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## N uptake as a function of concentration in streams

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**Abstract.** Detailed studies of stream N uptake were conducted in a prairie reach and gallery forest reach of Kings Creek on the Konza Prairie Biological Station. Nutrient uptake rates were measured with multiple short-term enrichments of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  at constant addition rates in the spring and summer of 1998.  $\text{NH}_4^+$  uptake was also measured with  $^{15}\text{N-NH}_4^+$  tracer additions and short-term unlabeled  $\text{NH}_4^+$  additions at 12 stream sites across North America. Concurrent addition of a conservative tracer was used to account for dilution in all experiments.  $\text{NH}_4^+$  uptake rate per unit area ( $U_i$ ) was positively correlated to nutrient concentration across all sites ( $r^2 = 0.41$ , log–log relationship). Relationships between concentration and  $U_i$  were used to determine whether the uptake was nonlinear (i.e., kinetic uptake primarily limited by the biotic capacity of microorganisms to accumulate nutrients) or linear (e.g., limited by mass transport into stream biofilms). In all systems,  $U_i$  was lower at ambient concentrations than at elevated concentrations. Extrapolation from uptake measured from a series of increasing enrichments could be used to estimate ambient  $U_i$ . Linear extrapolation of  $U_i$ , assuming the relationship passes through the origin and rates measured at 1 elevated nutrient concentration underestimated ambient  $U_i$  by ~3-fold. Uptake rates were saturated under some but not all conditions of enrichment; in some cases there was no saturation up to 50  $\mu\text{mol/L}$ . The absolute concentration at which  $U_i$  was saturated in Kings Creek varied among reaches and nutrients. Uptake rates of  $\text{NH}_4^+$  at ambient concentrations in all streams were higher than would be expected, assuming  $U_i$  does not saturate with increasing concentrations. At ambient nutrient concentrations in unpolluted streams,  $U_i$  is probably limited to some degree by the kinetic uptake capacity of stream biota. Mass transfer velocity from the water column is generally greater than would be expected given typical diffusion rates, underscoring the importance of advective transport. Given the short-term spikes in nutrient concentrations that can occur in streams (e.g., in response to storm events),  $U_i$  may not saturate, even at high concentrations.

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*Key words:* advective transport, ammonium, areal uptake, benthos, kinetics, nitrate, nitrogen, mass transport.

Quantifying nutrient dynamics is central to understanding aquatic eutrophication and ecosystem function. Human activities often lead to short-term and long-term increased  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  inputs to streams and groundwater. The impact of these nutrients on water quality and ecosystem function depends in large part on the pathways through which each cycles upon entering aquatic ecosystems. For example, if autotrophic uptake is a dominant pathway of nutrient retention, then undesirable algal blooms will often occur (Dodds and Welch 2000). If heterotrophic uptake is dominant, however, C degradation may be stimulated. Downstream transport of nutrients is important, as evidenced by the development of an anoxic zone that covers large areas in the coastal waters of the Gulf of Mexico (Rabalais et al. 1998) and toxic concentrations of  $\text{NO}_3^-$  in drinking water.

Small streams are key interfaces between terrestrial habitats and downstream receiving waters and can potentially regulate nutrient transport (e.g., Peterson et al. 2001). Nutrients can move from the water column into the benthos (uptake), or from the benthos into the water column (remobilization). The rate of remineralization should not respond quickly to short-term variations in water-column nutrient concentrations (Dodds 1993), so only uptake is considered in this paper. Characterizing benthic nutrient uptake as a function of variable in-stream nutrient concentrations is an important step in understanding how the stream benthic biota is linked to temporally and spatially variable nutrient concentrations in the water column.

At least 2 models can represent extremes on a possible continuum of the functional relationship between nutrient concentration in the water column and uptake rates by the benthos of the stream under the range of nutrient concentrations that typically occur in streams. At one end of the spectrum, uptake is linear and may be driven by hydrodynamic limitation of mass transport. Such linear uptake at moderate to low concentrations also could be related to abiotic sorption with low affinity and high saturation (i.e., low affinity uptake with a high half-saturation constant [ $K_s$ ] will lead to apparently lin-

ear uptake until very high water-column nutrient concentrations are reached). However, if uptake rates are limited by mass transport alone, they are controlled by diffusion rates, which is characterized by Fick's first law:

$$J = D \frac{\delta C_n}{\delta z} \quad [1]$$

where  $J$  is diffusion,  $D$  is the diffusion constant, and  $\delta C_n / \delta z$  is the gradient in nutrient concentration ( $C$ ), across distance ( $z$ ) (Denny 1993). Molecular diffusion is very slow, so the diffusion flux can be thought of as controlled by the nutrient gradient across a stream-wide average diffusion boundary layer (Vogel 1994). If only mass transfer limits uptake, a linear relationship between nutrient concentration and uptake rate will result:

$$U_t = K_t C_n \quad [2]$$

where  $U_t$  is uptake in units of mass per unit area benthos per unit time,  $C_n$  is the nutrient concentration, and  $K_t$  is an uptake constant that corresponds to  $D/dz$  in Fick's law, and is a function of the rate of advective transport. The relationship between uptake and concentration will hold constant over short time periods (i.e.,  $K_t$  will remain constant) if discharge does not change.

At the other end of the continuum,  $U_t$  can be controlled by the biotic capacity of organisms or abiotic sites of adsorption to immobilize nutrients. At this end of the continuum, capacity is a nonlinear saturating model where kinetics rather than mass transfer dominate  $U_t$ . Michaelis-Menten uptake kinetics generally describe the relationship between  $U_t$  and  $C_n$  for individual cells or cell cultures and  $K_s$  values are usually close to 1  $\mu\text{mol/L}$  for biotic uptake, ranging from 0.1–15  $\mu\text{mol/L}$  (Brezonik 1994). Regardless of whether biotic capacity or abiotic sorption controls  $U_t$ , saturation is expected as concentration increases with this type of model, where  $U_t$  is represented by a maximum uptake rate ( $V_{max}$ ).

It is unknown to what extent a linear model versus saturation kinetics models describe nutrient uptake in streams. If saturation kinetics occur,  $K_s$  values for  $U_t$  are not well known (ex-

cept see Bothwell 1989, Mulholland et al. 1990). A prior study of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  uptake in a forested stream indicated that a linear model did not fit uptake rate as a function of nutrient concentrations (Mulholland et al. 2001). A model coupled with data from marine mesocosms suggested that there is a broad region where both uptake capacity and mass transfer limit  $U_t$  across solid–water boundaries (Sanford and Crawford 2000), but such an analysis has not been applied to streams to our knowledge.

Three interrelated measures are typically used to characterize nutrient uptake by the benthos in streams: 1) spiraling length, 2) uptake rate per unit benthos area ( $U_t$ ), and 3) mass transfer velocity. Nutrient retention is a function of nutrient spiraling (Newbold et al. 1981) in streams. The most easily measured component of spiraling length is the uptake length ( $S_w$ ), which describes the average distance traveled by a dissolved nutrient in the water column before being immobilized (Webster and Ehrman 1996).  $S_w$  is the main component of spiraling length (Newbold et al. 1981), making it a good index of nutrient retention (Kim et al. 1990). Though easily measured,  $S_w$  is not only a function of the uptake capacity of the benthos, but is also strongly influenced by discharge and water depth.  $S_w$  is therefore not the best parameter to compare across streams of different size when the relationship between uptake and nutrient concentration is of interest (Davis and Minshall 1999).

The mass transfer velocity ( $V_f$ , also referred to as the mass transfer coefficient by some investigators) can be thought of as the average velocity of a nutrient toward the benthos, and is independent of depth (Stream Solute Workshop 1990, Wollheim et al. 2001). We concentrate on  $U_t$  and  $V_f$  to highlight processes controlling the rate that nutrients move into the benthos. We used  $^{15}\text{N}$  tracer additions and unlabeled short-term nutrient enrichments in a detailed assessment of  $U_t$  and  $V_f$  as a function of  $C_n$ . The study sites were prairie and gallery forest stream sites in Kansas and a cross-system comparison of 11 other streams across the United States as part of the Lotic Intersite Nitrogen eXperiment (LINX, Peterson et al. 2001).

We attempt to establish the general form of the relationship between  $U_t$  and  $C_n$  because this relationship is not well described for many streams. We test specific predictions that can be

made relative to a linear model versus a model that assumes saturation of  $U_t$ . In a pure linear mass transfer model,  $U_t$  will be linearly related to concentration with no saturation. In this case,  $V_f$  should not be a function of concentration because any increase in concentration should lead to a proportional increase in  $U_t$ , so average nutrient velocity toward the benthos should remain constant. If only biotic capacity limits  $U_t$ , then  $U_t$  should saturate at low to moderate nutrient concentrations (i.e.,  $<100 \mu\text{mol/L}$ ). In this case, values for  $K_s$  should be comparable to those of single cells whose uptake is not constrained by transport. If  $U_t$  saturates,  $V_f$  will decrease with increasing nutrient concentration; average velocity of nutrient molecules decreases because benthic uptake moves a lower proportion of the molecules downward and out of the water column per unit time. In intermediate cases, where transport limitation or sorption with very high  $K_s$  values have an influence,  $K_s$  for  $U_t$  should be greater than expected for purely biotic uptake. However, at very high nutrient concentrations  $U_t$  is still expected to saturate.

## Methods

### Study sites

A prairie reach and a gallery forest reach of Kings Creek on the Konza Prairie Biological Station were used for detailed enrichment studies. Descriptions of the site's ecology (Gray and Dodds 1998), hydrology (Gray et al. 1998), geology (Oviatt 1998), and N cycling and transport (Dodds et al. 1996, 2000, Kemp and Dodds 2001) are available. The 100-m prairie reach in watershed N04D of Kings Creek was autotrophic, with relatively little leaf input. It initially had a high discharge (50 L/s) and high algal biomass (Dodds et al. 2000). As the stream dried in early summer, the study was moved downstream to the gallery forest site. The 75-m gallery forest reach was characterized by greater allochthonous inputs and lower light than the prairie reach. Discharge at each Kings Creek site for each date is reported in Table 1.

Experiments were conducted at 11 additional stream sites of approximately similar discharge and order as Kings Creek, in conjunction with the LINX study (Table 2). Most of these sites were relatively pristine. Only Eagle Creek and the East Fork Little Miami River had substan-

TABLE 1. Discharge, nutrient concentration at uppermost measurement site closest to the addition point, uptake length ( $S_w$ ), uptake rate ( $U_i$ ), and mass transfer velocity ( $V_f$ ) for all nutrient additions at Kings Creek. SE for  $S_w$  in parentheses. See text for description of parameters.

Date (all 1998)	Site	Nutrient	Discharge (L/s)	Nutrient top conc. ( $\mu\text{mol/L}$ )	$S_w$ (m)	$U_i$ ( $\mu\text{mol m}^{-2}$ $\text{s}^{-1}$ )	$V_f$ (m/h)
2 April	Prairie	$\text{NO}_3^-$	55	4	168 (38)	0.53	0.446
23 June	Prairie	$\text{NO}_3^-$	4	15	300 (41)	0.13	0.031
23 June	Prairie	$\text{NO}_3^-$	4	29	311 (61)	0.25	0.030
23 June	Prairie	$\text{NO}_3^-$	4	61	402 (62)	0.40	0.024
23 June	Prairie	$\text{NO}_3^-$	4	105	225 (47)	1.23	0.042
5 April	Prairie	$\text{NH}_4^+$	47	2	228 (34)	0.21	0.314
8 April	Prairie	$^{15}\text{N-NH}_4^+$	48	0.1	56 (22)	0.05	1.417
27 April	Prairie	$^{15}\text{N-NH}_4^+$	8	0.08	24 (4)	0.015	0.675
8 May	Prairie	$\text{NH}_4^+$	2	3	145 (17)	0.03	0.029
8 May	Prairie	$\text{NH}_4^+$	2	7	261 (26)	0.03	0.016
12 May	Prairie	$^{15}\text{N-NH}_4^+$	11	0.01	38 (5)	0.001	0.360
9 June	Prairie	$\text{NH}_4^+$	5	9	66 (9)	0.38	0.159
9 June	Prairie	$\text{NH}_4^+$	5	84	248 (65)	1.00	0.043
6 July	Gallery	$\text{NH}_4^+$	29	49	97 (5)	5.87	0.429
13 July	Gallery	$\text{NH}_4^+$	29	5	91 (7)	0.61	0.459
13 July	Gallery	$\text{NH}_4^+$	29	9	247 (80)	0.42	0.169
13 July	Gallery	$\text{NH}_4^+$	29	24	115 (25)	2.36	0.362

TABLE 2. Site characteristics for  $^{15}\text{N}$  and unlabeled  $\text{NH}_4^+$  additions.

Site	Biome	Dis- charge (L/s)	Aver- age width (m)	$\text{NH}_4^+$ ( $\mu\text{mol/L}$ )	$\text{NO}_3^-$ ( $\mu\text{mol/L}$ )	Reference
Upper Ball Creek, North Carolina	Deciduous forest	51.4	2.2	0.16	0.07	Tank et al. 2000
Walker Branch, Tennes- see	Deciduous forest	9.8	2.2	0.19	1.11	Mulholland et al. 2000
Sycamore Creek, Ari- zona	Desert	70	7.1	0.14	1.20	
Bear Brook, New Hamp- shire	Deciduous forest	3.5	2.3	0.36	4.10	
Gallina Creek, New Mexico	Montane coniferous forest	4.2	2.1	0.37	0.54	
Quebrada Bisley, Puerto Rico	Tropical forest	17.9	1.8	0.33	10.07	Merriam et al. 2002
Eagle Creek, Michigan	Deciduous forest	208	4.9	1.28	2.06	Hamilton et al. 2001
Mack Creek, Oregon	Montane coniferous forest	55.8	7.3	0.21	3.88	
E1, Alaska	Tundra	20	1.3	0.10	2.55	Wollheim et al. 2001
Amity Creek, Michigan	Deciduous forest	71	2.2	0.48	0.62	
East Fork Little Miami River, Ohio	Deciduous forest	849	14.2	2.14	38.79	

tially elevated nutrient concentrations in the stream channel as a consequence of anthropogenic inputs. The sites were selected to maximize variation in type of biome, with discharge roughly similar across sites. Further descriptions of N cycling (Peterson et al. 2001) and metabolism (Mulholland et al. 2001) are published.

#### *Unlabeled nutrient enrichments*

We conducted multiple short-term elevated solute additions of NaNO<sub>3</sub> or NH<sub>4</sub>Cl at Kings Creek from April to September 1998. Concentrations in the stream water were elevated by adding nutrients with a peristaltic pump to achieve specific solute release rates ranging from 2 to 38 mL/min, based on the discharge of the stream, the concentration of the stock solution, and a target nutrient increase. Water samples were collected at 3 downstream sampling points prior to the first addition on each date to determine background nutrient concentrations. Each solute addition was conducted at successively higher concentrations over the series of experiments conducted in 1 d.

A conservative solute tracer of NaBr or NaCl in solution with the nutrients was used to account for abiotic dilution caused by groundwater influx and to ensure that the solute addition had reached steady state (Stream Solute Workshop 1990). These additions also confirmed that the first sampling station was far enough downstream from the addition point to allow for complete mixing. The concentration of Br<sup>-</sup> in the stream during the addition was monitored using ion-selective Br<sup>-</sup> electrodes (Orion 290A) placed at sampling points midway and the furthest downstream from the addition point. Multiple calibration points and a 2<sup>nd</sup>-order polynomial fit were employed for the Br<sup>-</sup> probe used at low concentrations to establish the standard curve. The maximum concentration of Br<sup>-</sup> was ~0.1 μmol/L and Cl<sup>-</sup> was ~0.5 μmol/L in the stream at plateau. The NaCl additions were assessed with standard conductivity probes. When ion concentrations had reached plateau downstream, water samples for nutrient analysis were collected from the center of the stream starting downstream and moving up to the enrichment site. Samples were transported back to the laboratory on ice. Ion additions probably did not interfere with abiotic exchange because they were done at low concentrations and we never

documented increases in NO<sub>3</sub><sup>-</sup> or NH<sub>4</sub><sup>+</sup> concentrations when only saline solutions were added.

Water samples were analyzed spectrophotometrically for NO<sub>3</sub><sup>-</sup> + NO<sub>2</sub><sup>-</sup> (hereafter referred to as NO<sub>3</sub><sup>-</sup>) following Cd reduction (Technicon 1973), and for NH<sub>4</sub><sup>+</sup> by the phenol hypochlorite method (APHA 1995). Bromide was analyzed in the laboratory using an ion-selective electrode. Care was taken to ensure stability of the electrode system (i.e., constant temperatures, standards made in stream water, and standardization before and after analyses of unknowns).

#### *Stable isotope tracer additions of <sup>15</sup>NH<sub>4</sub><sup>+</sup>*

NH<sub>4</sub><sup>+</sup> uptake at ambient concentration was also measured at all 12 sites. A solution of <sup>15</sup>NH<sub>4</sub>Cl was released into the stream, and disappearance of <sup>15</sup>NH<sub>4</sub><sup>+</sup> over distance was used to estimate *U<sub>t</sub>*. The <sup>15</sup>N tracer approach was necessary because at ambient nutrient concentrations remineralization is comparable to uptake at the whole-stream level (Dodds 1993). Furthermore, at 2 of the sites (East Fork Little Miami River and Eagle Creek) no change of concentration downstream could be detected even with elevated NH<sub>4</sub><sup>+</sup> additions. When <sup>15</sup>N is used as a tracer in the water column, assuming insignificant rates of <sup>15</sup>N regeneration from the benthos, the rate of disappearance of <sup>15</sup>NH<sub>4</sub><sup>+</sup> over distance allows calculation of *U<sub>t</sub>*. We can assume insignificant regeneration of <sup>15</sup>N with short-term releases because remineralized N from the benthos has such a small amount of <sup>15</sup>N content, and estimates were made in the first day of <sup>15</sup>N release. Isotopic discrimination, a minor (~0.3%) component of uptake, was ignored. A solution of NH<sub>4</sub><sup>+</sup> enriched with <sup>15</sup>N (10 mol %) was released at each site, producing <1% increase in background NH<sub>4</sub><sup>+</sup> concentrations. Samples were collected and shipped on ice by overnight carrier to The Ecosystems Center at the Marine Biological Laboratory, Woods Hole, Massachusetts, where <sup>15</sup>N:<sup>14</sup>N ratios in NH<sub>4</sub><sup>+</sup> were determined using a Finnigan Delta S mass spectrometer, following NH<sub>4</sub><sup>+</sup> diffusion under alkaline conditions (Holmes et al. 1998). <sup>15</sup>N results are reported as δ<sup>15</sup>N (‰) values calculated using the following equation:

$$\delta^{15}\text{N} = \left[ \left( \frac{R_{\text{compartment}}}{R_{\text{std}}} \right) - 1 \right] \times 1000 \quad [3]$$

where *R<sub>compartment</sub>* is the <sup>15</sup>N/<sup>14</sup>N analyzed in the



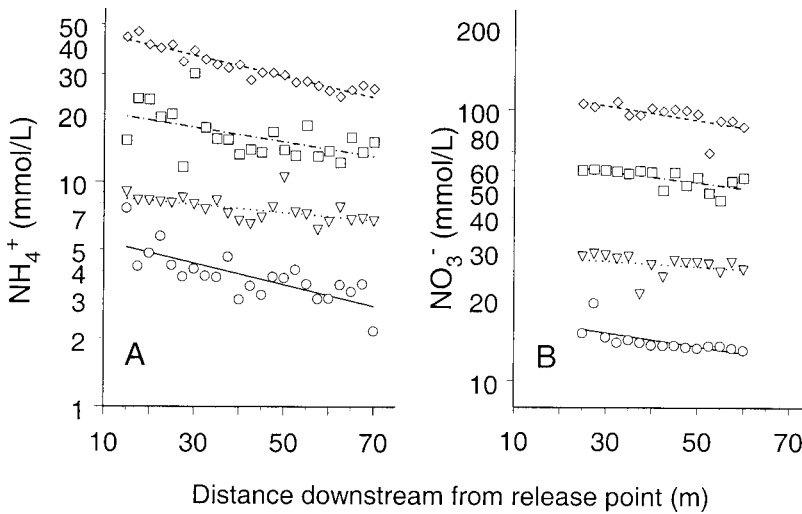


FIG. 1. Representative dilution-corrected concentrations of  $\text{NH}_4^+$  in the gallery forest reach, 6 July 1998 (A) and  $\text{NO}_3^-$  in the prairie reach, 23 June 1998 (B) as a function of distance over a range of unlabeled nutrient-enrichment levels. Note log scale on y-axis.

sample and the N isotope standard is air ( $R_{std} = 0.003663$ ).

#### Nutrient uptake calculations

$S_w$  was calculated using linear regression of the natural log of nutrient concentration (or  $\delta^{15}\text{N}$ ) corrected for dilution and background concentration versus distance. The slope of the line is uptake rate per unit distance (Webster and Ehrman 1996), and the inverse of the uptake rate ( $k_c$ ) is the  $S_w$ .  $U_t$  is calculated using the following equation:

$$U_t = \frac{C_n}{S_w} \times \frac{Q}{w} \quad [4]$$

where  $Q$  equals discharge, and  $w$  is average width.

Stream depth and wetted width were measured across 10 transects and averaged for the calculations of  $U_t$ . Plateau concentrations from the conservative solute tracer additions were used to calculate  $Q$  on each addition date using the following equation (Webster and Ehrman 1996):

$$Q = \frac{(C_t - C_b) \times Q_t}{(C_p - C_b)} \quad [5]$$

where  $C_t$  is the concentration of NaBr addition solution,  $C_p$  is the plateau conservative solute

concentration,  $Q_t$  is the addition rate, and  $C_b$  is the background concentration of conservative solute in the stream.

$V_f$  was calculated from the equation (Newbold et al. 1981, Stream Solute Workshop 1990):

$$V_f = \frac{Q/w}{S_w} = \frac{U_t}{C_n} \quad [6]$$

## Results

#### Konza Prairie nutrient additions

Representative data demonstrate how nutrient concentrations tended to decrease downstream from nutrient-addition points (Fig. 1). The uptake rates were proportional to the slopes of the lines fit to the logarithmic plots. In all cases there was a significant amount of variance in the nutrient concentrations. In some cases, particularly at lower  $\text{NH}_4^+$  concentrations, there was considerable variance inconsistent with sampling location (Fig. 1) longitudinally along the stream channel that could be caused by temporal or analytical variation. However, the regression analyses used to establish the lines all yielded significant slopes ( $p < 0.05$ ).

These data and similar data not shown were used to calculate  $S_w$  values for each concentration used in the additions (Table 1). In general,  $S_w$  values were longer at higher nutrient concen-



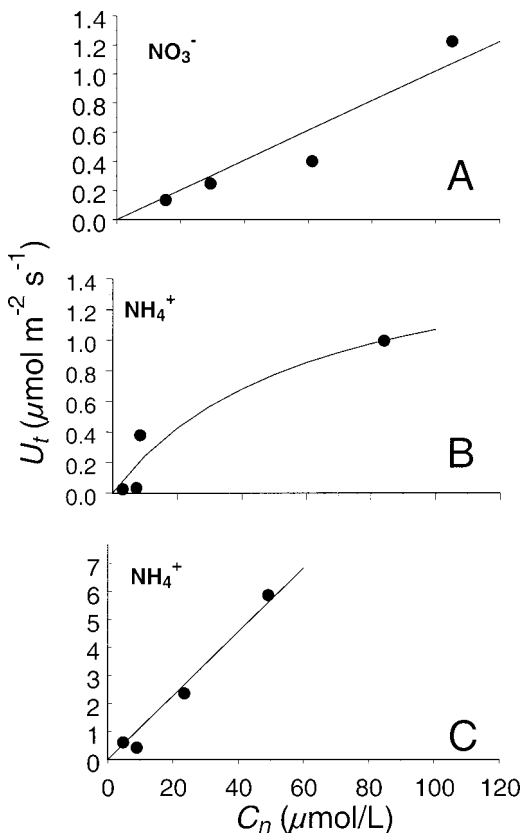


FIG. 2. Relationships of uptake rate ( $U_t$ ) versus nutrient concentration ( $C_n$ ) for (A)  $\text{NO}_3^-$  in the prairie reach, 23 June 1998, (B)  $\text{NH}_4^+$  in the prairie reach, 8 May and 9 June 1998 combined, and (C)  $\text{NH}_4^+$  in the gallery reach, 6 July 1998, with models for those relationships fit by regression (Table 3).

trations, and  $S_w$  values were longer for  $\text{NO}_3^-$  than  $\text{NH}_4^+$  at the prairie site.

$V_f$  values were variable across nutrients and across dates (Table 1). In general, values of  $V_f$  were higher in the gallery forest sites. In some cases there was a decrease in  $V_f$  with increasing concentration as is expected with kinetic uptake saturation (e.g., the addition of  $\text{NH}_4^+$  on 8 May and 9 June), but in other cases there was no relationship with increasing concentration as expected with a linear mass-transfer model (e.g.,  $\text{NO}_3^-$  additions on 23 June).

There was an increase in  $U_t$  as nutrient concentration increased for multiple additions at the 2 reaches on Kings Creek (Fig. 2). In all cases there must be no uptake at 0 nutrient concentration (i.e., no nutrient can leave the water column and enter the benthos if there is no nutrient in the water column), so these curves were fit with no intercept (forced through 0). The best-fit curves for these plots (Table 3) demonstrated that either a linear or a Michaelis–Menten model described a significant portion of the variance in these 3 cases. The best-fit curve was determined based upon the highest value for  $r^2$ . In 2 cases, nonlinear estimation fit the Michaelis–Menten model almost as well as a linear model, but  $V_{max}$  and  $K_s$  values were so great that the model was essentially a linear model at the concentrations of interest. The graph of  $U_t$  for  $\text{NH}_4^+$  in the prairie (Fig. 2B) illustrates a potential case of kinetic uptake saturation (i.e., a potential Michaelis–Menten relationship), but omission of a single point would make a linear model fit the relationship with a comparable  $r^2$ . The calculated  $K_s$  concentration for  $U_t$  was 67  $\mu\text{mol/L}$ .

TABLE 3. Modeled uptake rate ( $U_t$ ) versus concentration for 3 additions, model parameters, and calculated ambient  $U_t$  for best model. See Table 1 and Fig. 2 for data and modeled curves. 1<sup>st</sup> order is the linear model, M–M is a Michaelis–Menten model. Both models were constrained to go through 0 uptake at 0 nutrient concentration. Ambient  $U_t$  is calculated for best-fit model.  $V_{max}$  = maximum uptake rate,  $K_s$  = half-saturation constant,  $V_f$  = mass transfer velocity, – = not applicable.

Site	Nutrient	Model	Constant ( $V_{max}$ or slope)	$K_s$ ( $\mu\text{mol/L}$ )	$r^2$	Ambient		
						concentration ( $\mu\text{mol/L}$ )	$U_t$ ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ )	$V_f$ (m/h)
Prairie	$\text{NO}_3^-$	1 <sup>st</sup> order	0.01	–	0.95	4.10	0.042	0.036
		M–M	$8.3 \times 10^5$	$7.9 \times 10^7$	0.89	–	–	–
Prairie	$\text{NH}_4^+$	1 <sup>st</sup> order	0.012	–	0.87	–	–	–
		M–M	1.73	61.3	0.91	0.62	0.017	0.099
Gallery	$\text{NH}_4^+$	1 <sup>st</sup> order	0.11	–	0.98	2.35	0.268	0.410
		M–M	$1.2 \times 10^6$	$1.1 \times 10^7$	0.97	–	–	–

The graphs of the  $\text{NO}_3^-$  additions in the prairie reach (Fig. 2A) and the gallery forest  $\text{NH}_4^+$  additions (Fig. 2C) show a linear (1<sup>st</sup>-order) relationship between  $U_i$  and concentration. Furthermore, for each doubling of nutrient concentration, there is an approximate doubling of  $U_i$ , as a mass transport model (Eqn 2) would predict.

Once the best-fit model (linear or Michaelis-Menten) had been determined for the 3 data sets in Fig. 2, ambient concentrations were used with the appropriate model to calculate the ambient  $U_i$  (Table 3). Ambient  $U_i$  values estimated this way were lower than those measured with any short-term nutrient enrichments from these data (Table 1), regardless of which model was used to describe  $U_i$ . Ambient values of  $V_f$  were greater than all  $V_f$  values for short-term unlabeled nutrient enrichments at Kings Creek for  $\text{NO}_3^-$ . In 2 sets of calculations using  $\text{NH}_4^+$  data from the prairie and from the gallery forest, 1 of the lower short-term elevated additions had higher values of  $V_f$  than the value obtained by extrapolation to ambient concentration.

#### Tracer $^{15}\text{NH}_4^+$ additions

Using  $^{15}\text{NH}_4^+$  as a tracer of uptake at ambient  $\text{NH}_4^+$  concentrations, we observed that  $U_i$  values calculated from tracer additions were  $\sim 10$  times lower than those estimated from nutrient additions at all 12 sites (Fig. 3). This discrepancy occurred even though we attempted to keep our enrichments as small as possible. Uptake measured with elevated nutrient enrichments does not account for remineralization (i.e., elevated additions measure net uptake, tracers measure gross uptake). The 10 times greater  $U_i$  measured with enrichments indicates that, with nutrient enrichments, net uptake  $\approx$  gross uptake within  $\sim 10\%$ . The assumptions behind this approximation are explored in the discussion.

Two sites, Eagle Creek and East Fork Little Miami River, had very long  $\text{NH}_4^+ S_w$  values. When unlabeled additions were attempted it was impossible to calculate  $U_i$  because there was no detectable decrease in total  $\text{NH}_4^+$  concentration. Depletion of  $^{15}\text{NH}_4^+$  down from the isotope addition point could be detected at these sites, and  $U_i$  at ambient  $\text{NH}_4^+$  concentrations could be calculated (Hamilton et al. 2001, Donna Morrall, unpublished data).

The  $U_i$  values measured with  $^{15}\text{NH}_4^+$  and un-

labelled additions plotted across all sites demonstrated significant positive relationships between  $U_i$  and  $\text{NH}_4^+$  concentration (Fig. 3A). Combining all of the  $U_i$  data yielded the following relationship:

$$\begin{aligned} \log_e(\text{NH}_4^+ U_i) \\ = 0.251 + 0.212 \times \log_e(\text{NH}_4^+ \text{ concentration}), \\ r^2 = 0.41 \end{aligned} \quad [7]$$

with  $\text{NH}_4^+ U_i$  expressed in  $\mu\text{mol m}^{-2} \text{s}^{-1}$  and  $\text{NH}_4^+$  concentration in  $\mu\text{mol/L}$ .

There was evidence for saturation of uptake in the plot of  $U_i$  against concentration across all sites. When the untransformed data (not on a log scale) were fit with linear and Michaelis-Menten relationships, the Michaelis-Menten relationship explained more of the variance ( $r^2 = 0.20$  and  $0.33$  for linear and Michaelis-Menten curve fits, respectively). The 2-dimensional Kolmogorov-Smirnov test (Garvey et al. 1998) indicated that the data were bivariate ( $p = 0.001$ ) and that a breakpoint occurred at  $3.4 \mu\text{mol/L}$   $\text{NH}_4^+$ . Piecewise regression analysis also suggested a breakpoint at  $1.1 \mu\text{mol/L}$   $\text{NH}_4^+$ , and the slope of the regression line above this point was significantly less than below. Fitting the data with 2 lines explained 76% of the variance. These 3 statistical approaches independently suggest some saturation occurs even when data across all sites are compared.

$\text{NH}_4^+ V_f$  decreased with increasing nutrient concentration (Fig. 3B,  $r^2 = 0.37$ ,  $p < 0.0001$ , linear regression of log-transformed data). When all sites with both unlabeled addition and tracer measurements were considered together,  $V_f$  was always lower with enrichment. The lower  $V_f$  values with tracer additions indicated some degree of uptake saturation at elevated concentrations occurred.

## Discussion

### Saturation of uptake

$U_i$  generally increased for  $\text{NH}_4^+$  and  $\text{NO}_3^-$  as stream nutrient concentrations in Kings Creek were increased during the unlabeled nutrient enrichments.  $U_i$  continued to increase up to very high concentrations in some cases in Kings Creek and at other sites (i.e., Konza, Fig. 2A and C; Sycamore Creek, Fig. 3). This finding suggests that there are cases where biotic saturation

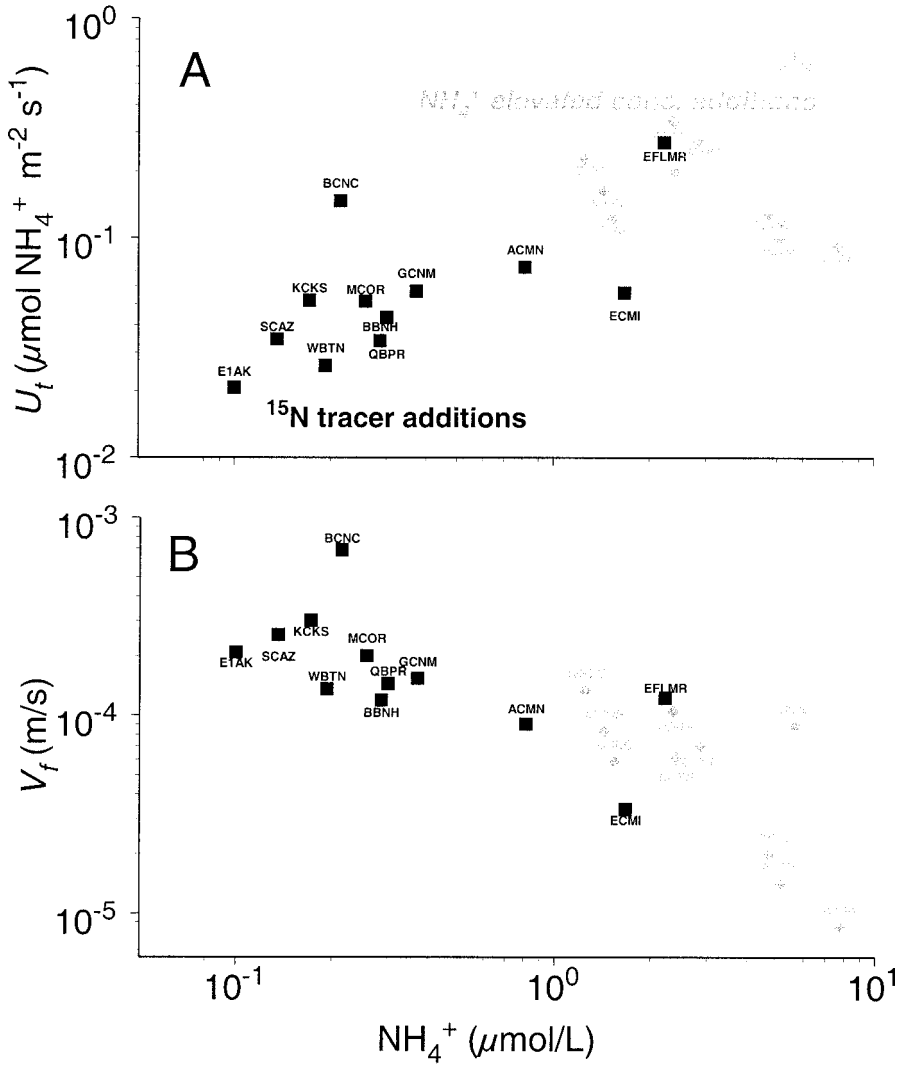


FIG. 3. Relationship between uptake rate,  $U_t$  (A) and mass transfer velocity  $V_f$  (B) and concentration of  $\text{NH}_4^+$  for 12 stream sites as measured by an unlabeled enrichment of  $\text{NH}_4^+$  or a tracer  $^{15}\text{NH}_4^+$  enrichment. WBTN = Walker Branch, Tennessee; BCNC = Ball Creek, North Carolina; SCAZ = Sycamore Creek, Arizona; BBNH = Bear Brook, New Hampshire; GCNM = Gallina Creek, New Mexico; QBPR = Quebrada Bisley, Puerto Rico; KCKS = Kings Creek, Kansas; MCOR = Mack Creek, Oregon, E1AK = E1, Alaska; ECMI = Eagle Creek, Michigan; EFLMR = experimental facility East Fork Little Miami River, Ohio; and ACMN = Amity Creek, Minnesota. Note log scales.

of uptake could not describe  $U_t$  as a function of  $C_n$ ;  $K_s$  values of periphyton are generally  $<10 \mu\text{mol/L}$  (Borchardt 1996), and data in Fig. 2A, B, and C indicated  $K_s$  values likely exceed  $60 \mu\text{mol/L}$ . If adsorption kinetics were important, uptake could eventually saturate, but only at higher concentrations than usually occur in the

systems we studied. Some clear cases of saturation did occur.

At Eagle Creek, downstream nutrient flux was so high relative to uptake that  $U_t$  could be considered saturated regardless of how much nutrient was added, even though  $U_t$  at that stream was similar to the other sites under com-

parable  $C_n$  values (Hamilton et al. 2001), and a similar situation occurred in the East Fork Little Miami River. These sites had  $U_t$  values for  $\text{NH}_4^+$  similar to those measured with  $\text{NH}_4^+$  enrichments in more pristine sites. This result suggests that high  $U_t$  values can be maintained in systems with high nutrient loading, but that remineralization rates also increase leading to higher  $C_n$  values and downstream transport of dissolved nutrients.

Mass transport limitation of  $U_t$  (the linear model) is probably operating simultaneously with limitation of uptake kinetics by abiotic sorption and biotic capacity (Michaelis–Menten). Bothwell (1989) found an increase in periphyton biomass with increased  $\text{PO}_4^{3-}$  concentrations up to  $0.9 \mu\text{mol/L}$ . When periphyton biomass was plotted against  $\text{PO}_4^{3-}$  concentrations (see fig. 7 in Bothwell 1989), the resulting curve could be broken into 3 sections. The 1<sup>st</sup> section ( $0\text{--}0.03 \mu\text{mol/L PO}_4^{3-}$ ) resembled Michaelis–Menten uptake kinetics. The 2<sup>nd</sup> section ( $\sim 0.06\text{--}0.9 \mu\text{mol/L PO}_4^{3-}$ ) showed a linear response at these higher levels of nutrient enrichment. The final section exhibited complete saturation at concentrations  $>0.9 \mu\text{mol/L PO}_4^{3-}$ .

Mulholland et al. (1990) found that uptake of  $\text{PO}_4^{3-}$  in Walker Branch may be saturated at concentrations  $>0.16 \mu\text{mol/L PO}_4^{3-}$ . Mulholland et al. (1990) suggested that biological processes control uptake at low  $\text{PO}_4^{3-}$  concentrations ( $<0.16 \mu\text{mol/L PO}_4^{3-}$ ), and physical/chemical adsorption dominated uptake when  $\text{PO}_4^{3-}$  concentrations were  $>0.16 \mu\text{mol/L PO}_4^{3-}$ . Thus, a combined model of biotic and abiotic limitation with potential hydrological effects applied to  $\text{PO}_4^{3-}$  uptake in Walker Branch.

#### *Do biotic uptake or mass transfer dominate uptake?*

The lack of saturation of  $U_t$  in some cases suggests the existence of a mass transfer component, high-saturation sorption kinetics, or dissimilatory processes such as nitrification and denitrification that may not saturate. We cannot rule out that such processes are in operation at least sometimes, although it is clear that assimilatory biotic uptake is important as well. More data are required on biotic conditions coupled with tracer measurements of  $U_t$ , and refined models including biotic uptake, abiotic uptake, and limitation by mass transfer rates (diffusion boundary layer effects) are necessary to under-

stand uptake as a function of  $C_n$  across a wide variety of small streams. Our data support the predictions of Sanford and Crawford (2000), who suggested that simultaneous limitation of benthic nutrient uptake by biotic affinity and transport phenomena should operate under a broad range of conditions.

Our experiments cannot separate abiotic uptake (adsorption) from biotic uptake, but saturation of adsorption generally occurs at higher concentration than does saturation of biotic uptake (Mulholland et al. 1990). Dissimilatory processes (denitrification and nitrification of  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , respectively) may also have high  $K_s$  values. Nitrification rates at our study sites were 20 to 30% of total  $\text{NH}_4^+$   $U_t$  (Peterson et al. 2001). Denitrification at Kings Creek is  $<1\%$  of  $\text{NO}_3^-$  uptake (Kemp 2001).

#### *Mass transfer velocity*

If there is hydrological limitation of  $V_f$ , it is overcome to some degree by channel characteristics, such as surface topography and advective transport into shallow subsurface channels. This advective transport can be demonstrated by a simple calculation that compares  $V_f$  in the diffusion boundary layer to values calculated for the water column. We will assume that the diffusion boundary layer ( $\delta z$  in eqn 1) is  $\sim 0.2 \text{ mm}$  thick (Glud et al. 1994, Bott et al. 1997), and that the diffusion coefficient of ions through the layer ( $D$ ) is  $0.07 \text{ cm}^2/\text{h}$  (CRC 1978).  $V_f$  then is  $D/\delta z = 0.035 \text{ m/h}$ , which is at least 1 order of magnitude less than most of the  $V_f$  values measured with tracers for all streams (Fig. 3B) and less than 15 of 20 values reported for Kings Creek (Tables 1, 3). We can rule out uptake in the water column (Dodds et al. 2000), which leaves benthic/hydrodynamic properties to explain how nutrients can move so quickly from the water column to the benthos.

The effective surface area for uptake must be at least several times greater than the actual streambed area given most of the calculated values for  $V_f$ . Flow through substrata with biofilms attached and flow through primary producers such as filamentous algae and bryophytes will increase the effective surface area of the stream bottom. It has been demonstrated that substantial flow occurs through filamentous algae (Dodds 1991). The effective increase in surface

area for diffusion may be one reason filamentous algae are so successful in many streams.

The  $K_s$  values we were able to calculate for Konza additions were well above the  $K_s$  values that have been documented previously for microbial uptake of nutrients (Borchardt 1996). This result indicates some influence of mass transport limitation (no saturation expected at all) or low-affinity abiotic sorption processes (saturation only at very high concentrations). It is not possible to distinguish the effects of these 2 processes.

#### *Using nutrient addition experiments*

The relationship between distance from the addition and nutrient concentration was well characterized with 20 data points for each addition (e.g., Fig. 1). With this many sampling points we could identify outliers more easily than if samples had been taken with more coarse spatial resolution (e.g., every 10 m over a 60-m reach). The need for many sampling points was particularly relevant for the low-level nutrient additions where the limits of detection of colorimetric assays were being approached. Many other studies have used additions of this type to examine nutrient dynamics, but most used ~7 sampling stations (e.g., Newbold et al. 1981, Mulholland et al. 1990, Martí and Sabater 1996, Butturini and Sabater 1998, Davis and Minshall 1999). Depending upon which 7 points are chosen for each data series in Fig. 1, very different results are possible for each level of nutrient enrichment, particularly at low enrichments. The best 7 points to choose would be evenly spaced over the entire length of the reach. However, there were some outliers and these few points could still lead to errors even if points were taken over sufficiently long reaches. For future studies, we recommend  $\geq 20$  sampling stations in the reach where nutrients are decreasing.

Isotopic tracers are the only way to determine nutrient uptake at ambient concentrations. Many investigators are limited to short-term nutrient enrichments at levels well above ambient nutrient concentrations because of the difficulty and cost involved in  $^{15}\text{N}$  tracer studies and the complications of using radioisotopes ( $^{33}\text{P}$  or  $^{32}\text{P}$ ) for P studies. Our data suggest that  $U_i$  values are substantially greater and  $V_f$  values are considerably less at increased nutrient levels than at

ambient concentrations. However, by conducting additions at a series of increasing solute concentrations well below the saturation point, investigators can determine the best-fit relationship between  $C_n$  and  $U_i$ . This relationship can be used to extrapolate to ambient concentrations and establish possible stream responses to ambient levels of nutrients. We tested the possibility of such extrapolation by using the  $^{15}\text{NH}_4^+$  and short-term pulsed addition data from 12 stream sites, and by comparing our extrapolations from nutrient-enrichment additions to  $^{15}\text{N}$  addition at Kings Creek.

#### *Estimating ambient uptake rates*

For each of 10 sites in different biomes, we could calculate a  $U_i$  at elevated nutrient concentrations, and a  $^{15}\text{N}$  tracer  $U_i$  determined at ambient concentrations. Gross uptake to the benthos must be 0 when ambient concentration in the water column is 0. Thus, there are 3 known points (0,0; ambient  $U_i$  and  $U_i$  with elevated  $\text{NH}_4^+$  enrichments) to evaluate the applicability of the linear model (eqn 2). We used the line that passes through the origin, and the  $U_i$  measured at an elevated concentration for each stream to estimate an expected  $U_i$  at ambient concentrations given a linear model.

We assumed that gross uptake approximates net uptake at elevated concentrations. This approximation is based upon several assumptions. Remineralization is probably not influenced by short-term nutrient additions to the water column because remineralization is a heterotrophic process that depends upon quantity and stoichiometry of organic material, which is coupled to water-column  $C_n$  over longer time scales than the measurements we took of  $U_i$  at elevated nutrient concentrations. We also determined previously that remineralization rates were less than ambient  $U_i$  across the study sites (Peterson et al. 2001), so remineralization rates were  $< 10\%$  of uptake at elevated concentration. The idea that remineralization is approximately equal to ambient  $U_i$  is further supported by the observation that  $\text{NH}_4^+$  varied little downstream from tracer release points. If ambient  $U_i$  exceeded remineralization, then concentrations would be expected to decrease downstream and vice versa.

If  $U_i$  follows a saturating curve, then this linear extrapolation using 2 points ( $U_i$  at elevated

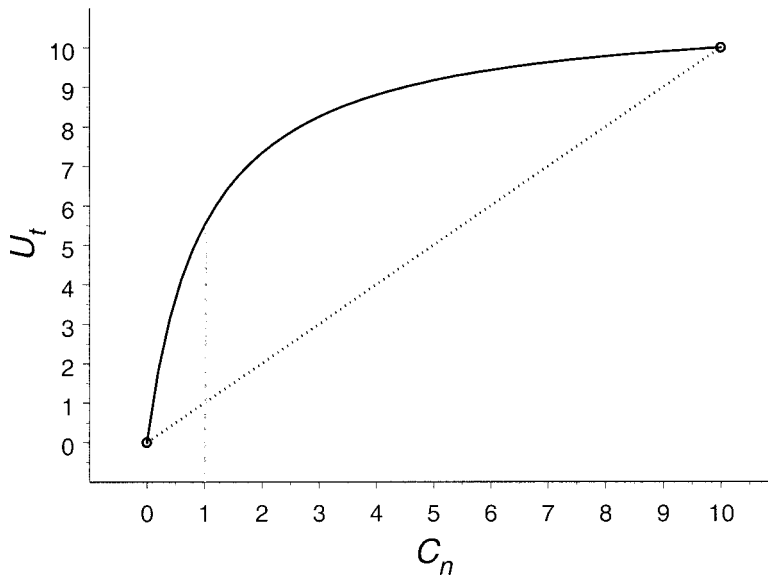


FIG. 4. A conceptual diagram of how estimation of uptake rate ( $U_t$ ) at ambient nutrient concentration ( $C_n$ ) using a single nutrient enrichment and extrapolation downward by a linear model through the origin will tend to underestimate actual uptake if a saturation model of uptake actually applies. Dashed vertical line illustrates how extrapolated uptake will be less than actual uptake if a linear model (dotted line) is used and a Michaelis-Menten model (dark line) actually applies.

nutrient concentration and 0) should underestimate ambient  $U_t$  (Fig. 4). When  $\text{NH}_4^+$   $U_t$  at ambient concentrations was estimated using the linear model,  $U_t$  was underestimated in all but Amity Creek. Uptake was substantially underestimated at E1 in Alaska, but a very high elevated  $\text{NH}_4^+$  addition was used for this site. Removing E1, the average ratio of measured to expected  $U_t$  was 3.1 (Fig. 5, SE = 0.7, paired difference  $t$ -test,  $p = 0.00005$ ).

Thus, we have 2 general methods that can be used to estimate  $\text{NH}_4^+$   $U_t$  at ambient concentrations in the absence of isotopic tracer data, and these methods were tested across biomes. The 1st is a simple relationship between  $U_t$  of  $\text{NH}_4^+$  and water-column nutrient concentration (Fig. 3). This simple log-log relationship has considerable variance, but it encompasses systems from a wide variety of biomes. The fact that 41% of the variance in  $U_t$  of  $\text{NH}_4^+$  can be ascribed to a single factor,  $\text{NH}_4^+$  concentration in the water column, could be viewed as surprising in light of all the other factors that could alter  $U_t$  (e.g., heterotrophic versus autotrophic uptake, temperature, discharge, microbial biomass, light for primary producers, organic C supply for heterotrophic microorganisms, grazing). However, this

relationship only constrains expected  $U_t$  at an individual instream concentration to within about an order of magnitude. The 2nd method to estimate the  $U_t$  at ambient concentrations is to use a linear extrapolation from a short-term unlabeled addition, and to multiply that rate by 3 (i.e., observed ambient  $U_t$  was 3.1 times higher than that calculated from unlabeled additions as discussed in the previous paragraph), which also entails considerable uncertainty. Neither method is as accurate as isotopic tracer techniques, but both are easier and more cost effective. It is not known how well such techniques will work for  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  uptake.

A 3rd alternative for estimating  $\text{NH}_4^+$  uptake at ambient concentrations was tested with the more detailed additions in Kings Creek. In this instance, the series of  $\text{NH}_4^+$  enrichments in Kings Creek were used to create a Michaelis-Menten model of  $\text{NH}_4^+$   $U_t$  (Fig. 2B) that could be compared to the tracer measurement of  $U_t$  at ambient concentration (Table 2). The  $^{15}\text{N}$  tracer and nonlinear estimates of  $U_t$  were 0.1 and 0.17  $\mu\text{mol m}^{-2} \text{s}^{-1}$ , respectively. This result suggests that extrapolation of  $U_t$  from a series of increased-concentration nutrient additions may provide a better estimate than extrapolating



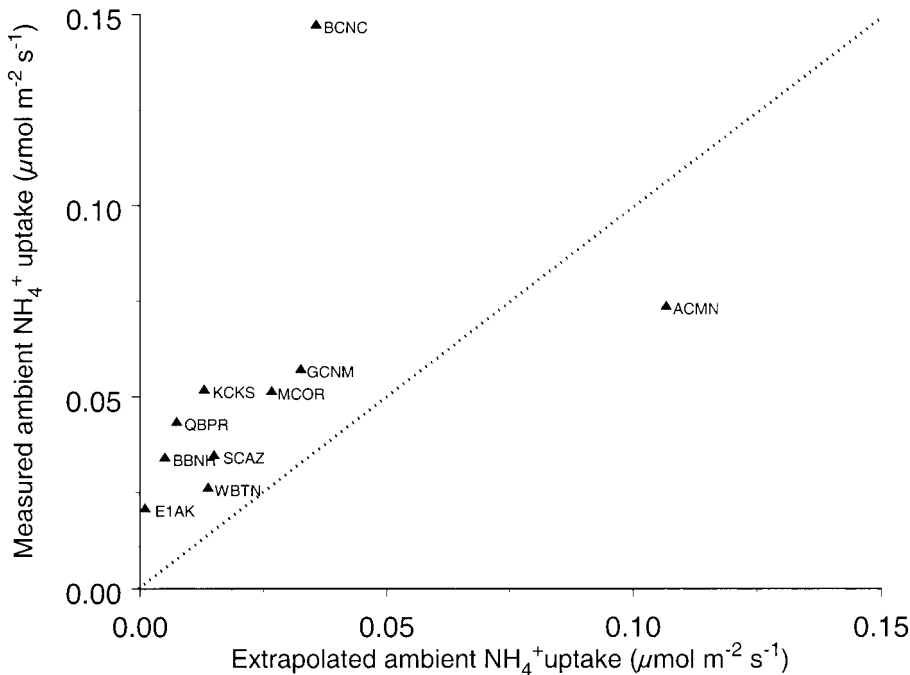


FIG. 5. Observed (using  $^{15}\text{N}$  tracer) versus calculated  $\text{NH}_4^+$  uptake rate ( $U_i$ ) at ambient  $\text{NH}_4^+$  concentration for 10 stream sites using observed data plotted in Fig. 4 and  $U_i$  calculated with a linear model from the elevated nutrient-enrichment experiments. Site acronyms as in Fig. 3. See text for a description of calculation methods.

from a single nutrient addition and using a linear model. We have demonstrated that values of  $U_i$  for  $\text{NO}_3^-$  and  $\text{NH}_4^+$  cannot be effectively estimated with a single short-term addition using our data from Kings Creek, and the same result has been demonstrated for  $\text{NH}_4^+$  in 11 other streams.

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#### Literature Cited

APHA (American Public Health Association). 1995. Standard methods for the examination of water

and wastewater. 19<sup>th</sup> edition. American Public Health Association, Washington, DC.

BORCHARDT, M. A. 1996. Nutrients. Pages 183–227 in R. J. Stevenson, M. L. Bothwell, and R. L. Lowe (editors). *Algal ecology: freshwater benthic ecosystems*. Academic Press, San Diego.

BOTHWELL, M. L. 1989. Phosphorus-limited growth dynamics of lotic periphytic diatom communities: areal biomass and cellular growth rate responses. *Canadian Journal of Fisheries and Aquatic Sciences* 46:1293–1301.

BOTT, T. L., A. BATRUUP-PETERSON, J. T. BROCK, P. A. CHAMBERS, W. K. DODDS, K. T. HIMBEAULT, J. R. LAWRENCE, D. PLANAS, E. SNYDER, AND G. M. WOLFAARDT. 1997. An evaluation of techniques for measuring periphyton metabolism in chambers. *Canadian Journal of Fisheries and Aquatic Sciences* 54:715–725.

BREZONIK, P. L. 1994. Chemical kinetics and process dynamics in aquatic systems. Lewis Publishers, Boca Raton, Florida.

BUTTURINI, A., AND F. SABATER. 1998. Ammonium and phosphate retention in a Mediterranean stream: hydrological versus temperature control. *Canadian Journal of Fisheries and Aquatic Sciences* 55: 1938–1945.



- CRC. 1978. Handbook of chemistry and physics. CRC Press, West Palm Beach, Florida.
- DAVIS, J. C., AND G. W. MINSHALL. 1999. Nitrogen and phosphorus uptake in two Idaho (USA) headwater wilderness streams. *Oecologia* (Berlin) 119: 247–255.
- DENNY, M. W. 1993. Air and water, the biology and physics of life's media. Princeton University Press, Princeton, New Jersey.
- DODDS, W. K. 1991. Microenvironmental characteristics of filamentous algal communities in flowing freshwaters. *Freshwater Biology* 25:199–209.
- DODDS, W. K. 1993. What controls the levels of dissolved phosphate and ammonium in surface waters? *Aquatic Sciences* 55:132–142.
- DODDS, W. K., J. M. BLAIR, G. M. HENEYRY, J. K. KOELLIKER, R. RAMUNDO, AND C. M. TATE. 1996. Nitrogen transport from tallgrass prairie by streams. *Journal of Environmental Quality* 25: 973–981.
- DODDS, W. K., M. A. EVANS-WHITE, N. GERLANC, L. GRAY, D. A. GUDDER, M. J. KEMP, A. L. LÓPEZ, D. STAGLIANO, E. STRAUSS, J. L. TANK, M. R. WHILES, AND W. WOLLHEIM. 2000. Quantification of the nitrogen cycle in a prairie stream. *Ecosystems* 3: 574–589.
- DODDS, W. K., AND E. WELCH. 2000. Establishing nutrient criteria in streams. *Journal of the North American Benthological Society* 19:186–196.
- GARVEY, J. E., E. A. MARSCHALL, AND R. A. WRIGHT. 1998. From star charts to stoneflies: detecting relationships in continuous bivariate data. *Ecology* 79:442–447.
- GLUD, R. N., J. K. GUNDERSEN, N. P. REVSBECH, AND B. B. JØRGENSEN. 1994. Effects on the benthic diffusive boundary layer imposed by microelectrodes. *Limnology and Oceanography* 39:462–467.
- GRAY, L. J., AND W. K. DODDS. 1998. Structure and dynamics of aquatic communities. Pages 177–189 in A. K. Knapp, J. M. Briggs, D. C. Hartnett, and S. L. Collins (editors). *Grassland dynamics*. Oxford University Press, New York.
- GRAY, L. J., G. L. MACPHERSON, J. K. KOELLIKER, AND W. K. DODDS. 1998. Hydrology and aquatic chemistry. Pages 159–167 in A. K. Knapp, J. M. Briggs, D. C. Hartnett, and S. L. Collins (editors). *Grassland dynamics*. Oxford University Press, New York.
- HAMILTON, S. K., J. L. TANK, D. F. RAIKOW, W. M. WOLLHEIM, B. J. PETERSON, AND J. R. WEBSTER. 2001. Nitrogen uptake and transformation in a midwestern US stream: a stable isotope enrichment study. *Biogeochemistry* 54:297–340.
- HOLMES, R. M., J. W. MCCLELLAND, D. M. SIGMAN, B. FRY, AND B. J. PETERSON. 1998. Measuring  $^{15}\text{N-NH}_4^+$  in marine, estuarine and fresh waters: an adaptation of the ammonium diffusion method for samples with low ammonium concentrations. *Marine Chemistry* 60:235–243.
- KEMP, M. J. 2001. Factors controlling spatial and temporal patterns of nitrogen cycling in prairie streams. PhD Dissertation, Kansas State University, Manhattan, Kansas.
- KEMP, M. J., AND W. K. DODDS. 2001. Spatial and temporal patterns of nitrogen in prairie streams. *Biogeochemistry* 53:125–141.
- KIM, B. M., A. P. JACKMAN, AND F. J. TRISKA. 1990. Modeling transient storage and nitrate uptake kinetics in a flume containing a natural periphyton community. *Water Resources Research* 26:505–515.
- MARTÍ, E., AND F. SABATER. 1996. High variability in temporal and spatial nutrient retention in Mediterranean streams. *Ecology* 77:854–869.
- MERRIAM, J. L., W. H. MCDOWELL, J. L. TANK, W. M. WOLLHEIM, C. L. CRENSHAW, AND S. L. JOHNSON. 2002. Characterizing nitrogen dynamics, retention and transport in a tropical rainforest stream using an *in situ*  $^{15}\text{N}$  addition. *Freshwater Biology* 47:143–160.
- MULHOLLAND, P. J., C. S. FELLOWS, J. L. TANK, N. B. GRIMM, J. R. WEBSTER, S. K. HAMILTON, E. MARTÍ, L. ASHKENAS, W. B. BOWDEN, W. K. DODDS, W. H. MCDOWELL, M. J. PAUL, AND B. J. PETERSON. 2001. Inter-biome comparison of factors controlling stream metabolism. *Freshwater Biology* 46:1503–1517.
- MULHOLLAND, P. J., A. D. STEINMAN, AND J. W. ELWOOD. 1990. Measurement of phosphorus uptake length in streams: comparison of radiotracer and stable  $\text{PO}_4$  releases. *Canadian Journal of Fisheries and Aquatic Sciences* 47:2351–2357.
- MULHOLLAND, P. J., J. L. TANK, D. M. SANZONE, J. R. WEBSTER, W. M. WOLLHEIM, B. J. PETERSON, AND J. L. MEYER. 2001. Ammonium and nitrate uptake lengths in a small forested stream determined by  $^{15}\text{N}$  tracer and short-term nutrient enrichment experiments. *Verhandlungen der Internationalen Vereinigung für theoretische und angewandte Limnologie* 27:1320–1325.
- MULHOLLAND, P. J., J. L. TANK, D. M. SANZONE, W. M. WOLLHEIM, B. J. PETERSON, J. R. WEBSTER, AND J. L. MEYER. 2000. Nitrogen cycling in a deciduous forest stream determined from a tracer  $^{15}\text{N}$  addition experiment in Walker Branch, Tennessee. *Ecological Monographs* 70:471–493.
- NEWBOLD, J. D., J. W. ELWOOD, R. V. O'NEILL, AND W. VAN WINKLE. 1981. Measuring nutrient spiralling in streams. *Canadian Journal of Fisheries and Aquatic Sciences* 38:860–863.
- OVIATT, C. G. 1998. Geomorphology of Konza Prairie. Pages 35–47 in A. K. Knapp, J. M. Briggs, D. C. Hartnett, and S. L. Collins (editors). *Grassland dynamics*. Oxford University Press, New York.
- PETERSON, B. J., W. M. WOLLHEIM, P. J. MULHOLLAND,

- J. R. WEBSTER, J. L. MEYER, J. L. TANK, N. B. GRIMM, W. B. BOWDEN, H. M. VALETT, A. E. HERSHEY, W. B. MCDOWELL, W. K. DODDS, S. K. HAMILTON, S. GREGORY, AND D. J. D'ANGELO. 2001. Stream processes alter the amount and form of nitrogen exported from small watersheds. *Science* 292:86–90.
- RABALAIS, N. N., R. E. TURNER, W. J. WISEMAN, AND Q. DORTCH. 1998. Consequences of the 1993 Mississippi River flood in the Gulf of Mexico. *Regulated Rivers: Research and Management* 14:161–177.
- SANFORD, L. P., AND S. M. CRAWFORD. 2000. Mass transfer versus kinetic control of uptake across solid–water boundaries. *Limnology and Oceanography* 45:1180–1186.
- STREAM SOLUTE WORKSHOP. 1990. Concepts and methods for assessing solute dynamics in stream ecosystems. *Journal of the North American Benthological Society* 9:95–119.
- TANK, J. L., J. L. MEYER, D. M. SANZONE, P. J. MULLHOLLAND, J. R. WEBSTER, B. J. PETERSON, AND N. E. LEONARD. 2000. Analysis of nitrogen cycling in a forest stream during autumn using a  $^{15}\text{N}$  tracer addition. *Limnology and Oceanography* 45:1013–1029.
- TECHNICON AUTOANALYZER II. 1973. Nitrate and nitrite in water and wastewater. Industrial method number 100–70W. Technicon Industrial Systems, Tarrytown, New York.
- VOGEL, S. 1994. *Life in moving fluids*. Princeton University Press, Princeton, New Jersey.
- WEBSTER, J. R., AND T. P. EHRLMAN. 1996. Solute dynamics. Pages 145–160 in F. R. Hauer and G. A. Lamberti (editors). *Methods in stream ecology*. Academic Press, New York.
- WOLLHEIM, W. M., B. J. PETERSON, L. A. DEEGAN, J. E. HOBBIIE, B. HOOKER, W. B. BOWDEN, K. J. EDWARDSON, D. B. ARSCOTT, A. E. HERSHEY, AND J. FINLAY. 2001. Influence of stream size on ammonium and suspended particulate nitrogen processing. *Limnology and Oceanography* 46:1–13.

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