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Longitudinal patterns in nutrient chemistry and algal chlorophyll below point sources in three northern Ozark streams

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Introduction

Stream water quality is strongly influenced by nutrient enrichment from both diffuse and point sources (Jarvie et al. 2006). Initial regulatory efforts in the United States to improve water quality largely focused on point sources because they are more easily identified and controlled than diffuse sources. In many locations nutrient enrichment from municipal point sources has been substantially reduced. Nutrient removal is expensive, however, and few small wastewater treatment plants (WWTP) include tertiary treatment to remove nitrogen and phosphorus. Nutrients from WWTP are an important component of the overall load received by many streams.

Diffuse sources can also deliver large nutrient loads to streams (Carpenter et al. 1998, Perkins et al. 1998). In rural areas, the impact of agricultural land use can far exceed that of point sources (Clesceri et al. 1986), and where agriculture is widespread the consequential effects of nutrient enrichment may be evident across entire river basins. In contrast, point source impacts may be localized but also more intense, and the impairment caused by high nutrient concentrations in stream reaches directly below WWTP can be severe (Haggard et al. 2001, Marti et al. 2004).

Our objective was to determine the impact of WWTP effluent on 3 small Missouri streams by measuring how far downstream nutrient concentrations remained elevated above background levels attributable to diffuse input from agricultural and forested watersheds.

Key words: nutrient enrichment, point source, water quality, wastewater treatment, Ozark streams

Site description

We sampled 3 streams (Straight Fork, Blythes Creek, and Maries River) located in the northern Ozark Border region in central Missouri along the lower course of the Missouri River (Fig. 1). This area represents a transitional zone between the deeply dissected and heavily forested terrain of the Ozark Plateau to the south and the more agricultural till plains of northern and western Missouri (Collier 1953). Bedrock geology is predominantly Jefferson City limestone and dolomite of lower Ordivician age. Forest covers more than 50 percent of the Maries River watershed; row crop and pasture predominate in the watersheds of Straight Fork and Blythes Creek.

Municipal WWTP occur near the headwaters of each stream. Design capacity (3624–5500 population equivalents) and permitted discharge (1360–2100 m^3/day) of the 3 WWTP were similar at the time of sampling, and none of the plants provided tertiary treatment (MDNR 1984).

Methods

In July 1986 and again in October 1986 we sampled 7 sites on Straight Fork spaced along a 20 km-reach downstream from the Versailles WWTP, 6 sites on Blythes Creek distributed across a 13 km-reach downstream from the Eldon WWTP, and 7 sites on a 20 km-length of the Maries River downstream from the Dixon WWTP (Fig. 1). Sites on a given stream were sampled on a single day, and collections took place across 3 consecutive days. Water temperature was similar among stream sites in each season, ranging from 23 to 31 °C in July and from 12 to 16 °C in October. Water was taken mid-depth at 3 intervals across the stream at each site and combined into one sample. We measured depth, width and current velocity and then used cross-sectional area to calculate discharge (Robins & Crawford 1954).

To compare diffuse and point source effects on stream nutrient concentrations we used water chemistry data collected from 8 other sites within the northern Ozark Border region that do not receive WWTP effluent. These sites occur either within the Maries or Moreau river drainages (6 sites) or in adjacent watersheds (2 sites). Four of the streams drain predominantly agricultural watersheds (row crop and pasture combined ranging from 76 to 84%), whereas the other 4 streams drain primarily forested watersheds (forest ranging from 55 to 66%). Each stream was sampled 14–15 times during low flow (comparable to Jul) and 19–20 times during moderate flow (comparable to Oct) during 1985–1986. We calculated the average values for 4 agricultural and 4 forested

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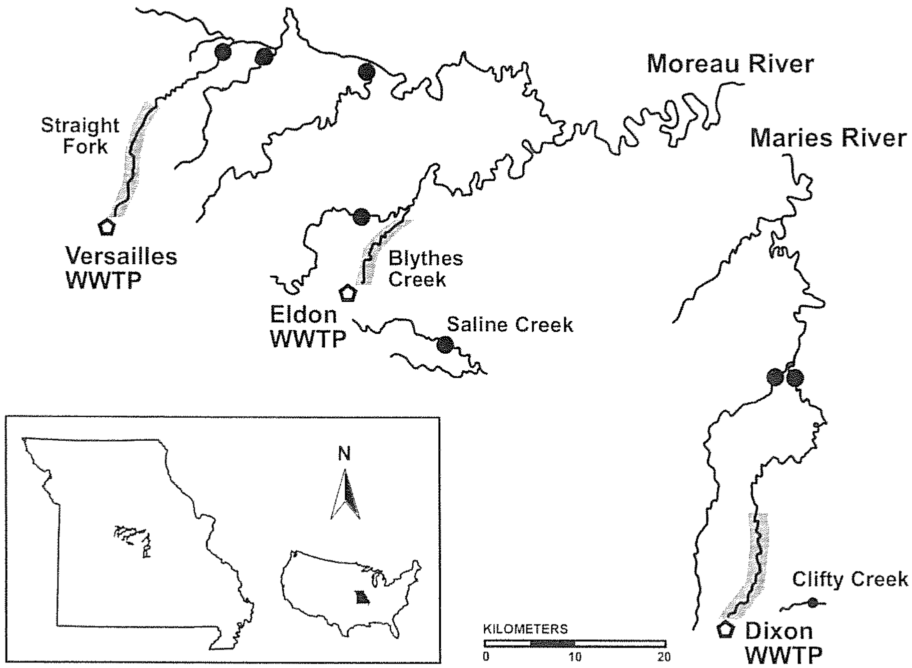

Fig. 1. Location of streams sampled in the northern Ozark Border region. Shaded areas show stream reaches (Straight Fork, Blythes Creek, Maries River) sampled below wastewater treatment plants (WWTP). Black circles indicate sampling sites for streams without point sources that were used as representative of streams draining predominantly agricultural and forested watersheds.

streams based on means for each individual stream for each flow period. Blythes Creek and Straight Fork are most similar to the agricultural streams, draining watershed that are 72 and 78 % agricultural, respectively. The Maries River is comparable to the forested streams, draining a watershed that is 55 % forested.

Methods for total phosphorus (TP), total nitrogen (TN), and chlorophyll *a* were described by LOHMAN et al. (1992). Nitrate (including nitrite and expressed as NO_3-N) was analyzed by cadmium reduction. We used the mercuric nitrate method to measure chloride (APHA 1984).

We used downstream changes in nutrient concentrations relative to chloride concentration to estimate net nutrient uptake lengths, S_{net} (MARTI et al. 2004). This approach is a variation on the solute injection technique in which a WWTP is treated as the nutrient injection source, and chloride is used as a conservative tracer (SEBETICH et al. 1984, MARTI et al. 2004). We assumed downstream changes in ambient nutrient concentrations were the net result of physical, chemical or biological uptake and release processes, whereas changes in chloride were the result of dilution. By regressing the natural logarithm of the proportion of dilution-corrected nutrient concentration against distance downstream, we obtained estimates of S_{net}, the negative, inverse slope:

$$\mathrm{Ln}\left(\frac{N_x / N_0}{Cl_x / Cl_0}\right) = kx, \text{ and } S_{net} = -\frac{1}{k}$$

where N = nutrient concentration and Cl = chloride concentration in mg/L, both at the upstream sampling point (o) and at each downstream sampling point (x); x = the distance downstream in km; and k = net nutrient change coefficient in km.

Assuming downstream decreases in chloride between sites were solely the result of dilution, nutrient losses greater than that predicted by changes in chloride concentration could be attributed to factors other than dilution, such as biological uptake, denitrification or physical adsorption/sedimentation. In July, nondilutional losses were calculated based on the distance between peak TP and NO_3-N values and the sites where these nutrients approached background levels (Straight Fork 0.1–5.7 km; Blythes Creek 2.0–9.4 km; Maries River 0.1–4.8 km). Losses in October were calculated between 0.1 and 13 km in all 3 streams. Nutrient depletion was estimated by multiplying nondilutional loss by mean discharge of the reach and dividing by streambed area between sampling stations.

Results

Nutrient concentrations showed clear longitudinal declines below WWTP in all 3 streams in July and October (Tables 1 and 2; Fig. 2). During summer low flow, dilution was minimal and stream water was primarily effluent, which resulted in much higher TP levels immediately below the point source discharges than at moderate flow (4814–9336 µg/L in Jul as compared to 704–2630 µg/L in Oct). As a consequence, TP values at sites below WWTP were consistently higher at low than at moderate flow, but downstream trends were similar. At summer low flow TP declined to < 3 % of peak values within 13 km, and at moderate flow TP declined to 7–19 % of peak values within this distance.

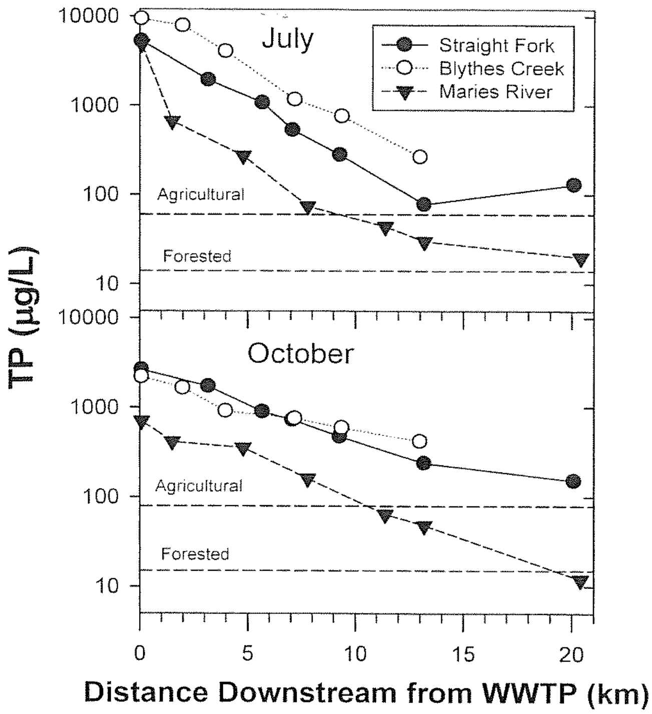

Fig. 2. Change in TP concentration with distance downstream from WWTP in 3 northern Ozark streams, Missouri, USA, in July (upper panel) and October (lower panel). Dashed lines for 'Agricultural' and 'Forested' indicate the average values for 4 streams draining agricultural watersheds and 4 streams draining forested watersheds during seasons of low (Jul) and moderate (Oct) flow.

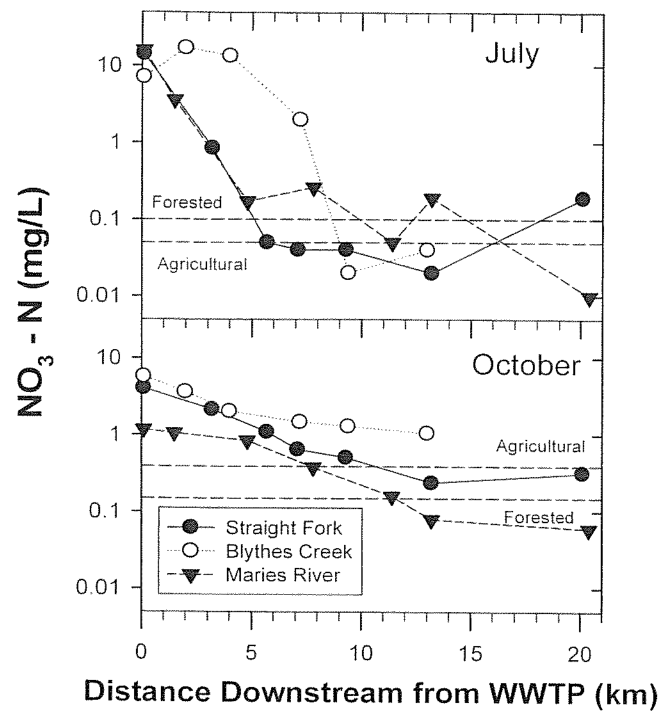

Fig. 3. Change in NO_3-N concentration with distance downstream from WWTP in 3 northern Ozark streams, Missouri, USA, in July (upper panel) and October (lower panel). Dashed lines for 'Agricultural' and 'Forested' indicate the average values for 4 streams draining agricultural watersheds and 4 streams draining forested watersheds during seasons of low (Jul) and moderate (Oct) flow.

Among July samples NO_3-N declined by 3 orders of magnitude from > 14 mg/L to < 0.2 mg/L at sites 5–9 km downstream from each WWTP facility (Fig. 3). At moderate flow in October, NO_3-N concentrations below WWTP were < 5.7 mg/L and the log-linear downstream decline was less sharp with values typically greater than July measurements (Tables 1 and 2; Fig. 3). On average, 55 % of TN was NO_3-N (median 55 %, minimum 4 % and maximum 100 %), and downstream trends in the study streams were similar between these 2 nitrogen measurements. Chloride dilution below the WWTP ranged between 56 and 88 % of initial values, and declines in conductivity ranged between 24 and 73 % within the sampled reaches (Tables 1 and 2).

Concentrations of TP averaged 60 µg/L in the agricultural streams in the region and 14 µg/L in forested streams during low flow (Table 1), and 79 and 15 µg/L, respectively, during moderate flow (Table 2). Concentrations of TP at sites 2–3 km downstream from WWTP were 1–2 orders of magnitude greater than these values from agricultural and forested streams during both flow regimes. Despite downstream declines, TP in streams receiving point source effluent remained higher than in comparable agricultural and forested streams for 13 km or greater (Fig. 2). Differences in TP between point source streams and streams in agricultural or forested areas were greatest at low flow. Concentrations of NO_3-N at sites 2–3 km downstream of WWTP were also 1–2 orders of magnitude greater than those in streams without point sources (Fig. 3). Increased dilution at moderate flow lowered NO_3-N at sites located within 2–3 km of WWTP. Concentrations NO_3-N at sites on Blythes Creek and Straight Fork remained greater than those in comparable agricultural streams for distances of 13 km or more at moderate flow, whereas NO_3-N values in the Maries River were greater than those seen in forested streams for 10 km or more. During summer low flow, however, within 5–10 km downstream NO_3-N concentrations declined to levels <0.10 mg/L in all 3 streams; these values were similar to those in forested and agricultural streams (<0.08 mg/L; Table 1).

All 3 streams had generally high benthic chlorophyll *a* values in July and October, but none were characterized by consistent longitudinal patterns (Tables 1 and 2). Ben-

Table 1. Water chemistry from longitudinal sampling of 3 streams in the northern Ozark Border, Missouri, USA, in July (low flow). Seasonal mean values are also presented from 4 streams draining primarily agricultural watersheds and from 4 streams draining primarily forested watersheds.

	Distance downstream from WWTP (km)	Q (m^3/s)	Conductivity (μS)	TP (μg/L)	TN (mg/L)	NO_3-N (mg/L)	Cl (mg/L)	Sestonic Chl *a* (μg/L)	Benthic Chl *a* (mg/m^2)
Low flow									
Blythes Creek	0.1	0.04	845	9336	14.06	7.08	70.8	14.4	298
	2.0	0.01	810	7802	19.14	17.02	75.5	5.7	99
	4.0	0.01	815	4026	14.87	13.46	73.5	5.9	167
	7.2	0.02	680	1157	2.42	1.98	57.5	2.2	426
	9.4	0.02	555	753	0.48	0.02	44.2	13.8	193
	13.0	0.01	510	265	0.23	0.04	31.2	2.9	58
Straight Fork	0.1	0.02	1900	5236	14.53	14.22	382.5	17.8	507
	3.2	<0.01	2090	1919	2.18	0.84	362.0	8.0	80
	5.7	0.01	1600	1068	0.58	0.05	246.2	39.0	57
	7.1	0.01	1320	528	0.54	0.04	211.2	5.9	118
	9.3	<0.01	810	279	1.00	0.04	98.8	9.0	92
	13.2	<0.01	770	78	0.46	0.02	71.2	7.5	84
	20.1	<0.01	560	130	1.04	0.19	71.0	32.2	NA
Maries River	0.1	<0.01	975	4814	16.44	15.86	71.2	1.4	77
	1.5	0.01	755	664	4.11	3.56	43.0	3.1	253
	4.8	0.01	595	272	0.62	0.17	36.0	11.8	291
	7.8	<0.01	490	74	0.37	0.26	19.2	0.4	55
	11.4	0.01	362	44	0.20	0.05	13.2	1.0	111
	13.2	0.01	362	30	0.38	0.19	10.5	0.4	68
	20.4	0.04	340	20	0.26	0.01	8.5	2.8	34
Agricultural Streams	–	0.03±0.01	420±22	60±7	0.30±0.04	0.05±0.01	7.9±0.8	10.6±2.3	36±8
Forested Streams	–	0.04±0.02	393±26	14±3	0.20±0.02	0.10±0.03	5.8±1.2	1.2±0.4	22±5

thic chlorophyll *a* was highly variable among sites in July (58–298 mg/m^2 on Blythes Creek, 57–507 mg/m^2 on Straight Fork, and 34–291 mg/m^2 on Maries River). Most sites on all 3 streams had higher values in October than July (100–313 mg/m^2 on Blythes Creek, 102–241 mg/m^2 on Straight Fork, and 13–450 mg/m^2 on Maries River). There were no consistent downstream trends in sestonic chlorophyll *a* in these streams in July (Table 1) but longitudinal declines were measured in October (Table 2). At most sites benthic chlorophyll *a* was greater than in agricultural and forested streams in both July and October. Levels of sestonic chlorophyll *a* in point source streams were similar to values in the surrounding non-point streams during both sampling periods with the exception of large October values in Straight Fork (Table 2).

Net uptake lengths for TP were generally shorter in July than in October, ranging from 5.1 to 7.1 km in July and from 6.0 to 16.0 km in October (Table 3). Net NO_3-N uptake lengths were also shorter in July, ranging from 0.9 to 1.1 km in July compared with 8.1 to 18.9 km in October.

Declines in TP and NO_3-N with distance downstream from point sources were only partially attributable to dilution. July nutrient losses not accounted for by dilution were 48–55 % and 50–64 % for TP and NO_3-N, respectively, and 16–32% for both nutrients in October (Table 4). Estimates of TP depletion rates were 98–286 mg/m^2/day in July and 62–110 mg/m^2/day in October. Depletion rates of NO_3-N were 394–742 mg/m^2/day in July and 96–305 mg/m^2/day in October.

Discussion

Nutrient concentrations in sites receiving WWTP effluent were substantially greater than in northern Ozark Border streams in central Missouri draining agricultural and forested watersheds. Although clearly dependent on

Table 2. Water chemistry from longitudinal sampling of 3 streams in the northern Ozark Border, Missouri, USA, in October (moderate flow). Seasonal mean values are also presented from 4 streams draining primarily agricultural watersheds and from 4 streams draining primarily forested watersheds.

	Distance downstream from WWTP (km)	Q (m^3/s)	Conductivity (µS)	TP (µg/L)	TN (mg/L)	NO_3-N (mg/L)	Cl (mg/L)	Sestonic Chl *a* (µg/L)	Benthic Chl *a* (mg/m^2)
Moderate flow									
Blythes Creek	0.1	0.05	550	2190	7.04	5.76	35.5	7.8	280
	2.0	0.04	475	1642	4.32	3.64	24.2	4.2	167
	4.0	0.07	429	906	2.54	2.04	18.0	3.6	313
	7.2	0.21	421	750	1.88	1.48	16.2	1.8	100
	9.4	0.26	420	590	1.50	1.30	15.0	1.4	220
	13.0	0.30	418	418	1.22	1.06	13.0	1.3	134
Straight Fork	0.1	0.05	780	2630	4.06	4.06	104.5	68.6	201
	3.2	0.04	575	1715	2.93	2.16	69.2	44.6	144
	5.7	0.05	490	894	1.64	1.10	45.2	25.4	243
	7.1	0.07	433	725	1.26	0.65	39.5	35.6	199
	9.3	0.10	415	472	0.98	0.51	35.0	17.8	183
	13.2	0.13	330	238	0.64	0.24	23.2	5.8	102
	20.1	0.18	346	152	0.72	0.32	21.5	6.8	117
Maries River	0.1	0.02	540	704	2.50	1.17	21.2	4.0	123
	1.5	0.14	410	413	1.26	1.06	14.2	1.2	194
	4.8	0.12	398	354	1.00	0.85	12.8	2.4	450
	7.8	0.17	405	160	0.56	0.38	10.0	1.2	171
	11.4	0.22	382	64	0.28	0.16	8.8	1.4	169
	13.2	0.34	358	48	0.17	0.08	7.8	0.4	13
	20.4	0.44	352	12	0.19	0.06	8.0	0.5	288
Agricultural Streams	–	0.60±0.11	358± 3	79±9	0.73±0.12	0.39±0.09	8.0±1.0	8.8±1.4	65±10
Forested Streams	–	0.70±0.22	338±22	15±3	0.28±0.06	0.15±0.05	3.8±0.4	1.8±0.7	35± 7

characteristics of the discharge and receiving stream, our results are consistent with studies showing point source input often has greater influence on ambient nutrient concentrations than diffuse sources (HAGGARD et al. 2001, JARVIE et al. 2006). Streams affected by point source effluent in our study area are small and discharges occur in headwaters, allowing only minimal dilution. Differences in nutrients between streams receiving continuous point source discharge and other streams in the area are magnified during low flow when dilution is reduced and contributions from diffuse sources are minimal. In large streams, or in streams that receive tertiary treated effluent, ambient nutrient concentrations may be similar to streams influenced only by diffuse sources (DUDA 1982, CLESCERI et al. 1986).

Elevated TP concentrations in streams receiving point source discharges persisted for distances of up to 20 km during both low (Jul) and moderate flow (Oct). Estimated losses of TP (98–286 mg/m^2/day in Jul and 62–110 mg/m^2/day in Oct; Table 4) were larger than those reported for soluble reactive phosphorus (38–50 mg/m^2/day; GRIMM et al. 1981, HILL 1982). In addition to uptake by algae and microbes in biofilms, physical adsorption by bed-sediments or coprecipitation with calcite may account for substantial reductions in stream phosphorus concentrations (MEYER 1979, HOUSE & DENISON 1997). Calcite precipitation is likely in these streams draining limestone and dolomite (alkalinity was typically around 160 mg/L as $CaCO_3$). Greater losses are likely during low flow periods when slow current velocities promote settling and adsorption. High rates of phosphorus removal during summer months suggest that large stores of phosphorus are retained in biota and sediments (KEUP 1968, RIGLER 1979, HOUSE & DENISON 1997).

Table 3. Net nutrient uptake lengths (Snet) in July and October for 3 streams in the northern Ozarks receiving effluent from waste-water treatment plants.

	S_{net} (km)	
	July	October
TP		
Blythes Creek	5.0	16.0
Straight Fork	6.5	13.3
Maries River	7.1	6.0
NO_3-N		
Blythes Creek	0.9	18.9
Straight Fork	1.0	8.9
Maries River	1.2	8.1

Table 4. TP and NO_3-N depletion rates (mg/m²/day) in streams receiving WWTP effluent in July and October. Values in parentheses are percent of nutrient loss not accounted for by dilution.

	TP		NO_3-N	
Stream	July	October	July	October
Blythes Creek	286 (54 %)	110 (22 %)	742 (58 %)	305 (22 %)
Straight Fork	98 (55 %)	62 (16 %)	394 (64 %)	96 (16 %)
Maries River	144 (48 %)	65 (32 %)	526 (50 %)	96 (32 %)

Release of phosphorus from the stream bed and scouring of fine sediments and biofilm material during elevated flow likely reduces phosphorus accumulation immediately below WWTP while elevating phosphorus in the lower reach of these streams.

Higher NO_3-N concentrations, as compared to streams receiving only diffuse nutrient loads, were measured at distances up to 13 km downstream at moderate flow, but low flow values were similar between the 2 stream types within 5–10 km of WWTP outflows. Estimated nitrate depletion rates in July (394–742 mg/m²/day; Table 4) were in the mid-range of nitrogen loss values (40–1400 mg/m²/day) reported during summer or low flow periods in other studies (Owens et al. 1972, Kaushik & Robinson 1976, Van Kessel 1977, Grimm et al. 1981, Hill 1981, House et al. 2001). By comparison, nitrate depletion in October (96–305 mg/m²/day; Table 4) was at the lower end of values reported in previous studies.

Nitrogen losses during low flow are attributed to denitrification (Kaushik & Robinson 1976, Hill 1981, Van Kessel 1977) or assimilation by algae or macrophytes (Brink & Widell 1967, Grimm et al. 1981). Both processes are probably important in small northern Ozark streams receiving sewage effluent. Nuisance benthic algal mats are common during low flow in these streams and nutrient demands are high (Lohman et al. 1992). Opportunities for denitrification are also enhanced below point sources during summer when nitrate concentrations are high and slow current velocities increase water residence time and water-sediment interactions.

Nutrient transport studies on more pristine streams have typically found net uptake lengths on the order of 10^1–10^2 m (Mulholland et al. 2004) as compared with the kilometer-scale lengths seen in this and other studies on highly enriched streams. Marti et al. (2004) calculated S_{net} values of 0.4–31.9 km for NO_3-N and 0.1–14.3 km for soluble reactive phosphorus (SRP) from Catalonian streams, whereas Haggard et al. (2001) reported a range of 3.1–12 km for NO_3-N and 9.0–31 km for SRP for a fifth-order stream in northern Arkansas. Some streams, however, are unable to effectively retain large nutrient load delivered by point sources; 40 % of Catalonian streams surveyed by Marti et al. (2004) did not exhibit consistent longitudinal declines in inorganic nitrogen, and 45 % did not show declines in SRP. In an Arkansas stream similar in size and chemistry to our streams, Haggard et al. (2006) did not observe significant uptake of inorganic nitrogen in 8 separate profiles conducted over a 9-mo period, indicating net release rather than net removal of nitrogen. In the same stream, net uptake lengths of 6.8–13.4 km for SRP occurred on 6 of the 8 sampling dates when net removal was greater than net release.

Northern Ozark streams were characterized by net retention of both TP and NO_3-N, but we suspect that net release occurs much of the year. Algal demand for nutrients, particularly nitrogen, is high in nitrogen-limited streams during low flow periods in this region (Lohman et al. 1991), and benthic chlorophyll *a* exceeded 100 mg/m², a level indicative of nuisance conditions (Horner et al. 1983), at half the sampled sites in July (Table 1). In October, algal demand may have been even greater, when benthic chlorophyll *a* was >100 mg/m² at all but one site (Table 2), and an extended flood-free period persisted in the northern Ozarks creating conditions ideal for the accumulation of benthic algal biomass (Lohman et al. 1992). During periods less conducive to benthic algal growth, nutrient storage within these reaches must be greatly reduced.

Longitudinal trends in both benthic and sestonic chlorophyll *a* in our study were less consistent and more difficult to interpret than nutrient patterns. Whereas the high values for benthic chlorophyll *a* at most sites in July and

October are characteristic of highly enriched streams, many sestonic chlorophyll *a* values are low relative to ambient nutrient levels (Van Nieuwenhuyse & Jones 1996). The patchy distribution of chlorophyll *a* peaks suggests factors other than nutrients (e.g., light, current velocity, water residence time, grazing) influence algal biomass in these enriched headwaters. The consistent decline in sestonic chlorophyll *a* below point sources in October suggests nutrient enrichment effects on algal accumulation are being diluted with distance. The absence of this pattern in July may also reflect the nature of small northern Ozark streams in summer, when low discharge creates a heterogeneous system of isolated pools separated by shallow riffles that might differentially favor algal growth.

Rural point sources, like those in the headwaters of northern Ozark streams, have a continuous impact on nutrients and stream processes both locally and regionally (Marti et al. 2004). Large nutrient loads, and associated algal blooms, can persist for substantial distances downstream. Within these reaches local biotic uptake serves only as temporary nutrient storage. At times of algal senescence and during substrate disturbing floods, nutrients will be further displaced downstream, ensuring that even small point sources will have long distance effects. These in-stream processes are consistent with the concepts of patch dynamics and nutrient spiraling in lotic systems (Pringle et al. 1988).

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