

OKLAHOMA STATE UNIVERSITY

CONTROLS OF NUTRIENT CONCENTRATIONS
IN A PRAIRIE STREAM

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CONTROLS OF NUTRIENT CONCENTRATIONS

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help in the

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INTRODUCTION

Although streams reflect the watersheds they drain (Hynes 1975), only recently have researchers identified ecological components within watersheds that have the greatest control on stream chemistry. Holmes et al. (1994) identified discrete, but interacting, subunits (e.g., hyporheic, parafluvial, and riparian zones) in a Sonoran desert stream ecosystem and measured ecological processes occurring within each component that affect stream solute concentrations. As a result, they determined which components exerted the strongest influence on stream water chemistry. Triska et al. (1989a), Smock et al. (1992) and Peterjohn and Correll (1984) also found this approach useful. The ability of a particular component to affect water chemistry is related to its degree of interaction with the stream. For example, upland areas may have less pronounced effects on surface water chemistry than stream-side riparian areas (McClain et al. 1994). Likewise, benthic sediments are in direct contact with the overlying water and likely exert marked effects on stream chemistry. In streams with unconsolidated sediments, surface water infiltrates the bed material, effectively increasing the sediment surface area in contact with stream water. Such infiltration, or underflow (*sensu* Munn and Meyer 1988), has been reported in several studies (see reviews by Jones and Holmes 1996, Brunke and Gosner 1997) and is recognized as an important area for nutrient retention (Gregory 1978; Mulholland 1992) and transformation (Triska et al. 1989b, Valett et al. 1990). Identification and measurement of processes occurring within benthic sediments are necessary to evaluate the importance of this component in the context of the whole stream ecosystem.

Stream sediments have the capability both to provide (Valett et al. 1990; Holmes

et al. 1994) and remove (Pinay et al. 1993, Meyer 1979, Triska et al. 1994) dissolved inorganic nutrients from stream water through a variety of physical, chemical and biological processes. Identification of these processes is of particular importance in nutrient limited ecosystems. That is, identification of source and sink areas affecting the limiting nutrient(s) is needed to understand whole ecosystem function. Net primary productivity in prairie streams of the central United States has been shown to be limited by the availability of both nitrogen and phosphorus (Tate 1990, E.H. Stanley pers. comm.). It is logical, then, to investigate the interactions between benthic stream sediments and the limiting nutrients nitrogen and phosphorus.

Streams gain nutrients through natural processes such as groundwater inputs (Hynes 1983), decomposition of allochthonous material (Fisher and Likens 1973), and hydrologic exchange with subsurface interstitial water (Valett et al. 1994, Jones and Holmes 1996), as well as other sources. Sediments interact either directly or indirectly involved in all of those nutrient sources mentioned above. For example, stream bed sediments function as a porous medium, allowing groundwater to discharge from the surrounding soils into the surface stream. Decomposition of allochthonous, as well as autochthonous, material occurs primarily on the stream bed where epilithic microbial communities are most abundant (Geesey et al. 1978). Stream water nutrient concentrations are also influenced by microbial activities occurring within sediments. The saturated sediments directly below the surface stream are often referred to as the hyporheic zone. This area is metabolically active and a site for microbial nutrient transformations (Jones et al. 1994, Jones et al. 1995). Nitrification, in particular, has been

measured in sediments of both desert (Holmes et al. 1994) and coastal streams (Triska et al. 1990). This process was shown to represent a valuable nitrate source in these systems. Similarly, Valett et al. (1994) showed that areas of hyporheic nitrification in a Sonoran Desert stream were biotic 'hot spots' and positively influenced algal development following a disturbance. Nutrients produced within sediments can become available to the surface stream through vertical hydrologic exchange (Grimm and Fisher 1984, Jones et al. 1995). That is, water in sediment interstices becomes available, through hydrologic linkage, to the surface stream. Although nitrification within sediments has been shown to be an important contributor to the nitrate budget of several streams (Grimm and Fisher 1984, Triska et al. 1990), it remains unmeasured in nutrient-limited prairie stream ecosystems.

Streams also lose nutrients through several processes associated with channel sediments. For example, sediments provide attachment sites for algal community development and concomitant nutrient depletion of surface water (Sebetich et al. 1984). Nitrate loss through denitrification has been reported in channel and riparian sediments (Triska et al. 1990, Peterjohn and Correll 1984) as well as in algal mats (Joye and Paerl 1994). Sediments have also been shown to retain nutrients as groundwater enters the stream channel. Many researchers have reported higher concentrations of nutrients in groundwater relative to stream water, indicating nutrient retention by stream channel sediments (Grimm and Fisher 1984, Ford and Naiman 1988, Mulholland 1992). Such retention of nutrients by sediments can temporarily prevent nutrient transport to the surface stream (Bencala et al. 1984, Froelich 1988).

Sediment-mediated retention is often referred to as sorption. Sorption can be partitioned into physical-chemical and biological processes. Adsorption describes the physical or chemical adhesion of a solute onto a solid (Green et al. 1978, Froelich 1988), whereas absorption describes cellular uptake of a solute (Gregory 1978). Many researchers, when referring to solute retention, have used the term sorption to describe the combined effects of adsorption and absorption (Bache and Williams 1971, Meyer 1979, Baldwin 1996). In this study, I too will use the term sorption to characterize both biotic and abiotic nutrient retention by stream sediments.

Sorption is not limited to stream ecosystems. Nutrient sorption has been observed in lake sediments (Harter 1968, Kuo and Lotse 1974), marine sediments (Boatman and Murray 1982), estuarine sediments (Pomeroy et al. 1965), and soils of terrestrial ecosystems (Coleman et al. 1960, Bache and Williams 1971). Nutrient retention by sorption, then, is an important control of nutrient concentrations in a variety of ecosystems. Studies of nutrient-sediment dynamics in streams have primarily focused on phosphate ($\text{PO}_4\text{-P}$) and ammonium ($\text{NH}_4\text{-N}$) sorption (Meyer 1979, Mulholland 1992, Triska et al. 1994). Nitrate ($\text{NO}_3\text{-N}$) sorption has received less attention because it has been shown to be unreactive with inorganic substrates (Sebetich et al. 1984, Richey et al. 1985).

As stated above, stream sediments are capable of nutrient sorption through physical (Meyer 1979, Froelich 1988), chemical (Taylor and Kunishi 1971, Baldwin 1996), and biological (Richey et al. 1985, Triska et al. 1994) processes. These processes will differentially effect nutrient sorption depending on sediment characteristics. For

example, Klotz (1988) found phosphate sorption to stream sediments to be negatively correlated with previously bound, or native, phosphate. Presumably, as sediment binding sites become occupied by sorbed nutrients, the proportion of available binding sites are reduced, thus decreasing the sorbing capacity of the sediments. Sediment texture, measured by particle size distribution, can also affect sorption ability. The research of Meyer (1979) and Klotz (1988) demonstrated that smaller sediment size particles had the greatest sorption ability. This is likely the result of the greater surface area to volume ratio of smaller particles. Geochemical characteristics of sediments also affect sorption ability. Triska et al. (1994) indicated that the minerals quartz and plagioclase are particularly important in $\text{NH}_4\text{-N}$ sorption processes. Other researchers (Taylor and Kunishi 1971, Baldwin 1996, Mulholland 1992) have identified aluminum and iron hydroxide surfaces on sediment particles as primary binding areas for $\text{PO}_4\text{-P}$.

Biological uptake by epilithic microbial communities is an important nutrient uptake process. Both Kaplan et al. (1975) and Klotz (1985) recognized microbial uptake of $\text{PO}_4\text{-P}$ as a significant retention mechanism in stream sediments. Likewise, Munn (1990) and Newbold et al. (1983) found stream water $\text{NH}_4\text{-N}$ concentrations effectively reduced as a result of microbial uptake. Klotz (1988) found a positive relationship between sediment organic content and $\text{PO}_4\text{-P}$ sorption. This finding suggests that epilithic microbes rapidly remove $\text{PO}_4\text{-P}$ from solution while decomposing sediment detritus. Similarly, Meyer (1979) showed that sediments high in organic content were most effective in phosphorus retention. Triska et al. (1994) found $\text{NH}_4\text{-N}$ sorption to be the greatest in autumn, possibly as a result of riparian leaf fall and a resultant organic matter

pulse to the stream.

Mechanisms aside, it is apparent that stream sediments are capable of removing or regenerating dissolved nutrients from the stream through various processes. Indeed, pools of sorbed $\text{NH}_4\text{-N}$ (Richey et al. 1985, Triska et al. 1994) and $\text{PO}_4\text{-P}$ (Meyer 1979, Klotz 1988) are associated with benthic stream sediments. Sediment-sorbed nutrients represent temporary storage areas that likely affect whole ecosystem properties. Storage or retention areas in sediments can reduce the availability of limiting nutrients, as well as slow the transfer of nutrients downstream. Conversely, nutrient retention can also stimulate in-stream microbial activities, namely nitrification.

Processes that govern inorganic nutrient generation (sources) and depletion (sinks) probably operate in all stream ecosystems, but vary in their timing, duration, location, and magnitude. For example, leaf decomposition can be both a nutrient source and sink to the stream. Once submerged, leaves are readily leached of their nutrients by the stream current and thus provide a nutrient source (Kaushik and Hynes 1971). As the leaf skeleton remains, however, it becomes a site for microbial colonization and subsequent nutrient removal from stream water (Suberkropp et al. 1975, Cummins et al. 1974). Similarly, riparian sediments of a Tennessee stream were found to be both a sink and a source of $\text{NH}_4\text{-N}$ and soluble reactive phosphorus (SRP) depending on the dissolved oxygen concentration in interstitial water (Mulholland 1992). When dissolved oxygen was available, nitrification reduced concentrations of $\text{NH}_4\text{-N}$ and increased concentrations of $\text{NO}_3\text{-N}$, while SRP became bound to metal oxides on sediment surfaces. Depletion of dissolved oxygen prevented nitrification but mobilized SRP as metal oxides became

reduced (Mulholland 1992). Therefore, sediments can be both a source and a sink of nutrients to the stream depending on prevailing physical, chemical and biological conditions of the sediments.

The objectives of this study were 1) to determine the ability of Wild Hog Creek sediments to regulate surface water concentrations of $\text{NH}_4\text{-N}$ and SRP through physical-chemical and biological uptake (sorption), 2) and to generate $\text{NO}_3\text{-N}$ to the surface stream through sediment nitrification. Both laboratory and field investigations were employed to examine the potential importance of nutrient-sediment interactions in controlling surface water concentrations of inorganic nitrogen and phosphorus.

STUDY SITE

The study was conducted in Wild Hog Creek, an intermittent prairie margin stream in the Nature Conservancy's Tallgrass Prairie Preserve, Osage County, Oklahoma. The geographic center of the 12.7 km² Wild Hog Creek watershed is located at 36°50' latitude and 96°21' longitude. Watershed elevation ranges from 297 m to 331 m. Although agricultural and oil pumping activities are absent in the watershed, the basin is subject to light cattle grazing (ca. 1 ha/head) from mid April to mid July. Average annual precipitation and air temperature for the watershed are 8.7 cm and 13.8° C respectively. Vegetation in the upper basin is dominated by a mixture of big bluestem (*Andropogon gerardii*), little bluestem (*Schizachyrium scoparium*), indian grass (*Sorghastum nutans*) and switch grass (*Panicum virgatum*). Main channel riparian species consist of oak

(*Quercus spp.*), sycamore (*Platanus occidentalis*), willow (*Salix spp.*), ash (*Fraxinus spp.*) and hackberry (*Celtis spp.*)

The Wild Hog Creek (WHC) watershed exhibits a dendritic drainage pattern with a drainage density of 0.46 km/km². Parent geology in the watershed is sedimentary and consists mainly of sandstone and limestone. Rock outcrops are common along the entire length of the stream. The main stem of WHC is third order (Strahler 1975), and has a low gradient (7.6 m/km). Recorded main channel discharge ranged from 6 to 1161 L/s, and averaged 23 L/s during the study.

Channel morphology is characterized by shallow, ephemeral runs in the upper basin, and distinct riffle and pool sequences along the main stem. Stream substrata is poorly sorted and consists of mud, silt, coarse sand, gravel, boulder and exposed bedrock. Water chemistry was monitored monthly at nine sites in the watershed (Fig. 1). Physical and chemical parameters for the study sites during the period of sediment collection are summarized in Table 1. pH and temperature varied little between study areas. Baseflow concentrations of NO₃-N, NH₄-N and SRP were consistently low and exhibited minimal variation between study areas.

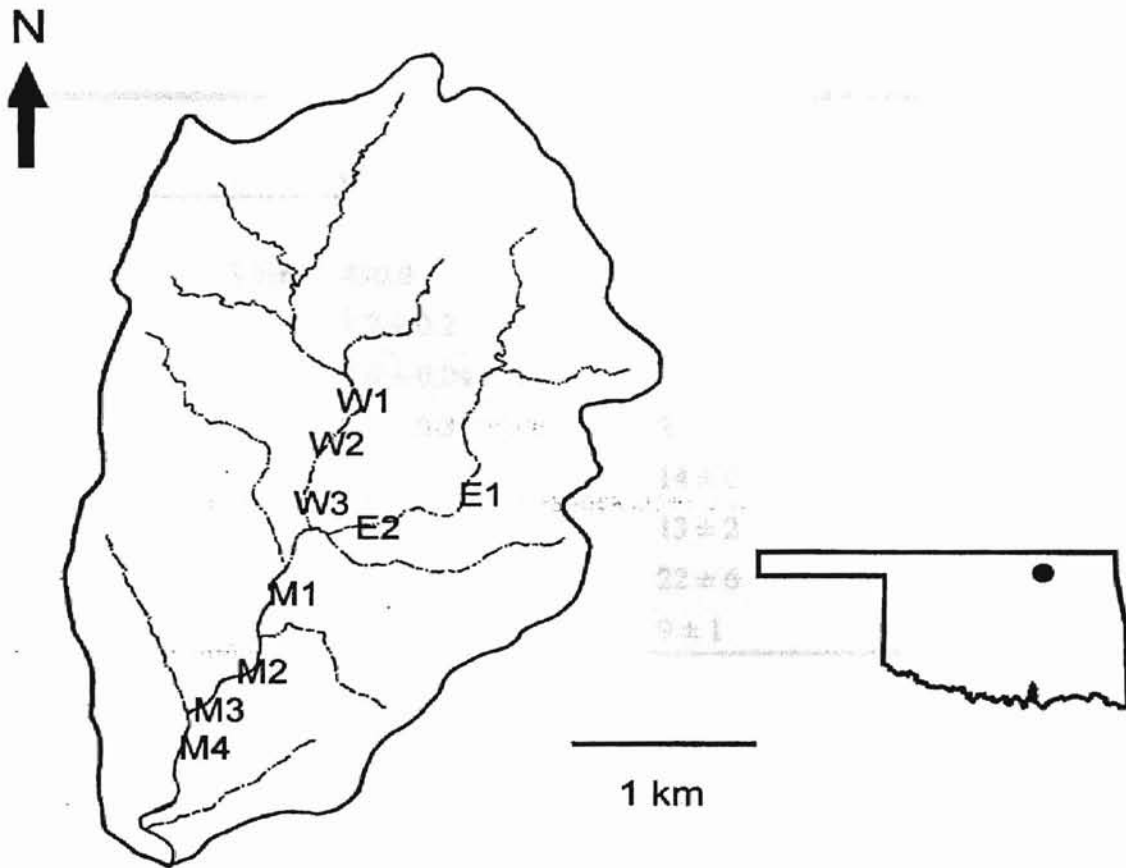


Figure I. Location of study sites within the Wild Hog Creek watershed, Osage County, Oklahoma.

Table I. Physical and chemical characteristics of stream water at study areas in Wild Hog Creek from June to August 1997. Values presented are means of 3 samples (± 1 SE), per month, of specific sites within each area.

	Main Channel (n = 4 sites)	West Branch (n = 3 sites)	East Branch (n = 2 sites)
Temperature ($^{\circ}\text{C}$)	24.5 \pm 0.4	23.8 \pm 0.3	24.5 \pm 0.3
Conductivity ($\mu\text{S}/\text{cm}$)	430.0 \pm 8.4	484.8 \pm 19.9	495.6 \pm 26.8
Turbidity (ftu)	1.7 \pm 0.2	3.5 \pm 0.3	6.2 \pm 0.9
pH	7.9 \pm 0.04	7.9 \pm 0.05	7.8 \pm 0.05
Cl (mg/l)	2.2 \pm 0.3	2.1 \pm 0.08	2.9 \pm 0.2
SO ₄ (mg/l)	10 \pm 0.6	14 \pm 0.9	23 \pm 1.6
NO ₃ -N ($\mu\text{g}/\text{l}$)	17 \pm 3	13 \pm 2	27 \pm 7
NH ₄ -N ($\mu\text{g}/\text{l}$)	11 \pm 3	22 \pm 6	16 \pm 3
SRP ($\mu\text{g}/\text{l}$)	8 \pm 1	9 \pm 1	9 \pm 1

METHODS

Sediment Collection

I collected stream sediments at 9 sites in the WHC watershed to examine nutrient-sediment dynamics in laboratory experiments. Riffles were selected as study areas because of their high potential for surface water-sediment interaction. Sediments were sampled at several different areas within each study site to incorporate local heterogeneity of sediment characteristics. Shallow stream sediments (1-5 cm) were removed from the stream using a trowel, placed in polyethylene bags and stored on ice during transport to the laboratory. Because I was solely interested in physical-chemical and microbial sorption processes, algal biomass on the sediment surface (0-1 cm) was removed prior to sampling. Upon return to the laboratory, all sediment samples were passed through a 4-mm standard sieve to isolate smaller sediment particles. Previous research has shown that smaller size sediments are the most active in nutrient sorption (Klotz 1988), so I used only this fraction (<4-mm) in the laboratory experiments. This collection procedure was used for all sediment analyses.

Nutrient Sorption Experiments

Nutrient sorption indices were determined in the laboratory for ammonium ($\text{NH}_4\text{-N}$) and soluble reactive phosphorus (SRP) using the methods of Bache and Williams (1971) as modified by Meyer (1979) and Klotz (1988). The index is a measure of the uptake potential, or the ability of sediments to sorb a large amount of nutrients (Klotz 1988). The sorption index was determined as:

$$I = \frac{X}{\log C}$$

where X is the amount of nutrient sorbed ($\mu\text{g/g}$ dry sediment) from an initial concentration of $2000 \mu\text{g/L}$ and C is the final nutrient concentration in solution after 1 h (Bache and Williams 1971, Klotz 1988). High values for the index indicate that sediments can remove a large amount of nutrients from solution. To separate biological and physical-chemical sorption processes, both living and autoclaved sediments were used in sorption measurements.

In the laboratory, 20-30 g of wet sediments were placed in 250 mL flasks and 100 mL of $2000 \mu\text{g/L}$ of $\text{NH}_4\text{-N}$ -or PO_4 -enriched stream water was added. Flasks were secured on a shaker table and agitated at low speed for 10 sec every 15 min for 1 h. After 1 h, 15 mL of solution was removed from each flask and placed in a 15 mL polystyrene centrifuge tube. The samples were centrifuged at 3500 rpm for 5 min using a Scientific Products model HN-S centrifuge. The supernatant of each sample was filtered ($0.7 \mu\text{m}$ Whatman GF/F filter) and analyzed for $\text{NH}_4\text{-N}$ or SRP. Phosphate concentrations were measured as soluble reactive phosphorus (SRP) using the methods of Murphy and Riley (1962) and $\text{NH}_4\text{-N}$ concentrations were determined using the phenol-hypochlorite method (Soloranzo 1969). Sediments in the flasks were transferred to aluminum pans and dried at 70°C for 48 h, at which time dry masses were measured. Sorption index measurements were replicated three times for both living and killed sediments. Results were analyzed by a two-way analysis of variance using least squares means; sampling site and sediment state

(living or killed) were used as independent variables (Wilkinson 1990). Sorption data were normally distributed and thus not transformed before analysis.

Factors affecting sorption

I examined three sediment characteristics: exchangeable (loosely sorbed) nutrients, organic content, and texture, to determine if there were correlations between these abiotic variables and nutrient sorption. Surface water concentrations of $\text{NH}_4\text{-N}$ and SRP were also measured during sediment collection to investigate a potential relationship between ambient nutrient concentration and sorption.

Sediment exchangeable $\text{NH}_4\text{-N}$ was measured using the methods of Richey et al. (1985). In the laboratory, 100 mL of 2 M KCl was added to 250 mL flasks containing 10-20 g of wet sediments. Flasks were secured on a shaker table and agitated at low speed for 30 min. Concentration of $\text{NH}_4\text{-N}$ in solution was determined following the procedures described above. Sediment exchangeable SRP was quantified using the methods of Ruttenberg (1992); 100 mL of 1 M MgCl was added to 250 mL flasks containing 10-20 g of wet sediments, and processed as described above. Quantity of sediment exchangeable $\text{NH}_4\text{-N}$ and SRP is expressed as μg nutrient/g sediment dry mass. Sediment exchangeable $\text{NH}_4\text{-N}$ and SRP were measured in triplicate. Organic content of sediment samples was calculated as mass loss following ignition at 550° C and are expressed as percent organic matter (Hauer and Lamberti 1996). Particle size classes were determined after drying sediments for 48 h (70°C). Sediments were passed through a series of standard sieves (> 2 mm, >1 mm, >0.5 mm, >0.35 mm) and each size fraction was weighed to the nearest

0.01 g. Proportions of the different size classes were expressed as a percent of the total mass of the sample. Sediment size classes were simplified to > 1.0 mm, > 0.5 mm, and < 0.5 mm for statistical analyses. The relationship between these independent variables and nutrient sorption was determined using stepwise multiple linear regression (Sokal and Roth 1995).

Net Nitrification

Net nitrification was determined for main channel sediments (sites M1-M4) on June 25 and 15 August 1997 using the methods described by Holmes et al. (1994). 100 mL of distilled water was added to 250 mL flasks containing 120-130 g of wet sediments. Net nitrification was measured as increase in $\text{NO}_3\text{-N}$ concentration between an initial (10 min) and final sample (24 h). Nitrate concentration in solution was determined by ion chromatography (Dionex DX-110). Sediments within each flask were placed in aluminum pans and stored at 70° C for 48 h, at which time sediment dry masses were determined. Nitrification rates were measured in triplicate for each site and expressed as $\mu\text{g NO}_3\text{-N/ g sediment dry mass/ h}$.

Field Experiments

To investigate nutrient-sediment interactions under field conditions, I constructed an experimental system of artificial stream channels. Field experiments were conducted on 27 September and 4 October 1997. On 27 September, sediments were collected, using previously described methods, and placed in the channels the day of the experiment. Upon

completion of that experiment, channels were filled with fresh sediments and submerged in the stream until 4 October. The experimental system consisted of two principal components: a central polyethylene tank containing stream water and eight artificial stream channels. Volume of water in the central tank was kept constant by pumping water from the stream to the tank using a battery powered pump. Stream water from the central tank was released through adjustable manifolds and delivered to the channels through rubber hoses. Plastic flat-bottomed rain gutters (100 cm x 11.2 cm x 6.7 cm) were used as the artificial stream channels. Approximately 2500 cm³ of unseived stream sediments lined each channel bottom. Stream water discharge in the artificial channels averaged 0.01 L/s during the two dates. I used fluorescein dye injections to determine residence time, or the amount of time a parcel of stream water had to interact with the sediments, in each channel. On 27 September residence time in the channels ranged from 27 s to 53 s and averaged 33 s. Residence time was not measured on 4 October.

Four of the channels were designated as control (no nutrient addition) replicates and the remaining channels served as treatment (NH₄-N and SRP addition) replicates. Four 11.4 L plastic buckets containing 10 L of NH₄-N and SRP enriched stream water were positioned above and behind the four treatment channels. Channels were covered to prevent solar input and subsequent autotrophic uptake of nutrients. Nutrient enriched stream water was delivered at 0.03 mL/min to treatment channels through a tube (1 cm OD) inserted in the rubber hose. My goal was to increase background nutrient concentrations in the treatment channels to 50 µg/L SRP and 100 µg/L NH₄-N on 27 September and 100 µg/L SRP and 200 µg/L NH₄-N on 4 October. Nutrient delivery to the

channels was variable and showed a gradual decrease on 27 September. As a result, sediments within treatment channels did not receive a consistent level of nutrient input during the experiment. Variation in nutrient delivery over time prevented me from investigating temporal dynamics of retention. Instead, I measured bulk retention of nutrients for the entire experimental period on each date.

I allowed unenriched stream water to pass through artificial channels for 30 min prior to starting the experiment. This pre-experimental rinse attempted to produce water chemistry uniformity between channels. Water was collected at the top and bottom of each channel. Samples were taken before application of the treatment (nutrient addition), and at 30 min, 120 min, and 180 min during the experiment. Stream water was removed from the top of the channel with a pre-rinsed 60 mL plastic syringe and injected into a 50 mL polyethylene centrifuge tube and a 25 mL $\text{NH}_4\text{-N}$ vial; each channel had a separate syringe. Outflow samples were collected by filling acid-washed 125-mL polyethylene bottles and 25-mL $\text{NH}_4\text{-N}$ vials as water exited the channel. Samples were stored on ice during transport to the laboratory where they were then filtered ($0.7\mu\text{m}$ Whatman GF/F filter) and analyzed for $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and SRP using the methods described above.

Bulk retention was calculated as the difference in nutrient flux between upstream and downstream ends of the channels. Bulk nutrient input was calculated as the product of total volume of stream water entering the channels and average upstream nutrient concentration, and was expressed as mg of nutrient. Because I had measured upstream nutrient concentration five times in each channel during the experimental period, I used a weighted average to approximate upstream nutrient concentration over time. Bulk

nutrient output was determined in the same manner. Values of bulk nutrient input and bulk nutrient output were compared at each sampling interval using a paired t-test.

The rate of $\text{NH}_4\text{-N}$ oxidation to $\text{NO}_3\text{-N}$, or net nitrification, was measured on both dates in treatment and control channels. Net nitrification was calculated by subtracting upstream $\text{NO}_3\text{-N}$ concentration from downstream $\text{NO}_3\text{-N}$ concentration for each channel at every sampling interval. A positive value for this calculation indicated nitrate production within channel sediments. Net nitrification rates were expressed as $\mu\text{g NO}_3\text{-N/g sediment/h}$.

Upon completion of the experiments, sediments in each channel were transferred to a clean polyethylene bag and stored on ice until return to the laboratory, at which point they were frozen. The quantity of exchangeable $\text{NH}_4\text{-N}$ and SRP on channel sediments were determined on thawed samples, using methods described earlier, for each channel on both dates.

RESULTS

Sorption Experiments

WHC sediments reduced concentrations of $\text{NH}_4\text{-N}$ and SRP in enriched stream water under laboratory conditions. Both living and killed sediments were effective in nutrient uptake. Composite sorption (living + killed) of SRP ($\bar{x} = 27.1$, $\text{SE} = 1.02$, $n = 18$) was significantly higher than $\text{NH}_4\text{-N}$ ($\bar{x} = 14.4$, $\text{SE} = 1.65$, $n = 18$) for all study sites (paired t-test, $p < 0.001$).

SRP uptake by living sediments was greater than killed sediments ($p < 0.005$; Fig. 2). Location of study site also affected composite SRP sorption ($p < 0.02$; Table 2). Sorption of SRP was greatest in east branch sediments and least in the west branch (Tukeys HSD, $p < 0.02$, Fig. 2). Pairwise multiple comparisons (Tukeys HSD) showed no difference in SRP sorption between main channel and west branch sediments ($p > 0.1$). Values for the abiotic variables used in multiple regression analyses are listed in Table 3. The proportion of sediment particles < 0.5 mm was positively correlated with SRP sorption by living sediments ($r^2 = 0.78$). SRP sorption by killed sediments was correlated with surface water SRP concentration, exchangeable $\text{NH}_4\text{-N}$ and exchangeable SRP ($r^2 = 0.21$, $r^2 = 0.14$, $r^2 = 0.25$ respectively, Table 4).

$\text{NH}_4\text{-N}$ uptake in living sediments exceeded uptake by killed sediments at each study site (Table 2, $p < 0.02$). $\text{NH}_4\text{-N}$ sorption varied between sites, but a site main effect was only marginally significant (Fig. 3, Table 2, $p = 0.057$). The absence of a significant interaction between state (living or killed) and site (Table 4), permitted interpretation of a site main effect. $\text{NH}_4\text{-N}$ sorption by living and killed sediments showed the same

Table II. Results of two-way ANOVA for sorption indices. The dependent variable is sorption index and site (main, west and east) and state (living versus killed) are independent factors.

Sorption Index	Factor	Error mean square	F statistic	P value
Ammonium	Site	100.25	3.67	0.057
	State	224.45	8.22	0.014
	Site * State	9.03	0.33	0.725
Phosphorus	Site	45.57	5.74	0.018
	State	120.59	15.19	0.002
	Site * State	17.22	2.17	0.157

Table III. Values for several environmental factors used in multiple linear regression analyses of sorption indices. Values listed are means \pm 1 SE.

Factor	Study Area		
	Main Channel (n = 4)	West Branch (n = 3)	East Branch (n = 2)
Organic Matter (%)	3.2 \pm 0.3	3.3 \pm 0.1	5.4 \pm 0
Exchangeable NH ₄ -N (μ g/g sed)	8.4 \pm 2.5	11.7 \pm 0.6	26.4 \pm 2.4
Surface NH ₄ -N (μ g/l)	16.5 \pm 3.3	23.7 \pm 1.2	19 \pm 0.7
Exchangeable SRP (μ g/g sed)	1.9 \pm 0.4	0.8 \pm 0.2	0.5 \pm 0.1
Surface SRP (μ g/l)	5.0 \pm 1.2	6.7 \pm 1.2	13.5 \pm 0.4
Sediment particles > 1.0 mm (%)	80.0 \pm 5.3	80.7 \pm 3.5	63.9 \pm 1.2
Sediment particles > 0.5 mm (%)	9.8 \pm 2.6	10.3 \pm 2.1	17.3 \pm 0.3
Sediment particles < 0.5 mm (%)	10.3 \pm 2.8	9.0 \pm 2.1	18.8 \pm 0.9

Table IV. Results of multiple linear regression analyses of ammonium (ASI) and phosphorus (PSI) sorption indices vs. eight independent variables. Variables which were not significant predictors of sorption ($p > 0.15$) are omitted.

Independent variable	Sorption Index			
	ASI living	ASI killed	PSI living	PSI killed
Surface water NH ₄ -N	0.30	0.09		
Exchangeable NH ₄ -N				0.14
Surface water SRP				0.21
Exchangeable SRP				0.25
Sediment size class <0.05 mm			0.78	

Figure II. Phosphorus sorption indices in Wild Hog Creek. Values are least squares means (+1 SE).

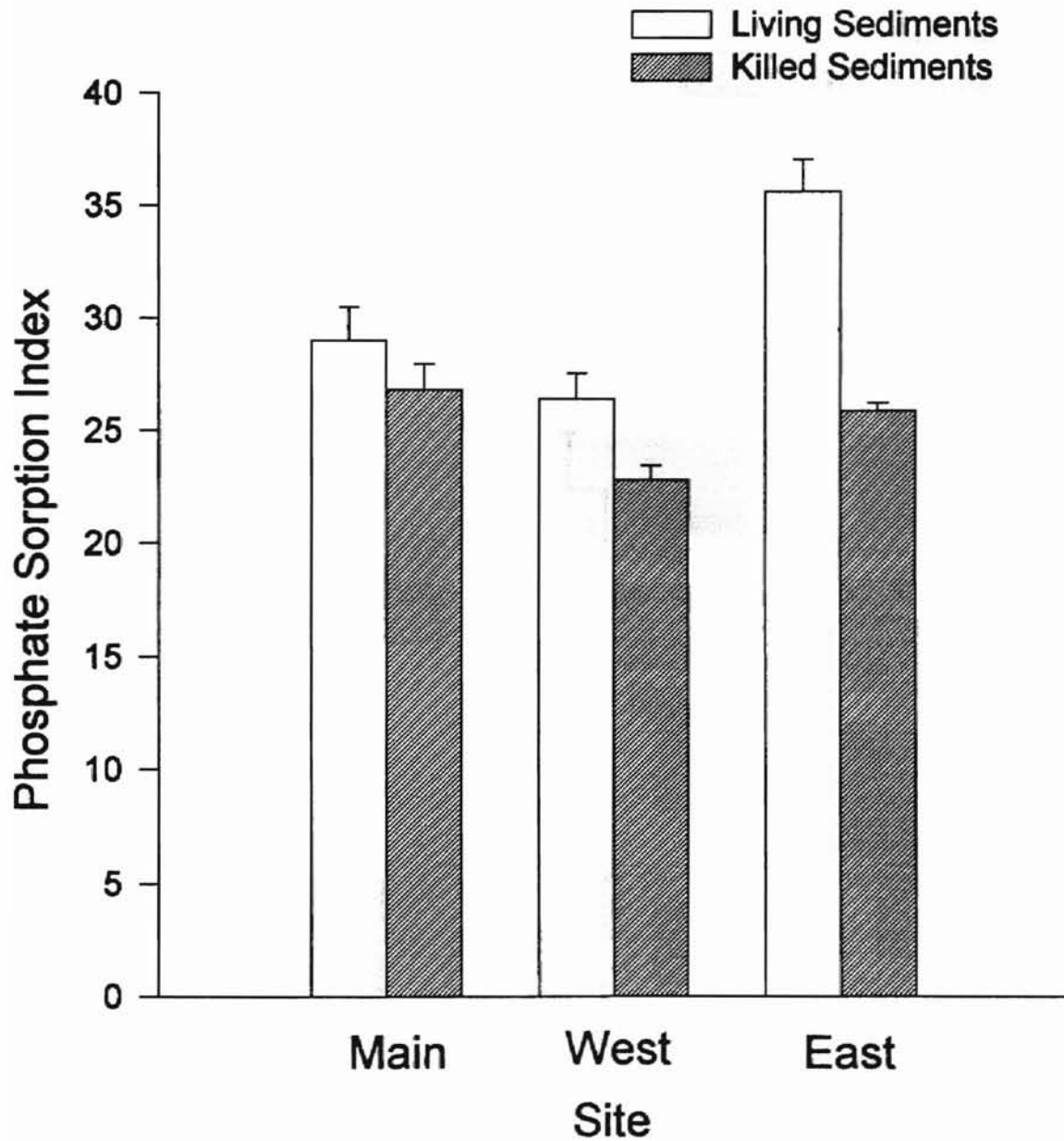
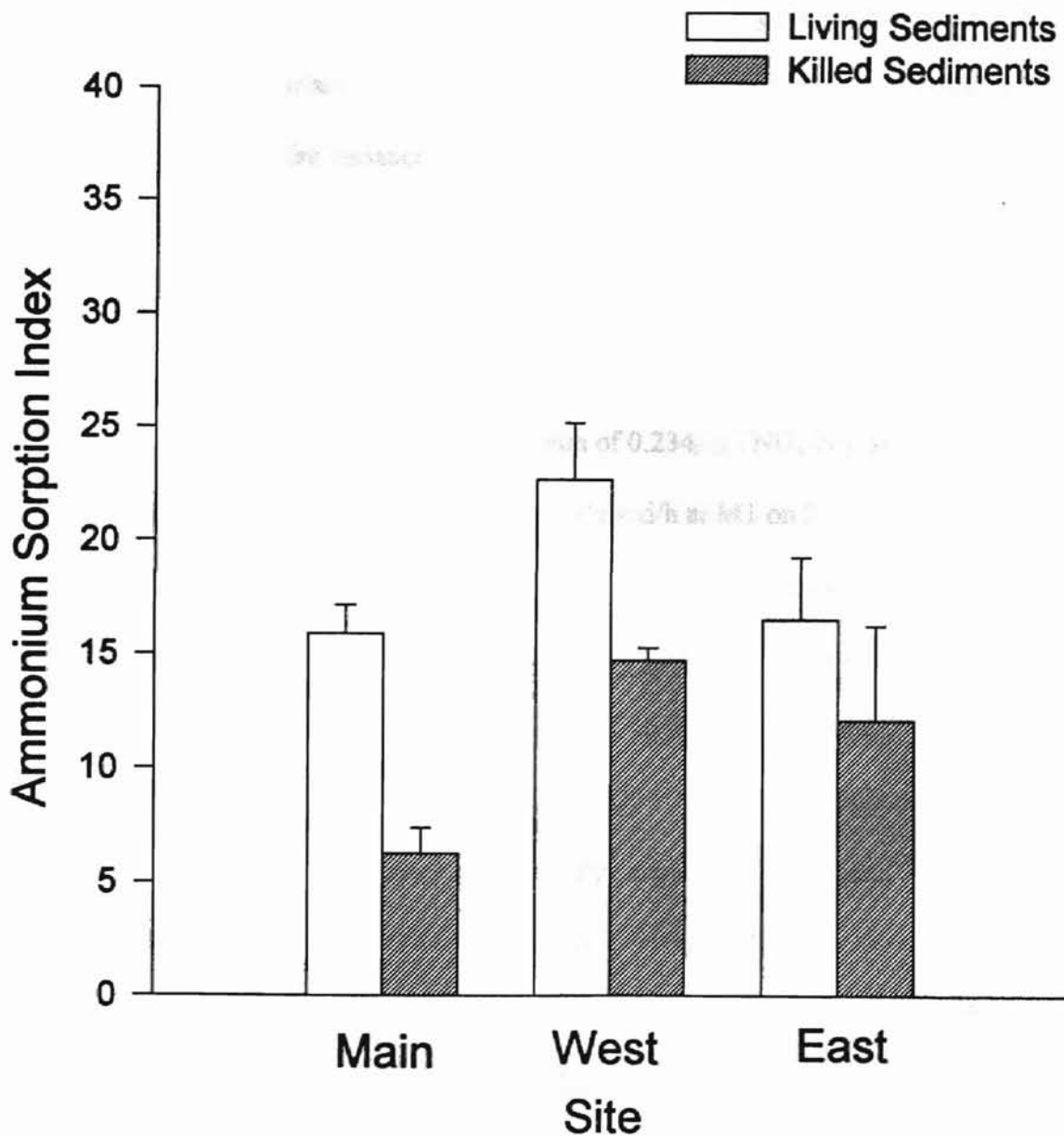


Figure III. Ammonium sorption indices in Wild Hog Creek. Values are least squares means (+1 SE).



site-to-site differences. $\text{NH}_4\text{-N}$ sorption by west branch living sediments was significantly greater than by living sediments at both main channel and east branch sites (Tukey's HSD, $p < 0.05$). Sorption by east branch sediments was not significantly different from main channel or west branch sediments (Fig. 3).

Although surface water concentration of $\text{NH}_4\text{-N}$ during sediment collection was the only independent variable correlated with $\text{NH}_4\text{-N}$ sorption (Table 4), it provided little explanatory power for the variance observed in living ($r^2 = 0.30$) and killed sediments ($r^2 = 0.09$).

Net Nitrification

Net nitrification rate reached a maximum of $0.234\mu\text{g/l NO}_3\text{-N/g sed/h}$ at M4 on 14 August and had a minimum of $0.004\mu\text{g/l NO}_3\text{-N/g sed/h}$ at M1 on 25 June (Fig. 4). Main channel net nitrification rates measured on 25 June differed significantly from rates measured on 14 August ($p < 0.001$; Table 5). There was also variation between sites on each sampling date ($p < 0.001$; Table 5). Nitrification rates at M1 and M3 were greater than rates at M2 and M4 on 25 June (Tukeys HSD, $p < 0.001$, both comparisons). Nitrification rates at study sites were also spatially variable on 14 August (Table 5). Pairwise comparisons (Tukeys HSD, $p < 0.05$) of sites on 14 August showed nitrification rate at M1 to be significantly less than rates measured at M2, M3 and M4. Nitrification rates at M2 and M3 on this date were not significantly different from each other (Tukeys HSD, $p > 0.5$), but were both less than the rate measured at M4 ($p < 0.002$). There was an inverse relationship between exchangeable $\text{NH}_4\text{-N}$ and net nitrification on both 25 June

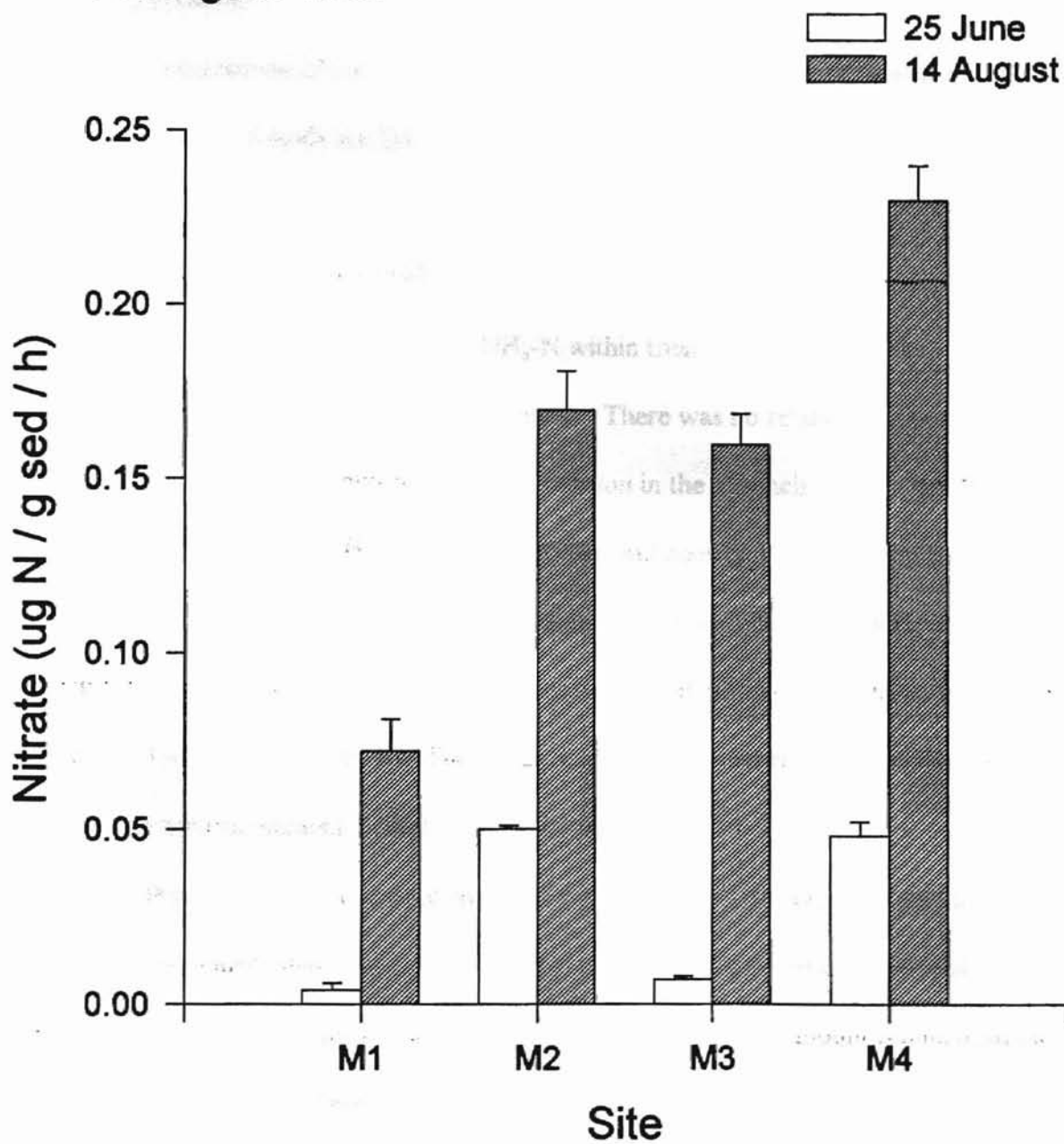
Table V. Results of two-way ANOVA for net nitrification rates measured on 25 June and 14 August 1997.

Source of variation	Sum of squares	Degrees of freedom	Mean square	F-ratio	P value
Date	0.104	1	0.104	627.69	0.001
Site	0.034	3	0.011	68.29	0.001
Date * Site	0.011	3	0.004	22.98	0.001
Error	0.003	16	0.000		

Table VI. Values (± 1 SE) of net nitrification and exchangeable $\text{NH}_4\text{-N}$ from main channel sediments collected on 25 June and 14 August 1997.

Site	M1	M2	M3	M4
25 June 1997				
Nitrification ($\mu\text{g N/ g sed/ h}$)	0.004 ± 0.002	0.050 ± 0.001	0.007 ± 0.001	0.048 ± 0.004
Exchang. $\text{NH}_4\text{-N}$ ($\mu\text{g/ g sed}$)	13.4 ± 1.1	2.7 ± 0.8	13.0 ± 2.4	4.4 ± 1.2
14 August 1997				
Nitrification ($\mu\text{g N/ g sed/ h}$)	0.072 ± 0.009	0.170 ± 0.011	0.160 ± 0.009	0.230 ± 0.010
Exchang. $\text{NH}_4\text{-N}$ ($\mu\text{g/ g sed}$)	29.4 ± 2.6	3.7 ± 1.4	3.3 ± 0.9	1.9 ± 1.1

Figure IV. Net nitrification rates (+1 SE) for main channel sediments measured on 25 June and 14 August 1997



and 14 August (Table 6). During 25 June, the site with the highest rate of net nitrification had the lowest amount of exchangeable $\text{NH}_4\text{-N}$; the same pattern was observed on 14 August.

Field Experiments

Concentrations of nutrients delivered to treatment and control channels during both experimental periods are listed in Tables 7 and 8.

Experiment I: 27 September 1997

There was an overall release of $\text{NH}_4\text{-N}$ within treatment channels, while control channels exhibited retention of $\text{NH}_4\text{-N}$ (Table 9). There was no relationship between $\text{NH}_4\text{-N}$ retention and upstream $\text{NH}_4\text{-N}$ concentration in the channels on this date ($r^2 = 0.24$, $p > 0.1$). Exchangeable $\text{NH}_4\text{-N}$ on treatment and control sediments was 5.7 (0.5 SE) mg and 5.1 (0.8 SE) mg respectively; these values were not significantly different ($p > 0.5$; Fig. 5). Interestingly, similar amounts of exchangeable $\text{NH}_4\text{-N}$ were present in treatment and control sediments, although treatment sediments showed no retention of $\text{NH}_4\text{-N}$ whereas control sediments retained 1.2 (0.1 SE) mg of $\text{NH}_4\text{-N}$.

SRP was retained by both control and treatment sediments on this date. Retention of SRP in the control channels was greater than retention in the treatment channels ($t = 2.98$, $df = 9$, $p < 0.02$, Table 9). Retention of SRP was inversely related to upstream SRP concentration in both treatment and control channels ($r^2 = -0.53$, $p < 0.02$; Fig. 6) during this experiment. Exchangeable SRP extracted from treatment and control sediments were

Table VII. Upstream nutrient concentration for control and treatment channels during the experiment on 27 September 1997. Values presented are means of the four channels (± 1 SE).

Time	Control (n=4)		Treatment (n=4)	
	SRP ($\mu\text{g/l}$)	$\text{NH}_4\text{-N}$ ($\mu\text{g/l}$)	SRP ($\mu\text{g/l}$)	$\text{NH}_4\text{-N}$ ($\mu\text{g/l}$)
Background	16.3 \pm 2.2	25.5 \pm 6.7	13 \pm 0	11.8 \pm 4.3
15 min	14.5 \pm 0.4	19.8 \pm 6.4	63.5 \pm 17.1	146.3 \pm 37.1
1 h	14.0 \pm 0.5	7.0 \pm 5.2	48.3 \pm 11.9	124.8 \pm 44.1
2 h	18.0 \pm 1.7	10.3 \pm 8.9	32.5 \pm 2.8	47.8 \pm 9.0
3 h	17.0 \pm 0	10.3 \pm 1.2	25.8 \pm 2.0	34.8 \pm 3.9

Table VIII. Upstream nutrient concentration for control and treatment channels during the experiment on 4 October 1997. Values presented are means of the four channels (± 1 SE).

Time	Control (n=4)		Treatment (n=4)	
	SRP ($\mu\text{g/l}$)	$\text{NH}_4\text{-N}$ ($\mu\text{g/l}$)	SRP ($\mu\text{g/l}$)	$\text{NH}_4\text{-N}$ ($\mu\text{g/l}$)
Background	13.8 \pm 1.3	3.5 \pm 0.9	14.5 \pm 0.8	2.5 \pm 1.0
15 min	14.0 \pm 0.9	1.8 \pm 0.6	102.0 \pm 9.1	194.3 \pm 28.3
1 h	17.0 \pm 0.7	16.8 \pm 5.5	89.0 \pm 6.8	191.3 \pm 22.2
2 h	15.0 \pm 0.7	14.0 \pm 6.0	123.3 \pm 12.5	252.0 \pm 23.5
3 h	15.0 \pm 1.2	10.0 \pm 1.7	92.3 \pm 13.2	208.5 \pm 29.5

Table IX. Bulk retention of SRP and $\text{NH}_4\text{-N}$ by benthic sediments in experimental channels on 27 September 1997. Values presented are means ($n=5$) \pm 1 SE.

Nutrient	Input flux (mg)	Output flux (mg)	Retention (mg)	Exch. nutrients ($\mu\text{g/g}$ sediment)
SRP				
Treatment	4.5 ± 0.6	3.6 ± 0.6	0.9 ± 0.1	1.1 ± 0
Control	2.6 ± 0.3	1.2 ± 0.2	1.4 ± 0.1	1.3 ± 0.3
$\text{NH}_4\text{-N}$				
Treatment	8.8 ± 1.7	8.9 ± 1.4	-0.1 ± 0.6	5.7 ± 0.5
Control	2.3 ± 0.2	1.1 ± 0.3	1.2 ± 0.1	5.1 ± 0.8

1.3 (0.3 SE) mg and 1.1 (0 SE) mg respectively. The amount of exchangeable SRP on treatment sediment did not significantly differ from control sediments ($p > 0.3$, Fig. 5). Exchangeable SRP removed from control sediments was slightly less than the amount of SRP retained, whereas treatment sediments had slightly greater amount of exchangeable SRP relative to retained SRP (Table 9).

Net nitrification rate in control channels was significantly greater than treatment channels ($p < 0.001$, t-test, Fig. 7). Net nitrification was not limited by availability of $\text{NH}_4\text{-N}$, as there was no relationship between sorbed $\text{NH}_4\text{-N}$ and net nitrification rate (simple linear correlation, $p > 0.6$ for control and treatment).

Experiment II: 4 October 1997

Retention of $\text{NH}_4\text{-N}$ and SRP was observed in both treatment and control channels on this date. Retention of $\text{NH}_4\text{-N}$ in treatment channels was significantly greater than retention in control channels ($t = 2.77$, $df = 9$, $p < 0.04$; Table 10). Upstream $\text{NH}_4\text{-N}$ concentration was positively correlated with net $\text{NH}_4\text{-N}$ retention during this experimental period ($p < 0.01$ $r^2 = 0.61$, Fig. 8). There was no significant difference in exchangeable $\text{NH}_4\text{-N}$ between treatment and control channels ($p > 0.1$; Fig. 6). Quantities of exchangeable $\text{NH}_4\text{-N}$ on channel sediments were 2.5 (0.1 SE) mg and 2.1 (0.1 SE) mg for treatment and control channels respectively. The amount of exchangeable $\text{NH}_4\text{-N}$ on treatment and control sediments was considerably greater than the amount retained (Table 10).

Retention of SRP in treatment channels exceeded retention in control channels

Figure V. Exchangeable SRP and NH₄-N (+1 SE) extracted from channel sediments on 27 September and 4 October 1997.

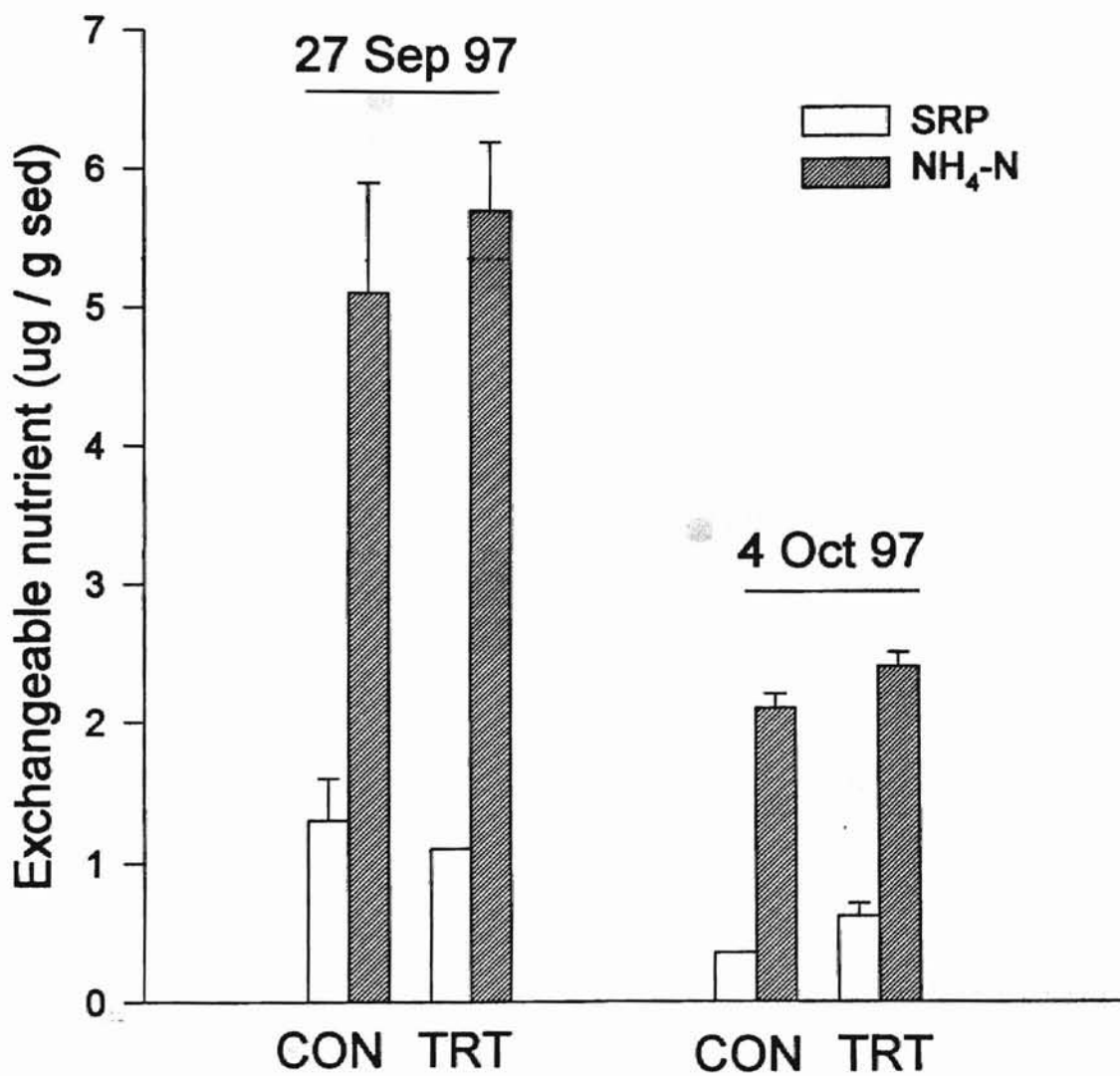


Figure VI. SRP retention versus upstream SRP concentration in experimental channels on 27 September 1997.

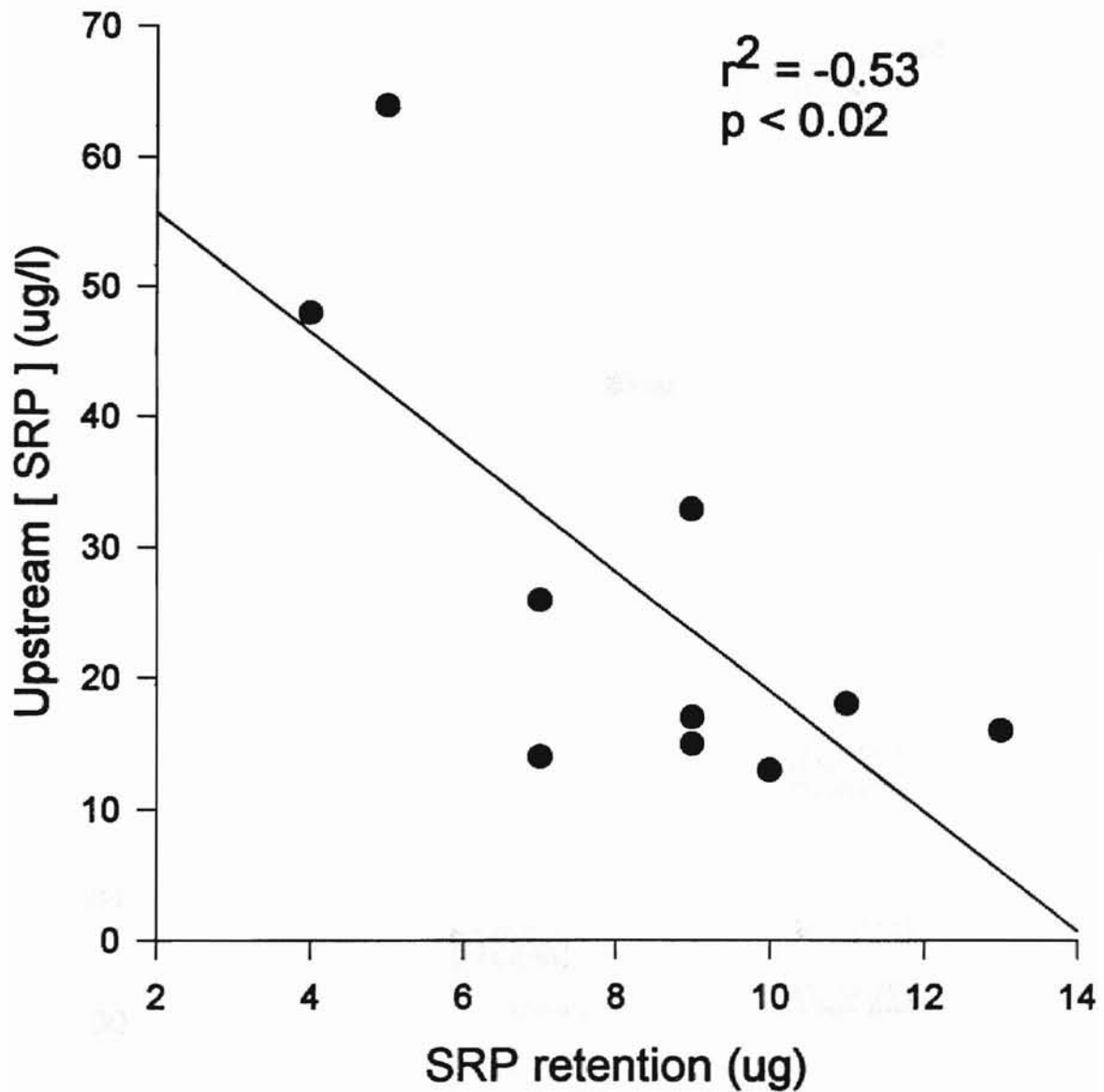


Figure VII

Figure VII. Net nitrification (+1 SE) in experimental channels on 27 September and 4 October 1997.

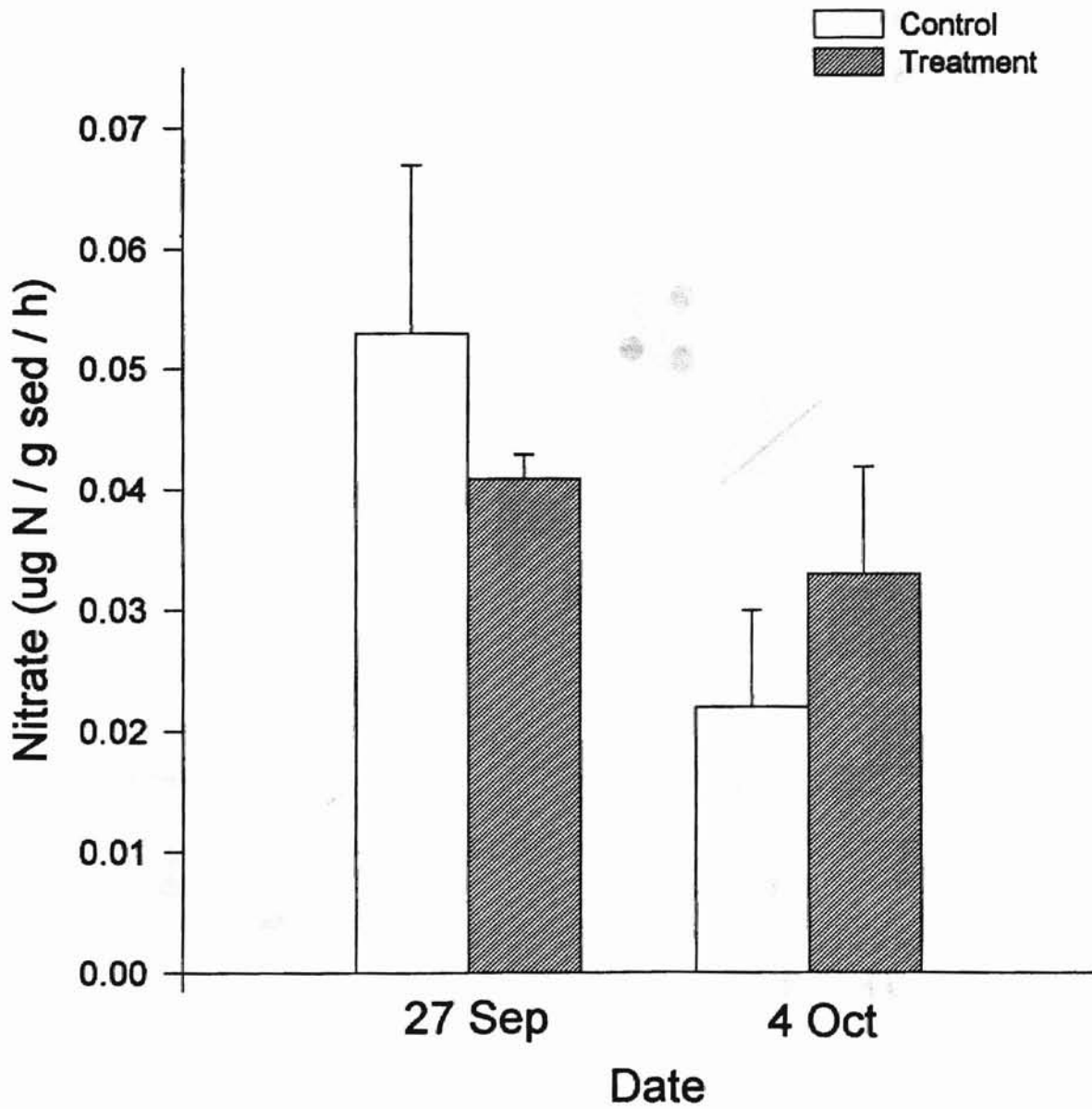


Figure VIII. $\text{NH}_4\text{-N}$ retention versus upstream $\text{NH}_4\text{-N}$ concentration in experimental channels on 4 October 1997.

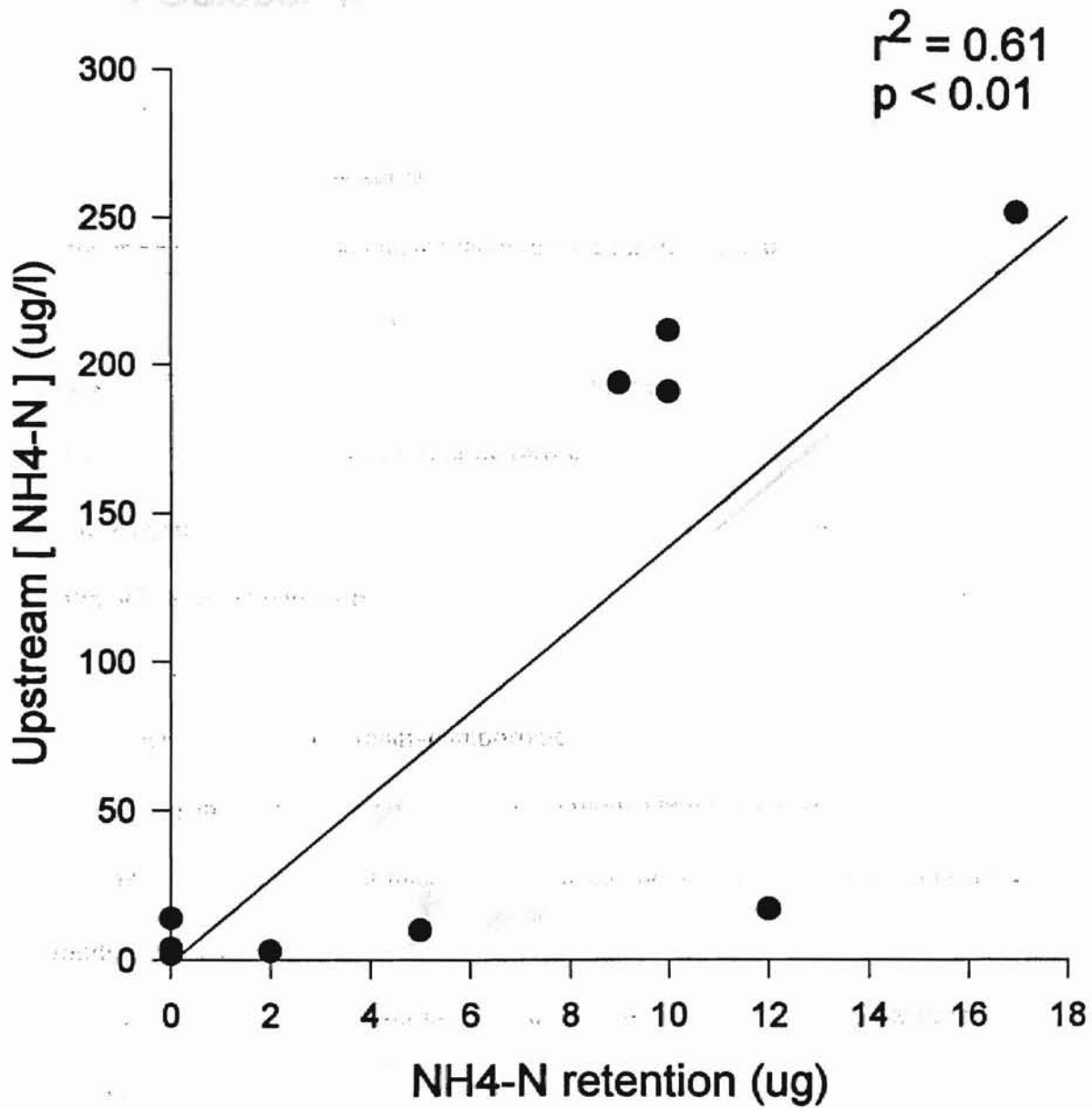
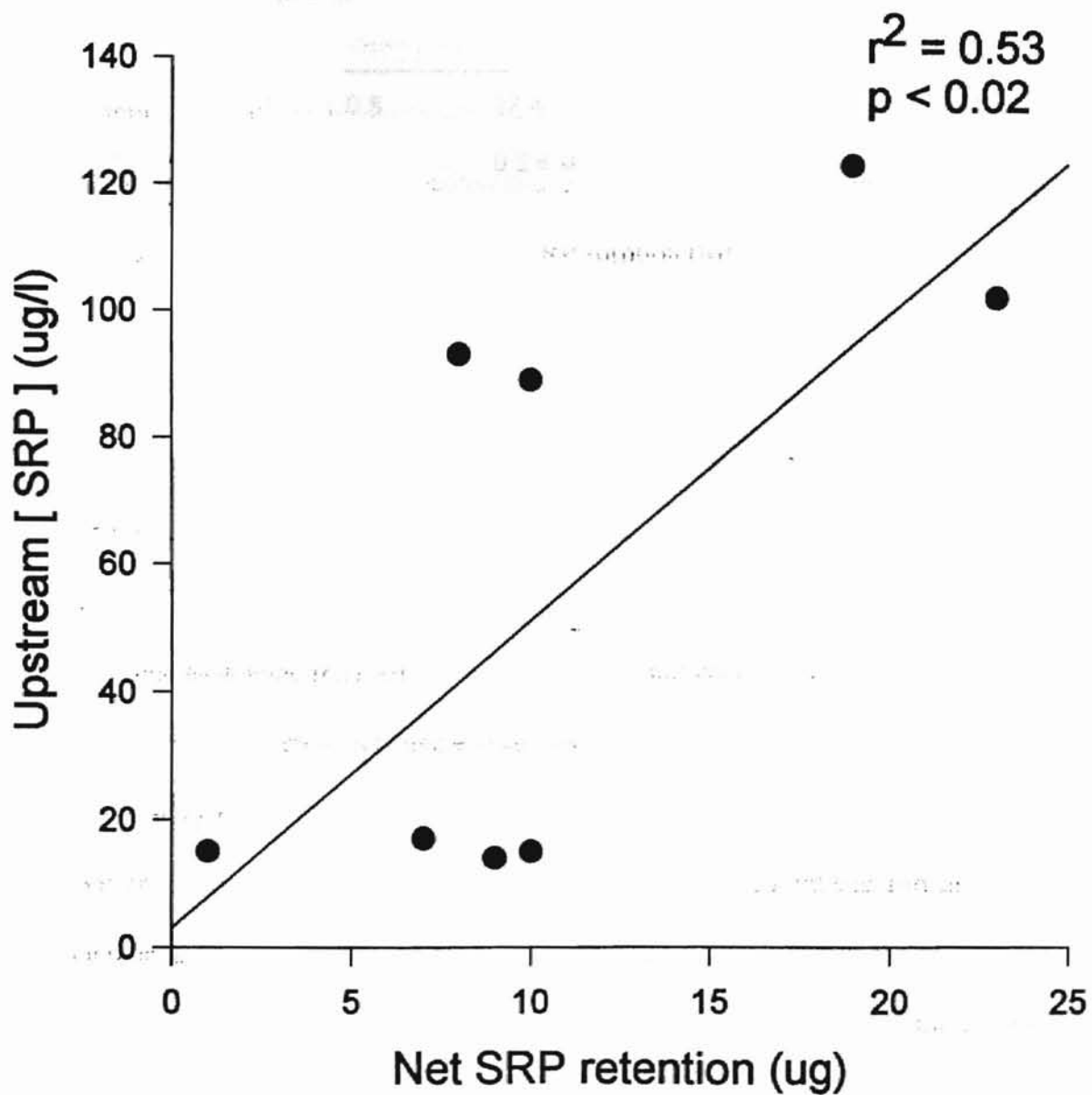


Figure IX. SRP retention versus upstream SRP concentration in experimental channels on 4 October 1997.



during the experiment ($t = 2.56$, $df = 9$, $p < 0.04$; Table 10). In contrast to the 27 September experiment, SRP retention was positively correlated with upstream SRP concentration in the channels on this date ($p < 0.02$, $r^2 = 0.53$; Fig. 9). Treatment channel sediments had a significantly greater amount of exchangeable SRP relative to the controls ($p < 0.03$; Fig. 6). 0.6 (0.09 SE) mg and 0.4 (0 SE) mg of SRP were extracted from treatment and control sediments respectively (Table 10).

Treatment channels exhibited a significantly higher rate of net nitrification than control channels (t-test, $p < 0.006$). Similar to experiment 1, $\text{NH}_4\text{-N}$ availability did not limit net nitrification in either treatment or control channel sediments (simple linear correlation, $p > 0.2$).

DISCUSSION

Laboratory Experiments

The results from the laboratory sorption experiments demonstrate that benthic sediments in WHC are active in removing $\text{NH}_4\text{-N}$ and SRP from the stream through biological and physical-chemical sorption processes. As surface water infiltrates the shallow stream sediments, both $\text{NH}_4\text{-N}$ and SRP are removed from the stream by sediment sorption processes. Once sorbed, these nutrients may be temporarily retained or transformed, and consequently affect stream water nutrient concentrations.

SRP uptake by living sediments results from both biological and physical-chemical sorption processes, whereas physical-chemical processes are solely responsible for SRP uptake in killed sediments. Although living sediments exhibited the greatest SRP removal,

biological processes appeared to be a minor component of SRP sorption (Fig. 2).

Physical-chemical processes dominated SRP uptake and were responsible for nearly all of the SRP removed from solution. Abiotic uptake constituted 92%, 86% and 73% of the total SRP sorption at main, west and east sites respectively. Results from previous studies indicate that the importance of sediment microorganisms in SRP sorption is unclear.

Meyer (1979) found little difference in SRP sorption between autoclaved (killed) and untreated (living) sediments, suggesting biological uptake was negligible. Similarly, Klotz (1985) found SRP uptake by agricultural stream sediments to be largely abiotic. Some reports of SRP sorption in sediments fail to even consider a biological influence, and focus solely on physical-chemical mechanisms of SRP sorption (McCallister and Logan 1978, Green et al. 1978). On the other hand, Munn and Meyer (1990) found biological uptake of SRP within stream sediments primarily responsible for maintaining low SRP levels in the streams examined in their study. Likewise, the laboratory experiments of Gregory (1978) and the field experiments of Elwood et al. (1981) illustrated the importance of biological uptake of SRP.

When evaluating the relative importance of biotic versus abiotic sorption processes, it is important to recognize what methods were used to reach conclusions. Elwood et al. (1981) state that microbial uptake can be underestimated if inappropriate methods are employed. If the concentration of SRP used in sorption experiments is considerably greater than ambient levels found in the stream from which the sediments were collected, the capacity for microbial uptake could be exceeded and abiotic processes would appear to be more important in SRP sorption (Elwood et al. 1981). That is, SRP

enriched solutions may saturate the microbial community, thus negatively affecting the uptake ability of the microorganisms. For instance, in Bear Brook, New Hampshire, Meyer (1979) found microbial uptake to be unimportant in SRP sorption during experimental delivery of SRP enriched stream water to benthic sediments. However, this method likely underestimated biological uptake and consequently overestimated abiotic sorption processes (Elwood et al. 1981).

Interestingly, my results show that biological processes were active, albeit relatively unimportant, in SRP sorption despite the fact that the SRP concentrations used in sorption experiments were approximately 250 X greater than ambient SRP levels in WHC. The fact that microbial uptake was observed at these extremely elevated levels suggests that sediment microorganisms in WHC have an unusually high SRP uptake capacity.

SRP sorption by living sediments was strongly correlated with the proportion of smaller sediment particles (Table 4). The laboratory sorption experiments indicated SRP uptake in living sediments was largely abiotic. The relationship between SRP sorption and sediment size is likely due to the greater surface area provided by small sediment particles. In other words, small sediment particles would have a greater number of SRP binding sites relative to larger sediment particles. My results show that SRP sorption was greatest in the east branch, where the proportion of smaller sediment particles is the greatest. Meyer (1979) and Klotz (1988) also found small sediment particles to have the greatest SRP sorption ability.

Although microbial uptake of SRP was found to be relatively unimportant in WHC

sediments, this process was most active in the east branch sediments. Perhaps the greater surface area provided by small sediment particles promoted the development of an active microbial community capable of SRP uptake. It is interesting to note that uptake of SRP by living sediments was greatest in east branch sediments, where organic content and exchangeable $\text{NH}_4\text{-N}$ were highest and exchangeable SRP was lowest (Table 3). It is possible that the greater SRP uptake measured in these sediments resulted from an increased demand for SRP during bacterial decomposition of sediment organic matter. The large amounts of exchangeable $\text{NH}_4\text{-N}$ associated with these sediments support the idea of organic matter decomposition. Although a relationship between exchangeable $\text{NH}_4\text{-N}$, exchangeable SRP, organic matter and SRP sorption by living sediments was not found in my study, further examination of those variables and SRP sorption would certainly be useful.

Despite evidence for the role of biota in SRP sorption, many investigators contend that abiotic, or physical-chemical, processes are primarily responsible for SRP sorption in stream sediments (Green et al. 1978, Klotz 1988). This appears to be the case in the benthic sediments of WHC. Abiotic sorption processes in my study were responsible for the majority of SRP uptake from solution (Fig. 2). SRP sorption by killed sediments was correlated with three independent variables: exchangeable $\text{NH}_4\text{-N}$, exchangeable SRP and surface water SRP concentrations (Table 4). Although related, the partial correlation coefficients of these variables were too low to infer strong relationships with SRP sorption.

Abiotic SRP sorption processes have been shown to be influenced by water

chemistry (Stewart 1988), sediment mineral composition (McCallister and Logan 1978) and chemical coatings on the surfaces of sediment particles (Green et al. 1978, Baldwin 1996). Phosphorus was found to readily sorb to precipitated carbonates in Brier Creek, a prairie stream in Oklahoma (Stewart 1988). Moreover, the calcareous sediments of that stream appeared to promote carbonate precipitation, and subsequent SRP removal from the stream (Stewart 1988). The presence of limestone in the WHC watershed indicates channel sediments have a calcareous composition. Thus, it is likely that the SRP sorption process observed in Brier Creek also operates in WHC. Another recognized abiotic SRP sorption process involves a chemical reaction between SRP and iron (Fe^{3+}). This process can occur in solution or on the surfaces of sediment particles (Baldwin 1996). The chemical reaction transforms SRP into a insoluble iron-based compound (i.e., FePO_4), thereby removing SRP from solution. This process is reversible, and under certain conditions (e.g., anoxia), bound SRP may be released into solution. Preliminary data collected at WHC suggests this sorption-desorption process may occur within WHC sediments (E.H. Stanley, pers. comm.).

Mechanisms aside, SRP was removed from solution through abiotic sorption processes. The amount of exchangeable, or loosely sorbed, SRP on sediment surfaces indicates the magnitude of such sorption processes. Loosely bound SRP was extracted from sediments collected at each study site. I then calculated partition coefficients for SRP sorption (sensu Triska et al. 1994) to demonstrate the importance of exchangeable SRP on the sediment particles. The partition coefficient is the ratio of sediment-sorbed SRP to the concentration of SRP in solution. Partition coefficients were always >10:1 and

usually >100:1, indicating a considerable amount of SRP is stored on sediment surfaces (Table 11).

Similar to SRP sorption, $\text{NH}_4\text{-N}$ sorption was always greater in living sediments. Unlike SRP sorption, however, the importance of physical-chemical processes in $\text{NH}_4\text{-N}$ sorption varied. Abiotic sorption accounted for 40%, 65% and 73% of the total $\text{NH}_4\text{-N}$ removed from solution at main, west and east sites respectively. Thus, it appears that biotic processes are more active in $\text{NH}_4\text{-N}$ sorption relative to SRP sorption.

Munn (1990) also found $\text{NH}_4\text{-N}$ uptake by stream sediments to be positively influenced by biological sorption processes. Similarly, other researchers have recognized the importance of biotic uptake of $\text{NH}_4\text{-N}$ during laboratory (Richey et al. 1985) and field experiments (Newbold et al. 1983). Biological uptake of $\text{NH}_4\text{-N}$ will probably be most pronounced in sediments taken from hydrologically stable areas, where robust epilithic microbial communities are permitted to develop. This appeared to be the case in my study. Microbial uptake of $\text{NH}_4\text{-N}$ was greatest in sediments taken from the perennial main channel and least in sediments taken from the ephemeral east branch.

The fact that sediments removed $\text{NH}_4\text{-N}$ through physical-chemical processes was also interesting. This finding indicates that there is an abiotic, passive retention of $\text{NH}_4\text{-N}$ as the stream infiltrates the benthic sediments. This process may be particularly important in streams subject to frequent hydrologic extremes (e.g., flooding and drying), where microbial communities in sediments are often disturbed. Although void of microbial communities, sediment particles will still be capable of $\text{NH}_4\text{-N}$ retention through physical-chemical sorption.

$\text{NH}_4\text{-N}$ sorbed to the sediment particles would likely help to establish an epilithic microbial community, consequently increasing the ability of the sediments to retain $\text{NH}_4\text{-N}$. The relative importance of biotic versus abiotic sorption processes may, then, be closely associated with the hydrologic regime of the stream.

Considerable quantities of sorbed $\text{NH}_4\text{-N}$ were found on sediments from each study area confirming that sediments were active in $\text{NH}_4\text{-N}$ removal from the stream.

Exchangeable $\text{NH}_4\text{-N}$ in the benthic sediments of WHC ranged from 2.7 to 29.9 $\mu\text{g NH}_4\text{-N/g}$ sediment. These values are similar, albeit higher, to those values reported by Richey et al. (1985) and Triska et al. (1994), who found <1.0-9.0 $\mu\text{g NH}_4\text{-N/g}$ sediment and 0.4-1.7 $\mu\text{g NH}_4\text{-N/g}$ sediment respectively. Partition coefficients calculated for $\text{NH}_4\text{-N}$ were always >100:1 and commonly >500:1 (Table 12), indicating benthic sediments possess a large pool of $\text{NH}_4\text{-N}$. Triska et al. (1994) found similar partition coefficients of >10:1 and >100:1 for channel and riparian sediments respectively. Thus, benthic stream sediments in WHC represent a large reservoir of sorbed $\text{NH}_4\text{-N}$ available for microbial uptake and transformation.

Multiple linear regression analyses revealed that $\text{NH}_4\text{-N}$ concentration in the surface water was the only independent variable related to $\text{NH}_4\text{-N}$ sorption in both living and killed sediments. Despite the weak correlation between surface water $\text{NH}_4\text{-N}$ concentration and $\text{NH}_4\text{-N}$ sorption, this relationship may still provide insight into the

Table XII. Ammonium partition coefficients for each site sampled in Wild Hog Creek.

Site	Exchangeable $\text{NH}_4\text{-N}$ ($\mu\text{g NH}_4\text{-N/g sed.}$)	Surface water $\text{NH}_4\text{-N}$ ($\mu\text{g NH}_4\text{-N/g water}$)	Partition Coefficient
Main Channel 1	13.3	0.026	511.5
Main Channel 2	2.7	0.018	150.0
Main Channel 3	13.3	0.014	950.0
Main Channel 4	4.4	0.008	550.0
West Branch 1	10.2	0.024	425.0
West Branch 2	12.3	0.026	473.1
West Branch 3	12.7	0.021	604.8
East Branch 1	29.9	0.020	1495.0
East Branch 2	23.0	0.018	1277.8

mechanisms controlling $\text{NH}_4\text{-N}$ sorption processes. Triska et al. (1994) recognized a relationship between stream water $\text{NH}_4\text{-N}$ concentrations and $\text{NH}_4\text{-N}$ sorption. They stated that in streams with low ambient $\text{NH}_4\text{-N}$ concentrations, sediment sorption ability is directly related to ambient $\text{NH}_4\text{-N}$ concentration (Triska et al. 1994). Their reasoning was that sediments consistently exposed to low stream water $\text{NH}_4\text{-N}$ concentrations may have a greater capacity to remove $\text{NH}_4\text{-N}$ from the stream. That is, the full potential of biotic and abiotic sorption processes are unrealized in streams with low $\text{NH}_4\text{-N}$ concentrations. This appears to be the situation in my study. The benthic sediments of WHC have an intrinsic ability to remove $\text{NH}_4\text{-N}$ from solution through physical-chemical sorption processes. Development of an active microbial community within the sediments can result in increased $\text{NH}_4\text{-N}$ sorption and further reduce stream water $\text{NH}_4\text{-N}$ concentrations.

Net Nitrification

Net nitrification was measured in main channel benthic sediments on June 25 and August 14, 1997. All of the sediments collected were capable of $\text{NO}_3\text{-N}$ production through nitrification (Fig. 4). Thus, nitrification within the benthic sediments of WHC represents a source of $\text{NO}_3\text{-N}$ to the surface stream. Net nitrification rates were spatially and temporally variable. This variability may be related to factors which limit nitrification; specifically availability of $\text{NH}_4\text{-N}$ and dissolved oxygen.

There was an inverse relationship between net nitrification and the quantity of exchangeable $\text{NH}_4\text{-N}$ present on sediments (Table 6). On both dates, sites with the highest rate of net nitrification had the lowest amount of exchangeable $\text{NH}_4\text{-N}$ and sites with the

lowest net nitrification had the greatest amounts of exchangeable $\text{NH}_4\text{-N}$. The fact that sorbed $\text{NH}_4\text{-N}$ was present on sediments having the highest rates of net nitrification suggests that nitrification was not limited by $\text{NH}_4\text{-N}$ availability. It is plausible, then, that the availability of dissolved oxygen within the sediments limited nitrification.

Within each study site, sediments were collected from several areas to incorporate local heterogeneity of sediment characteristics. Perhaps the interstitial water of some of the sediments collected was low in dissolved oxygen. This situation may occur if sediment metabolic rates are high or sediment infiltration is minimal. Although the sediments were homogenized before net nitrification rates were determined, a greater proportion of those sediments exposed to low dissolved oxygen levels could have resulted in minimal net nitrification. This may explain the spatial and temporal variation in net nitrification rates measured in WHC benthic sediments.

Net nitrification rates measured in WHC sediments are comparable to annual rates measured within the sediments of a Sonoran Desert stream. Jones et al. (1995) found average annual net nitrification in shallow sediments (2-17 cm) to range from $0.002 \mu\text{g/l NO}_3\text{-N/g sed/d}$ to $0.013 \mu\text{g/l NO}_3\text{-N/g sed/d}$ in Sycamore Creek, Arizona. Net nitrification in benthic sediments of WHC ranged from 0.004 to $0.050 \mu\text{g/l NO}_3\text{-N/g sed/d}$ in June and 0.072 to $0.234 \mu\text{g/l NO}_3\text{-N/g sed/d}$ in August. It should be noted, however, that channel morphology and sediment distribution differs within these two systems. Thus, comparisons of sediment net nitrification rates are only meaningful when such differences are recognized.

Sycamore Creek flows through a channel filled with deep (~ 1 m) unconsolidated

coarse grained sediments, and consequently has considerable subsurface flow (Valett et al. 1990, Jones et al. 1995). In contrast, WHC often flows over bedrock reaches and through patchy accumulations of poorly sorted sediments. The small accumulations of sediments often found in bedrock reaches or pools could retain $\text{NH}_4\text{-N}$ through sorption, and through nitrification, provide a source of $\text{NO}_3\text{-N}$ to the surface stream in those areas. It is certainly possible that the spatial distribution of the nutrient limited primary producers may also indicate the spatial distribution of sediment nitrification. Thus, microbial communities within the shallow stream sediments of WHC are capable of producing $\text{NO}_3\text{-N}$ through nitrification, providing a source of $\text{NO}_3\text{-N}$ to the overlying stream water.

Field Experiments

Similar to the laboratory sorption experiments, benthic sediments within artificial stream channels exhibited sorption when exposed to nutrient enriched stream water (except for $\text{NH}_4\text{-N}$ treatment in September). Unlike the laboratory experiments, however, sediments lining the channels were not agitated, potentially limiting the number of binding sites on sediment surfaces in contact with the stream water. As a result, the total sorption capacity of the sediments used in the field experiments was probably underestimated.

Field Experiment: 27 September 1997

The laboratory sorption experiments demonstrated that SRP sorption was largely due to physical-chemical sorption processes. Thus, it was surprising not find a positive relationship between stream water SRP concentration entering the channel (upstream) and

SRP retention in the treatment channels (Fig. 7). If SRP sorption was mainly abiotic, it is logical to expect greater sorption in response to greater SRP. Instead, SRP retention within the control channel sediments was greater.

The difference in SRP retention between the treatment and the control channels may be related to flow patterns through the sediments. Theoretically, the flow path of a solution through sediments will vary little over time, assuming the velocity of that solution remains relatively constant. Using this logic, sediment surfaces in contact with the flow path should also remain constant over time. As SRP sorption occurs, binding sites on the surfaces of sediment particles become increasingly occupied by SRP, resulting in fewer available binding sites. Assuming solution flow paths remain stable over time, SRP retention will decrease as SRP continues to sorb to sediment particles. This mechanism could have been responsible for the relatively minor amount of SRP retained in the treatment channels. Sediment surfaces could have become rapidly covered with SRP upon delivery of the SRP enriched solution. This certainly would have resulted in less retention over time.

The greater SRP retention observed in the control channels agrees with this proposition. More sediment binding areas would probably be available in sediments exposed to a solution with low SRP concentrations, thus allowing more SRP to be removed from solution.

Interestingly, a similar situation may have developed if biological uptake was responsible for the majority of SRP sorption. Microbial uptake of SRP is believed to operate most efficiently under SRP concentrations to which the microorganism are

normally exposed (Elwood et al. 1981). This is described in more detail above. The difference in the amount of SRP retained by treatment and control sediments support the possibility of this mechanism. Although possible, it is unlikely that only one of these processes was responsible for the $\text{PO}_4\text{-P}$ retained by sediments in the experimental channels. Rather, the retentive ability of sediments was likely a combination of physical-chemical and biological processes.

The reason $\text{NH}_4\text{-N}$ was not retained by treatment sediments during this experiment may also be explained by sediment flow patterns. That is, sediment surfaces likely become readily occupied by NH_4^+ ions upon delivery of the $\text{NH}_4\text{-N}$ enriched stream water. As a result, sediment surfaces available for $\text{NH}_4\text{-N}$ sorption became limited and retention was not observed over the course of the experiment. Conversely, the low amount of $\text{NH}_4\text{-N}$ delivered to control sediments did not saturate the available binding sites, thus allowing a greater amount of $\text{NH}_4\text{-N}$ to be retained. It is possible that the nutrient retention ability of channel sediments was underestimated. That is, if the channel sediments were not completely infiltrated by the delivery solution, all of the sediment surfaces would not be in contact with the solution. That situation would prevent the full retentive capacity of the sediments from being realized.

Field Experiment: 4 October 1997

The benthic sediments used during the October 4 experiment were placed in the experimental channels and submerged in the stream one week before the experiment was conducted. This incubation period appeared to enhance the nutrient retention ability of the

sediments. The amount of SRP and $\text{NH}_4\text{-N}$ retained by channel sediments were similar to the amounts retained during the September experiment, even though the concentrations of SRP and $\text{NH}_4\text{-N}$ in the delivery solution were twice as high (Table 8). Leaving the channel sediments submerged in the stream for a week before the experiment may have promoted the development of a stable microbial community. Sediments that were used in the September experiment were taken from several areas within the main channel, mixed together in a bucket and evenly distributed between the eight experimental channels, perhaps preventing the full capacity of microbial uptake to be realized. Robust microbial communities capable of considerable nutrient uptake undoubtedly became homogenized with less efficient, even dead, microbial communities, thus reducing the overall uptake capacity of the sediments.

Retention of both SRP and $\text{NH}_4\text{-N}$ during the October experiment was positively correlated with upstream nutrient concentration. This finding could be interpreted from both a biological and physical-chemical standpoint. Microbial communities may have been more active in these undisturbed sediments, thus allowing greater nutrient retention. On the other hand, the increased nutrient retention during this experiment may have been related to sediment flow paths. It is certainly possible that more sediment surfaces were in contact with solution, that is, sediment infiltration was greater during this experiment. These processes are not mutually exclusive, and likely operated together to produce the nutrient retention observed during this date.

Net nitrification was greatest in treatment channel sediments during this experiment. Interestingly, net nitrification rates for both treatment and control sediments

on this date were slightly lower than the rates measured on 27 September (Fig. 7). At first, this result appears to refute the idea of the development of an active microbial community within sediments used in this experiment. However, $\text{NH}_4\text{-N}$ concentrations delivered to the treatment sediments were nearly twice as high as the concentrations used during the 27 September experiment. Such high $\text{NH}_4\text{-N}$ concentrations may have negatively affected the nitrification potential of the sediment microorganisms.

CONCLUSION

Stream water concentrations of dissolved inorganic nitrogen and phosphorus in WHC may be influenced by processes occurring within benthic sediments. Ambient concentrations of SRP and $\text{NH}_4\text{-N}$ could be reduced through biotic or abiotic sorption to sediment particles. Stream water $\text{NO}_3\text{-N}$ levels may be increased through nitrification within benthic sediments. WHC sediments may be active area in controlling the availability of these nutrients in the stream water.

SRP dynamics in WHC may be strongly influenced by stream-sediment interactions. SRP sorption to sediment particles could certainly contribute to the low SRP concentrations observed throughout the watershed. SRP becomes bound to sediment particles through abiotic, or physical-chemical processes. Epilithic uptake of SRP can also occur, however, this process may be of secondary importance. Following sorption, sediment-bound SRP is retained and may be temporarily unavailable for uptake by stream autotrophs.

Sediment sorption processes may also affect N dynamics in WHC. $\text{NH}_4\text{-N}$ becomes bound to sediments through biological and physical-chemical processes. Epilithic uptake of $\text{NH}_4\text{-N}$ is most pronounced in hydrologically stable areas, where active microbial communities are able to develop. Conversely, physical-chemical sorption of $\text{NH}_4\text{-N}$ becomes important in ephemeral areas. Biotic and abiotic $\text{NH}_4\text{-N}$ sorption processes are not mutually exclusive, but rather operate in concert to remove $\text{NH}_4\text{-N}$ from solution.

Unlike SRP, sorbed $\text{NH}_4\text{-N}$ is not tightly retained by sediment particles and can become available for autotrophic uptake. Similarly, sorbed $\text{NH}_4\text{-N}$ can be transformed to

$\text{NO}_3\text{-N}$ through sediment nitrification.

The concentrations of SRP, $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ in WHC are not solely the result of sediment sorption processes or nitrification. Rather, the stream water concentration of these nutrients result from an interaction of processes occurring in upland, riparian and instream areas. Identification and measurement of the processes affecting nutrient concentrations within each area are needed in order to completely understand the nutrient dynamics of WHC. The nutrient-sediment interactions examined in this study provide an appropriate starting point from which further research may be conducted.

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Scope and Method of Study: The objectives of this study were 1) to determine the ability of Wild Hog Creek benthic sediments to regulate surface water concentrations of inorganic nitrogen and phosphorus through physical-chemical and biological uptake (sorption), and 2) to generate nitrate to the surface stream through sediment nitrification. Both laboratory and field investigations were employed to examine the potential importance of nutrient-sediment interactions in controlling surface water concentrations of inorganic nitrogen and phosphorus.

Findings and Conclusions: Benthic sediments of Wild Hog Creek have the ability to influence stream water chemistry through nutrient retention and transformation. Biological and physical-chemical sorption processes are capable of reducing concentrations of inorganic nitrogen and phosphorus, thereby maintaining low levels of these nutrients in the stream water. Nitrification occurs within the benthic sediments of Wild Hog Creek and represents an important nitrate source to this ecosystem. The benthic sediments of Wild Hog Creek need to be recognized as an important stream ecosystem component which regulates the instream availability of nitrogen and phosphorus.

ADVISOR'S APPROVAL: _____

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