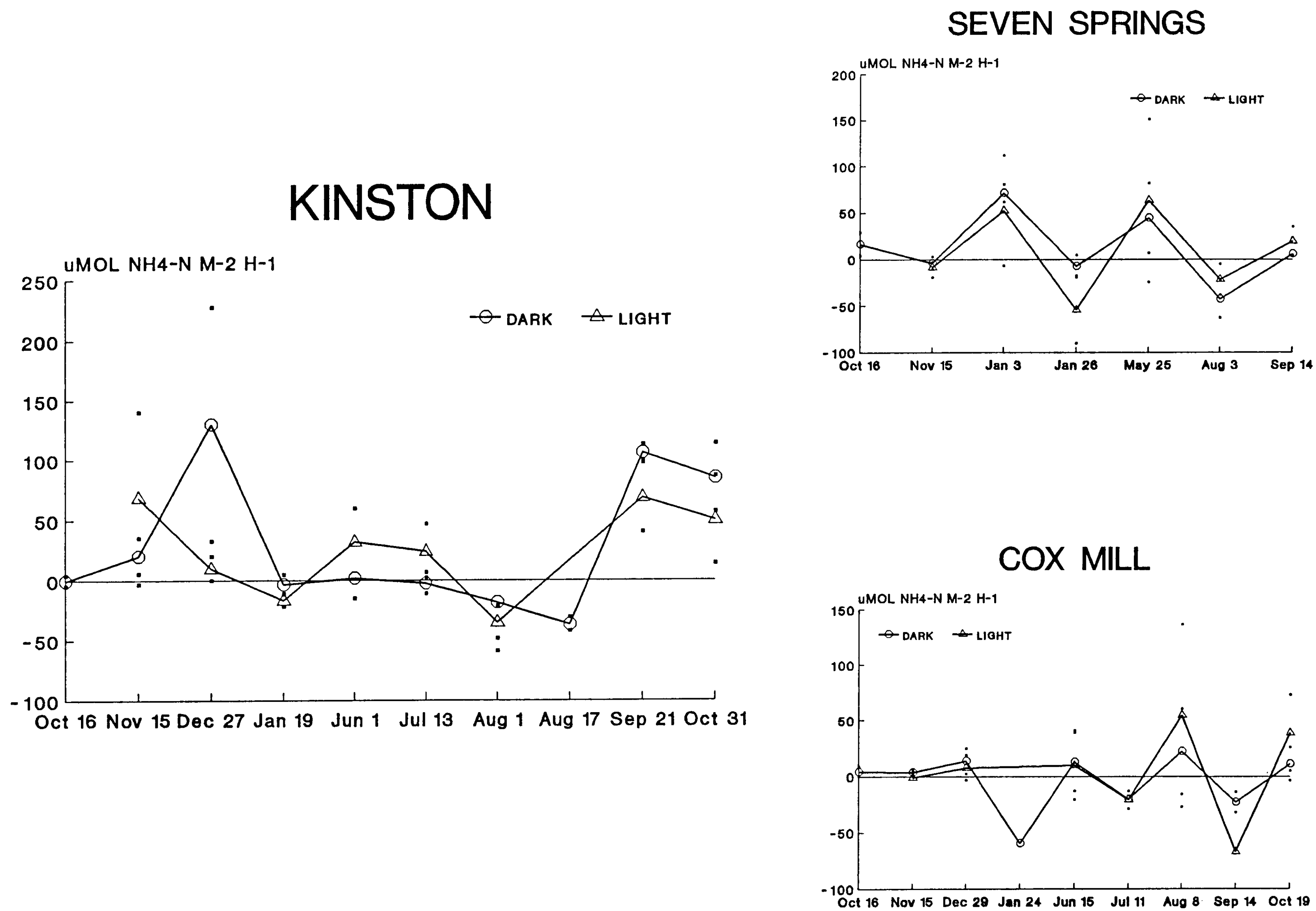

Figure 5. Means (+ standard deviations) of NH4 fluxes.

River stations could be explained by differences in rate of mineralization by aerobic respiration (see discussion of oxygen uptake below; Table 4), this would not explain the Chowan River data.

NO_3 + NO_2 Exchanges. The sediments were net sinks for NO_3 + NO_2 except for light-incubated cores at Seven Springs and dark-incubated cores at Cox Mill. Like NH_4 fluxes, mean values do not indicate the general behavior of sediment-water NO_3 + NO_2 exchanges. NO_3 + NO_2 was released in 50-75% of all incubations (Figure 6). Very low releases of NO_3 + NO_2 were also characteristic of Chowan River sediments, but Cowpen Landing sediments were strong NO_3 + NO_2 sinks (Table 4). The consistently high concentrations of NO_3 + NO_2 in the water column make it seem unlikely that diffusion would consistently direct NO_3 + NO_2 fluxes out of the sediments. A possible explanation is that nitrification in the surficial sediments results in NO_3 + NO_2 formation and release. This hypothesis is supported by the typical removal of NH_4 by sediments. The NO_3 + NO_2 uptake at Cowpen Landing is probably linked to high rates of denitrification. Further study is needed to resolve the dominant nitrogen cycling processes within Neuse River sediments.

Oxygen Exchanges. The sediments at all sites were net oxygen sinks. Mean respiration (primarily community respiration, but including chemical demand) was similar among sites (Table 4) and showed no seasonal pattern at any site (Figure 7). Maximum respiration occurred at Cox Mill and Seven Springs, and high

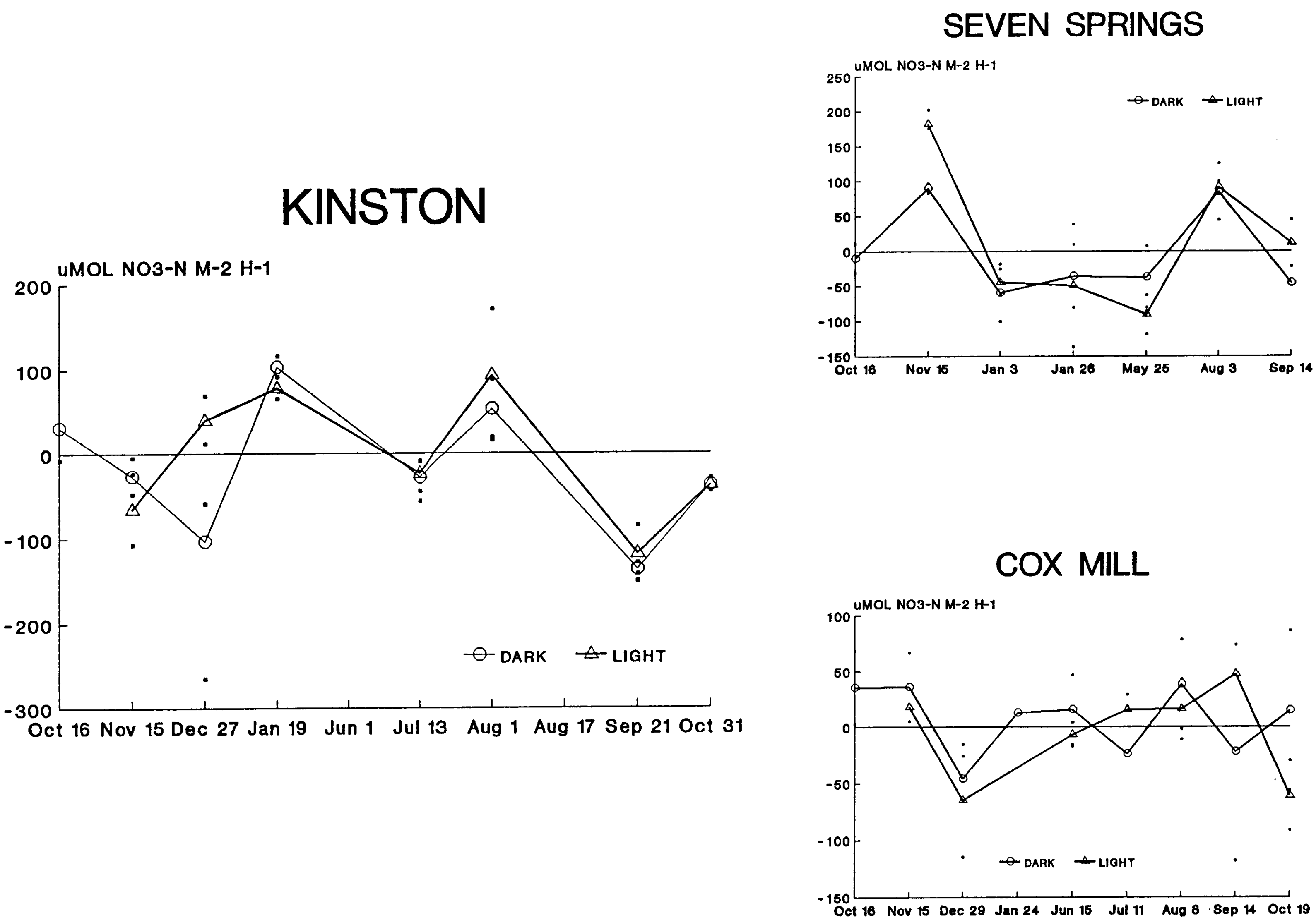

Figure 6. Means (+ standard deviations) of NO3+NO2 fluxes.

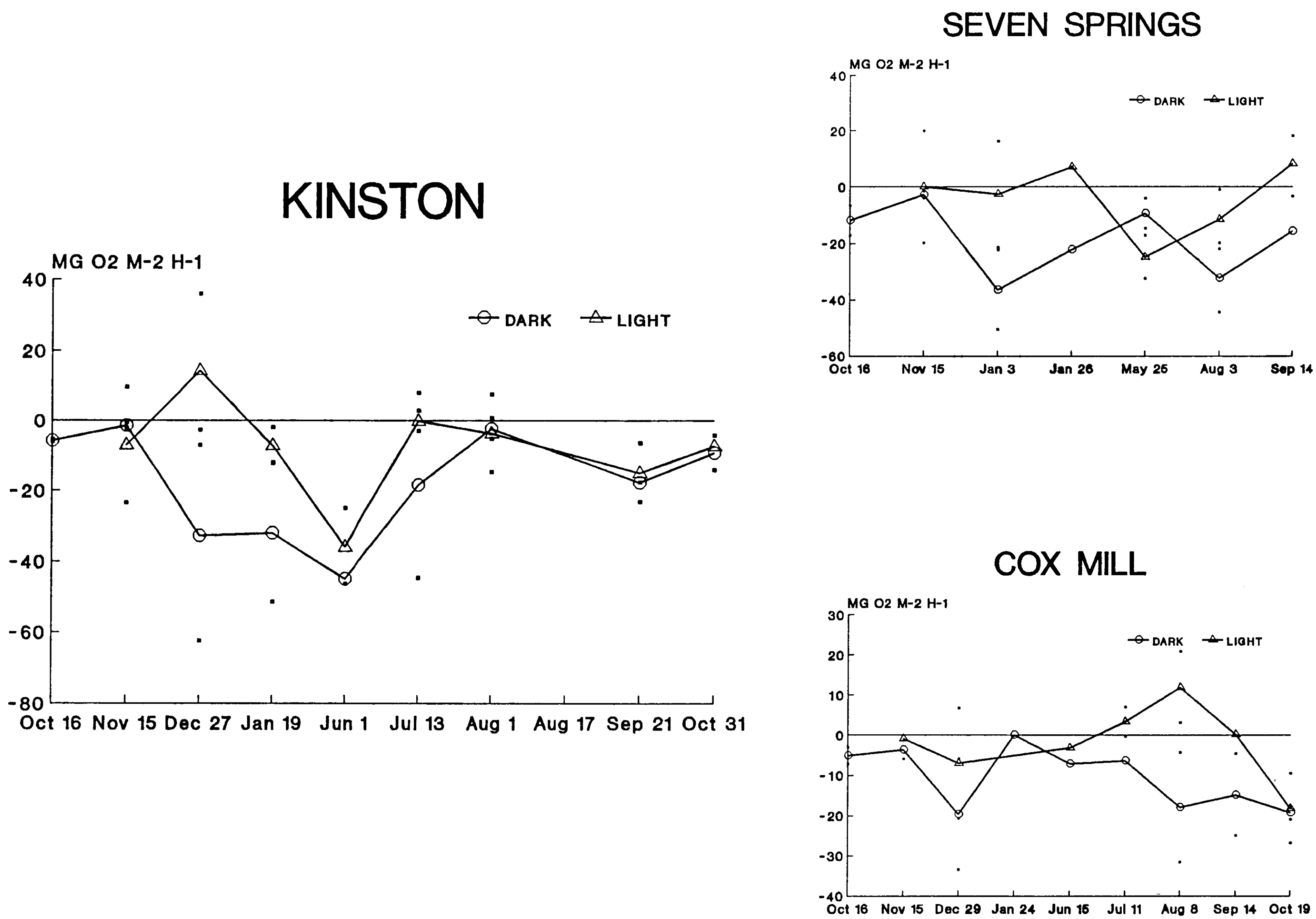

Figure 7. Means (+ standard deviations) of oxygen fluxes.

respiration rates occurred at Kinston, during the December 1988 - January 1989 period, coincident with large releases of FRP and NH_4. The oxygen data thus support the idea of a benthic heterotrophic response to an input of labile organic matter such as the crash of a phytoplankton bloom.

Net oxygen production (net community productivity; NCP) by the sediments occurred in 3 of 7 samples at Cox Mill, 1 of 8 at Kinston, 3 of 4 (sand) and 0 of 2 (mud) at Seven Springs (Figure 7). Thus Kinston sediments and muddy sediments at Seven Springs were dominated by heterotrophic processes while autotrophic processes were of about equal importance at Cox Mill and sandy sediments at Seven Springs. The lack of oxygen production during some light-incubations may be due to reduction or elimination of the benthic algal community by scouring. Also, it is possible that photoinhibition may have occurred at the irradiance used if the benthic microalgal communities were extremely dark-adapted due to water depth and turbidity effects.

Other Influences on Material Exchanges

Changes in pH, the sediment grain size changes at Seven Springs, and the presence of bivalves at all sites affected material exchanges. The impact of these variables were analyzed in additional experiments given in appendices B-D. Changes in pH promoted release of FRP and inhibited release of NH_4, sometimes reversing the direction of flux. Fluxes from muddy sediments were significantly different than fluxes from sandy sediments, often occurring in opposite directions.

Active bivalve metabolism (respiration rates significantly greater than sediment respiration in cores without bivalves) significantly increased releases of FRP and NH_4, and caused sediments to remove NO_3 + NO_2 instead of releasing it as was the case in non-bivalve containing cores. The estimated size of the bivalve population was considerable at all sites, but was nearly four-fold higher at Cox Mill than the two lower river sites. At Cox Mill, bivalve metabolism in summer converted sediments from nutrient sinks to nutrient sources for the water column. The ecological significance of the filter-feeding pathway is such that even nutrient-poor sediments can be sources of internal loading to the water column as long as water column particulate concentrations will support the population.

Effects of Light Treatment on Flux Rates of Cores Samples

Light-incubated cores differed significantly in FRP exchange from dark-incubated cores in 2 of 8 samples at Kinston, 4 of 6 at Seven Springs, and 3 of 7 at Cox Mill (Table 5). In all but a few instances, light-incubated cores either released FRP at lower rates or took up FRP while dark-incubated cores released FRP. Mean FRP release in the light was only 34%, 54% and 61% of mean dark-incubation release for Kinston, Seven Springs and Cox Mill, respectively. Statistically, light-incubation had less effect on nitrogen exchanges. Only 21% of the NH_4 exchanges and 14% of the

Table 5. Tests of FRP flux rates (μmol-P m^{-2} h^{-1}) vs. PAR treatment by initial FRP concentration. Positive values denote release from sediment. A = ambient FRP concentration. Results are significant at $P \leq 0.05^*$ or $P \leq 0.10^+$.

Site	Date	Conc. (μM)	Treatment Light	Treatment Dark	Prob.
Kinston	27 Dec 88	2.40	85	152	0.083^+
		6.16	65	124	0.043^*
		12.17	51	200	0.021^*
		4.40 A	57	263	0.021^*
	19 Jan 89	2.85	47	58	0.248
		4.90	11	60	0.020^*
		10.78	64	3	0.275
		3.77 A	-5	186	0.724
	01 Jun 89	2.39	68	47	0.021^*
		7.15	21	24	0.439
		10.76	-4	57	0.564
		3.77 A	92	74	0.034^*
	13 Jul 89	16.65	6	40	0.564
		17.65	96	61	0.724
		9.21 A	1	-8	0.724
	01 Aug 89	5.77	-5	74	0.028^*
		8.85	-3	70	0.022^*
		23.88	-24	24	0.034^*
		5.21 A	2	11	0.505
	31 Oct 89	1.65	22	20	0.285
		6.25	5	72	0.034^*
		10.85	-20	3	0.285
		2.23 A	45	32	0.513
Seven Springs	03 Jan 89	3.05	231	505	0.083^+
		4.72	113	406	0.021^*
		13.08	312	255	0.999
		4.58 A	243	518	0.021^*

Table 5. Continued.

Site	Date	Conc. (µM)	Treatment Light	Treatment Dark	Prob.
Seven Springs	26 Jan 89	4.38	77	94	0.858
		5.10	57	24	0.180
		13.40	85	67	0.643
		6.19 A	156	20	0.050*
	03 Aug 89	2.12	3	49	0.020*
		6.52	71	101	0.355
		10.52	-6	-4	0.561
		4.21 A	-11	40	0.028*
Cox Mill	29 Dec 88	2.32	18	133	0.050*
		8.76	8	125	0.020*
		12.63	0.3	170	0.050*
		4.89 A	19	99	0.021*
	24 Jan 89	4.91	48	190	0.221
		10.51	27	617	0.050*
		3.65 A	90	273	0.248
	15 Jun 89	1.95	8	2	0.999
		2.51	9	8	0.561
		4.11	7	9	0.480
		7.14 A	-26	-34	0.034*
	11 Jul 89	2.05	11	12	0.643
		5.72	-0.3	5	0.060+
		18.42	-110	-151	0.034*
		4.28 A	1	-1	0.083+
	08 Aug 89	1.98	8	30	0.034*
		1.98 A	10	44	0.034*
	19 Oct 89	2.12	64	20	0.083*
		6.72	-4	20	0.083*
		13.22	-1	4	0.825
		5.51 A	37	11	0.157

NO_3 + NO_2 exchanges differed significantly between light and dark incubations. Nevertheless, NH_4 release at Kinston and Seven Springs was considerably affected by light incubation (Table 4). Light-incubated cores released only 63-73% of the NH_4 released by dark-incubated cores. Sediments at Cox Mill released NH_4 in the light compared to dark uptake but fluxes were much lower than at the two downstream sites. There were no seasonal patterns in NO_3 + NO_2 flux. However, dark incubation seemed to promote NO_3 + NO_2 uptake at the lower two stations. At Kinston, mean NO_3 + NO_2 uptake was four times greater in the dark than in the light, and at Seven Springs uptake occurred in the dark but not in the light (Table 4). At Cox Mill however, sediments removed NO_3 + NO_2 in the light and released it in the dark.

Several studies have shown that benthic microalgae limit release of either nitrogen or phosphorus, depending on which particular nutrient may be growth-limiting (Nowicki and Nixon, 1985; Carlton and Wetzel, 1988; Sundback and Graneli, 1988; Forsberg, 1989; Rizzo, 1990; Sundback et al. 1991). In all cases where the comparison could be made, significant differences in FRP flux rates between light and dark treatments co-occurred with high benthic microalgal production (i.e. when sediments either released oxygen or when oxygen uptake in the light was two-fold to three-fold lower than dark uptake). This suggests that some cases of non-significant light treatment effects were due to low benthic microalgal productivity. Also, exclusion of bivalve-containing cores occasionally led to reduced sample sizes.

Coupled with natural spatial variability, significant differences would be harder to detect statistically, and may have led to some of the non-significant results.

Response of Sediment-Water Exchanges to Manipulations of Light and FRP Concentration in Core Samples

Under experimental FRP concentrations light-incubated cores often released less FRP than dark-incubated cores. At low concentrations (< 4 μM), FRP releases were significantly lower in 25% of the experiments, 38% at intermediate concentrations, and 41% of the experiments at high initial FRP concentrations (> 8 μM), compared to 53% of the ambient incubations (Table 5).

Samples from Kinston showed significant concentration effects on FRP exchange in 2 of 6 dark-incubated samples, and 1 of 6 light-incubated samples (Table 6). At Seven Springs, FRP concentration did not affect sediment-water exchanges in light-incubated cores, but significantly affected FRP exchange in 1 of the 3 dark incubation experiments. At Cox Mill, FRP concentrations significantly affected flux rates in only 1 of 6 experiments for dark-incubated cores, and in 2 of 5 experiments for light-incubated cores. Although most experiments did not show statistical significance between FRP treatments (Table 6), light-incubated cores with high initial FRP concentrations consistently released less FRP than other treatments or removed FRP compared to release at lower concentrations (Figure 8).

Table 6. Tests of FRP flux vs. initial FRP concentration by PAR treatment. Results are significant at $P \leq 0.05^{*}$ or $P \leq 0.10^{+}$.

Site	Date	PAR	Concentrations (μM)	Prob.
Kinston	27 Dec 88	Light	2.40 x 6.16 x 12.17	0.298
		Dark		0.098^{+}
	19 Jan 89	Light	2.85 x 4.90 x 10.78	0.618
		Dark		0.049^{*}
	01 Jun 89	Light	2.39 x 7.15 x 10.76	0.082^{+}
		Dark		0.146
	13 Jul 89	Light	10.98 x 16.65 x 17.65	0.157
		Dark		0.855
	01 Aug 89	Light	5.77 x 8.85 x 23.88	0.027^{*}
		Dark		0.538
	31 Oct 89	Light	1.65 x 6.25 x 10.85	0.082^{+}
		Dark		0.027^{*}
Seven Springs	03 Jan 89	Light	3.05 x 4.72 x 13.08	0.232^{+}
		Dark		0.437
	26 Jan 89	Light	4.38 x 5.10 x 13.40	0.841
		Dark		0.852
	03 Aug 89	Light	2.12 x 6.52 x 10.52	0.056^{+}
		Dark		0.023^{*}
Cox Mill	29 Dec 89	Light	2.32 x 8.76 x 12.63	0.195
		Dark		0.328
	24 Jan 89	Light	1.97 x 4.91 x 10.51	0.248
		Dark		0.807
	15 Jun 89	Light	1.95 x 2.51 x 4.11	0.617
		Dark		0.330
	11 Jul 89	Light	2.05 x 5.72 x 18.42	0.010^{*}
		Dark		0.065^{+}
	08 Aug 89	Dark	1.98 x 5.61 x 11.98	0.015^{*}
	19 Oct 89	Light	2.12 x 6.72 x 13.22	0.030^{*}
		Dark		0.174

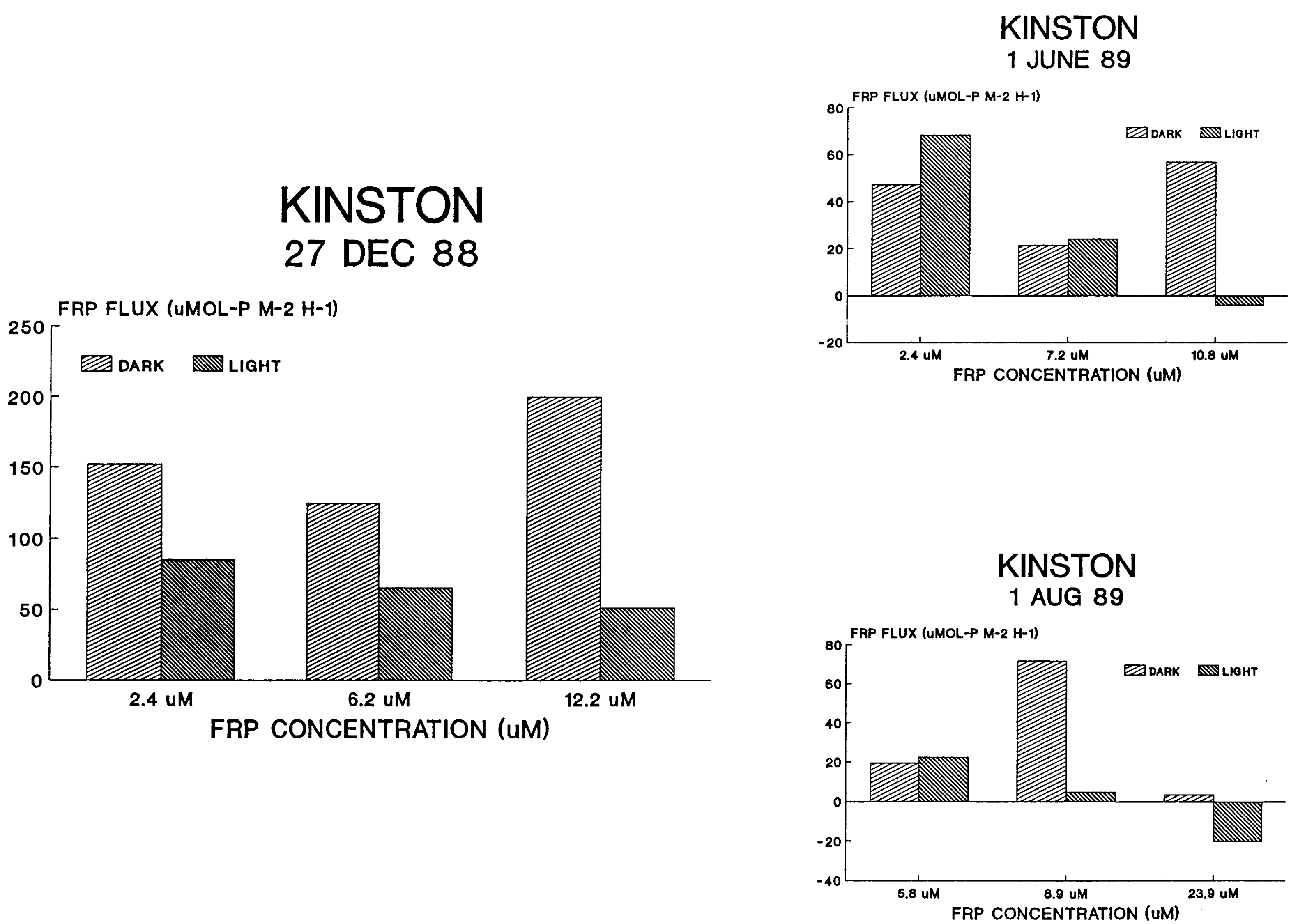

Figure 8. FRP flux vs. initial concentration.

Also, FRP release from light-incubated cores at initial concentrations ≈ 2 μM was generally twofold greater than at intermediate concentrations. Although significant concentration effects occurred with about equal frequency in dark-incubated cores, a consistent pattern of response was not evident (Figure 9). However, the most noticeable differences among concentration treatments in dark-incubated cores also occurred in the highest FRP treatment, especially for concentrations representative of low flow maximum concentrations, where sediments became FRP sinks (Figures 8 and 9).

The lack of statistical significance in some individual experiments probably results from sample variability arising from patchiness and because of the treatment concentrations which were chosen. As the Cowpen Landing data and the ambient core incubation data from this study indicate, Neuse River sediments switch roles as FRP source or sink at FRP concentrations between 4-6 μM. This range encompasses the intermediate treatment concentration. Thus in this range cores may show greater variability in response to water column concentrations; sometimes acting as sources and sometimes as sinks. Greater variability in exchanges at intermediate concentrations is supported by the average coefficients of variation (including both light- and dark-incubated samples: 49% at 2 μM, 92% at 10 μM compared to 156% at 5 μM). Also, the range of treatment concentrations was relatively narrow, especially between the low and intermediate treatments (≈ 2 μM). Responses to such subtle treatments could be more easily obscured by high spatial variability.

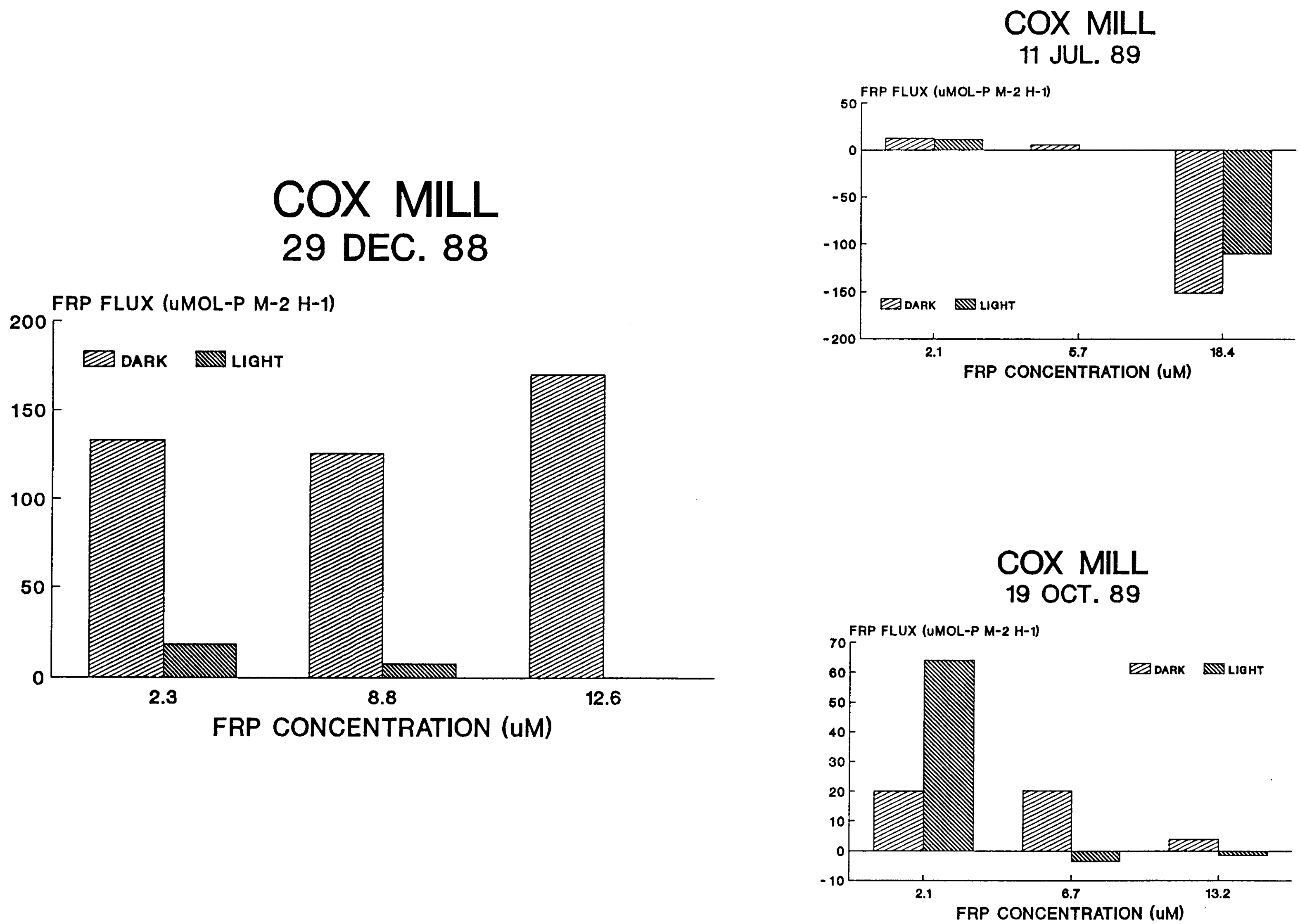

Figure 9. FRP flux vs. initial concentration.

Microcosm Studies

The microcosm studies were undertaken as an alternative to short incubations. Microcosms would minimize spatial variability by increasing the area of sediment involved in exchanges. Also, sediment-water exchanges would not be subject to an additional source of variability from fluctuating concentrations of ambient water column FRP.

Table 7 gives the beginning and ending values for the chemical and physical parameters monitored during the microcosm experiments. Temperature remained very constant (± 1°C) during each experiment. In general, pH remained constant from day to day also (± 0.1), but there were occasional fluctuations of 0.5-1.0 units within a 24 h period. Daily fluctuations in dissolved oxygen were usually ± 0.2 mg l^{-1}, but occasionally as much as 0.5 mg l^{-1}.

Experiment 1. In the first experiment, initial and final FRP concentrations in the ambient treatment were very similar although concentrations fluctuated considerably from day to day (Figure 10). At initial concentrations of 5.15 and 10.49 μM, sediments removed FRP. Sediments released FRP in the microcosm with a low (2.42 μM) initial FRP concentration. There were considerable day-to-day fluctuations within the microcosms, especially in the final 24-h. Prior to the final 24-h, all microcosms in which FRP concentration had been manipulated (microcosms B,C and D) had reached similar FRP concentrations (3.95-5.53 μM). These trends indicate a source/sink switch at a concentration similar to that suggested by the core studies (4-5

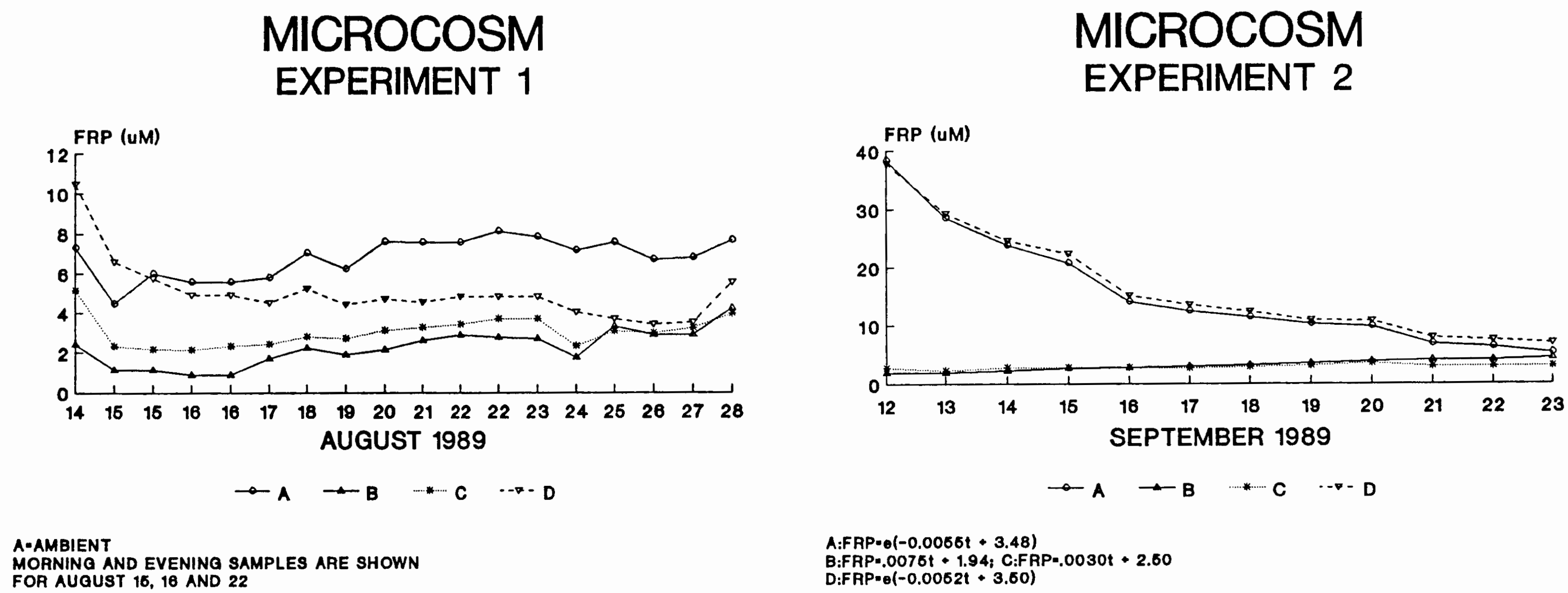

Figure 10. Microcosm Experiments, FRP Concentration vs. Time.

μM). However, the changes over the final 24 hours cannot be readily explained. FRP concentrations increased and oxygen concentrations decreased in all microcosm, especially in the ambient treatment, indicating a burst of heterotrophic activity. A hatch of gastropods also occurred near the end of the experiment and may have caused the changes over the final 24-hour period. (The gastropods disappeared by the beginning of experiment two).

Table 7. Initial and final values for parameters determined for the microcosm experiments. I = Initial value. F = Final value. UD = Undetectable.

Experiment 1

MICROCOSM	A		B		C		D	
	I	F	I	F	I	F	I	F
FRP (μM)	7.29	7.65	2.42	4.21	5.15	3.95	10.49	5.53
NH_4 (μM)	2.70	2.12	10.63	2.60	11.70	2.76	11.39	2.60
NO_3+NO_2 (μM)	23.91	0.34	33.11	0.28	30.59	0.45	34.59	0.34
O_2 (mg l^{-1})	8.20	7.65	8.30	8.00	8.35	8.15	8.20	8.35
TC (%DW)	0.10	0.49	0.29	0.09	0.25	0.045	0.07	0.04
TN (%DW)	0.01	0.01	0.02	<0.01	0.01	UD	UD	UD
Temp. (½C)	21.0	21.5						
pH	7.2	7.6	7.9	7.7	7.9	7.8	8.3	7.8

Experiment 2

MICROCOSM	A		B		C		D	
	I	F	I	F	I	F	I	F
FRP (μM)	38.40	5.26	1.96	4.44	2.76	2.89	37.87	6.90
NH_4 (μM)	1.88	1.43	1.28	1.44	1.28	2.98	1.08	0.77
NO_3+NO_2 (μM)	UD	UD	UD	UD	UD	UD	UD	UD
O_2 (mg l^{-1})	7.65	8.55	7.40	7.80	7.30	8.45	7.40	8.30
Temp. (½C)	21.0	21.5						
pH	7.8	7.4	7.7	7.4	7.7	7.6	7.8	7.5

The greater day-to-day fluctuations in FRP concentrations and the anomalous behavior of the ambient treatment relative to the other microcosms may have arisen from differences in sediment metabolism, although this was not directly measured. In the ambient treatment microcosm (microcosm A), TC concentrations increased, TN concentrations were unchanged, and final oxygen concentration was 0.55 mg l^{-1} less than the initial value. In the other microcosms, both TC and TN declined and oxygen concentrations changed much less ($\leq$ 0.30 mg l^{-1}). This suggests that the benthic community was greatly diminished in the non-ambient microcosms. The sharp reduction in sediment TN and the rapid removal of DIN (Table 7) from the water suggest that nitrogen limitation may have caused the decline. This is also consistent with the lack of TN depletion in the ambient treatment which received two replenishments with DIN-rich river water during the course of the experiment. Ambient sediment cores also generally removed ammonium, suggesting that nitrogen cycling may be an important control on phosphorus cycling in the Neuse River.

<u>Experiment 2</u>. In experiment two, nitrogen limitation was imposed on the microcosms in an attempt to reduce the daily fluctuations in FRP shown in experiment 1. Total DIN concentrations remained < 2 μM over the experiment. FRP concentrations were chosen to reflect the historical ranges of Neuse River during low flow and high flow conditions (Table 7). The resulting daily changes in FRP concentrations showed little fluctuation (Figure 10) and were easily fitted to regression

equations (Table 8). The intersection of the linear equations with the exponential curves provides an empirical indication of the ambient FRP concentration at which sediment-water FRP exchange would be zero. FRP would be removed by sediments at greater water column concentrations and released at lower concentrations. The water column FRP concentration for zero exchange lies between 3.74 - 4.38 μM, in good agreement with both the core studies and microcosm experiment 1.

Table 8. Regression equations expressing the changes in FRP (μM) with time (h), for microcosm experiment two. n = sample size.

Chamber	Equation	r^2	n
A	FRP = $e^{-0.0055t + 3.48}$	0.97	9
B	FRP = 0.0075t + 1.94	0.94	9
C	FRP = 0.0030t +2.50	0.60	9
D	FRP = $e^{-0.0052t + 3.50}$	0.98	9

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GLOSSARY

Abbreviations

A. Units of Measurement

°C	Degrees Celsius
μM	Micromolar or micromoles per liter
cm	Centimeter(s)
$mg\ l^{-1}$	Milligrams per liter
m	Meter(s)
$\mu E\ m^{-2}\ s^{-1}$	MicroEinsteins per square meter per second (light quantity)
μm	Micrometer(s)
mm	Millimeter(s)
cc	Cubic centimeter(s)
g	Gram(s)
mg	Milligram(s)
l	Liter(s)
m^{-1}	Per meter
$\mu mol\text{-}N\ m^{-2}\ h^{-1}$	Micromoles of nitrogen per square meter per hour (quantity rate of change)
$\mu mol\text{-}P\ m^{-2}\ h^{-1}$	Micromoles of phosphorus per square meter per hour (quantity rate of change)
$mg\ O_2\ m^{-2}\ h^{-1}$	Milligrams of dissolved oxygen per square meter per hour (quantity rate of change)

B. Parameters

FRP	Filterable reactive phosphorus. Consists primarily of ortho-phosphate, the form used by plants.
PO_4	Phosphate or ortho-phosphate. The primary form of dissolved inorganic phosphorus and the form used by plants.
$NH_4\text{-}N$	Ammonium nitrogen, or nitrogen derived from ammonium; the most common reduced form of inorganic nitrogen at most natural pH's, and the form most usable by plants.
$NO_3\text{-}NO_2\text{-}N$	Combined nitrate and nitrite nitrogen; nitrite usually contributes only a very small amount to this combined form. Can be used by plants after expending energy to reduce it to ammonium.
DIN	Dissolved inorganic nitrogen. Primarily the sum of ammonium and nitrate concentrations.

TOM	Total organic matter; both particulate and dissolved.
TC	Total carbon. Both particulate and dissolved forms.
TN	Total nitrogen. Both particulate and dissolved forms.
Fe^{+2}	Ferrous or reduced iron; the common form under anoxic conditions.
Fe^{+3}	Ferric or oxidized iron; the common form under oxic conditions.
$FeOOH-PO_4$ complexes	Iron hydroxide and phosphate (FRP) omplexes; form under oxic conditions by adsorption to particles and desorb and dissolve under anoxic conditions.
Eh	Oxidation-reduction potential. A measure of the potential of sediments for promoting oxidation (+ Eh) or reduction (- Eh) of chemical compounds. Since oxygen is the primary contributor to high oxidation potentials, Eh is an indirect measurement of sediment oxygen status.
pH	Negative log of the hydrogen ion concentration; a measure of acidity.
hypoxia	Low oxygen concentrations, in the water column, borderline for supporting many organisms. Approximately in the range of 2-4 mg l^{-1}.
anoxia	Absence or near-absence of oxygen. A major cause of fish and benthic organism mortality.
oxic	Containing oxygen.
adsorption/ desorption	Adherence or dissolution of elements orchemical compounds to a charged surface e.g. a clay particle.
diffusion	The physical movement of gases or chemical compounds from areas of high concentration to areas of low concentration. Dependent on

	random molecular motion, it is highly temperature dependent.
bioturbation	Sediment disturbance caused by organismal activity. Promotes nutrient exchanges.
loading	The rate of nutrient input to an aquatic ecosystem; either from external (watershed) sources or internal (sediment) sources.
autotrophic	Organisms which build organic matter from inorganic constituents and energy not derived from organic matter; most commonly, green plants.
PAR	Photosynthetically active radiation. Visible light in the range of 400-700 nm. The range of electromagnetic radiation usable by plants for photosynthesis.
light saturation	The light level at which further increases in light quantity will not increase the rate of photosynthesis.
photo-inhibition	The reduction of photosynthesis by high light levels.
chl _a_	Chlorophyll _a_. Chlorophyll concentration corrected for pheophytin. The most common pigment used by plants for light capture. An indirect measure of microalgal biomass.
pheophytin	A degradation product of chlorophyll formed by loss of magnesium.
net community productivity	The amount of autotrophic organic matter production after community aerobic respiration is subtracted; can be negative when respiration exceeds autotrophic production.
heterotrophic	Organisms deriving their nutrition from sources of pre-formed organic matter; all organisms except plants and a few bacteria.
aerobic respiration	The energy-yielding oxidation of organic matter by reduction of oxygen.

chemical oxygen demand The amount of oxygen consumption which is attributable to the chemical oxidation of reduced chemical compounds.

APPENDIX

Appendix Table 1-A.
Mean hourly material fluxes ± stan. dev. (μmol N or P m^{-2}; mg O_2 m^{-2}) in ambient cores incubated in light or dark at Kinston. Positive values denote release from sediment.

Date	FRP	NH_4	$NO_3 + NO_2$	O_2
Oct 88				
Dark	47.1 ±31.4	-0.3 ±4.3	30.8 ±38.8	-5.9 ±0.3
Nov 88				
Dark	22.9 ±8.4	20.2 ±14.9	-26.6 ±21.4	-1.5 ±0.9
Light	10.0 ±24.9	68.4 ±71.8	-65.7 ±41.6	-7.1±16.5
Dec 88				
Dark	262.8 ±60.3	129.9 ±97.3	-103.2 ±162.2	-32.7±29.8
Light	57.3 ±24.9	9.8 ±10.0	40.9 ±28.4	14.4±21.5
Jan 89				
Dark	186.0±181.8	-3.4 ±7.9	102.8 ±12.5	-32.0±19.6
Light	-5.4 ±6.6	-16.7 ±5.2	78.0 ±13.0	-7.1 ±5.0
Jun 89				
Dark	40.8	2.0	-44.9	
Light	74.1 ±52.1	32.1 ±47.2		-35.9±10.6
Jul 89				
Dark	-7.9 ±26.0	-2.6 ±8.7	-27.8 ±17.4	-18.5±26.3
Light	1.1 ±28.8	24.2 ±22.3	-23.9 ±32.7	-0.2 ±2.9
Aug 89				
Dark	11.4 ±12.6	-18.3 ±40.8	52.9 ±34.7	-2.4 ±3.0
Light	2.4 ±4.7	-34.9 ±13.5	92.8 ±77.6	-3.7±11.1
Aug 89				
Dark	30.3 ±29.3	-36.8		
Sep 89				
Dark	0.0 ±0.0	105.6 ±6.9	-136.2 ±6.7	-17.7±0.03
Light	1.6 ±16.9	68.6 ±28.4	-118.1 ±32.5	-15.0 ±8.3
Oct 89				
Dark	29.2 ±17.0	85.0 ±28.3	-52.4 ±36.6	-9.3 ±5.0
Light	42.2 ±26.7	50.0 ±36.1	-37.4 ±7.8	-7.4

Appendix Table 1-B.
Mean hourly material fluxes ± stan. dev. (μmol N or P m^{-2}; mg O_2 m^{-2}) in ambient cores incubated in light or dark at Seven Springs. Positive values denote release from sediment.

Date	FRP	NH_4	$NO_3 + NO_2$	O_2
Oct 88				
Dark	28.1 ±20.5	16.1 ±12.5	-10.3 ±20.7	-12.0±5.2
Nov 88				
Dark	-1.9 ±7.5	-4.1 ±7.1	89.2 ±7.4	-2.9 ±1.3
Light	-50.9 ±22.8	-8.5 ±10.9	182.0 ±19.3	.03±19.9
Jan 89				
Dark	518.3 ±27.8	70.9 ±9.4	-59.2 ±41.1	-36.5±14.1

Light	242.5 ±23.8	52.5 ±59.2	-44.5 ±69.7	-2.5±18.8
Jan 89				
Dark	22.6 ±24.1	-7.7 ±11.9	-36.2 ±44.9	-22.2
Light	156.4 ±60.8	-54.2 ±36.4	-49.7 ±87.5	7.1 ±0.1
May 89				
D-sand*	17.3 ±7.5	-3.7 ±19.5	38.0 ±19.5	-4.6 ±3.5
D-mud	168.6±108.1	44.1 ±37.5	-37.4 ±43.7	-9.4 ±5.3
L-mud	55.8 ±10.3	62.9 ±87.9	-91.1 ±27.9	-24.8 ±7.6
Aug 89				
Dark	39.6 ±29.8	-43.1 ±19.8	-84.3 ±40.5	-32.2±12.3
Light	-10.5 ±1.1	-21.9 ±16.5	91.1 ±8.6	-11.5±10.5
Sep 89				
Dark	14.6	5.3	-45.7	-15.7
Light	27.9 ±24.3	19.4 ±15.5	10.9 ±33.1	8.4 ±9.7

* All means are significantly different ($P \leq 0.05$) between D-sand and D-mud for May, 1989. D=dark, L=light.

Appendix Table 1-C.
Mean hourly material fluxes ± stan. dev. (μmol N or P m^{-2}; mg O_2 m^{-2}) in ambient cores incubated in light or dark at Cox Mill. Positive values denote release from sediment.

Date	FRP	NH_4	$NO_3 + NO_2$	O_2
Oct 88				
Dark	187.2 ±92.9	4.3 ±4.6	35.4 ±32.8	-5.2 ±2.1
Nov 88				
Dark	-5.7 ±6.2	3.4 ±1.9	35.9 ±30.8	-3.7 ±2.3
Light	19.5	-0.9	17.7	-0.9
Dec 88				
Dark	98.6 ±44.7	13.4 ±11.0	-46.0 ±20.2	-19.7±13.8
Light	19.4 ±8.7	7.7 ±11.3	-65.1 ±49.6	-7.0±13.7
Jan 89				
Dark	272.8	-59.6	12.4	0.0
Jun 89				
Dark	-34.4 ±1.3	12.9 ±26.0	-15.5 ±31.0	-7.1
Light	-25.8 ±6.1	9.9 ±30.7	-6.7 ±10.6	-3.2
Jul 89				
Dark	-1.4	-20.0	-24.0	-6.3
Light	1.0 ±1.7	-20.7 ±7.9	23.5 ±5.0	3.3 ±3.6
Aug 89				
Dark	43.7 ±9.3	22.2 ±37.9	38.1 ±40.1	-17.9±13.6
Light	10.4 ±7.5	54.6 ±81.9	15.9 ±27.3	12.0 ±8.9
Sep 89				
Dark	14.6	-22.9 ±9.2	-22.3 ±95.9	-14.8±10.2
Light	14.2	-67.5	47.3	0.2
Oct 89				
Dark	11.4 ±13.2	10.9 ±14.8	14.6 ±71.1	-19.3 ±1.7
Light	36.6 ±27.2	38.4 ±34.0	-61.1 ±30.7	-18.2 ±8.7

Appendix Table 2.
Results of experiments on the effects of reduced pH on nutrient exchanges between sediment and water. Reduced pH was achieved by adding drops of concentrated sulfuric acid. Nutrient exchanges are μmol N or P m^{-2} h^{-1}, oxygen in mg O_2 m^{-2} h^{-1}.

Experiment 1: Acidification of sandy and muddy sediments.

Sediment	Type	pH	FRP	NH_4	O_2
Sand	7.3	15	-1	9	
Sand	6.7	28	3	11	
Mud	7.3	56	644	19	
Mud	6.7	117	469	28	

Experiment 2. Acidification of sandy sediments at varying pH.

Sand	7.1	-49	193	11
Sand	6.5	-19	58	17
Sand	6.0	25	-35	9

Appendix Table 3.
Comparison of material exchanges between bivalve-containing cores (B) and non-bivalve-containing cores (NB) for two conditions: bivalve-core respiration > ambient, and ≤ ambient. Exchanges are mean (± stan. dev.) μmol N or P m^{-2} h^{-1} and mg O_2 m^{-2} h^{-1}. Positive fluxes indicate release from sediments. * indicates t-test significant at P ≤ 0.05.

	*FRP	*NH_4	NO_3 + NO_2	*O_2
Bivalve core respiration > ambient.				
B	41 ± 25.8	53 ± 12.8	-76 ± 2.2	47 ± 8.9
NB	10 ± 6.6	-9 ± 37.1	-24 ± 14.3	12 ± 3.7
Bivalve core respiration ≤ ambient.				
B	58 ± 113.0	4 ± 66.9	-23 ± 34.5	2 ± 1.5
NB	58 ± 110.0	5 ± 36.1	-0.4 ± 28.9	5 ± 4.3

Appendix Table 4.
Comparison of net FRP and NH_4 fluxes due to bivalves (B), water column processes and sediment-water exchanges for Kinston (K), Seven Springs (S) and Cox Mill (C). Bivalve rates are based on data given in Lauritsen and Mozley (1989), and apply to conditions where bivalve respiration exceeds ambient sediment respiration. Water column rates are based on light- and dark-incubations of BOD bottles and integrated for a depth of 1 m. L=light incubation, D=dark incubation. Positive fluxes denote release from sediments. Rates are μmol N or P m^{-2} h^{-1}. Bivalve population estimates were derived from the core samples and agree well with data from the Chowan River (Lauritsen and Mozley, 1989).

	FRP			NH_4		
	K	S	C	K	S	C
B	41	42	167	235	241	958
D. Sed.	62	113	65	40	12	-4
L. Sed.	23	70	11	25	8	3
D. Water	-203	260	245	47	175	268
L. Water	-257	0	85	-43	160	-183