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

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ABSTRACT

The prevailing 'puzzle' in watershed phosphorus (P) management is how to account for the non-conservative behavior (retention and remobilization) of P along the land-freshwater continuum. This often hinders our attempts to directly link watershed P sources with their water quality impacts. Here, we examine aspects of within-river retention of wastewater effluent P and its remobilization under high flows. Most source apportionment methods attribute P loads mobilized under high flows (including retained and remobilized effluent P) as non-point agricultural sources. We present a new simple empirical method which uses chloride as a conservative tracer of wastewater effluent, to quantify within-river retention of effluent P, and its contribution to river P loads, when remobilized under high flows. We demonstrate that within-river P retention can effectively mask the presence of effluent P inputs in the water quality record. Moreover, we highlight that by not accounting for the contributions of retained and remobilized effluent P to river storm-flow P loads, existing source apportionment methods may significantly over-estimate the non-point agricultural sources and under-estimate wastewater sources in mixed land-use watersheds. This has important implications for developing

effective watershed remediation strategies, where remediation needs to be equitably and accurately apportioned among point and non-point P contributors.

INTRODUCTION

Phosphorus (P) is a major cause of freshwater eutrophication and associated impairment of water quality and ecology[1]. Across the world, ever greater scrutiny is being focused on the sources of P entering rivers and the effectiveness of remediation measures[1, 2]. In the U.S., total maximum daily loads (TMDLs)[3] have been implemented to attain target total phosphorus (TP) water quality criteria, through control of both point and non-point sources[4, 5]. Setting TMDLs and identifying remedial options relies on appropriate and accurate apportionment of P loads across the watershed. This usually necessitates empirical or modeling methods which link detailed data on land use, land management and P application rates, and wastewater effluent P discharges, with routine water-quality monitoring data which are used to calculate P loads in receiving waters[6]. Based on a wealth of evidence demonstrating the hydrologic controls on P transport and delivery[7-9], the widespread assumption is that P loads mobilized during storm events equate to non-point sources delivered via run-off and erosion from the land surface[10, 11]. Loads measured under low flows are assumed to equate to the contributions from point-source effluent discharges, together with any 'background' baseflow groundwater contributions[12, 13].

While there are increasing concerns about a 'global P crisis puzzle', linked to dwindling P resources[14], the prevailing 'puzzle' in watershed P management is the non-conservative behavior of P. This puzzle relates to its storage and remobilization across the land-freshwater continuum[15, 16], which consistently hinder attempts to directly link P source and impact[17, 18]. Storage and remobilization of P occur across a range of timescales and account for a large 'legacy' of P in watersheds. This means that loads measured at the watershed outlet can often reflect stored and remobilized 'intermediate' P sources rather than 'direct' P delivery from a particular watershed source[17].

'Within-river retention' encompasses a wide range of physical and biogeochemical processes which retain both point and non-point sources of P during downstream transport[19]. In this study, we focus on within-river storage and subsequent physical (flow-dependent) remobilization of P derived from wastewater treatment plant (WWTP) effluent. Within-river retention and cycling of effluent P, through a range of abiotic and biotic processes (e.g., sorption to stream sediments or uptake into periphyton), often represents a relatively short-term P store[20], typically retained in the order of weeks to months and remobilized during storm events[19, 21, 22]. Within-river P retention has an important influence on the timing of P delivery at the watershed outlet[19, 23, 24], and is responsible for large-scale reductions in effluent P concentrations and loads over short distances (just a few km), particularly under low-flow conditions when water retention times are highest[22, 25-27]. Although recent studies have alluded to the importance of physical remobilization of this stored effluent P during high flows [28, 29], the contribution to P budgets is rarely considered because of the difficulty of directly quantifying within-river effluent P retention at the watershed scale[30]. Physical remobilization of retained effluent P includes erosion of fine superficial bed sediments (to which P has sorbed), advective release of dissolved P in pore waters, or sloughing of biologically-incorporated P from benthic or attached periphyton Currently, most source apportionment methods attribute this effluent P, remobilized during high flows, to non-point agricultural sources. This potentially leads to over-estimation of P from agricultural sources and under-estimation of wastewater sources. Therefore, quantifying the contribution of stored and remobilized effluent P to storm-event and annual river P loads is a vital missing piece of the watershed P puzzle.

Here, we present a new simple empirical method which uses a routinely-measured analyte, chloride (Cl^-), as a conservative tracer of WWTP effluent[31-33], to quantify (i) the retention of point-source TP, and (ii) how this retained effluent P contributes to river TP loads mobilized under storm-flows and annual river TP loads at the watershed scale. This method complements earlier modeling approaches: river load apportionment modeling[6, 34, 35] and extended end-member mixing analysis (E-EMMA), which evaluates the aggregated effects of P retention and release on river TP fluxes from both point and non-point inputs, along the land-river continuum[16]. We examine (a) whether remobilization of retained effluent P provides a significant contribution to measured storm-event and annual river TP loads, and consequently (b) the risk that existing P source apportionment approaches may overestimate the contribution of non-point (usually agricultural) sources to measured river TP loads.

As a case study, we apply the method to the Illinois River Watershed (IRW), U.S., a mixed land-use watershed (c. 4330 km^2), which spans the states of Arkansas and Oklahoma. The IRW exemplifies regional, national and international concerns about P sources, their eutrophication impacts and the need to demonstrate and quantify the sources and the impacts of remediation measures at the watershed scale[36, 37]. Indeed, there are few watersheds in the world where P has received such intense scrutiny; in the IRW, there have been numerous and continuing lawsuits over P sources, between downstream water users and upstream land managers. Details of the watershed characteristics can be found in Haggard (2010)[36] and Scott et al (2011)[37] and so only a brief overview is provided here. The upper part of the IRW drains an area of northwest Arkansas which is one of the fastest growing metropolitan areas of the U.S. Agriculture in the IRW is dominated by poultry and beef cattle production. The portion of northwest Arkansas, in which the IRW is located, is the top producing area for beef cattle in Arkansas and second in the USA for poultry production behind Georgia[38, 39]. There were 1.04 billion birds reared in 2011 in about 1600 active poultry houses in the IRW[38, 40] , with about 30% of the poultry litter generally applied to pastureland in the IRW and the remainder exported out of the watershed[41, 42]. The Illinois River is impounded by the Lake Tenkiller dam and Lake Tenkiller has been subject to nuisance algal blooms since the 1970s[40]. Concerns that the aesthetic and recreational quality of the lake and river were being compromised by upstream land use activities in Arkansas, releasing P into the Illinois River, have led to a series of disputes and lawsuits, initiated by Oklahoma against Arkansas entities (see SI). These disputes have reached as far the U.S. Supreme Court[40, 43-46]. A crucial area of dispute in these lawsuits is the relative contribution of P sources at various points along the river network and entering Lake Tenkiller, and the impact of remedial measures on P loads and concentrations.

MATERIALS AND METHODS

Data

The USGS collects long-term streamflow and water quality data across the Illinois watershed (see http://waterdata.usgs.gov/ar/nwis/qw). We selected data from USGS sites where flow, TP and Cl concentration data were available at the same locality, with measurements on at least a monthly basis for a 10-year period (1997 through 2007). Our study focused on two key sites 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) (see supporting Information; SI)). Data from an additional eight USGS flow and water quality monitoring stations across the Illinois River and its tributaries were also examined; Fig SI-1). Details describing the USGS data resource for the

Illinois Watershed, and sampling and analysis protocols, are available in Haggard (2010)[36] and Scott et al (2011)[37].

Total P loads from municipal WWTP effluents were provided by individual facilities or from the Arkansas Department of Environmental Quality (Table SI-1). Improvements to wastewater treatment at Springdale WWTP in 2002 resulted in a major reduction in effluent P inputs to the Illinois River. Average annual effluent TP inputs declined at Siloam from 88 t-P yr^{-1} (1997-2002; units are metric tonnes, t) to 21 t-P yr^{-1} (2003-2007), and at Tahlequah from 105 t-P yr^{-1} (1997-2002) to 36 t-P yr^{-}. Improvements in wastewater treatment at Rogers WWTP were largely negated by increases in TP effluent loads from Springdale WWTP between 1997 and 2002.

Identifying the influence of effluent discharges and use of chloride as a conservative tracer of effluent P

Despite the urban land-use in the upper IRW and numerous WWTP discharges, the relationships between TP concentration and flow for the Illinois River at Siloam and Tahlequah showed no evidence of dilution with increasing flow, a pattern which is typical of point source P inputs[6, 47] (Fig 1a). Of the wider tributary monitoring sites (see Fig SI-2a), only one site showed a well-defined TP-flow dilution effect; this was located just a few hundred meters downstream of the effluent discharge from Siloam Springs WWTP on a headwater stream. Nevertheless, spatial patterns in TP concentrations showed higher average P concentrations at sites draining the major centres of population and WWTP discharges and these were mirrored by Cl^- concentrations, which also showed a dominant WWTP source (Fig SI-3). Chloride is commonly used as a tracer of sewage effluent, as (a) Cl^- concentrations in wastewater are greatly elevated above background riverine/groundwater concentrations and (b) Cl^- is chemically conservative and, unlike P, does not undergo significant uptake by sediments or biota [28, 31, 33, 48]. Boron has also been widely used as a tracer of wastewater effluent and could be used as an alternative tracer[13, 49, 50], but B was not routinely measured in the IRW. In contrast to TP, Cl^- showed a well-defined dilution pattern at all the monitoring sites, reflecting hydrological dilution of the effluent discharges with increasing river flow (Fig 1b; Fig SI-2b). The absence of dilution patterns in the TP concentration-flow relationships, therefore, belies the point source influence in these rivers; the low TP concentrations under low flows reflect very efficient within-river retention of effluent P, when water residence times are highest.

To examine the magnitude of within-river P retention, we used the riverine Cl^- concentrations to calculate 'conservative' TP concentrations (i.e. the concentration of TP if the effluent P were simply mixing conservatively with the river water, with hydrological dilution but no uptake by within-river processes). The 'conservative' TP concentrations were calculated by taking the ratio of TP:Cl^- entering the river from effluent discharges upstream of a monitoring station (Table 1), and applying this ratio to the river water Cl^- concentrations. For the IRW, Cl^- was not measured directly in effluent discharges. Therefore we took the river baseflow endmember Cl^- load (in this case, the mean Cl^- load for the lowest 25% of recorded river flows) as a surrogate for effluent Cl^- (Table 1). The average effluent TP:Cl ratio for the IRW was 0.03 before nutrient remediation at Springdale WWTP in 2002 and 0.008 afterwards. These TP:Cl ratios are fully consistent with direct measurements of final treated wastewater effluent elsewhere[33], demonstrating that the use of the baselow Cl^- load was, in this case, a suitable surrogate for effluent Cl^- discharge (also see SI).

Modeling approach

We compared river loads derived from measured river TP concentrations, with an estimate of corresponding 'conservative' TP loads (i.e. where TP from effluent discharges was only subject to hydrological dilution, with no in-stream retention processes). This allowed us 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. Both measured river TP concentrations and 'conservative' TP concentrations (derived from applying effluent TP:Cl^- ratios to the river water Cl^- concentration data) were modeled as a function of river flow (Fig 2a), according to Load Apportionment Model algorithms[6, 51, 52], and the details of the modelling approach and algorithms used here are provided in the SI. For the measured river TP concentrations, the loads of TP from 'continuous' or 'flow independent' inputs (typically point sources, which dilute with increasing flow) and 'flow-dependent' inputs (which are mobilized by increasing flow), were modeled as a power-law function of river flow. Conservative TP loads were modeled as continuous or flow independent source loads. A 'combined' TP model (Fig 2b), tracks the conservative TP model until Q_c is reached (the intersection of Conservative River TP models i.e. the point above which no net TP retention occurs), then tracks the River TP model above Q_c. TP retention is then modelled as the difference between the 'Combined' and River TP models.

Both the River TP and Combined models were then applied to the daily timeseries to generate daily river TP concentration and load timeseries (Fig SI-4). Annual river TP loads were derived by summation of the daily loads for each calendar year. The stormflow TP load was then calculated as the difference between the annual TP load and the annual baseflow TP load (where baseflow TP load was the average daily TP load for the lowest 25% of recorded river flows).

This method takes forward the existing Load Apportionment Modeling method[6, 51, 52], by accounting for within-river retention of the point source signal in the measured river TP concentrations. Using this method, we were able to quantify the contributions of stored and remobilized effluent P to storm event and annual river TP loads. There are two key assumptions, that:

(1) River TP concentration – flow relationships cover a fully representative range of flow conditions, such that, when applied to the daily flow timeseries, the modeled storm-event and annual river TP loads provide an accurate reflection of the actual annual river TP loads. In the case of the Illinois River, monitoring was typically monthly, with sampling also targeted at high flows. Supporting Information and Fig SI-5 show how this sampling protocol was effective in capturing a representative range of higher flows over the monitoring period. Additionally, to ensure best representation of the wider flow regime (i.e., a higher probability of capturing a greater range of river flows), the modeling was not undertaken on an annual basis, but using datasets collected over several years: six years before effluent P remediation (1997-2002) and five years post-remediation (2003-2007).

(2) Within-river effluent storage enters a short residence-time retention pool, which is fully flushed out of the river system on an annual time scale. This pool can includes P sorbed to fine sediment on the river bed and P which is taken up into periphyton. These in-channel P stores are among the first P sources to be mobilized when river flows increase[21]. Unlike non-point sources, delivery of in-channel stores is not reliant upon surface runoff generation and establishing hydrological connectivity between the source and the stream network. In the case of the Illinois River, much of the drainage network is via shallow rivers and tributary streams which have a high ratio of river-bed surface area to water volume and where light penetrates to the benthic interface. The river bed is largely armoured and lacks extensive fine surface sediment accumulation[53] Earlier studies have indicated that, in the Illinois

river, P uptake by periphyton (up to 8.14 µg P cm^{-2} day^{-1}) exerts a major control on within-river P retention[54]. Other studies have also shown that aquatic microbiota tend to dominate P retention in streams and rivers where the proportion of fine sediments is low[54].It is also postulated that periphyton sloughing off substrates during the frequent scouring events, export total P in biologically immobilized form and this may be a dominant mechanism for P export in these rivers[55]. However, even in more hydrologically-damped river systems (e.g., Chalk groundwater-fed rivers), and where the dominant process of P retention is uptake by fine sediment, the P storage times were only few months [22].

RESULTS AND DISCUSSION

Impacts of point-source P remediation on river TP concentrations and loads in the Illinois River

Annual TP loads in the Illinois River varied significantly according to weather conditions; the highest annual river TP loads occurred in 1999/2000 and 2004, which were wetter years with the greatest magnitude and frequency of storm events (Fig 3; Table SI-2). These external hydrological forcing effects had a much greater impact on annual TP loads than the reductions in effluent inputs (Fig 3). Although the effectiveness of P remediation measures are typically assessed through 'before and after' comparisons of river P loads and concentrations; these are often misleading because of year-to-year variability in weather[56]. The relationships TP concentration and flow, and TP load and flow before and after effluent P remediation (Fig 4) allow any differences in load or concentration for a specific flow to be evaluated and quantification of P remediation impacts, independent of any variability in hydrology. Figure 4 shows that, at both Siloam and Tahlequah, there was a well-defined reduction in TP concentrations and loads relative to flow after 2002. Therefore, independent of external hydrological forcing effects, P remediation had a significant impact in lowering TP loads and concentrations. The greatest impact of effluent P remediation in reducing TP concentrations and loads in the Illinois River was at intermediate to high flows rather than under baseflow conditions. This was surprising as the greatest impact of effluent P is often under baseflow conditions, when hydrological dilution is lowest. There are, therefore, two possible explanations for these results: (1) effluent P remediation reduced in-channel P storage, resulting in lower TP concentrations remobilized under intermediate to higher flows; and (2) other non-point P remediation measures, such as implementation of land-based best management practices, may have reduced P concentrations and loads over the same time period.

To investigate the relative importance of point and non-point remediation during this time, a very simple mass balance was calculated for 1997-2001 and 2004-2007 (Table 2). This showed that, on average, point source remediation accounted for a greater proportion of reductions in average annual river TP load than non-point source reductions (60% of the annual river TP load at Siloam and 68% at Tahlequah). Correspondingly, reductions in non-point source P inputs to the Illinois River accounted for 40% and 32% of the decrease in annual river TP loads at Siloam and Tahlequah, respectively. Unlike the TP load-flow and TP concentration-flow relationships, these mass balance comparisons do not take account of variations in weather, so at least some of the reduction in non-point source contributions may result from changes in external hydrological forcing.

Within-river retention of effluent TP loads

Within-river retention of effluent P accounted for losses in river TP load of up to c. 100 t-P yr^{-1} at Tahlequah and up to c. 50 t-P yr^{-1} at Siloam (Fig 3; Fig SI-6; Table 1). At both Siloam and Tahlequah, within-river retention of effluent TP dropped dramatically (by a factor of c. 9) after 2002, as a result of enhanced nutrient removal at Springdale WWTP and the resulting reductions in effluent P input loading. Earlier studies have suggested that P uptake by periphyton exerts a major control on within-river P retention in the Illinois River[54]. The decline in P retention with decreasing effluent P load also suggests a biological control mechanism: reductions in effluent P inputs may reduce the periphyton biomass that can be supported, thus leading to a decline in P retention. This has potentially important implications for achieving P criteria in the Illinois River, since further reductions in P inputs may simply serve to further limit biological P retention and result in diminishing returns in improving baseline P concentrations.

Throughout the monitoring period, within-river retention of TP at Tahlequah was approximately twice as high as at Siloam (Fig 3; Fig SI-6; Table SI-2). This reflects the longer river reach lengths and time-of-travel to Tahlequah (greater opportunity for P retention), and also higher effluent inputs (additional effluent loadings from Siloam Springs and Gentry WWTPs via Flint Creek tributary; Fig SI-1; Table SI-2). However, when reach length (i.e., total distance travelled along the river network from each WWTP effluent input to the monitoring point) was taken into account, within-river retention of effluent P was, on average, 45% lower in the lower reaches of the Illinois River, downstream of Siloam (Table SI-3). This is consistent with higher rates of nutrient retention in smaller tributaries and headwater streams, where shallower water, light penetration to the benthic interface and lower water volume to benthic surface area provide greater potential for biological P uptake[19]. These results also support the P spiraling concept, where the majority of P transport should occur in the form of particulate P[57].

Although annual river TP loads showed large year-to-year variability, within-river retention of effluent P remained relatively constant at both sites before and after effluent P remediation (Fig 3; Fig SI-6; Table SI-2). For example, the coefficients of variation in TP retention at Tahlequah were 15% for both 1997-2002 and 2003-2007, compared with 31% and 70% of the corresponding annual river TP loads at Tahlequah. This indicates that the processes of within-river retention of effluent TP were decoupled from the total annual riverine P fluxes, which were largely mobilized during storm events.

Impacts of within-river effluent TP retention and remobilization on river TP concentrations and loads

By comparing the conservative TP concentrations with the modeled river TP concentrations (Fig SI-4), it is clear that within-river processes, which retain effluent P, have a major impact in reducing TP concentrations, particularly under baseflow conditions (Table 3; Fig. SI-4). Conservative baseflow TP concentrations were up to c. 0.5 mg-P L^{-1} before effluent P-remediation and up to c. 0.2 mg-P L^{-1} afterwards. In contrast, river baseflow TP concentrations were typically below c.0.1 mg-P L^{-1} throughout the monitoring period (Table 3). Total P concentration-flow relationships are often used as a simple water-quality screening tool to assess the influence of point and non-point source influences in rivers[13, 47, 58]. However, the results from the Illinois River clearly demonstrate how these TP-flow relationships can underestimate the true influence of point sources, owing to the retention and removal of TP from the water column under low flows. Here, within-river P retention was capable of reducing P concentrations under low flows, to the extent of eliminating the diagnostic point-source P dilution pattern with increasing river flow. Within-river effluent P retention therefore provides an important ecosystem service by dramatically reducing the concentrations of TP to downstream reaches (by up to several hundred µg-P L^{-1}) during the most ecologically sensitive low-flow conditions. After effluent P remediation within-river P retention reduces ambient P concentrations to levels which, while still above the numerical water standard adopted by Oklahoma, may still be capable of limiting nuisance algal growth[59, 60].

Under storm-flow conditions, the retained effluent P becomes physically remobilized effluent P. Net effluent TP load retention, in absolute terms, remained relatively constant from year to year, both before and after effluent P remediation. However, the percentage contribution of the remobilized effluent TP to annual river TP loads and to annual river stormflow loads varied with year-to-year changes in weather and hydrological forcing (Fig 3; Table SI-2). Prior to effluent P remediation (i.e., 1997-2002), remobilized effluent P contributed an average of 21% (and up to 32%) of the annual river TP flux at Siloam, and an average of 26% (and up to 37%) of the annual storm-flow TP load at Siloam. At Tahlequah, the contributions of remobilized effluent P were higher, accounting for an average of 49% (and up to 68%) of the annual river TP load and an average of 52% (and up to 74%) of the annual storm-flow river TP load. Conventional source apportionment approaches would (mistakenly) attribute this remobilized effluent P to non-point, usually agricultural, sources.

After effluent P remediation, the absolute and percentage contributions of remobilized effluent TP to river TP loads fell. However, there was large year-to-year variability: between 2003 and 2007, remobilized effluent P contributed between 1% and 19% of the annual stormflow load at Siloam and between 4 and 34% of the annual storm flow load at Tahlequah. In wetter years, remobilized effluent P contributed a negligible contribution to river TP loads in wetter years. However, during drier years, retained and remobilized effluent P contributed up to a third of river TP loads. Nevertheless, after P remediation, irrespective of how wet or dry the year was and the magnitude of river TP loads, within-river retention still had a major impact on reducing ecologically-critical baseflow TP concentrations in the Illinois River by c. 0.1 mg-P L^{-1} to potentially ecologically-limiting levels of c. 0.05 – 0.07 mg-P L^{-1} [60, 61].

Wider implications

This study shows that the remobilization of retained effluent P can potentially provide a major contribution to the measured storm-flow and annual TP loads. For the Illinois River, the contribution of remobilized effluent P to river P loads was greatest before point source remediation. Nonetheless, remobilized effluent P could account for up to a third of stormflow TP loads, even after remediation and during the driest years. The major puzzle in watershed P management is how to account for the non-conservative behaviour (storage and remobilization) of P along the land-freshwater continuum, in order to identify and target sources for P remediation most effectively. Within-river P retention and its subsequent remobilization is a key missing piece in this watershed P puzzle, as it exerts a major control on magnitude and timing of downstream delivery of riverine P loads and concentrations. Also, remobilized effluent P is generally mistaken for non-point P from agricultural sources. Critically, retention and remobilization of P within the stream / river continuum still remains a black box in models, which are used in setting TMDLs for impaired waters[62]. This piece of the P puzzle must be better defined to determine reliable source load allocations from which to derive target P load reductions as part of watershed implementation plans to restore desired water quality [63]. Failing to adequately account for within-river retention and remobilization of effluent P, will continue to hinder accurate estimation of P source load allocations in watersheds and further contribute to contentious TMDL development and implementability. We show how the use of Cl^- as a conservative tracer of wastewater effluent, allowed us to directly quantify within-river effluent P retention and its impact on river TP loads and concentrations at the watershed scale, to provide this vital information. Further studies are now required to evaluate this approach and its assumptions across a wider range of river and watershed environments.

We demonstrate that within-river P retention can effectively mask the presence of point source P inputs in the water quality record. Moreover, we highlight that, by not accounting for the contributions of retained and remobilized effluent P to river storm-flow TP loads, existing source apportionment methods can significantly over-estimate the contributions of non-point agricultural sources to river TP loads in mixed land-use watersheds. Clearly, this has important implications for development of effective watershed remediation strategies, where remediation needs to be equitably and accurately apportioned among point and non-point P contributors and stakeholders. Unless this piece of the P puzzle is solved watershed remediation to address local and regional water quality impairments will remain flawed, continue to attract litigation, and limit successful outcomes.

SUPPORTING INFORMATION

Information about monitoring sites in the IRW and patterns in TP and Cl^- concentrations; background to the lawsuits and numerical P criteria development in the IRW; model algorithms; daily timeseries TP model output; tables of annual TP effluent and river loads and within-river effluent TP retention. This information is available free of charge via the Internet at http://pubs.acs.org.

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	Siloam		Tahlequah	
	Effluent TP load (t-P yr^{-1})	Efluent TP:Cl	Effluent TP load (t-P yr^{-1})	Effluent TP:Cl
1997	80	0.030	98	0.034
1998	67	0.025	85	0.029
1999	86	0.033	105	0.036
2000	109	0.041	127	0.044
2001	104	0.036	121	0.031
2002	80	0.028	95	0.025
2003	29	0.01	44	0.011
2004	20	0.008	35	0.009
2005	24	0.009	40	0.01
2006	18	0.006	34	0.008
2007	13	0.005	29	0.007

Table 1: Yearly average effluent TP loads (metric tonnes P per year) and average TP:Cl ratios in WWTP effluent discharges to the Illinois River at Siloam and Tahlequah

	Reduction in average river TP load (t-P yr^{-1})	Reduction in point source TP load (t-P yr^{-1})	Reductions in non-point source TP load (t-P yr^{-1})	Non-point source reductions, expressed as % of river TP load reductions
Siloam	116	69	47	40
Tahlequah	107	72	34	32

Table 2 Reductions in (i) average river TP load, (ii) point source TP load and (iii) non-point TP load (by difference, (i)minus (ii)), comparing the period 1997-2001 with 2004-2007 for the Illinois River at Siloam and Tahlequah

		Mean river baseflow TP (mg L^{-1})	Mean conservative baseflow TP (mg L^{-1})
Siloam	1997-2002	0.134	0.361
	2003-2007	0.073	0.194
Tahlequah	1997-2002	0.058	0.508
	2003-2007	0.074	0.172

Table 3 Mean TP concentrations under baseflow conditions from the river TP model and conservative TP model for the Illinois River at Siloam and Tahlequah, before point-source P remediation (1997-2002) and after remediation (2003-2007).

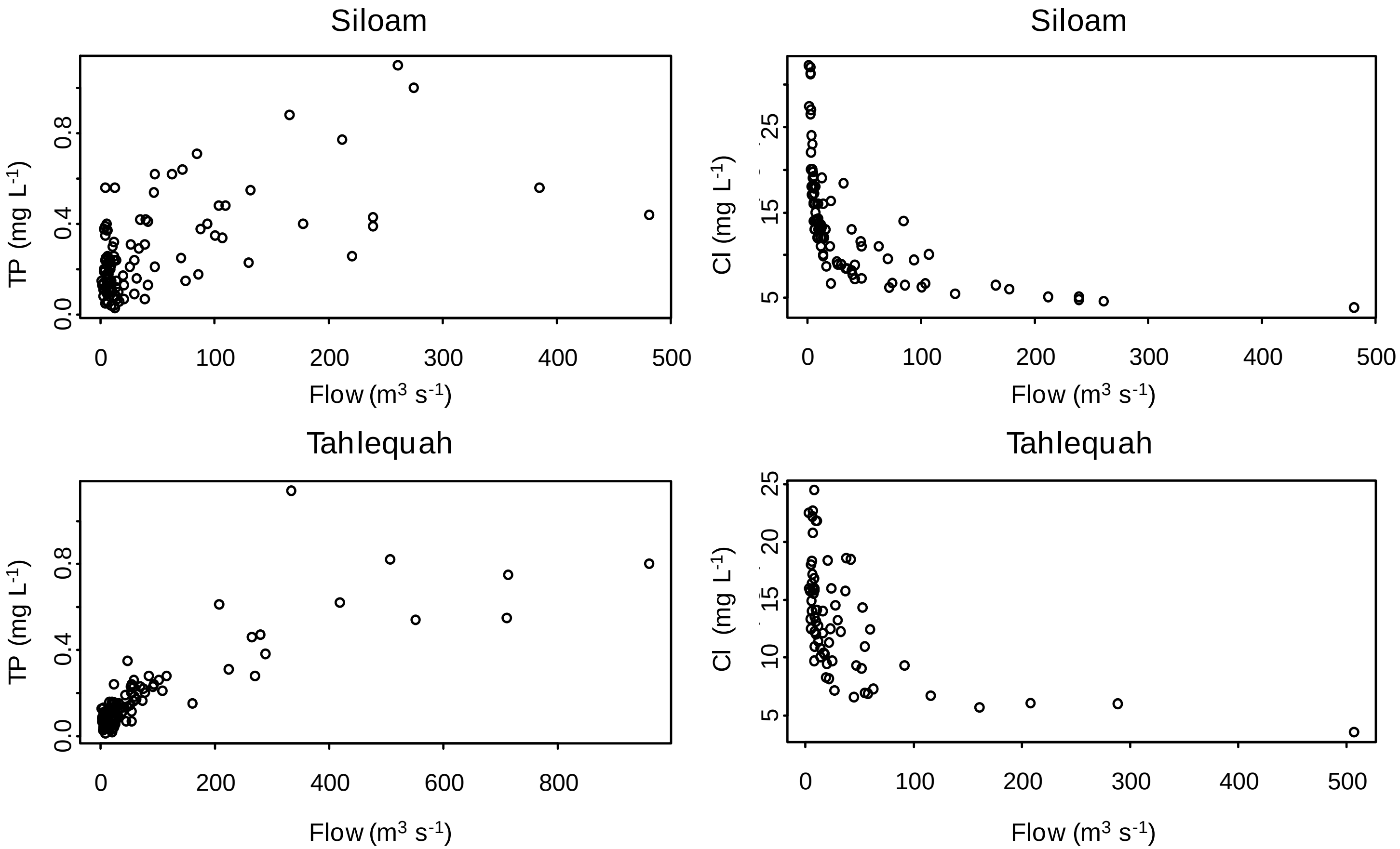

Fig 1: Relationships between (a) river TP concentrations and flow and (b) river Cl^- concentrations and flow, for the Illinois River at Siloam and Tahlequah

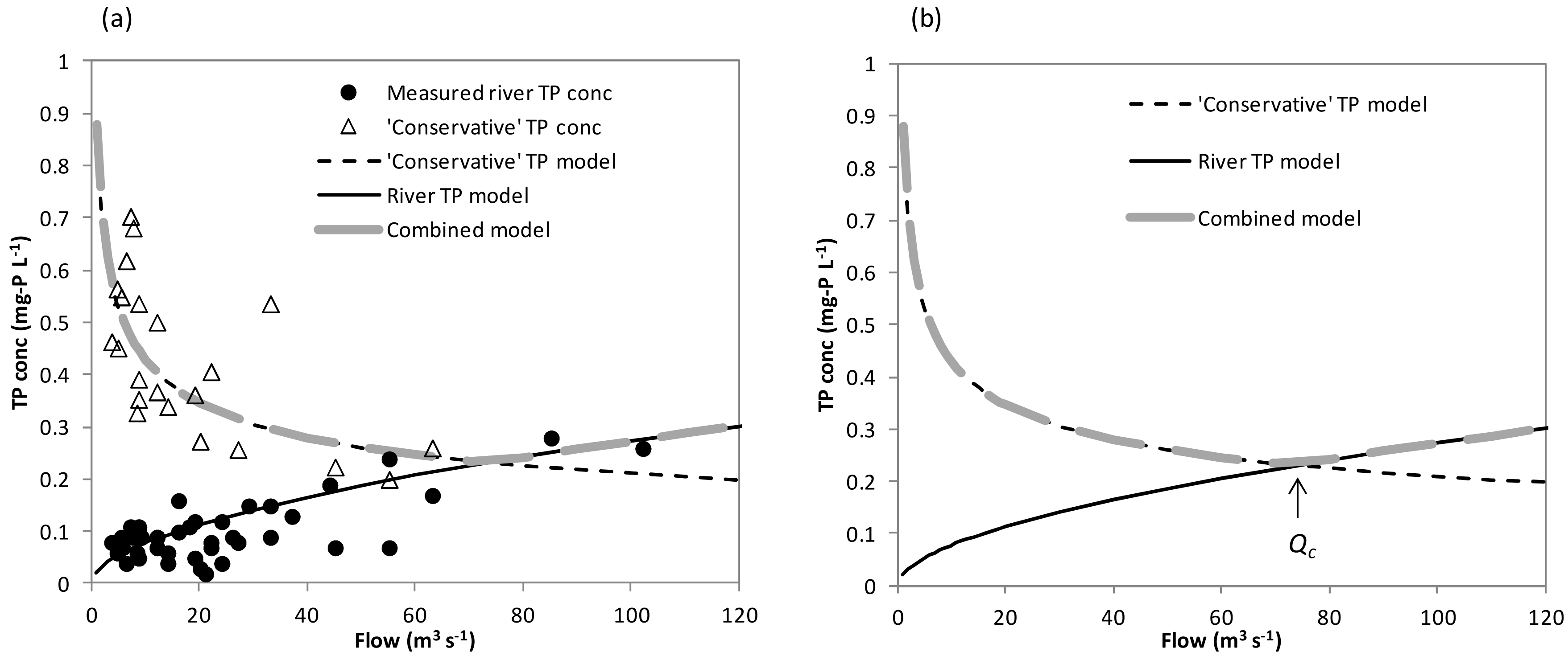

Fig. 2: Modeling P retention in the Illinois River at Tahlequah (1997-2002):

(a) model fits to the Measured (River) data and Conservative TP data (derived from the conservative Cl tracer);

(b) model fits showing Q_c which denotes the intersection between the Conservative and River TP models i.e. the threshold flow above which no net TP retention occurs. The 'Combined model' tracks the Conservative model until Q_c is reached, then tracks the River TP model. Within-river TP retention is therefore modeled as the difference between the Combined and River TP models.

N.B. A restricted flow range is presented (up to 120 $m^3 s^{-1}$) to show more clearly the intersection of the River TP and Conservative TP models and the effects of within-river P retention on TP concentrations under low flows.

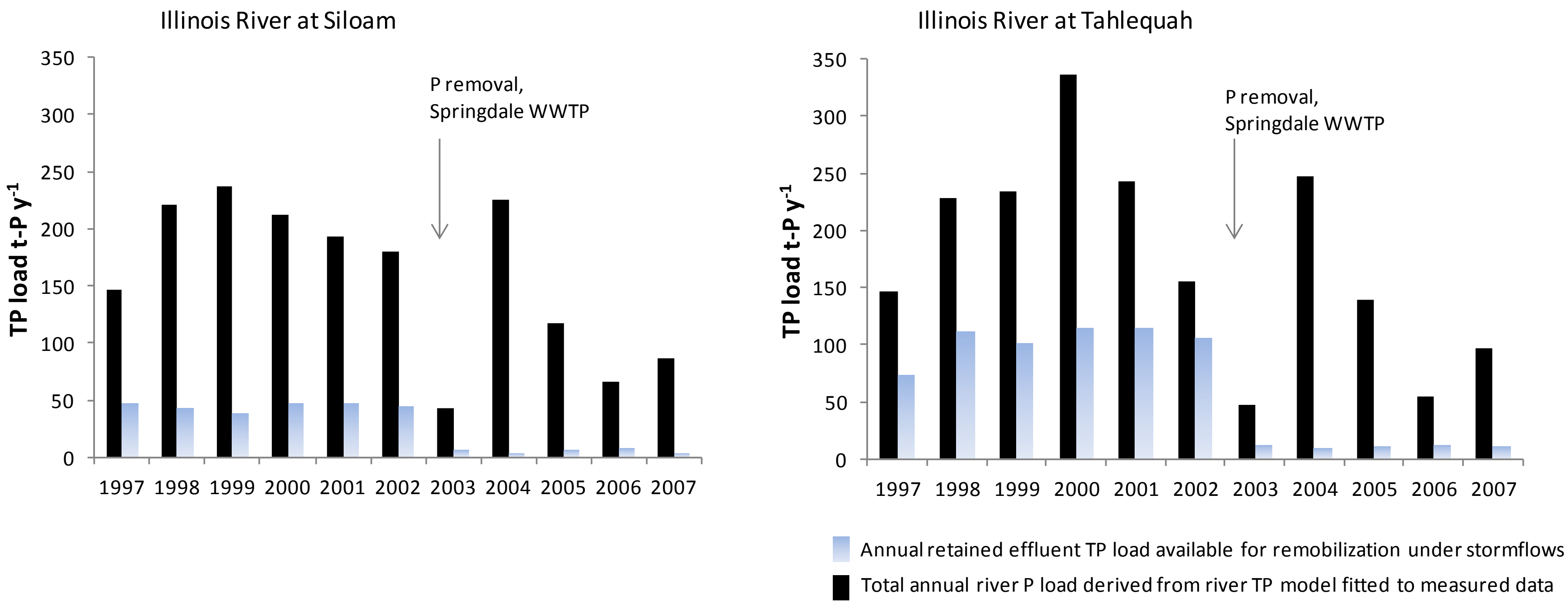

Fig. 3 Annual timeseries of total P load and the retained effluent P load in the Illinois River at Siloam and Tahlequah
(the annual timeseries of retained effluent P, presented at an expanded scale, is shown in the Supporting Information, Fig SI-6)

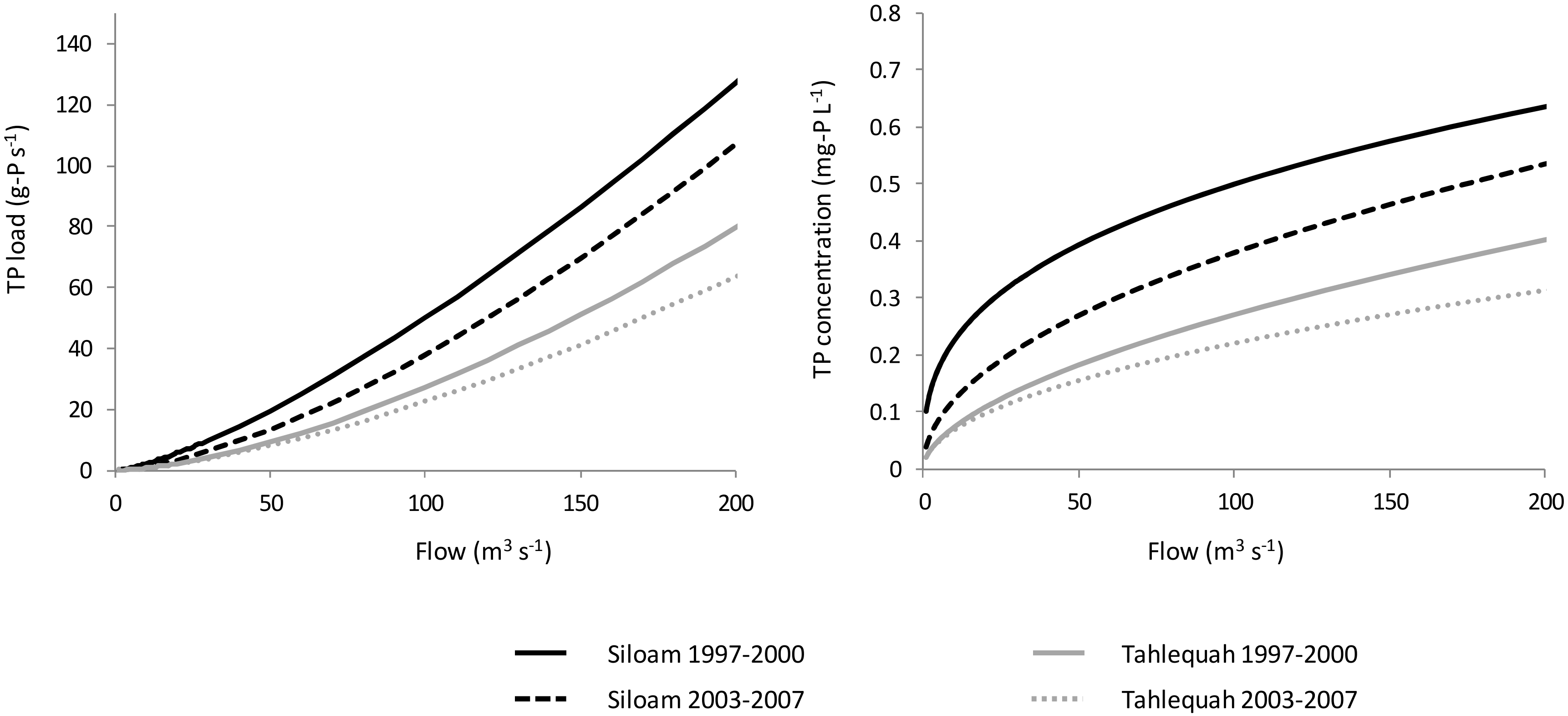

Fig 4: River TP model output load-flow and concentration-flow plots for the Illinois River at Siloam and Tahlequah