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Role of river bed sediments as sources and sinks of phosphorus across two major eutrophic UK river basins: the Hampshire Avon and Herefordshire Wye

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Abstract

The Equilibrium Phosphorus Concentration (EPC_0) of river bed sediments has been measured for a wide range of agricultural subcatchments and main river sites across two major eutrophic river basins: the Hampshire Avon and Herefordshire Wye catchments, to examine whether bed sediments are acting as sources or sinks of soluble reactive phosphorus (SRP) under low flows and times of greatest eutrophication risk. A conceptual reach-based model of interactions between bed sediment and river water has been used to estimate relative differences in bed-sediment SRP flux transfers. In this model, processes of SRP uptake and release are assumed to occur within an operationally defined 0.1 m river water 'boundary layer' and the uptake and release of SRP is assumed to be driven by a differential between the EPC_0 of the sediment and SRP concentration in the boundary layer. Most of the river monitoring sites in the Wye and Avon catchments had elevated SRP and boron (B) concentrations in the water column at low flows, linked to sewage effluent discharges. At these sites, bed sediments consistently acted as net sinks for SRP, demonstrating the role of bed sediments in riverine 'self-cleansing' mechanisms. In contrast, bed sediments were found to act as net sources of SRP under three circumstances: (i) where there was minimal sewage influence (in headwater streams of the Avon), (ii) where sewage inputs were subject to large hydrological dilution by water of low SRP concentration (in the main River Wye), (iii) where EPC_0 values were relatively high, as a result of deposition of particulates with high exchangeable P concentrations from diffuse sources or from effluents (immediately downstream of sewage treatment works (STWs)). Under baseflow conditions, high SRP concentrations from sewage effluent in the tributaries appear to 'swamp out' any potential release of SRP from the bed sediments. For rivers that are subject to effluent P-stripping, reductions in SRP in the overlying water could potentially result in changes to the in-stream P-cycling mechanisms, with bed sediments possibly switching from net sinks to net sources of SRP. This feature is of potential importance in relation to environmental management and phosphorus mitigation operations.

Keywords: Phosphorus; Bed sediments; Equilibrium phosphorus concentration; Flux; River; River Avon; River Wye

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1. Introduction

Phosphorus (P) plays a key role in eutrophication of surface waters (OECD, 1982; Hecky and Kilham, 1988; Mainstone and Parr, 2002). The impacts of elevated phosphorus concentrations in rivers include increasing rates of plant growth, changes in species composition and proliferation of planktonic, epiphytic and epibenthic algae, resulting in shading of higher plants (Mainstone and Parr, 2002). Further, microbial breakdown of the enhanced amounts of biomass in eutrophic rivers can result in low dissolved oxygen and fish-kills. Phosphorus enters rivers from diffuse catchment sources (particularly agriculture) and point (effluent) sources. However, river systems have an important internal capacity to remove or release phosphorus from/to the water column and to transform phosphorus between organic, inorganic, particulate and dissolved forms. This occurs as a result of a diverse array of physical, chemical and biological processes (e.g. Reddy et al., 1996, 1998, 1999; Webster et al., 2001; House and Denison, 2002; Bowes et al., 2003; House, 2003). River bed sediments can play an important role in buffering concentrations of soluble reactive phosphorus (SRP) in surface waters (House and Denison, 1998, 2002; House and Warwick, 1999). This buffering is strongest under low-flow conditions, when there is a relatively long contact time between the water column and the bed sediment and where the sediment surface area to water volume is high.

Over the last few years, there has been a vast research effort to quantify and model diffuse-source phosphorus and sediment losses from agriculture (e.g. Johnes, 1996; Haygarth and Jarvis, 1999; Chambers et al., 2000; Heathwaite and Dils, 2000; Withers et al., 2001a,b; Hutchins et al., 2002; Heathwaite, 2003; Robertson, 2003; Withers and Bailey, 2003). However, there has been very little research to directly examine within-river ecological impacts of diffuse agricultural P inputs. Greatest diffuse agricultural P flux contributions tend to be generated as a result of winter storm events, when in-stream ecological impacts are minimal. However, a proportion of the agricultural diffuse-source sediment-associated P, which is flushed into the stream channel under high flows, will be deposited and stored on the river bed during downstream transport and potentially be available for release of dissolved P under stable low-flow conditions. River bed sediments therefore potentially provide a key '*missing link*' between sediment-associated diffuse sources of P delivered to the stream channel during rainfall events and the subsequent impacts at times of ecological sensitivity. The critical time for impacts of P in rivers is during spring/summer low-flows, when eutrophication risk is greatest. At this critical time, diffuse sources of sediment-associated P stored on the river bed may potentially release SRP, the main dissolved bioavailable form of P (Ekholm and Krogerus, 2003). Information is therefore required on whether river bed sediments, derived from diffuse inputs, act as a sources or sinks of SRP at times of greatest eutrophication risk and the net contribution of river bed sediments to in-stream SRP flux modification under baseflow conditions.

The internal reservoir of P stored in bed sediments may potentially be available for re-release as soluble P, particularly following reductions in concentrations of SRP in overlying river water following introduction of P-mitigation measures. For example, the Lough Neagh study (Foy et al., 1995) demonstrated increases in SRP loads, despite reductions in point-source P discharges in the catchment. However, other studies (Jarvie et al., 2002a,b) have demonstrated more rapid recovery of water-column SRP concentrations following point-source P-reductions. Timescales of retention and release of P by river bed sediments, and thus the rate of response to point-source reductions, is likely to be controlled by a variety of factors, including the P-sorption characteristics of the bed sediments, the SRP concentration in the overlying water column, stream transport characteristics and residence times of bed sediments. New information is therefore required about the P-exchange characteristics of bed sediments upstream and downstream of STWs and their dissolved P flux contribution to/from the overlying river water in order to assess what the actual changes will be.

In this study, the P-exchange characteristics of bed sediments are examined for a wide range of sites across the Herefordshire Wye and the Hampshire Avon Rivers. Equilibrium Phosphorus Concentration measurements, EPC_0 (Taylor and Kunishi, 1971; House et al., 1995) were undertaken to provide information about whether the river bed sediments will extract or release SRP from the overlying river water. The kinetics of the interactions between bed sediments and SRP were undertaken and used in conjunction with EPC_0 measurements to provide simple estimates of fluxes of SRP to/from the river bed sediments. River bed sediment samples were collected from a range of locations, corresponding with different agricultural land uses (from intensive grassland and livestock production and arable land to low intensity grassland), geological types (from upland igneous /metamorphic to lowland sandstone and limestone lithologies) and human impacts (from rural environments to sites draining urban areas and upstream and downstream of STWs).

This research examines the circumstances under which river bed sediments may act as sources or sinks of SRP and any seasonal or spatial variability in SRP-exchange characteristics of bed sediments, linked to land use, the impact of STW discharges and geology. This work is part of a wider research project, PSYCHIC (**P**hosphorus and **S**ediment **Y**ield **CH**aracterisation **I**n **C**atchments), which seeks to examine the impact of agricultural land use and land management practices on losses of phosphorus and sediment at the catchment scale.

2. Study areas

The Hampshire Avon and the lower (Herefordshire) Wye (Fig. 1a–d) have been chosen within PSYCHIC as two case study catchments where diffuse loads of sediment and phosphorus from agriculture are of great concern (Environment Agency, 2002; Jarvie et al., 2004a). Both rivers have been designated Special Areas of Conservation under the EU Habitats Directive. The Wye catchment (4136 km^2) spans a wide range of riverine environments from base-poor upland streams, to the silty lowland rivers, which are of concern in terms of phosphorus and sediment loss. Within the lower Wye catchment, the Rivers Lugg and the Monnow are the two major tributaries, flowing

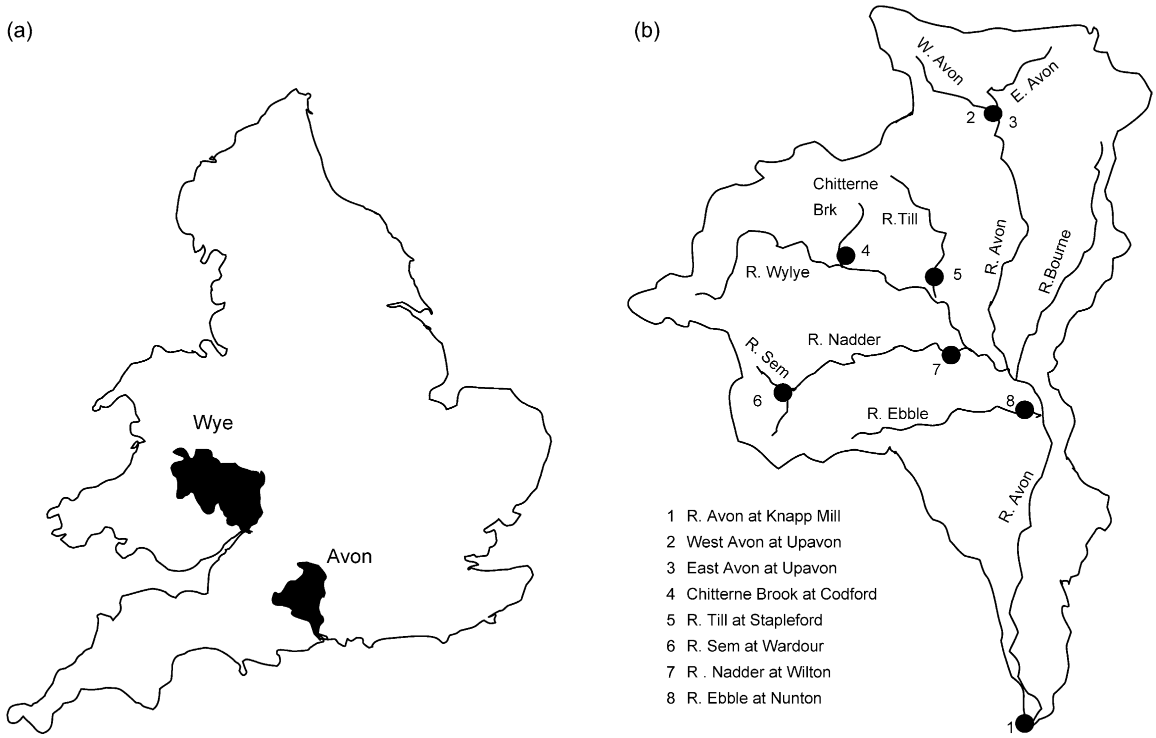

Fig. 1. (a) Map of England and Wales showing the locations of the Wye and Avon catchements, (b) the PSYCHIC sampling sites in the Avon catchment, (c) the PSYCHIC sampling sites in the Wye catchment, (d) additional main river sampling sites in the Wye catchment.

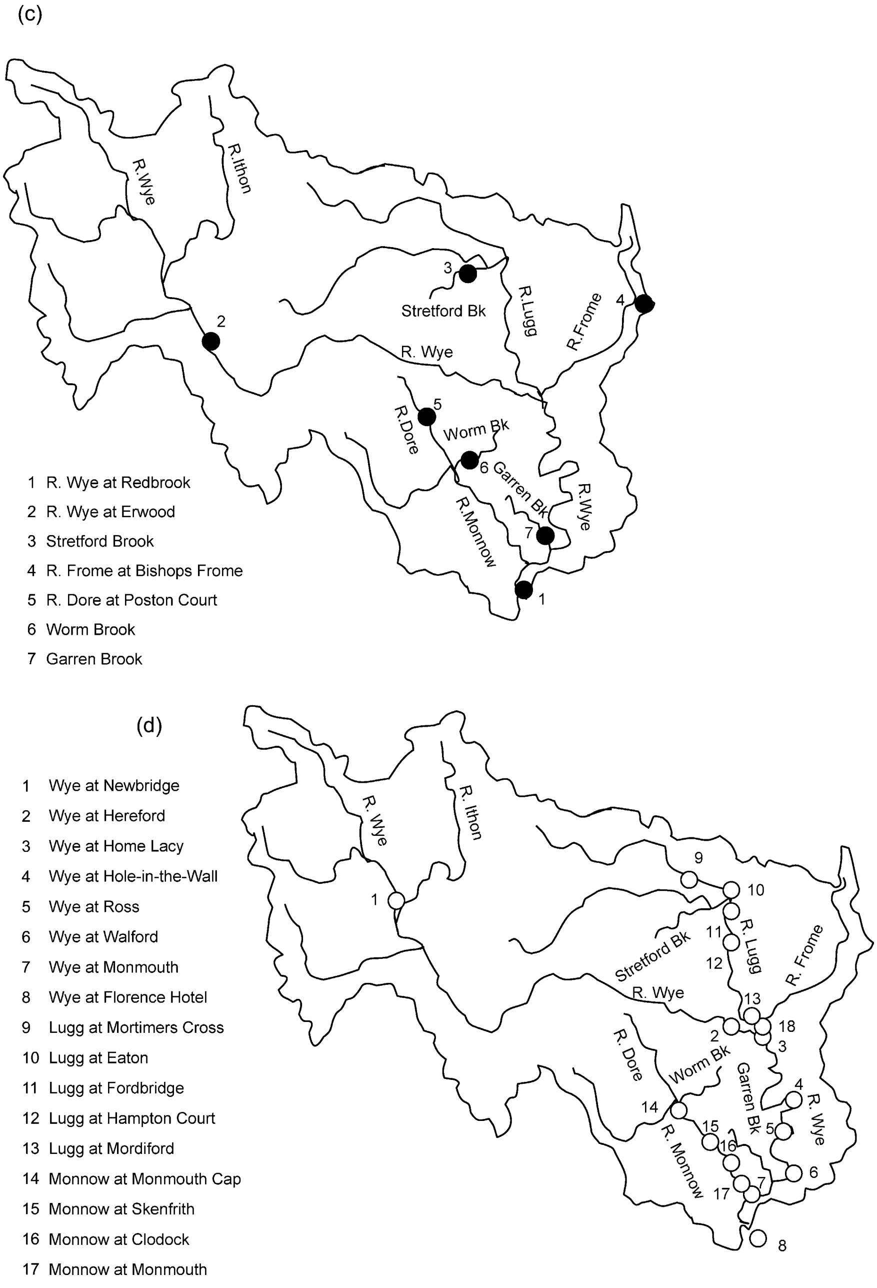

Fig. 1 (*continued*)

into the main River Wye downstream of Hereford. After Hereford, the Wye flows southwards to the Severn Estuary. The Hampshire Avon ($1650\,km^2$) rises on the Chalk down-land north of Pewsey in southern England, as two tributaries: the East and West Avon. The upper Avon catchment is composed of a radial pattern of major tributaries (Ebble, Nadder, Wylye, Avon and Bourne) which converge close to the town of Salisbury, from where the Avon flows south via Ringwood to the English Channel.

Table 1a
Catchment characteristics for Avon PSYCHIC sites

	Avon @ Knapp Mill	East Avon @ Upavon	West Avon @ Upavon	Chitterne @ Codford	Till @ Stapleford	Nadder @ Wilton	Sem @ Wardour	Ebble @ Nunton
Catchment area (km^2)	1715	171	84.6	68.1	125	216	34.2	107
Mean SAAR[a] (mm)	843	776	765	818	763	943	941	924
Est. mean flow (m^3s^{-1})	19.0	1.54	0.737	0.727	1.10	3.05	0.495	1.43
Elevation (m)								
Mean	120	141	137	157	128	138	162	128
Range	3–294	93–294	23–294	81–230	62–218	52–275	96–275	44–262
Land use								
%Arable	33.4	45.3	48.9	18.5	46.4	33.9	26.7	20.8
%Settlement	7.5	9.9	7.1	1.9	10.7	5.1	4.3	2.6
%Urban	1	3.3	0.1	0.2	3.9	0.2	0.4	0
%Lowland pasture	12.1	15.6	11.4	9.5	15.5	13.2	14.1	20.1
%All grazing land	38.9	31.1	36.2	71.9	31.5	40.6	58.2	58.4

[a] SAAR, Standard Annual Average Rainfall.

For the PSYCHIC project, 15 ‘core’ stream monitoring sites have been established in the Wye and Avon catchments (Fig. 1b and c, Tables 1a and b). Twelve of these PSYCHIC stream sites drain agricultural subcatchments, which are typically <100 km^2. In addition, PSYCHIC river monitoring sites have also been set up at the catchment outlets, on the River Wye (at Redbrook) and the River Avon (at Knapp Mill), and at the upland/lowland transition of the River Wye at Erwood, to examine inputs from the upland portion of the Wye catchment. More limited sampling was also undertaken at an additional 17 main river sites along the main Rivers Wye, Lugg and Monnow (Fig. 1d). Sampling was undertaken at these main river sites, to examine changes in bed-sediment SRP uptake and release: (i) upstream and downstream of sewage treatment works (STWs) on the Rivers Wye and Lugg, (ii) along the transition in agricultural land-use from grassland to arable farming on the River Monnow (Table 1c). These 17 main river sites were only sampled for EPC_0 determination. In contrast, the PSYCHIC sites have been subject to weekly water

Table 1b
Catchment characteristics for Wye PSYCHIC sites

	Wye @ Redbrook	Wye @ Erwood	Stretford Brook	Frome @ Bishops Frome	Dore @ Poston Court	Worm Brook	Garron Brook
Catchment area (km^2)	4017	1283	55.9	78.1	41.4	73.4	90.1
Mean SAAR[a] (mm)	1054	1413	780	744	972	767	781
Est. mean flow (m^3 s^{-1})	75.6	39.9	0.547	0.695	0.674	0.7	0.908
Elevation (m)							
Mean	267	343	114	157	230	114	114
Range	14–735	109–723	74–287	77–252	112–471	72–292	21–359
Land use							
%Arable	17.3	1.7	32.9	31.6	17.9	43.5	34.6
%Settlement	3.6	0.9	3.8	8.5	4.2	5.8	4.2
%Urban	0.2	0	0.2	0.6	0.6	0.2	0.2
%Lowland pasture	21	16.5	25.8	22.1	28	16.9	25.4
%All grazing land	52.1	54	49.5	48.4	63.3	33.4	47.4

[a] SAAR, Standard Annual Average Rainfall.

Table 1c
Wider Wye monitoring sites

Site	Reason for monitoring
Wye @ Newbridge	Upper catchment (low intensity farming)
Wye @ Hereford	U/s Hereford STWs
Wye @ Holme Lacy	D/s Hereford STWs and d/s confluence with Lugg
Wye @ Hole-in-Wall	D/s confluence with Frome
Wye @ Ross	U/s Ross-on-Wye STW
Wye @ Walford	D/s Ross-on-Wye STW
Wye @ Monmouth	U/s Monmouth STW
Wye @ Florence Hotel	D/s Monmouth STW
Lugg @ Mortimer's Cross	U/s Leominster STW
Lugg @ Eaton	D/s Leominster STW
Lugg @ Fordbridge	U/s Cadbury factory effluent (food processing)
Lugg @ Hampton Ct	D/s Cadbury Factory effluent (food processing)
Lugg @ Mordiford	Lower Lugg just u/s of confluence with Wye
Monnow @ Skenfrith	Grassland to Arable Transition
Monnow @ Monmouth Cap	↓
Monnow @ Clodock	
Monnow @ Monmouth	

quality monitoring and continuous flow measurement, as well as measurements of bed-sediment EPC_0 and P-sorption kinetics to estimate sediment–water SRP fluxes.

The PSYCHIC subcatchment monitoring sites (Tables 1a and b) and cover a range of land uses and geological types, but without any major settlements or large sewage treatment works. These subcatchments were chosen to examine the impact of different agricultural practices on phosphorus and sediment losses. The catchment characteristics for each of the PSYCHIC sampling sites are show in Tables 1a and b. Catchment boundaries for each sampling site were delineated from the Institute of Hydrology Digital Terrain Model (IHDTM; Morris and Flavin, 1990). Catchment areas, Standard Annual Average Rainfall (SAAR), estimated mean flow, and mean and ranges in elevation were also derived from the IHDTM. Land use data were derived from the Centre for Ecology and Hydrology Landcover Map (Fuller et al., 1994). Catchment boundaries were superimposed on the spatial datasets using Arcview GIS and the data for each subcatchment were extracted using a geoprocessing function.

Both the Wye and Avon catchments are predominantly rural. In the Avon catchment, 7.5% of the land area is covered by settlement and within the subcatchments, the areal percentage of settlement is lowest in the Chitterne (1.9%) and highest in the Till (10.7%; NB this may be influenced by military land use on Salisbury plain, as there are no major towns located in this catchment). In the Wye, 3.6% of the land area is covered by settlements within the subcatchments. Settled land ranges from 0.9% at Erwood to 8.5% on the Frome. Agriculture is the dominant land use in both catchments. In the Avon, the highest areal percentages of arable land (>45%) are in the West and East Avon and Till subcatchments. The Chitterne, Ebble and Sem subcatchments have higher proportions of livestock grazing land. In the Wye, the subcatchment with the highest arable influence is Worm Brook (44%) and the lowest percentage of arable land is at Erwood (1.7%). The Dore has the highest proportion of grazing land (63%), with 28% of the land area lowland pasture. The Wye catchment encompasses a wider range of topography: the upper catchment draining to Erwood has a mean elevation of 343 m a.o.d., rising from 109 to 723 m a.o.d and has a SAAR of 1413 mm. The Wye subcatchments in the east (Stretford Brook, Garren Brook, Worm Brook and River Frome) all have mean elevations below 160 m a.o.d and SAAR of less than 785 mm. The Avon catchment is low-lying with maximum elevation of 294 m a.o.d and mean elevations across all the subcatchments <165 m a.o.d. SAAR is highest in the west of the catchment in the Nadder (943 mm) and lowest in the Till (763 mm). In the Avon, permeable Cretaceous Chalk and less permeable Upper Greensand and Gault are the dominant geologies in all the PSYCHIC subcatchments, although the Sem and Nadder have smaller proportions of Cretaceous Chalk and significant proportions (ca. 20%) of impermeable clays of Cretaceous and Upper Jurassic age. The lower Avon has a geology which includes ca. 10% Eocene sediments (the acidic Barton, Bracklesham and Bagshot Beds). In contrast, the lower Wye catchment is dominated by Old Red Sandstone series, with Ordovician Slates and Shales in the upper catchment above Erwood.

3. Theory of P-sorption experiments and flux calculations

3.1. Equilibrium batch experiments for equilibrium phosphorus concentration (EPC_0) determination

The Equilibrium Phosphorus Concentration (EPC_0) of sediment provides information about whether sediments will take up or release SRP when placed in contact with a freshwater of known SRP concentration and can be used with measurements of sediment sorption kinetics to calculate flux transfers (House and Denison, 1998, 2000). EPC_0 is measured by batch equilibrium experiments: it is the concentration of SRP which, when placed in contact with the sediment, produces no change in SRP in solution over a 24 h period (Taylor and Kunishi, 1971; House et al., 1995). EPC_0 (measured in μmol l^{-1}) is calculated by plotting the relationship between the change in the amount of SRP sorbed after a 24 h incubation, relative to the initial amount (ΔN_a, in μmol g^{-1}), against the concentration of SRP in solution after 24 h (C_i, in μmol l^{-1}), and fitting an isotherm to the data using a least squares method (House and Denison, 2000) (Fig. 2). The Freundlich model (Drever, 1997; House and Denison, 2000) was used in this study for this purpose. The Freundlich model is derived from: $\Delta N_a = K_f C_i^n$, where K_f is the Freundlich sorption constant and n is a constant.

When $EPC_0 > SRP$ in the surrounding water, the sediment will release SRP to the water column and when $EPC_0 < SRP$, the sediment will take up SRP from the water column. If the EPC_0 is close to the SRP in the water column, the bed sediment and the river water are approximately in equilibrium with respect to SRP: N.B., this may also indicate that sediments exert a dominant control on water column P-availability (Haggard et al., 1999).

In this study, EPC_0 and SRP measurements are compared using a 'EPC_0 Percentage Saturation' (EPC_{sat}) term, which is defined as $EPC_{sat} = 100 (EPC_0 - SRP)/EPC_0\%$. Negative values of EPC_{sat} indicate potential for uptake of SRP from the water column by bed sediments. Correspondingly, positive values of EPC_{sat} indicate a potential for the release of SRP by bed sediments to the water column. A value of zero corresponds to an equilibrium situation. In this study, for pragmatic reasons, we have placed an EPC_{sat} cut-off of up to $\pm 20\%$ to define an approximate equilibrium between bed sediments and

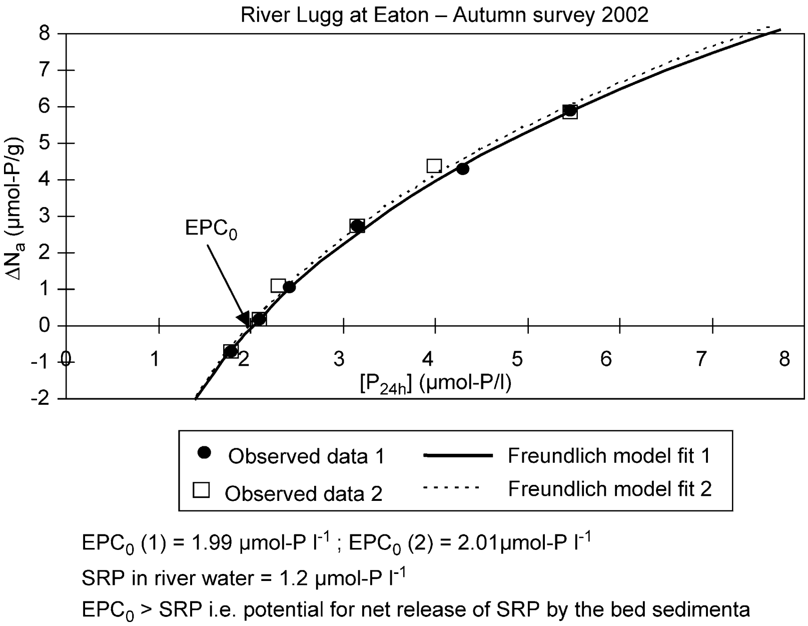

Fig. 2. Duplicate sorption isotherms for a bed sediment sample collected from the River Lugg during the Autumn 2002 survey. The plot shows how EPC_0 is calculated and demonstrates the very high precision for the method.

river water. A sorption constant (K_d; units: $l\,kg^{-1}$), describing the linear portion of the isotherm was also calculated and the magnitude of this measurement reflects the 'sorption affinity' of the sediment for SRP (House and Warwick, 1999). In this study, EPC_0 measurements were taken for both the PSYCHIC sites and the Wye main river sites.

3.2. Conceptual model of river interactions between river bed sediments and the overlying water column

Here, the river system is conceptualised as a series of inter-connected reaches, each of which has a known mass of fine (<2 mm) sediment on the surface of the river bed, which interacts with the overlying water to take up or release SRP. The bed sediment does not undergo full mixing with the volume of river water in the reach. In this study, we define a 'boundary layer', which is in intimate contact with the bed sediment. SRP is taken up into the sediment from the boundary layer or released from the sediment to the boundary layer. The depth of the water boundary layer is operationally defined as 0.1 m above the sediment surface. SRP is exchanged between the river bed and the volume of water contained in the boundary layer during the residence time of the river water within the reach. This exchange is characterised according to (i) a measured initial SRP concentration in the water column, (ii) the equilibrium phosphorus concentration of the bed sediment and (iii) kinetic parameters for P-sorption, which are derived experimentally. Since both sorption and kinetics experiments are undertaken on a suspension of a representative sample of sediment, the experiments reproduce the full mixing between sediment and the water in the boundary layer. Therefore this methodology provides an estimate of *maximum* SRP release/uptake rates. Here, SRP flux estimates to/from bed sediments have been calculated for the PSYCHIC core sites because there are river flow measurements at the sampling points at these sites, as well as estimates of channel geometry and bed-sediment depth. The fluxes calculated in this study are for an operationally defined boundary layer. They are not absolute values of SRP uptake and release for the PSYCHIC river reaches. Rather, they provide a guide to the *relative* differences in SRP uptake/release *potential* of different types of river bed sediment.

3.3. Kinetic experiments

The kinetics of the uptake and release of SRP by river bed sediments are described by the general equation (House and Warwick, 1999)

$$R = K_r(C_t - C_0)^n \tag{1}$$

where R is the change in amount of SRP sorbed ($\mu mol\ g^{-1}\ h^{-1}$), C_t is SRP concentration ($\mu mol\ l^{-1}$) in the overlying water, C_0 is the SRP concentration in the overlying water after 24 h ($\mu mol\ l^{-1}$), K_r is a rate constant ($\mu mol^{1-n}\ l^n\ g^{-1}\ h^{-1}$) and n is a power term.

A linear regression of $ln(R)$ with $ln(C_t - C_0)$ yields appropriate values of K_r and n. The amount of SRP released from the sediment or removed from solution at any time, dt, may then be obtained from

$$dM = K_r(C_t - EPC_0)^n S\, dt \tag{2}$$

where M is the amount of SRP sorbed (μmol), C_t is the concentration in solution at any time, t, EPC_0 is the equilibrium P concentration, and S is the estimated mass of fine (<2 mm) sediment (g) in the reach.

The fine bed-sediment Mass (S, g) within the 1 km reach is calculated using

$$S = V_{sed} S_{dens} \tag{3}$$

where S_{dens} is the average specific density for fine (<2 mm) bed sediments; and

$$V_{sed} = D_{sed} W_{cs} L_{riv} \tag{4}$$

where V_{sed} is the volume of sediment within the 1 km reach in (m^3). D_{sed} is an estimate of the mean depth of fine (<2 mm diameter particle size) bed sediment undergoing P exchange (in m), W_{cs} is the average width of the cross-section (m) L_{riv} is the length of the reach in m.

In this study an average S_{dens} of $1.2\times10^6\ g\ m^{-3}$ was used. The flux of SRP to/from the bed sediment is then calculated in g by integration (Eq. (2)) over the residence time (T_{res}) of river water within the 1 km river reach: $T_{res} = (D_{cs} W_{cs} L_{riv})/Q$, where D_{cs} is the mean cross-sectional depth of the reach and Q is the flow rate at the time of sampling. Bed sediment fluxes are therefore expressed as g-P T_{res}^{-1}

4. Methods

4.1. Bed-sediment sampling

Three surveys were carried for selected sites on both the Avon and Wye PSYCHIC during spring, summer and autumn (prior to the onset of autumn/winter high flows) under stable baseflow conditions. For the Avon, eight PSYCHIC sites were sampled as follows: 'spring' survey (23–24 April 2003), 'summer' survey (28–29 July 2003) and 'autumn' survey (6–7 October 2003). An earlier winter sample could not be collected on the Avon, due to restrictions on river bed disturbance during the salmon spawning and development period. For the Wye, seven PSYCHIC sites were sampled during the three main surveys: 'autumn' (17th Sept–10th October 2002), 'winter' (27th Feb–28th March 2003); and 'summer': (30 June–3rd July 2003). A preliminary survey was also carried out on the Wye in May 2002, and a restricted number of analyses were performed on these samples. The additional 18 sites along the main rivers (Wye, Lugg and Monnow) were sampled twice: during the autumn survey of 7 Sept–10 October 2002, and the winter survey of 27th Feb–28th March 2003.

Samples of fine (<2 mm) bed sediment were collected, as this fraction is the most geochemically reactive fraction. A vacuum sampling technique was used for collection of an integrated and representative sample from across the river reach and to a distance of 10 m upstream and 10 m downstream of the water quality sampling point. The sediment–water slurry is pumped through a 2 mm sieve (10 cm diameter) into a continuous-flow centrifuge system. The 2 mm sieve is fixed to a handle, which allows the sieve to be moved across the surface of the bed sediments, with sampling to a maximum depth of 5 cm. A sample of the overlying river water was also collected, filtered in the field and returned to the laboratory for SRP analysis. This measurement provides the water-column SRP concentration for comparison with the sediment EPC_0 measurement.

4.2. Sorption experiments for EPC_0 determination

Sediment samples were stored at 5–8 °C (to minimise biological activity in the samples) prior to carrying out the sorption experiments within 1 week of sample collection. Sorption experiments were undertaken using an 'artificial river water matrix' (2 mmol l^{-1} $CaCl_2$ solution). This solution was chosen to produce similar calcium concentrations and conductivity to those of the hard-waters of the Avon and lower Wye. Sorption experiments were undertaken at 10 °C (to reproduce average annual temperature conditions in groundwater-dominated rivers) and in the dark to minimise biological activity. For each sediment sample, known weights of wet sediment (equivalent to 0.5 g dry sediment) were placed in six polypropylene bottles with 200 ml of $CaCl_2$ solution, pre-chilled to 10 °C. All but one bottle was then spiked with KH_2PO_4 to provide a range of initial SRP concentrations (0, 2.5, 5, 10, 15 and 20 μmol l^{-1}). Bottles were then placed in an orbital incubator in the dark and shaken at 150 rpm at 10 °C for 24 h. After 24 h, each bottle was centrifuged and the supernatant was analysed for SRP concentrations. Sorption experiments for the autumn survey in the River Wye were carried out in duplicate (Fig. 2). The results of duplicate analyses demonstrate a high degree of analytical precision: $r^2=0.997$ with a gradient of 1.006 (±0.02) and a statistically insignificant intercept. Percentage deviation from the mean was 2.8%. Given the high labour intensity of undertaking batch sorption analyses and the high degree of precision of the method used, subsequent surveys were undertaken on single rather than duplicate samples.

4.3. Kinetic experiments to determine rates of SRP uptake or release

Rates of SRP release were measured for bed-sediment samples where EPC_0 exceeded SRP, and rates of SRP uptake were measured for bed-sediment samples where SRP exceeded EPC_0. For the SRP release experiments, known weights of wet sediment (equivalent to 0.5 g dry sediment) were placed in six polypropylene bottles with 200 ml of $CaCl_2$ solution, pre-chilled to 10 °C, with no additions of KH_2PO_4. For the SRP uptake experiments, the $CaCl_2$ solution in each bottle was spiked with KH_2PO_4 to an appropriate SRP concentration (higher than the EPC_0 of the sediment and close to the measured SRP concentration in the water column at the time of sediment sampling). Bottles were then placed in the orbital incubator in the dark and shaken at 150 rpm at 10 °C and removed after specific time intervals (5 mins, 15 mins, 30 mins, 1 h, 3 h, 6 h, 15 h, 24 h), centrifuged and analysed for SRP concentrations.

4.4. Water chemistry analysis

At each of the PSYCHIC sites in the Wye and Avon catchments, weekly water-quality monitoring data were collected over the period of the bed-sediment sampling programme. Soluble reactive phosphorus concentrations in river water samples, and in the artificial river water matrix during sorption experiments, were analysed colorimetrically on samples filtered through 0.45 μm membranes, using the method of Murphy and Riley (1962), modified by Neal et al. (2000). For the weekly water-quality monitoring, concentrations of total phosphorus (TP) and total dissolved phosphorus (TDP) were analyzed using an acid-persulphate digestion and colorimetry (see Jarvie et al., 2002d for further details). The Particulate Phosphorus (PP) fraction is calculated as the difference between TP and TDP and the Dissolved Hydrolysable Phosphorus (DHP) is calculated as the difference between TDP and SRP. In addition, calcium (Ca), iron (Fe) and boron (B) were measured on weekly filtered water samples, using an Inductively Coupled Plasma Optical Emission Spectrometer. Boron was measured to provide an indication of the influence of sewage effluent sources at each of the sites, since B is derived predominantly from detergents discharged via effluent (Neal et al., 1998; Jarvie et al., 2002a,b; Wyness et al., 2003). Ca and Fe were analysed to provide information on the overall river-water matrix chemistry, along with pH and Gran alkalinity. Nitrate (NO_3) was measured by Ion Chromatography (Dionex) to provide an indicator of agricultural diffuse nutrient leaching. The value of NO_3 as an indicator of agricultural sources can be gauged when an estimate of the point sewage effluent sources are evaluated using B as a marker. Neal et al. (2005) has shown that the average NO_3/B ratio in sewage treatment effluent averages 0.0236 mg-NO_3 l^{-1} μg-B l^{-1}. The nitrate range for the waters considered here is 0–69 mg-NO_3 l^{-1} and the estimated sewage effluent contribution is 0–2 mg-NO_3 l^{-1}.

5. Results

5.1. Water chemistry and characteristics of the PSYCHIC sites

A summary of nutrient and major and minor element chemistry are presented in Tables 2a and b to provide information on the range in P concentrations and likely sources of runoff and P at each of the sampling sites. The water chemistry of the Avon sampling sites is typical of Chalk groundwater dominated streams, with high pH (mean values c. 8) and alkalinity (mean values ca. 4000 μEql^{-1}). Highest Ca concentrations (>100 mg l^{-1}) are found in the catchments with the highest proportions of calcareous geologies (Chalk, Greensand and Gault) where calcite ($CaCO_3$) weathering and groundwater inputs are at their highest. Highest nitrate concentrations occur in those subcatchments with high areal percentages of arable land and which are largely groundwater-fed. The lowest Ca and nitrate concentrations are found in the Sem, reflecting lower groundwater and weathering contributions and higher near-surface runoff from the impermeable Jurassic clays. The high Fe concentration in the Sem suggests a lithogenous source and higher concentrations of particulate matter from near-surface runoff; the Sem also has the highest proportion of PP. Highest mean TP concentrations are found in the East and West Avon (330 μg-P l^{-1}, 245 μg-P l^{-1}, respectively) and in the Sem (291 μg-P l^{-1}). Lowest mean TP concentrations are found in the Chitterne (27 μg-P l^{-1}), Ebble (52 μg-P l^{-1}) and Till (57 μg-P l^{-1}). SRP accounts for most of the TP concentration in all the Avon rivers, with SRP on average accounting for between 52% of TP (Sem) to c. 80% of TP (East and West Avon). Mean DHP concentrations range from 7 μg-P l^{-1} in the Chitterne to 35 μg-P l^{-1} in the Sem. DHP on average accounts for between 6% of TP (West Avon) and 32% of TP (Chitterne). B concentrations range between 6 and 17 μg l^{-1} on the Chitterne to between 23 and 98 μg l^{-1} on the Sem. Studies from a neighbouring Chalk river, the Kennet, showed that the 'background' B concentration the upper headwaters with no major sewage influence ranged from 5 to 30 μg l^{-1}, while immediately downstream of major STWs, B concentrations ranged from 20 to 100 μg l^{-1} (Jarvie et al., 2002a). The results from the Avon therefore indicate

Table 2a
Summary water quality data for Avon PSYCHIC monitoring sites

River		pH	Alkalinity (μEq l^{-1})	SRP (μg-P l^{-1})	DHP (μg-P l^{-1})	PP (μg-P l^{-1})	B (μg l^{-1})	SRP/B	SRP as % of TP	DHP as % of TP	PP as % of TP	NO_3 (mg-$NO_3 l^{-1}$)	Ca (mg l^{-1})	Fe (μg l^{-1})
Avon Knapp Mill	Mean	8.00	4036	112	26	20	29.2	3.9	70.7	14.9	14.7	24.5	95.6	39.8
	Median	8.02	4113	104	14	21	28.9	3.8	73.6	10.9	13.5	23.5	96.8	23.1
	Max	8.35	4613	222	193	49	47.3	6.5	96.9	87.5	51.4	32.5	111	168
	Min	7.64	3266	7	0	0	20.1	0.2	3.0	0.0	0.0	17.0	70.9	11.8
Chitterne	Mean	7.76	4296	12	7	10	11.2	1.0	42.4	31.6	33.4	25.7	101	13.4
	Median	7.65	4289	7	4	7	11.2	0.8	40.8	21.4	26.4	27.0	101	4.4
	Max	8.40	4918	55	43	93	16.5	3.5	100	100	100	29.5	113	319
	Min	7.42	3276	0	0	0	6.1	0.0	0.0	0.0	0.0	17.5	91.3	1.1
E. Avon	Mean	7.94	4894	196	15	37	43.7	4.5	80.7	6.2	14.6	36.0	123	29.6
	Median	7.93	4899	189	10	34	43.0	4.1	80.4	3.9	15.0	36.5	124	15.5
	Max	8.24	5602	339	75	123	51.3	8.4	100	33.3	35.2	40.0	140	357
	Min	7.62	4160	111	0	5	37.7	2.6	47.2	0.0	2.5	28.0	99.5	6.8
Ebble	Mean	7.91	4270	31	11	14	15.2	2.0	58.9	23.3	24.8	30.0	100	8.5
	Median	7.90	4223	26	7	10	14.8	1.8	58.3	14.1	21.9	29.5	99.7	7.4
	Max	8.22	4861	147	42	109	34.0	10.1	100	88.2	100	36.5	110	48.5
	Min	7.67	3821	0	0	0	12.1	0.0	0.0	0.0	0.0	24.0	91.4	2.2
Nadder	Mean	7.95	4024	116	20	41	23.9	4.7	64.4	11.6	24.5	28.0	98.9	30.2
	Median	7.95	4160	121	15	32	23.0	4.7	68.2	9.1	19.7	25.8	99.7	15.8
	Max	8.23	4655	264	72	254	45.3	8.7	98.9	49.0	82.6	39.5	110	139
	Min	7.65	2365	0	0	0	17.4	0.0	0.0	0.0	0.0	19.0	68.6	5.1
Sem	Mean	7.69	3172	153	34	108	65.6	2.5	52.1	12.1	36.9	9.7	70.3	204
	Median	7.73	3383	140	35	84	68.1	2.4	53.9	11.2	31.4	9.0	74.3	158
	Max	8.05	4447	346	131	348	97.8	10.1	81.8	60.0	100	40.0	86.8	616
	Min	7.10	1193	13	0	5	23.3	0.2	5.6	0.0	3.0	2.5	26.9	52.8
Till	Mean	7.85	4471	33	12	11	16.2	1.9	57.7	22.3	20.1	26.7	107	6.5
	Median	7.85	4432	26	8	10	16.2	1.7	65.3	16.9	16.7	26.5	106	5.1
	Max	8.10	4718	91	68	49	20.9	4.5	91.1	80.9	55.7	31.5	117	34.5
	Min	7.60	3827	0	0	0	10.9	0.0	0.0	0.0	0.0	21.0	101	1.3
W. Avon	Mean	7.99	5250	263	21	49	52.7	4.9	78.8	6.4	15.5	22.5	125	22.3
	Median	7.98	5314	222	12	38	48.2	4.9	79.9	4.2	11.5	18.8	125	15.7
	Max	8.35	5764	460	165	260	75.6	6.6	100	43.4	47.7	38.0	140	103
	Min	7.64	3576	127	0	0	33.2	2.8	48.0	0.0	0.0	13.5	111	9.5

Table 2b
Summary water quality data for Wye PSYCHIC monitoring sites

River		pH	Alkalinity (μEq l^{-1})	SRP (μg-P l^{-1})	DHP (μg-P l^{-1})	PP (μg-P l^{-1})	B (μg l^{-1})	SRP/B	SRP as % of TP	DHP as % of TP	PP as % of TP	NO_3 (mg-$NO_3$$l^{-1}$)	Ca (mg l^{-1})	Fe (μg l^{-1})
Dore	Mean	7.82	4129	105	22	28	17.2	5.9	71.0	15.4	15.2	16.2	86.2	20.2
	Median	7.86	4392	86	14	10	16.8	4.9	74.8	10.4	9.8	16.5	90.9	10.7
	Max	8.09	4783	258	190	190	28.7	11.6	100	91.6	71.2	19.5	103	127
	Min	7.39	1901	16	0	0	9.2	0.7	23.2	0.1	0.0	12.0	43.1	4.3
Frome	Mean	7.97	4679	400	29	38	39.9	9.4	84.3	6.2	9.8	28.5	88.1	53.4
	Median	7.98	5153	398	18	27	39.3	10.1	86.7	5.4	6.6	28.0	91.2	25.1
	Max	8.22	5712	809	212	236	59.5	16.8	100	28.9	33.2	43.0	102	457
	Min	7.47	0	121	0	0	23.8	4.1	61.3	0.0	0.0	16.5	39.4	7.4
Garren Brook	Mean	8.00	4844	69	19	20	27.6	2.4	63.2	19.4	18.0	51.3	95.5	24.2
	Median	7.99	4900	65	10	12	27.3	2.4	65.6	11.7	13.8	51.8	98.9	15.3
	Max	8.24	5657	212	164	123	38.8	7.4	94.0	93.3	51.6	59.5	113	101
	Min	7.83	3745	0	0	0	0.0	0.0	0.0	0.0	0.0	38.5	0.0	0.0
Stret-ford Brook	Mean	7.97	4845	439	24	24	36.2	10.4	86.3	6.0	8.1	37.6	110	34.4
	Median	7.97	4926	285	19	18	31.6	8.4	87.8	5.3	6.5	38.8	111	20.0
	Max	8.25	5665	1292	208	80	68.3	22.9	100	18.8	27.3	59.5	123	484
	Min	7.62	3074	85	0	0	19.8	2.8	64.6	0.0	0.0	18.0	77.6	0.0
Worm Brook	Mean	7.93	4743	130	21	27	25.1	5.0	73.5	11.6	15.1	33.6	103	27.4
	Median	7.96	5067	119	15	17	25.2	4.9	73.5	11.4	13.5	31.8	109	19.3
	Max	8.22	5597	444	123	178	37.4	14.5	100	36.1	38.2	69.0	126	188
	Min	7.33	2144	33	0	0	0.1	1.3	51.0	0.0	1.8	12.5	0.0	0.0
Wye at Erwood	Mean	7.59	798	22	15	19	10.2	1.5	32.5	40.4	29.7	5.8	16.7	124
	Median	7.54	463	10	10	9	9.1	1.3	33.8	27.7	27.3	3.5	10.2	100.0
	Max	8.61	5597	444	123	212	37.4	2.3	100	100	100	69.0	126	277
	Min	6.85	251	0	0	0	0.1	0.4	0.0	0.0	0.0	1.0	0.0	0.0
Wye at Red-brook	Mean	7.92	2278	45	20	31	21.0	2.3	48.8	20.3	31.5	14.1	45.2	53.4
	Median	7.93	2318	42	14	22	21.3	2.1	53.4	15.6	28.8	14.0	47.6	46.0
	Max	8.47	3646	121	128	162	32.1	5.3	74.3	115.8	71.2	23.0	67.1	187
	Min	7.39	969	10	0	0	10.7	0.4	12.9	0.0	0.0	6.5	20.1	0.0

that the West Avon, Sem, Nadder and the River Avon at Knapp Mill all show sewage influence. Only the Chitterne, Ebble and Till appear relatively unaffected by sewage effluent.

In the Wye catchment, the lower tributaries are also well-buffered, with high pH, alkalinity and Ca concentrations, characteristic of high weathering rates and groundwater discharge from the calcareous cements within the Old Red Sandstone series. The upper main River Wye at Erwood, draining the Silurian and Ordovician slates and shales, has considerably lower pH, alkalinity and Ca concentrations. The main River Wye at Redbrook also has low Ca and alkalinity, reflecting the large flow contribution from the upper Wye catchment. Mean Ca and NO_3 concentrations appear to be spatially correlated, as in the Avon, with highest concentrations of NO_3 linked to groundwater-fed subcatchments dominated by arable farming. The River Frome and Stretford Brook show the greatest influence of sewage effluent, with highest mean B concentrations (>35 μg l^{-1}) and highest SRP concentrations (400 and 439 μg-P l^{-1}, respectively). Lowest mean SRP concentrations are found at Erwood and Redbrook (22 and 45 μg-P l^{-1}, respectively). There is a comparatively little variation in mean PP concentrations, which range from 19 μg l^{-1} at Erwood to 38 μg-P l^{-1} on the Frome, and mean DHP concentrations, which range from10 μg-P l^{-1} at Erwood to 38 μg-P l^{-1} on the Frome. In the Frome and Stretford Brook, on average, SRP accounts for 84 and 86% of TP, repectively. DHP and PP fractions have greater proportional significance at other sites: at Erwood, DHP accounts for 40% of TP and PP accounts for 30% of TP.

5.2. Equilibrium phosphorus concentrations (EPC_0), percentage EPC saturation (EPC_{sat}) and sorption constants (K_d)

EPC_0 values for the Avon PSYCHIC sites range from 0.06 μmol l^{-1} in the Chitterne, to 5.74 μmol l^{-1} in the West Avon with a mean value of EPC_0 across the sites of 1.84 μmol l^{-1} (Table 3a). For the Wye

Table 3a
EPC_0, SRP EPC_{sat} and K_d measurements for the Avon PSYCHIC monitoring sites

	Site	EPC_0 (μmol l^{-1})	SRP (μmol l^{-1})	EPC_{sat} (%)	UPTAKE/ RELEASE	K_d (l kg^{-1})
Spring 2003 (April)[a]	R. Avon @ Knapp Mill	0.74	1.58	−114	UPTAKE	3094
	W. R. Avon @ Upavon	1.72	6.31	−267	UPTAKE	1959
	E. R. Avon @ Upavon	2.33	6.1	−162	UPTAKE	639
	R. Till @ Stapleford	2.59	1.05	59	RELEASE	221
	R. Chittern @ Codford	0.67	0.32	52	RELEASE	630
	R. Sem @ Wardour	0.46	2.74	−496	UPTAKE	1339
	R. Nadder @ Wilton	1.03	1.89	−83	UPTAKE	1630
	R. Ebble @ Nunton	0.68	0.32	53	RELEASE	920
Summer 2003 (July)	R. Avon @ Knapp Mill	1.04	5.05	−386	UPTAKE	2524
	W. R. Avon @ Upavon	4.7	14.3	−204	UPTAKE	786
	E. R. Avon @ Upavon	2.02	6.1	−202	UPTAKE	307
	R. Till @ Stapleford	0.89	0.63	29	RELEASE	582
	R. Chittern @ Codford	0.19	0.07	63	RELEASE	1335
	R. Sem @ Wardour	0.51	9.05	−1675	UPTAKE	3114
	R. Nadder @ Wilton	1.01	6	−494	UPTAKE	3165
	R. Ebble @ Nunton	1.78	0.84	53	RELEASE	556
Autumn 2003 (October)	R. Avon @ Knapp Mill	1.60	4.63	−189	UPTAKE	1157
	W. R. Avon @ Upavon	5.74	13.4	−133	UPTAKE	394
	E. R. Avon @ Upavon	0.87	5.89	−576	UPTAKE	1153
	R. Till @ Stapleford	0.98	0.53	46	RELEASE	685
	R. Chittern @ Codford	0.06	0.32	−482	UPTAKE	12,183
	R. Sem @ Wardour	0.54	3.37	−526	UPTAKE	4342
	R. Nadder @ Wilton	2.45	5.68	−132	UPTAKE	743
	R. Ebble @ Nunton	0.66	1.26	−92	UPTAKE	1258

[a] NB winter sampling was not permitted between November and end of March, to minimise disturbance to spawning grounds.

Table 3b
EPC_0, SRP EPC_{sat} and K_d, and measurements for Wye PSYCHIC sites

	Site	EPC_0 (μmol l^{-1})	SRP (μmol l^{-1})	EPC_{sat} (%)	UPTAKE/ RELEASE	K_d (l kg^{-1})
Spring 2002 (May)	R. Dore @ Poston Court Farm	2.52	2.42	4	EQUILIBRIUM[a]	298
	R. Frome @ Bishops Frome	2.52	7.58	−201	UPTAKE	711
	Stretford Brook	2.79	8.21	−194	UPTAKE	135
	Garren Brook	1.26	2.42	−92	UPTAKE	190
	Worm Brook	5.65	4.95	12	EQUILIBRIUM	172
Autumn 2002 (September–October)	R. Wye @ Redbrook	0.83	0.32	61	RELEASE	2829
	R. Wye @ Erwood	0.09	0.28	−68	UPTAKE	3800
	R. Dore @ Poston Court Farm	1.16	4.74	−309	UPTAKE	1312
	R. Frome @ Bishops Frome	6.29	20.2	−221	UPTAKE	438
	Stretford Brook	4.99	24.2	−385	UPTAKE	720
	Garren Brook	1.32	1.69	−28	UPTAKE	603
	Worm Brook	3.86	5.16	−34	UPTAKE	496
Winter 2003 (February–March)	R. Wye @ Redbrook	0.27	0.32	−19	EQUILIBRIUM	2993
	R. Wye @ Erwood	0.08	0.1	−25	UPTAKE	7377
	R. Dore @ Poston Court Farm	0.64	2.32	−263	UPTAKE	1739
	R. Frome @ Bishops Frome	0.86	4.94	−474	UPTAKE	702
	Stretford Brook	1.24	2.84	−129	UPTAKE	1072
	Garren Brook	1.02	0.03	97	RELEASE	1384
	Worm Brook	1.47	1.47	0	EQUILIBRIUM	465
Summer 2003 (June)	R. Wye @ Redbrook	0.65	1.37	−111	UPTAKE	2818
	R. Wye @ Erwood	<0.01	0.42	>4000	UPTAKE	1544
	R. Dore @ Poston Court Farm	1.4	4.53	−224	UPTAKE	677
	R. Frome @ Bishops Frome	4.49	21.3	−373	UPTAKE	702
	Stretford Brook	6.24	21.5	−244	UPTAKE	440
	Garren Brook	2.44	3.26	−34	UPTAKE	386
	Worm Brook	4.82	8.21	−70	UPTAKE	435

[a] Eqilibrium between bed sediments and river water where EPC_{sat} is up to ±20%.

PSYCHIC sites, EPC_0 values (Table 3b) range from <0.01 μmol l^{-1} at Erwood to 6.29 μmol l^{-1} in the Frome (mean EPC_0=2.29 μmol l^{-1}). For the main river sites on the Wye, EPC_0 values range from 0.03 on the Wye at Newbridge to 5.12 on the Monnow at Monmouth Cap (mean EPC_0=0.74 μmol l^{-1}) (Table 3c). Examining the changes in EPC_0 along the Rivers Lugg and Wye, EPC_0 values increase markedly downstream of the first major STWs (Leominster STW on the Lugg and Hereford STWs on the Wye). Increases in SRP are also detectable downstream of Ross-on-Wye and Monmouth STWs on the Wye during the autumn, but not in winter. There is a positive relationship between EPC_0 and SRP concentrations for the PSYCHIC and main river sites ($r^2=0.46$, $n=84$, $P<0.001$, gradient=0.23(± 0.06), intercept=0.81(±0.34)). The correlation between EPC_0 and SRP is highest for the Wye PSYCHIC sites ($r^2=0.65$, $n=25$, $P<0.01$, gradient=0.212 (±0.06), intercept=1.11 (±0.61)), compared with the Avon PSYCHIC sites ($r^2=0.19$, $n=27$, $P=0.05$, gradient=0.217 (±0.17), intercept=1.0 (±0.95)) and the Wye main river sites ($r^2=0.1$, $n=32$, $P=0.08$, gradient=0.54 (±0.6), intercept=0.38 (±0.52)). If there had been equilibrium across the sites then EPC_0 equals SRP and the regression lines would have a gradient of unity. The observed regression gradients are less than unity and the higher correlation for the Wye reflects increases in the amount of SRP sorbed by sediment as a result of exposure to waters with higher ambient SRP concentrations. For the Wye and the strongly sewage-impacted Avon sites (Knapp Mill, Nadder and West Avon), EPC_0 and SRP concentrations tend to be lower for the winter survey (Tables 3a–c). Lower SRP values in winter reflect higher winter baseflows and thus greater dilution of point sources of SRP. In the Sem, EPC_0 values remain largely constant

Table 3c
EPC_0, SRP EPC_{sat} and K_d measurements for wider Wye monitoring sites

	Site	EPC_0 ($\mu mol\ l^{-1}$)	SRP ($\mu mol\ l^{-1}$)	EPC_{sat} (%)	UPTAKE/ RELEASE	K_d ($l\ kg^{-1}$)
Autumn 2002 (September)	Wye @ Newbridge	0.05	0.14	−180	UPTAKE	5937
	Wye @ Hereford	0.09	0.2	−122	UPTAKE	5757
	Wye @ Holme Lacy	0.64	0.74	−16	EQUILIBRIUM[a]	3996
	Wye @ Hole-in-Wall	0.71	1.26	−77	UPTAKE	2276
	Wye @ Ross	0.55	0.64	−16	EQUILIBRIUM	2269
	Wye @ Walford	0.64	1.26	−97	UPTAKE	2274
	Wye @ Monmouth	0.63	0.95	−51	UPTAKE	1945
	Wye @ Florence Hotel	1.15	1.58	−37	UPTAKE	838
	Lugg @ Mortimer's Cross	0.42	0.53	−26	UPTAKE	358
	Lugg @ Eaton	1.99	1.2	39	RELEASE	3351
	Lugg @ Fordbridge	1.89	1.7	9	EQUILIBRIUM	356
	Lugg @ Hampton Ct	1.46	1.93	−32	UPTAKE	438
	Monnow @ Skenfrith	0.52	1.89	−263	UPTAKE	454
	Monnow @ Monmouth Cap	5.12	0.46	91	RELEASE	438
	Monnow @ Clodock	1.77	0.57	68	RELEASE	811
	Monnow @ Monmouth	1.4	1.6	−14	EQUILIBRIUM	1146
Winter 2003 (February–March)	Wye @ Newbridge	0.03	0.1	−233	UPTAKE	5775
	Wye @ Hereford	0.07	0.1	−43	UPTAKE	12,628
	Wye @ Holme Lacy	0.06	0.32	−433	UPTAKE	2664
	Wye @ Hole-in-Wall	0.18	0.32	−78	UPTAKE	5000
	Wye @ Ross	0.17	0.53	−212	UPTAKE	2023
	Wye @ Walford	0.26	0.32	−23	EQUILIBRIUM	1073
	Wye @ Monmouth	0.27	0.65	−141	UPTAKE	3836
	Wye @ Florence Hotel	0.07	0.53	−657	UPTAKE	679
	Lugg @ Mortimer's Cross	0.06	0.32	−433	UPTAKE	2277
	Lugg @ Eaton	0.74	0.1	86	RELEASE	1200
	Lugg @ Fordbridge	0.46	0.84	−83	UPTAKE	381
	Lugg @ Hampton Ct	0.5	0.74	−48	UPTAKE	508
	Monnow @ Skenfrith	0.53	0.32	40	RELEASE	330
	Monnow @ Monmouth Cap	0.44	0.05	89	RELEASE	525
	Monnow @ Clodock	0.23	0.05	78	RELEASE	507
	Monnow @ Monmouth	0.5	0.32	36	RELEASE	519

[a] Eqilibrium between bed sediments and river water where EPC_{sat} is up to ±20%.

during all three surveys. On the East Avon, Chitterne and Till, SRP and EPC_0 concentrations actually decrease as baseflows fall from spring to autumn.

EPC_{sat} percentages for the Avon PSYCHIC sites range from −1675% in the Sem to +63% in the Chitterne. For the Wye PSYCHIC sites, EPC_{sat} percentages range from −474% in the Frome to >4000 in the River Wye at Erwood. For the main Wye rivers, EPC_{sat} percentages range from −657% on the Wye at Florence Hotel to +91% for the Monnow at Monmouth Cap. The majority of bed sediments from the Wye and Avon have negative EPC_{sat} percentages of >20%, indicating that most of the river bed sediments in the PSYCHIC subcatchments are acting as a net sink for SRP. For the Avon, 37% of the PSYCHIC monitoring sites showed significant potential for SRP release from bed sediments, i.e. positive EPC_{sat} percentages >20%. Within the Avon, sites Rivers Till, Chitterne and Ebble show potential for SRP release; these are the chalk streams, which are largely unimpacted by sewage effluent. For the Wye, 8% of the PSYCHIC sites and 28% of the main river sites showed significant potential for SRP release from bed sediments. Within the Wye catchment, the Lugg at Eaton (located downstream of Leominster STW) and sites on the Monnow showed consistent potential for SRP release, while Garren Brook show potential for SRP release in winter and Wye at Redbrook showed potential for SRP release in autumn. The greatest potential for SRP uptake into bed sediments (i.e. highest negative EPC_{sat} percentages) generally occur where SRP concentrations are highest. This suggests that the potential for SRP uptake by bed sediments is greatest at sites where bed-sediments are exposed to highest SRP concentrations (i.e. heavily sewage-impacted sites). The strongest negative relationship between EPC_{sat} and SRP is for the Wye PSYCHIC sites ($r^2=0.4$, $n=25$ $P=<0.01$), compared with the Avon PSYCHIC sites ($r^2=0.18$, $n=27$, $P=0.03$). There is no significant relationship between EPC_{sat} and SRP for the Wye main river sites.

K_d values for the Avon PSYCHIC sites range from 221 to 12,183 l kg^{-1} (mean $K_d=1863$ l kg^{-1}) and for the Wye PSYCHIC sites, K_ds vary from 135 to 7377 l kg^{-1} (mean $K_d=1325$ l kg^{-1}). For the Wye main river sites, K_ds vary from 330 to 12628 l kg^{-1} (mean $K_d=4004$ l kg^{-1}). The range in K_d values from this study are consistent with K_d values for a wide range of bed sediments, reported by House and Warwick (1999). At EPC_0 values above ca. 2 μmol l^{-1}, K_d values are relatively low (ca. <750 l kg^{-1}) and show low variability. However, below EPC_0 values of ca. 2 μmol l^{-1}, the variability in K_d values increases as EPC_0 decreases. For all sites, the highest K_d values (ca. >2500 l kg^{-1}) are found at the lowest EPC_0 values, showing that sediments with the lowest EPC_0 values tend to have the highest sorption affinity for SRP. K_ds tend to be higher in the winter in the Wye, reflecting the lower EPC_0 values. In the Avon catchment, Knapp Mill, West Avon and Wylye also have higher winter K_ds, reflecting the lower EPC_0 s of the winter bed sediments. In contrast, the East Avon Till, Chitterne and Sem have highest K_d values in autumn.

5.3. Results of the kinetic experiments to examine rates of SRP uptake and release

The kinetic experiments demonstrated that uptake and release of SRP by bed sediments occur very quickly where there is full mixing of the sediment and water. An example of the typical kinetics curve for SRP uptake is shown in Fig. 3. Typically, most of the SRP flux transfer between the sediment and water occurs in less than 1 hour, well within the average water residence time calculated for the 1 km reaches at the PSYCHIC monitoring sites under baseflow conditions (Avon: mean $T_{res}=1.4$ h, range $=0.7$–3.2 h; Wye mean $T_{res}=1.4$ h, range $=$ 0.5–5.4 h). For the Avon, the average value of the rate constant, K, is 10.6 μmol^{1-n} l^{n} g^{-1} h^{-1} (range 0.84–54 μmol^{1-n} l^{n} g^{-1} h^{-1}), compared with 4.9 μmol^{1-n} l^{n} g^{-1} h^{-1} for the Wye (range 0.54–18.9 μmol^{1-n} l^{n} g^{-1} h^{-1}). Values of the power term n are close for the two catchments (Avon mean $=1.8$ and Wye mean $=1.7$) and n values vary across a relatively small range (0.6–2.7 for the Avon and 1.25–2.32 for the Wye). These values are consistent with the work of House and Warwick (1999), which suggested that SRP uptake and release by bed sediments follows a parabolic function, in which n approximates to 2.

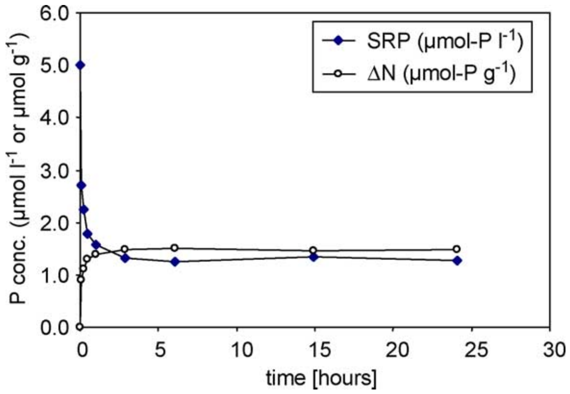

Fig. 3. Example graph showing rate of SRP uptake by sediments (ΔN, μmol g^{-1}) and SRP loss from the river water matrix (SRP, μmol l^{-1}), measured during kinetic experiments (River Wye at Redbrook, Summer 2003).

5.4. SRP fluxes to and from river bed sediments

SRP uptake fluxes on the Avon range from 1.6 g-P T_{res}^{-1} on the Chitterne in autumn to 239 g-P T_{res}^{-1} at Knapp Mill in summer (mean SRP uptake for the Avon $=72$ g-P T_{res}^{-1}) (Table 4a). SRP release fluxes on the Avon range from 0.74 g-P T_{res}^{-1} on the Chitterne in summer to 19 g-P T_{res}^{-1} on the Till in spring (mean SRP release for Avon $=7.8$ g-P T_{res}^{-1}). SRP uptake fluxes tend to be lowest during the spring, but no consistent trend is observed for the release fluxes. Uptake fluxes over 1 km of reach, expressed as a percentage of the SRP load entering

Table 4a
Bed-sediment SRP fluxes for the Avon rivers, calculated for a 10 cm water boundary layer along a 1 km reach

		Spring 2003	Summer 2003	Autumn 2003
Avon @ Knapp Mill	Release/uptake by sediments	Uptake	Uptake	Uptake
	Sediment–water P flux (g)	52.7	239	188
	P flux as % of SRP load entering reach	2.7	5.7	6.5
	Corresponding change in river-water SRP (μg-P/l)	1.3	9	9.4
West Avon @ Upavon	Release/uptake by sediments	Uptake	Uptake	Uptake
	Sediment–water P flux (g)	35.6	72.9	59.1
	P flux as % of SRP load entering reach	7.3	8.2	11.4
	Corresponding change in river-water SRP (μg-P/l)	14.2	36	47
East Avon @ Upavon	Release/uptake by sediments	Uptake	Uptake	Uptake
	Sediment–water P flux (g)	35.1	36.9	46.7
	P flux as % of SRP load entering reach	6.2	7.2	12.2
	Corresponding change in river-water SRP (μg-P/l)	12	14	22
Till @ Stapleford	Release/uptake by sediments	Release	Release	Release
	Sediment–water P flux (g)	19.1	6.30	5.58
	P flux as % of SRP load entering reach	18	16.1	21.2
	Corresponding change in river-water SRP (μg-P/l)	6.0	3.2	3.5
Chitterne @ Codford	Release/uptake by sediments	Release	Release	Uptake
	Sediment–water P flux (g)	2.17	0.744	1.61
	P flux as % of SRP load entering reach	21.9	68.6	40.6
	Corresponding change in river-water SRP (μg-P/l)	2	1.49	4.03
Sem @ Wardour	Release/uptake by sediments	Uptake	Uptake	Uptake
	Sediment–water P flux (g)	24.7	92.5	30.7
	P flux as % of SRP load entering reach	20.8	36.3	41.9
	Corresponding change in river-water SRP (μg-P/l)	18	102	43.8
Nadder @ Wilton	Release/uptake by sediments	Uptake	Uptake	Uptake
	Sediment–water P flux (g)	93.4	124	74.4
	P flux as % of SRP load entering reach	26.6	14.5	10.6
	Corresponding change in river-water SRP (μg-P/l)	15.6	26.9	18.6
Ebble @ Nunton	Release/uptake by sediments	Release	Release	Uptake
	Sediment–water P flux (g)	6.54	17.5	11.1
	P flux as % of SRP load entering reach	13.7	31	18.9
	Corresponding change in river-water SRP (μg-P/l)	1.4	8.1	7.4

Fluxes are calculated for the residence time of river water within the reach (T_{res}). Fluxes are also shown as a percentage of the riverine SRP load entering the reach. Corresponding changes in river-water SRP concentrations as a result of bed sediment fluxes are calculated, based on mixing of the boundary layer with the full water volume within the reach.

the reach (% uptake), vary from 2.7% at Knapp Mill in spring to 42% on the Sem in autumn, with a mean uptake of 17%. Correspondingly, percentage SRP releases from bed sediment range from 14% on the Ebble to 69% on the Chitterne, with a mean release of 27%. Changes in riverine SRP concentrations which would result from these bed-sediment fluxes were also calculated (Table 4a), assuming full mixing of the boundary layer with the entire water volume within the 1 km reach. The bed-sediment uptake fluxes on the Avon would result in reductions in riverine SRP concentrations between 1.3 μg-P l^{-1} (Knapp Mill in spring) and 102 μg-P l^{-1} (Sem in summer). The bed sediment release fluxes on the Avon would result in increases in SRP concentration of between 1.4 μg-P l^{-1} (Ebble in spring) and 8.1 μg-P l^{-1} (Ebble in summer).

SRP uptake fluxes on the Wye range from 1.1 g-P T_{res}^{-1} at Erwood in winter to 156 g-P T_{res}^{-1} on the Frome in summer (mean SRP uptake for the Wye = 47 g-P T_{res}^{-1}) (Table 4b). SRP flux uptakes in the Wye are consistently highest in summer. Only two instances of SRP release were recorded on the Wye (39.5 g-P T_{res}^{-1} at Redbrook in the autumn and 10.7 g-P T_{res}^{-1} in the Garren Brook in winter). Uptake fluxes expressed as a percentage of SRP load entering the reach vary from

Table 4b
Bed-sediment SRP fluxes for the Wye rivers, calculated for a 10 cm water boundary layer along a 1 km reach

		Autumn 2002	Winter 2003	Summer 2003
Wye @ Redbrook	Release/uptake by sediments	Release	[uptake]	Uptake
	Sediment–water P flux (g)	39.5	3.6	55.8
	P flux as % of mass entering reach	11	0.7	3.1
	Corresponding change in river-water SRP (μg-P/l)	1.1	2.57	1.3
Wye @ Erwood	Release/uptake by sediments		Uptake	Uptake
	Sediment–water P flux (kg)		1.09	26.0
	P flux as % of mass entering reach		2.19	18.2
	Corresponding change in river-water SRP (μg-P/l)		0.07	2.4
Dore @ Poston Ct	Release/uptake by sediments		Uptake	Uptake
	Sediment–water P flux (g)		15.6	29.1
	P flux as % of mass entering reach		14.4	23.0
	Corresponding change in river-water SRP (μg-P/l)		10.4	32.3
Frome @ Bishops Frome	Release/uptake by sediments	Uptake	Uptake	Uptake
	Sediment–water P flux (kg)	130	37.9	156
	P flux as % of mass entering reach	23.1	10.3	20.1
	Corresponding change in river-water SRP (μg-P/l)	145	16	133
Stretford Brook	Release/uptake by sediments		Uptake	Uptake
	Sediment–water P flux (g)		14.9	142
	P flux as % of mass entering reach		4.7	23.6
	Corresponding change in river-water SRP (μg-P/l)		4.1	157
Garren Brook	Release/uptake by sediments		Release	Uptake
	Sediment–water P flux (g)		10.7	8.89
	P flux as % of mass entering reach		660	12.6
	Corresponding change in river-water SRP (μg-P/l)		6.1	12.7
Worm Brook	Release/uptake by sediments		[uptake]	Uptake
	Sediment–water P flux (g)		2.88	31.5
	P flux as % of mass entering reach		2.6	13.8
	Corresponding change in river-water SRP (μg-P/l)		1.20	35

Fluxes are calculated for the residence time of river water within the reach (T_{res}). Fluxes are also shown as a percentage of the riverine SRP load entering the reach. Corresponding changes in river-water SRP concentrations as a result of bed sediment fluxes are calculated, based on mixing of the boundary layer with the full water volume within the reach. (Parentheses [ ] indicate sites where the EPC_{sat} was below $\pm 20\%$ and therefore bed sediments and river water were close to equilibrium).

0.7% (Redbrook in winter) to 24% (Stretford Brook in summer), with a mean uptake of 12% of the incoming riverine SRP load. If subject to mixing with the full water volume, these flux transfers would translate into reductions in riverine SRP concentrations between 0.07 μg-P l^{-1} (Erwood in winter) and 157 μg-P l^{-1} (Stretford Brook in summer) and increases in SRP concentrations of between 1.1 μg-P l^{-1} (Redbrook in autumn) and 6.1 μg-P l^{-1} (Garren Brook in winter).

6. Discussion

Although the PSYCHIC agricultural subcatchments in the Wye and Avon have been chosen to examine the impacts of agriculture on phosphorus losses at the catchment scale, the results of the weekly water-quality monitoring programme indicate that the majority of these subcatchments are subject to significant influence by sewage effluent (particularly the River Frome and Stretford Brook in the Wye catchment and the West Avon). The influence of sewage at these sites is evident from:

(i) Concentrations of boron (a trace of sewage effluent) above ‘background’ levels of ca. 30 μg-P l^{-1}.
(ii) High SRP concentrations (mean SRP concentrations are 263 μg-P l^{-1} in the West Avon, 400 μg-P l^{-1} in the Frome and 439 μg-P l^{-1} in

Stretford Brook), with SRP constituting a high percentage of TP (79% TP in West Avon, 84% TP in Frome, 86% TP in Stretford Brook).

In contrast, the Ebble, Chitterne and Till in the Avon appear to be less affected by sewage inputs. They have lower B concentrations (typically $<30\ \mu g\ l^{-1}$), lower SRP concentrations (mean SRPs are $<35\ \mu g\text{-P}\ l^{-1}$) with SRP constituting a lower proportion of TP (owing to larger DHP contributions) and poorer correlations between SRP and B concentration. The high degree of scatter in the positive relationships between SRP and B for individual sites indicates that SRP is behaving non-conservatively (i.e. is undergoing in-stream uptake and release).

The bed sediment surveys have shown that EPC_0 values are correlated with SRP concentrations analysed for the overlying water at the time of bed-sediment sampling. Thus, bed sediments, which have been exposed to higher SRP concentrations, generally have higher concentrations of exchangeable P. However, river-water SRP concentrations are typically not in equilibrium with the bed sediment EPC_0 values, even under stable baseflow conditions, when water residence times are highest. This may be because water residence times over a particular locality of sediment on the river bed are insufficiently long for equilibrium to be established between the sediment and the boundary layer. Alternatively, or in conjunction, non-equilibrium conditions may be inferred because the EPC_0 value represents an integrated measure of the exposure history of sediment to SRP, while the river-water SRP concentrations are subject to fluctuation over shorter timescales.

Mean EPC_0 values are highest in the PSYCHIC Wye sites and lowest in the Wye main river sites. This reflects greater exposure to sewage-derived high SRP concentrations and a stronger relationship between EPC_0 and SRP for the Wye PSYCHIC sites. In contrast, the main river sites are exposed to lower SRP concentrations, owing to higher dilution of effluent in the main river channels and the main river sites exhibit a much weaker relationship between EPC_0 and SRP. In the main rivers Wye and Lugg, EPC_0 concentrations increased markedly downstream of Leominster and Hereford, where the first major STWs were located. However, the highest EPC_0 values in the main river sites were on the Monnow, which is not subject to major effluent inputs. The highest EPC_0 values on the Monnow were in the upper grassland portion of the catchment. This suggests that sediments derived from grazing land of the Monnow catchment potentially provides an important source of exchangeable P. Within the Avon and Wye PSYCHIC sites, highest EPC_0 concentrations were found in the rivers which had the highest sewage impact and the highest SRP concentrations.

Within the Wye catchment, EPC_0 and SRP values in the strongly sewage-impacted rivers tend to be lower in winter. The reductions in SRP are linked to higher winter baseflows and thus greater hydrological dilution of point source effluent inputs. The reductions in EPC_0 values in winter may be related to the lower ambient riverine SRP concentrations, but also to the delivery and in-channel deposition of freshly eroded sediment during winter storms. These freshly deposited sediment sources may have lower exchangeable P concentrations, compared with the sediments which settle out during extended summer low flows, which may be, in part, derived from effluent sources. Indeed, increases in EPC_0 downstream of STWs on the main Rivers Wye and Lugg are only clearly discernable during the autumn survey, following extended period of summer low-flows. For bed sediments with EPC_0 values of $>2\ \mu mol\ l^{-1}$, the adsorption affinity of the sediment (measured as the K_d) is relatively constant. However, at EPC_0 values below $2\ \mu mol\ l^{-1}$, the variability of adsorption affinity increases with decreasing EPC_0 and highest adsorption affinities are found at the lowest EPC_0 values. These results indicate that sediments with low concentrations of exchangeable P have the highest affinity for taking up SRP from the water column. However, the high variability in adsorption affinity at these low EPC values indicates that other factors, such as sediment composition and particle size distribution, become more important for adsorption affinity at low EPC_0 values.

Three quarters of the bed sediments sampled in the Wye and Avon catchments showed potential for uptake of SRP (i.e. were acting as net sinks for SRP) with EPC_{sat} values of $<-20\%$. However, 37% of the Avon PSYCHIC sites showed potential for SRP release (i.e. were acting as net sources of SRP, with EPC_{sat} $>+20\%$), compared with 28% of the Wye main river sites and just 8% of the Wye PSYCHIC sites. The sites that act as net sources of SRP release into the overlying river water column, tended to be those with minimal sewage influence. These sites were subject to relatively low SRP concentrations in river water, either as a result of no major effluent inputs upstream (Ebble, Till and Chitterne and Garren Brook) or where the hydrological dilution of those inputs was high (such as on the main River Wye and Monnow). The sites with the greatest potential for SRP uptake (i.e. highest negative EPC_{sat} values) tend to be those with the highest SRP concentrations (i.e. those sites with the greatest sewage impact, such as the Frome and Stretford Brook on the Wye and West Avon and Knapp Mill for the Avon). However, there is high degree of scatter in the negative relationships between EPC_{sat} and SRP, demonstrating that other factors are important for determining the EPC_{sat}. Clearly, the EPC_0 and EPC_{sat} terms will vary according to sediment type and factors such as particle composition (such as mineralogy and organic content), particle size distribution and the exposure history of the sediment to differing SRP concentrations.

The negative relationships between SRP and EPC_{sat} for the PSYCHIC sites suggest that the high SRP concentrations derived from sewage effluent at baseflow 'swamp out' any potential release of sediment-bound P from the river bed at many of the sites. SRP release from bed sediments is dependent on a diffusion gradient across the benthic interface, with higher concentrations of particulate-bound exchangeable P in the sediment compared with SRP concentrations in the overlying river water. The particulate bound exchangeable P may be derived from diffuse sources (in the Ebble, Till and Chitterne and Garren Brook and Monnow) or from sewage-derived particulates (downstream of Leominster STW (Lugg at Eaton), and Monmouth STW (Wye at Redbrook)). This suggests that deposition of sewage-derived particulates enriched with P, particularly during an extended period of low summer baseflows, may also provide localised bed-sediment 'hotspot sources' of SRP immediately downstream of STWs. The P within these hotspots may then be available for release, in circumstances where the SRP discharged in effluents is subject to a large hydrological dilution (as in the main river systems), promoting a diffusion gradient between relatively high EPC_0 on the river bed and lower SRP concentrations in the water column.

The appropriateness of the estimated bed-sediment SRP flux transfers depend on the validity of the conceptual reach-based model of bed-sediment water interactions. The kinetics experiments have shown that rates of SRP uptake and release occur very rapidly, with the vast majority of mass flux transfers occurring within 1 hour of mixing. Baseflow water residence times within the 1 km river reaches were estimated to be typically 1–2 h. Therefore, within this conceptual model, bed sediment SRP fluxes would not be rate-limited, but controlled largely by the mass of sediment in the reach and the concentration differential between the bed-sediment EPC_0 and the river-water SRP concentration. Mass flux estimates dependent on reliable data on reach/boundary layer water volumes, river flow rates and fine-sediment storage on the river bed. Although the PSYCHIC monitoring sites were gauged, estimates of water volume and sediment storage were based on crude observations at the sampling sites and thus do not necessarily accurately represent the whole 1 km reach. Therefore, the SRP fluxes presented in this study provide a guide to the relative SRP flux potential from different bed sediments, rather than definitive mass flux transfers.

SRP flux uptake and percentage uptake is typically higher for the Avon bed sediments compared with the Wye bed sediments. The rate constants derived from the kinetics experiments were also higher for the Avon. The same is true for the K_d values derived from the equilibrium batch experiments. These results seem to indicate that, on average, the Avon bed sediments have a greater adsorption capacity for SRP than the Wye bed sediments. The highest uptake fluxes (>100 g-P T_{res}^{-1}) occurred in the rivers with the highest sewage influence at times of highest riverine SRP concentration: the Frome and Stretford Brook in summer and Knapp Mill in summer and autumn. SRP release fluxes were relatively low (<40 g-P T_{res}^{-1}). The SRP uptake as a percentage of baseflow riverine load is relatively high, with an average of 17% of the riverine flux for the Avon and 12% for the Wye. However, SRP uptake by bed sediment may be over-estimated because:

(i) The actual contact time between the boundary layer and the bed sediment may be shorter than the crude estimates of water residence time used in this study.

(ii) The effective boundary layer in intimate contact with the bed sediment may be less than the operationally defined 0.1 m boundary layer.
(iii) The bed sediment fluxes are based on full mixing of bed sediments and the boundary layer, whereas interactions within the river bed may be more limited.

The net reductions in SRP loads along a 1 km river reach are likely to be lower than the bed-sediment uptake fluxes estimated here. This is because of other effects, particularly (i) the release of SRP by other P-cycling mechanisms, such as the activities of riverine plants and microbes and (ii) other SRP inputs (point and diffuse) along the reach.

6.1. Recommendations for further work

In order to place this work in context and examine the validity of the conceptual model of bed sediment–river water interactions and flux estimates, we recommend three lines of further research:

(a) Intensive riverine SRP flux monitoring along experimental reaches to calculate in-stream flux modification. It is not possible to directly isolate and validate the bed-sediment flux modification in natural river channels, owing to a multitude of in-stream P-cycling processes. However, *net* SRP flux changes along a give reach may be undertaken by detailed monitoring of flows and concentrations simultaneously at the upstream and downstream reach limits, covering timescales of the reach water residence time (e.g. House and Warwick, 1999). Choosing reaches where bed sediment interactions are likely to dominate in-stream cycling processes would be advantageous (e.g. reaches with low macrophyte and algal growth), although it is not possible to eliminate biofilm and other microbial activity, which can potentially also have important effects on in-channel SRP cycling (Jarvie et al., 2002c; Hartley et al., 1996)
(b) Measurement of diffusion gradients across the bed-sediment surface and calculation of diffusive flux transfers using simple diffusion models. The authors are currently investigating alternative techniques for in-situ measurement of concentration gradients in bed sediment porewaters, through the benthic interface and into the boundary layer, using DGT (Diffusive Gradients in Thin Films) gel probes (Zhang et al., 1998). These data could be used to test an alternative P release/uptake model where the sorptive equilibrium processes occur within the sediment porewater and transfer of SRP is controlled by diffusion. Such models already exist for pesticides (Adriaanse, 1997) and could be modified to consider P.
(c) Incorporating the EPC_0 and kinetic parameters derived in this study together with diffusive flux data in reach-based water quality models, such as QUESTOR (Boorman, 2003a–c) and INCA (Wade et al., 2002a,b). These models are able to predict the hydrological conditions such as water residence times and mixing of boundary layer within the reach volume more accurately than the hydrological observations used in this study and, in the case of INCA-P, offer the prospect of quantifying the relative importance of bed-sediment–water interactions in relation to cycling by in-stream plants.
(d) The fractionation of P in bed sediments and the K_d values for important components of the fine bed sediments need identifying. Sorption will be associated with inorganic components such as iron oxides (and perhaps solubilisation/co-precipitation with calcite, $CaCO_3$) and also onto organic fractions of the sediment, which are currently poorly defined.
(e) Examining the importance of redox profiles, seasonal changes in redox and biological degradation for P exchange between bed sediments and the water column. This is needed, for example, to examine iron mobilization and iron phosphate solubility. The biological interactions not only affect/control redox, but also the heterotrophic degradation of organic components in the sediments, which may provide an internal source of P.

7. Conclusions

The main findings of the research are as follows:

- The water quality profiles of the monitoring sites (including the 'agricultural' subcatchments) show that most of the rivers have elevated SRP and B concentrations linked to sewage inputs, particularly under low flows.

- At sites that are subject to sewage influence, bed-sediments predominantly act as net sinks for SRP, demonstrating the natural 'self-cleansing' capacity of rivers.
- SRP release from bed sediments is dependent on a diffusion gradient across the benthic interface, with higher EPC_0 in the sediment compared with the water column. However, at most of the sites, sewage effluent discharges result in riverine SRP concentrations exceeding the EPC_0 of the sediment.
- Bed sediments were found to act as sources of SRP where:
  1. There is minimal sewage influence, resulting in very low SRP concentrations, typically $<$ 50 μg-P l^{-1};
  2. Sewage inputs are subject to large hydrological dilution with water of low SRP concentration to concentrations below the EPC_0 of the sediment;
  3. EPC_0 values are relatively high owing to deposition of diffuse particulate-associated P on the river bed or deposition of effluent-derived particulate P.
- Deposition of sewage-derived particulates enriched with P, particularly during an extended period of low summer baseflows, may also provide localised bed-sediment 'hotspots', which can act as sources of SRP, where the point-source discharge is subject to sufficiently large hydrological dilution to reduce riverine SRP concentrations below EPC_0.
- Relatively high EPC_0 values indicate the potential importance of diffuse-source bed sediment in rural, grassland catchments with high stocking densities.
- Kinetic experiments on bed sediment suspensions showed that rates of SRP uptake and release were very high, with the majority of SRP flux transfer occurring within one hour of mixing between the bed-sediment and the water column. Baseflow water residence times were estimated to be typically in the order of 1–2 h. Therefore, according to the conceptual model, bed sediment SRP fluxes would not be rate-limited, but controlled largely by the mass of sediment in the reach and the concentration differential between the bed-sediment EPC_0 and the river-water SRP concentration.
- The highest SRP bed-sediment fluxes were uptake fluxes from the boundary layer into the bed sediments in the rivers with the highest sewage influence at times of highest riverine SRP concentration.
- Under baseflow conditions, the high SRP concentrations from sewage in the Wye and Avon typically 'swamp out' any potential release of SRP from the bed sediments. This has considerable implications in rivers subject to effluent P-stripping, which may reduce SRP concentrations below sediment EPC_0 levels. In these circumstances, bed sediments may potentially switch from net sinks to net sources of SRP, and the major sources of SRP at times of greatest eutrophication risk (summer low flows) may change from point sources to in-stream sediment sources, with major changes to the in-stream P-cycling system, including biological interactions.

8. Wider comment

Research of the type undertaken in this study is important for understanding nutrient cycling in major lowland UK river systems that are sensitive to eutrophication, linked to point and diffuse nutrient inputs. Phosphorus is often the limiting nutrient in rivers and water-sediment dynamics, as well as biological uptake and release processes, potentially play an important role in regulating river-water SRP concentrations and fluxes, especially under low flows, when risks of eutrophication are highest. Knowledge of the extent of the water-sediment interactions is important in assessing the driving mechanisms for in-stream SRP regulation.

Recent studies from the River Kennet, a chalk stream adjacent to the River Avon, have shown that there have been unexpected perturbations to the stream ecology in the aftermath of P-stripping (proliferation of nuisance epiphytes, Jarvie et al., 2004b), which may be associated with changes in the in-stream P-cycling system. A key requirement is now to take the PSYCHIC work further and examine whether river bed sediments have the capacity to switch to SRP sources following reductions in SRP inputs from point sources, and the resultant impacts on P-cycling system and in-stream ecology.

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