

# Stream Discharge and Riparian Land Use Influence In-Stream Concentrations and Loads of Phosphorus from Central Plains Watersheds

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**Abstract** Total annual nutrient loads are a function of both watershed characteristics and the magnitude of nutrient mobilizing events. We investigated linkages among land cover, discharge and total phosphorus (TP) concentrations, and loads in 25 Kansas streams. Stream monitoring locations were selected from the Kansas Department of Health and Environment stream chemistry long-term monitoring network sites at or near U.S. Geological Survey stream gauges. We linked each sample with concurrent discharge data to improve our ability to estimate TP concentrations and loads across the full range of possible flow conditions. Median TP concentration was strongly linked ( $R^2 = 76\%$ ) to the presence of cropland in the riparian zones of the mostly perennial streams. At baseflow, discharge data did not improve prediction of TP, but at high flows discharge was strongly linked to concentration (a threshold response occurred). Our data suggest that on average 88% of the total load occurred during the 10% of the time with the greatest discharge. Modeled reductions in peak discharges, representing increased hydrologic retention, predicted greater decreases in total annual loads than reductions of ambient concentrations because high discharge and elevated phosphorus concentrations had multiplicative effects. No measure of land use provided significant predictive power for

concentrations when discharge was elevated or for concentration rise rates under increasing discharge. These results suggest that reductions of baseflow concentrations of TP in streams without wastewater dischargers may be managed by reductions of cropland uses in the riparian corridor. Additional measures may be needed to manage TP annual loads, due to the large percentage of the TP load occurring during a few high-flow events each year.

**Keywords** Total phosphorus · Discharge · Riparian zones · Watershed management · Perennial streams

Eutrophication of freshwater ecosystems is a key environmental concern worldwide (Smith 2003; Smith and others 2006). Protecting biological integrity requires control of in-stream concentrations, but protecting downstream systems requires characterization and control of loading rates (Dodds 2006). Understanding mechanisms of nutrient mobilization and transport is critical for effective management. Nutrient mobilization has greatly increased over natural rates and global anthropogenic mobilization of phosphorus now exceeds three times the natural mobilization rate (Smil 2000). Point source discharges of nutrients have been targeted by regulatory agencies for improvements in treatment technology to reduce loadings from these sources of nutrients in many developed countries. However, in the United States many surface waters remain impaired by nutrients (US EPA 2007), much of which may be attributed to nonpoint source loadings (Dodds 2002).

The relationship between land use variables and observed stream water concentrations of nutrients and

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major ions has been documented (e.g., Jones and others 2001; Sponseller and others 2001; Dodds and Oakes 2006; Dow and others 2006; Sonoda and Yeakley 2007). These studies generally predict average concentrations of nitrogen or phosphorus over seasons or years as a function of land cover and land use (Dodds and Oakes 2006, 2008). Nitrogen concentrations have correlated more closely with land use than phosphorus (Dodds and Oakes 2006). Nitrogen has a substantial dissolved component and loadings may be more related to baseflow conditions and groundwater sources (Hill 1996).

Sharpley and others (2008) have established that phosphorus loadings occur primarily as a function of runoff conditions, because phosphorus is associated with sediments and enters surface waters primarily when particles are moved into streams, rivers, lakes, and ponds (Royer and others 2006). In nonpoint influenced watersheds phosphorus has a complex relationship with stream sediment (Reddy and others 1999) and stream sediment has a complex relationship with discharge (Porterfield 1972). The difference in sources of nitrogen and phosphorus has led some to speculate that the weaker relationships between land use and phosphorus are an artifact of sampling procedures that miss large runoff events which would be expected to have higher phosphorus concentrations (Dodds and Oakes 2006). Tile drains have also been implicated in phosphorus losses from agricultural watersheds in the upper Midwest United States (Gentry and others 2007) but are not common in our region so are not considered in this paper.

Because of the high cost of obtaining regular monitoring data, especially discharge data, we wanted to know how gauge data can improve estimates of typical concentrations and loads of total phosphorus (TP) in streams. If concentrations can be strongly correlated with land use variables without gauge data, management decisions can be based on results from a representative set of grab samples. If, however, gauge data provide a strong predictive power across a range of flow conditions, then grab samples alone may be insufficient to identify potential responses to management actions.

Effective management of total loads of phosphorus to surface waters requires an understanding of how concentrations change over naturally variable flow conditions in lotic systems. Gauge data can also prove useful for characterizing these TP loads, by providing the needed volume estimate to calculate total mass from concentration measurements. If large exports of phosphorus occur in high-discharge events, these short duration conditions can contribute greatly to long-term nutrient loading.

Water resource managers need to know what factors are associated with observed concentrations and loads and what steps may be taken to mitigate the impact of TP

loading (Litke 1999). Understanding the effects of discharge on phosphorus transport across a range of flow conditions is particularly important for protecting downstream waters. Appropriate management strategies for control of phosphorus loading require more information. If phosphorus concentration and load differ between high-flow and baseflow conditions, management strategies need to be adjusted to influence concentrations during the discharge levels of concern.

Literature on the watershed scale effectiveness of best management practices (BMPs) to mitigate the impact of phosphorus transport during high-flow events is lacking, and some BMPs could be unimportant during high-rainfall/high-runoff events. An understanding of the distribution of total loads across a flow duration curve for a stream may assist in determining which BMPs will be most effective at reducing total loads and which measures will address project specific management objectives. Targeting BMPs also requires an awareness of the linkages between land use and concentrations across the spectrum of flow conditions occurring in a waterbody.

In this study we extracted data from a long-term monitoring dataset maintained by the Kansas Department of Health and Environment (KDHE) for collection points colocated with U.S. Geological Survey (USGS) gauging stations, to determine if differentiation of high and low flow conditions improved our ability to adequately describe phosphorus concentrations across a flow duration curve. We also wanted to determine which, if any, land cover characteristics were most strongly linked to median and high flow concentrations. Regulations in the United States require (Code of Federal Regulations, 130.7) establishment of total maximum daily loads (TMDLs) for impaired waters, so we constructed models of daily load and discharge across the flow duration curve to determine the temporal pattern of annual phosphorus loading and estimate what percentage of annual loading occurs during baseflow and high-flow events.

The potential combined influence of elevated flows and elevated concentrations leads to another important question: What impact does management of ambient conditions have on total loading of these nutrients to the system? Finally, because typical cropland has greater runoff rates than perennial vegetation and Gerla (2007) showed that conversion of cropland to prairie can reduce peak discharge by as much as 55%, we wanted to explore the relative load reduction impacts of increased hydraulic retention compared to concentration reductions during baseflow conditions. We used the models developed to estimate daily loads and subjected them to concentration changes or discharge changes to estimate annual phosphorus loads for scenarios that reflect decreased baseflow concentration or increased hydrologic retention.

## Methods

### Stream Chemistry Data

We used KDHE data from 25 monitoring stations sampled in even months 1 year and odd months the next year so that over 2 years each station is sampled once in every month. Station visits are scheduled 1 year in advance, resulting in an unbiased selection of weather and discharge conditions throughout the year. Water is collected only when streams are flowing. Samples are collected from a bridge in a stainless-steel bucket in the thalweg of the stream, 0–25 cm below the water surface. Subsamples for TP concentration (TP<sub>c</sub>) analysis are immediately collected from the first pour-off into a collection bottle, preserved in a 250-mL bottle with 1 mL of 1.1 molar H<sub>2</sub>SO<sub>4</sub>, and analyzed following persulfate digestion using automated colorimetry (Kansas Department of Health and Environment 2007). Nearly all streams in this study exhibited perennial flow (small first-order headwater streams were not included in this analysis), and all were designated for the support of aquatic and semiaquatic life as listed in the most recently approved Kansas Surface Water Register (Kansas Department of Health and Environment 2004) at the time of our study.

Sites included in our analysis met the following criteria: (1) located within 10 km (with no major intervening tributaries) of a USGS gauging station with at least 30 years of recorded daily mean data, (2) having a stream chemistry data record going back to at least 1990 and up to 2005, (3) watershed completely or nearly completely (>95%) within Kansas, and (4) not downstream of either a major point source discharger or a major federal reservoir. This resulted in the selection of 25 monitoring stations (Table 1, Fig. 1). No watershed included in this analysis had extensive tile drainage.

A parallel analysis of 169 additional unnested sites with complete chemistry but no discharge data was used to extend the results of correlations of median TP<sub>c</sub> with land use. The criteria for the 169 sites were the same as for the original 25 sites except discharge data were mostly not available and some were sampled only six times per year every fourth year. For each site, stream TP<sub>c</sub> data from 1990 to 2005 were extracted from the KDHE database.

### Discharge Data

USGS-approved mean daily discharge ( $\bar{x}Q$ ) data were downloaded from the National Water Information System Web Interface associated with each sample. A characteristic flow duration curve was also developed for each site for modeling purposes, based on the percentile of time a flow was exceeded (%<sub>xc</sub>) between October 1, 1970, and

**Table 1** Site numbers, names, and USGS gauging station numbers with location of sites included in this analysis

Site	River	USGS gauge	Longitude	Latitude
011	Saline River	06867000	-98.815	38.971
036	SF Ninnescah River	07145200	-97.854	37.562
038	Whitewater River	07147070	-97.013	37.796
207	Little Osage River	06917000	-94.704	38.010
217	Caney River	07172000	-96.316	37.004
220	Medicine Lodge River	07149000	-98.470	37.039
239	Soldier Creek	06889500	-95.725	39.100
501	Stranger Creek	06892000	-95.028	39.006
505	Black Vermillion River	06885500	-96.506	39.646
507	Mill Creek (Washington)	06884200	-96.937	39.921
512	Salt Creek	06876700	-97.724	39.103
515	Chapman Creek	06878000	-97.040	39.031
521	Mill Creek (Paxico)	06888500	-96.006	39.090
525	NF Ninnescah River	07144780	-97.936	37.844
529	Chikaskia River	07151500	-97.529	37.080
545	Bow Creek	06871500	-99.323	39.553
546	NF Solomon River	06871000	-99.309	39.674
547	SF Solomon River	06873000	-99.585	39.374
549	Prairie Dog Creek	06847900	-100.077	39.771
565	Lightning Creek	07184000	-95.044	37.237
574	Otter Creek	07167500	-96.224	37.709
577	Dragoon Creek	06911900	-95.779	38.699
586	Pawnee River	07141200	-99.526	38.199
596	Walnut Creek	07141780	-99.567	38.468
600	Crooked Creek	07157500	-100.209	37.031

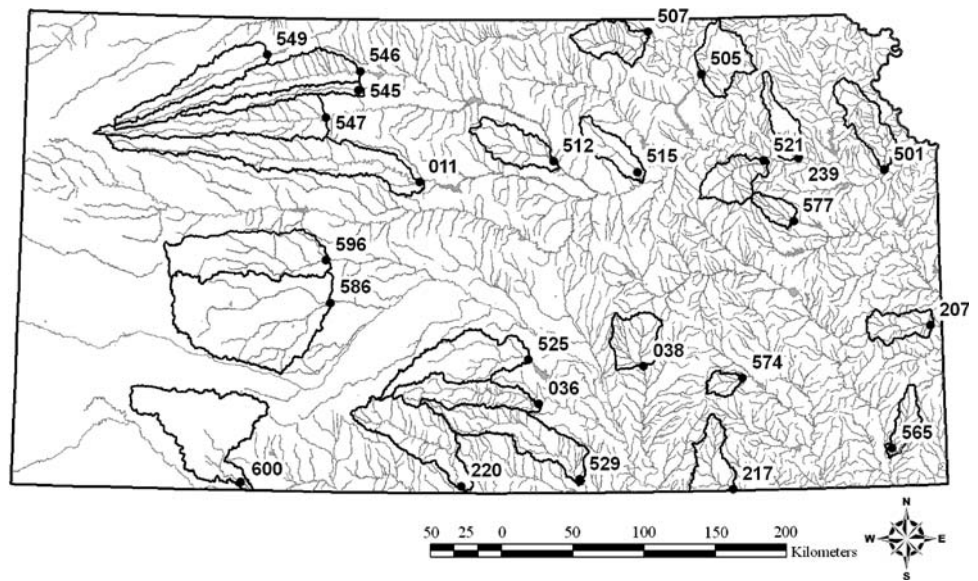
September 30, 2006. The gauge for the Chikaskia River was not online until October 1, 1975, so the flow duration curve was fitted to the 1976–2006 water years.

Our flow exceedance term denotes the percentage of the year that has  $\bar{x}Q$  greater than the value for that day's  $\bar{x}Q$ . This terminology is opposite the typical phrasing of flood probability (100-year flood, etc. [Dunne and Leopold 1978]). For each chemistry data collection event the average daily flow and the percent flow exceedance were derived from the gauge data. Using a percentage exceedance approach allowed comparison of concentration and discharge across streams with widely varying flow duration curves (Table 2).

### Land Use Data

Geospatial data were analyzed using ArcGIS 9.2 with a spatial analyst extension. Geospatial data analyzed included watershed average slope (generated from a 30-m pixel digital elevation map [USGS Seamless 2006]), soil permeability (Natural Resources Conservation Service 2006), whole watershed land cover (National Land Cover Dataset

**Fig. 1** Sampling locations included in this study and attendant watershed boundaries. Gray lines indicate waters included in the Kansas Surface Water Register (2004). Site coordinates are included in Table 1



**Table 2** Mean daily discharge (L/s) at selected points on the flow-duration curve

Site	5%	10%	25%	50%	75%	90%	95%
011	6,247	3,908	1,699	680	227	88	51
036	14,476	9,430	5,918	4,134	3,058	2,152	1,812
038	19,408	7,079	2,407	963	481	232	139
207	27,218	12,290	4,021	1,133	102	11	3
217	37,661	18,859	6,173	1,472	201	20	2
220	12,997	8,184	4,531	2,747	1,727	595	311
239	17,925	7,900	2,888	1,048	425	176	102
501	38,964	14,798	4,587	1,501	425	99	42
505	19,086	7,334	2,407	906	368	176	105
507	11,036	4,630	1,472	566	212	110	71
512	7,221	3,171	906	368	153	62	34
515	8,219	3,681	1,501	736	425	272	207
521	18,621	10,251	4,531	1,501	566	266	156
525	10,919	6,428	3,681	2,265	1,416	736	481
529	22,874	13,167	6,173	3,143	1,699	821	456
545	708	453	275	153	62	6	0
546	1,841	1,218	566	173	0	0	0
547	2,464	1,614	765	178	12	0	0
549	368	278	142	48	2	0	0
565	24,483	8,416	1,642	368	42	1	0
574	8,382	3,766	1,388	311	54	9	2
577	6,088	2,662	878	224	28	0	0
586	2,577	934	198	0	0	0	0
596	1,756	793	311	42	0	0	0
600	1,019	651	396	266	167	82	34

[NLCD], MRLC 2007), land cover along all water features excluding lagoons (Kansas Riparian Areas Inventory-Natural Resources Conservation Service 2001), and land cover

along the Kansas Surface Water Register. Riparian land use adjacent to registered streams was characterized by converting the stream network into a 30-m raster pixel coverage to ensure correction for small errors in stream location and to allow for stream width, then buffered by 30 m on each side, resulting in a 90-m-wide coverage of the length of the stream. The 90-m-wide zone was used to extract land cover data from the 2001 NLCD (MRLC 2007).

### Concentration and Load Modeling

Paired %<sub>xc</sub> and TP<sub>c</sub> data were subjected to a breakpoint regression analysis (segmented regression) with SegRegW (Oosterbaan 2008) to determine if a threshold response existed that justified the use of more than one concentration model across the flow duration curve. The breakpoint analysis tests if the breakpoint model explains significantly more variance than a single line, and if it does not, then the breakpoint is not supported (Oosterbaan and others 1990). Breakpoint regression (Jones and Molitoris 1984) has been used previously to determine ecologically relevant thresholds (Dodds and others 2002; Toms and Lbsperance 2003). The TP<sub>c</sub> data were normalized by log<sub>10</sub> transformation (Helsel and Hirsch 1991) before determination of discharge breakpoints (BpQ) and modeling annual loads. Where BpQ existed, and at least one sloping line was indicated, we determined the relationship between %<sub>xc</sub> and log<sub>10</sub> transformed TP<sub>c</sub>. Statistically significant ( $P < 0.05$ ) regression slopes (BpR) of %<sub>xc</sub> and TP<sub>c</sub> as well as the point of intersection of the regression line with the baseflow median concentration were recorded for further analysis. Statistics were calculated using Minitab version 15.

When significant ( $P < 0.05$ ) discharge/concentration relationships existed we developed models of discharge and TP daily load ( $TP_{dl}$ ) to determine distribution of the total estimated load by flow frequency. These models used the baseflow median concentration (BfM) to model moderate to low flow (ambient) conditions and estimated high-flow concentrations using the regression equations of  $TP_c$  and  $\%_{xc}$  developed in conjunction with the breakpoint analysis.

The modeling procedure can be explained by the following determinations and equations,

$$\text{If } \bar{x}Q < BpQ \rightarrow TP_c = BfM$$

$$\text{If } \bar{x}Q \geq BpQ \rightarrow TP_c = BpR * \%_{xc} + BpI,$$

unless( $BpR * \%_{xc} + BpI$ ) < BfM,  
inwhich case  $TP_c = BfM$

$$TP_{dl}(\text{kg/day}) = TP_c * \bar{x}Q(\text{L/s}) * 60(\text{s/min}) * 60(\text{min/h}) * 24(\text{h/day})/1,000,000 \text{ mg/kg}$$

As shown, for flow conditions where discharge was greater than the breakpoint value identified in the breakpoint analysis, each flow value was assigned a  $TP_c$  value equal to the BfM value for the site. For discharge values that exceed BpQ the  $TP_c$  value is equal to the algebraic solution to the previously determined regression equation unless this  $TP_c < BfM$ , in which case  $TP_c$  is assigned the BfM value. The breakpoint intercept (BpI) is the algebraic solution where  $\%_{xc} = 0$ , a condition that occurs during the single largest flow event included in the gauge record (0% of flows exceed the discharge value). This results in a negative BpR value for the regressions in this study, because the concentrations decline with declining discharge, which corresponds to increases in the value of  $\%_{xc}$ . For each site the actual value of discharge is determined through a lookup table relating  $\%_{xc}$  to the discharge record, which returns  $\bar{x}Q$  for the site. Once both a TP concentration estimate and a discharge estimate are generated, a daily load estimate as milligrams is calculated as  $TP_c$  (mg/L) \* average daily discharge (L/s) \* 60 s \* 60 min \* 24 h.

To generate a generalized model of flow conditions and concentrations likely to occur, we used the flow percentile data to create a “year” during which the range of flow conditions recorded by the USGS gauge data was consolidated into 365 data points per station. Day 1 represented a flow likely to be met or exceeded 99.73% of the time, day 2 represented a flow likely to be met or exceeded 99.45% of the time, and so on, until day 365, a flow likely to be met or exceeded 0.07% of the time, based on a 365.25-day year. Day 365 was adjusted to fit total discharge to the 365-day average total discharge for the period of gauge record used. For each “day” a load estimate from the above calculation

was developed. This approach can only be considered an estimated load, because the flow data used are mean daily flow, and no cross-sectional sediment sampling was done to generate more precise TP concentrations (Gray and others 2000).

For each “day” estimated  $TP_{dl}$  was summed with all preceding “days” to generate a cumulative load estimate, where the sum of all estimated daily loads corresponds to “day” 365, and can be interpreted as an estimated annual TP load ( $TP_{al}$ ). Each estimated daily load was plotted as both cumulative load and percentage of  $TP_{al}$  to determine the distribution of the loads and evaluate potential strategies for total load reductions. The procedure can be understood in the following equation, where  $n$  equals the “day” of the year, and  $TP_{al}$  is equal to the solution where  $n = 365$ .

$$TP \text{ Cumulative Load} = \sum_{TP_{dl}=1}^{TP_{dl}=n} TP_{dl}$$

Estimated daily load models were then used to evaluate the efficacy of concentration reductions at baseflow on total load reductions.

Finally, to determine the effect of alterations to peak discharge, the models were fixed to their total modeled discharge volume while redistributing a portion of the peak flow volumes across a longer time period. Stated differently, the new models exhibited the same total water discharge, while approximating conditions that could occur if the stream peak discharges slowed down by increased hydraulic retention of storm flows. In the event that watershed management improved hydraulic retention of storm flows, it is possible that the annual discharge would decline somewhat due to increased evapotranspiration and increased deep groundwater recharge. It is also possible that an increase in hydraulic retention would alter the relationship between discharge and TP concentration at high flows. However, we had no data on the relative impact of these factors and, instead, chose to model results as if the concentration/discharge relationship remains as currently described and all existing discharge continues, but is distributed into longer periods of more moderately high flow from existing peak discharges. The discharge values developed through this hydraulic redistribution were paired with the previously developed discharge/concentration models, and the new estimated  $TP_{dl}$  was calculated, as well as the estimated cumulative annual loads detailed above.

Specifically the annual load models either were adjusted by assigning all current baseflow  $TP_c$  to 0.068 mg/L for an ambient concentration reduction or were assigned new  $\bar{x}Q$  values according to the following scheme. For the 70% and 80% peak flow reduction models, the 19 days with the greatest  $\bar{x}Q$  were assigned new  $\bar{x}Q$  values equal to 70% and

80% of the current  $\bar{x}Q$ . For the 90% peak flow reduction model the 37 days with the greatest  $\bar{x}Q$  were assigned new  $\bar{x}Q$  values equal to 90% of the current  $\bar{x}Q$ . Remaining days were fitted to the model by stepwise increases in  $\bar{x}Q$  multiplication factors from 70%, 80%, and 90% values until the total annual discharge under the new model was equal to the current annual discharge. This results in somewhat higher baseflow  $\bar{x}Q$  values and a gradient of change for  $\bar{x}Q$  values between the adjusted peak  $\bar{x}Q$  and the new baseflow  $\bar{x}Q$  values. Because of the wide variation in stream discharge each model was fitted to the site-specific annual discharge total, resulting in somewhat variable changes in baseflow  $\bar{x}Q$ .

### Land Use Regressions

Data were also summarized by median concentration and seasonal (spring [April–July], summer-fall [August–October], and winter [December–March]) median concentrations. BfM, median  $TP_c$ , and seasonal median  $TP_c$  were regressed against land use measures for the restricted set of sites (25) (Table 3) and the expanded set of 169 sites from

the GIS dataset using best subsets regression with best fit models selected by Mallows' CP statistic. BpR, BfM, and overall median  $TP_c$  were also regressed against land use parameters using best subsets regression. Kruskal–Wallis was used to test for seasonal differences of the flow percentiles.

## Results

### Land Use and Seasonality

$TP_c$  and hydrologic conditions varied widely across the included watersheds (Tables 2 and 4) but showed generally consistent patterns, with exceptions in arid and very low cropland impact watersheds. Overall median concentrations ranged from 0.046 to 0.33 mg/L, with interquartile ranges typically approximating the median plus or minus half the median (quartile  $\bar{X} = 0.0747$  mg/L; range, 0.0135–0.21 mg/L). Median concentrations at flows less than the breakpoint, baseflow, were highly correlated with overall median concentration ( $R^2 = 97.4\%$ ,  $P < 0.0001$ ,

**Table 3** Land use parameters for sites included in this analysis: the first four land use columns are whole watershed land use, and the last four columns are land use in the Kansas Surface Water Register riparian (RR) buffer area

Site	Area (km <sup>2</sup> )	Crop	Grass (%)	Forest (%)	Dev. (%)	RR crop	RR grass (%)	RR forest (%)	RR dev. (%)
011	3,850	46	50	0	1	14	56	4	0
036	1,530	50	43	1	1	13	51	13	1
038	1,090	48	42	4	1	20	24	27	0
207	810	17	59	20	0	9	22	60	0
217	1,060	4	87	5	0	3	68	24	0
220	2,370	25	69	2	0	10	60	9	0
239	760	19	67	9	1	22	20	37	1
501	1,230	24	52	17	1	12	21	52	1
505	1,300	52	36	7	1	36	13	40	1
507	1,060	44	46	6	1	31	22	40	0
512	1,210	41	53	2	0	42	24	23	0
515	840	34	57	5	1	21	16	48	1
521	1,080	6	86	4	1	11	45	29	1
525	2,240	53	41	1	1	14	60	6	0
529	2,320	57	36	2	0	18	44	16	0
545	900	63	33	0	0	25	25	8	1
546	2,420	48	48	0	0	24	46	3	0
547	2,650	48	48	0	1	17	55	1	0
549	1,540	66	30	0	0	36	46	1	0
565	610	37	45	5	1	10	25	24	1
574	320	3	87	6	0	6	43	38	0
577	430	17	72	6	1	14	32	43	1
586	5,970	60	37	0	0	21	60	2	0
596	3,170	62	34	0	0	18	63	3	0
600	3,680	72	25	0	0	9	67	5	0

**Table 4** Total phosphorus (TP) concentrations for all data at each sample location and details of breakpoint analysis

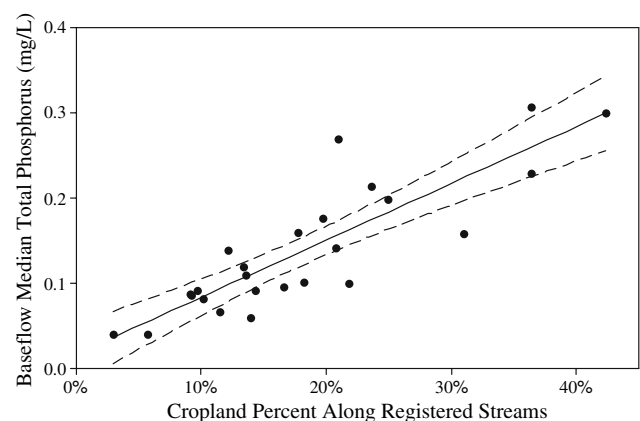
Site	Overall TP median (mg/L)	TP IQR (mg/L)	BfM TP <sub>c</sub>	N	BpQ	Regression R <sup>2</sup> (%)	BpR	BpI
011	0.065	0.079	0.060	92	13	53	-0.105	0.025
036	0.130	0.088	0.120	95	25	32	-0.025	-0.328
038	0.191	0.160	0.176	93	17	66	-0.048	0.031
207	0.090	0.070	0.087	101	21	50	-0.028	-0.344
217	0.040	0.027	0.040	88	a	a	a	a
220	0.101	0.087	0.091	90	30	23	-0.041	-0.216
239	0.117	0.122	0.100	94	24	74	-0.065	0.287
501	0.176	0.225	0.139	95	35	65	-0.030	0.110
505	0.231	0.119	0.229	90	22	53	-0.038	0.206
507	0.189	0.203	0.159	89	26	37	-0.033	0.155
512	0.324	0.230	0.300	91	30	16	-0.017	-0.168
515	0.160	0.153	0.142	93	16	42	-0.048	-0.006
521	0.070	0.067	0.066	91	10	96	-0.230	0.852
525	0.120	0.100	0.110	91	40	22	-0.010	-0.572
529	0.132	0.142	0.102	91	17	52	-0.056	0.089
545	0.210	0.210	0.199	91	6	99	-0.402	1.546
546	0.250	0.225	0.214	59	25	11	-0.013	-0.336
547	0.097	0.075	0.097	70	a	a	a	a
549	0.310	0.420	0.308	61	46	9	-0.007	-0.337
565	0.100	0.081	0.082	77	33	54	-0.021	-0.286
574	0.046	0.037	0.040	88	17	57	-0.081	-0.302
577	0.110	0.100	0.091	104	14	48	-0.089	0.060
586	0.330	0.354	0.270	47	10	67	-0.127	0.440
596	0.188	0.252	0.160	88	10	35	-0.063	-0.058
600	0.087	0.110	0.097	80	a	a	a	a

Regression columns are the results of log<sub>10</sub> transformed TP<sub>c</sub> as a function of %<sub>xc</sub> for samples collected during discharge conditions that exceeded the identified breakpoint for each watershed. BpI reported here is the log<sub>10</sub> transformed TP<sub>c</sub> that would be expected during the single largest flow event in the discharge record (i.e., %<sub>xc</sub> = 0)

<sup>a</sup> No breakpoint was indicated; no high-flow regression was conducted

BfM = -0.00393 + 0.915 \* overall median). Relationships between land use and TP<sub>c</sub> were generally consistent between overall median and BfM, though there tended to be a slight improvement (<5%) in R<sup>2</sup> when land use was regressed against baseflow median versus overall median TP<sub>c</sub>.

BfM was best predicted by a linear regression model of percentage cropland in the 90-m buffer of registered streams, adjusted for watershed size (median = -0.0066 + 0.671 [registered riparian cropland%] + 0.000013 [watershed area; km]; R<sup>2</sup> = 79.4%). Use of overall median TP<sub>c</sub> performed similarly, with a slightly lower R<sup>2</sup> value (76.0%). Results were nearly as strong (R<sup>2</sup> = 74.5%) when BfM was regressed along the buffer without inclusion of watershed size (Fig. 2). Riparian Inventory land use and total watershed land use both provided statistically significant models but fit more poorly than the registered riparian regression. Neither permanent grasslands nor forestlands



**Fig. 2** Simple linear regression of median total phosphorus concentrations and the percentage of all land in the buffer zone along Kansas Surface Water Register (2004) streams in cropland. Dashed lines are 95% confidence intervals. Some additional improvement to R<sup>2</sup> occurs when watershed area is added as a regression factor

along the riparian corridor provided statistically significant improvement to regression  $R^2$ .

Seasonal median  $TP_c$ , when regressed against land use variables, continued to support the registered stream riparian corridor as the primary predictor of both BfM and overall median  $TP_c$ . Best subsets regression indicated that spring baseflow was strongly related to the registered stream corridor, and forested areas were correlated with a reduction in  $TP_c$  (spring BfM =  $0.0557 + 1.07$  [registered riparian cropland%] –  $0.215$  [registered riparian forest%];  $R^2 = 76.1\%$ ). Summer-fall BfM regression benefited from inclusion of watershed area but not riparian forest ( $R^2 = 71.5\%$ ), and winter BfM values were best predicted by the registered riparian cropland predictor alone ( $R^2 = 54.8\%$ ). Similar results were found when best subsets regression was done on the seasonal overall median TP, though the spring season did not benefit from inclusion of forest parameters in this model (spring  $R^2 = 66.8\%$ , summer-fall  $R^2 = 65.9\%$ , winter  $R^2 = 53.2\%$ ), and all seasonal regressions performed less well than the  $R^2$  for overall BfM and riparian land use relationships regardless of season ( $R^2 = 79.4\%$ ). Generally the greatest median  $TP_c$  occurred in spring, and the lowest in winter (Table 5). The interacting impacts of flow and land management were not examined directly in this study, but a Kruskal–Wallis test of flow percentiles indicated statistically significant differences between seasons ( $P < 0.001$ , median flow percentiles: spring-32%, summer-fall-67%, winter-44%) for all sites combined.

We determined if the strength of the results held up with a larger unnested sample set of sites ( $N = 169$ ) from the same monitoring network. Similarly to the 25 sites initially analyzed, each monitoring station captured an independent watershed (results not shown). We found that cropland percentages along registered streams were usually the strongest predictor across seasons of median  $TP_c$ . Results were strongest in the spring and weakest in the winter (spring  $R^2 = 47.1\%$ , winter  $R^2 = 23.2\%$ ). Results for these generally smaller watersheds (average size =  $540 \text{ km}^2$ ) benefited modestly from additional landscape elements to improve  $R^2$ , including average watershed slope, average annual rainfall, and either whole watershed grassland percentage or riparian grassland percentage. Of the significant factors, only registered riparian cropland had a positive coefficient. Consideration of forested lands did not significantly improve explained variation in the model, but native vegetation in many of the watersheds is grassland. Median concentrations were highest during spring and lowest during winter when described by the median of all site seasonal medians (spring =  $0.149 \text{ mg/L}$ , summer-fall =  $0.130 \text{ mg/L}$ , winter =  $0.087 \text{ mg/L}$ ).

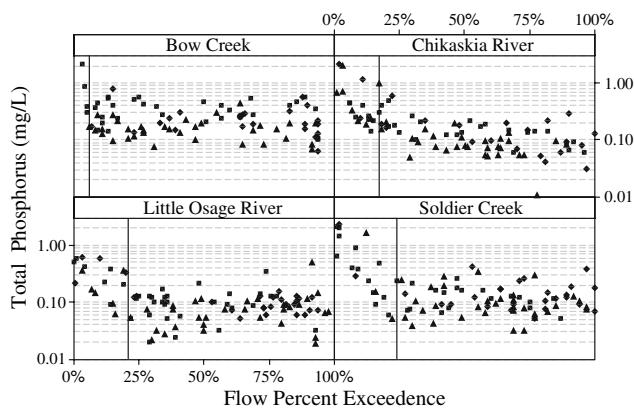
**Table 5** Seasonal median concentrations of total phosphorus for sites included in this analysis

Site	Spring median (mg/L)	Summer-fall median (mg/L)	Winter median (mg/L)
011	0.114	0.061	0.050
036	0.182	0.140	0.110
038	0.291	0.197	0.140
207	0.114	0.104	0.070
217	0.047	0.050	0.026
220	0.110	0.106	0.100
239	0.155	0.127	0.081
501	0.246	0.140	0.175
505	0.281	0.231	0.196
507	0.286	0.156	0.121
512	0.422	0.321	0.166
515	0.270	0.150	0.110
521	0.090	0.070	0.040
525	0.190	0.141	0.084
529	0.168	0.157	0.090
545	0.373	0.200	0.148
546	0.371	0.240	0.180
547	0.130	0.076	0.080
549	0.577	0.310	0.150
565	0.120	0.109	0.077
574	0.050	0.050	0.022
577	0.136	0.100	0.110
586	0.390	0.490	0.115
596	0.325	0.212	0.069
600	0.121	0.094	0.080

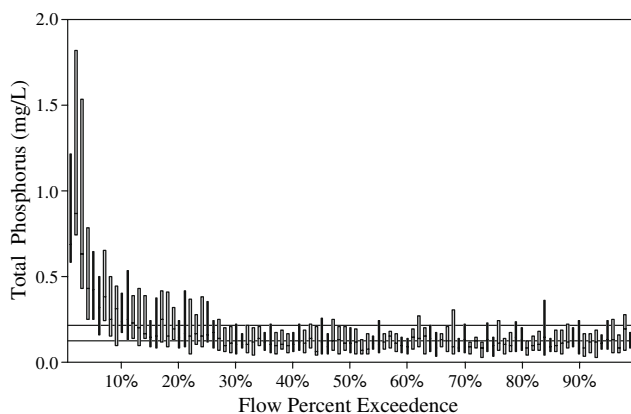
#### Concentration–Discharge Relationships

A wide range of flow conditions existed throughout the watersheds (Table 2). In some western Kansas streams extended periods of no flow were common throughout the years of measured flow. For eastern streams no-flow periods were relatively rare. The magnitude of the highest flows relative to the median flows also varied widely. In areas of highly permeable soil (Natural Resources Conservation Service 2006), e.g., sites 036 (South Fork Ninnescah) and 525 (North Fork Ninnescah), the ratio of 5% exceedance flows to medians flows was lower than in areas with lower soil permeability, e.g., site 565 (Lightning Creek). Watershed area was inversely related to 5% exceedance flows ( $P = 0.039$ ), reflecting site placement decisions required to monitor streams expected to be flowing most of the time. Western streams typically require larger contributing areas to generate similar flows due to the lower available rainfall in those areas.



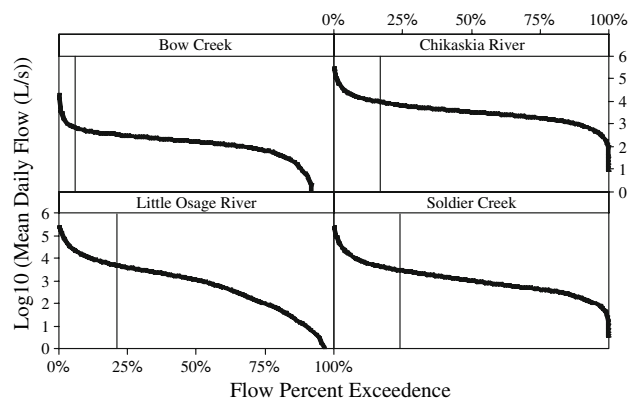


**Fig. 3** Concentrations of total phosphorus at selected sampling points as a function of percentage flow exceedance. Spring samples are represented by squares; summer-fall, by diamonds; winter, by triangles. The line indicates the location of the breakpoint



**Fig. 4** Boxplot of median concentration and interquartile range across all sites for each flow percentage exceedance. Overall mean (0.216 mg/L) and median concentration (0.13 mg/L) shown as lines

Contrary to prediction,  $TP_c$  was not linked to flow condition most of the time in most watersheds (Figs. 3 and 4). Breakpoint analysis indicated that 22 of 25 total watersheds had a  $TP_c$  relationship with flow at high flows and that, at flows less than the BpQ, flow and concentration were not linked. Rapid rise rates at and above 10% exceedance flows were the norm (Fig. 5), though the average breakpoint after model fitting was a 22% exceedance flow (range, 6–46%). No relationship between land use, watershed area, or soil permeability was found to influence the position of the breakpoint along the flow spectrum or the BpR or BpI of the line for flows larger than the breakpoint. Slopes for concentration/percentage exceedance lines at flows larger than the breakpoint generally performed well ( $R^2$   $\bar{X}$  = 48%; range, 9–98%) (Table 4), though three poorly fitting models ( $R^2 < 20\%$ ) were found for western Kansas streams. The negative



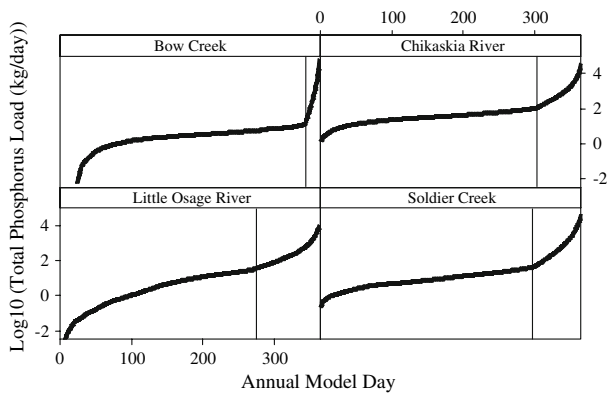
**Fig. 5** Flow-duration curves for selected sites. Both the Little Osage River and Bow Creek have periods of no flow, as indicated by the intercept at less than 100% exceedance. Vertical line indicates breakpoint value. Flow values to the left of the breakpoint are high flow; those to the right are baseflow

coefficient of BpR (Table 4) occurs because the percentage exceedance flow value declines as discharge increases.

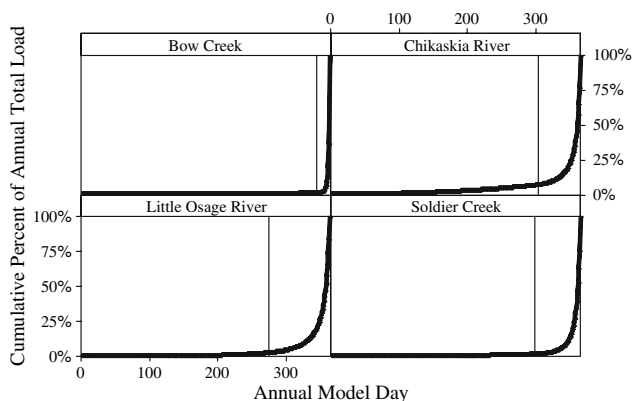
Generally regression lines were based on fewer than 20 data points, due to the random nature of the sampling and the fact that high discharges are relatively rare, particularly for sites with breakpoints higher on the duration curve (e.g., sites 521 and 545). As expected from a random sampling design, sites with somewhat fewer than 100 samples typically had  $<1$  sample per % exceedance flow. In some watersheds anomalous high-concentration events occurred at times other than a high-flow event. In most cases (data not shown) these could be linked to either rising or falling limbs of multiday high-flow events, where sampling occurred during a period of transitional flow. It is possible that some of these points represent contaminated samples or were influenced by otherwise unknown factors. As noted previously, flow has some correlation with season, but due to limited high-flow sample size, regressions were based on all sample data, regardless of season.

#### Total Annual Phosphorus Loads

$TP_{al}$  models where breakpoints existed indicated a strong interacting effect of increasing flows and increasing concentrations. For sites with higher peak flows relative to median flows the impact was particularly notable. Under current conditions (Fig. 6) a substantial increase in total estimated load per day is present during days of elevated discharge for all sites with breakpoints, though the effect is more pronounced where steeper regression line slopes (BpR) and/or greater peak discharge occur. The cumulative impact of each  $TP_{dl}$  is more apparent when plotted as a cumulative load chart (Fig. 7). The largest percentage of the total estimated annual load ( $>50\%$ ) occurs during a few days each year, typically less than 15 days per year, and an



**Fig. 6** Annual model total daily load for selected sites. Both the Little Osage River and Bow Creek have periods of no flow, indicated by no load during the first days of each model year. Vertical line indicates breakpoint. Daily loads to the left of the line are baseflow conditions; those to the right are high flow conditions



**Fig. 7** Cumulative percentage of the total annual load that has occurred up to and including a model day for selected sites. Vertical line indicates breakpoint. Cumulative loads to the left of the line occur during baseflow conditions; those to the right occur during high flow conditions

average of 88% of the total annual load occurred during only 10% of the time. The most extreme examples of a combined effect due to increasing discharge and increasing concentrations co-occurring are present when both discharge and concentration rise rates are steep, e.g., site 521, where 90% of the estimated total annual load occurs during 8 days of high flows (2% exceedance flows and greater), with a high-concentration discharge. The absolute largest estimated  $TP_{al}$  occurred in streams in the eastern part of the state, where rainfall and discharge were the greatest. A model fitting the current flow-duration curve with the current peak flow-concentration relationship, but reducing ambient concentrations (those at flows less than the breakpoint) to the current ecoregional guidance, 0.068 mg/L TP (US EPA 2001), resulted in relatively small reductions in  $TP_{al}$ , typically <5%. Three sites were not modeled for ecoregional guidance due to an existing BfM less than

the guidance concentration. Conversely, the interacting effects of high discharge and high concentration result in notable reductions to  $TP_{al}$  where peak flows are reduced and the flow duration curve is redistributed to allow for the same total annual discharge. Models with the same  $\bar{x}Q/TP_c$  equations developed by regression analysis for flows beyond the breakpoint, but adjusted by reducing peak discharges, consistently indicated major reductions in  $TP_{al}$ , as much as 30% and more than 10% at half of the modeled sites, from a reduction to 90% peak flows (Table 6). Sites with very low peak discharges, like site 549, were less affected by a reduction in peak flows. Further reductions in peak discharges, to 80 and 70% of current conditions, continued to reduce  $TP_{al}$  by as much as 48%, and generally more than 20%, at most sites.

## Discussion

### Land Use

Previous studies of land use and nutrient concentrations from large monitoring datasets have suggested that some unexplained variation may result from unmeasured influences of discharge (e.g., Dodds and Oakes 2006, 2008). Our results suggest not only that there is a strong relationship among riparian land use along perennial streams, watershed size, and median TP concentration ( $R^2 = 76.0\%$ ), but that flow data are largely unnecessary for characterizing typical concentrations when robust metrics, such as median concentrations, are used. Mean concentrations may require flow weighting, but medians are much less influenced by flow extremes for the streams included in this study. Some high-flow targeted sampling may be desirable if sediment-bound pollutant transport, rather than stream water concentration, is of concern to researchers. The 30-m buffer area (30 m on each side of a 30-m stream corridor) found to be most significant is consistent with previous work on a much smaller watershed (McDowell and others 2001) and disagrees with the results modeled by Weller and others (1998), who suggested that riparian influence would be limited to the protection afforded by the narrowest buffer areas in the watershed. Our results suggest that a proportional reduction in  $TP_c$  should occur as cropland in the near-stream area is replaced with more permanent vegetation. Our results also suggest that monitoring programs should ensure that sampling occurs over an extended time period, especially when elevated runoff conditions are likely to occur, so transport rates can be accurately estimated.

Our results, particularly the disparities between the 169-site analysis and the 25-site analysis, when considered in the context of the existing literature (McDowell and others

**Table 6** Total phosphorus annual loads (metric tons; t) for modeled scenarios indicated in “load” columns (reported to two significant digits) and modeled percentage reductions from current conditions for each management scenario indicated in “reduction” columns (reported to the nearest integer)

Site	TP <sub>ai</sub> (t), current conditions	TP <sub>ai</sub> (t), 90% peak flow	TP <sub>ai</sub> reduction (t), 90% peak flow	TP <sub>ai</sub> (t), 80% peak flow	TP <sub>ai</sub> reduction (t), 80% peak flow	TP <sub>ai</sub> (t), 70% peak flow	TP <sub>ai</sub> reduction (t), 70% peak flow	TP <sub>ai</sub> (t), ambient conc.	TP <sub>ai</sub> (t), ambient conc. reduction	TP <sub>ai</sub> reduction (t), ambient conc. reduction	TP <sub>ai</sub> reduction (%), (largest 10% of all discharge)
011	32	27	16	24	26	35	32	32	a	95	
036	49	46	5	46	8	10	44	44	10	66	
038	140	130	11	120	18	25	140	140	2	94	
207	75	69	8	64	14	17	75	75	1	90	
220	41	37	9	35	14	19	40	40	3	79	
239	190	160	13	140	22	29	180	180	<1	96	
501	230	210	8	190	15	20	230	230	1	91	
505	190	170	10	150	17	21	180	180	2	93	
507	94	86	9	80	16	19	93	93	1	92	
512	37	35	5	34	9	11	35	35	5	86	
515	53	47	11	43	18	24	51	51	3	91	
521	460	350	23	300	34	45	460	460	a	99	
525	27	27	2	27	3	4	26	26	5	66	
529	150	130	12	120	19	25	150	150	2	91	
545	100	71	30	61	39	48	100	100	1	99	
546	6	6	3	6	5	5	6	6	7	71	
549	3	2	2	2	3	3	2	2	3	77	
565	70	66	6	63	11	11	70	70	0	92	
574	26	22	14	21	21	26	26	26	a	97	
577	42	36	14	32	24	34	42	42	1	97	
586	55	46	17	41	27	38	55	55	1	99	
596	13	11	11	11	17	21	12	12	3	95	

Flow reduction and ambient concentration (conc.) reduction models are explained in the text. Generally, a given percentage peak discharge model predicts the total annual load when the current peak daily discharges (10%, 5%, and 5% highest percentiles) are reduced by 10%, 20%, or 30% mean daily discharge, respectively. Ambient condition models predict reductions in annual loads when concentrations at discharges below the breakpoint are set to the current ecoregional guidance. Sites that were not modeled were excluded for lack of a statistically significant breakpoint resulting in at least one sloping line. The rightmost column indicates the percentage of the total current modeled annual load occurring during the largest 10% of all discharge days

<sup>a</sup> Current median less than ecoregional guidance values

2001; Dodds and Oakes 2006), suggest that different factors are likely to influence  $TP_c$  across watersheds of differing sizes, with small watersheds more strongly impacted by conditions along small headwater streams, and large watersheds such as those included in the 25-site analysis presented here experience greater impacts from land use along larger perennial streams. In-stream processing of nutrients may influence downstream nutrient concentrations (Mulholland and others 2008). Our study specifically excluded regulated rivers, and further research will be needed to determine the role of large reservoir releases in regulating  $TP_c$  in downstream waters.

We cannot be certain about the mechanisms that drive the observed relationships because our study is correlative. Perennial stream riparian-area cropland could be a good predictor of  $TP_c$  because of an ongoing steady supply of sediment-bound nutrients from overland flow and/or bank erosion and sloughing where cropland abuts streams. Conversely, sediments delivered during high-flow events could provide a larger pool of available TP by depositing sediment and sediment-bound nutrients. The high  $R^2$  values in our regression model suggest that efforts to reduce  $TP_c$  during baseflow conditions may be best focused on reducing cropland uses very near perennial streams. Implementing best management practices to improve water quality may be more manageable by focusing on those areas that appear to be more strongly linked to in-stream  $TP_c$ .

Our results also indicate a generally robust relationship between high-flow events and elevated  $TP_c$  (22 of 25 sites), particularly in areas with greater annual rainfall and more cropland. While such events are rare, and have little influence on median  $TP_c$  (Helsel and Hirsch 1991), they are very important in annual TP loading. These results support concerns from previous research that samples taken during high-flow events may skew concentration means if discharge data are not available.

A recent USGS study of sediment sources, which often correspond to TP sources, indicated that in a large watershed in Kansas, the primary source of sediment to downstream reservoir was channel bank supply, and the strength of the relationship increased with downstream distance from headwaters of the watershed (Juracek and Ziegler 2007). We did not measure or account for streambank stability or overland flow sources of sediment or TP so we cannot attribute TP sources during high-flow events in these watersheds. Determining TP sources in the watershed will require measurement of the relative contributions of each of the potential sources.

#### Total Phosphorus Loads

The results of our modeled analysis point to the importance of managing high-flow concentrations and discharge to

address downstream impacts resulting from absolute loads. Our results are consistent with a recently completed study on a large Kansas river (Rasmussen and others 2005) using continuous water quality monitoring, which found that 40% of total annual TP load occurred during 10% of the time. Our study found that an average of 88% of the total annual load happens during flows that occur only 10% of the time. Our results are also consistent with results from Illinois (Royer and others 2006), where a set of three heavily cropped ( $\bar{x} = 89\%$ ) watersheds was analyzed. They found similarly large portions of the total annual load occurring during a few days of high-flow events each year and very small reductions in total load from management of baseflow concentrations. The similarities in total load patterns did not extend in our study to the least intensively cropped watersheds and the most arid watersheds, potentially indicating a threshold below which other influences control total loading of TP in prairie watersheds.

Our results indicate that the combination of elevated discharge with elevated concentration results in large load increases to downstream receiving waters. Significant efforts have been made to reduce ambient loads in rivers and streams from point source discharges (Kansas Department of Health and Environment 2008) and Kansas waters have shown notable improvement from reductions in some nutrients. Estimates by Rasmussen and others (2005) indicate that only 12% of the TP load near the outlet of the Kansas River comes from point source discharges, further supporting the need to address widespread nonpoint sources of nutrients.

The largest reduction in peak modeled flow condition, 30% in peak discharge, corresponds with the pattern of discharge documented previously on Soldier Creek (station 239) prior to extensive channelization and headcutting (Juracek 2002). The widespread impacts of channelization (National Research Council 1992) combined with changes to soil infiltration rates expected from conversion of permanent grasslands to row crop production may explain why such large increases in peak discharge occur in some streams. Gerla (2007) recently demonstrated that reductions in peak discharge even greater than those modeled here, as much as 55%, could result from conversion of cropland to native prairie grasses. Restoration of forest lands in some areas has been associated with a return to peak discharges 25–55% less than under the deforested conditions (Jones 2000). Wetland restoration has also been identified as an important factor in mitigating flood magnitude by increasing storage and reducing peak flow (Zedler 2003; Hey and Philippi 2006). Few long-term gauging stations occur on smaller streams without upstream impoundments, limiting our ability to test the extent of changes to peak discharges in the relatively wet eastern portion of the state. Conversely, streams in the

western portion of our study area have decreased current peak and total discharges over the past decades, a change largely associated with the withdrawal of groundwater for irrigation (Schloss and others 2000).

Our results point to the importance of finding strategies that reduce both peak concentration and discharge if TP loading is to be controlled. Strategies that reduce ambient TP<sub>c</sub> will probably reduce peak concentrations somewhat because efforts to reduce sediment transport should dampen extreme flows by increasing water retention on the landscape.

Attempts to reduce TP loading may be most effective when managers implement measures that reduce peak discharge, which should correspond to reduced peak concentrations in many watersheds. Small watershed impoundments have commonly been built to address downstream high flows, but their downstream impact can be negated in short distances (Dunne and Leopold 1978). The Soldier Creek example (Juracek 2002) suggests that increased channel complexity and connection with the surrounding floodplain, together with increased total channel length, may provide reductions in peak discharge. Off-channel deposition in riparian areas and wetlands can potentially retain nutrients (Venterink and others 2003) in large rivers and was historically common in many stream channels that are now channelized. Restoration of meandering and floodplain connection could lower downstream TP loads (Yarbo and others 1984); TP is generally bound to sediment, which is more likely to deposit in a floodplain (Reddy and others 1999) that has a low relative water velocity. Improving hydrologic retention at all points on the landscape may be the most effective method of reducing downstream loading of TP.

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