Long-term changes in sediment phosphorus below a rural effluent discharge

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Abstract

Effluent discharge often increases the amount of phosphorus (P) in the water column and bed material of receiving water bodies. The goal of this study was to evaluate changes in sediment-P interactions in an effluent-driven stream over a 4-year period where hydrology and watershed P management changed dramatically. Specifically, this study evaluated (i) the equilibrium between benthic sediments and stream water dissolved P; and (ii) the amounts of select P fractions in the bed material within the fluvial channel. Sediment and water samples were collected at Columbia Hollow in northwest Arkansas from October 2003 through September 2007, and the sampling site was approximately 3 km downstream from the Decatur wastewater treatment plant (WWTP). Monthly average effluent total P (TP) concentrations were highly variable (0.30–4.80 mg L$^{-1}$) from October 2003 until December 2005; however, the Decatur WWTP implemented new P management strategies in 2006 that reduced the variability in effluent TP (0.28–0.95 mg L$^{-1}$). Soluble reactive P (SRP) concentrations at Columbia Hollow 3 km downstream from the effluent discharge followed the same pattern; these concentrations were positively correlated to the effluent TP ($r=0.73$; $p<0.001$). Sediment equilibrium concentrations (EPC$_0$) were significantly less (ln transformed data, $p<0.001$) after the WWTP effluent reduced TP concentrations, and sediment EPC$_0$ suggested that the stream bed material acted as a P source to the overlying water at Columbia Hollow. The effects of this effluent discharge and the WWTP management changes on sediment P dynamics were profound. Prior to implementation of WWTP P management, the effluent TP concentrations were the driving factor related to SRP concentrations in the water column and sediment EPC$_0$. Conversely, after the P management changes the benthic sediments became the important factor likely regulating dissolved P concentrations in the stream water.
1 Introduction

Effluent discharge contributes significant amounts of phosphorus (P) to receiving aquatic ecosystems (Foy et al., 1995; Beklioglu et al., 1999; Marti et al., 2004; Demars et al., 2005). Wastewater treatment plant (WWTP) effluent discharge increases not only the amount of P in the water column (Neal, 2001; Haggard et al., 2005; Ekka et al., 2006), but also in the sediments (Jarvie et al., 2005, 2008; Popova et al., 2006). Effluent P inputs profoundly decrease the ability of sediments within the fluvial channel to buffer the transport of P from other watershed sources (Dorioz et al., 1998; House and Denison, 1998; Haggard et al., 2001). When reductions in effluent P concentrations have been implemented, relatively rapid reductions in P concentrations have been observed in the water column of streams (Ekka et al., 2006) and even lakes (Beklioglu et al., 1999; Phillips et al., 2005). However, the eutrophic expression of aquatic ecosystems to effluent P reductions maybe delayed because the sediments may become an internal P source (Novak et al., 2004; Haggard et al., 2005; Ekka et al., 2006). For example, the recovery from elevated P inputs into a well-flushed lake (i.e., ∼16 day hydraulic retention time) in England took over 15 yrs (Phillips et al., 2005).

In effluent-driven streams, benthic sediments typically act as temporary P storage zones (Haggard et al., 2001), representing both a short- and long-term source of bioavailable P (Reddy et al., 1999). The ability of sediments to adsorb dissolved P from the aqueous solution is influenced by many abiotic and biotic factors, such as sediment particle size (Meyer, 1979; McDowell et al., 2002), Al and Fe mineral content (Fox, 1989; Klotz, 1988), and sediment-associated microbes (Gächter et al., 1988; Haggard et al., 1999). Many studies (e.g., Taylor and Kunishi, 1971; Meyer, 1979) have suggested that benthic sediments can regulate dissolved P concentrations in the water column at or near the sediment equilibrium P concentration (EPC₀; Froelich, 1988). Thus, benthic sediments have the unique characteristic of being both a potential sink of dissolved P in streams as well as a potential source. For example, sediments act as a P sink when dissolved P concentrations exceed sediment EPC₀ and act as a
source when dissolved P concentrations are less than sediment EPC₀ (Taylor and Kunishi, 1971; Meyer, 1979; Jarvie et al., 2005; Novak et al., 2004). Therefore, the result of new P management strategies at a WWTP effluent discharge might shift the sediments from acting primarily as a P sink to a source of dissolved P to the overlying stream water (e.g., Ekka et al., 2006). The benthic sediments within the fluvial channel become an internal P source that must be considered within the watershed.

The overall objective of the study was to evaluate changes in sediment-P interactions in an effluent-driven stream over a 4-year period where hydrology and watershed P management changed dramatically. Specifically, this study evaluated (1) the amount of select P fractions (e.g., easily exchangeable and Mehlich-3 extractable) in the bed material within the fluvial channel from October 2003 through September 2007, and (2) the equilibrium between benthic sediments and stream water dissolved P concentrations. The effects of the effluent discharge (i.e., prominent watershed P source) on the receiving stream and further downstream aquatic ecosystem were evaluated.

2 Material and methods

2.1 Study site description

Stream bed material and water samples were collected on an approximate monthly basis at Columbia Hollow approximately 3.0 km downstream from the effluent discharge near Decatur, Arkansas, USA from October 2003 through September 2007 (Fig. 1). Columbia Hollow, also known as Decatur Branch, is a 3rd order Ozark stream within the Eucha-Spavinaw Basin which extends from northwest Arkansas to northeast Oklahoma. The topography of the study region include hill top pastures, steep terrain and flat flood plains with underlying karst geology, and the fluvial channels are chert-gravel beds.

The Decatur WWTP effluent discharge is released into Columbia Hollow, which empties into Spavinaw Creek, a tributary stream to Lake Eucha and eventually Lake
Spavinaw. The Decatur municipal WWTP receives wastewater from a population of approximately 1600 people based on a 2006 census and a poultry processing plant. The facility treats wastewater using secondary treatment, and a lawsuit settled in 2003 required the effluent discharge to meet a monthly average of 1 mg L\(^{-1}\) (US District Court Case No. 01-CV-0900-EA(C)). The management change made by the Decatur WWTP to meet the effluent limits was through the use of alum to flocculate particulates and adsorb dissolved P (personal communication, James Boston, City of Decatur, Arkansas, USA). Average monthly effluent TP concentration data was available from the Arkansas Department of Environmental Quality (http://www.adeq.state.ar.us/home/pdssql/pds.asp). The WWTP effluent discharge is a large contributor to stream flow and supports up to, but often less than, 83% of the seasonal base flow at Columbia Hollow (Haggard et al., 2005). The Decatur WWTP contributes approximately 23% of TP load to Lake Eucha (Storm et al., 2002) and has increased water column SRP concentrations and P content of sediments in Columbia Hollow and Spavinaw Creek (Haggard et al., 2001; Popova et al., 2006). Historically, the effluent discharge has also reduced P retention (Haggard et al., 2005) and decreased sediment P buffer capacity within the fluvial channel (Popova et al., 2006).

2.2 Sediment collection and extractions

Sediments were collected in 3.78 L plastic bags from the top 5 cm of stream bed along three transects perpendicular to stream flow using a shovel, and placed into a cooler until return to laboratory. At each transect, approximately 1 L of stream water was collected and placed into a cooler. Upon return to laboratory, sediments were sieved (4.5 mm) and <4.5 mm sediments were retained for further analysis. Approximately 25 g of retained fresh wet sediments were added to 250-mL Erlenmeyer flasks containing 100-mL filtered stream water spiked with an additional 0.0, 0.5, 1.0, 2.0, and 5.0 mg P L\(^{-1}\). All flasks were shaken at low speed (60 oscillations per min) for 1 h and allowed to settle for approximately 20 min. A 20-mL aliquot from each flask was filtered through a 0.45-µm membrane and acidified to pH<2 using concentrated HCl. The remaining
material in each flask was transferred to pre-weighed Al pans which were oven-dried for 48 h at approximately 80°C in order to determine sediment dry weight. Soluble reactive P (SRP) concentrations were determined colorimetrically using the ascorbic acid method (APHA, 1995) on a Skalar San Plus Wet Chemistry Auto Analyzer (Skalar, the Netherlands). Equilibrium P concentration (EPC₀) is the concentration at which P is neither desorbed nor adsorbed by the sediments (Taylor and Kunishi, 1971), and was determined by plotting the amount of P sorbed (mg kg⁻¹ dry sediments) against the final SRP concentration (mg L⁻¹) where the x-intercept represents the EPC₀ (Fig. 2). Benthic sediments and the aqueous solution were assumed to be in equilibrium when stream water SRP was within ±20% of sediment EPC₀ (based on Jarvie et al., 2005).

Sediment exchangeable P (EXP) was extracted using 100 mL of a 1.0 M MgCl₂ solution and approximately 25 g wet sediments. The sediment slurry was shaken for 1 h, and SRP in the aqueous solution was measured as previously described. The dry weight of sediments in the extraction was determined by transferring the sediment slurry to a pre-weighed Al pan and dried at approximately 80°C.

Oven-dried sediments were sieved at 2.8 mm, and then 2.5 g of material were extracted with 25 mL of 0.2 N CH₃COOH, 0.001 M EDTA, 0.013 N HNO₃, 0.015 N NH₄F, and 0.25 N NH₄NO₃ for 5 min (Mehlich, 1984), centrifuged for 5 min (4000 rpm), and then filtered (Whatman No. 42 filter paper). The filtrate was analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES) for multiple elements. Mehlich-3 (M3) extractable P, Al, and Fe were used to determine P saturation ratios (PSR) on stream sediments and PSR was determined on a molar basis using Eq. (1) (Sims et al., 2002).

\[
PSR = \frac{M3P}{(M3Al + M3Fe)}
\]  

Daily discharge data were not available at Columbia Hollow, so continuous discharge was determined using the United States Geological Survey (USGS) discharge monitoring data from locations at Spavinaw Creek upstream (USGS site number 07191160, Spavinaw Creek near Maysville, Arkansas) and downstream (USGS site number 07191160).
site number 07191179, Spavinaw Creek near Cherokee, Arkansas) of its confluence with Columbia Hollow. These two locations were used to estimate Columbia Hollow discharge since Columbia Hollow is the only tributary on Spavinaw Creek between these two discharge monitoring stations.

2.3 Statistics

Geometric means were used to represent the data from the three transects sampled each month in order to minimize the influence of extreme values on the temporal data set. Linear regression and Pearson correlation analyses were performed on the data to evaluate the relations between experimental parameters using a significance level of 0.05 (Microsoft Excel, 2003). Data parameters met the normal distribution assumption using the natural logarithm (ln) transformation, and then a t-test of the ln-transformed data was used to determined differences between effluent total P, SRP, sediment EPC₀, sediment EXP, and M3P prior to and after January 2006.

3 Results

Average monthly effluent TP concentrations at the Decatur WWTP were highly variable (0.30–4.80 mg L⁻¹) prior to 2006 when this WWTP started operating with P management strategies (Fig. 3a). Following this change in WWTP management, effluent TP concentrations were less variable (0.28–0.95 mg L⁻¹). Average monthly effluent TP concentrations were significantly greater prior to 2006 (ln transformed data, t-test with unequal variance, p<0.001) having an average of 2 mg L⁻¹, which was four times greater than the average effluent TP concentration (0.46 mg L⁻¹) after WWTP management changes.

Effluent TP concentrations were positively correlated (r=0.73, p<0.001) to SRP concentrations in the water column approximately 3 km downstream from the point source (Fig. 4). Stream water SRP concentrations at Columbia Hollow followed similar tem-
poral patterns to that observed with the effluent TP concentrations (Fig. 3b), where SRP concentrations were highly variable (0.24–2.14 mg L\(^{-1}\)) prior to 2006 and less variable (0.16–0.87 mg L\(^{-1}\)) thereafter. Stream water SRP was significantly greater prior to 2006 (In transformed data, t-test with unequal variances, \(p<0.001\)) with an average of 0.97 mg L\(^{-1}\) and was two fold greater than average SRP (0.50 mg L\(^{-1}\)) after WWTP management changed. Stream water SRP concentrations increased as effluent TP concentrations increased \((r^2=0.39, p=0.001)\) prior to 2006. Conversely, after the WWTP implemented P management strategies, effluent TP was not related to stream water SRP at the site 3 km downstream. In general, SRP concentrations in the water column typically decreased during the winter (e.g. November to February).

Similar to effluent TP and stream water SRP at Columbia Hollow, sediment EPC\(_0\) at the study site approximately 3 km downstream from the point source was highly variable (0.34–2.61 mg L\(^{-1}\)) prior to 2006 and less variable (0.40–1.58 mg L\(^{-1}\)) through the end of the study period (Fig. 5a). Average sediment EPC\(_0\) showed the same magnitude of decrease before (1.51 mg L\(^{-1}\)) and after (0.80 mg L\(^{-1}\)) the WWTP management changes that average SRP concentrations in the stream water did (In transformed data, t-test, \(p<0.001\)). Overall, sediment EPC\(_0\) compared to stream water SRP concentrations suggested that the bed material within the fluvial channel was a source of dissolved P to the water column at Columbia Hollow; the sediments were a likely P source on approximately 75% of the sampling dates (Fig. 6). There was a significant linear relation between sediment EPC\(_0\) and SRP concentrations in the water column both prior to 2006 \((r^2=0.31, \text{SRP}=0.44\times\text{EPC}_0+0.30, p=0.004)\) and after WWTP management changes \((r^2=0.73, \text{SRP}=0.56\times\text{EPC}_0+0.05, p<0.001)\). However, the relation between sediment EPC\(_0\) and stream water SRP was much stronger from 2006 through the end of the sampling period. Sediment EPC\(_0\) and dissolved P in the water column tended to move toward equilibrium from June through October during this study (Fig. 7), as indicated from the linear regression of the data \((r^2=0.84, \text{SRP}=0.84\times\text{EPC}_0-0.07, p<0.001)\) where the slope was much closer to one. Sediment EPC\(_0\) also shifted in relation to large discharge events in between sampling dates, where discharge increased
more than six fold at any time between successive sampling dates. Following these
 discharge events, sediment EPC$_0$ decreased approximately 75% of the time.

Sediment EXP showed the same long-term trends that the other parameters did, be-
cause sediment EXP was positively correlated to sediment EPC$_0$ ($r=0.74$, $p<0.001$),
stream water SRP ($r=0.74$, $p<0.001$), and effluent TP ($r=0.44$, $p=0.003$). These cor-
relations with sediment EPC$_0$ and water column SRP existed before and after P man-
agement changes at the Decatur WWTP. Exchangeable P in the sediments decreased
in content and variability once WWTP P management strategies were implemented
(Fig. 5b). The amount of exchangeable P in the benthic sediments showed some sea-
sonal variation where EXP was generally greater from May to August and less from
October to February.

Mehlich-3 extractable P content of benthic sediments followed a similar trend
($r=0.63$, $p=0.011$) as sediment EXP prior to the management changes at the WWTP.
However, after P management strategies were implemented, EXP and M3P contents
were not correlated. Mehlich-3 P contents of benthic sediments in Columbia Hollow
throughout the study ranged from 44.3 to 250 mg kg$^{-1}$ and tended to increase, espe-
cially after the occurrence of episodic large discharge events relatively ceased (Fig. 5c).
The M3P contents of the benthic sediments showed a sharp decrease from June
2007 (220 mg kg$^{-1}$) to July 2007 (89.0 mg kg$^{-1}$), and M3P increased to 141 mg kg$^{-1}$
in September 2007. Phosphorus saturation ratios based on M3 extractable P, Al, and
Fe followed the same pattern as M3P, where PSRs generally increased throughout the
study until June 2007 when a noticeable decrease occurred; sediment PSRs ranged
from 0.20 to 0.53 (Fig. 5d).

4 Discussion

Soluble reactive P concentrations at Columbia Hollow upstream of the effluent dis-
charge from October 2003 through September 2007 had a geometric mean of
0.11 mg L$^{-1}$ (unpublished data, BE Haggard), whereas SRP concentrations down-
stream from the WWTP were an order of magnitude greater on average. Many studies have shown effluent discharge increases dissolved P concentrations in the receiving water column (Neal, 2001; Marti et al., 2004; Haggard et al., 2005; Ekka et al., 2006). In our study, the Decatur WWTP not only significantly increases dissolved P in the water column at Columbia Hollow (Haggard et al., 2005; Popova et al., 2006), but also that observed in Spavinaw Creek approximately 9 km downstream from the WWTP (Haggard et al., 2001; Tortorelli, 2006). Dissolved and total P concentrations at Spavinaw Creek were approximately eight times greater downstream from the Columbia Hollow inflow compared to upstream concentrations (Fig. 8). The elevated P concentrations persisted tens of km downstream from the Spavinaw Creek and Columbia Hollow confluence (Tortorelli, 2006). Haggard et al. (2001) showed that dissolved P traveled 10 to 30 km downstream at Spavinaw Creek before net uptake occurred within the fluvial channel. The Decatur WWTP has far reaching impacts on P concentrations within the Eucha-Spavinaw watershed, and it will be interesting to see how downstream stream water P concentrations change in the future following these WWTP management changes.

The Decatur municipal WWTP began treating the wastewater with alum (aluminum sulfate) in November 2005, and plant operators took several months (i.e., until January 2006) to determine the proper amount of alum needed to effectively reduce effluent TP concentrations (personal communication, James Boston, City of Decatur, Arkansas, USA). Alum is commonly used to remove P during the treatment of wastewater. The addition of alum at the Decatur WWTP decreased the concentration and variability of effluent P discharge, which resulted in subsequent reductions in both dissolved P concentrations in the water column and exchangeable P within the benthic sediments at Columbia Hollow. Several studies have observed reductions in P concentrations at aquatic systems in response to WWTP management changes (Beklioglu et al., 1999; Phillips et al., 2005; Ekka et al., 2006). However, it could take decades for P concentrations to reduce to background concentrations because of the legacy P stored within the fluvial channel (Novak et al., 2004; Haggard et al., 2005; Phillips et al., 2005).
Many studies (e.g. Dorioz et al., 1998; House and Denison, 1998; Jarvie et al., 2005) have shown benthic sediments are typically a P sink in streams receiving effluent discharge. However, bottom sediments within the fluvial channel of Columbia Hollow were a potential P source to the overlying water column on approximately 75% of the sampling dates. The benthic sediments at Columbia Hollow likely continued to be a P source due to the lack of large storm events after 2005 capable of scouring bottom sediments downstream and providing fresh sediments to adsorb additional P from the water column (House and Denison, 1998; Jarvie et al., 2005). The Columbia Hollow catchment experienced few large storm events from 2006 through the end of the study, but when large storms occurred between successive sampling dates, sediment EPC often decreased.

Stream-bottom sediments and dissolved P in the water column tended to move toward P equilibrium during warmer months when seasonal base flow was lowest. The increased interaction time between the stream water and sediments might allow for the aqueous and solid phase to approach P equilibrium (Meyer and Likens, 1979). Biological activity at Columbia Hollow also likely increased during these periods, and Lottig and Stanley (2007) showed biological processes were important in regulating P equilibrium between the aqueous solution and coarse sediments. Numerous studies have shown microorganisms increase the ability of benthic sediments to adsorb P, where microbial uptake accounted for 23 to 43% of total P sorption (Klotz, 1985; Haggard et al., 1999; McDowell and Sharpley, 2003).

Phosphorus can be adsorbed to sediments in many forms including those that are easily exchangeable (e.g., EXP) and plant available (e.g., M3P). The amount of easily exchangeable P in the bottom sediments within the fluvial channel dramatically decreased after WWTP management changes. However, M3P contents in the benthic sediments continued to increase at Columbia Hollow, even after the WWTP started using alum to reduce effluent P inputs. This observation might suggest that sediments continually exposed to the effluent P sources can integrate dissolved P from the water column into less available forms (e.g., M3P) within the solid phase. Thus, these sedi-
ments at Columbia Hollow may be a potential long-term source of P to aquatic systems further downstream.

Sediment M3P contents at Columbia Hollow (44.3 to 250 mg kg\(^{-1}\)) were generally greater than contents observed in soils considered optimal for agricultural production (50 mg kg\(^{-1}\); Maguire and Sims, 2002) and were several orders of magnitude greater than M3P contents in USA streams that do not receive effluent discharge (3–39 mg kg\(^{-1}\); Haggard et al., 2007; McDowell and Sharpley, 2003). The M3P contents in Columbia Hollow sediments often exceeded the threshold (i.e., 300 mg kg\(^{-1}\)) that limits poultry litter application to pastures within the Eucha-Spavinaw Basin (DeLaune et al., 2006). The Decatur WWTP input not only increased the amount of various P fractions in the sediments of Columbia Hollow, the WWTP also increased the degree with which these sediments were saturated compared to other USA streams (e.g., see Haggard et al., 2007). The P saturation ratios (PSR) in sediments of Columbia Hollow were well-above so called environmental thresholds in USA soils (0.11 to 0.15; Sims et al., 2002).

The Decatur WWTP effluent discharge had profound impacts on this stream (i.e., Columbia Hollow) and the Eucha-Spavinaw Basin. Prior to 2006, effluent P was the important factor increasing P concentrations in the water and sediments from Columbia Hollow downstream through Spavinaw Creek (Haggard et al., 2001). The effluent was strongly correlated \((r=0.62, p=0.001)\) to SRP concentrations in the stream water approximately 3 km downstream from the point source, and stream water SRP was positively correlated to sediment EPC\(_{0}\) \((r=0.56, p=0.004)\). However, after the Decatur WWTP P management strategies were implemented a paradigm shift occurred. The effluent discharge was no longer correlated to stream water SRP, and the benthic sediments then became an important factor regulating stream water P \((r=0.86, p<0.001)\) approximately 3 km downstream from the effluent discharge.

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References


Changes in stream phosphorus below an effluent discharge

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Fig. 1. Sample site was located approximately 3 km downstream of the City of Decatur wastewater treatment plant effluent discharge in the Columbia Hollow catchment in northwest Arkansas, USA.
Fig. 2. Relation between phosphorus (P) sorbed (mg kg\(^{-1}\)) by the sediments as a function of the final soluble reactive P (SRP) concentration (mg L\(^{-1}\)) in the aqueous solution; the point where the linear regression crossed the x-axis was used to determine sediment equilibrium P concentration (EPC\(_0\)) in this study.
Fig. 3. Average monthly effluent total phosphorus (TP) concentrations (mg L\(^{-1}\)) from the wastewater treatment plant (WWTP) at Decatur, Arkansas, USA (A), and soluble reactive P (SRP) concentrations (mg L\(^{-1}\)) (B) at Columbia Hollow approximately 3 km downstream from the effluent discharge from October 2003 through September 2007; the solid line represents estimated discharge (m\(^3\) s\(^{-1}\)) from the Columbia Hollow catchment into Spavinaw Creek, and the dotted line represents when WWTP management changed.
Fig. 4. Relation between average monthly effluent total phosphorus (TP) concentrations (mg L\(^{-1}\)) at the wastewater treatment plant at Decatur, Arkansas, USA and stream water soluble reactive P (SRP) concentrations (mg L\(^{-1}\)) at Columbia Hollow approximately 3 km downstream from the effluent discharge.
Fig. 5. Sediment equilibrium phosphorus concentration (EPC_0; mg L\(^{-1}\)) at Decatur, Arkansas, USA (A); soluble reactive P (SRP) concentrations (mg L\(^{-1}\)) (B); sediment Mehlich-3 P (M3P) content (mg kg\(^{-1}\)) (C); and P saturation ratios in sediments (D) at Columbia Hollow approximately 3 km downstream from the effluent discharge from October 2003 through September 2007; the solid line represents estimated discharge (m\(^3\) s\(^{-1}\)) from the Columbia Hollow catchment into Spavinaw Creek, and the dotted line represents when WWTP management changed.
Fig. 6. Relation between sediment equilibrium phosphorus concentration (EPC$_0$; mg L$^{-1}$) and stream water soluble reactive P (SRP) concentration (mg L$^{-1}$) approximately 3 km downstream of Decatur, Arkansas, USA wastewater treatment plant. Solid diagonal line represents 1:1 relationship where points above represent when sediments are adsorbing P from the water column and points below represent when sediments are releasing P to the water column. The diagonal dotted line above and below the solid line represent ±20% of sediment EPC$_0$ and range when sediments are in equilibrium with the water column with respect to P (Jarvie et al., 2005).
Fig. 7. Relation between the difference of stream water soluble reactive phosphorus (SRP) concentrations (mg L\(^{-1}\)) and sediment equilibrium P concentration (EPC\(_0\); mg L\(^{-1}\)) and discharge (m\(^3\) s\(^{-1}\)) from October 2003 through September 2007; the solid line represents estimated discharge (m\(^3\) s\(^{-1}\)) from the Columbia Hollow catchment into Spavinaw Creek.
**Fig. 8.** Box plots of total phosphorus concentrations (mg L\(^{-1}\)) at Spavinaw Creek during base flow conditions from October 2003 through December 2005 (top) and January 2006 through September 2007 (bottom) in the Eucha-Spavinaw watershed, Arkansas and Oklahoma, USA; distance represents river km upstream (negative values) or downstream (positive values) from the Spavinaw Creek and Columbia Hollow confluence. Box plots with different letters represent significant differences between sample sites (ln transformed data, ANOVA LSD, \(p<0.05\)) and asterisks represent significant differences before and after P management changes at the Decatur, AR wastewater treatment plant (ln transformed data, ANOVA LSD, \(p<0.05\)) (data from Tortorelli, 2006).