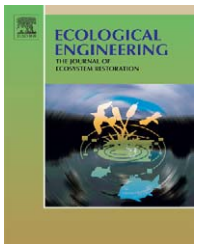
ECOLOGICAL ENGINEERING 26 (2006) 375–391

available at www.sciencedirect.com

SCIENCE DIRECT®

journal homepage: www.elsevier.com/locate/ecoleng



Dissolved phosphorus concentrations and sediment interactions in effluent–dominated Ozark streams☆

S.A. Ekka[a], B.E. Haggard[b,c,*], M.D. Matlock[b], I. Chaubey[b]

[a] Graduate Research Assistant, Biological Systems Engineering Department, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

[b] Associate Professors, Biological and Agricultural Engineering Department, 203 Engineering Hall, University of Arkansas, Fayetteville, AR 72701, USA

[c] Former Hydrologist, USDA-ARS, Poultry Production and Product Safety Research Unit, University of Arkansas, Fayetteville, AR 72701, USA

ARTICLE INFO

Article history:
Received 9 August 2005
Received in revised form 11 January 2006
Accepted 24 January 2006

Keywords:
Phosphorus
Effluent discharge
Wastewater treatment plant
Stream sediment
Arkansas

ABSTRACT

Phosphorus (P) loads from point sources have a significant influence on dissolved P concentrations in streams and sediment-water column dynamics. The goal of this study was to quantify dissolved P concentrations and sediment-P interactions in Ozark (USA) headwater streams with high point source P loads. Specifically, the objectives were to: (1) compare soluble reactive P (SRP) upstream and downstream from wastewater treatment plant (WWTP) effluent discharges; (2) examine longitudinal gradients in SRP downstream from WWTPs; (3) evaluate the effect of WTTP P inputs on sediment-water column P equilibrium and sediment exchangeable P. Water and sediment samples were collected, extracted and analyzed from July 2002 through June 2003 at these Ozark streams. Mean SRP concentrations in the select Ozark streams were significantly greater downstream from effluent discharges (0.08–2.10 mg L^{-1}) compared to upstream (0.02–0.12 mg L^{-1}). Effluent discharge from the WWTPs increased equilibrium concentrations between stream sediments and the water column; mean sediment equilibrium P concentration (EPC_0) was between 0.01–0.07 mg L^{-1} upstream from WWTP and the increase downstream was proportional to that observed in water column SRP. Sediment exchangeable P (EXP) was greater downstream from the effluent discharges (0.3–6.8 mg kg^{-1}) compared to upstream (0.03–1.4 mg kg^{-1}), representing a substantial transient storage of P inputs from WWTPs. Furthermore, P was generally not retained in these stream reaches when dilution was considered using a hydrologic tracer and was released in one stream reach where effluent P concentrations decreased over the study period. Thus, the effect of the WWTPs was profound in these streams increasing water column and sediment-bound P, and also reducing the ability of these stream reaches to retain P. In P-enriched streams, effluent P discharges likely regulate sediment and aqueous phase P equilibrium and sediment bioavailable P, not the sediments.

Published by Elsevier B.V.

☆ Mention of a trade name, proprietary product, or specific equipment does not constitute a guarantee or warranty by the USDA and does not imply its approval to the exclusion of other products that may be suitable.

* *Corresponding author*. Tel.: +1 479 575 2879; fax: +1 479 575 2846.
E-mail address: haggard@uark.edu (B.E. Haggard).

0925-8574/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.ecoleng.2006.01.002

1. Introduction

Although substantial improvements in water quality have been made following implementation of the 1972 Clean Water Act in the United States, point sources such as municipal wastewater treatment plant (WWTP) effluent discharges still exert a prominent influence on dissolved phosphorus (P) concentrations and transport in Ozark streams, particularly in Northwest Arkansas, USA (Haggard et al., 2001, 2004, 2005). Dissolved P concentrations have been observed in Ozark streams as great as 10 mg L^{-1} downstream from regional municipal WWTPs (Haggard et al., 2005). In some Ozark catchments, municipal WWTP inputs are 25–45% of estimated annual P export in streams (Haggard, unpublished data).

Effluent discharges from municipal WWTPs not only increase water column P concentrations in streams, but several studies have also shown an increase in benthic sediment-bound P (House and Denison, 1997; Dorioz et al., 1998; Haggard et al., 2001). The influence of WWTP effluent discharge on benthic sediments is generally much greater than other external factors, such as agricultural land use and nonpoint source pollution in the Ozarks (Popova et al., 2006). Dissolved P in the water column has an affinity for benthic sediments, and it is likely that adsorption and desorption processes may regulate dissolved P concentrations in streams (Klotz, 1988; Froelich, 1988), especially in P-enriched streams (Haggard et al., 2004, 2005). However, the ability of benthic sediments to adsorb P is often much less downstream from effluent discharges compared to sites upstream (House and Denison, 1997; Dorioz et al., 1998; Haggard et al., 2001). The adsorption of P from the water column to benthic sediments represents only a temporary transient storage zone, because sediments may release P back into the water column when effluent concentrations are low (Haggard et al., 2005). Sediment P release mechanisms are likely controlled by the equilibrium P concentration (EPC_0) (Froelich, 1988) between benthic sediments and the water column (Novak et al., 2004), and the amount of easily exchangeable P in the sediments (Haggard et al., 2005).

The overall goal of this study was to quantify dissolved P concentrations and sediment-water column P dynamics in effluent–dominated headwater Ozark streams. Specifically, the objectives were to: (1) compare soluble reactive P (SRP) concentrations upstream and downstream from WWTP effluent discharges; (2) examine longitudinal gradients in SRP concentration downstream from WWTP effluent discharges; (3) evaluate the effect of the effluent discharge on dissolved P equilibrium between stream sediments and water; (4) assess changes in $MgCl_2$ extractable P (sediment EXP) in benthic sediments upstream and downstream from the effluent discharge. The focus of this study was on four headwater streams in the Illinois River Drainage Area (IRDA) in Northwest Arkansas, USA that receive municipal WWTP effluent discharge. The Illinois River drains a *trans*-boundary watershed between Arkansas and Oklahoma and has recently been a subject of political concern, environmental debate and litigation. Thus, the intent of this study was to focus data collection on the headwater streams receiving effluent discharge in the Illinois River Basin and understand the influence of these effluent discharges on stream P retention mechanisms.

2. Materials and methods

2.1. Study site description

The headwater streams of the Illinois River Basin originate in Northwest Arkansas, and the Illinois River and other tributaries flow from Northwest Arkansas into Northeast Oklahoma. Phosphorus sources in the IRDA include municipal WWTPs and various potential nonpoint sources (commercial fertilizers, biosolids, poultry litter, and other animal manure). The Illinois River and its two main tributaries (Flint Creek and Baron Fork) are designated as scenic rivers in Oklahoma. The Oklahoma Water Resources Board (OWRB, 2002) recently established total P criterion of 0.037 mg TP L^{-1} in rivers designated as scenic. In 1992, the U.S. Supreme Court rendered a decision that the U.S. Environmental Protection Agency (USEPA) may require upstream states to meet downstream state water quality standards at the state border (Arkansas versus Oklahoma, 503 U.S. 91; http://laws.findlaw.com/us/503/91.html). Consequently, P concentrations in these Arkansas streams may be required to meet the TP criterion promulgated in Oklahoma Scenic Rivers where these streams cross the Arkansas and Oklahoma state boundary. Green and Haggard (2001) measured average annual flow-weighted TP concentration at the Illinois River near the Arkansas-Oklahoma border to be approximately 0.40 mg L^{-1}, 10 times greater than the Scenic River TP criterion. The average annual TP load in the Illinois River is about 208,000 kg, and almost half of this load (45%) is attributed to inputs from municipal WWTPs. Elevated P concentrations near the Arkansas-Oklahoma border at the Illinois River can be largely traced to one municipal WWTP over 47 km upstream in the headwaters of Spring Creek (Haggard, unpublished data).

Specifically, we selected study reaches on Mud Creek, Osage Creek, Spring Creek, and Sager (and Flint) Creek, which receive WWTP effluent discharge from the cities of Fayetteville, Rogers, Springdale and Siloam Springs, respectively, in Northwest Arkansas, USA (Fig. 1, Table 1); the Siloam Springs WWTP discharges into Sager Creek, which is a tributary to Flint Creek. The Illinois River and its headwater streams are representative streams of the central United States (Brown and Matthews, 1995), and the southwestern Ozark streams in this study are located in USEPA Region VI of the conterminous USA. The headwater streams of this region are unique because of their uniformly spaced alluvial gravel riffle-pool geomorphology (Brussock et al., 1985). All these stream reaches commonly exhibit a typical riffle-pool geomorphology with bedrock outcroppings at some sites. The study reach length selected at each headwater stream was variable from 3.3 to almost 14 km (Table 1). In general, the upper portions of the catchments drained a mixture of small urban neighborhoods, pasture and forest, but the proportion of urban–suburban land use varied between streams, with Mud Creek draining the greatest urban proportion.

Only Fayetteville's WWTP had effluent P limits of 1.0 mg L^{-1} in its discharge. The other facilities had no P limits or regulations during this study period, although Rogers WWTP has operated with voluntary P management practices (effluent P concentration less than 1.0 mg L^{-1} since circa 1997). For the

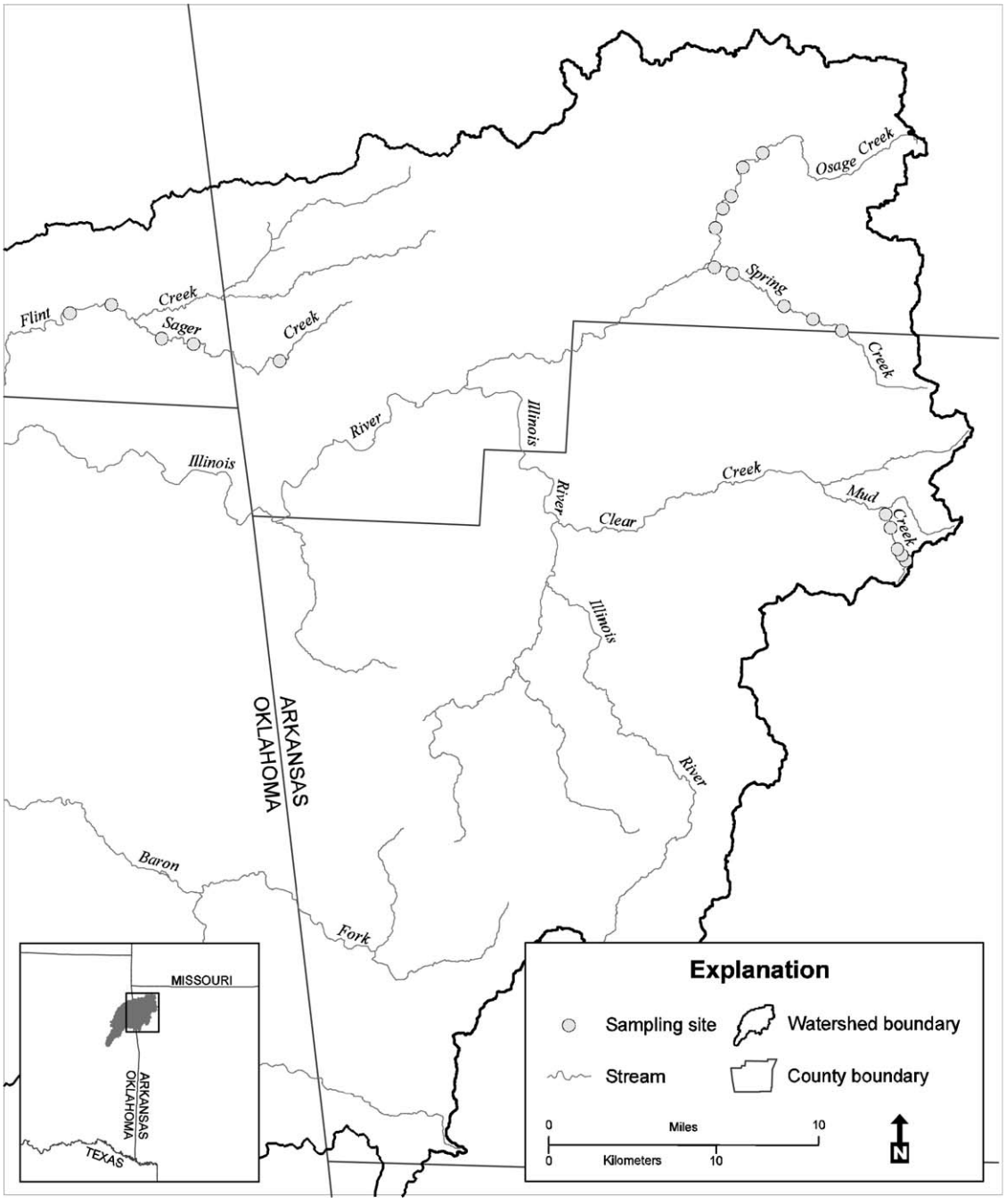


Fig. 1 – Selected water quality monitoring sites and map of the Illinois River and its tributaries Baron Fork and Flint Creek in the Ozarks of Northwest Arkansas and Northeast Oklahoma, USA.

past few years, however, recent concerns with regard to the TP criterion in Scenic Rivers have prompted regional municipalities to adopt a 1.0 mg TP L^{-1} limit in all effluent discharges in the IRDA. Specifically, the city of Springdale and its WWTP started making these efforts during this study period (see Section 3). These municipal facilities treat very different populations and industrial sources where treatment populations vary from 10,000 to almost 60,000 individuals at Siloam Springs and Fayetteville, respectively. The most prominent influent sources with respect to P are poultry and food processing plants. Several poultry processing facilities exist in Northwest Arkansas, one of the leading poultry producing areas in the United States. Arkansas produces about 1.2 billion birds annually with the greatest portion occurring in the Ozark region of Arkansas.

2.2. *Field techniques*

Five water quality sampling sites (one reference site upstream from the WWTP effluent discharge and four sites downstream)

Table 1 – Samplings sites and respective distance from effluent discharge and global positioning system coordinates at Mud Creek, Osage Creek, Sager (and Flint) Creek, and Spring Creek in the headwaters of the Illinois River Basin in the Ozarks of Northwest Arkansas and Northeast Oklahoma, USA

Sampling site	Sampling stream	Municipal WWTP	Distance[a] (km)	Latitude	Longitude
1	Mud Creek	Upstream	−0.5	36°05.271	94°06.560
2	Mud Creek	Fayetteville, AR, USA	0.4	36°05.444	94°06.733
3	Mud Creek	Fayetteville, AR, USA	0.9	36°05.638	94°06.912
4	Mud Creek	Fayetteville, AR, USA	2.2	36°06.323	94°07.200
5	Mud Creek	Fayetteville, AR, USA	3.1	36°06.753	94°07.400
1	Osage Creek	Upstream	−0.2	36°18.374	94°12.446
2	Osage Creek	Rogers, AR, USA	1.5	36°17.901	94°13.240
3	Osage Creek	Rogers, AR, USA	3.4	36°16.964	94°13.687
4	Osage Creek	Rogers, AR, USA	4.2	36°16.565	94°14.021
5	Osage Creek	Rogers, AR, USA	5.5	36°15.935	94°14.295
1	Sager Creek	Upstream	−3.3	36°11.446	94°31.592
2	Sager Creek	Siloam Springs, AR, USA	2.0	36°11.933	94°35.016
3	Sager Creek	Siloam Springs, AR, USA	3.9	36°12.106	94°36.294
4	Flint Creek	Siloam Springs, AR, USA	7.5	36°13.156	94°38.304
5	Flint Creek	Siloam Springs, AR, USA	10	36°12.872	94°39.955
1	Spring Creek	Upstream	−1.1	36°12.660	94°09.213
2	Spring Creek	Springdale, AR, USA	2.0	36°13.017	94°10.372
3	Spring Creek	Springdale, AR, USA	3.9	36°13.431	94°11.532
4	Spring Creek	Springdale, AR, USA	4.6	36°14.461	94°13.586
5	Spring Creek	Springdale, AR, USA	7.5	36°14.663	94°14.322

[a] Negative values for distance are estimated stream lengths upstream from the effluent discharge and positive values are estimated stream lengths downstream from the effluent discharge.

were selected at each stream reach. One water sample was collected from each site on the stream reaches at least once a month under base flow conditions from July 2002 through June 2003. The water samples were collected using a high density polyethylene (HDPE) syringe from the middle of the stream channel. The stream should be well mixed in the middle of the channel; a previous study (Haggard, unpublished data) showed that within site variability was less than that between sites when water samples were collected at these sites in Spring 2002. The water samples collected were filtered through 0.45-μm nylon membranes into two 20 mL scintillation vials; one vial was acidified to pH < 2 with concentrated HCl at each site. All the water quality samples collected were stored on ice and kept in the dark until return to the laboratory.

Physico-chemical parameters were also measured at a single point (mid-stream) at each sampling site. These measurements included specific conductivity and temperature (Orion conductivity Meter 115A plus, Beverly, MA), dissolved oxygen (DO) (YSI-Model 85, Yellow Springs, OH), and pH (pH Testr 2 double junction pH meter, Oakton Instruments, West Caldwell, NJ). Water velocity was measured on a transect divided in equally spaced intervals with an electromagnetic flow meter (Flo-Mate 2000; Marsh-McBirney Inc., Frederick, MD), and depth was measured at mid-points of the width intervals across the transect at all sampling sites; discharge was estimated as a product of water velocity and cross-sectional area (Gore, 1996).

A single sediment sample was collected in July and October 2002, and January, April and June 2003 at the reference site upstream and three sites downstream from the WWTP effluent discharges. Sediments were collected with a trowel at various points along a transect perpendicular to the stream flow from the top 2 to 5 cm of the streambed. The sediment samples were composited along each transect, placed in a plastic bag, and stored in the dark until transported to the laboratory. Approximately 1-L of stream water was also collected at each sediment sampling site in a HDPE bottle and stored on ice in the dark until return to the laboratory.

2.3. *Laboratory techniques*

After return to the laboratory, all water samples were frozen until specific analyses were completed. Filtered, acidified water samples were analyzed for soluble reactive P (SRP) using the ascorbic acid reduction method (APHA, 1998). Total P (TP) was measured using persulfate digestion in an autoclave (APHA, 1998) and colorimetric analysis for SRP as described in the preceding sentence. Chloride (Cl^-) is a good hydrologic tracer in effluent dominated streams (Haggard et al., 2005; Martí et al., 2004), Cl^- was measured using mercuric thiocyanate reaction on unfiltered, unacidified water samples (Skalar Method, The Netherlands). SRP concentrations at sites downstream from WWTP effluent discharges were dilution-corrected using the Cl^- concentrations measured at the first site downstream from the effluent discharge and Cl^- concentration at respective sites further downstream. Since Cl^- is a conservative solute, a longitudinal decline in Cl^- concentrations usually indicates ground water and lateral contributions to the streamflow. So we evaluated the longitudinal variation in dilution-corrected SRP concentration to determine if the ground water and lateral tributaries were responsible for downstream gradients in SRP concentration.

After return to the laboratory, sediments were immediately sieved through a 4.5-mm sieve, and particles <4.5 mm in diameter were used in the following extraction procedures. One-L stream water samples collected in conjunction with the composite sediment samples were filtered through 0.45-μm nylon membranes and used in subsequent extraction procedures as defined. Fresh, wet sediments were used in all extractions because dried sediments yield significantly greater sediment EXP and EPC_0 (Klotz, 1988; Srivastava, 1998), especially in P-enriched streams (Erickson et al., 2004).

To measure EXP, we added 100 mL of 1 M $MgCl_2$ to 20–30 g of fresh, wet sediments in an Erlenmeyer flask (Ruttenburg, 1992). The flasks and sediment slurry were shaken in a reciprocating type shaker for 1 h and also shaken vigorously by hand for 5 s every 15 min. The sediment slurry was allowed to settle for 30 min, and then a 15–20 mL aliquot was filtered through a 0.45-μm nylon membrane into 20-mL scintillation vials for SRP analysis; this filtrate was acidified and analyzed for SRP as previously described. The remaining sediment slurry was transferred into aluminum pans and dried for about 48 h at 80 °C to determine sediment dry mass for each sample.

Equilibrium P concentration (EPC_0 *sensu* Froelich, 1988) may be defined as the dissolved P concentration when stream sediments and the water column are in equilibrium (i.e., there is negligible net adsorption or release of P from stream sediments to the aqueous solution; Taylor and Kunishi, 1971). We used filtered stream water spiked with additional dissolved P at rates from 0.00, 0.25, 0.50, 2.00–4.00 mg P L^{-1}. For example, if the filtered stream water had an ambient concentration of 0.10 mg SRP L^{-1}, the series of P solutions would contain 0.10, 0.35, 0.60, 2.10, and 4.10 mg SRP L^{-1}. We added 100 mL of the various P solutions to 20–30 g fresh, wet sediments, and the sediment slurries were shaken and processed as previously described in the EXP methods. Simple linear regression of P sorbed (mg P sorbed kg^{-1} dry sediment) against initial SRP concentration in the solution was used to estimate sediment EPC_0, where the *x*-intercept represents the point of negligible P adsorption or release from the sediments to the aqueous solution. The slope of this relation was used as a measure of the ability of stream sediments to adsorb added P. Greater slope values suggest an increase in amount of P sorbed (mg P kg^{-1} dry sediment) per unit increase in P concentration (mg L^{-1}).

2.4. *Statistical analysis*

Water quality data were natural-logarithm (ln)–transformed to achieve normality requirements; this is typically used in comparisons of water quality data (Hirsh et al., 1991). Simple linear regression was used to determine sediment EPC_0 and to evaluate the relation between SRP, sediment EPC_0, and sediment EXP across the streams. A one-tail paired *T*-test of the ln-transformed data was used to determine the differences between SRP, sediment EPC_0, and sediment EXP at sites upstream and the first site downstream from the WWTP. A two-tailed paired *T*–test of the ln-transformed data was used to determine the differences between SRP and sediment EPC_0 at an individual sediment samples sites. An *a priori* significance level of 0.10 was used for all statistical comparisons and regression analyses.

3. Results

3.1. *Physico-chemical parameters*

Effluent discharge from the municipal WWTPs significantly altered physico-chemical parameters in the water column at Mud Creek (Table 2), Osage Creek (Table 3), Sager and Flint Creeks (Table 4), and Spring Creek (Table 5). The downstream effect of the effluent input on these parameters was dependent on the amount of stream flow attributable to WWTP effluent discharge. Mean discharge downstream from the effluent input increased from two to 57 times that measured upstream. Thus, these headwater streams are effluent dominated, and Mud Creek, Spring Creek and Sager Creek would likely be intermittent streams without the surface water contribution from the WWTPs.

The effluent discharge did not have a consistent effect on DO concentrations in these streams (Tables 2–5). Dissolved oxygen concentrations upstream and downstream from the effluent discharge were similar across all sampling dates. Dissolved oxygen concentrations measured at all sites across streams were highly variable, ranging from 1.0 to 14.8 mg L^{-1}; low DO concentrations occurred upstream and downstream from effluent discharges. Overall, mean and median DO concentrations were between 7.1 and 10.2 mg L^{-1} across all sites and streams. Similar to DO concentrations, pH was not consistently influenced by the effluent discharge and was generally between 6 and 9 pH units.

Stream water temperatures consistently increased at all streams downstream from the effluent discharge (Tables 2–5), where the greatest increase typically occurred in the colder winter months. The greatest increase in water temperature at individual streams was observed in the streams that were most dominated by effluent discharge, i.e. Mud Creek, Spring Creek and Sager Creek. In these streams (Mud Creek, Spring Creek and Sager Creek), almost 90% of the streamflow at sites downstream of WWTP input can be attributed to the effluent discharge. Often, stream water temperatures remained elevated compared to upstream conditions throughout the study reach used in this investigation.

Conductivity was substantially greater at sites downstream from the effluent discharge compared to upstream (Tables 2–5), and conductivity decreased with increasing distance downstream from the effluent input likely from dilution. Chloride concentrations were also substantially greater downstream from the effluent input, following longitudinal gradients similar to decreases in conductivity resulting from dilution. The effluent input has significant amounts of Cl^- and stream water Cl^- concentrations changed similar to conductivity and discharge. Therefore, the longitudinal patterns in Cl^- concentrations may be used to correct SRP concentrations for dilution from ground water and lateral tributaries in these headwater streams. Chloride concentrations showed the greatest decrease with increasing distance downstream from the WWTP effluent discharge in Spring Creek and Sager (and Flint) Creek; mean Cl^- concentrations at the furthest downstream sites were 68 and 45% of that observed just downstream from the WWTP. In contrast, Cl^- concentrations did not show a distinct longitudinal gradient in Mud Creek or

Table 2 – Descriptive statistics for soluble reactive phosphorus (SRP), chloride (Cl^-), stream discharge (Q), conductivity, dissolved oxygen (DO), temperature, and pH observed at Mud Creek from July 2002 through June 2003

Parameter	Distance[a]	n	Mean	Standard deviation	Median	Minimum	Maximum
SRP ($mg\,L^{-1}$)	−0.5	21	0.02	0.03	0.01	0.00	0.16
	0.4	20	0.11	0.09	0.09	0.04	0.42
	0.9	21	0.10	0.05	0.08	0.02	0.24
	2.2	21	0.10	0.09	0.07	0.02	0.40
	3.1	21	0.09	0.05	0.09	0.02	0.23
Cl^- ($mg\,L^{-1}$)	−0.5	20	9	7	5	4	22
	0.4	20	43	18	48	8	64
	0.9	21	44	16	46	9	66
	2.2	21	47	20	49	3	90
	3.1	19	43	18	44	14	93
Q ($L\,s^{-1}$)	−0.5	21	3	4	1	0	15
	0.4	21	172	127	170	4	428
	0.9	21	181	125	183	3	442
	2.2	21	190	109	202	6	393
	3.1	21	209	115	225	5	417
Conductivity ($\mu S\,cm^{-1}$)	−0.5	21	205	52	217	126	294
	0.4	21	586	150	607	283	909
	0.9	21	597	136	604	290	911
	2.2	21	580	139	591	270	911
	3.1	21	566	144	562	269	913
DO ($mg\,L^{-1}$)	−0.5	19	7.7	3.1	7.4	2.4	14.8
	0.4	19	7.7	1.9	7.0	3.0	10.8
	0.9	19	8.2	2.1	7.5	3.9	12.3
	2.2	19	8.1	2.4	7.6	2.5	12.4
	3.1	19	8.5	2.6	7.8	2.3	13.2
Temperature (°C)	−0.5	20	14.3	7.0	16.0	4.0	23.8
	0.4	20	18.1	5.4	17.0	10.0	26.9
	0.9	20	18.1	5.3	16.9	10.6	26.8
	2.2	20	17.2	5.4	17.6	9.5	26.1
	3.1	20	17.0	5.6	17.9	8.7	25.6
pH	−0.5	20	7.9	0.4	8.1	6.6	8.4
	0.4	20	7.8	0.2	7.8	7.4	8.1
	0.9	20	8.0	0.2	8.0	7.6	8.5
	2.2	20	8.1	0.3	8.0	7.6	8.7
	3.1	20	8.2	0.3	8.1	7.7	9.0

[a] Negative values for distance are estimated stream lengths upstream from the effluent discharge and positive values are estimated stream lengths downstream from the effluent discharge.

Osage Creek; mean Cl^- concentrations at the most downstream site were greater than 93% of that measured at the first site below the WWTP effluent discharge.

3.2. *Soluble reactive P concentrations*

Mean effluent P concentrations varied between the municipal WWTPs during this study period (July 2002 through June 2003). The Fayetteville and Rogers municipal WWTPs discharged an average TP concentration of 0.25 and 0.35 $mg\,L^{-1}$ into Mud and Osage Creeks, respectively. The Springdale municipal WWTP discharged an average effluent TP concentration of 4.4 $mg\,L^{-1}$ into Spring Creek. Average effluent P concentration was not available from the Siloam Springs facility, but it appears that the change in dissolved P concentration in Sager (and Flint) Creek is somewhere between that of Spring Creek and Mud or Osage Creek.

Soluble reactive P (SRP) concentrations downstream from the WWTP effluent discharges increased significantly (ln-transformed data, paired *T*-test, $P < 0.01$) compared to concentrations measured upstream at these headwater streams (Tables 2–5, Fig. 2). The magnitude of the increase was much less at Mud Creek and Osage Creek compared to the other headwater streams (Tables 2 and 3). Mean SRP concentrations upstream at Mud Creek and Osage Creek were 0.02 and 0.03 $mg\,L^{-1}$, whereas mean concentrations downstream were 0.11 and 0.08 $mg\,L^{-1}$ at sites immediately downstream from the WWTP input. The most profound effect of WWTP effluent discharge on SRP concentrations was observed at Spring Creek, which had the greatest SRP concentration measured in this study (7.0 $mg\,L^{-1}$) in August 2002 (Table 5). However, due to changes in WWTP operation, SRP concentrations had been reduced from 7 to less than 1 $mg\,L^{-1}$ in June 2003 at Spring Creek (Fig. 2).

Monthly mean SRP concentrations measured during this study were compared with TP concentrations reported in WWTP effluent for the cities of Fayetteville, Springdale, and Rogers (Fig. 2); no data was available from Siloam Springs.

Table 3 – Descriptive statistics for soluble reactive phosphorus (SRP), chloride (Cl^-), stream discharge (Q), conductivity, dissolved oxygen (DO), temperature, and pH observed at Osage Creek from July 2002 through June 2003

Parameter	Distance[a]	*n*	Mean	Standard deviation	Median	Minimum	Maximum
SRP ($mg\,L^{-1}$)	−0.2	21	0.03	0.03	0.02	0.01	0.12
	1.5	21	0.08	0.07	0.07	0.02	0.27
	3.4	21	0.07	0.04	0.06	0.02	0.16
	4.2	21	0.07	0.04	0.06	0.02	0.16
	5.5	21	0.07	0.03	0.07	0.03	0.12
Cl^- ($mg\,L^{-1}$)	−0.2	20	10	8	7	4	37
	1.5	20	32	10	31	15	49
	3.4	21	31	9	30	13	45
	4.2	21	31	8	30	17	45
	5.5	21	30	8	30	17	45
Q ($mg\,L^{-1}$)	−0.2	21	286	131	267	89	579
	1.5	21	605	185	590	363	1004
	3.4	21	650	156	677	360	913
	4.2	21	625	167	653	265	947
	5.5	21	630	169	642	332	957
Conductivity ($\mu S\,cm^{-1}$)	−0.2	21	275	38	264	212	337
	1.5	21	405	62	412	318	560
	3.4	21	375	52	382	297	460
	4.2	21	377	51	386	291	476
	5.5	21	374	53	377	288	476
DO ($mg\,L^{-1}$)	−0.2	19	7.1	2.4	7.1	1.1	10.4
	1.5	19	7.9	2.3	7.8	1.3	11.2
	3.4	19	8.7	3.0	8.7	1.2	14.3
	4.2	19	8.7	2.7	8.3	1.4	14.0
	5.5	19	9.1	2.8	9.5	1.4	13.8
Temperature (°C)	−0.2	21	15.4	3.9	17.2	8.3	20.3
	1.5	21	16.9	4.2	18.0	10.1	22.6
	3.4	21	16.9	5.0	18.7	8.5	24.0
	4.2	21	16.6	5.1	18.3	7.9	23.4
	5.5	21	16.9	5.7	19.5	7.3	24.4
pH	−0.2	20	7.6	0.2	7.6	7.1	8.0
	1.5	20	7.6	0.2	7.6	7.0	7.7
	3.4	20	7.8	0.2	7.8	7.5	8.1
	4.2	20	7.9	0.2	7.8	7.5	8.3
	5.5	20	8.0	0.2	8.0	7.4	8.3

[a] Negative values for distance are estimated stream lengths upstream from the effluent discharge and positive values are estimated stream lengths downstream from the effluent discharge.

Monthly mean SRP concentrations in Mud Creek and Osage Creek generally were related to TP concentrations measured in the effluent discharge. However, effluent concentrations were much greater than that observed in the stream at Mud Creek and Osage Creek in one month. Total P concentrations in the effluent discharge at Spring Creek decreased throughout the study period (July 2002 through June 2003), as did SRP concentrations measured in the Spring Creek. A significant correlation ($TP_{effluent} = 0.52 \times SRP_{stream} - 0.12$, $r^2 = 0.60$, $P < 0.01$) was observed between SRP concentrations measured in the study streams at the first site downstream from the effluent discharge and the values obtained from the municipal WWTP (Fig. 2).

Soluble reactive P concentrations at Mud and Osage Creeks did not decline appreciably with increasing distance downstream from the WWTP effluent discharges. Thus, minimal P retention generally occurred at these two streams during the study period. However, SRP concentrations in Spring Creek and Sager (and Flint) Creek showed a decline with increasing distance downstream from the municipal WWTP input. These decreasing gradients in SRP concentrations may suggest some P retention is occurring, while the longitudinal decline in Cl^- concentrations indicates dilution from ground water and lateral contributions as a substantial factor for SRP decline. Thus, dilution-corrected SRP concentrations were used to evaluate potential P retention at Spring Creek and Sager (and Flint) Creek, and dilution-corrected concentrations showed no significant change with distance downstream from the effluent input. On eight of approximately 20 sampling dates, we observed a significant decrease in dilution-corrected SRP concentrations at Sager (and Flint) Creek. At Spring Creek, a different phenomenon was observed; dilution-corrected SRP

Table 4 – Descriptive statistics for soluble reactive phosphorus (SRP), chloride (Cl^-), stream discharge (Q), conductivity, dissolved oxygen (DO), temperature, and pH observed at Sager (and Flint) Creek from July 2002 through June 2003

Parameter	Distance[a]	n	Mean	Standard deviation	Median	Minimum	Maximum
SRP ($mg\,L^{-1}$)	−3.3[b]	20	0.12	0.12	0.08	0.01	0.46
	2.0[b]	21	1.03	0.46	0.96	0.36	2.24
	3.9[b]	21	0.98	0.41	1.09	0.40	1.94
	7.5[c]	21	0.25	0.09	0.25	0.11	0.53
	10[c]	21	0.22	0.09	0.21	0.03	0.47
Cl^- ($mg\,L^{-1}$)	−3.3[b]	20	9	4	8	4	22
	2.0[b]	21	42	11	38	28	66
	3.9[b]	19	40	14	33	24	68
	7.5[c]	19	20	7	18	15	41
	10[c]	20	19	6	18	10	29
Q ($L\,s^{-1}$)	−3.3[b]	21	42	26	35	2	95
	2.0[b]	21	275	117	269	115	473
	3.9[b]	21	265	134	252	102	545
	7.5[c]	21	772	354	666	363	1447
	10[c]	21	893	452	729	300	1887
Conductivity ($\mu S\,cm^{-1}$)	−3.3[b]	21	204	19	203	174	241
	2.0[b]	21	444	86	439	286	601
	3.9[b]	21	424	85	401	273	601
	7.5[c]	21	302	45	310	228	375
	10[c]	21	301	46	315	221	369
DO ($mg\,L^{-1}$)	−3.3[b]	19	9.3	2.9	10.2	1.1	12.0
	2.0[b]	19	8.7	3.4	8.5	1.0	14.5
	3.9[b]	19	8.5	3.4	8.1	1.2	14.3
	7.5[c]	19	8.7	2.7	8.6	1.5	12.1
	10[c]	19	8.8	3.4	8.4	1.3	14.2
Temperature (°C)	−3.3[b]	21	16.0	5.4	17.8	6.7	22.4
	2.0[b]	21	18.6	7.0	21.0	8.0	28.4
	3.9[b]	21	17.5	7.4	19.5	6.6	27.4
	7.5[c]	21	17.5	6.7	20.0	7.2	26.9
	10[c]	21	17.4	7.4	19.7	6.5	27.4
pH	−3.3[b]	19	7.4	0.5	7.6	5.8	8.0
	2.0[b]	19	7.8	0.3	7.8	7.0	8.5
	3.9[b]	19	7.8	0.3	7.8	6.8	8.5
	7.5[c]	19	7.8	0.3	7.8	7.1	8.1
	10[c]	19	7.9	0.3	7.9	6.9	8.4

[a] Negative values for distance are estimated stream lengths upstream from the effluent discharge and positive values are estimated stream lengths downstream from the effluent discharge.
[b] These sites are at Sager Creek upstream from the confluence of Sager Creek and Flint Creek.
[c] These sites are at Flint Creek downstream from the confluence of Sager Creek and Flint Creek.

concentrations increased with distance downstream from the effluent discharge on six of 14 sampling dates after October 2002. Overall, minimal P retention was observed in these headwater streams and potential P release was observed in Spring Creek following reductions in effluent dissolved P concentrations.

The percent of TP as SRP in water samples collected in July and October 2002, and January, April and June 2003 were compared (Fig. 3), showing that measured SRP was a good surrogate for TP in Spring Creek at high concentrations (greater than $2\,mg\,L^{-1}$). The proportion of TP as SRP was between 50 and 100% when TP concentrations were between 0.4 and $2.0\,mg\,L^{-1}$. The variability in the proportion of TP as SRP increased at TP concentrations less than $0.4\,mg\,L^{-1}$, where SRP concentrations comprised from 10 to 100% of measured TP concentrations in this study.

3.3. *Dissolved P equilibrium between stream sediments and water*

Effluent discharge from the WWTPs also increased equilibrium concentrations between stream sediments and the water column. Across all streams, sediment EPC_0 significantly (ln-transformed data, paired *T*-test, $P < 0.01$) increased at the first site downstream from the effluent discharge compared to that measured upstream (Tables 6–9 and Fig. 2). Mean sediment EPC_0 upstream from the effluent discharge ranged from 0.01 to $0.07\,mg\,L^{-1}$ across all streams, whereas sediment EPC_0 downstream varied with the level of P enrichment from the WWTPs. At Mud Creek and Osage Creek, mean sediment EPC_0 was from 0.10 to $0.18\,mg\,L^{-1}$ with the greater values generally occurring in Mud Creek (Tables 6 and 7). Mean sediment EPC_0 at sites downstream from the effluent discharge in Sager Creek was

Table 5 – Descriptive statistics for soluble reactive phosphorus (SRP), chloride (Cl^-), stream discharge (Q), conductivity, dissolved oxygen (DO), temperature, and pH observed at Spring Creek from July 2002 through June 2003

Parameter	Distance[a]	n	Mean	Standard deviation	Median	Minimum	Maximum
SRP ($mg\,L^{-1}$)	−1.1	20	0.08	0.08	0.06	0.03	0.41
	2.0	21	2.10	2.24	1.95	0.13	7.60
	3.9	21	1.93	1.86	1.83	0.25	6.05
	4.6	21	1.66	1.45	1.36	0.27	5.09
	7.5	21	1.58	1.16	1.19	0.20	3.80
Cl^- ($mg\,L^{-1}$)	−1.1	21	12	6	11	7	30
	2.0	21	63	15	62	41	89
	3.9	21	51	12	53	29	71
	4.6	21	46	12	46	24	72
	7.5	20	43	11	41	22	66
Q ($L\,s^{-1}$)	−1.1	21	14	16	4	0	53
	2.0	21	698	267	762	255	1189
	3.9	21	601	254	670	88	979
	4.6	21	761	299	766	277	1438
	7.5	21	753	307	710	298	1466
Conductivity ($\mu S\,cm^{-1}$)	−1.1	21	278	55	273	191	365
	2.0	21	567	97	549	402	726
	3.9	21	532	90	526	370	721
	4.6	21	496	84	487	339	671
	7.5	21	470	92	472	294	661
DO ($mg\,L^{-1}$)	−1.1	19	8.4	3.5	8.0	1.7	14.0
	2.0	19	8.2	2.1	8.4	1.9	12.3
	3.9	19	8.6	2.3	8.8	1.9	12.8
	4.6	18	9.7	2.3	9.3	5.6	14.3
	7.5	18	9.6	2.3	9.0	5.8	13.7
Temperature (°C)	−1.1	21	15.1	6.4	16.7	2.8	25.0
	2.0	21	18.5	5.3	19.9	10.4	26.3
	3.9	21	18.0	5.4	19.3	9.7	26.2
	4.6	21	17.2	6.1	18.5	7.3	26.1
	7.5	21	17.1	6.3	18.8	6.8	25.5
pH	−1.1	20	7.9	0.4	7.9	7.4	8.9
	2.0	20	7.6	0.2	7.7	7.1	7.9
	3.9	20	7.8	0.2	7.8	7.4	8.2
	4.6	20	8.2	0.2	8.2	7.7	8.5
	7.5	20	8.3	0.3	8.2	7.8	8.9

[a] Negative values for distance are estimated stream lengths upstream from the effluent discharge and positive values are estimated stream lengths downstream from the effluent discharge.

1.02–1.13 $mg\,L^{-1}$; mean sediment EPC_0 downstream from the Sager and Flint Creek confluence was 0.49 $mg\,L^{-1}$ (Table 8). Sediment EPC_0 at Spring Creek was highly variable at sites downstream from the effluent discharge ranging from 0.50 to 6.99 $mg\,L^{-1}$; mean sediment EPC_0 was between 2.62 and 3.44 $mg\,L^{-1}$ at these sites (Table 9).

Sediment EPC_0 did not change with time or distance downstream from the WWTP at Mud Creek and Osage Creek (Tables 6 and 7). However, sediment EPC_0 at Sager (and Flint) Creek was surprisingly less in June 2003 compared to that observed on the preceding sampling dates (Table 8). Sediment EPC_0 downstream from the Sager and Flint Creek confluence was also less than half of that measured at sites on Sager Creek downstream from the effluent discharge. Sediment EPC_0 at Spring Creek changed drastically with time and distance downstream from the WWTP (Table 9), just as stream water SRP concentrations and effluent TP concentrations did (Table 5, Fig. 2). Sediment EPC_0 at Spring Creek observed in June 2003 was only 8–9% of the values reported in July 2002 at sites downstream from the effluent discharge, when effluent dissolved P concentrations were high.

Sediment EPC_0 showed a significant correlation with water column SRP (ln-transformed data, $\ln(EPC_0) = 0.78 \times \ln(SRP) + 0.14$, $r^2 = 0.60$, $P < 0.001$) across all streams (Fig. 4). However, this relation was not apparent within individual streams, except at Spring Creek. It is likely that the wide range in sediment EPC_0 and SRP concentrations in the water column at Spring Creek contribute to this relation. None-the-less, sediment EPC_0 was related to water column SRP concentrations that were generally related to effluent dissolved P concentrations (Fig. 2).

The slope of the relation used to estimate sediment EPC_0 generally decreased at the first site downstream from the effluent discharge compared to that measured upstream, indicating that the effluent influenced the ability of the sediment to adsorb P from the aqueous solution in the laboratory experiments. However, the slopes of this relation at sites further

Table 6 – Sediment easily exchangeable phosphorus (EXP), equilibrium phosphorus concentrations (EPC_0) and linear adsorption isotherm data for sediment sampling stations in Mud Creek from July 2002 through June 2003

Sampling Date	Distance[a] (km)	Sed EXP (mg kg^{-1})	Data from linear adsorption isotherms				Water column SRP (mg L^{-1})
			Sed EPC_0 (mg L^{-1})	Slope (k)	r^2	P	
July 2002	−0.5	0.24	<0.01	6.08	0.99	<0.01	<0.001
July 2002	0.4	2.51	0.18	4.07	0.99	<0.01	0.08
July 2002	0.9	0.68	0.06	5.71	0.99	<0.01	0.16
July 2002	3.1	1.12	0.09	3.72	0.98	<0.01	0.16
October 2002	−0.5	0.22	0.01	5.00	0.99	<0.01	0.01
October 2002	0.4	0.86	0.04	4.48	0.99	<0.01	0.04
October 2002	0.9	0.31	0.05	5.38	0.99	<0.01	0.06
October 2002	3.1	0.60	0.05	3.59	0.99	<0.01	0.04
January 2003	−0.5	0.10	0.01	5.94	0.99	<0.01	0.01
January 2003	0.4	1.84	0.21	4.49	0.99	<0.01	0.04
January 2003	0.9	2.48	0.29	4.77	0.99	<0.01	0.06
January 2003	3.1	0.91	0.17	4.19	0.99	<0.01	0.03
April 2003	−0.5	0.03	0.01	5.24	0.99	<0.01	0.01
April 2003	0.4	1.88	0.23	4.16	0.99	<0.01	0.14
April 2003	0.9	1.65	0.25	4.36	0.99	<0.01	0.16
April 2003	3.1	1.32	0.19	4.75	0.99	<0.01	0.15
June 2003	−0.5	0.02	0.01	5.40	0.99	<0.01	0.01
June 2003	0.4	1.98	0.23	4.71	0.99	<0.01	0.13
June 2003	0.9	2.18	0.26	4.56	0.99	<0.01	0.13
June 2003	3.1	1.07	0.19	4.75	0.99	<0.01	0.12

[a] Negative values for distance are estimated stream lengths upstream from the effluent discharge and positive values are estimated stream lengths downstream from the effluent discharge.

Table 7 – Sediment easily exchangeable phosphorus (EXP), equilibrium phosphorus concentrations (EPC_0) and linear adsorption isotherm data for sediment sampling stations in Osage Creek from July 2002 through June 2003

Sampling date	Distance[a] (km)	Sed EXP ($mg\,kg^{-1}$)	Data from linear adsorption isotherms				Water column SRP ($mg\,L^{-1}$)
			Sed EPC_0 ($mg\,L^{-1}$)	Slope (k)	r^2	P	
July 2002	−0.2	0.22	0.02	6.35	0.99	<0.01	0.02
July 2002	1.5	1.16	0.14	5.19	0.99	<0.01	0.08
July 2002	3.4	1.49	0.12	4.70	0.99	<0.01	0.08
July 2002	5.5	1.11	0.14	6.13	0.99	<0.01	0.08
October 2002	−0.2	0.37	0.03	5.68	0.99	<0.01	0.02
October 2002	1.5	0.87	0.04	5.01	0.99	<0.01	0.25
October 2002	3.4	1.22	0.07	4.99	0.99	<0.01	0.09
October 2002	5.5	1.36	0.08	4.83	0.99	<0.01	0.07
January 2003	−0.2	0.38	0.15	5.79	0.99	<0.01	0.02
January 2003	1.5	1.61	0.22	5.78	0.99	<0.01	0.04
January 2003	3.4	0.77	0.08	5.78	0.99	<0.01	0.03
January 2003	5.5	1.48	0.19	5.56	0.99	<0.01	0.03
April 2003	−0.2	0.47	0.04	5.93	0.99	<0.01	0.01
April 2003	1.5	2.08	0.20	6.10	0.99	<0.01	0.04
April 2003	3.4	1.52	0.15	5.71	0.99	<0.01	0.09
April 2003	5.5	1.07	0.09	5.06	0.99	<0.01	0.12
June 2003	−0.2	0.48	0.07	5.93	0.99	<0.01	0.01
June 2003	1.5	0.83	0.10	5.79	0.99	<0.01	0.03
June 2003	3.4	0.96	0.09	4.96	0.99	<0.01	0.04
June 2003	5.5	0.97	0.08	4.87	0.99	<0.01	0.05

[a] Negative values for distance are estimated stream lengths upstream from the effluent discharge and positive values are estimated stream lengths downstream from the effluent discharge.

Table 8 – Sediment easily exchangeable phosphorus (EXP), equilibrium phosphorus concentrations (EPC_0) and linear adsorption isotherm data for sediment sampling stations in Sager (and Flint) Creek from July 2002 through June 2003

Sampling Date	Distance[a] (km)	Sed EXP (mg kg^{-1})	Data from linear adsorption isotherms				Water column SRP (mg L^{-1})
			Sed EPC_0 (mg L^{-1})	Slope (k)	r^2	P	
July 2002	−3.3	0.75	0.12	5.20	0.99	<0.01	0.38
July 2002	2.0	4.01	1.05	4.94	0.99	<0.01	1.70
July 2002	3.9	5.07	1.27	5.04	0.99	<0.01	1.43
July 2002	10	1.30	0.32	5.22	0.99	<0.01	0.47
October 2002	−3.3	0.70	0.02	5.29	0.99	<0.01	0.08
October 2002	2.0	7.18	1.18	4.67	0.98	<0.01	0.78
October 2002	3.9	5.24	1.13	5.02	0.99	<0.01	1.20
October 2002	10	1.59	0.25	5.67	0.99	<0.01	0.29
January 2003	−3.3	1.42	0.04	5.13	0.99	<0.01	0.05
January 2003	2.0	6.28	1.17	4.37	0.99	<0.01	0.54
January 2003	3.9	4.64	1.29	4.73	0.94	<0.01	0.47
January 2003	10	1.82	0.37	4.75	0.99	<0.01	0.17
April 2003	−3.3	0.61	0.01	5.35	0.99	<0.01	0.08
April 2003	2.0	6.77	1.18	5.65	0.99	<0.01	1.23
April 2003	3.9	6.73	1.36	6.23	0.99	<0.01	1.30
April 2003	10	1.88	1.36	5.66	0.99	<0.01	0.28
June 2003	−3.3	0.06	0.01	4.14	0.99	<0.01	0.06
June 2003	2.0	4.42	0.50	4.49	0.99	<0.01	1.03
June 2003	3.9	3.68	0.60	5.17	0.99	<0.01	0.62
June 2003	10	1.25	0.15	4.71	0.99	<0.01	0.20

[a] Negative values for distance are estimated stream lengths upstream from the effluent discharge and positive values are estimated stream lengths downstream from the effluent discharge.

Table 9 – Sediment easily exchangeable phosphorus (EXP), equilibrium phosphorus concentrations (EPC_0) and linear adsorption isotherm data for sediment sampling stations in Spring Creek from July 2002 through June 2003

Sampling date	Distance[a] (km)	Sed EXP ($mg\,kg^{-1}$)	Data from linear adsorption isotherms				Water column SRP ($mg\,L^{-1}$)
			Sed EPC_0 ($mg\,L^{-1}$)	Slope (k)	r^2	P	
July 2002	−1.1	0.86	0.13	5.85	0.99	<0.01	0.41
July 2002	2.0	10.71	6.99	5.13	0.97	<0.01	7.03
July 2002	3.9	11.62	5.19	5.12	0.96	<0.01	6.05
July 2002	7.5	10.33	3.68	5.03	0.99	<0.01	3.80
October 2002	−1.1	0.80	0.07	5.43	0.99	<0.01	0.03
October 2002	2.0	16.37	6.30	9.82	0.90	0.01	3.70
October 2002	3.9	10.76	6.08	9.59	0.99	<0.01	4.71
October 2002	7.5	10.77	6.09	11.73	0.99	<0.01	3.59
January 2003	−1.1	0.90	0.08	5.20	0.99	<0.01	0.03
January 2003	2.0	7.63	2.62	5.23	0.99	<0.01	2.37
January 2003	3.9	7.26	2.59	4.21	0.94	<0.01	0.83
January 2003	7.5	7.26	1.99	4.66	0.99	<0.01	1.50
April 2003	−1.1	0.52	0.01	4.63	0.99	<0.01	0.04
April 2003	2.0	4.57	0.73	5.22	0.99	<0.01	0.35
April 2003	3.9	4.42	0.71	4.72	0.99	<0.01	0.40
April 2003	7.5	6.76	0.85	5.49	0.99	<0.01	0.55
June 2003	−1.1	0.61	0.04	5.64	0.99	<0.01	0.10
June 2003	2.0	2.78	0.55	4.33	0.99	<0.01	0.63
June 2003	3.9	3.08	0.55	4.72	0.99	<0.01	0.52
June 2003	7.5	5.05	0.50	4.41	0.99	<0.01	0.61

[a] Negative values for distance are estimated stream lengths upstream from the effluent discharge and positive values are estimated stream lengths downstream from the effluent discharge.

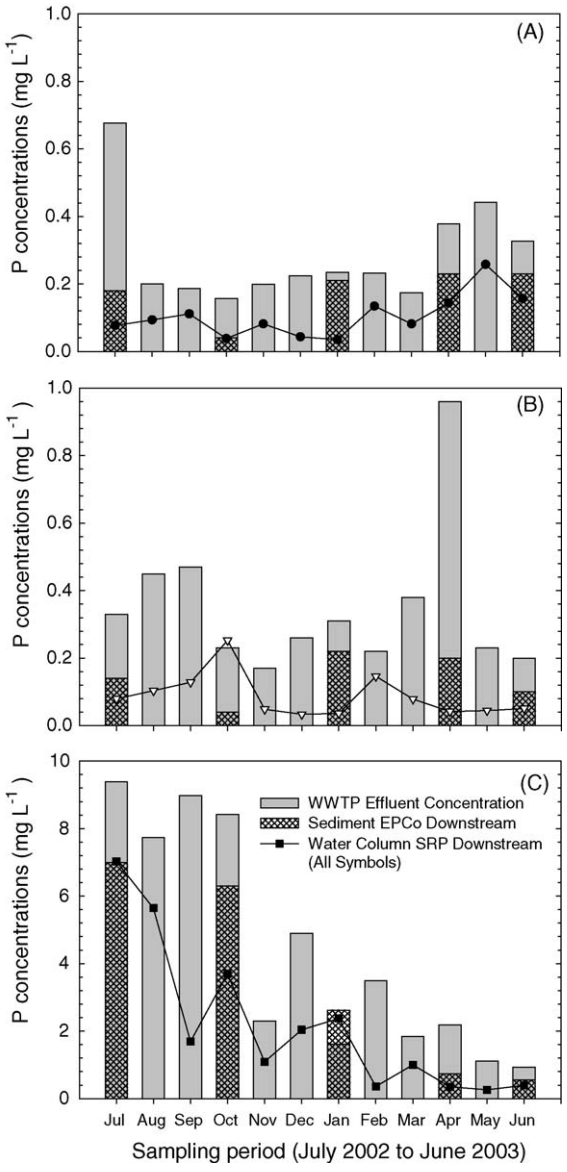


Fig. 2 – Wastewater treatment plant (WWTP) effluent total phosphorus (TP) concentrations, water column soluble reactive phosphorus (SRP) concentrations at the first site downstream from the effluent discharge, and sediment equilibrium phosphorus concentrations (EPC_0) at the first site downstream from the effluent discharge at Mud Creek (A), Osage Creek (B) and Spring Creek (C).

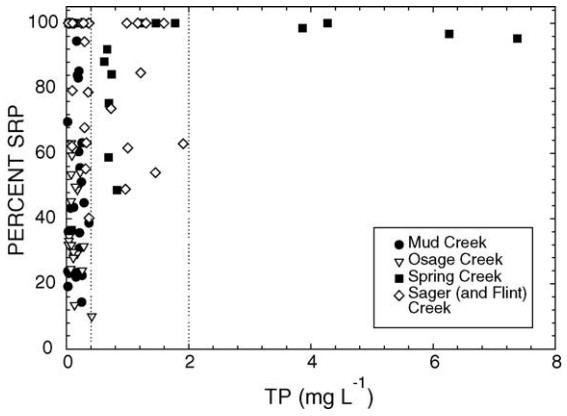


Fig. 3 – Percent of total phosphorus (TP) as soluble reactive phosphorus (SRP) measured in various water samples collected at Mud Creek, Osage Creek, Sager (and Flint) Creek and Spring Creek from July 2002 through June 2003.

downstream from the effluent discharge were often similar to that observed upstream.

3.4. *Easily exchangeable P in sediments*

Mean sediment EXP at all sites downstream from the effluent discharge was greater (ln-transformed data, paired *T*-test, $P<0.01$) than that observed upstream across all streams (Fig. 4). Sediment EXP differences across streams followed patterns similar to that observed with sediment EPC_0 and SRP concentrations in the water column across all streams. Sediment EXP and EPC_0 were strongly correlated (ln-transformed data, $\ln(EXP) = 0.69 \times \ln(EPC_0) + 1.50$, $r^2 = 0.85$, $P<0.0001$) across all streams (Fig. 4); this relation was also apparent within individual streams, especially the effluent-driven Spring Creek. Sediment EXP and SRP concentrations in the water column were also strongly correlated (ln-transformed data, $\ln(EXP) = 0.56 \times \ln(SRP_{stream}) + 1.65$, $r^2 = 0.56$, $P<0.001$), but this relation appeared to rise to a maximum ($EXP = 11.38 \times (1 - \exp(0.90 \times SRP_{stream}))$, $r^2 = 0.73$, $P<0.0001$). Thus, the maximum amount of sediment EXP would be estimated to be approximately 11.4 mg P sorbed kg^{-1} dry sediment in these streams.

4. Discussion

4.1. *Effects of WWTP effluent discharge on water quality*

Several studies have demonstrated the impact that municipal WWTP effluent may have on P concentrations in streams and sediments (Fox et al., 1989; House and Denison, 1997; Dorioz et al., 1998; Haggard et al., 2001, 2005). Results from this study showed that stream SRP concentrations increased several fold downstream from effluent inputs, and these municipal WWTPs have also influenced general water chemistry (particularly conductivity and water temperature) of the receiving streams. Dissolved P concentrations in streams generally show a longitudinal decline with increasing distance downstream from municipal WWTPs (House and Denison, 1998; Haggard et al., 2001, 2005), even after correcting for dilution from ground water or lateral tributaries. This study showed that in Mud Creek, Osage Creek, and Spring Creek dilution was generally responsible for decreases in SRP concentration with increasing distance downstream from the effluent input, not biotic and abiotic processes that occur within the stream reach. However, P retention was significant at Sager and Flint Creek on less than half of the sampling dates, where it required km-scale lengths (3.6–8.2 km) to significantly retain approximately 63% of the municipal WWTP P input. These distances are comparable to those measured downstream

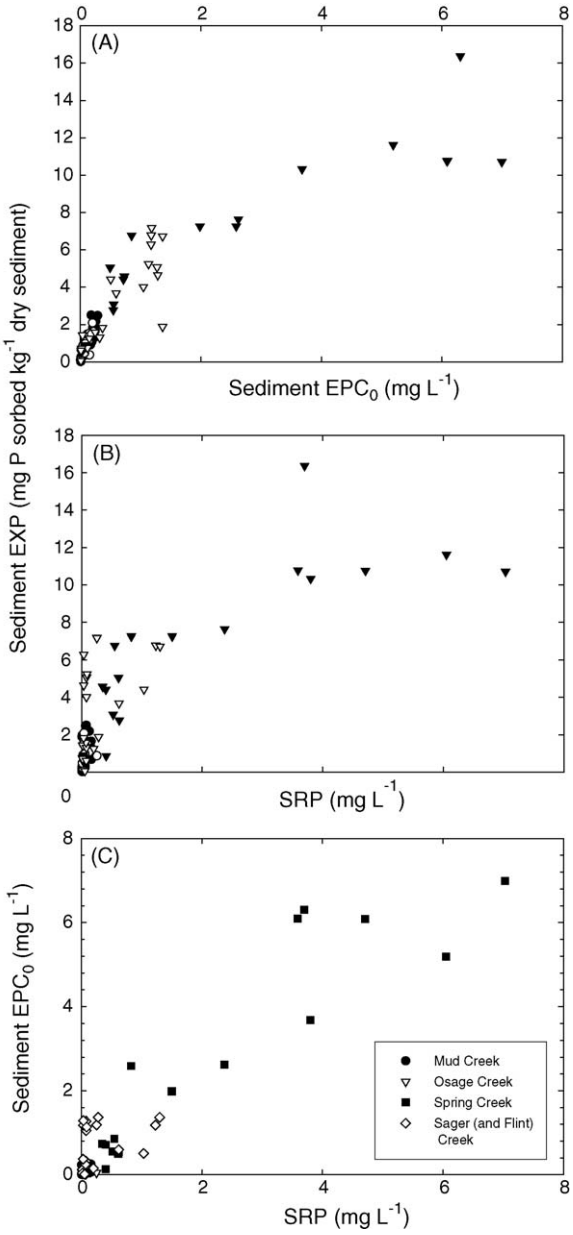


Fig. 4 – The relation between sediment equilibrium phosphorus concentrations (EPC_0) and easily exchangeable phosphorus (EXP) (A), water column soluble reactive phosphorus (SRP) and sediment EXP (B), and water column SRP and sediment EPC_0 (C) across all study streams at the Illinois River Basin.

from another regional WWTP (Haggard et al., 2001, 2005) and reported in other effluent-driven streams across the world (Martí et al., 2004).

The Springdale municipal WWTP adopted voluntary P management strategies and started implementing this strategy in Fall 2002. In fact, this municipal facility and those in Fayetteville, Rogers, and Siloam Springs, Arkansas all agreed to reduce effluent TP concentrations to less than 1 mg L^{-1} because of the Oklahoma Scenic Rivers TP criterion (0.037 mg L^{-1}) and potential lawsuits that may be filed regarding the Illinois River and Flint Creek exceeding this criterion. Springdale's WWTP effluent TP concentrations decreased from June 2002 through July 2003, translating into subsequent decreases in SRP concentration of the water column at Spring Creek. Although SRP concentrations at Spring Creek show a decrease with distance downstream from the effluent input, dilution-corrected concentrations did not significantly decrease on any sampling dates. In contrast, dilution-corrected SRP concentrations often increased after effluent P reductions, suggesting that legacy P stored within the stream reach was released back into the water column. Haggard et al. (2005) showed an internal P loading mechanism in an Ozark stream when effluent P concentrations were low (<3 mg L^{-1}). Many other studies have shown that P-saturated wetland sediments release P to the water column when dissolved P concentrations are low (e.g., see Novak et al., 2004; Fisher and Reddy, 2001). It is not known how long P may be released from stream sediments back into the water column, maintaining elevated SRP concentrations. Water quality monitoring of the Illinois River near the Arkansas-Oklahoma border and upstream to the headwater streams has not shown SRP concentrations less than the Scenic River TP criterion, except on one sampling date in 2004 (Haggard, unpublished data). If the goal is a quick response to reduced effluent P concentrations, then watershed managers may have to consider chemical remediation techniques such as treating stream sediments with aluminum sulfate (Haggard et al., 2004) as often used in reducing sediment P flux in reservoirs (Welch and Schrieve, 1994; Rydin and Welch, 1999).

4.2. *Sediment-phosphorus interactions downstream from effluent discharges*

As dissolved P moves downstream, benthic sediments and associated biota often play a major role, potentially regulating dissolved P concentrations in the water column and temporarily reducing downstream transport, especially under baseflow conditions (Fox et al., 1989; Svendsen et al., 1995; Schulz and Herzog, 2004). During storm events, dissolved and total P transport may be influenced by resuspension of sediment-bound P within the stream channel, as well as nonpoint sources of pollution. Suspended sediments in streams affect dissolved P equilibrium between water and benthic sediments (House et al., 1995) and likely impact dissolved P concentrations occurring during surface runoff events in streams.

In this study, effluent discharge from municipal WWTPs significantly increased $MgCl_2$ extractable P (EXP) in sediments of these Ozark streams, consequently increasing the sediment EPC_0 and reducing the P buffering capacity of the sediments. Sediment sorption (as an abiotic process) has been shown as a substantial factor in P retention (Fox et al., 1989; House and Warwick, 1999). However, biotic uptake associated with benthic sediments often accounts for a large portion of P removal (Haggard et al., 1999; Khoshmanesh et al., 1999); the cited studies showed biotic processes were responsible for 38 and 45% of P removal. Furthermore, the organic matter content of sediments also influences the ability of sediments to adsorb P (Smith et al., 2005). However, many factors influence sediment EPC_0 and the ability of sediments to adsorb P, and this study focused solely on the effect of WWTP effluent input. Future

investigations into sediment-P interactions in these streams should consider the influence of exchangeable Al, Fe, and Ca (Meyer, 1979; Klotz, 1988) and biotic processes. Sediment particle size and organic matter content also play a large role in sediment-P sorption and sediment EPC_0 (Haggard et al., 1999; Klotz, 1988; Hill, 1982, McDowell et al., 2002), but these Ozark streams are dominated by coarse sediments (chert gravel with few fine particles) with relatively low organic matter content.

In these Ozark headwater streams, the sediments were a significant transient storage of P downstream from WWTPs. The increased P bioavailability downstream from effluent discharge may influence sediment – associated biotic processes in these streams and potentially in aquatic systems further downstream. The increase in sediment EPC_0 downstream from effluent discharges supports the idea that in P-enriched systems, it is P inputs from the WWTP that control sediment-aqueous phase P equilibrium and not the sediments. However, Klotz (1985, 1988) showed that sediments and associated biotic processes were likely controlling dissolved P concentrations in a stream with relatively low dissolved P concentrations. In the current study, sediment EPC_0 at Spring Creek downstream from the effluent discharge seem to have responded quickly to reduced effluent P concentrations, similar to water column SRP concentrations. However, the stream reach downstream from the effluent discharge at Spring Creek showed that dilution-corrected SRP concentrations often increased with increasing distance downstream.

Acknowledgments

This research was supported by the Arkansas Water Resources Center, the U.S. Geological Survey State Water Resources Research Institute Program, and the U.S. Department of Agriculture – Agricultural Research Service. The authors would like to thank Theo Dillaha, Tess Wynn, and Laura Thorne for providing valuable comments on an earlier version of this article. This article also benefited from technical reviews provided by several anonymous reviewers. This work would not have been completed without field support from Ray Avery, laboratory support from Stephanie Williamson and GIS support from Chad Cooper.

REFERENCES

APHA, 1998. Standard Methods for Examining Water and Wastewater, 18th ed. American Public Health Association, Washington, DC.

Brown, A.V., Matthews, W.J., 1995. Stream of the Central United States. In: Cushing, C.E., Minshall, G.W. (Eds.), River and Stream Ecosystems. Elsevier Press, Amsterdam, The Netherlands, pp. 89–116.

Brussock, P.P., Brown, A.V., Dixon, J.C., 1985. Channel form and stream ecosystem models. Water Resour. Bull. 21, 859–866.

Dorioz, J.M., Cassell, E.A., Orand, A., Eisenman, K.G., 1998. Phosphorus storage, transport and export dynamics in the Foron River watershed. Hydrol. Process. 12, 285–309.

Erickson, A.L., Williamson, S.M., Haggard, B.E., 2004. Method analysis of laboratory measures of stream sediment and water phosphorus equilibrium. Discov. Undergraduate Res. J. 5, 10–15.

Fisher, M.M., Reddy, K.R., 2001. Phosphorus flux from wetland soils affected by long-term nutrient loading. J. Environ. Qual. 30, 261–271.

Fox, I., Malati, M.A., Perry, R., 1989. The adsorption and release of phosphate from sediments of a river receiving sewage effluent. Water Res. 23, 725–732.

Froelich, P.N., 1988. Kinetic control of dissolved phosphate in natural rivers and estuaries: a primer on the phosphate buffer mechanism. Limnol. Oceanogr. 33, 649–668.

Gore, J.A., 1996. Discharge measurements and streamflow analysis. In: Hauer, F.R., Lamberti, G.A. (Eds.), Methods in Stream Ecology. Academic Press, San Diego, CA, USA, pp. 53–74.

Green, W.R., Haggard, B.E., 2001. Phosphorus and Nitrogen Concentrations and Loads at Illinois River South of Siloam Springs, Arkansas, 1997–1999. U.S. Geological Survey Water-Resources Investigations Report. 01-4217.

Haggard, B.E., Stanley, E.H., Hyler, R., 1999. Sediment-phosphorus relationships in three northcentral Oklahoma streams. Trans. Am. Soc. Agric. Eng. 42, 1709–1714.

Haggard, B.E., Storm, D.E., Stanley, E.H., 2001. Effect of a point source input on stream nutrient retention. J. Am. Water Resourc. Assoc. 37, 1291–1299.

Haggard, B.E., Ekka, S.A., Matlock, M.D., Chaubey, I., 2004. Phosphate equilibrium between stream sediments and water: potential effect of chemical amendments. Trans. Am. Soc. Agric. Eng. 47, 1113–1118.

Haggard, B.E., Stanley, E.H., Storm, D.E., 2005. Nutrient retention in a point-source enriched stream. J. North Am. Benthol. Soc. 24, 29–47.

Hill, A.R., 1982. Phosphorus and major cation mass balances for two rivers during low summer flows. Freshwater Biol. 12, 293–304.

Hirsh, R.M., Alexander, R.B., Smith, R.A., 1991. Selection of methods for the detection and estimation of trends in water quality. Water Resourc. Res. 27, 803–813.

House, W.A., Denison, F.H., 1997. Nutrient dynamics in a lowland stream impacted by sewage effluent: great Ouse, England. Sci. Total Environ. 205, 25–49.

House, W.A., Denison, F.H., 1998. Phosphorus dynamics in a lowland river. Water Res. 32, 1819–1830.

House, W.A., Denison, F.H., Armitage, P.D., 1995. Comparison of the uptake of inorganic phosphorus to suspended and bed sediments. Water Res. 29, 767–779.

House, W.A., Warwick, M.S., 1999. Interactions of phosphorus with sediments in the River Swale, Yorkshire, UK. Hydrol. Process. 13, 1103–1115.

Khoshmanesh, A., Hart, B.T., Duncan, A., Becket, R., 1999. Biotic uptake and release of phosphorus by a wetland sediment. Environ. Technol. 29, 85–91.

Klotz, R.L., 1985. Factors controlling phosphorus limitation in stream sediments. Limnol. Oceanogr. 30, 543–553.

Klotz, R.L., 1988. Sediment control of soluble reactive phosphorus in Hoxie Gorge Creek, New York. Can. J. Fish. Aquat. Sci. 45, 2026–2034.

Martí, E., Autmatell, J., Godé, L., Poch, M., Sabater, F., 2004. Nutrient retention efficiency in streams receiving inputs from wastewater treatment plants. J. Environ. Qual. 33, 285–293.

McDowell, R.W., Sharpley, A.N., Chalmers, T.A., 2002. Land use and flow regime effects on phosphorus chemical dynamics in the fluvial sediment of the Winooski River, Vermont. Ecol. Eng. 18, 477–487.

Meyer, J.L., 1979. The role of sediments and bryophytes in phosphorus dynamics in a headwater stream ecosystem. Limnol. Oceanogr. 24, 365–375.
Novak, J.M., Stone, K.C., Szogi, A.A., Watts, D.W., Johnson, M.H., 2004. Dissolved phosphorus retention and release from a coastal plain in-stream wetland. J. Environ. Qual. 33, 394–401.
OWRB, 2002. Water Quality Standards. Oklahoma Water Resources Board, Oklahoma City, OK, USA, http://www.owrb.state.ok.us/.
Popova, Y.A., Keyworth, V.G., Haggard, B.E., Storm, D.E., Lynch, R.A., Payton, M.E., 2006. Stream nutrient limitation and sediment interactions in the Eucha – Spavinaw Basin, USA. J. Soil Water Cons. 61, 105–115.
Ruttenburg, K.C., 1992. Development of a sequential extraction method for different forms of phosphorus in marine sediments. Limnol. Oceanogr. 37, 1460–1482.
Rydin, E., Welch, E.B., 1999. Dosing alum to Wisconsin lake sediments based on possible in vitro formulation of aluminum - bound phosphate. Lake Reserv. Manage 15, 324–331.
Schulz, M., Herzog, C., 2004. The influence of sorption processes on the phosphorus mass balance in a eutrophic German lowland river. Water Air Soil Pollut. 155, 291–301.
Smith, D.R., Haggard, B.E., Warnemuende, E.A., Haung, C., 2005. Sediment phosphorus dynamics for three tile fed drainage ditches in Northeast Indiana. Agri. Water Manage 71, 19–32.
Srivastava, S.C., 1998. Microbial contribution to extractable N and P after air-drying of tropical soils. Biol. Fert. Soils 26, 31–34.
Svendsen, L.M., Kronvang, B., Kristensen, P., Græsbøl, P., 1995. Dynamics of phosphorus compounds in a lowland river system: importance of retention and non-point sources. Hydrol. Process. 9, 119–142.
Taylor, A.W., Kunishi, H.M., 1971. Phosphate equilibria on stream sediment and soil in a watershed draining an agricultural region. J. Agri. Food Chem. 19, 827–831.
Welch, E.B., Schrieve, G.D., 1994. Alum treatment effectiveness and longevity in shallow lakes. Hydrobiologia 275/276, 423–431.