

Nutrient retention in a point-source-enriched stream

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Abstract. The capacity of a 3rd-order Ozark Plateau stream (Arkansas, USA) to take up (or remove) nutrient inputs from a rural wastewater treatment plant (WWTP) was examined using nutrient spiraling methods. Short-term nutrient additions often are used to assess nutrient uptake length, where an exponential decline in the concentration of the added nutrient reflects gross nutrient uptake. We applied this quantitative framework using WWTP effluent as a stream nutrient addition, and estimated net nutrient uptake length (S_{net}), mass transfer coefficient ($v_{f,net}$), and uptake rate (U_{net}) in Columbia Hollow, Arkansas. Water samples were collected at a reference site upstream of the WWTP input and at 6 sites downstream of the WWTP (0.3–2.7 km). Input from the WWTP significantly increased discharge, temperature, conductivity, soluble reactive P (SRP), and $\text{NH}_4\text{-N}$, and decreased pH and $\text{NO}_3\text{-N}$ 0.3 km downstream from the point source. When P additions from the WWTP were low, stored SRP was released from the stream reach to maintain high water-column concentrations. Dissolved inorganic N was not retained in Columbia Hollow. Most or all of the $\text{NH}_4\text{-N}$ added from the point source was converted to $\text{NO}_3\text{-N}$, resulting in net nitrification rates of 7 to 31 g $\text{NO}_3\text{-N m}^{-2} \text{d}^{-1}$. The relationship between dilution-corrected concentrations and distance from the WWTP input indicated no significant nutrient retention, or that several stream kilometers were required before N and P were taken up. U_{net} typically was >7- to 10-fold higher and $v_{f,net}$ estimates were 10- to 100-fold lower than values reported for undisturbed streams, indicating low relative nutrient demand. Rather than acting as a nutrient sink, Columbia Hollow appeared to be acting as a short-term storage zone for P and a transformer of N. Thus, the effect of this rural WWTP on the stream was profound, distorting N and P cycling in Columbia Hollow.

Key words: effluent, nitrogen, phosphorus, nitrification, nutrient uptake, retention, wastewater treatment plants.

In the last decade, scientific investigation in the Ozark Plateaus, USA, has focused on the effects of animal manure application to pastures on nutrient concentrations and fluxes in surface runoff (e.g., Edwards and Daniel 1993, Sauer et al. 2000). Nutrient concentrations and fluxes in Ozark streams often increase with the proportion of pasture or agricultural land use in the basin (Petersen et al. 1999, Haggard et al. 2003a). These observations have received more attention than the potential effects of municipal wastewater treatment plant (WWTP) inputs on

aquatic systems. However, WWTPs continue to pose a threat to regional water quality despite nationwide efforts to reduce WWTP nutrient inputs. WWTPs and other point sources contribute almost 50% of the total nutrient load to some aquatic systems in this region (Haggard et al. 2003b). Within individual basins throughout the world, WWTP inputs often contribute 50% to 90% of annual nutrient inputs (e.g., Newman 1995, House and Denison 1997, Koning and Roos 1999, Kim et al. 2002, Albek 2003, Martí et al. 2004).

The effects of WWTPs on stream nutrient concentrations and cycling are substantial; the distance required to retain >63% of WWTP nutrient inputs temporarily can be as long as 30

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km (Haggard et al. 2001a, Martí et al. 2004). Effluents can cause sediment deoxygenation several kilometers downstream (Rutherford et al. 1991), and they decrease the P buffering capacity of benthic sediments (Dorioz et al. 1998, House and Denison 1998, Haggard et al. 2001a). In short, WWTPs can have significant effects on nutrient loads and on nutrient transformations and general limnological conditions in the stream, and the effects may persist for several kilometers downstream of the input. Unfortunately, few measures of nutrient uptake have been made using spiraling methods (Stream Solute Workshop 1990) in highly enriched systems, especially in streams receiving nutrient-enriched WWTP effluent.

The objective of our study was to evaluate the impact of a rural WWTP on physical properties, nutrient concentrations, and net nutrient retention during baseflow conditions in a 3rd-order Ozark Plateau stream. The relationships between stream flow, net nutrient retention, and the level of nutrient addition from the WWTP were evaluated to determine potential mechanisms causing or limiting nutrient retention below a point-source input.

Site Description

The focus of our study was Columbia Hollow, a 3rd-order tributary to Spavinaw Creek in the Ozark Plateau of northwest Arkansas. We determined stream order from 1:24,000-scale US Geological Survey topographic maps and included intermittent and perennial streams (Fig. 1). Spavinaw Creek empties into Lakes Eucha and Spavinaw, important drinking-water-supply reservoirs for the cities of Jay and Tulsa, Oklahoma. The area lies within the Springfield Plateau section of the Ozark Plateaus, and its groundwater chemistry is dominated by limestone dissolution. Total P and NO₃-N concentrations in groundwater samples collected from the Spavinaw Creek basin (Lake Eucha Basin) were <0.05 and <4 mg/L, respectively, during the study period (OWRB 2002).

Columbia Hollow receives effluent from a municipal WWTP with secondary treatment in the City of Decatur, Arkansas. This facility receives wastewater from a poultry processing plant and a residential population of ~1000 inhabitants. The facility provides secondary treatment of influent using lagoon anaerobic and

aerobic digestion with a finishing (clarification) pond. Mean discharge from the Decatur WWTP is ~5000 m³/d (60 L/s), and the effluent has permit limits of 10, 15, and 10 mg/L of carbonaceous biochemical oxygen demand (CBOD), NH₄-N, and NO₃-N, respectively. Currently, no regulations exist for P at this facility (ADPCE 1985, 1997). The Decatur WWTP contributes almost 25% of the annual P load to Lake Eucha (Storm et al. 2002) and is ~9 stream km from Spavinaw Creek and >30 stream km from Lake Eucha. The effect of inputs from Columbia Hollow on nutrient retention in Spavinaw Creek was evaluated in a previous study in a 3.5-km study reach downstream from the confluence of Spavinaw Creek and Columbia Hollow, where Spavinaw Creek received no tributary inputs other than from Columbia Hollow (Haggard et al. 2001a).

We selected 7 sampling sites at Columbia Hollow (Fig. 1); 6 sites were located along a 2.7 km reach downstream of the WWTP input, and one was located upstream of the WWTP input and served as a reference for physicochemical conditions and nutrient concentrations (Fig. 1). The first sampling site below the WWTP was 0.3 km from the outfall, and downstream distances of sampling sites from the WWTP increased to 2.7 km at the most-downstream site. Within the study reach, Columbia Hollow is a typical Ozark Mountain stream with a chert-gravel bed and karst topography in the upland areas. The basin area above the most-downstream site is 18 km², with 73% of the land used for agriculture and pasture. Agriculture in this region consists of poultry, swine, and cattle operations, and animal manure is applied to pastures as fertilizer. The headwaters of Columbia Hollow drain the city of Decatur, but urban-suburban land use is only 4% of total basin area.

Methods

Field and laboratory methods

We sampled the 7 sites at Columbia Hollow almost monthly from June 1999 through February 2000. We estimated discharge at each site from depth and velocity measurements at ~0.3-m intervals across a transect perpendicular to stream flow. We measured velocity using an electromagnetic flow meter (Flo-Mate 2000, Marsh-McBirney, Frederick, Maryland). At each

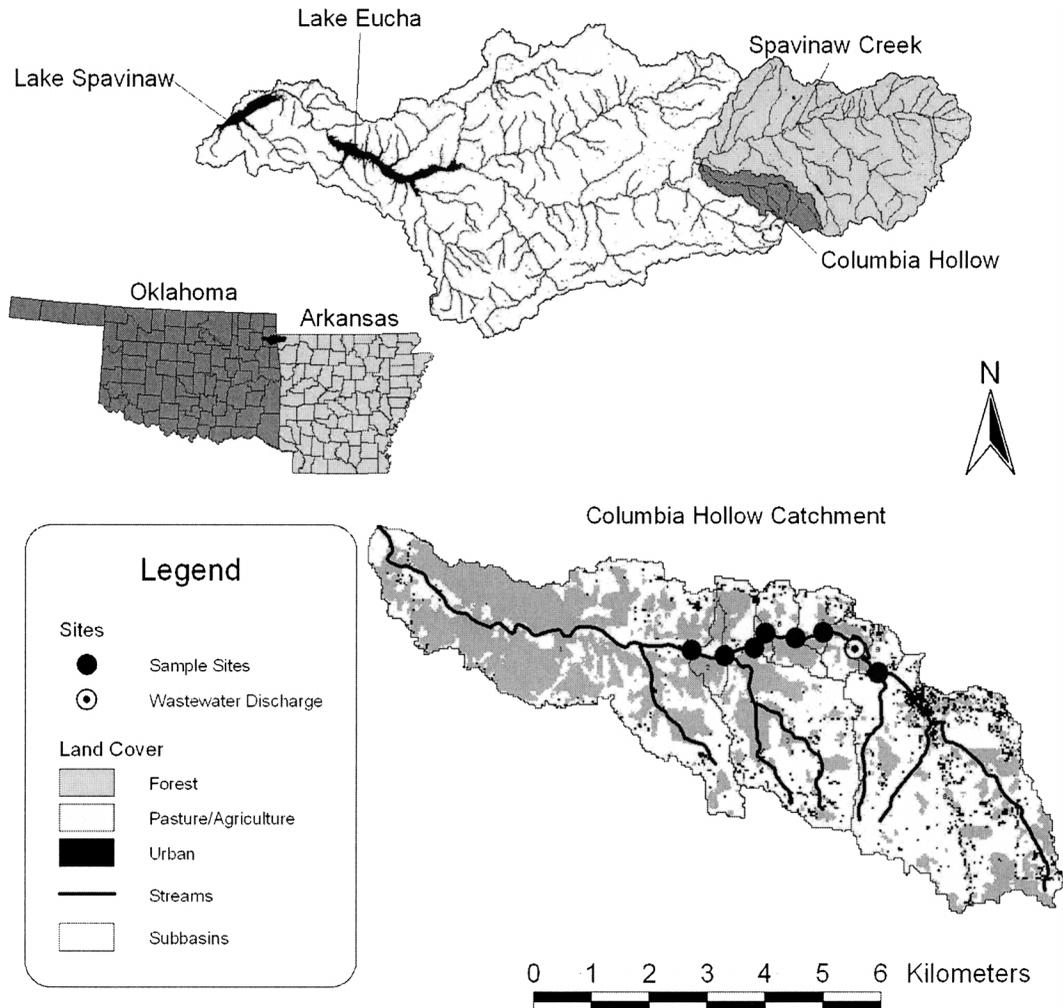


FIG. 1. Columbia Hollow catchment (lat 36°20.6'N, long 94°28.6'W), Eucha-Spavinaw basin, and water-quality sampling sites.

site, we measured electrical conductivity (YSI Model 30 SCT Meter), temperature, and pH (Oakron pH Tester 2) at a single point, and we collected surface water samples at 3 points perpendicular to stream flow. We filtered water samples immediately on site using 0.7- μm pore diameter, Whatman GF/F glass fiber filters and acidified them with H_2SO_4 to $\text{pH} < 2$. We put water samples on ice, stored them in the dark, and analyzed them within 48 h of collection. Field surveys specifically targeted baseflow conditions at Columbia Hollow.

Upon return to the laboratory, we determined dissolved inorganic nutrient and Cl^- concentrations using a Lachat QuikChem 9000 (Lachat,

Milwaukee, Wisconsin). We determined soluble reactive P (SRP) using the molybdate and ascorbic acid reduction method (QuikChem Method 10-115-01-1A). We analyzed NO_3^- -N using Cd-Cu reduction (QuikChem 10-177-04-1-A). We determined NH_4^+ -N via alkaline phenol, sodium hypochlorite, and nitroprusside reaction (QuikChem Method 10-107-06-1-B). We measured Cl^- using mercuric thiocyanate (QuikChem Method 10-117-07-1-C).

Calculation of nutrient uptake and retention

We used nutrient spiraling methods (Newbold et al. 1981, Stream Solute Workshop 1990)

to estimate transport and retention of nutrients from the WWTP. Short-term solute additions often are used to estimate nutrient uptake length (S_w), the average distance a nutrient molecule travels downstream in the dissolved form before being removed by benthic abiotic and biotic processes (Newbold et al. 1981). Nutrient uptake length is an indicator of stream nutrient retention efficiency; the shorter the length the greater the efficiency and vice versa. This parameter is estimated from the decline in nutrient concentration with distance from the solute addition point, assuming that nutrient additions are sufficiently low that resulting stream concentrations are below saturation (e.g., Webster et al. 1991, Martí and Sabater 1996, Haggard et al. 2001b). We used this method of determining downstream declines in nutrient concentrations to make a whole-reach estimate of nutrient retention. However, nutrient concentrations were elevated far beyond typical saturating concentrations because the nutrient addition from the WWTP was substantial (see Results) and continuous (e.g., see Dodds et al. 1997, Dodds et al. 2002). Therefore, a key assumption for the determination of S_w was violated. Moreover, in nutrient spiraling studies, short-term nutrient additions are limited in duration to ensure measurement of only nutrient uptake. However, at our site, the observed longitudinal pattern in nutrient concentrations downstream from continuous WWTP inputs was the net result of nutrient uptake and release. Therefore, we used downstream declines in nutrient concentrations to estimate a different parameter: net nutrient uptake length (S_{net}) (Martí et al. 1997, Haggard et al. 2001a).

S_{net} is the negative, inverse slope of the regression between the natural logarithm of the proportion of dilution-corrected nutrient concentration remaining in the water column and distance from the nutrient source (in this case, the WWTP). WWTP effluent is often high in Cl^- , and because Cl^- is a conservative ion, we used downstream changes in Cl^- concentrations to correct for dilution from groundwater and lateral inflows. Hyporheic Cl^- concentrations upstream and downstream of the outfall were similar to concentrations in overlying surface waters at each site (Hunt 2000), demonstrating that groundwater was not a substantial source of Cl^- . Median and mean groundwater Cl^- concentrations in the Eucha Basin were <8 mg/L

(OWRB 2002); this concentration was slightly less than that measured upstream (11 mg/L) from the WWTP at Columbia Hollow. Thus, we were able to use the Cl^- addition from the WWTP to correct for dilution throughout the study reach (see also Kim et al. 2002, Martí et al. 2004).

We used changes in the dilution-corrected nutrient concentration downstream from the WWTP to estimate S_{net} on each sampling date using the following equations:

$$C_x = C_o e^{kx} \quad \ln(C_x/C_o) = kx \quad S_{net} = -1/k$$

where C_x is the dilution-corrected nutrient concentration (mg/L) at distance x (m) from the WWTP, C_o is the nutrient concentration (mg/L) at the most-upstream site below the WWTP, and k is the nutrient change coefficient (1/m). The calculations of S_w and S_{net} are identical, but interpretation of their meanings differ. S_w is a component of the spiraling length and a measure of the nutrient retention efficiency of a stream (Newbold 1992). S_{net} is a measure of net retention efficiency because the nutrient additions are continuous, and dissolved inorganic nutrient molecules are retained from and released into the water column continuously. We used simple linear regression to determine if the relation between dilution-corrected nutrient concentrations and distance downstream (i.e., S_{net}) was significant at $\alpha = 0.05$. We applied this same level of significance to other correlation analyses and to paired t -tests of physical and chemical conditions upstream and downstream of the WWTP effluent discharge.

Once we calculated S_{net} , we were able to calculate mass transfer coefficients and uptake rates. The mass transfer coefficient (v_f) is the vertical velocity at which a nutrient molecule travels from the water column to the stream substrate (Stream Solute Workshop 1990). The parameter is related to S_{net} through average water depth and velocity as

$$v_{f-net} = hu/S_{net} = Q/(S_{net}w)$$

where h is the average water depth (m), u is the average water velocity (m/s), Q is the average discharge (m^3/s), and w is the average stream width (m). Net nutrient uptake rate (U_{net} , $\text{mg m}^{-2} \text{s}^{-1}$) of nutrients added by the WWTP also can be calculated from S_{net} as

$$U_{net} = (C_o Q)/(S_{net} w) = v_{f-net} C_o$$

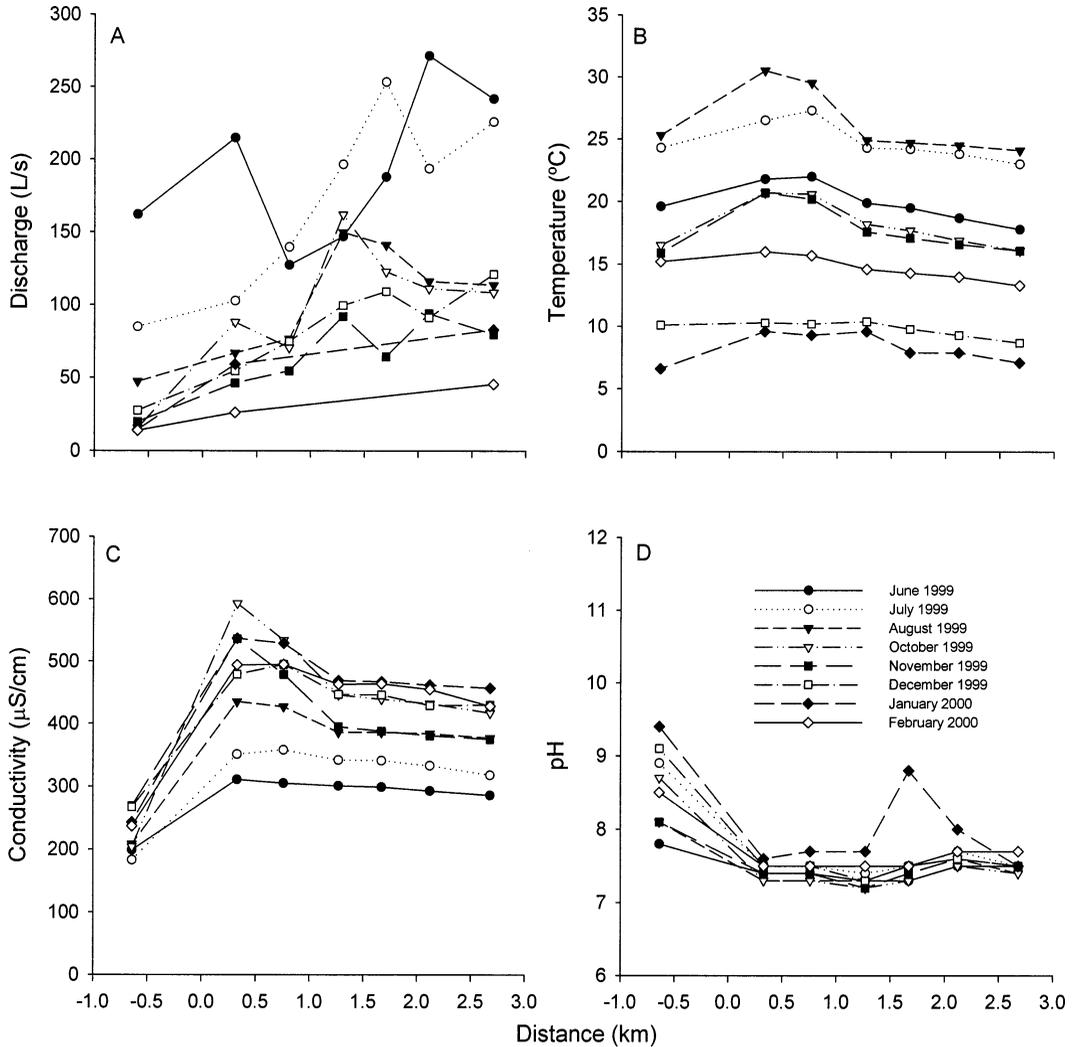


FIG. 2. Discharge (A), temperature (B), conductivity (C), and pH (D) with respect to distance upstream (negative value) and downstream (positive values) from the Decatur wastewater treatment plant at Columbia Hollow over the study period. Symbols represent the means of 3 samples collected at each site; lines are used between symbols only to aid visualization.

Because we calculated S_{net} , we have redefined these terms in our study as the net mass transfer coefficient (v_{f-net}) and the net nutrient uptake rate (U_{net}). We estimated the level of nutrient addition (i.e., ΔSRP , Δ dissolved inorganic N [DIN], ΔNO_3-N , and ΔNH_4-N) as the difference between concentrations measured upstream and downstream from the WWTP input.

We modeled linear nitrification rate (K_{NIT} , 1/m) using equations and methods described by Bernhardt et al. (2002). We determined K_{NIT} by

fitting the model to longitudinal changes in NO_3-N concentration (see also Mulholland et al. 2000). We determined NO_3-N uptake/m (K_{NO_3-N}) and K_{NIT} simultaneously using MS Excel Solver and minimizing the sum of squares between predicted and observed NO_3-N concentration. MS Excel Solver was constrained so that K_{NIT} , K_{NO_3-N} and NH_4-N uptake/m (K_{NH_4-N}) were ≥ 0 . We estimated the fraction of NH_4-N nitrified and the modeled nitrification rate ($g\ m^{-2}\ d^{-1}$) using the following equations from Bernhardt et al. (2002):

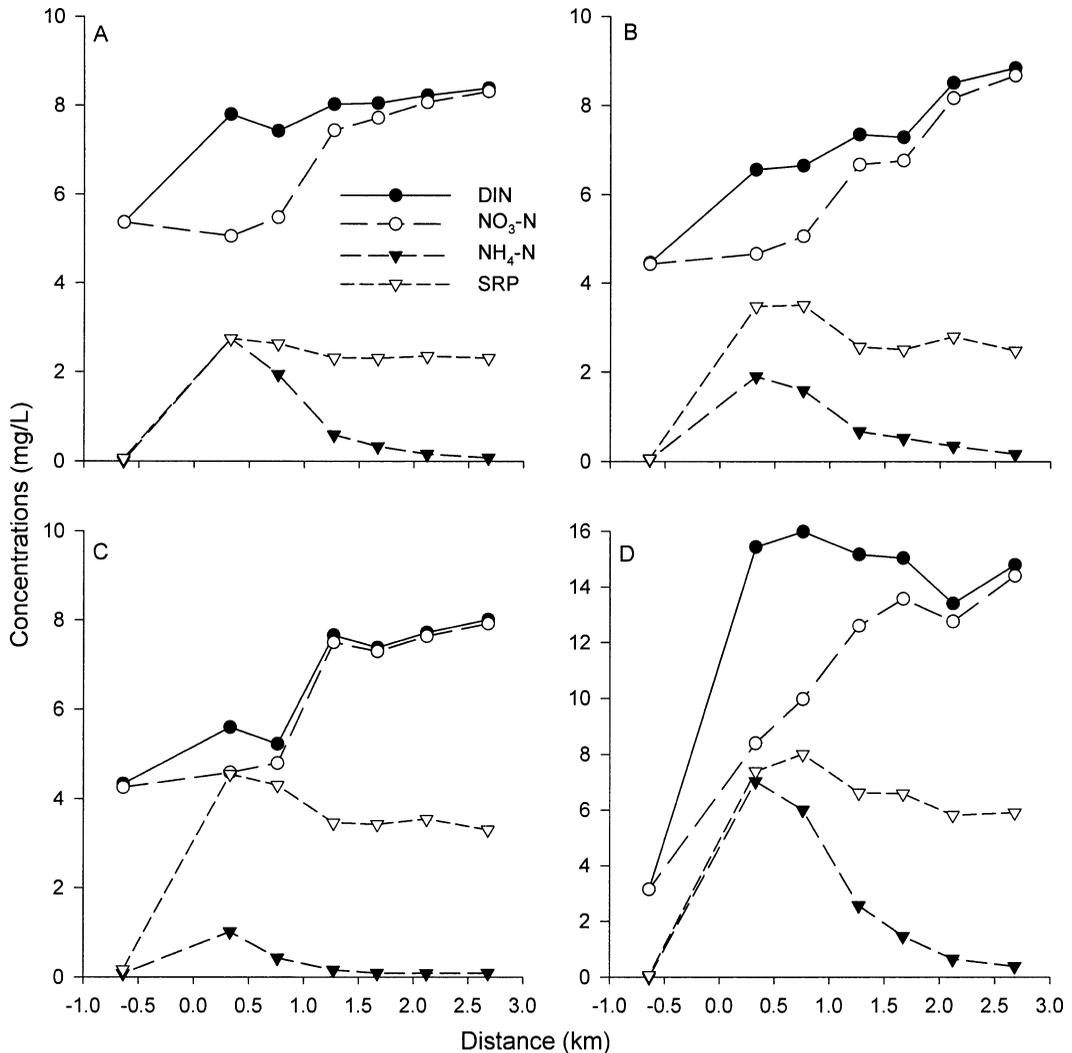


FIG. 3. Dilution-corrected nutrient concentrations with respect to distance upstream (negative value) and downstream (positive values) from the Decatur wastewater treatment plant at Columbia Hollow in June 1999 (A), July 1999 (B), August 1999 (C), October 1999 (D), November 1999 (E), December 1999 (F), January 2000 (G), and February 2000 (H). Symbols represent the means of 3 samples collected at each site; lines are used between symbols only to aid visualization. DIN = dissolved inorganic N, SRP = soluble reactive P.

$$\% \text{NH}_4\text{-N nitrified} = K_{\text{NIT}} / K_{\text{NH}_4\text{-N}}$$

$$\text{modeled nitrification rate} = (K_{\text{NIT}} / K_{\text{NH}_4\text{-N}}) U_{\text{net}} - \text{NH}_4\text{-N}$$

Results

Discharge, temperature, pH, and conductivity

Stream discharge generally decreased in Columbia Hollow over the study period. At the up-

stream site, discharge ranged from a maximum of 162 L/s in June to a minimum of 14 L/s in January and February (Fig. 2A). On all sampling dates, discharge increased by 20% to almost 500% between the upstream site and the first site downstream from the Decatur WWTP input. If we assume no inputs other than the WWTP over the 0.9 km between the 2 sampling stations, then the point source discharge contributed 17 to 83% of the stream flow in Columbia Hollow at the 0.3 km site. Discharge grad-

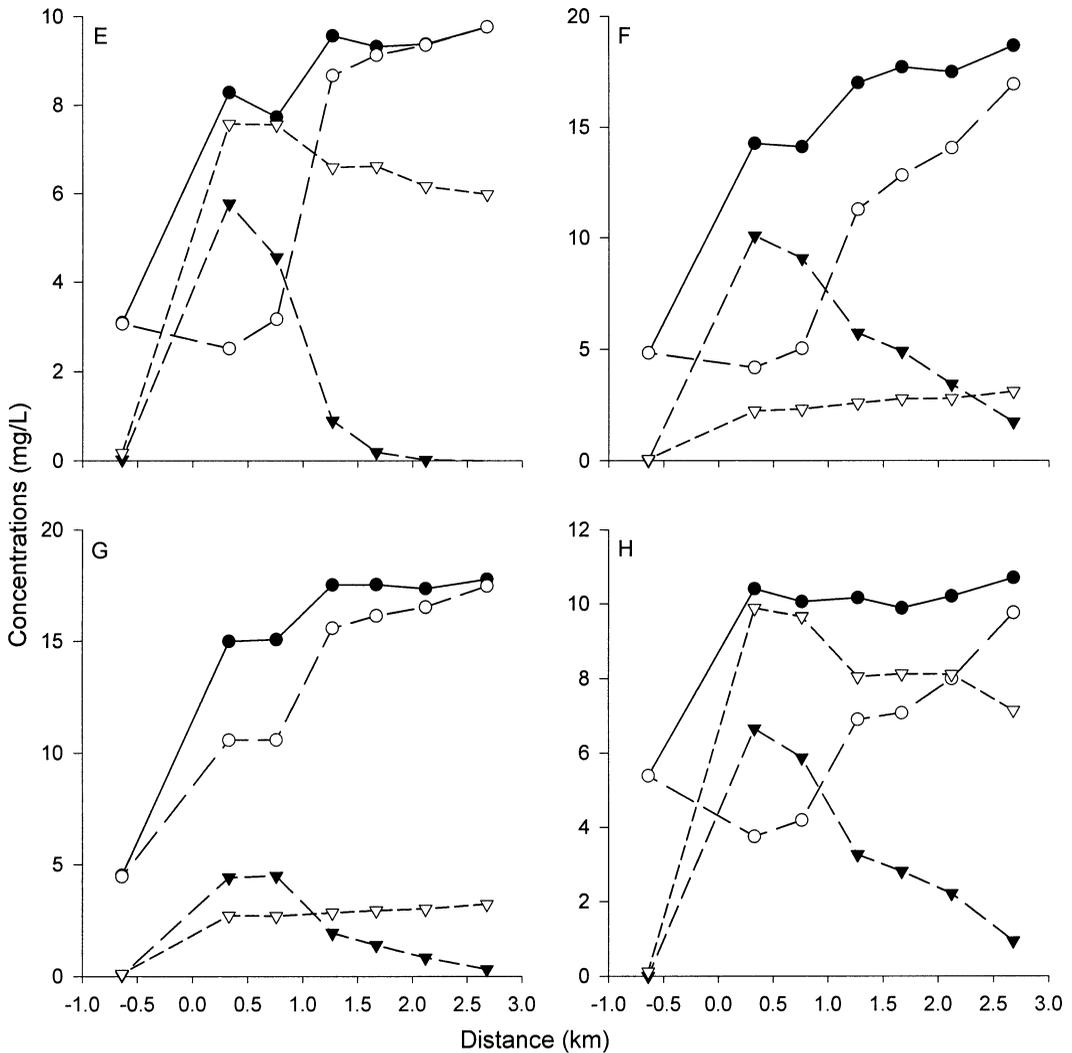


FIG. 3. Continued.

ually increased with distance downstream from the WWTP input, except between the 2.1 and 2.7 km sites, where flow decreased slightly despite the presence of a small tributary that contributed flow from June to August. The most notable increase in surface flow occurred between sites 0.8 and 1.3 km, where we observed groundwater inflow through karst bedrock on the steep stream bank. For the entire study reach, the ratio of WWTP discharge to groundwater discharge varied from 0.1 to 3.7, averaging 1.2 across the 8 sampling dates.

Discharge from the Decatur WWTP had a substantial effect on water temperature, pH,

and conductivity in Columbia Hollow. Water temperature increased significantly immediately downstream from the WWTP input (paired *t*-test, $p < 0.01$, Fig. 2B) then decreased in the downstream direction. At the most-downstream site, temperature was similar to that observed at the upstream reference site. Similarly, conductivity 0.3 km below the WWTP was $>2\times$ that observed upstream (paired *t*-test, $p < 0.0001$, Fig. 2C) and decreased in the downstream direction, but conductivity remained elevated relative to the upstream reference site. pH decreased significantly below the WWTP (paired *t*-test, $p < 0.001$, Fig. 2D) and remained

at neutral conditions throughout the study reach.

Cl^-

Cl^- concentrations upstream of the Decatur WWTP ranged from 5.8 to 20.3 mg/L and increased to 23.2 to 67.9 mg/L immediately below the point source. Assuming no groundwater inputs over the 0.9 km between these 2 sampling stations, these increases translate to a Cl^- loading rate of 1.0 to 5.8 g/s from the WWTP, and effluent Cl^- concentrations of 74 to 152 mg/L. Cl^- concentration declined along the 2.4-km reach on all dates. Rates of decline ranged from a minimum of 2.6 mg/L to a maximum of 17.7 mg/L. Thus, dilution estimated from Cl^- declines between the 0.3 and 2.7 km sites accounted for 16 to 41% of the observed change in the various soluble N and P concentrations. Within the study reach, the greatest decline in Cl^- concentration (7–33%) occurred between the 0.8 and 1.3 km sites and coincided with the greatest increases in stream discharge.

SRP concentrations and net retention

SRP concentration upstream from the WWTP input varied from 0.06 to 0.17 mg/L over the study period. The Decatur WWTP input increased significantly downstream SRP concentration on all sampling dates (paired *t*-test, $p < 0.001$ for ln-transformed data), resulting in concentrations that were as much as 50-fold greater than upstream of the WWTP input (Fig. 3A–H). The highest concentration measured at Columbia Hollow 0.3 km downstream from the WWTP input was 9.9 mg/L in February 2000 (Fig. 3H). SRP concentration decreased with increasing distance downstream from the WWTP, but concentrations at the most-downstream site were still 30-fold greater than at the reference site, and averaged 3.0 mg/L across all dates.

After correcting for dilution, we observed decreases in SRP concentration with downstream distance from the WWTP on 6 of 8 sampling dates and increases on the other 2 dates. For dates with significant SRP decreases, S_{net} -SRP ranged from 6.8 to 13.4 km (Table 1). The increasing gradient in SRP resulted in negative S_{net} -, $v_{f\text{-net}}$ - and U_{net} -SRP values in December and January and indicated that net P release was greater than net removal along the study reach.

These negative values coincided with the lowest P inputs from the WWTP. S_{net} -SRP did not show any particular temporal variation over the sampling dates (Table 1, Fig. 4A), nor was S_{net} -SRP related to stream discharge or ambient SRP concentration 0.3 km downstream from the WWTP input.

Temporal patterns were not evident with S_{net} -SRP, but $v_{f\text{-net}}$ -SRP decreased with time during our study period, and was fastest in late spring and summer and slowest in winter (Table 1). The relationship with time was not surprising given that $v_{f\text{-net}}$ -SRP was strongly correlated with water temperature downstream from the WWTP input ($v_{f\text{-net}} = -7.1 \times 10^{-6} + 5.4 \times 10^{-7}$ [temperature], $r^2 = 0.86$, $p < 0.001$). Excluding dates with negative values, $v_{f\text{-net}}$ -SRP generally decreased with increasing SRP concentration 0.3 km downstream from the WWTP input or with increasing ΔSRP (Fig. 4B). $v_{f\text{-net}}$ -SRP and S_{net} -SRP were greatest when SRP concentrations 0.3 km downstream from the WWTP input were approaching the shift from SRP uptake to SRP release within the study reach (i.e., the shift from positive to negative values).

U_{net} -SRP averaged 0.015 mg m⁻² s⁻¹, and ranged from -0.009 to 0.029 mg m⁻² s⁻¹. The relationship between U_{net} -SRP and SRP concentration 0.3 km downstream from the WWTP input appeared to shift from P uptake (positive values) to release (negative values) at ~2.8 mg/L. The relationship became relatively constant when P was >3.4 mg/L (Fig. 4C).

DIN concentrations and net retention

DIN was dominated by $\text{NO}_3\text{-N}$ upstream of the WWTP. Background $\text{NO}_3\text{-N}$ concentrations varied from 3.03 to 5.47 mg/L (average = 4.37 mg/L), whereas the background $\text{NH}_4\text{-N}$ concentration was ≤ 0.10 mg/L on all dates and averaged 0.02 mg/L. $\text{NH}_4\text{-N}$ concentration immediately downstream from the WWTP input was 10- to 100-fold greater than upstream concentration (paired *t*-test, $p < 0.01$ for ln-transformed data; Fig. 3A–H). $\text{NH}_4\text{-N}$ concentrations showed a consistent longitudinal decrease along the study reach on all sampling dates (Fig. 3A–H). At the most-downstream site, $\text{NH}_4\text{-N}$ concentration declined to ≤ 1 mg/L and was < 0.1 mg/L on most dates. $\text{NO}_3\text{-N}$ decreased immediately downstream from the WWTP input on some dates, indicating that the effluent discharge diluted this form of DIN. However, $\text{NO}_3\text{-N}$

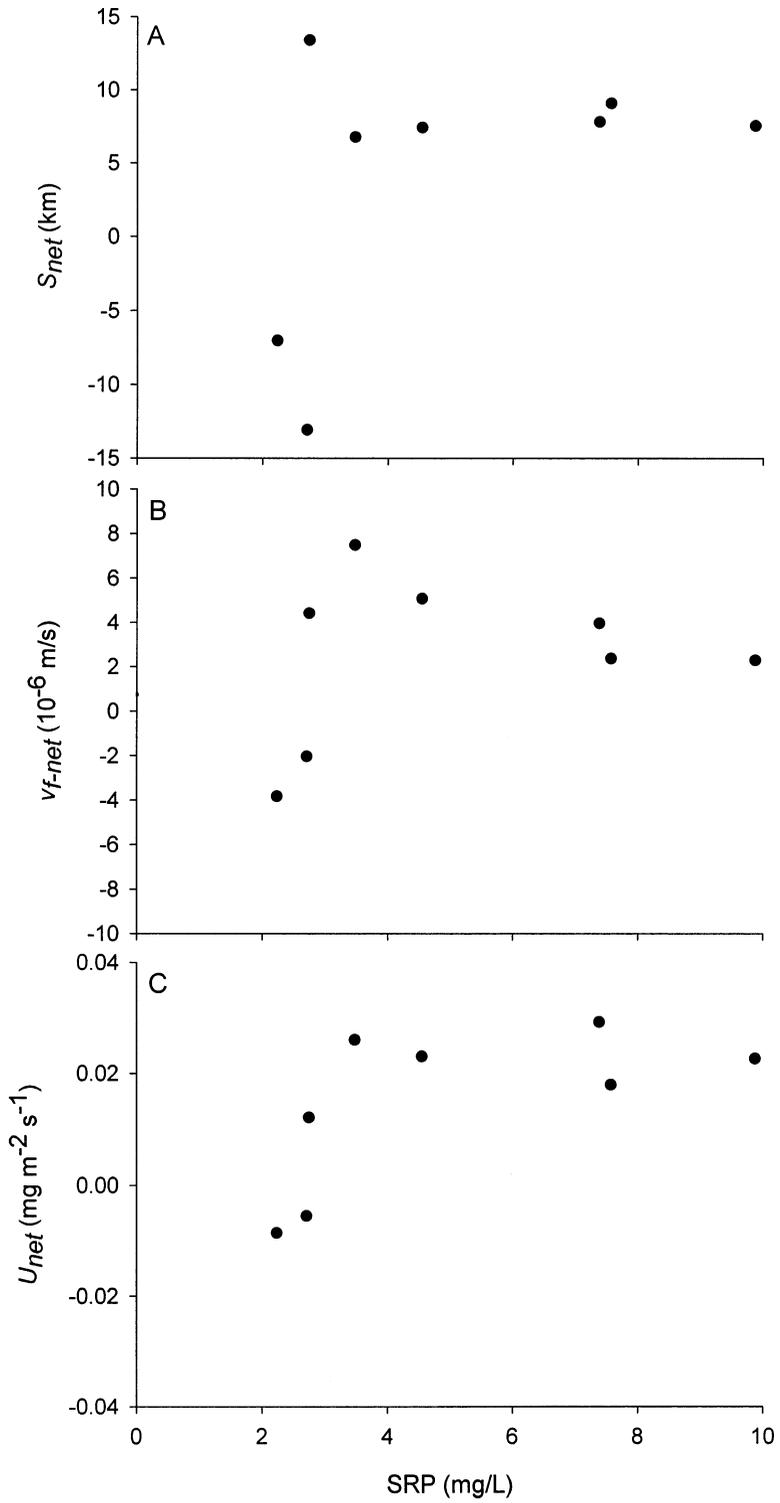
TABLE 1. Regression statistics (r^2 and p) for dilution-corrected concentration vs downstream distance, net nutrient uptake lengths (S_{net}), mass transfer coefficients (v_{f-net}), and uptake rates (U_{net}) in Columbia Hollow (Arkansas, USA) downstream from a point-source input. NS = S_{net} linear regression was not significant. SRP = soluble reactive P, DIN = dissolved organic N.

Date	r^2	p	S_{net} (km)	v_{f-net} (10^{-6} m/s)	U_{net} ($\text{mg m}^{-2} \text{s}^{-1}$)
SRP					
17 June 1999	0.69	0.04	13.4	4.4	0.012
23 July 1999	0.65	0.05	6.8	7.5	0.026
11 August 1999	0.77	0.02	7.4	5.1	0.023
21 October 1999	0.80	0.02	7.8	4.0	0.029
11 November 1999	0.92	<0.01	9.1	4.0	0.018
22 December 1999	0.96	<0.01	-7.0	-3.8	-0.009
28 January 2000	0.95	<0.01	-13.1	-2.0	-0.006
29 February 2000	0.87	<0.01	7.5	2.3	0.023
NH ₄ -N					
17 June 1999	0.98	<0.01	0.6	98	0.270
23 July 1999	0.98	<0.01	1.0	53	0.101
11 August 1999	0.99	<0.01	0.5	74	0.075
21 October 1999	0.98	<0.01	0.8	41	0.289
11 November 1999	0.93	0.04	0.4	56	0.325
22 December 1999	0.96	<0.01	1.4	20	0.200
28 January 2000	0.95	<0.01	0.9	31	0.137
29 February 2000	0.95	<0.01	1.3	14	0.092
NO ₃ -N					
17 June 1999	0.85	<0.01	-4.4	-13	-0.068
23 July 1999	0.95	<0.01	-3.6	-14	-0.066
11 August 1999	0.77	0.02	-4.0	-9.5	-0.043
21 October 1999	0.82	0.01	-4.6	-6.6	-0.056
11 November 1999	0.76	0.02	-1.6	-13	-0.033
22 December 1999	0.88	<0.01	-1.6	-17	-0.071
28 January 2000	0.81	0.01	-4.2	-6.4	-0.067
29 February 2000	0.93	<0.01	-2.4	-7.2	-0.027
DIN					
17 June 1999	0.71	0.03	-23.9	-2.5	-0.019
23 July 1999	0.93	<0.01	-7.3	-6.9	-0.045
11 August 1999	0.72	0.03	-5.5	-6.7	-0.038
21 October 1999	0.43	0.16	NS	NS	NS
11 November 1999	0.64	0.06	NS	NS	NS
22 December 1999	0.84	0.01	-8.0	-3.4	-0.048
28 January 2000	0.72	0.03	-12.8	-2.1	-0.031
29 February 2000	0.11	0.52	NS	NS	NS

N gradually increased downstream from the WWTP input on all sampling dates (Fig. 3A–H). Overall, we observed a decline in DIN concentrations along the study reach on most dates (6 of 8); however, after dilution correction, we did not observe significant uptake of DIN on any sampling dates (Table 1, Fig. 3A–H).

Downstream changes in NO₃-N concentration resulted in negative values for S_{net} -NO₃-N (Fig.

5A) and S_{net} -DIN. On 3 dates, removal or release of DIN were not significant, i.e., S_{net} was not estimated (Table 1). v_{f-net} -NO₃-N was variable and was not significantly related to water temperature, discharge, or NO₃-N concentration 0.3 km downstream of the WWTP input (Fig. 5B); the same was true for DIN. U_{net} -NO₃-N was positively correlated to SRP concentration 0.3 km downstream from the WWTP discharge (U_{net} =



$-0.081 + 0.005[\text{SRP}]$, $r^2 = 0.78$, $p < 0.01$) and ranged from -0.071 to $-0.027 \text{ mg m}^{-2} \text{ s}^{-1}$ (Table 1, Fig. 5C). Modeled $K_{\text{NO}_3\text{-N}}$ was negligible on all sampling dates.

In contrast to $\text{NO}_3\text{-N}$, the longitudinal decrease of $\text{NH}_4\text{-N}$ with downstream distance was significant on all sampling dates, and $S_{\text{net}}\text{-NH}_4\text{-N}$ ranged from 0.4 to 1.4 km (Table 1, Fig. 6A). $v_{f\text{-net}}\text{-NH}_4\text{-N}$ generally decreased throughout our study period and were lowest in winter, but $v_{f\text{-net}}\text{-NH}_4\text{-N}$ was not significantly related to temperature. $U_{\text{net}}\text{-NH}_4\text{-N}$ generally was greatest when $\text{NH}_4\text{-N}$ concentrations 0.3 km downstream were high (Fig. 6B). $v_{f\text{-net}}\text{-NH}_4\text{-N}$ decreased significantly with increasing $\text{NH}_4\text{-N}$ concentration 0.3 km downstream from the WWTP input ($v_{f\text{-net}} = 8.2 \times 10^{-5} - 6.7 \times 10^{-6} [\text{NH}_4\text{-N}]$, $r^2 = 0.51$, $p < 0.05$), regardless of discharge (Fig. 6B). $U_{\text{net}}\text{-NH}_4\text{-N}$ ranged from 0.075 to $0.325 \text{ mg m}^{-2} \text{ s}^{-1}$ (Table 1, Fig. 6C), but was not related to discharge, time, or temperature. The ratio of modeled $K_{\text{NIT}}/K_{\text{NH}_4\text{-N}}$ was between 0.80 and 2.93, and modeled nitrification rates were between 0.081 and $0.354 \text{ mg m}^{-2} \text{ s}^{-1}$ (Table 2). Modeled nitrification rates and $U_{\text{net}}\text{-NH}_4\text{-N}$ were positively correlated ($r^2 = 0.59$, $p < 0.05$).

Discussion

Hydrologic effects of point-source inputs

Streams in the southwestern Ozark Plateaus include losing and gaining systems, depending on local variation in channel morphology. Excluding the effects of the point-source input, discharge increased in a downstream direction along the study reach except at the most-downstream end of it (i.e., 2.1 and 2.7 km sites), indicating that our study reach was a gaining reach. However, effluent discharge was often greater than downstream groundwater or lateral inputs. Effluent discharge was even greater than upstream discharge at Columbia Hollow. Thus, the stream's natural flow regime was strongly affected by the point source. Altered stream hydrology because of effluent augmentation is apparently widespread, particularly in arid zones

where otherwise intermittent streams may be converted to perennial systems (Dennehy et al. 1993, Martí et al. 2004).

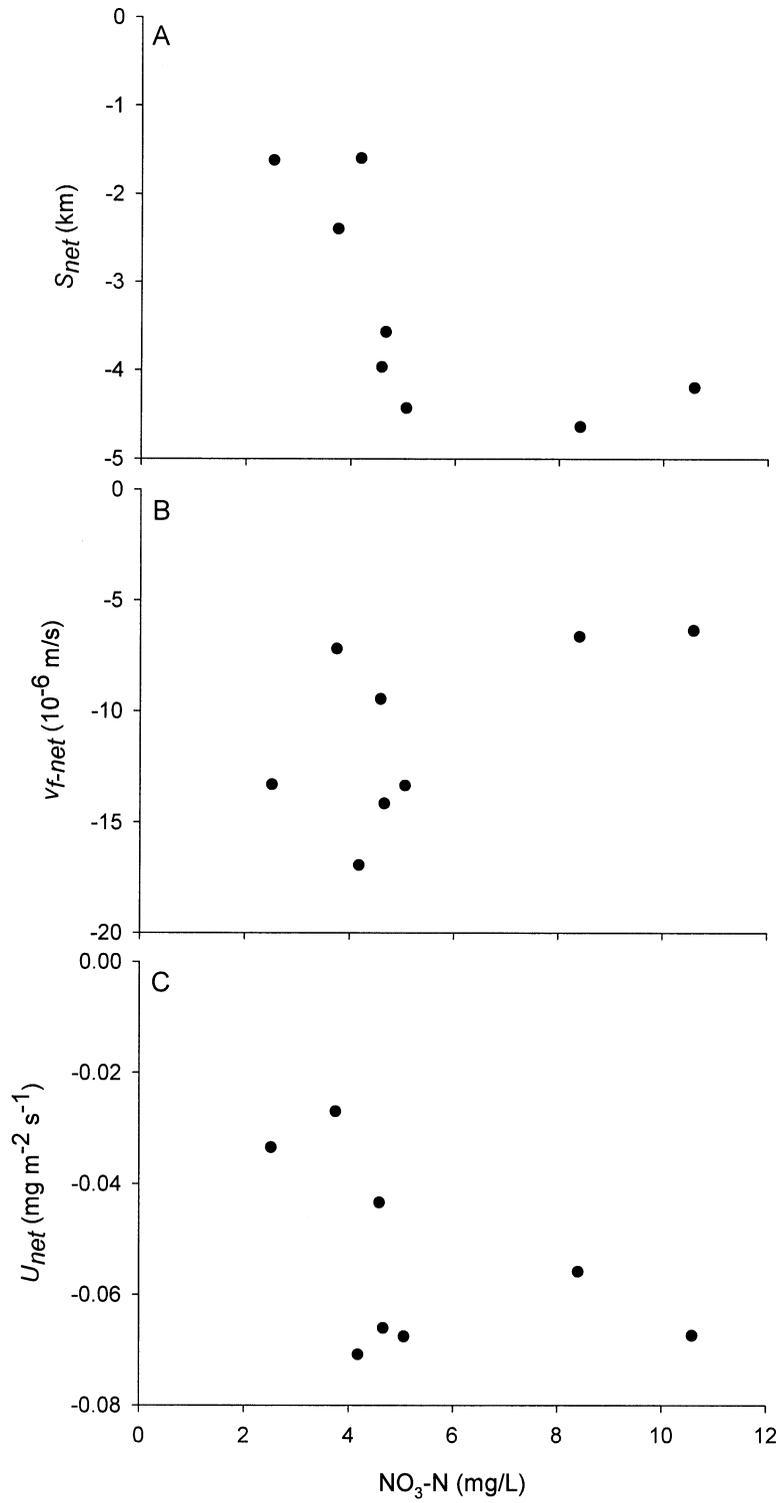
Given the volume of effluent released into Columbia Hollow, it is not surprising that stream water chemistry was significantly altered by the WWTP input. Increased water temperature caused by the point source did not decrease to pre-input levels until the water was 2.7 km from the point source, and altered pH and conductivity caused by the point source did not return to pre-input conditions along the study reach.

P dynamics

Conditions upstream from the WWTP discharge were not pristine. SRP concentrations were generally greater than concentrations that typically saturate algal growth (Bothwell 1985, Dodds et al. 1997). The Decatur WWTP had a profound effect on SRP in Columbia Hollow, further increasing concentrations to levels 3 to 4 orders of magnitude beyond concentrations that saturate algal growth. Despite downstream declines in concentration on most dates, SRP remained elevated as far as 9 km downstream of the point source. At 9 km downstream of the WWTP, Columbia Hollow became a point-source input to Spavinaw Creek where SRP concentrations were elevated 25-fold (Haggard et al. 2001a). Columbia Hollow's SRP contribution to Spavinaw Creek resulted in $S_{\text{net}}\text{-SRP}$ distances of 9 to 31 km in Spavinaw Creek (Haggard et al. 2001a). These values are generally longer than those observed at Columbia Hollow, probably because discharge is greater in Spavinaw Creek (380–1240 L/s; Haggard et al. 2001a) than in Columbia Hollow. $v_{f\text{-net}}\text{-SRP}$ ($2.7 \times 10^{-6} - 6.8 \times 10^{-6} \text{ m/s}$) at Spavinaw Creek was within the range reported at Columbia Hollow (BEH, unpublished data). Nonetheless, $S_{\text{net}}\text{-SRP}$ lengths in both Columbia Hollow and Spavinaw Creek were substantially longer than uptake lengths (0.2–0.9 km) in other streams in the same basin that drained forested and agricultural lands but lacked point-source inputs (Hag-

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FIG. 4. Net P uptake length (S_{net}) (A), mass transfer coefficient ($v_{f\text{-net}}$) (B), and uptake rate (U_{net}) (C) at Columbia Hollow as a function soluble reactive P (SRP) concentration 0.3 km downstream from the Decatur wastewater treatment plant.



gard et al. 2001b). Kilometer-scale uptake lengths for both creeks also show that the effects of the point source are spatially extensive, and extend from Columbia Hollow downstream to Spavinaw Creek and Lake Eucha in this basin.

v_{f-net} -SRP in Columbia Hollow was ~ 10 - to 100-fold lower than typical values for unenriched streams of similar size (reviewed by Doyle et al. 2003). However, U_{net} -SRP was 7- to 15-fold greater than P uptake rates estimated using short-term additions in Idaho (Davis and Minshall 1999) and Spain (Martí and Sabater 1996). Taken together, these uptake parameters suggest that net SRP uptake rate is high in Columbia Hollow. The demand for this nutrient relative to its supply (Stream Solute Workshop 1990) is 12 orders of magnitude lower than in unenriched streams.

Net retention of P on most dates contrasted to net release of P in December and January, when point-source enrichment was relatively moderate and SRP concentration 0.3 km downstream from the WWTP input was ≤ 2.7 mg/L. Equilibrium P concentrations (EPC₀) for sorption on the coarse cherty sediments in Columbia Hollow were between 2.9 and 3.3 mg/L (Popova 2000, BEH unpublished data). These values correspond well with the observed transition between P retention and release in our study and, thus, suggest that sediment sorption is involved in P dynamics in this stream. However, rather than maintaining low and relatively constant P concentrations in the stream, the P buffering mechanism (sensu Froelich 1988) appears to reinforce chronically high P conditions in Columbia Hollow. The correlation between v_{f-net} -SRP and water temperature suggests that the P buffering mechanism was not solely a physical process, but also may have been dependent on biotic uptake (e.g., see Klotz 1985, Gachter and Meyer 1993). At the high end of P additions (> 3.4 mg/L), net uptake rates were not responsive to P concentration. At the low end of P additions (< 2.7 mg/L), stored P was released back into the water column, perpetuating the effects of the point-source enrichment. The release of P during low enrichment conditions is reminis-

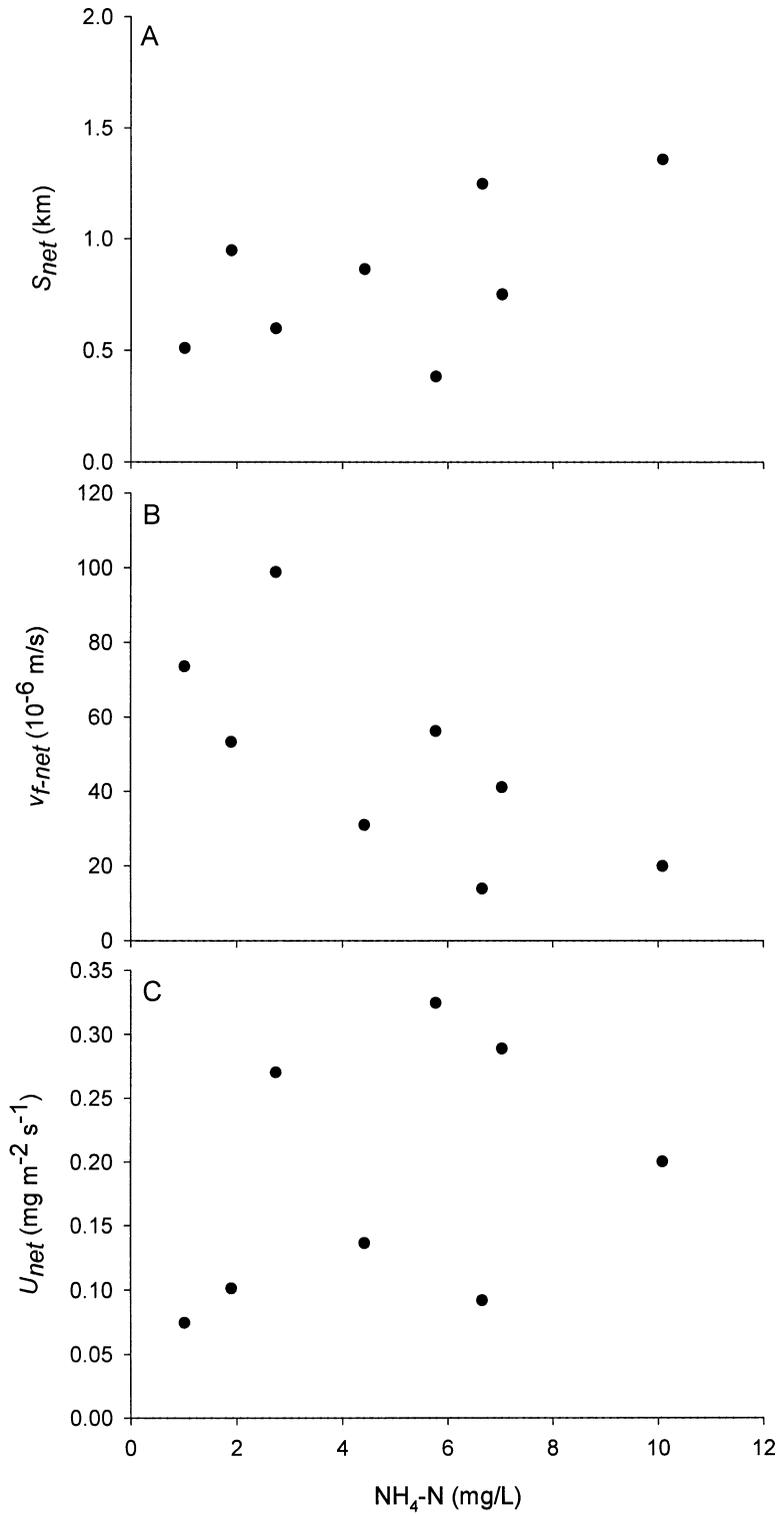
cent of internal loading in eutrophic lakes, and suggests that even if the P content of the effluent is substantially reduced, the effects of the WWTP will persist for some time after any reduction in effluent P concentrations are made.

N transformation and retention

N dynamics in Columbia Hollow were dominated by transformation rather than retention. Apparent retention of NH₄-N was counterbalanced by increases in NO₃-N, indicating that active nitrification in the reach on all sampling dates may be characteristic of streams receiving NH₄-N-rich effluents (Martí et al. 2004). The downstream increase in NO₃-N probably was not related to groundwater influx because NO₃-N concentrations in groundwater throughout the Eucha Basin were < 4 mg/L (OWRB 2002), similar to upstream conditions. Furthermore, other Ozark streams draining pasture- and agriculture-dominated basins generally have NO₃-N concentrations < 4 mg/L (Petersen et al. 1999, Haggard et al. 2001a, b). Modeled nitrification rates were between 7 and 31 g NO₃-N m⁻² d⁻¹, and were several orders of magnitude greater than rates in prairie and agricultural stream sediments (Kemp and Dodds 2002) and a desert stream with extensive hyporheic sediments capable of nitrification (Jones et al. 1995). U_{net} -NH₄-N (and U_{net} -NO₃-N) generally were within the same order of magnitude as modeled nitrification rates. Modeled nitrification in Columbia Hollow could account for 80 to almost 300% of NH₄-N lost, in contrast to nitrification in low-N streams where nitrification typically is responsible for $\sim 10\%$ of NH₄-N uptake (Dodds et al. 2000, Kemp and Dodds 2002). Modeled nitrification often exceeded NH₄-N uptake, suggesting that other reduced N sources were nitrified in addition to NH₄-N inputs from the WWTP. These additional sources may have included organic N that was subsequently mineralized, stored NH₄-N, or groundwater sources. The Decatur WWTP probably increased organic N in Columbia Hollow, and stream sediments were also a storage pool of NH₄-N (Popova 2000);

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FIG. 5. Net NO₃-N uptake length (S_{net}) (A), mass transfer coefficient (v_{f-net}) (B), and uptake rate (U_{net}) (C) at Columbia Hollow as a function of NO₃-N concentration 0.3 km downstream from the Decatur wastewater treatment plant.



however, groundwater was not a likely source of additional reduced N because $\text{NH}_4\text{-N}$ concentration was <0.05 mg/L (OWRB 2002). Regardless of the additional sources of $\text{NH}_4\text{-N}$, overall rates of nitrification in our system were remarkably high and may have affected processes beyond N cycling. Assuming a 25:1 molar ratio of NO_3 produced to CO_2 fixed (Wood 1986), chemoautotrophic production by nitrifying bacteria was 200 to >800 mg C m^{-2} d^{-1} in Columbia Hollow, a rate comparable to photoautotrophic production in some pristine streams (see Mulholland et al. 2001).

Enhanced nitrification may play an important role in reducing the effects of point-source inputs, both by reducing concentrations of $\text{NH}_4\text{-N}$ that are potentially lethal to resident biota and by converting inorganic N to a form that can be removed from the stream via denitrification. However, the lack of overall net retention of DIN in Columbia Hollow suggests that, despite conversion of inorganic N to a form that could have been removed from the ecosystem, little such removal actually occurred. Instead, the transformation of $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$ made Columbia Hollow a significant $\text{NO}_3\text{-N}$ source to Spavinaw Creek (as was the case for SRP). In Spavinaw Creek, $S_{\text{net-NO}_3}$ was 3 to 12 km in a study reach with no other tributary inputs other than Columbia Hollow, demonstrating that the seemingly distant WWTP had an impact on net N retention far downstream in the basin (Haggard et al. 2001a). Modeled $K_{\text{NO}_3\text{-N}}$ at Columbia Hollow was estimated as 0, suggesting that $\text{NO}_3\text{-N}$ uptake was negligible when determining nitrification. $\text{NO}_3\text{-N}$ uptake during short-term additions generally was not significant in other streams within the basin (Haggard et al. 2001b).

Nitrification appears to dominate DIN dynamics, but downstream decrease in $\text{NH}_4\text{-N}$ may also be affected by biotic uptake and sediment sorption. Benthic sediments in Columbia Hollow have a significantly greater extractable $\text{NH}_4\text{-N}$ content than sediments in other streams draining agricultural areas in the basin (Popova 2000). This observation suggests that sorption also may play a role in N processing and reten-

TABLE 2. Fraction of $\text{NH}_4\text{-N}$ uptake nitrified ($K_{\text{NIT}}/K_{\text{NH}_4\text{-N}}$) and modeled nitrification rates at Columbia Hollow using equation and methods of Bernhardt et al. (2002). See text for details. $K_{\text{NO}_3\text{-N}}$ estimated as 0 on all sampling dates. K_{NIT} = linear nitrification rate, $K_{\text{NH}_4\text{-N}}$ = $\text{NH}_4\text{-N}$ uptake rate.

Date	$K_{\text{NIT}}/K_{\text{NH}_4\text{-N}}$	Modeled nitrification rates (mg m^{-2} s^{-1})
17 June 1999	1.08	0.292
23 July 1999	1.91	0.193
11 August 1999	2.93	0.219
21 October 1999	0.80	0.231
11 November 1999	1.09	0.354
22 December 1999	1.38	0.277
28 January 2000	1.53	0.209
29 February 2000	0.88	0.081

tion. As with SRP, storage of $\text{NH}_4\text{-N}$ in sediments has the potential to allow the effects of the point-source input to be expressed during low- or no-effluent discharge periods. Potential nitrification of this sediment storage pool of $\text{NH}_4\text{-N}$ probably explains some of the differences between $U_{\text{net-NH}_4\text{-N}}$ and modeled nitrification.

Nutrient retention in streams receiving point-source inputs

Nutrient retention in Columbia Hollow was characterized by very long uptake lengths and, in some cases, no net uptake and release of previously retained nutrients. The results of the handful of studies with nutrient concentrations and distance from a point-source input demonstrate that this phenomenon is widespread, especially for SRP (Table 3). We estimated $v_{f\text{-net}}$ (and U_{net}) parameters that should have provided robust comparisons of ecological services for point-source-affected streams because the parameters removed the effects of discharge by accounting for differences in stream velocity and depth (Stream Solute Workshop 1990). It remains to be seen whether enhanced U_{net} and

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FIG. 6. Net $\text{NH}_4\text{-N}$ uptake length (S_{net}) (A), mass transfer coefficient ($v_{f\text{-net}}$) (B), and uptake rate (U_{net}) (C) at Columbia Hollow as a function of $\text{NH}_4\text{-N}$ concentration 0.3 km downstream from the Decatur wastewater treatment plant.

TABLE 3. Net nutrient uptake lengths (S_{net}) from studies that reported nutrient concentrations with distance from a high-nutrient-contributing source. – = no data, NS = not significant, SRP = soluble reactive P, DIN = dissolved inorganic N.

Stream or basin	S_{net} -SRP (km)	S_{net} -NO ₃ (km)	S_{net} -NH ₄ (km)	S_{net} -DIN (km)	Citation
Columbia Hollow, Arkansas, USA	–13.1––3.4	–4.6––1.6	0.4–1.4	–23.9––5.5	Our study
Spavinaw Creek, Arkansas, USA	9.0–31	3.1–12	–	–	Haggard et al. 2001a
Various streams, Catalonia, Spain	0.1–14.3	0.4–31.9	0.1–26.9	0.1–29.5	Martí et al. 2004 ^a
Otter Creek, Florida, USA	3.4–11.1	–	–	–	Reddy et al. 1996
South Elkhorn Creek, Kentucky, USA	19.4	–	–	–	Birge et al. 1989 ^b
River Wey, England	7.4–15.2	–13.8–17.6	–	–	House and Denison 1998 ^c
Sand and Caddo Creeks, Oklahoma, USA	45.7–50.9	NS	2.6–29.4	16.2–22.5	Wesolowski 1999 ^d

^a Did not report negative S_{net} when nutrient concentrations showed a consistent increase in concentration downstream from the WWTPs, and a large number of the streams showed no significant retention

^b Mean PO₄-P concentrations with distance downstream from the WWTP were used to estimate S_{net} without dilution correction

^c Nutrient concentrations from 4 sampling dates, S_{net} reported without dilution correction on 3 dates, and no significant retention observed on 1 date

^d Nutrient concentrations during 3 time frames, S_{net} calculated without dilution correction, NO₃ retention not significant during any period, PO₄ and DIN retention not significant during one period

greatly depressed v_{f-net} characterize uptake dynamics in nutrient-rich systems. Nonetheless, it seems apparent that overall retention efficiency of Columbia Hollow, in particular, and effluent-dominated streams, in general, is often minimal (see also Martí et al. 2004).

Point-source effluent discharges often enter streams that already have elevated nutrient concentrations because of human activity in the basin. In Columbia Hollow, upstream NO₃-N and SRP concentrations were elevated prior to the addition of nutrients from the WWTP. The impact of any point source depends on the combination of ambient nutrient concentrations in the receiving stream, the nutrient concentration of the effluent, and the magnitude of the point-source discharge relative to stream discharge. In our study, the effluent discharge from the WWTP fundamentally changed water chemistry in Columbia Hollow for several kilometers downstream.

Point-source nutrient loading to Columbia Hollow has created an unusual mixture of biogeochemical characteristics. The mix includes high areal uptake rates that contrast with ex-

tremely low v_{f-net} for nutrients, a P-exchange mechanism that apparently helps maintain high ambient P concentrations, and distorted N cycling in which absolute and relative rates of transformation are substantially different from those in unenriched streams. Thus, rather than acting as a nutrient sink, Columbia Hollow appears to act more as a short-term storage zone for P and a transformer of N. Limited retention emphasizes that point-source inputs may have long-term and large-scale effects on water quality (see also Martí et al. 2004), and that the key to managing point sources will be to understand the biogeochemical distortions created by focused N and P loading and the circumstances that foster a return to more normal nutrient cycling conditions.

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