Quantifying Phosphorus Retention and Release in Rivers and Watersheds Using Extended End-Member Mixing Analysis (E-EMMA)

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Extended end-member mixing analysis (E-EMMA) is presented as a novel empirical method for exploring phosphorus (P) retention and release in rivers and watersheds, as an aid to water-quality management. E-EMMA offers a simple and versatile tool that relies solely on routinely measured P concentration and flow data. E-EMMA was applied to two river systems: the Thames (U.K.) and Sandusky River (U.S.), which drain similar watershed areas but have contrasting dominant P sources and hydrology. For both the Thames and Sandusky, P fluxes at the watershed outlets were strongly influenced by processes that retain and cycle P. However, patterns of P retention were markedly different for the two rivers, linked to differences in P sources and speciation, hydrology and land use. On an annual timescale, up to 48% of the P flux was retained for the Sandusky and up to 14% for the Thames. Under ecologically critical low-flow periods, up to 93% of the P flux was retained for the Sandusky and up to 42% for the Thames. In the main River Thames and the Sandusky River, in-stream processes under low flows were capable of regulating the delivery of P and modifying the timing of delivery in a way that may help to reduce ecological impacts to downstream river reaches, by reducing ambient P concentrations at times of greatest river eutrophication risk. The results also suggest that by moving toward cleaner rivers and improved ecosystem health, the efficiency of P retention may actually increase.

Throughout North America and Europe, requirements to protect the ecological status of surface waters and reduce river and lake eutrophication have resulted in increasing scrutiny and regulatory controls on phosphorus (P) sources entering rivers (USEPA 1998, 2008; EC, 2000; Neal and Jarvie, 2005). Phosphorus enters the hydrographic network of ditches, streams, and rivers in different forms, at different times, and at variable locations within the watershed and is subject to "landscape filtering" (attenuation and processing) along the watershed–river continuum (Heathwaite, 2010; Smith, 2009). The downstream ecological impacts of these variable P inputs are heavily dependent on the extent to which they are physically retained and/or chemically and biologically processed (Edwards and Withers, 2007; Withers and Jarvie, 2008). The net effects of the attenuation, retention, and processing of P are poorly understood and rarely considered in watershed management, where the primary focus is on source control. However, in-stream processing of P fluxes may account for the apparent disconnect between measures implemented to reduce P inputs and improvements in water quality and ecology at the watershed scale (Sharpley et al., 2009). A better understanding of the net effects of P retention and release in watersheds is of central importance for managing streamwater quality and ecology and for targeting remediation and restoration measures most effectively.

New analytical technologies are greatly advancing our understanding of the biotic and abiotic processes controlling P-cycling at the molecular- to microscale, such as synchrotron X-ray fluorescence spectromicroscopy (Diaz et al., 2009) and P-31 nuclear magnetic resonance spectroscopy (Cade-Menun et al., 2006). New in situ monitoring techniques for measuring sediment–water P fluxes such as diffusive equilibrium in thin film technology (Jarvie et al., 2008; Palmer-Felgate et al., 2010), high-resolution bankside water P analyzers (Jordan et al., 2007; Palmer-Felgate et al., 2008), and detailed in-stream nutrient spiraling and process studies (Demars, 2008; Stutter and Lumsdon, 2008) are providing greater detail on mechanisms of P flux regulation at the river reach scale. However, such interactions between sediments, biota,

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Abbreviations: EMMA, end-member mixing analysis; E-EMMA, extended end-member mixing analysis; PP, particulate phosphorus; Q, flow; SRP, soluble reactive phosphorus; STW, sewage treatment works; TP, total phosphorus; TRP, total reactive phosphorus.

and river water are highly heterogeneous, and detailed process studies are by necessity small-scale relative to whole watersheds. Scaling up to quantify the significance of these effects on P delivery at the watershed scale remains a fundamental analytical and conceptual challenge.

Traditionally, watershed nutrient mass balance modeling to quantify delivery, retention, and release of P at the watershed outlet relies on detailed geographical data on land use, fertilizer inputs, and livestock numbers, as well as point source inputs. These inputs are used to estimate P export from all nonpoint and point sources within the watershed. The P export estimates are then compared with stream and river P loads to infer crude net gains or losses within the hydrographic network of ditches, streams, and rivers, usually on an annual timescale. However, large uncertainties in P inputs, export, and storage, especially for large watersheds, mean that P delivery estimates are subject to considerable uncertainty, and there are lag times that are poorly defined (Moss et al., 1988; Marcé and Armengol, 2009). Process-based semidistributed watershed simulation models, which rely on complex mathematical algorithms for nutrient export and delivery, are usually calibrated against observed river nutrient data. Deviations between observations and model outputs are often simply compensated for by varying nutrient retention and/or watershed process rates, and the modeled systems are often overparameterized (Wade et al., 2008; Hejzlar et al., 2009). Improved understanding of the variability and controls on nutrient retention capacities at the watershed scale has been identified as a major research need to support water-quality modeling and to understand the downstream impacts of macronutrient cycling and transport (Marcé and Armengol, 2009).

In this study, we present a simple empirical approach for quantifying P delivery, by taking forward the extended end-member mixing analysis approach (E-EMMA; Neal et al., 2010a) to explore P net retention and release along the watershed–river continuum. This new approach enables us to utilize existing routine water-quality monitoring data to quantify the impacts of in-stream and in-watershed P processing on P delivery at the watershed scale. E-EMMA can also be used to examine the scale and variability of P retention and release, as an aid to watershed management. The methodology has widespread applicability, as it relies solely on routinely measured water chemistry and flow data. E-EMMA does not require any geographic information system (GIS) land use, population, or livestock density data nor does it rely on any estimates of nutrient export. Here, we compare P delivery for two major river systems: the River Thames (U.K.) and Sandusky River (U.S.). These rivers were chosen because they drain very similar watershed areas but have contrasting dominant P sources and hydrology. We used E-EMMA to explore P retention and release characteristics within the two watersheds and the impacts of P mitigation measures on patterns in P retention/release.

Materials and Methods
Study Areas

The Sandusky watershed (3240 km^2) drains into the shallow southwestern part of Lake Erie, which has been subject to major eutrophication problems since the late 1960s, including hypoxia in late summer and extensive blooms of *Cladophora* and cyanobacteria (Richards et al., 2008). The Thames at Wallingford (3448 km^2) flows via London and the Thames estuary into the southernmost portion of the North Sea. Algal blooms and eutrophication are major problems in the lower slow-flowing reaches of the River Thames, where long residence times during the summer favor development of cyanobacteria, which are associated with the production of microcystin toxins (Ruse and Love, 1997, Johnson et al., 2009).

The geology of the Sandusky watershed is predominantly limestone, dolomite, and shale of Silurian and Devonian age. Glacial drift and lacustrine deposits are thin, with relatively low permeability. In contrast, the Thames drains the more permeable lithologies of Jurassic Limestone and Cretaceous Chalk, with a much higher groundwater contribution to flow than for the Sandusky. This is reflected in the hydrology of the two watersheds: the Sandusky is characterized by a much flashier flow regime, with a Richards-Baker (R-B) flashiness index (Baker et al., 2004) of 0.37, compared with a R-B index of 0.13 for the Thames, indicating a greater groundwater component.

Land use in the Thames compared with the Sandusky shows broadly similar proportions of agricultural, urban, and forest land (Table 1). Land use in the Sandusky watershed is predominantly arable: corn (*Zea mays* L.), soybean [*Glycine max* (Merr.) L.], and wheat (*Triticum aestivum* L.) production. By contrast, the Thames has a much lower proportion of arable land, with a higher proportion of the agricultural land used for livestock grazing. Arable land use in the Thames is predominantly wheat, oilseed rape (*Brassica napus* L.), and fodder maize (*Zea mays* L.). The Thames watershed has a population density approaching 1000 km^{-2} (Evans et al., 2003), with urban settlements of Swindon, Oxford, Bicester, and Abingdon all located along the main stem of the Thames or on the major tributaries. The Sandusky watershed has a population density of ~45 km^{-2}, with the population concentrated in the urban settlements of Bucyrus, Fremont, Tiffin, and Upper Sandusky (OH).

For both the Thames and Sandusky rivers, large-scale watershed management interventions have attempted to reduce eutrophication by reducing P inputs to limit algal productivity. For the Thames, attention has been directed at reducing point-source inputs from sewage treatment works (STWs), by major investment in tertiary wastewater treatment over the last decade. Chemical dosing (typically with ferric chloride) to reduce P concentrations in final effluent began in 1999 and continued through the following decade (Neal et al., 2005, 2010a). To examine the impacts of point-source P remediation on net P retention or release in the

Table 1. Summary of land use characteristics for the Thames, Sandusky, and Cherwell watersheds.

River	Catchment area	Cropland	Grassland	Urban	Forest
	km^2			%	
Thames	3445	47	34	7	11
Sandusky	3420	78	2	8	9
Cherwell	552	33	50	6	9

Thames, data are presented for 3 yr: 1998 (before introduction of tertiary treatment), 1999 (after the commencement of tertiary treatment), and 2006 (after widespread introduction of tertiary treatment). Data are also presented for a second site in the Thames basin: the River Cherwell (552 km²), just downstream of the town of Banbury, receives wastewater from a major food processing plant with correspondingly high organic loadings in the sewage effluent. Major upgrades to effluent treatment at Banbury STW took place in February 2001, and river monitoring data are presented for the immediate aftermath of P remediation until June 2002. The proportions of agricultural land, urban land, and forest in the Cherwell are similar to those in the wider Thames watershed (Table 1).

For the Sandusky, point sources are of lesser significance for watershed P budgets compared with the Thames, and remediation has focused on introduction of cost-effective measures to reduce P loading from agricultural land. Since the 1970s, there has been widespread introduction of conservation tillage and other measures to reduce erosion and transport of sediment and particulate P. Since 1975, conservation tillage increased from virtually zero to nearly 50% of cropland in corn and soybean in 1995 (Richards et al., 2002). At present, about 80% of soybean and wheat receive conservation tillage, but only about 30% of the corn does.

A 35-yr water-quality data record has been collected on the Sandusky as part of a major initiative to monitor nutrient inputs to Lake Erie (Richards et al. 2009). For this study, 3 yr of data from the Sandusky were chosen to evaluate effects of P retention and release on delivery at the watershed outlet: 1975 (before widespread introduction of conservation tillage and point-source remediation), 1998 (after widespread introduction of conservation tillage and point-source remediation, but with similar flow patterns to 1975), and 2006 (after widespread introduction of conservation tillage and point-source remediation, but a higher flow year).

Extended End-Member Mixing Analysis

In this study, we applied E-EMMA to explore the net P retention and release along the watershed-river continuum. In the original version of end-member mixing analysis (EMMA; Christophersen et al., 1990), concentrations of a chemical pollutant were plotted against a conservative tracer, such as chloride. These relationships were used to examine whether the pollutant behaved conservatively (i.e., did not undergo in-stream uptake or release) during mixing of baseflow and stormflow "end-member" waters of differing chemical composition. A linear two-component mixing series between baseflow and stormflow end-members is observed if the pollutant behaves conservatively. With E-EMMA, a similar process is used, except that the flux of the pollutant (P) is plotted against flow for the two component mixing series. The underlying assumption is that there are two dominant and distinct sources of water (both with different P concentrations) contributing to P fluxes at the watershed outlet: (i) a baseflow end-member source composed largely of effluent and/or groundwater, and (ii) a stormwater end-member source composed of an integrated watershed-wide nonpoint source that, under the highest flows, is delivered directly to the watershed outlet. As for EMMA, when the two water sources mix, a linear relationship between baseflow and stormflow P flux end-mem-

bers would indicate that P was behaving conservatively, that is, that P was not undergoing significant net uptake or release as a result of deposition of particulate P, remobilization of P, sorption to sediments, or interaction with biota. In contrast, a nonlinear mixing series would indicate that P was behaving nonconservatively (i.e., was therefore subject to physical or biogeochemical retention or release). Nonlinear behavior under low-flow conditions is assumed to result from within-river processes, whereas nonlinear behavior under intermediate and higher flows represents the net effects of both in-stream and watershed retention/ mobilization. By comparing an observed nonlinear relationship between river P flux and river flow measurements, with a theoretical linear conservative mixing series between the baseflow and stormflow end-member P fluxes, the net effects of P retention and release can be directly quantified (Fig. 1). This type of analysis can be conducted for different forms of P, over different timescales and for different reaches along the river system, providing a useful means of evaluating sources, and the temporal and spatial dimensions to nutrient delivery. E-EMMA provides information about net P retention and release, and external process data would be required to identify the mechanisms and locations and stages along the river–watershed continuum at which retention or release occurred.

Total P (TP) data for the Thames and Sandusky were used to illustrate how extended end-member mixing analysis can be used to estimate net losses and gains of P at the watershed outlet. For the Thames, weekly manual water-quality samples were collected; full details of the sampling and analysis program are provided in Neal et al. (2010a). For the Sandusky, autosamplers were used to collect three or four discrete samples per day at even intervals. All samples collected during storm runoff periods were analyzed; at other times, only one sample per day was analyzed and the remaining samples were discarded.

Analytical Methods and Data

Data on soluble reactive P fractions are presented to show P fractionation within the two rivers. Soluble reactive P (SRP) and TP analyses on both the Thames and Sandusky follow standard analytical methods using the Murphy and Riley (1962) ammonium molybdate/ascorbic acid method (USEPA 1978; Neal et al., 2000; Richards et al., 2009). Total P was determined from an unfiltered sample subject to acid-persulphate digestion. Soluble reactive P was determined on a river water sample filtered through a 0.45-µm membrane without acid-persulphate digestion.

Effluent data for the Thames were supplied by the Environment Agency for a total reactive phosphorus fraction (TRP; sometimes known as unfiltered molybdate reactive P) measurement, which is the Murphy and Riley colorimetric analysis on an unfiltered sample (Jarvie et al., 2003) and is a measure of SRP plus easily hydrolyzable particulate P fractions (Haygarth and Sharpley, 2000). Soluble reactive P typically accounts for >90% of TP in final sewage effluent (Neal et al., 2005). Measurements of TRP will therefore be even closer to the TP concentration in final effluent and, for this study TRP in effluent is assumed to be broadly comparable with TP.

Defining the Baseflow End-Member Source Flux

The baseflow end-member P flux ($Pflux_{baseflow}$) represents the sources of P to the river that contribute under dry weather
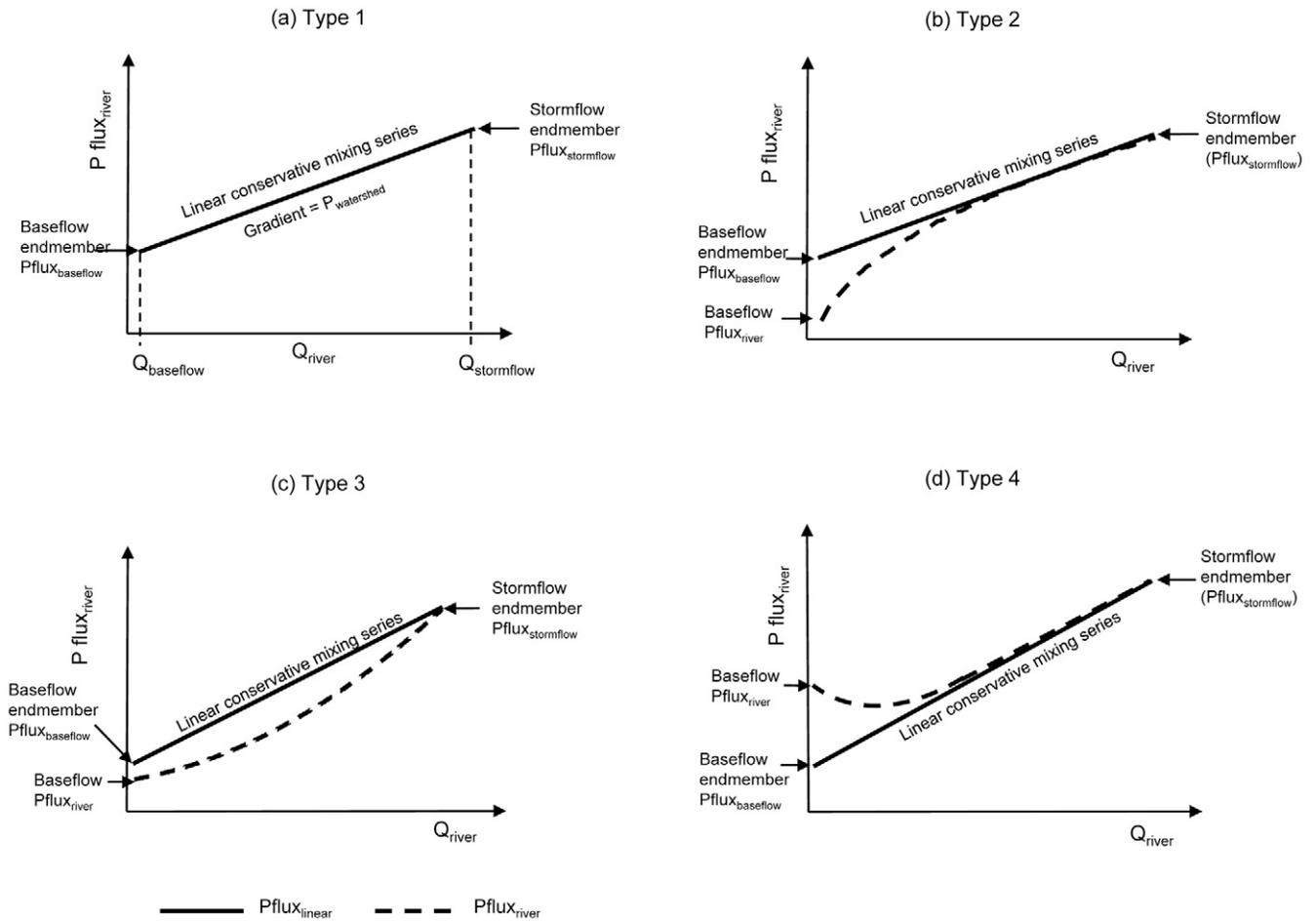
Fig. 1. Schematic diagram showing the four main types of relationships between river phosphorus (P) flux (Pflux$_{river}$) and river flow (Q_{river}): (a) Type 1 (conservative mixing series); (b) Type 2 (greatest P retention as flows decline); (c) Type 3 (greatest P retention at intermediate/high flows); (d) Type 4 (P release at low flows). The P flux retained or released ($P_{process}$) is calculated as the difference between Pflux$_{river}$ and the P flux from the conservative mixing series (Pflux$_{linear}$)

flow conditions. These fluxes are typically composed of effluent (Pflux$_{effluent}$) and any background groundwater sources of P (Pflux$_{groundwater}$):

$$\text{Pflux}_{baseflow} = \text{Pflux}_{effluent} + \text{Pflux}_{groundwater} \qquad [1]$$

The P effluent flux for each upstream wastewater treatment plant is calculated as the product of the average concentration of P in the sewage effluent (P_{stw_i}) and the long-term effluent dry weather flow (dwf) for each works ($Q_{dwf\_stw_i}$). The total upstream effluent flux is then:

$$\text{Pflux}_{effluent} = \sum_{i=1}^{n} \left(P_{stw_i} Q_{dwf\_stw_i} \right) \qquad [2]$$

To establish the significance of groundwater contributions to the Pflux$_{baseflow}$, the magnitude of the groundwater contribution to river flow under baseflow conditions ($Q_{groundwater}$) first needs to be established:

$$Q_{groundwater} = Q_{river\_min} - Q_{effluent} \qquad [3]$$

where Q_{river_min} is the minimum river flow during the monitoring period and

$$Q_{effluent} = \sum_{i=1}^{n} \left(Q_{dwf\_stw_i} \right) \qquad [4]$$

The groundwater P flux is then

$$\text{Pflux}_{groundwater} = Q_{groundwater} \, P_{groundwater} \qquad [5]$$

where $P_{groundwater}$ is the average groundwater P concentration from boreholes or springs in the upstream watershed.

In many cases, the Pflux$_{groundwater}$ is such a small proportion of the Pflux$_{baseflow}$ that it can be effectively ignored. This reflects the often negligible concentrations of P in groundwater (e.g., 0.01–0.03 mg P L^{-1}) compared with the high concentration of P found in sewage effluent (1.0–10.0 mg P L^{-1}) (Edwards and Withers, 2008).

Defining the Stormflow End-Member Flux

The stormflow end-member (Pflux$_{stormflow}$) is an integration of all the watershed-wide sources of P including from the watershed surface and mobilized from within the hydrographic network of ditches, streams, and rivers. Under these highest river flows, there is greatest hydrological connectivity and thus most efficient delivery between the watershed surface and the watershed outlet. Here, Pflux$_{stormflow}$ is estimated from the relationship between Pflux$_{river}$ and river flow (Q_{river}) by applying a LOESS fit (a locally weighted scatterplot smoothing regression) to the Pflux$_{river}$ vs. Q_{river} relationship on an annual basis (Fig. 2). Pflux$_{stormflow}$ is the

predicted Pflux$_{river}$ on the LOESS curve at the 99th percentile of the river flow distribution for the period of investigation. This is a pragmatic operationally defined approach, since there is always the possibility of flows being higher than those measured during a routine sampling program. Although hydrological connectivity between the watershed and the outlet monitoring point is greatest under highest flows, it is acknowledged that some P retention may impact the Pflux$_{stormflow}$. However, given the low water residence times and greatest efficiency of P delivery under highest flows, the impact of P retention on Pflux$_{stormflow}$ is likely to be relatively low. Therefore, the Pflux$_{stormflow}$ is taken as the reference point for the integrated watershed stormflow end-member, at which there is no net P retention.

It might be expected that the stormwater end-member P concentrations would be highly variable between storm events and seasons, especially for particulate components, for example, as a result of changes in crop cover, fertilizer use, water flow pathways, soil moisture, and sediment exhaustion and hysteresis effects (Haygarth et al., 2004). However, data such as those presented by Neal et al. (2010a) indicate that for many river basins, the integrated stormwater end-member flux signal at the watershed outlet shows a relatively high degree of uniformity, at least on an annual timescale, possibly because the flux term tends to be dominated by flow. As there was a relatively high degree of uniformity in the stormwater end-member flux for the Thames and Sandusky, extended end-member mixing analysis was performed on an annual time-step. However, in situations where there is temporal variability in the stormflow end-member P fluxes—for example, where there are clear seasonal differences in Pflux$_{river}$ versus flow relationships—then it may be more appropriate to use subannual time-steps for the extended end-member mixing analysis.

Observations of relationships of Pflux$_{river}$ and river flow (Q_{river}) have revealed four typical patterns (Fig. 1), which are outlined below, together with the methods for quantifying net P retention/release:

Type 1: Conservative Transport along the Watershed–River Continuum

The simplest situation is where there is conservative mixing between the baseflow and stormflow end-members, Pflux$_{stormflow}$ and Pflux$_{baseflow}$, where Pflux$_{baseflow}$ is derived from effluent and groundwater flow and concentration data, $Q_{baseflow}$ is the minimum observed river flow, $Q_{stormflow}$ is the 99th percentile of river flow, and Pflux$_{stormflow}$ is the LOESS value predicted at $Q_{stormflow}$. For any conservative determinand (i.e., which does not undergo biogeochemical processing, retention, or release within the watershed or hydrographic network of ditches, streams, and rivers), the two-component mixing series would be a single straight line relationship, whereby the upper and lower limits are defined by the fluxes of the two end-member sources (Fig. 1a).

For P, this relationship can be represented (Neal et al,, 2010a), as follows:

$$\text{Pflux}_{river} = P_{watershed}(Q_{river} - Q_{baseflow}) + P_{baseflow}Q_{baseflow} \qquad [6]$$

Rearranging terms on the righthand side of the equation gives

$$\text{Pflux}_{river} = P_{watershed}Q_{river} + (P_{baseflow} - P_{watershed})Q_{baseflow} \qquad [7]$$

where Pflux$_{river}$ is the river water P flux, Q_{river} is the river flow, $P_{baseflow}$ is the P concentration at baseflow, and $P_{watershed}$ is the concentration of P mobilized from an integration of the upstream watershed. Therefore, for the conservative mixing model, the relationship between Pflux$_{river}$ and Q_{river} should reveal a straight line relationship with a gradient equal to $P_{watershed}$.

The aim of the extended end-member mixing approach is to examine deviations from linearity and directly compare the observed (nonlinear) Pflux$_{river}$ versus Q_{river} relationship with the linear conservative mixing model, P_{linear} versus Q_{river} (Fig. 1b to d). This allows direct evaluation of the net effects of any physical and/or biogeochemical processes on P retention or release along the watershed–river continuum. Further description of the mixing model approach and its limitations can be found in Neal et al. (2010a).
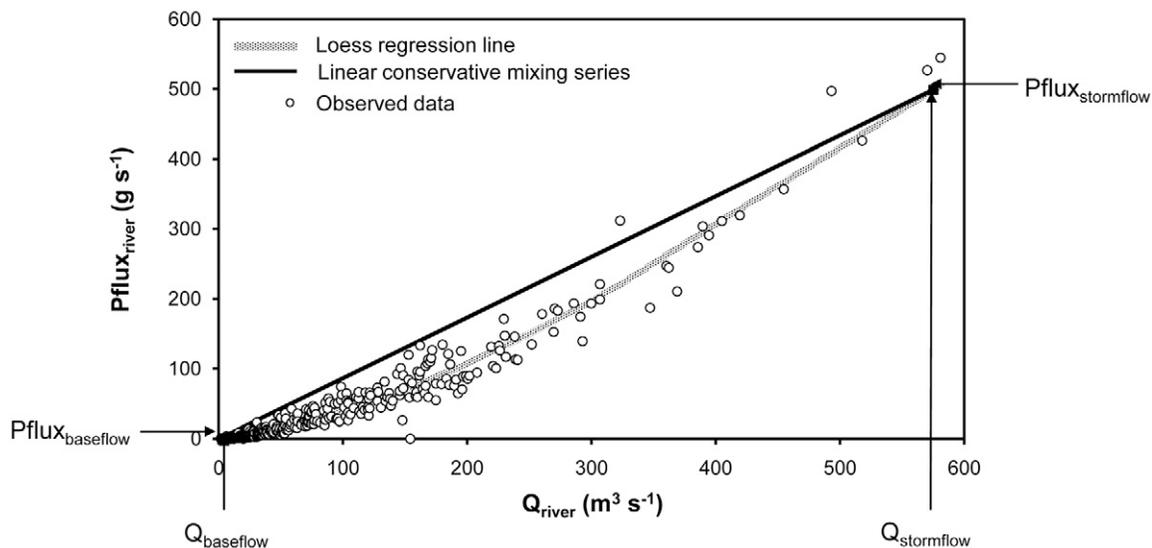

Fig. 2. Example plot showing baseflow and stormflow end-members, the LOESS regression line used to define the stormflow end-member, and the linear conservative mixing series, for the Sandusky River in 2006.

Type 2: Greatest Phosphorus Retention as Flows Decline

Figure 1b shows a typical pattern whereby $Pflux_{river}$ decreases relative to the conservative mixing series ($Pflux_{linear}$) as river flows decline. In this case, P retention increases as flows approach baseflow, when water residence times are highest, allowing greater time for interaction with sediments and biota. It is assumed that the main portion of this P retention is a direct result of processes occurring within the stream or in near-stream environments, such as hyporheic or riparian zones or in ponds and ditches that are in direct hydrological connectivity with the river under baseflow conditions. These processes include physicochemical sorption to sediments, precipitation reactions, biological uptake, or physical retention by sedimentation and deposition of particulate P and/or water storage in riparian or hyporheic zones (Withers and Jarvie, 2008).

Type 3: Greatest Phosphorus Retention at Intermediate to High Flows

Figure 1c depicts a pattern where $Pflux_{river}$ shows greatest deviation from the conservative mixing series ($Pflux_{linear}$) at intermediate to high flows. This reflects the net effects of both in-stream and watershed retention/mobilization linked to complex particulate/sediment transport processes.

Type 4: P Release at Low Flows

Figure 1d shows a situation whereby $Pflux_{river}$ increases relative to the conservative mixing series ($Pflux_{linear}$) as river flows decline. This is the reverse of Type 2: highest P release occurs as flows approach baseflow. It is therefore assumed that the main portion of this P release results from in-stream or near-stream processes.

Calculation of Net Phosphorus Retention or Release

For each study year, an annual riverine P flux (annual $Pflux_{river}$) was calculated from the observed river water P concentrations and the corresponding flow values at the time of sampling. For the Thames, where manual sampling was undertaken on a weekly basis, annual fluxes were calculated using an interpolation algorithm based on the product of the flow-weighted mean concentration and the average annual flow (Littlewood, 1992):

$$\text{annual Pflux}_{river} = K \left[\sum_{i=1}^{n} \left(P_{river\_i} Q_{river\_i} \right) \middle/ \sum_{i=1}^{n} \left(Q_{river\_i} \right) \right] Q_r \qquad [8]$$

where P_{river_i} is the instantaneous P concentration in the river; Q_{river_i} is the instantaneous river flow at the time of sampling; Q_r is the annual average river flow; K is a conversion factor to take account of the units and period of record; and n is the number of samples.

For the Sandusky, where more intensive daily and subdaily automated storm event samples were collected, the riverine P loads were calculated by multiplying P_{river_i} by the Q_{river_i} and the sample time window (Richards et al., 2009). These sample loads were then summed to give an annual P flux.

The gradient ($P_{watershed}$) and intercept ($Pflux_{intercept}$) of the conservative mixing series (Fig. 1a) were then applied to the observed flow data to derive corresponding $Pflux_{linear\_i}$ values:

$$Pflux_{linear\_i} = Q_{river} P_{watershed} + Pflux_{intercept} \qquad [9]$$

The corresponding instantaneous P concentrations for the conservative mixing series (P_{linear_i}) were then calculated as follows:

$$P_{linear\_i} = Pflux_{linear\_i} / Q_{river\_i} \qquad [10]$$

An annual P flux for the conservative mixing series was then calculated (annual $Pflux_{linear}$). For the Thames, annual $Pflux_{linear}$ was calculated using the interpolation algorithm, as follows:

$$\text{annual Pflux}_{linear} = K \left[\sum_{i=1}^{n} \left(P_{linear\_i} Q_{river\_i} \right) \middle/ \sum_{i=1}^{n} \left(Q_{river\_i} \right) \right] Q_r \qquad [11]$$

For the Sandusky, P loads for the conservative mixing series were calculated by multiplying P_{linear_i} by Q_{river_i} and the sample time window. These loads were then summed to provide the annual $Pflux_{linear}$.

To estimate the annual net P retention or release, annual $Pflux_{river}$ was then compared with the corresponding annual P flux derived from the conservative mixing model (annual $Pflux_{linear}$). The net P retention or release over the annual cycle (annual $P_{process}$) is then

$$\text{annual } P_{process} = \text{annual Pflux}_{river} - \text{annual Pflux}_{linear} \qquad [12]$$

Negative values of annual $P_{process}$ (Types 2 and 3) denote net P retention over the annual cycle. Positive values of annual $P_{process}$ (Type 4) denote net P release over the annual cycle.

Using the same principle, instantaneous $Pflux_{river\_i}$ values were used to derive average daily net retention/release rates ($P_{process}$) under different observed flow conditions. In this study, we examined differences in average daily $P_{process}$ under low-flow conditions (the lowest 20% of flows), high-flow conditions (highest 20% of flows), and the intervening "intermediate" flow conditions. This provided a simple differentiation between P retention/release as a result of (i) processes that occur under low flows (within the stream or in near-stream environments) and (ii) wider P processes along the watershed–river continuum, under intermediate to higher flows. These processes occurring under intermediate to high flows will be increasingly dominated by processes linked to flow dynamics, incorporating watershed runoff processes/mobilization/retention effects as well as in-stream sediment storage and remobilization. The impact of $P_{process}$ on increases or decreases in P concentrations was evaluated by subtracting P_{linear_i} from P_{river_i}.

Results

General Patterns in Flow and Phosphorus Concentrations in the Thames and Sandusky

Average TP concentrations were higher on the Thames and its tributary, the Cherwell (median 0.311–0.744 mg P L^{-1}), compared with the Sandusky (median 0.157–0.244 mg P L^{-1}) (Table 2). For the Thames, SRP accounted for the vast majority (>70%) of TP concentrations. In contrast, SRP accounted for <30% of TP concentrations on the Sandusky. Total P concentrations were highest on the Thames in 1998 (mean 0.858 mg P L^{-1}), before the introduction of tertiary effluent P treatment. As effluent P loadings decreased, mean river water TP concentrations in the Thames fell by 62% between 1998 and 2006. In the Sandusky, average TP concentrations were lower in 1998 than in 1975 or 2006. Despite point-source reductions in the Sandusky watershed over the monitoring period, SRP as a percentage of TP was highest in 2006. Mean flows were lower in

the Thames than the Sandusky, but median flows were higher in the Thames, reflecting a much more flashy flow regime on the Sandusky and higher baseflow contributions and more moderate runoff response in the groundwater-fed Thames. For both the Thames and Sandusky, 2006 was a relatively high-flow year, compared with the other years chosen for this study.

Relationships between Pflux$_{river}$ and Q_{river}

Example relationships between Pflux$_{river}$ and Q_{river} for the Thames, Sandusky, and Cherwell are shown in Fig. 3. In all cases, the Pflux$_{river}$ versus Q_{river} relationships were nonlinear, with none approximating to a conservative mixing series (Type 1). For the Thames, Pflux$_{river}$ versus Q_{river} corresponded with Type 2 behavior, with a clear reduction in Pflux$_{river}$ as flows declined toward lowest baseflow values, indicating net removal of P under low flows. This effect was most marked in 1998, when Pflux$_{river}$

was highest, before introduction of tertiary treatment to remove P from final effluent. Over the following 8 yr, improvements in effluent treatment resulted in a reduction in Pflux$_{river}$ values relative to Q_{river} across the flow range, but in each case, the most marked decline was under the lowest river flows. The Sandusky exhibited Type 3 behavior: a curvilinear pattern showing greatest absolute Pflux$_{river}$ losses at intermediate to high river flows. However, there did not appear to be any marked change in the relationship between Pflux$_{river}$ and Q_{river} for the Sandusky between 1975, 1998, and 2006. The Cherwell exhibited Type 4 behavior, with a marked rise in Pflux$_{river}$ as river flows declined toward the lowest baseflow values, indicating net release of P.

Baseflow and Stormflow End-Members

There are 123 STWs upstream of the Wallingford sampling site, which provide a combined dry weather flow ($Q_{effluent}$) of

Table 2. Summary of flow and phosphorus concentrations in the Thames, Sandusky, and Cherwell rivers for each of the study years.

River	Year	River flow		River TP†		River SRP†	
		Mean	Median	Mean	Median	Mean	Median
		——— m³ s⁻¹ ———		——— mg L⁻¹ ———		——— % of TP ———	
	1998	33.0	25.0	0.858	0.744	90	93
Thames	1999	32.3	22.5	0.520	0.504	86	88
	2006	41.1	19.5	0.324	0.311	72	73
	1975	50.4	14.9	0.372	0.244	25	18
Sandusky	1998	56.9	18.7	0.236	0.157	12	11
	2006	63.6	22.7	0.282	0.227	29	28
Cherwell	2001–2002	5.1	2.5	0.522	0.365	72	80

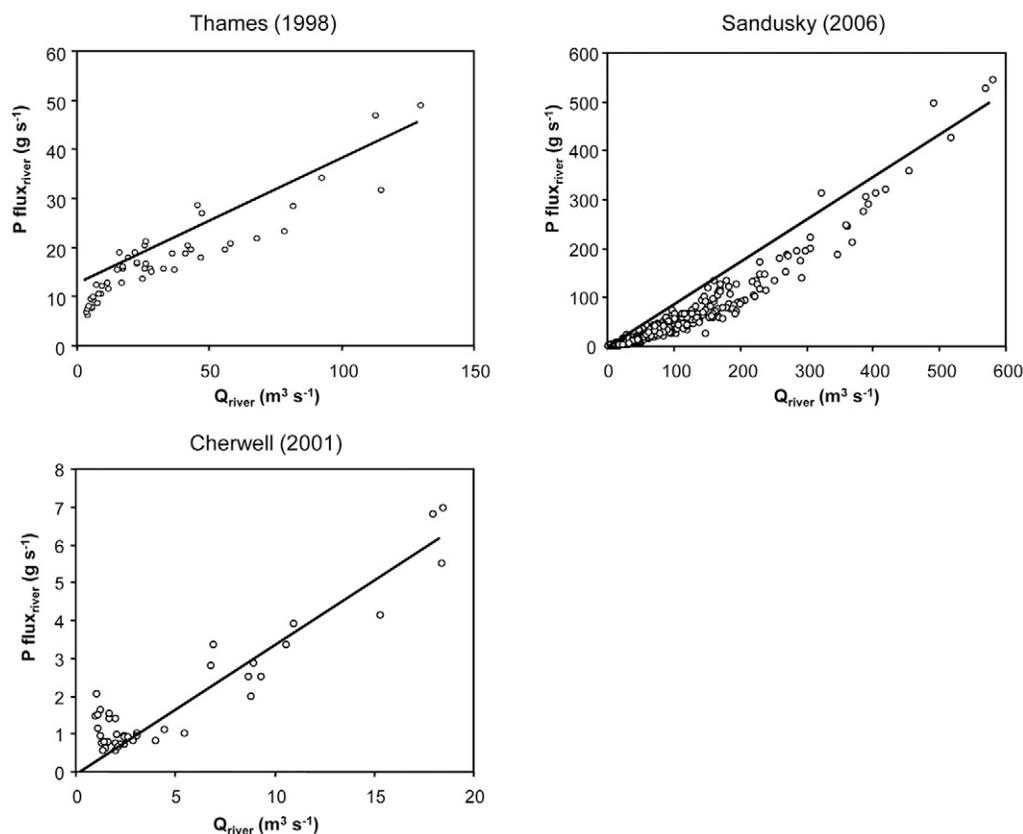† TP, total phosphorus; SRP, soluble reactive phosphorus.

Fig. 3. Example plots of P flux (Pflux$_{river}$) and river flow (Q_{river}) for the Thames, Sandusky, and Cherwell, showing the corresponding linear conservative mixing series between baseflow and stormflow end-member fluxes.

2.32 m^3 s^{-1} (Neal et al., 2010a). The corresponding effluent P load (Pflux$_{effluent}$) (from Eq. [2]) ranged from 13.3 g P s^{-1} in 1998 (before introduction of tertiary P removal) to 2.4 g P s^{-1} in 2006 (after widespread upgrades to tertiary effluent treatment). Minimum river flows (Q_{river_min}) ranged from 3.2 m^3 s^{-1} (in 2006) to 4.8 m^3 s^{-1} (in 1999). Therefore, from Eq. [3], $Q_{groundwater}$ ranged from 0.87 m^3 s^{-1} (in 2006) to 2.48 m^3 s^{-1} (in 1999). Using an average $P_{groundwater}$ for the Thames watershed of 20 μg P L^{-1} (Neal et al., 2002), Pflux$_{groundwater}$ ranges from 0.017 g s^{-1} (1999) to 0.05 g s^{-1} (2006). As Pflux$_{groundwater}$ therefore accounts for <1% of Pflux$_{baseflow}$ (ranging from 0.24% in 1998 to 0.75% in 1999) for the Thames, Pflux$_{groundwater}$ was deemed negligible and Pflux$_{baseflow}$ = Pflux$_{effluent}$. End-member fluxes are presented in Table 3.

For the Sandusky, the baseflow end-member flux derived from seven point sources upstream (Baker and Richards, 2002; Ohio EPA, 2004) varied from 1.33 g P s^{-1} in 1975 and 0.40 g P s^{-1} in 1998 to 0.33 g P s^{-1} in 2006 (Table 3). In the absence of effluent dry weather flow data, the $Q_{effluent}$ was operationally defined as the 98th flow percentile (1.11 m^3 s^{-1}). The Sandusky had much lower baseflow end-member P fluxes than the Thames but dramatically higher stormflow end-member P fluxes, which are about an order of magnitude higher than for the Thames (Table 3).

For the Thames, baseflow end-member P fluxes declined by 82% between 1998 and 2006. For the Sandusky, there was an 75% reduction in baseflow end-member P fluxes between 1975 and 2006. However, neither the Thames or Sandusky showed a corresponding decrease in stormflow end-member fluxes with time.

Patterns in Observed River Phosphorus Fluxes

Annual observed river P fluxes were broadly similar in the Thames (1.0–1.67 kg P ha^{-1} yr^{-1}), Sandusky (1.46–1.99 kg P ha^{-1} yr^{-1}), and Cherwell (1.18 kg P ha^{-1} yr^{-1}) (Table 4). Average daily low-flow P fluxes were consistently higher in the Thames (199–729 kg P d^{-1}) than the Sandusky (7–56 kg P d^{-1}) (Table 5). However, at high flows, average daily river P fluxes were consistently lower in the Thames (1792–2608 kg P d^{-1}) compared with the Sandusky (10,624–10,861 kg P d^{-1}).

Table 3. Baseflow and stormflow end-member P fluxes and river flows for the Thames, Sandusky, and Cherwell for each of the study years.

River	Year	End-member	Flow	P flux
			m^3 s^{-1}	g s^{-1}
Thames	1998	Baseflow	2.32	13.3
		Stormflow	129	45.7
	1999	Baseflow	2.32	7.2
		Stormflow	124	37.9
	2006	Baseflow	2.32	2.4
		Stormflow	147	39.8
Sandusky	1975	Baseflow	1.11	1.33
		Stormflow	440	402
	1998	Baseflow	1.11	0.40
		Stormflow	490	332
	2006	Baseflow	1.11	0.33
		Stormflow	575	499
Cherwell	2001–2002	Baseflow	0.17	0.008
		Stormflow	18.3	6.19

For the Thames, annual observed river P fluxes declined by 40% between 1998 and 2006 (Table 4). A higher percentage decline was observed for the average daily low-flow P fluxes, which fell by 73% from 1998 to 2006 (Table 5). There was also a 54% decline in average daily P fluxes at intermediate flows on the Thames over the same period. However, daily high-flow fluxes did not show a similar declining trend. For the Sandusky, annual P fluxes remained relatively constant between 1975 and 1998. However, for the high-flow year of 2006, the annual P flux was 36% higher. Annual and daily P fluxes (for low, high, and intermediate flows) on the Sandusky River were all lowest in 1998.

Impacts of Phosphorus Retention/Release at the Watershed Outlet

Net P retention or release was quantified by comparing the observed curvilinear Pflux$_{river}$ versus Q_{river} relationships with corresponding P fluxes calculated using the corresponding linear mixing model (Fig. 3). These net impacts were examined for annual flux estimates (Table 4), average daily fluxes delivered during low, high, and intermediate flows (Table 5), and changes in ambient P concentrations during low, high, and intermediate flows (Table 6).

Annual Fluxes

Both the Thames and Sandusky exhibited P flux retention on an annual scale at the watershed outlet, whereas net P flux gains were observed for the Cherwell (Table 4). Absolute and

Table 4. Comparison of observed annual river P fluxes (Pflux$_{river}$) and annual river P fluxes derived from the conservative mixing model (Pflux$_{linear}$). Differences between observed and conservative fluxes constitute either P retention (net loss) or P release (net gain).

River	Year	Annual Pflux$_{river}$	Annual Pflux$_{linear}$	Retention (−)/release (+)	Retention (−)/release (+)
		——————————— kg P ha^{-1} yr^{-1} ———————————			%
Thames	1998	1.67	1.94	−0.27	−14
	1999	1.25	1.35	−0.1	−7
	2006	1.0	1.14	−0.14	−12
Sandusky	1975	1.46	2.82	−1.36	−48
	1998	1.48	2.24	−0.76	−34
	2006	1.99	3.71	−1.72	−46
Cherwell	2001–2002	1.18	0.97	+0.21	+22

percentage annual retention of P fluxes was greatest for the Sandusky: observed annual P loads were up to 48% lower than the corresponding annual loads predicted from the conservative mixing model. For the Thames, observed annual loads were up to 14% lower than the conservative load estimates. For the Cherwell, there was 22% net gain in annual P load, relative to the annual load predicted from the conservative mixing model.

Average Daily Fluxes Delivered during Low, High, and Intermediate Flow Conditions

For the Thames, the retention in average daily percentage P flux was greatest under low-flow conditions, ranging from 27 to 42% of the conservative P flux estimate (Table 5). Under low flows, absolute P flux retention declined from 490 kg P

d^{-1} in 1998 to 75 kg P d^{-1} in 2006. Under high flows, the percentage P retention was consistently smaller, ranging from 3 to 12% of the conservative P flux estimate.

The Sandusky also showed greatest percentage P flux retention under low flows, ranging from 82 to 93% of the average daily conservative flux. However, for the Sandusky, the absolute P flux losses at low flows (up to 233 kg P d^{-1}) were small compared with losses at intermediate and high flows (where average losses of up to 4965 kg P d^{-1} were recorded).

For the Cherwell, greatest P flux release occurred under low flows in both absolute and percentage terms, with an average daily increase in P flux of 250% (77 kg P d^{-1}) under low flows. Under intermediate flows, there was a daily net P flux release of 13% (12 kg P d^{-1}). However, under high flows, there was

Table 5. Observed average daily river P fluxes (Pflux$_{river}$), average daily P flux retention/release (difference between average daily observed and conservative fluxes), and percentage P flux retention (relative to the conservative P flux estimate), for the Thames, Sandusky, and Cherwell for the lowest 20% of flows ("low flow"), highest 20% of flows ("high flow"), and intermediate flow.

River	Year		Low flow	Intermediate flow	High flow
Thames	1998	Observed Pflux$_{river}$ (kg P d^{-1})	729	1405	2608
		Retention (–)/Release (+) (kg P d^{-1})	−490	−256	−348
		% retention (–)/release (+)	−40	−15	−12
	1999	Observed Pflux$_{river}$ (kg P d^{-1})	428	1081	1792
		Retention (–)/Release (+) (kg P d^{-1})	−304	−51	−61
		% retention (–)/release (+)	−42	−5	−3
	2006	Observed Pflux$_{river}$ (kg P d^{-1})	199	651	2514
		Retention (–)/Release (+) (kg P d^{-1})	−75	−133	−163
		% retention (–)/release (+)	−27	−17	−6
Sandusky	1975	Observed Pflux$_{river}$ (kg P d^{-1})	45	618	10861
		Retention (–)/Release (+) (kg P d^{-1})	−206	−1064	−4162
		% retention (–)/release (+)	−82	−63	−28
	1998	Observed Pflux$_{river}$ (kg P d^{-1})	7	564	10624
		Retention (–)/Release (+) (kg P d^{-1})	−89	−838	−1484
		% retention (–)/release (+)	−93	−60	−12
	2006	Observed Pflux$_{river}$ (kg P d^{-1})	56	949	10816
		Retention (–)/Release (+) (kg P d^{-1})	−233	−2503	−4965
		% retention (–)/release (+)	−81	−99	−31
Cherwell	2001–2002	Observed Pflux$_{river}$ (kg P d^{-1})	108	99	365
		Retention (–)/Release (+) (kg P d^{-1})	+77	+12	−20
		% retention (–)/release (+)	+250	+13	−5

Table 6. Observed average daily P concentrations (conc.) and average daily P concentration increases/decreases (relative to P concentrations predicted by the conservative mixing series) for the Thames, Sandusky, and Cherwell for the lowest 20% of flows ("low flow"), highest 20% of flows ("high flow"), and intermediate flows.

River	Year		Low flow	Intermediate flow	High flow
Thames	1998	Observed P conc. (mg P L^{-1})	1.58	0.74	0.37
		P conc. decrease (–)/increase (+) (mg P L^{-1})	−1.15	−0.17	−0.06
	1999	Observed P conc. (mg P L^{-1})	0.71	0.53	0.36
		P conc. decrease (–)/increase (+) (mg P L^{-1})	−0.55	−0.04	−0.02
	2006	Observed P conc. (mg P L^{-1})	0.44	0.31	0.25
		P conc. decrease (–)/increase (+) (mg P L^{-1})	−0.18	−0.05	−0.02
Sandusky	1975	Observed P conc. (mg-P L^{-1})	0.18	0.36	0.59
		P conc. decrease (–)/increase (+) (mg P L^{-1})	−0.87	−0.58	−0.33
	1998	Observed P conc. (mg P L^{-1})	0.03	0.19	0.55
		P conc. decrease (–)/increase (+) (mg P L^{-1})	−0.48	−0.46	−0.13
	2006	Observed P conc. (mg P L^{-1})	0.13	0.24	0.54
		P conc. decrease (–)/increase (+) (mg P L^{-1})	−0.58	−0.62	−0.36
Cherwell	2001–2002	Observed P conc. (mg P L^{-1})	1.08	0.40	0.31
		P conc. decrease (–)/increase (+) (mg P L^{-1})	+0.79	+0.08	−0.02

an average daily net P flux retention of 5% (20 kg P d⁻¹) was recorded for the Cherwell.

Ambient Phosphorus Concentrations under Low, High, and Intermediate Flow Conditions

For the Thames, the greatest reductions in ambient P concentrations as a result of in-stream P retention occurred under low-flow conditions in 1998, with an average daily reduction in P concentration of 1.15 mg P L⁻¹ (Table 6). With the introduction of tertiary effluent treatment across the Thames watershed, in-stream P retention declined. By 2006, net in-stream removal of P resulted in average reductions in ambient P concentrations of 0.18 mg P L⁻¹ during the most ecologically important low-flow conditions. However, despite declining effluent P inputs, average daily low-flow P concentrations in 2006 for the Thames still exceeded 0.4 mg P L⁻¹.

Large reductions in ambient P concentrations under low-flow conditions were also seen on the Sandusky, ranging from 0.58 to 0.87 mg P L⁻¹ and resulting in observed in-stream P concentrations at the watershed outlet ranging from 0.03 mg P L⁻¹ in 1998 to 0.13 mg P L⁻¹ in 2006.

For the Thames, P concentration reductions, as a result of P retention, declined consistently between low-, intermediate-, and high-flow conditions. However, for the Sandusky, there was no clear pattern in concentration changes at low, intermediate, and high flows. Reductions in ambient P concentrations resulting from P retention were considerably higher in the Sandusky at intermediate and high flows compared with the Thames.

Discussion

Extended End-Member Mixing Analysis as a Tool to Estimate Net Retention/Release for Rivers

E-EMMA provides a new means of exploring the nonconservative behavior of P and is demonstrated here for two major U.K. and U.S. river systems. In both cases, relationships between Pflux$_{river}$ and Q_{river} were nonlinear, which suggests that riverine P fluxes at the watershed outlets were strongly controlled by processes that retain and cycle P. Differences in the patterns of net P uptake and release between the Sandusky and Thames–Cherwell, under changing flow conditions, provide insights into the relative importance of different processes controlling P cycling at the watershed scale for these contrasting river types.

E-EMMA requires representative sampling across the full flow regime, and particularly capture of a range of storm events to ensure that the stormflow end-member flux is adequately represented. For example, monthly sampling may not allow us to characterize the high-range Pflux$_{river}$ versus Q_{river} relationships. More intensive sampling and inclusion of targeted storm event sampling would greatly increase the robustness of the end-member mixing analysis, particularly for rivers with flashier flow regimes. The method also relies on good characterization of baseflow end-member P fluxes. Information on point-source discharges (effluent dry weather flow and P concentrations) upstream of the monitoring point as well as groundwater P concentrations is required to fully characterize the baseflow end-member P flux. Further study is needed to gain fuller understanding of the balance of processes that deter-

mine the stormflow end-member flux, especially in watersheds dominated by nonpoint export, such as differential erosion associated with storms of different magnitudes, intensities, seasons, and preexisting conditions; redeposition and other processing active during overland flow; and in-stream processing.

Contrasting Characteristics of the Thames and Sandusky and Implications for Phosphorus Delivery

The Thames is a groundwater-dominated river, with a "damped" hydrological response to rainfall events, and a relatively large proportion of farmland in the Thames watershed is grassland on well-drained chalk soils, with lower potential for erosion and particulate P export than arable land. The Thames has a relatively high population density with the major settlements located along the river corridor from Swindon to Oxford. This results in large demands for water abstraction from the Thames and discharge of treated sewage effluent back into the river. The net effects of the land use and hydrology within the Thames watershed means that the dominant source of phosphorus in the River Thames is sewage effluent (Neal et al., 2010a, Jarvie et al., 2006b), with a high proportion of highly bioavailable SRP (up to 93% of TP in the River Thames is as SRP).

The relationships between Pflux$_{river}$ and Q_{river} for both the Thames and its tributary, the Cherwell, showed strong nonconservative behavior under the lowest flows. Low flows correspond with highest water residence times, allowing greater interaction with sediments and biota and thus greatest potential for biogeochemical cycling. For the Thames, P retention was greatest under the lowest flows, which is strongly indicative of biological processing of P, particularly uptake by algae and/or sorption to sediments. There is also potential for P retention as a result of an increased proportion of total flow being stored in hyporheic sediments under baseflow conditions (Neal et al., 2010a,b).

In contrast, in the Cherwell, net release of P occurred under low flows, and the magnitude of P release increased as flows declined toward baseflow. The processes and sources controlling this net release of P on the Cherwell are subject to some speculation, and may include the following:

- Soluble reactive P release from riverbed sediments as a result of reductive dissolution of Fe–P complexes under summer low flows, associated with a legacy of high organic matter content of bed sediments from discharge of effluent from the food-processing industries. McDowell and Sharpley (2001) and Jarvie et al. (2010) observed similar patterns of net release during summer from organically enriched sediments.

- A change in P diffusion gradient between sediment porewaters and the overlying river water following a dramatic reduction in SRP concentrations in the overlying water as a result of introduction of tertiary effluent P treatment (Jarvie et al., 2006a).

- Potential increased P concentrations in the effluent discharged from the STW under summer baseflow conditions cannot be ruled out. Under usual circumstances, reduced efficiency of effluent treatment would be expected to occur during high flows, when inflows to the treatment works exceed the hydraulic and treatment capacity, resulting in storm overflows. Any increases in

P concentration in the final effluent under baseflow may therefore be linked to remobilization in final settling tanks and may be classed here as a "near"-river process, as the final effluent is in direct hydrological connectivity with the river under baseflow conditions.

For both the Thames and Cherwell, while nonlinear (non-conservative) P behavior occurred under low-flow conditions, in contrast, relationships between $Pflux_{river}$ and Q_{river} were roughly linear under intermediate- to high-flow conditions. As the dominant form of P in the Thames and Cherwell is SRP, this suggests that although SRP is subject to intensive biogeochemical processing under low flows, SRP is transported more conservatively under higher flows.

In contrast to the Thames, the Sandusky is characterized by surface runoff, with a flashy hydrological regime and greater extremes in flow. Land use across the watershed is dominated by arable land, and despite introduction of conservation tillage measures to reduce soil erosion, nonpoint inputs from farming are the major sources of P in the Sandusky River, composed predominantly of particulate P (PP). Differences in P sources between the Sandusky and Thames were clearly exemplified by the baseflow and stormflow flux characteristics: the Sandusky had much lower baseflow end-member fluxes compared with the Thames but dramatically higher stormflow end-member fluxes.

The Sandusky showed a strong concave curvilinear P flux–flow relationship. The processes causing this curvilinear relationship are open to interpretation. Complexities in the P concentration–flow relationship in flashy cropland-dominated watersheds such as the Sandusky reflect inter- and intrastorm variability in source availability and mobilization, antecedent conditions, rainfall intensity, and land-use management. However, this variability was not observed for the annual P flux–flow relationship, which showed a simple curvilinear relationship at the watershed outlet and for which flow was the key driving variable. Given the well-defined baseflow and integrated watershed stormflow end-members derived from the Sandusky P flux–flow scatterplot, the interpretation here is that the curvilinear relationship reflects net P retention along the river–watershed continuum during mixing of the stormflow and baseflow end members. Indeed, this is consistent with a large body of published evidence showing P retention along the river–watershed continuum (Withers and Jarvie, 2008).

Like the Thames, the Sandusky exhibited net P retention on an annual timescale; however, the nature and timing of P retention contrasted dramatically with the Thames. Greatest net P retention in the Sandusky watershed occurred under intermediate- to high-flow conditions, which are likely the result of net deposition of particulate P along the watershed–river continuum. This may result from floodplain storage or from in-stream deposition of particulates as flows decline. Phosphorus retention under low flows on the Sandusky was still important in absolute terms and was comparable with P retention for the Thames.

Phosphorus that becomes stored along the river–watershed continuum (either through physical deposition or by biogechemical processes such as sorption to sediments or uptake by biota) will subsequently be available for remobilization and thus contribute to the nonpoint-source load (and to the stormflow end-member flux) as flows rise. However, within the Sandusky, Thames, and Cherwell, there was no evidence of any significant net gains in flux in excess of the linear conservative mixing series. For the Sandusky, remobilization of any stored P was low compared with retention of P moving across the watershed surface and through the hydrographic network of ditches, streams, and rivers under elevated flows, at least on an annual timestep.

Temporal Patterns in Phosphorus Fluxes for the Thames and Sandusky

Point-source P remediation had a dramatic impact on riverine P fluxes for the Thames, with the greatest impacts under the lowest flows. Reductions in P fluxes under intermediate flows as a result of point-source reductions also suggested lower in-channel storage of effluent P and thus lower availability for subsequent re-release and/or remobilization as flows increase. However, reductions in in-channel storage and re-release of P were of minor significance at higher flow levels when there was greater P mobilization from across the watershed. For the Sandusky, despite major changes in land-use management between 1975, 1998, and 2006, there was no direct evidence of any major reduction in annual P loads. In contrast to the Thames, P loads in the Sandusky were governed by nonpoint-source P delivery of particulate P under high flows. Highest annual loads occurred during 2006, which was a considerably higher flow year than 1975 or 1998, and hydrology may mask any reductions in annual P loads linked to land-use management. However, average daily low-flow P loads were also highest in 2006, despite a dramatic reduction in point-source contributions.

Magnitude of Phosphorus Flux Retention/Release in the Thames, Cherwell, and Sandusky

Both the River Thames and the Sandusky River exhibited considerable net P retention on an annual timescale: up to 48% of the total conservative P flux estimate for the Sandusky and up to 14% for the Thames. However, under ecologically critical low-flow periods, up to 93% of the river P flux was retained under low flows in the Sandusky and up to 42% for the Thames. The results indicate that in-stream processes under low flows may regulate delivery of nutrients and modify the timing of delivery in a way that may help to reduce ecological impacts to downstream river reaches at times of greatest river eutrophication risk. This corresponds with earlier reach-based studies (Svendsen et al., 1995; Haggard et al., 2001a,b; Bukaveckas et al., 2005; McDaniel et al., 2009), which show that in-stream processes can provide an important ecosystem service in reducing ambient P concentrations. Whereas absolute P flux retention for the Sandusky under low flows was comparable with net P flux retention under low flows in the Thames, the low-flow P flux retention in the Sandusky was dwarfed by the net retention under higher flows, reflecting a combination of in-watershed and in-channel retention of PP. In contrast, the Thames was dominated by in-stream processing of SRP under low flows, when water residence times were highest, as a result of uptake by biota and sediments. The results indicate that P sources and speciation, hydrology, and land use likely play a major role in patterns of P flux retention at the watershed scale.

There was no evidence of significant net release or remobilization of P fluxes under intermediate to high flows relative to the linear conservative mixing series in these two watersheds. This indicates that remobilization of transient in-channel and

watershed stores of P was small relative to P flux retention under intermediate and higher flows. The only instance of significant P release occurred under low-flow conditions in the river Cherwell, which had been subject to high organic matter loadings from food-industry effluent. This P release resulted in a 22% increase in the annual P flux of the Cherwell but a 250% increase in low-flow P flux.

Under low-flow conditions, the magnitude of P retention for both the Thames and Sandusky appeared to be closely linked to the magnitude of low-flow river fluxes. This is consistent with other work (Hejzlar et al., 2009), which showed that modeled nutrient export from nonpoint sources was directly proportional to retention rates, for four European watersheds, subject to wide variations in climate, hydrology, and nutrient loads. In this study, under low-flow conditions, P retention as a proportion of the conservation P flux was much lower in the Thames than the Sandusky. This suggests that in-stream P processing and retention was much less efficient in the Thames. This may be linked to the higher ambient P concentrations under low flows in the Thames; indeed, other studies have also observed that heavily nutrient-enriched streams tend to show lower P retention efficiency than those with lower nutrient concentrations (Marcé and Armengol, 2009).

Impacts of Phosphorus Retention and Release on Ambient Phosphorus Concentrations at Low Flows

The impacts of P retention on river water P concentrations potentially has greatest ecological impact under low-flow conditions, particularly during spring and summer, the periods of greatest ecological sensitivity and eutrophication risk (Jarvie et al., 2006b; Edwards and Withers, 2007; McDaniel et al., 2009). The magnitude of change in ambient low-flow P concentrations in the Thames and Sandusky, as a direct result of in-stream P retention, were remarkably similar. In both the Thames and Sandusky, the reductions in P concentrations as a result of in-stream P retention declined in line with reductions in point-source inputs. This indicates that SRP from sewage effluent (the most highly bioavailable form of P) is most readily retained as a result of biological uptake and/or sorption to sediments. For the Sandusky, this in-stream P retention resulted in reductions in ambient low-flow P concentrations to levels close to, or below, the environmental thresholds at which P may become limiting for algal growth in rivers (<0.06–0.1 mg P L^{-1}; Bowes et al., 2007). This suggests that in-stream P retention in the Sandusky may play an important role in reducing P concentrations to levels capable of regulating in-stream algal growth. In contrast, for the Thames, despite the combined effects of point-source P control measures and in-stream P retention, ambient low-flow P concentrations remained in excess of 0.4 mg P L^{-1}. This is a result of effluent inputs from a multitude of smaller-scale wastewater plants, which have not been subject to tertiary treatment. This suggests that much wider effluent P remediation may be required across the Thames watershed to reduce P concentrations and eutrophication risk. Whether the required reductions in P concentrations may at least be partially achieved by increased efficiency of in-stream P retention, as a result of wider long-term improvements in the ecological health and function of the river, is of profound environmental management significance. In the Cherwell, release of P under low flows resulted in an increase in average ambient P concentrations of 0.79 mg P L^{-1}, and an observed P concentration at low flows of 1.08 mg P L^{-1}, thus providing a large oversupply of P for primary productivity and contributing to a significant degradation in water quality.

Conclusions

E-EMMA has been applied to two contrasting U.K. and U.S. river systems (Thames and Sandusky). Phosphorus fluxes at the watershed outlets were strongly influenced by processes that retain and cycle P, with retention of up to 48% of annual P fluxes and up to 93% of low-flow P fluxes. In-stream processes under low flows regulated P delivery in ways that may help to reduce ecological impacts to downstream river reaches at times of greatest river eutrophication risk. The results also suggest that cleaner rivers with better ecosystem health may have greater capacity to retain P. For the Sandusky, P retention under low flows resulted in reductions in ambient river water P concentration to levels close to, or at, thresholds where algal growth starts to be inhibited. However, for the Thames, even after substantial P concentration reductions as a result of the combined effects of point-source remediation, and in-stream P retention, P concentrations remained well above environmental P thresholds for algal growth in rivers.

These analyses suggest that E-EMMA provides a means of quantifying P delivery and exploring the nonconservative behavior of macronutrients at the watershed scale, using routine water-quality monitoring data. E-EMMA allows us to explore differences in the relative importance of in-stream biogeochemical processing under low flows versus sedimentation and remobilization of transient stores of P, and mobilization of nonpoint upstream watershed P sources, under higher flow conditions. E-EMMA can be used to examine the scale and variability in P retention and release as an aid to watershed management and may provide useful datasets to help constrain nutrient retention parameter values for process-based water quality and watershed simulation modeling.

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