SUPPORTING INFORMATION

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Within-river phosphorus retention: accounting for a missing piece in the watershed phosphorus puzzle

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Sampling strategy

Our study focused on two USGS monitoring sites (see http://waterdata.usgs.gov/ar/nwis/qw) which characterize the P loads and concentrations for the upper Illinois River leaving Arkansas (Siloam) and the lower Illinois River in Oklahoma, draining into Lake Tenkiller (Tahlequah) (Fig SI-1):

- 'Siloam' (ILSiloam): the Illinois River on Highway 59 south of Siloam Springs, Arkansas (drainage area 1489 km^2; USGS station no. 07195430), close to where the Illinois River flows across the state boundary into Oklahoma
- 'Tahlequah' (ILTahlequah): the Illinois River near Tahlequah, Oklahoma (drainage area 2484 km^2,USGS station no. 07196500), close to the inflow into Lake Tenkiller.

Sampling was typically monthly, with some sampling targeted at high flows. Figure SI-5, and the table therein, show how this sampling strategy provided good coverage of a full range of representative flows, including peak flows. This coverage of a full range of representative flows was required to characterise the flow dependence of TP concentrations, since TP was modelled as a function of river flow (see modelling approach below).

Disputes, lawsuits and P criteria in the Illinois River

Disputes and lawsuits between downstream water users and upstream land managers began in the 1980s with concerns about point-source P loadings from WWTPs in NW Arkansas. Since the early 1990s, attention has focused on non-point source inputs from pastures and land application of poultry litter. The dispute reached the U.S. Supreme Court in 1992, with a landmark ruling that the downstream State's (Oklahoma's) water quality laws must be met. In 1997, Arkansas and Oklahoma agreed to a goal of a 40% reduction in total P loads to Lake Tenkiller. In 2002, Oklahoma adopted a numerical water quality standard for P in the Illinois River (in accordance with its Scenic River status) that the 30-day geometric mean TP concentration should not exceed 0.037 mg L^{-1}. To meet these goals, nutrient removal was implemented at WWTPs in the watershed and both states have introduced best management practices for pasture and animal manure management. Despite these measures, river water P concentrations are consistently above the P criterion value and responses in P concentrations to remediation measures have been difficult to quantify[4]. Consequently, the transstate boundary disputes over land use and P inputs continue and, in 2005, the Oklahoma Attorney General filed a lawsuit against several poultry producers in Arkansas[4,5], and is still subject to ongoing litigation.

Modeling approach

River TP loads (derived from measured river TP concentrations) were compared with an estimate of corresponding 'conservative' TP loads (i.e. if the TP from effluent discharges was only subject to hydrological dilution, with no within-river P retention processes). By comparing the 'conservative' TP and river TP concentrations and loads, we were able to directly quantify the net retention of effluent P under low flows and its contribution (when physically remobilized under higher flows) to storm-flow and annual TP loads.

Conservative TP concentrations were derived from applying effluent TP:Cl^- ratios to the river water Cl^- concentration data . This allowed us to quantify the effects of hydrological dilution of effluent TP during mixing with river water and downstream transport, without any influence of within-river processes. As there were no direct measurements of effluent Cl^-, we took the river baseflow endmember Cl^- load (in this case, the mean Cl^- load for the lowest 25% of river flows) as a surrogate for the effluent Cl^- load . The use of the baseflow Cl^- load as a surrogate for effluent Cl^- load relies on an assumption that baseflow Cl^- is overwhelmingly dominated by effluent point sources. There are several independent strands of evidence to support this assumption:

- The spatial patterns in river water Cl^- concentrations (Figure SI-3) show highest concentrations at sites in closest proximity to WWTPs, and the strong dilution patterns with increasing flow (Fig SI-2b) are, together, indicative (i) of a dominant WWTP effluent source of Cl^- in the Illinois River, and (ii) that under baseflow conditions, the majority of the Cl^- in the river is derived from WWTP discharges.
- Using the baseflow Cl^- load as a surrogate for the effluent TP load, the resulting effluent TP:Cl^- ratios are entirely consistent with direct measurements of effluent TP:Cl^- ratios in other published WWTP effluent from domestic sources (see manuscript). This demonstrates that the use of the baseflow Cl^- load was a suitable surrogate for the effluent Cl^- load.

- We have also used the load apportionment model[1,2,3], which indicated that >80% of baseflow Cl^- in the Illinois River at Tahlequah is derived from flow-independent ('point') sources.

Both measured river and 'conservative' TP concentrations were modeled as a function of river flow, as follows:

1. Measured river TP concentrations were modeled according to the Load Apportionment Model algorithms; full details are supplied in Bowes et al. (2008-2010)[1,2,3] and only a brief description is provided here. The loads of P from 'continuous' or 'flow independent' inputs (typically point sources) (F_p) and 'flow-dependent' inputs, which are mobilized by increasing flow, (F_d), were modeled as a power-law function of river flow (Q; $m^3\ s^{-1}$):

$$F_p = A * Q^B \text{ and } F_d = C * Q^D \quad (1)$$

where A, B, C and D are parameters determined empirically.

The total measured river load (F_t; mg-P s^{-1}) was then calculated as a linear combination of the loads from continuous and flow-dependent sources:

$$F_t = F_p + F_d = A * Q^B + C * Q^D \quad (2)$$

The river TP concentration at any given time (C_r; mg m^{-3}) was then equal to the load divided by the flow, expressed as:

$$C_r = A * Q^{B-1} + C * Q^{D-1} \quad (3)$$

Eq. (3) was fitted to the data using non-linear least square regression in the Solver function in Microsoft EXCEL©. In the case of the Illinois River at Siloam and Tahlequah, there was no dilution under low flows because within-river processing was efficient at removing any point source signal and therefore $F_p = 0$.

2. Conservative TP loads (F_c) were modeled as continuous or flow independent source loads above, where:

$$F_c = A * Q^B \quad (4)$$

And the conservative TP concentration at any given time (C_c; mg m^{-3}) was then equal to the load divided by the flow, expressed as:

$$C_c = A * Q^{B-1} \tag{5}$$

Figure 2a shows an example of the model fits for measured river TP and conservative TP concentrations as a function of river flow for the Illinois River at Tahlequah for 1997-2000. Figure 2b shows the intersection of the Conservative TP model and the River TP model (Q_c, at which C_r=C_c), which is the threshold river flow above which no net TP retention occurs.

3. TP retention was modeled using a 'combined' TP model (Fig 2b), which tracks the conservative TP model until Q_c is reached, then tracks the measured river TP model above Q_c. The combined model TP concentration (C_m; mg m^{-3}) is calculated:

$$\text{Where } Q<Q_c,\ C_m = C_c \text{ and where } Q>Q_c,\ then\ C_m = C_r \tag{6}$$

The reduction in TP concentration (R_c in mg m^{-3}) as a result of within-river retention at any given time (Fig 2b) was then calculated as:

$$R_c = C_m - C_r \tag{7}$$

And the TP load reduction (L_c in mg m^{-3}) was calculated as:

$$L_c = R_c * Q \tag{8}$$

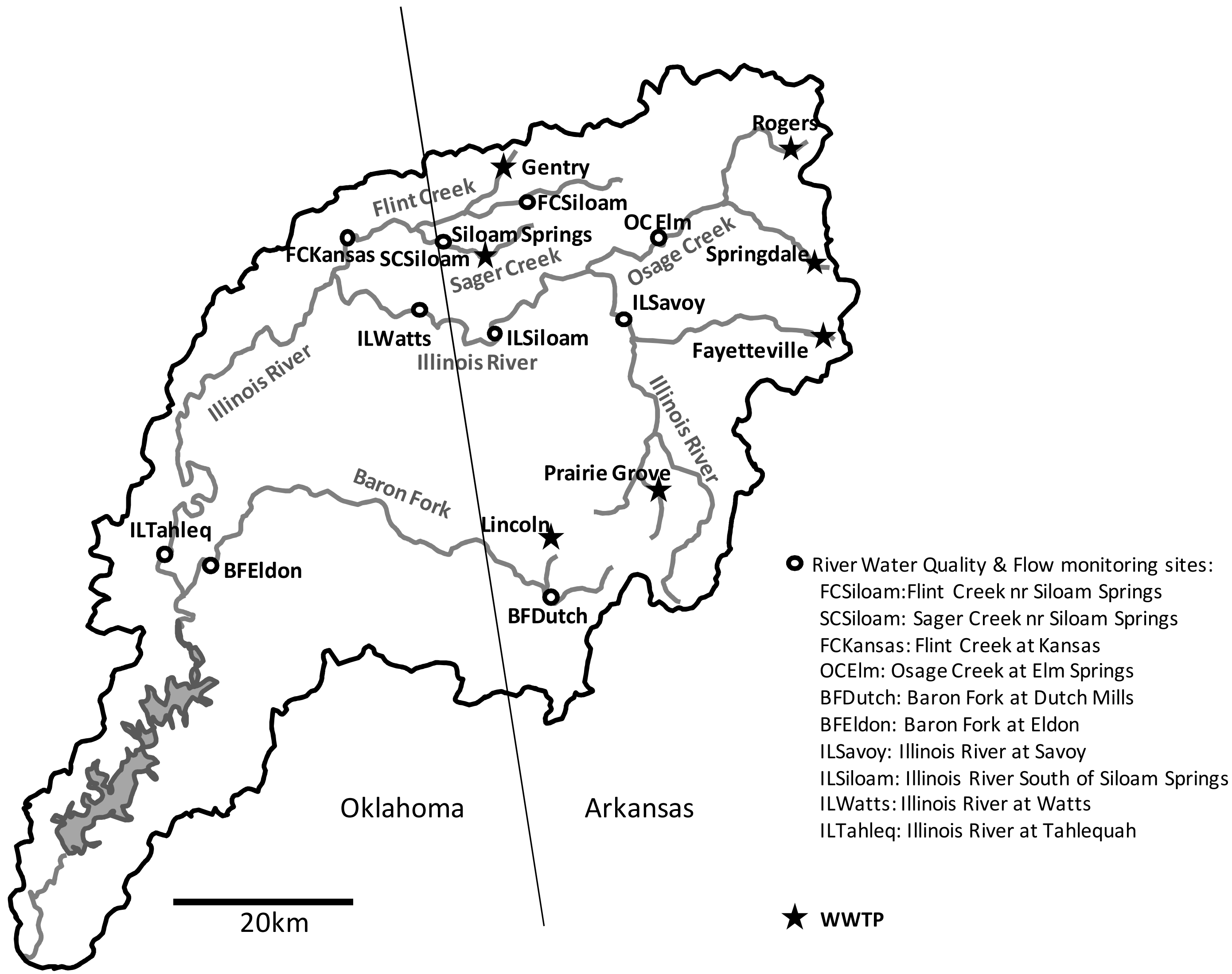


Fig SI-1: Map of the Illinois River watershed

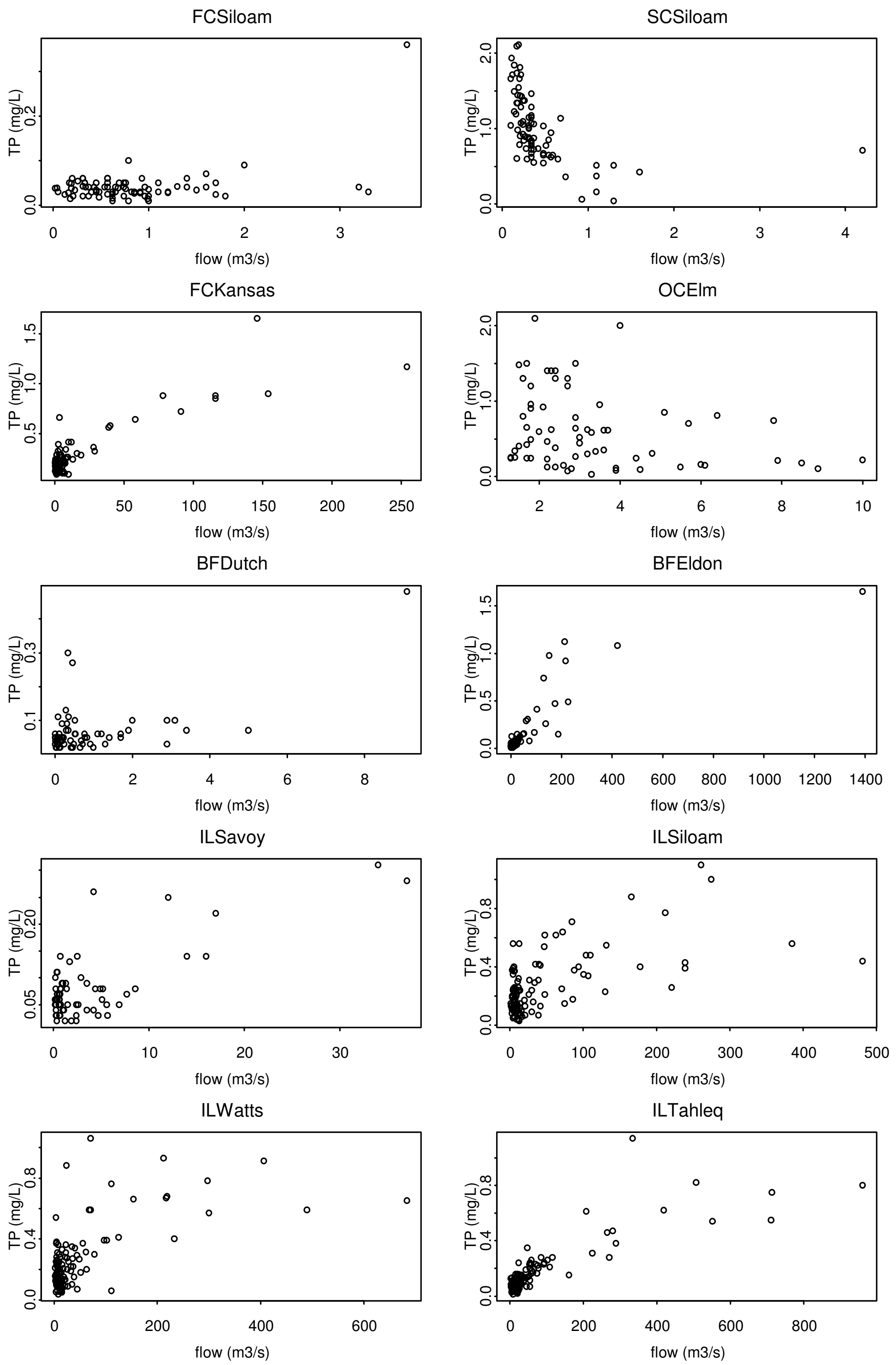


Fig SI-2a: Relationships between Total Phosphorus (TP) concentration and flow for the Illinois River and its tributaries (1997-2007) (for site codes and locations, see Fig SI-1)

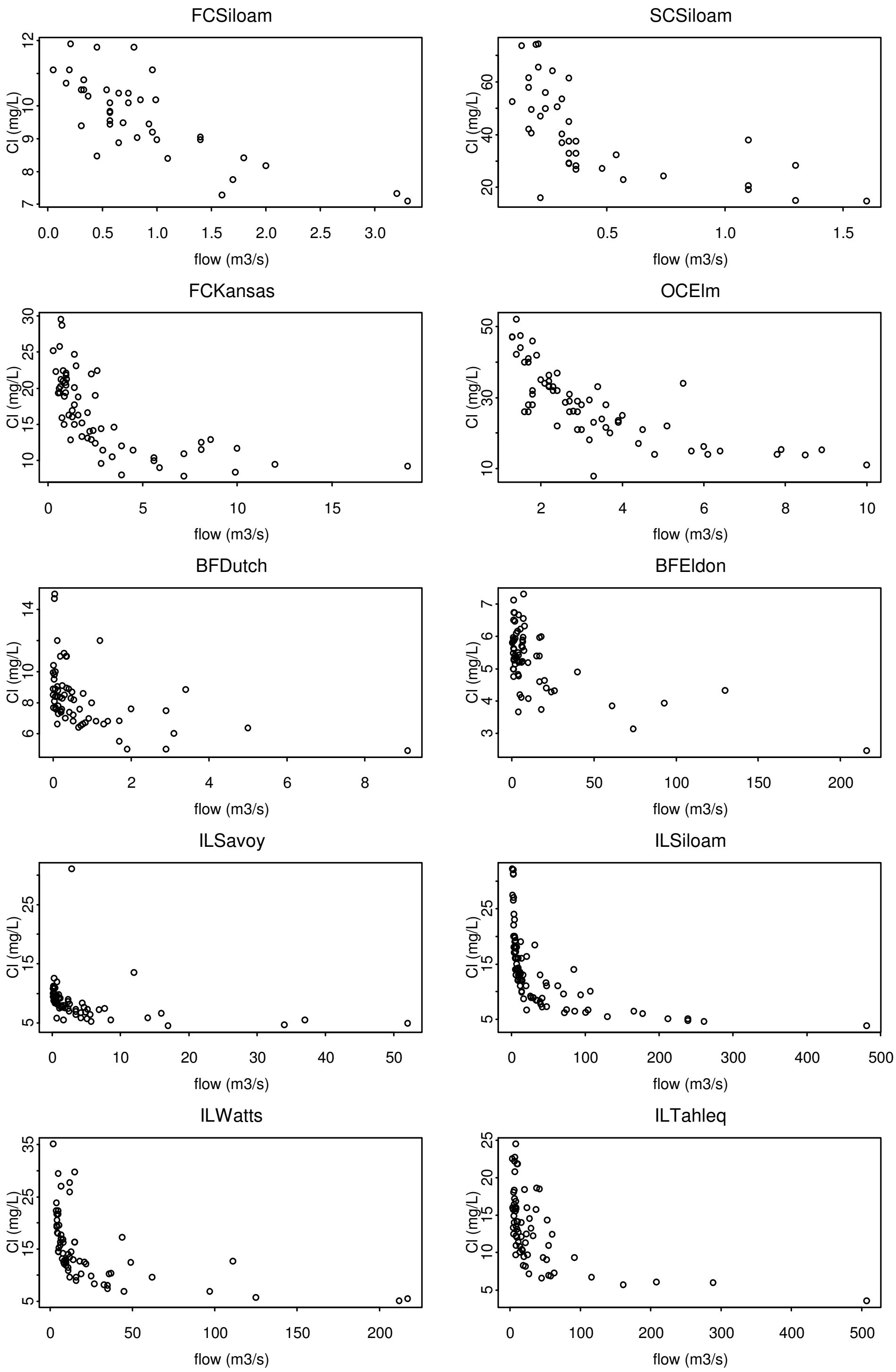
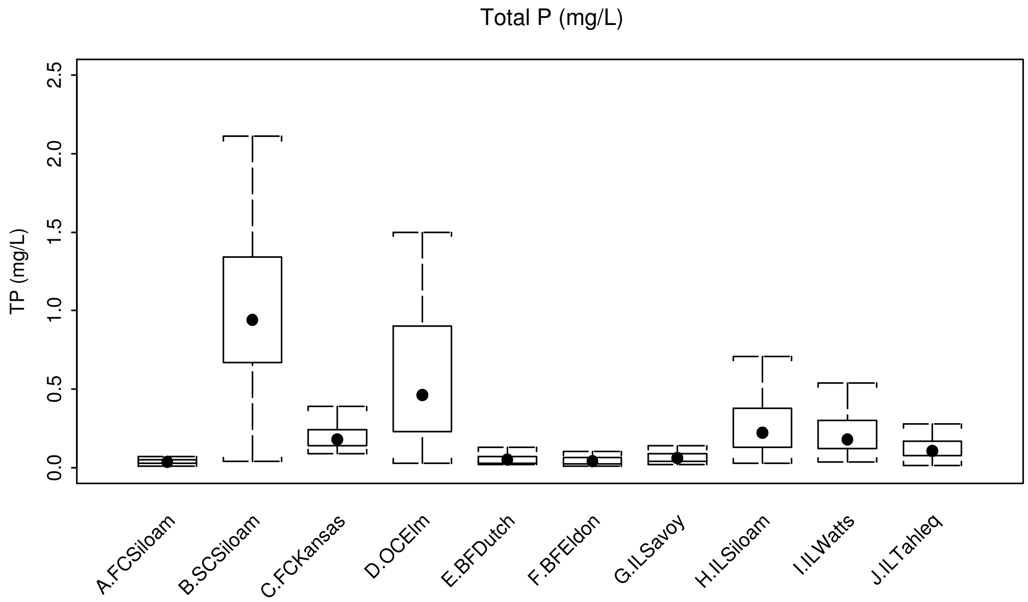


Fig SI-2b: Relationships between chloride (Cl^-) concentrations and flow for the Illinois River and its tributaries (1997-2007) (for site codes and locations, see Fig SI-1)



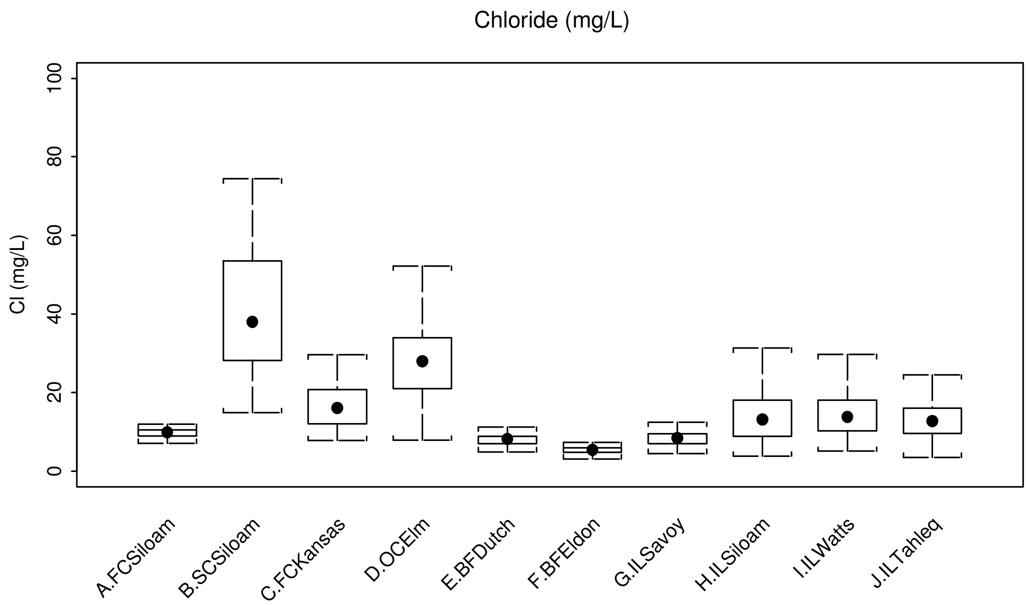


Fig SI-3: Boxplots summarizing Total Phosphorus and Chloride concentrations across the Illinois River and its tributaries (1997-2007) (for site codes and locations, see Fig SI-1).

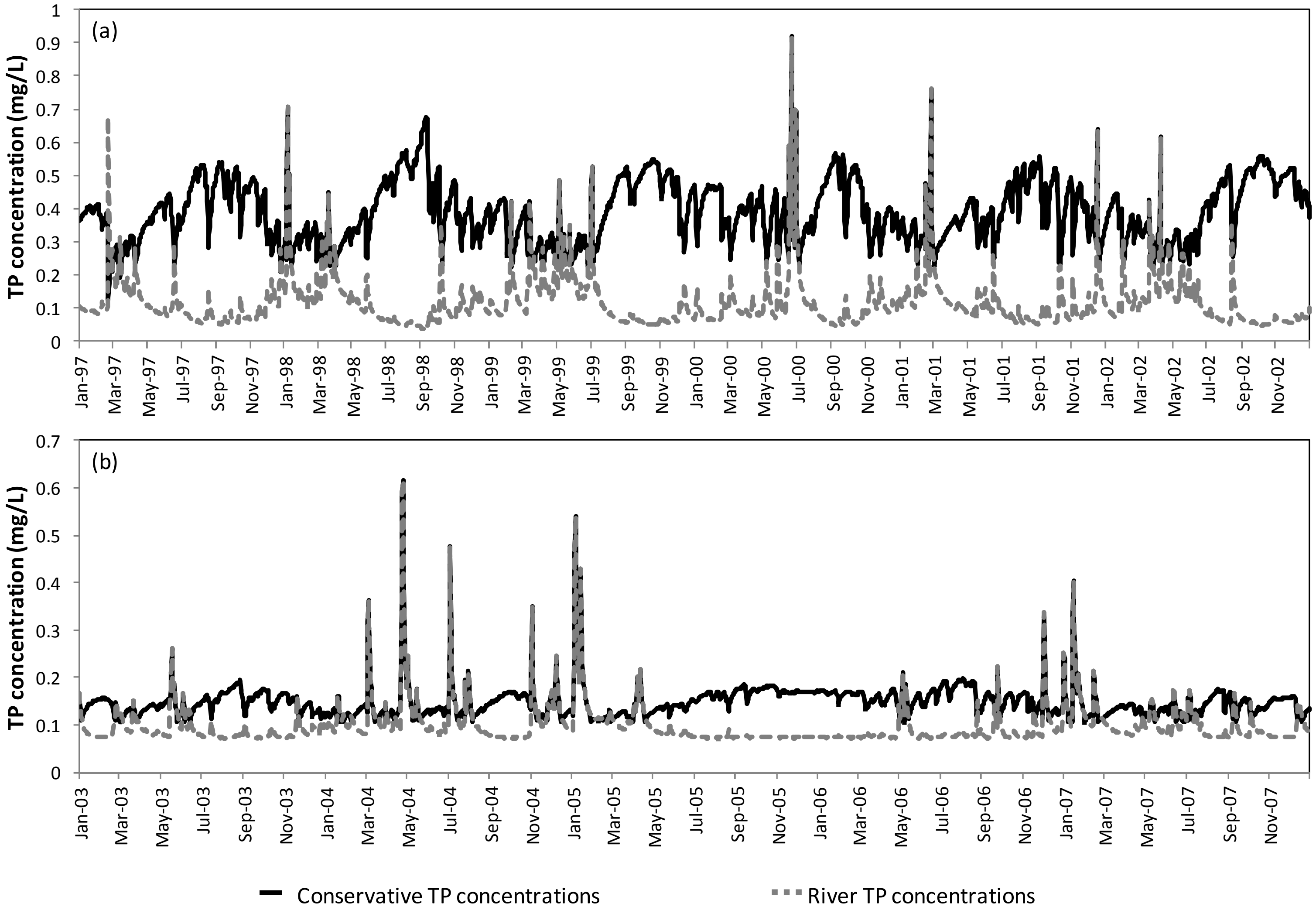
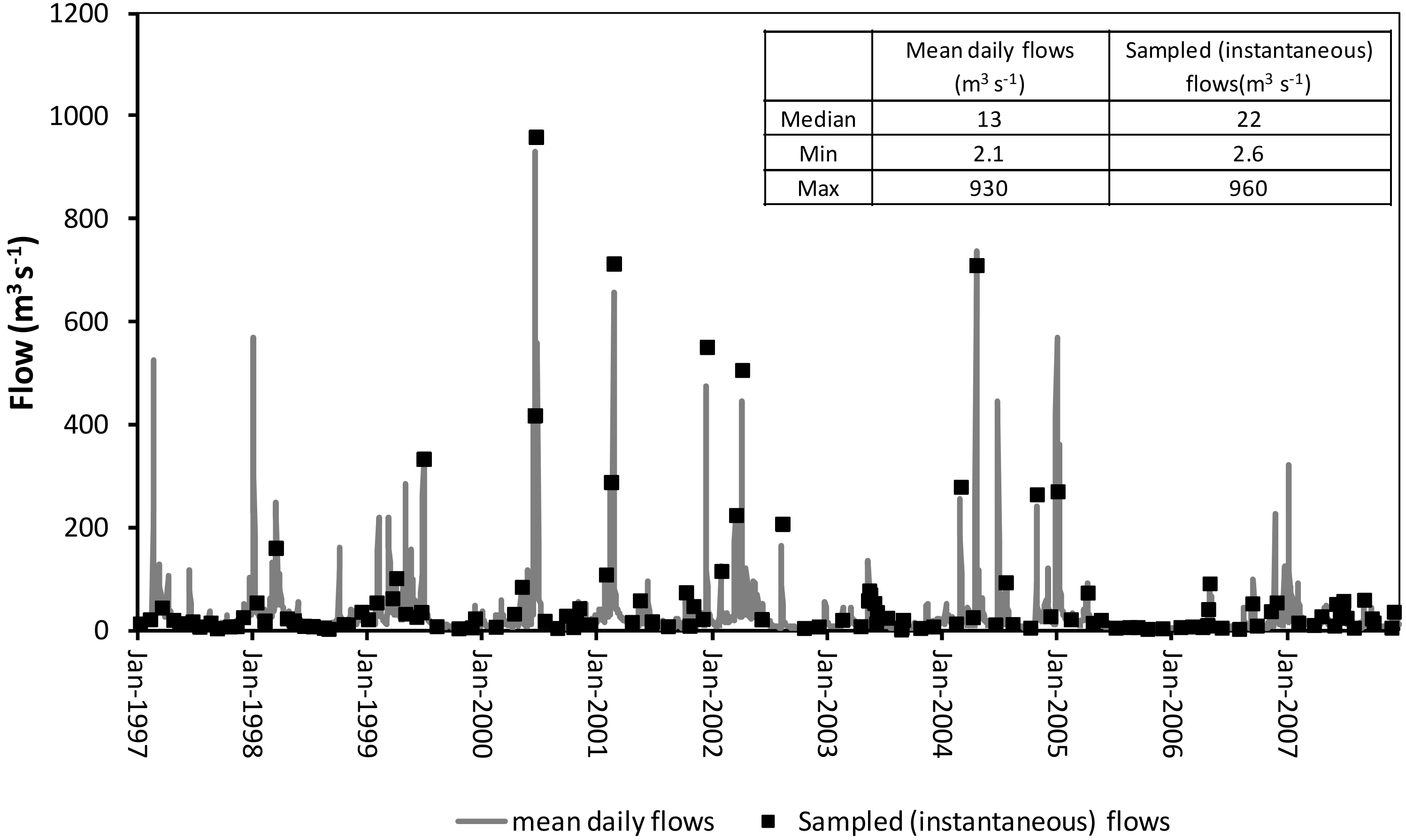


Fig SI-4: Modeled daily river TP and conservative TP concentrations in the Illinois River at Tahlequah (a) before P remediation at Springdale WWTP (b) after P remediation at Springdale WWTP



	Mean daily flows ($m^3 s^{-1}$)	Sampled (instantaneous) flows($m^3 s^{-1}$)
Median	13	22
Min	2.1	2.6
Max	930	960

Fig SI-5: Comparison of mean daily flows and instantaneous flows at the time of water-quality sampling, for the Illinois River at Tahlequah (1997-2007)

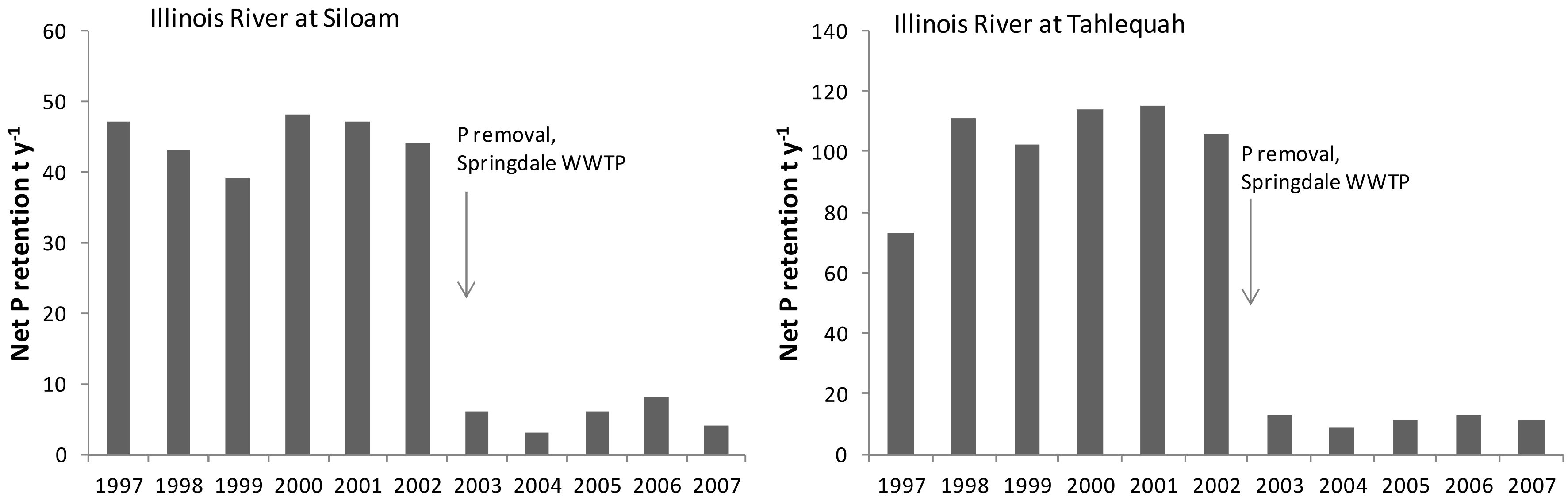


Fig. SI-6 Annual timeseries of in-stream effluent TP retention in the Illinois River at Siloam and Tahlequah

	Effluent TP loads (t-P yr^{-1})					
Year	Springdale	Rogers	Fayetteville	Prairie Grove	Gentry	Siloam Springs
1997	56	20.1	1.9	1.8	3.3	14
1998	53	9.7	2.5	1.8	3.8	14
1999	76	7.4	1.6	1.8	3.3	15
2000	101	4.0	2.3	1.5	3.5	15
2001	96	3.2	1.4	2.8	3.2	14
2002	73	3.9	1.8	1.2	2.9	12
2003	22	3.4	2.1	1.2	2.9	13
2004	12	3.9	2.7	1.4	4.0	11
2005	16	3.4	2.6	1.7	2.6	14
2006	9	3.8	3.1	2.0	2.2	13
2007	5	3.7	2.3	2.7	2.3	13

Table SI-1: Annual effluent TP loads (metric tonnes per year) for the wastewater treatment plants discharging into the Illinois River and tributaries upstream of Siloam and Tahlequah

	year	River TP load (t-P yr^{-1})	Conservative TP load (t-P yr^{-1})	Net within-river effluent TP load retention (t-P yr^{-1})	Baseflow TP load (t-P yr^{-1})	Stormflow TP load (t-P yr^{-1})	Contribution of retained effluent TP to annual river TP flux (%)	Contribution of retained effluent TP to river storm event TP flux (%)
Illinois River at Siloam	1997	147	194	47	18.4	129	32	37
	1998	221	264	43	18.4	203	19	21
	1999	237	276	39	18.4	219	16	18
	2000	212	260	48	18.4	194	23	25
	2001	194	241	47	18.4	176	24	27
	2002	180	224	44	18.4	162	24	27
	2003	43	49	6	10.7	32	14	19
	2004	225	228	3	10.7	214	1	1
	2005	118	124	6	10.7	107	5	6
	2006	67	75	8	10.7	56	12	14
	2007	87	91	4	10.7	76	5	5
Illinois River at Tahlequah	1997	147	220	73	11.9	135	50	54
	1998	228	339	111	11.9	216	49	51
	1999	234	336	102	11.9	222	44	46
	2000	336	450	114	11.9	324	34	35
	2001	243	358	115	11.9	231	47	50
	2002	156	262	106	11.9	144	68	74
	2003	48	61	13	9.7	38	27	34
	2004	247	256	9	9.7	237	4	4
	2005	140	151	11	9.7	130	8	8
	2006	54	67	13	9.7	44	24	29
	2007	97	108	11	9.7	87	11	13

Table SI-2: Annual river TP loads and effluent TP load retention in the Illinois River at Siloam and Tahlequah

	Withn-river effluent TP retention (kg-P km^{-1})	
	Upper watershed (Arkansas)	**Lower watershed (Oklahoma)**
1997	221	51
1998	202	133
1999	183	123
2000	225	129
2001	221	133
2002	207	121
2003	28	14
2004	14	12
2005	28	10
2006	38	10
2007	19	14

Table SI-3: Within-river TP retention normalised to river reach length

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