Environment Agency

Evidence

Phosphorus cycling in rivers

Report – SC120037

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This report was produced by the Scientific and Evidence Services team within Evidence. The team focuses on four main areas of activity:

- **Setting the agenda**, by providing the evidence for decisions;
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- **Carrying out research**, either by contracting it out to research organisations and consultancies or by doing it ourselves;
- **Delivering information, advice, tools and techniques**, by making appropriate products available.

Miranda Kavanagh

Director of Evidence

Executive summary

This project sought to:

- evaluate the relative importance of phosphorus cycling processes in rivers in relation to other sources of phosphorus
- develop an approach and method for a decision support tool to screen rivers for the likelihood and extent of phosphorus cycling from in situ sediments
- test this methodology on available national datasets

Achieving these objectives required a detailed understanding of the fate and behaviour of in situ sediment-bound phosphorus in relation to phosphorus loading, river flow and the variability of equilibrium phosphorus concentration (EPC_0) (that is, the concentration of phosphorus in water at which there is no net adsorption or desorption to/from sediment). Such an understanding was realised through a comprehensive literature review which examined the fate and behaviour of in situ sediment-bound phosphorus along the river continuum and the links between phosphorus and river ecology.

Development of a screening tool incorporated the key findings from the literature review in terms of water quality and ecology, with consideration given to the availability of national datasets. Findings from the literature review were also used to develop risk scores and weighting factors for different aspects of sediment accumulation and potential phosphorus release.

The following important findings and associated datasets were used to develop the screening tool.

- The phosphorus available to water–sediment equilibrium reactions (that is, the labile pool) is determined by different sources of phosphorus inputs from the catchment. Sources of phosphorus that have been included in the screening tool are (data sources are in brackets):
  - sediment phosphorus loads from the catchment (PSYCHIC model)
  - diffuse sources of phosphorus (SAGIS model)
  - point sources of phosphorus (SAGIS model)
- Accumulation of sediment within a river reach can potentially increase the sediment labile pool of phosphorus. An estimate of where sinks are within a river reach has been included in the screening tool, considering:
  - river velocity data (calculated from a digital terrain model and the SAGIS model)
  - scouring (using Base Flow Index data)
  - River Macrophyte Hydraulic Index as an indicator of flow based on a plant community's preference for flow conditions (LEAFPACS).
- Sediments downstream of a wastewater treatment works (WTW) act as a sink for phosphorus. Introducing tertiary phosphorus removal makes these sediments vulnerable to phosphorus release. An estimate of this legacy has been included in the screening tool using phosphorus load reduction as a result of phosphorus removal at WTWs (SAGIS).

To test the importance of in situ cycling processes in relation to other sources of phosphorus, the EPC_0 based model theory for sediment phosphorus exchange was tested by incorporating the relevant algorithms into an existing dynamic river quality model of the River Nene. This indicated that, while losses to the sediment are substantial, releases from the sediment are unlikely to be significant in relation to other sources of phosphorus. However, there is uncertainty regarding this model formulation and the variability of rate processes in relation to the range of conditions represented within a time series model.

Options for further developing the screening tool and time series models are discussed, along with ways to improve the supporting evidence. In taking the work forward, it is important to bear in mind the scientific uncertainties associated with sediment phosphorus dynamics. These uncertainties need to be addressed before the influence of sediment phosphorus on river ecology can be confidently quantified with regard to the magnitude of phosphorus inputs and how long these impacts are likely to last.

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1 Introduction

1.1 Background

Soluble reactive phosphorus (SRP) is defined as a supporting element to determine ecological status under the Water Framework Directive (2000/60/EC). Ecological responses to elevated SRP concentrations include a shift in the composition and abundance of plant species, which subsequently has an impact on higher aquatic ecology. The single largest cause of water bodies not achieving good ecological status is exceedance of SRP standards (Environment Agency 2013).

Discharges from wastewater treatment works (WTWs) are a major contributor to non-compliance with SRP standards and UK water companies have put in place a major investment programme since the late 1990s to reduce their emissions. A range of measures have also been introduced to reduce diffuse sources of phosphorus (for example, Catchment Sensitive Farming). However, the effectiveness of reducing phosphorus loading from these sources might be limited by in situ sediment phosphorus cycling. The focus of this work is to understand the implications of this process in terms of the extent and likelihood of its occurrence and the degree to which it is likely to be important.

There are two questions about the benefits of reducing sources of phosphorus.

- Will the reduction of SRP loads from WTWs or diffuse sources result in the release of sediment-bound phosphorus?
- If sediments release phosphorus, how long will it be before the benefits are realised with respect to lower river SRP concentrations and improvements in ecological status?

The Environment Agency requires a decision support tool to screen rivers for the likelihood and extent of phosphorus cycling from in situ sediments. The development of such a tool requires an understanding of the fate and behaviour of in situ sediment-bound phosphorus in relation to phosphorus loading, river flow and the variability of equilibrium phosphorus concentration (EPC_0). The EPC_0 value is the concentration of phosphorus in water at which there is no net adsorption or desorption when in contact with sediment (Badha et al. 2012).

In addition to the EPC_0, other factors that will influence the release of phosphorus from sediments include:

- the size of the labile pool of phosphorus in the sediment
- the rate constants of adsorption and desorption of phosphorus from the sediments

The labile pool of phosphorus can be defined as that phosphorus which takes part in water–sediment equilibrium reactions. Sediment transport processes and the degree to which sediment accumulates in rivers are also important in determining how these processes vary between reaches.

1.2 Project aims and objectives

The overall aim of this project was to develop an approach and method for a decision support tool to screen rivers for the likelihood and extent of phosphorus recycling from in situ sediments.

The project’s specific objectives are to:

1. Summarise through a literature review the evidence on the impact of river sediments on phosphorus retention/release and bioavailability within river reaches and implications for water quality and ecology.
2. Evaluate the fate and behaviour of in situ sediment-bound phosphorus along the river continuum for representative river reaches/types in response to changes in phosphorus loading and river discharge (flow), taking into account the relationship between river concentrations, the variability of EPC_0 in different river types and microbial processes.
3. Evaluate the likely links between phosphorus and river ecology (dose–response) including macrophytes and epiphytic algae and diatoms.
4. Identify the data (and licensing) required to develop a decision support tool.
5. Test the method against detailed data and time series modelling to determine rates of change in contrasting river types as identified in steps 1 and 2.
6. Use the data to test the hypothesis that, at high phosphorus levels where water column phosphorus exceeds EPC_0, there is minimal uptake/loss to sediments and the response of phosphorus in the water column to reduced inputs is rapid; but where water column phosphorus is close to or less than EPC_0, sediment exchange has more influence on water column phosphorus.

2 Literature review

2.1 Introduction

The literature review outlines the evidence for the most important parameters and processes that need to be considered in the development of a 'sediment and phosphate screening tool'. The aims of the screening tool are to assess:

- the extent to which sediment potentially acts as a source or sink for SRP
- where problem areas of sediment may occur and become a source of SRP to river and stream waters, thus contributing to water bodies failing to achieve good ecological status under the Water Framework Directive (WFD)

2.1.1 Current limits of SRP[1] concentrations

Current limits for annual mean water SRP concentrations were developed by the WFD UK Technical Advisory Group (UKTAG) in 2008 (Table 2.1). However, proposed standards for the second round of river basin management planning are more stringent (Defra 2014).

UKTAG has suggested that, in the future, site-specific standards be adopted where WFD status is assessed using the worst of either the diatom or macrophyte Ecological Quality Ratio (EQR) (UKTAG 2012). The EQR is defined as the ratio between the reference value and the observed value for a given metric.

Table 2.1 Current annual mean limits developed by UKTAG in 2008 for river and stream waters SRP concentrations

River type	Altitude (m)	Alkalinity ($CaCO_3$ mg l^{-1})	SRP concentration (µg P l^{-1})			
			High	Good	Moderate	Poor
1n	<80	<50	30	50	150	500
2n	>80	<50	20	40	150	500
3n	<80	>50	50	120	250	1000
4n	>80	>50	50	120	250	1000

Source: UKTAG (2012, Table 1)

2.1.2 Role of phosphorus

Although essential, phosphorus plays a fairly small role in the production of biomass. It is not a structural component of cellulose or lignin, for example. Because it is a component of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), it is necessary for:

[1] SRP is a measure of the reactive phosphorus in filtered samples (without digestion). Orthophosphate (OP) refers specifically to inorganic orthophosphate (PO_4^{3-}), but as SRP usually consists largely of OP, the terms are often used interchangeably and measurements referred to as OP are comparable with SRP values.

- cell division and growth
- production of adenosine triphosphate (ATP), responsible for energy transfer within cells
- phospholipids, components of all biological membranes

The phosphate anion also plays a role in the regulation of enzymes, via phosphorylation. However, the quantity of phosphorus required for this is tiny: 0.16% of dry weight of maize, for example (Troah and Thompson 1993). The relative proportion of phosphorus to other elements in algae is somewhat higher due to the lower proportions of structural tissue.

The commonly cited Redfield ratio, for example, suggests a typical carbon to nitrogen to phosphorus ratio of 106:16:1, as moles (Redfield 1958). Although the practical validity of the Redfield ratio has been questioned, it gives a broad indication of the relatively minor role that phosphorus plays in the physiology of individual organisms. The significance of phosphorus in freshwater ecology derives, instead, from its scarcity relative to other potentially limiting nutrients.

2.1.3 Forms of phosphorus

Phosphorus can exist in many forms, including inorganic soluble forms, organic bioavailable and non-available forms, and attached to particulates. This latter condition includes labile phosphorus that is only loosely attached to particles, and firmly bound phosphorus that has been incorporated into the matrix of the particles.

Phosphorus immediately available for plant growth (bioavailable phosphorus) essentially consists of inorganic soluble forms, organic forms of low molecular weight, and labile phosphorus that can rapidly desorb from particulates under certain conditions.

Phosphorus in complex organic compounds is released as the compounds are broken down by biological processes, but the long-term availability of phosphorus firmly bound to particulates is unclear. Once in the river, phosphorus is chemically and biologically active, undergoing numerous transformations and moving between the particulate and dissolved phases, between the sediment and water column, and between the biota and abiotic environment – as demonstrated in Figure 2.1.

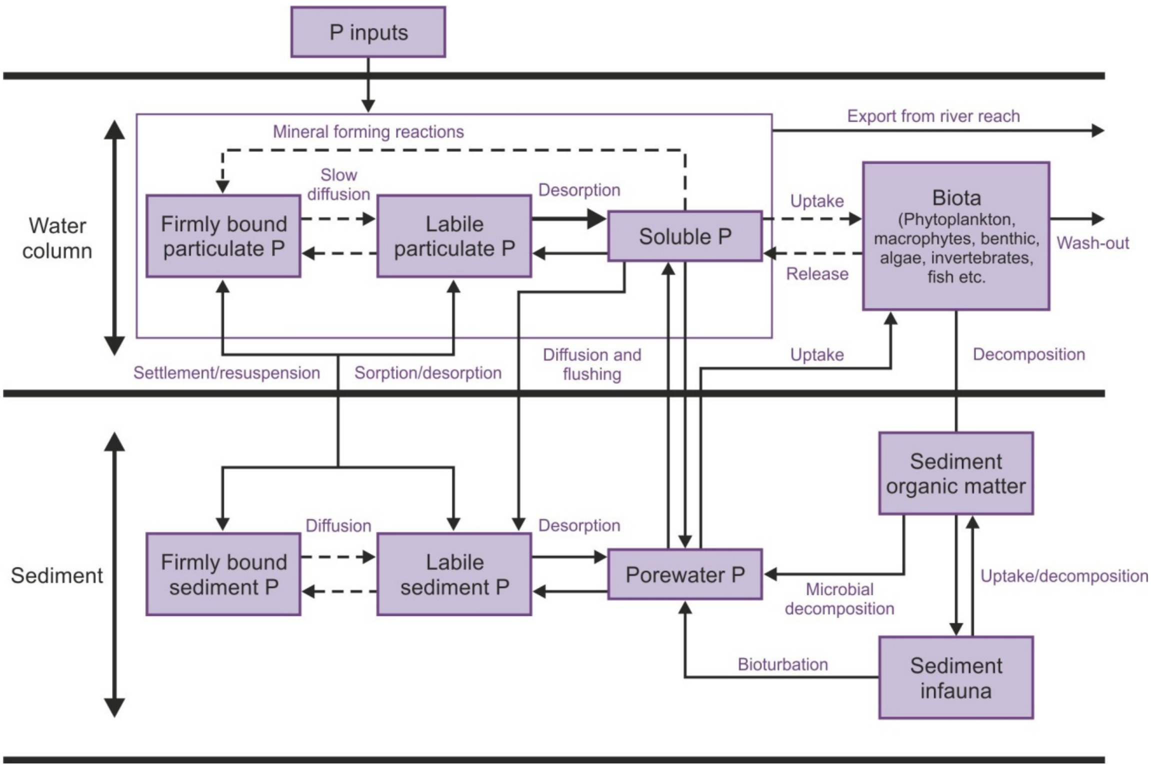

Figure 2.1 Phosphorus behaviour in rivers (after Mainstone et al. 2000)

2.1.4 Concept of equilibrium phosphate concentration

The basis of the proposed screening tool lies in the concept of 'equilibrium phosphate concentration', which describes the potential for sediments to act as sources or sinks for SRP. This concept was originally developed by White and Beckett (1964) for soils and used for stream sediments by Taylor and Kunishi (1973) and discussed further by Froelich (1988).

The methodology determines an equilibrium point where there is no net sorption or desorption of SRP. This is termed the EPC_0. When EPC_0 is greater than water SRP concentrations, the sediment is likely to become a source of SRP, while a sink for SRP is suggested when water SRP concentrations are greater than EPC_0 values. Thus the EPC_0 concept represents a methodology through which sediment–phosphorus interactions can be incorporated into wider management strategies for WFD compliance (Jarvie et al. 2013, Sharpley et al. 2013).

Figure 2.2 shows a conceptual model that describes how EPC_0 fits in within the broader sediment–SRP interactions.

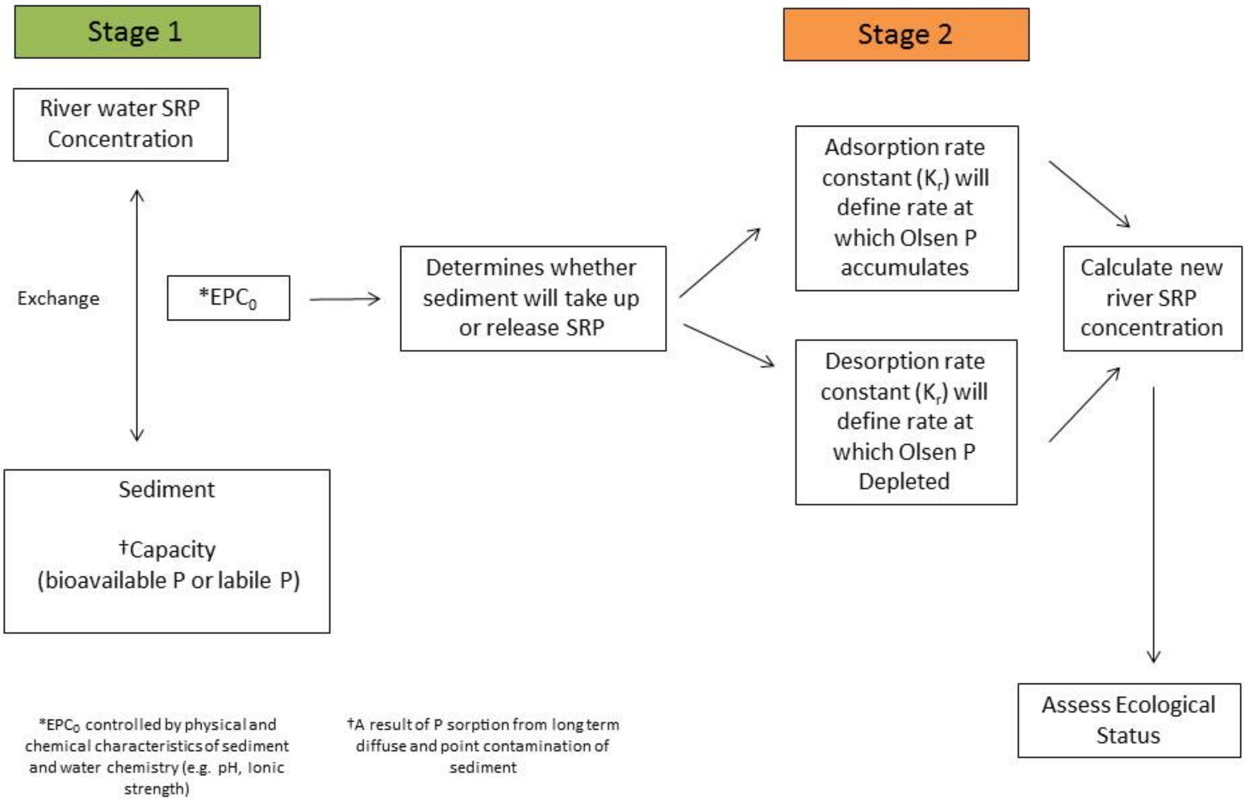

Figure 2.2 Conceptual model showing how the concept of EPC_0 links into sediment-bound SRP

2.2 Sediment properties in UK rivers and streams

If sediment is interacting with SRP within water channels, the first part of a screening tool will require an appreciation of the locations, quantities and chemical properties of channel sediment along with methods by which to identify and rank their potential.

2.2.1 Sediment inputs

Water bodies have a natural sediment regime with a dynamic balance of inputs and outputs to which the ecosystem is adapted. Human activities such as farming, urbanisation, dredging, land drainage and industry can disrupt this natural balance – amplifying, suppressing or otherwise changing it.

Sediment is largely derived from the erosion of the land surface, followed by transport into watercourses. According to the transport properties of the stream or river (for example, slope, water velocity, morphology of the channel) and sediment properties (for example, size and quantity), the eroded sediment will gradually be transported down the river system, with deposition occurring when water velocity is insufficient to transport particles of a given size. Thus, the geological properties (texture) and morphology (erosion potential and river gradient) will determine sediment deposition properties and the sediment architecture that develops within a river channel. The properties of this sediment deposition and its architecture will determine whether it acts as a source or sink for SRP based on the EPC_0.

Typical sources of sediment include:

- **Agriculture** – run-off from fields, tracks and roadside verges are the most important components. The timing and quantity depend largely on land management and rainfall patterns.
- **Forestry** – where forestry land use is extensive and specific high-risk practices are used.
- **Urban areas** through run-off from residential and trading/industrial estates, erosion of roadside verges, misconnections of foul sewer to surface drainage, and point source inputs of suspended solids from urban WTW.
- **Construction** – disruption to the land surface during construction projects increases the risk of soil erosion and can result in increased sediment delivery and potential mobilisation of contaminants.
- **Abandoned mines** are a common source of sediment through erosion of spoil tips.
- **Bank erosion** from boat wash, animal poaching, recreational activity, morphological change and activity of invasive species can result in significant sediment inputs to water bodies.

Important pathways for sediment include:

- rural (field) or urban run-off
- field tracks, roads and drains (field and road) which enable or amplify run-off through increased land–water connectivity
- combined sewer overflows (CSOs)
- wind erosion and atmospheric deposition

Direct diffuse run-off is the most significant pathway, especially where it is amplified by increased connectivity such as by tracks and roads. Run-off tends to be worst in regions with soil vulnerable to erosion and run-off, sloping land (slopes >3%), high rainfall and a dense drainage network.

Direct inputs of soil via erosion have started to decline in recent years as a result of the introduction of agri-environment measures including (Fullen 2003, Boardman 2013):

- adoption of soil management plans and minimal cultivation systems
- avoiding over-winter tramlines and high-risk crops on fields at risk of erosion
- addressing soil compaction
- improving farm tracks
- cultivating across slopes
- establishing buffer strips

2.2.2 Sediment deposition and architecture within channels

After sediment enters into a river, its deposition and resulting architecture is determined by:

- channel properties such as gradient and morphology

- role played by vegetation in trapping sediment
- role played by man-made structures in trapping sediment
- variation in stream velocity and shear strength

The different stream and river types within a catchment are the major determinant of the accumulation of sediment within the river channel.

In general, there is very little published data on sediment deposition and architecture for rivers. However, within the decision support tool, consideration should be given to knowledge of sediment depth as it may provide a basis on which sediment removal, as a remediation option, is assessed.

The use of a classification for individual river water bodies could be used within the screening tool as the best way to assess fine sediment status and likely build-up. Table 2.2 summarises the modified Montgomery–Buffington (MMB) typology which has been used by the Department for Environment, Food and Rural Affairs (Defra) as a basis of sediment management (Defra and Environment Agency 2011). For the purpose of the WFD, rivers are divided up into water bodies and it would be on this basis that this classification could be used.

Table 2.2 Modified Montgomery-Buffington typology

MMB type	Channel description	Morphological description	Style of adjustment
1	Steep headwater channels	Cascades, step-pool, poorly sorted grain size with boulders and exposed bedrock. Confined by valley sides resulting in strong coupling. Absence of floodplain. Steep slopes (>0.03)	Limited lateral movement – commonly the result of avulsion. Channel bed elevations periodically aggrade and incise in response to slope–channel connecting events often in association with generation of a sediment wave. Bed morphology can be destroyed by high magnitude events but re-form step pools. Where present, woody debris contributes to aggradation and sediment accumulation creating steps in long profile.
2	Pool-riffle/plan bed	Can exist in meandering partially confined and unconfined states. Characterised by lateral oscillating sequences of bars, pools and riffles. The gradient of such channels is low–moderate and the width depth ratio high. The bed is predominantly gravel with occasional patches of cobbles and sand. Interactions between the	The banks are typically resistant to erosion, and lateral migration of the channel is limited, resulting in relatively narrow and intermittently deep channels. Lateral channel adjustment occurs via avulsion and chute cut-offs across meander bends. Bar erosion and development coupled with pool infilling and riffle

MMB type	Channel description	Morphological description	Style of adjustment
		stream and the riparian zone result in over-bank flood flows and wetland areas.	erosion characterise the bed adjustment particularly in presence of a sediment wave. Where present, woody debris creates local scour and sedimentation and can force the formation of pools/pool-riffle sequences.
3	Wandering gravel bed rivers	Generally, they can be viewed as a transition channel type between braided and active meandering channels. These reaches exhibit characteristics of braided and meandering channels simultaneously, or if studied over a number of years, display a switching between divided and undivided channel types. Wandering channels typically occur where a reduction of bed material size and channel slope is combined with a widening of the valley floor. Presence of lateral, point and mid-channel bars with pool and rifle sequences.	Wandering channels are susceptible to channel avulsions during high flow events, particularly where the channel can re-occupy an old channel. Bank erosion processes are active with lateral migration and channel widening forced by bend curvature and sediment accumulation into mid-channel bars. Phases of incision and aggradation build sequences of terraces on the valley floor. Woody debris is an important part of island formation and flow deflection resulting in bank erosion and channel migration.
4	Braided rivers	Braided reaches can occur in a variety of settings. Typically characterised by relatively high gradients and/or abundant bedload with high width:depth ratio. Channel splits into a number of threads around in-stream bars. Nevertheless, poor bank strength renders them highly dynamic and channels will generally change even in relatively small flood events.	Braided channels are rare in the UK. They are susceptible to channel avulsions, chute cut-off and bar development during high flow events. Bank erosion processes are active with lateral migration and channel widening forced by sediment accumulation and flow deflection. Phases of incision and aggradation build sequences of terraces on the valley floor. Confluence–difluence processes of scour and aggradation maintain divided planform. Woody debris is important part of island formation.

MMB type	Channel description	Morphological description	Style of adjustment
5	Active meandering	Bordered by floodplains, the single channel is characterised by pool-riffle sequences and point bars. Counter-point bars occur at overwide bends. Silt berms extend from point bars, often colonised by riparian vegetation. Wooded riparian corridors. Bed material typically gravel with fines.	Bank erosion and lateral migration of the channel dominated adjustment processes. Bends develop through a range of forms, leading in some cases to meander cut-off. Chute cut-off processes also prevalent where the channel is not incised. Sinuosity changes over time resulting in progressive reduction in slope and accumulation of sediments on bars. Riffle-pool sequence is dynamic with addition riffles and pool units developing as channel length extends with bend migration. Laterally stable reaches often occur in between active bends. Large wood creates complex bar and flow structures that can influence bend, pool and bar development.
6	Passive meandering	Generally lower slopes, flowing through resistant materials, for instance boulder or marine clay deposits. They are generally sinuous – meandering. Channels are often incised and display low width:depth ratios. The beds typically comprise shallow layer of armoured or paved gravels with fine sedimentary materials (sands and silts). Bars are typically low amplitude and have high fines content. Fine sediment berms also prevalent where channel width increases. Pool and riffle sequences occur but often in association with other transitional bed forms such as glides and runs. Primary production is strong in these channels and, coupled with stable beds of with much	Combination of low slopes and resistant bank materials result in limited rates of lateral adjustment often characterised by widening or narrowing through deposition of fines. Woody debris is an important feature of adjustment processes, resulting in localised chute cut-off channels at bends, widening around jams and local plunge and scour pools and upstream backwater pools at dams. Bar migration occurs but typically in response to large wood dynamics.

MMB type	Channel description	Morphological description	Style of adjustment
		fine sediment, allows extensive growth of macrophyte vegetation. Riparian corridor is typically wooded.	
7	Groundwater dominated	Groundwater-dominated rivers have low gradient channels and are characterised by a stable flow regime, though limestone rivers with cave systems may display hydrological characteristics similar to freshet rivers. Typically, sediments are derived from catchment sources, although large macrophyte beds provide a source of in-stream organic detritus. Lack of bed disturbance promotes the accumulation of large quantities of fine sediment. Substrate generally comprises gravels, pebbles and sands. Glides and runs are the dominant flow types. Localised areas of riffle may be present, particularly where woody debris is available. Dense macrophyte beds and wooded riparian corridor.	Bed and bank migration is infrequent and sediments are predominantly transported in suspension. Lateral channel migration is absent or at very low rates. Bar development and gravel transport is highly localised resulting in stable channel morphology. Large wood is present in the channel for long periods, and creates local scour and deposition and possibly avulsion where the main stream is blocked. Macrophyte development controls much of the flow and fine sediment transport. Development of marginal berms of fine sediment frequent where channels are overwidened.
8	Channelised high energy – specific stream power (w) >35 W m^{-2}	Simplified cross-section and straightened planform, often with embankments. Typically incised, with bank protection necessary to maintain cross-section and prevent bank erosion. Bed can be armoured especially where river is incised with coarse bed material. If the channel is overwidened, shoals of sediment will accumulate, especially if upstream reaches are more efficient at transporting sediment. Limited riparian vegetation due to mowing regime and wood management. Steep bank	Bank erosion and undercutting in incised channels with armoured coarse stable beds. Reaches upstream of the channelised reach may be experiencing incision and active bank erosion. In widened reaches, adjustment will be through sediment accumulation in shoals and berms. These in turn will result in a meandering flow and the potential to initiate bank erosion.

MMB type	Channel description	Morphological description	Style of adjustment
		profiles with limited aquatic margins. Bed morphology typically simplified with shallow runs and glides, with occasional riffles. Pool habitats limited.	
9	Channelised medium energy (35 W m^{-2}< w > 10 W m^{-2})	Simplified cross-section and straightened planform, often with embankments. Typically incised, with some limited bank protection. Bed can be armoured especially where river is incised with coarse bed material. Generally absence of shoaling. Limited riparian vegetation due to mowing regime and wood management. Steep bank profiles with limited aquatic margins. Bed morphology typically simplified with shallow runs and glides, with occasional riffles. Pool habitats limited.	Limited erosion and depositional adjustment. Bed tends to be armoured and bank stable. What sediment transport occurs is in the form of small finer gravel shoals and marginal fine sediment berms. Overall the reach would be expected to be stable across most of the flow regime.
10	Channelised low energy (w <10 W m^{-2})	Simplified cross-section and often a straightened planform. Often with embankments and often over-deepened by dredging. Often disconnected from floodplain, with flows contained within the channel and embankments. Bed material often dominated by fine sands and silts, with emergent vegetation and limited riparian vegetation due to mowing regime and wood management. Steep bank profiles with limited margins. Absence of regular or frequent pool-riffle sequences, and typically deeper glide, pool and ponded habitats dominate.	Adjustment is primarily by fine sediment processes, typically the formation of marginal silt berms that are colonized by emergent vegetation, and the trapping of fines on the bed by vegetation. Banks typically fail by geotechnical slippage due to over-deepening, otherwise banks tend to be stable. Overwidening promotes fine sediment berm development out into the channel to reduce capacity to normal low flows particularly on the inside of meander bends.
11	Armoured channels (culverts, bed and bank protected)	Simplified cross-section with artificial bank and or bed. At one extreme is the culvert, and the other is the reach in	Adjustment will be dependent on the extent and success of armouring. At one end, adjustment can

MMB type	Channel description	Morphological description	Style of adjustment
		which one bank is armoured. Channel adjustment is therefore constrained in one or all dimensions. The presence of armouring (concrete, gabions and so on) impacts on the ecology by limiting vegetation development (steep margins) and providing poor quality substrates for aquatic organisms. Where the channel is overwidened and receives a sediment load from upstream, the bed may have a residual layer of natural substrate including some bars. Where the bed is armoured, pool development will be limited.	only occur through deposition on the bed. Where both banks are armoured, and the channel is not overwide, incision and erosion of the bed will be evident from undercutting of the bank protection and the presence of a coarse, compact bed substrate. Upstream structures may also exhibit undercutting, while downstream structures may show evidence of sediment deposition. Where one bank is armoured, the bed and opposite banks may show signs of undercutting and incision. Rates of adjustment will be conditioned by the power available to undertake sediment movement and bank erosion – lower stream power channels (<10 W m^{-2} bank full stream power) may not show evidence of erosional adjustment.
12	Tide locked channels	Often straightened and embanked. Flows are contained within the channel. During flood tide, flows are stopped and flow velocity declines as water levels rise. On the ebb tide, water levels drop and flows increase in velocity. Bed and banks rapidly accumulate fine sediment. In freshwater sections of these transitional waters, marginal vegetation colonises the fine sediments leading to extensive berms.	Adjustment is primarily by fine sediment accumulation on the bed and banks. The rate is dependent on the supply of fines from upstream. The bank processes are dependent on the tidal range. In systems where the tidal range is large and there are high levels of incoming fine sediment, accumulation on the banks occurs rapidly and adjustment is by bank slips and slides. Vegetation growth across the bed and on the margins can occur where tidal range is small and ponded freshwater flows occur.

Notes: Descriptions taken from Defra and Environment Agency (2011).

2.3 Evidence of sediment deposition depth and architecture in rivers and streams

River gradients and morphology control sediment movements and deposition within channels as they control river water velocity. This is often referred to as ‘stream power’. It describes the energy (W, watts) of flowing water expended on the bed and banks of a channel. High stream power values generally correspond with steep, straight, scoured reaches while low stream power values occur in broad alluvial flats and floodplains. Thus there is a general tendency for stream power to decrease as distance from the headwater increases, leading to a general deepening and fining of stream sediment. This was demonstrated on the River Nene by Tye et al. (2013), where average sediment depth increased from 15 to 45 cm through the non-tidal water bodies.

As the gradient decreases and water velocity slows, sediment size distribution will change, potentially with an increase in fine particles. This will potentially influence the extent that SRP may be adsorbed by the particles as a function of particle surface area. Walling et al. (1998) estimated the amount of fined grained sediment (<150 µm) stored in the channel bed of the rivers Ouse and Wharfe in Yorkshire. Average values were found to be between 0.017 and 0.924 g cm^{-2}, and tended to increase downstream. These figures translate to approximate sediment depths ranging from 0.02 cm to 0.9 cm, assuming a bulk density of 1 g cm^{-3}. These depths would double if a bulk density of 0.5 g cm^{-3} is used, as was recorded by Jarvie et al. (2005) and Tye et al. (2013).

Heppell et al. (2009) examined the quantity of sediment that plants trapped in the Frome and Piddle catchment in Dorset. Peak sediment deposition was 66.8 kg m^{-2} in July 2003 at Maiden Newton and 23.5 kg m^{-2} at Snatford Bridge; these equate to depths of 4.5 and 2.35 cm, respectively, if spread evenly across 1 m^2. If a bulk density of 0.5 g cm^{-3} were used, these sediment depths would increase to 9 and 4.7 cm, respectively. The depths of sediment can be hugely variable in river channels. For example, Lansdown et al. (2012) found sediment as deep as 1 m in the River Leith, Cumbria.

The structure of the drainage network within catchments is also important in determining sediment architecture. Variations in local geomorphology, natural disturbance regimes (for example, tributaries) and human interactions (for example, land drainage) produce a continuum set of in-stream conditions (Naiman et al. 2000, Fisher et al. 2004). Fisher et al. (2004), for example, suggest that tributaries flowing into a river will provide pulses of fresh material and energy that can affect sediment deposition.

2.3.1 Effects of infrastructure on sediment deposition

It is recognised that infrastructure placed in rivers such as weirs, bridge supports, locks and sluice gates can influence sediment transport and deposition, largely through changes in water velocity (SEPA 2010, Defra and Environment Agency 2011). Areas of increased deposition generally occur in the leeward side of locks and sluices as the water velocity decreases (Defra and Environment Agency 2011). However, there is very little published information on the extent of siltation that occurs due to infrastructure in UK rivers. Such information may be available through historical dredging records.

2.3.2 Effects of vegetation on sediment accumulation

According to the MMB river typology (Table 2.2), it is groundwater-dominated and channelised low energy rivers that are particularly susceptible to increased macrophyte growth as a result of sediment building up, primarily because many macrophytes require reasonable sediment depths for rooting. Macrophyte growth also encourages further sedimentation. Water velocity affects river macrophytes directly through physical damage (stretching, breaking and mechanical damage) and indirectly due to changes in gas exchange and light (turbidity).

Dawson and Robinson (1984) suggested that the force acting on the rooted macrophytes under field conditions is related to water velocity and plant biomass through the equation:

$$F = K \times Vl \times Bm \qquad (2.1)$$

where:

F = force in Newtons

V = velocity in m s^{-1}

B = biomass (kg fresh weight per macrophyte)

K, l, m = coefficients specific to season and macrophyte species

The force is the tension expressed to the stem securing the shoots to the root. Table 2.3 shows the force acting on whole macrophytes in stream beds calculated using equation 2.1 (from Dawson and Robinson, 1984).

Table 2.3 Approximate force acting on a range of macrophyte species within their beds in streams

Species	Force (N)
Ranunculus pseudofluitans	2–4
Potamogeton pectinatus L.	5
Elodea Canadensis	5
Potamogeton X zizii	6
Myriophyllum spicatum L.	7

As demonstrated in Table 2.3, different plants can withstand different forces caused by different water velocities. Thus, plant communities are likely to impact on the rate of possible sediment accumulation because of their effects on water velocity. This is summed up by Madsen et al. (2001), who reviewed the most important factors relating to submersed plant growth in channels (Table 2.4).

Table 2.4 Conceptual model of the effects of current velocity and species composition of submersed macrophytes in streams and rivers

Base velocity (growing season)	Low temporal flow variability	High temporal flow variability
Slow (<0.10 m s^{-1})	High biomass High diversity of angiosperms (few bryophytes, benthic	Early in the season: • delayed onset of growth • community typical of higher velocities

	periphyton)	Late in the season: • sediment movement • reduced biomass
Moderate (0.10–0.60 m s^{-1})	Intermediate between low and fast water velocity	Intermediate between low and fast water velocity
Fast (0.60–0.90 m s^{-1})	Low biomass Few angiosperm spp. + bryophytes	Early in the season: • delayed onset of growth Late in the season: • biomass and diversity maintained • no new growth
Very fast (>0.90 m s^{-1})	Periphyton, bryophytes	Unvegetated

Notes: Modified from Madsen et al. (2001).

A literature review of macrophyte growth and sediment deposition in UK river waters illustrates the aspects discussed above. Heppell et al. (2009) examined the quantity of sediment that plants trapped by monthly mapping of macrophyte and sediment at two sites in the Frome and Piddle catchments, Dorset. A cyclical pattern of sediment storage was found with respect to macrophyte growth and dieback. Significantly more sediment was stored under vegetation, peaking at 66.8 kg m^{-2} in July 2003 at Maiden Newton and 23.5 kg m^{-2} at Snatford Bridge. At both sites sediment generally built up during the spring and summer before declining over the winter period. Winter values for the Maiden Newton were ~20 kg m^{-2} and at Snatford Bridge were <10 kg m^{-2}. The increase in sedimentation rates caused by plant growth is likely to be a result of the effects vegetation has on decreasing water velocity.

2.3.3 Effects of high stream flow and flooding

Within the context of developing a screening tool for sediment and phosphate, a major process that needs to be accounted for is the likelihood of extensive losses of river channel sediment during episodes of high stream flow and flooding. Both Pinay et al. (2002) and Fisher et al. (2004) emphasised the importance of flooding in resetting the sediment structure and texture within the channel and the floodplain. In addition, there is very little information on residence times of sediment in river channels.

While suspended sediment measurements in river and stream waters have been shown to increase with rainfall, it is not clear how much of this is re-suspended sediment from the river channel and how much enters the water via erosion and land drains. However, extensive scouring during flood times can be regarded as an important natural process that can move considerable sediment from the river channel to the estuary, thus cleaning rivers of phosphate-bound sediment. In addition, scouring during flooding can remove substantial amounts of vegetation. For example, extensive scouring after flooding has been described for the River Nene (Brierley et al. 1989, Tye et al. 2013). These reports indicate that large-scale scouring of sediment occurred in both 1976 to 1977 and 2012 to 2013. However, there is relatively little information on the scale of scouring experienced by UK rivers. Important questions are:

- How often do these events occur?
- What are the threshold conditions for large-scale scouring to be initiated?
- How quickly does it occur?

The ability to re-mobilise sediment is most likely linked to an increase in shear stress at the river bed and sediment cohesiveness. During periods of flooding, the increase in shear stress will be associated with increased velocity (slope/discharge) and/or increased water depth. Thus within a screening model, excess shear stress could be determined by examining the average height of a river compared with its likely flood height.

2.3.4 Summary

There is limited knowledge about depths of sediment and its movement in UK river channels. However, based on the literature, there are a number of important points that can be looked at to identify the locations, quantities and chemical properties of channel sediment. These steps will go towards forming the foundation of the screening tool.

- A description of river/water body type may be required to determine whether sediment is likely to accumulate.
- Sediment input sites need to be identified, including the extent of under field drainage.
- Categorisation is needed of catchments or inputs of sediment with ‘likely phosphorus status’.
- The degree to which river sediment may be flushed through via flooding should be analysed.
- The degree of vegetation cover/type will provide an indication of sediment deposition; areas of high vegetation are most likely to trap greater quantities of sediment.
- An analysis of where infrastructure may cause sediment to accumulate is required.
- Historical dredging records should be analysed to provide locations where siltation is a problem.
- Seasonal variation in sediment trapping should be accounted for.

2.4 Phosphate dynamics in UK river sediments

The second part of this review examines likely phosphorus dynamics in relation to sediment in river channels. Phosphorus enters rivers either from point (for example, WTWs) and diffuse sources.

Background or natural sources of phosphorus are generally low and can include:

- atmospheric deposition
- soil weathering
- river bank erosion
- riparian vegetation
- migratory fish returning to spawning grounds

Anthropogenic phosphorus inputs come from both point and diffuse sources.

Point sources of phosphorus include wastewater, septic tank and industrial effluents, and generally contain a high proportion of soluble, more bioavailable phosphorus (Jarvie et al. 2006).

Diffuse non-agricultural sources include run-off from roads and urban areas, and generally contain a high proportion of particulate forms of phosphorus (that is, phosphorus sorbed to soil particles). Unlike point sources, diffuse sources of phosphorus are largely storm-dependent and occur only when it rains.

Sources of phosphorus on farms can be separated into those originating from impervious surfaces (farmyards, tracks and roads) and those originating from pervious surfaces (farmed land). Impervious surfaces by definition have no or limited infiltration capacity and usually rapidly transfer phosphorus to the watercourse directly. Pervious surfaces allow infiltration of water and therefore show much greater variation in surface and sub-surface run-off, both spatially and temporally depending on storm intensity and soil infiltration rates.

Once mobilised, phosphorus is delivered to the watercourse by a number of mechanisms including overland flow, bypass flow in to artificial field drainage systems, sub-surface lateral flow or soil matrix flow via groundwater. Opportunities for retention of phosphorus during the delivery process are dictated by the speed of transfer, degree of connectivity and type of landscape (for example, presence of ditches and ponds).

Once entering the river, both SRP and particle adsorbed phosphorus may participate in water–sediment interactions. In addition there will be a small proportion of organic phosphorus, which may be broken down by microbial life and may enter the phosphorus cycle as SRP at a later date. Within river phosphorus cycling is included within the INtegrated CAtchment Model – Phosphorus (INCA-P) model (Wade et al. 2002).

2.4.1 Sorption processes of SRP onto sediment

The sorption of phosphorus onto sediment can be considered a two stage process, where initially fast sorption (Step 1) of SRP is followed by a slower diffusion phase where the phosphorus ion enters the particle/oxide (Step 2). Factors influencing Step 1 are predominantly the particle surface area and charge balance of the sediment sample. Step 2 is dependent on the type and composition of the solid phase particle. Iron and aluminium oxides, or surfaces coated with them, tend to have a higher slow sorption capacity, possibly due to the reaction process (exchange with hydroxyls, chemisorption, precipitation as iron or aluminium phosphates) or because many oxides or aluminium sesquioxides in natural systems are poorly crystalline.

Pure clays have a limited ability to adsorb phosphorus beyond the initial sorption phase (Step 1), suggesting that it is in fact their covering with oxides which results in high values of K_d (adsorption affinity) and low values of EPC_0. Borggaard (1983) suggested that clays stripped of oxide coverings demonstrate rapid initial sorption (Step 1) but little capacity for the slow diffusion reactions (Step 2).

2.4.2 How labile is labile?

Within the pool of phosphorus that is considered labile or bioavailable, there is a continuum of availability based on how easily desorbed from the sediment SRP is. The most easily desorbed SRP is that which takes part in rapid solid–solution equilibria (that is, the calculation of EPC_0), while other phosphorus, such as the more strongly held orthophosphate, may become available to plants and other sediment living biota in the longer-term. Many techniques have been used to try and characterise the phosphorus attached to sediments based on the binding energy strength. The purpose of this is to define pools that could be described as labile, loosely bound, exchangeable, algal-available and are operationally defined (Logan 1982). These include extractions such as Olsen P or resin-available P. Sequential extraction procedures have been used to further categorise the progressively more strongly bound SRP by its associations with different mineral phases. For example, SRP bound to clay is likely to be less strongly bound than that to manganese and iron oxides. Over time SRP can move from easily exchangeable sites to be increasingly incorporated or fixed within the structures of oxides/minerals or precipitate out as minerals. This SRP can be considered non-labile.

2.4.3 Why is labile or bioavailable phosphorus important?

The labile pool of phosphorus can be defined as that phosphorus which takes part in water–sediment equilibrium reactions, while the bioavailable pool is that available for biota to utilise (for example, bacteria, macrophytes). These pools of phosphorus differ from the total pool of phosphorus where the vast majority of phosphorus is occluded or fixed within a variety of mineralogical forms, such as co-precipitation with calcium phosphates or within aluminium, manganese or iron oxides.

2.4.4 Interactions of labile P with water

Interactions between labile sediment PO_4-P and water (SRP) are controlled by the solid–solution equilibrium. This will depend on river water chemistry properties (pH, ionic strength and competing anions such as HCO_3^-), which will determine the surface sorption properties of particles, the size of the labile pool and the capacity of the sediment to sorb SRP. The most appropriate measure of the pool of phosphate that is in equilibrium with the river water would be made using isotopic exchange (using ^{32}P) such as has been carried out in soils. However, this has rarely been undertaken using river sediments.

Methods used to assess the labile pool in sediments could include extractions such as Olsen P (Tye et al. 2013), while resin exchange is often the preferred measure of bioavailable phosphorus (Palmer-Felgate et al. 2009). Extractions such as Olsen P (0.5 M $NaHCO_3$) work by flooding the system with ions (HCO_3^-) that compete with phosphate (PO_4^{3-}) ions on the anion exchange complex of the sediment, leading to the desorption of phosphate which can be measured. Resin extractable phosphorus (Resin-P) is a measure of the algal-available phosphorus fraction and is assayed using an anion exchange resin technique (Sibbesen 1977, Uusitalo and Ekholm 2003). It represents a pool of easily available phosphorus that may be available for uptake by plants and algae. These extractions have typically been used for lake sediments more than for river sediments. However, there are two examples for river sediment.

Olsen P example

Tye et al. (2013) used Olsen extractable phosphorus (Olsen P) to look at labile pools in sediments of six water bodies in the River Nene and found concentrations of labile sediment phosphate up to ~90 mg kg^{-1}. Mean values ±1SD are shown (Figure 2.3). These values exceed those recommended by the UK government for agricultural soils. The Fertiliser Manual (RB209) (Defra 2010) sets a target value for Olsen P of 16–25 mg l^{-1} (P Index 2) for the major arable crops and grass, which equates to 20.8–32.5 mg kg^{-1} assuming a bulk density of 1.3 g cm^{-3}; this is based on the P index measurement being traditionally undertaken on a volume of soil (5 ml) and assuming a bulk density of 1 g cm^{-3}. Although there was a large geological control on the total phosphorus concentrations of the sediments down the catchment, estimates of bioavailable phosphorus were <5% of total phosphorus and in most cases were <2% of total phosphorus.

Results showed that within a reasonably large river system such as the Nene, an increase in Olsen P was found from the headwaters (WB 1–3 in Figure 2.3) to lower water bodies (WB 4–6 in Figure 2.3) (Tye et al. 2013). This may represent a greater intensification of agriculture and a greater number of potential SRP inputs as distance increased from the headwaters. While the reasonably large standard deviation (SD) suggests a degree of local heterogeneity within the sampled sediments from each water body, the similarity of the mean value also suggest mixing of the sediments appropriate to the inputs of SRP from the catchment.

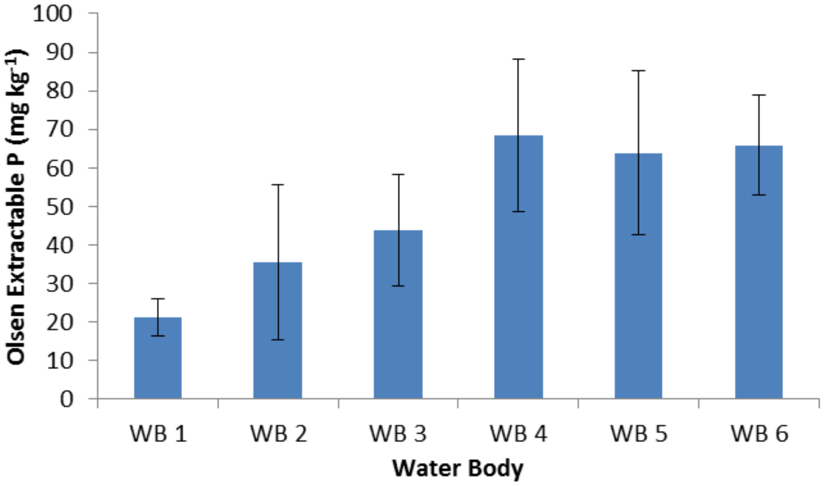

Figure 2.3 Mean Olsen extractable phosphorus concentrations for each water body sampled from the River Nene

Notes: Error bars are ± 1 SD
Data from Tye et al. (2013)

Resin-P example

Resin-P extractions, often referred to as algal-available P, were used by Palmer-Felgate et al. (2009) to examine differences in sediment concentrations in pools, riffles and separation zones in three paired headwater stream systems with different levels of agricultural intensification of the rivers Wye, Avon and Welland. They examined ‘control’ and ‘agriculturally impacted’ headwater streams within each catchment. Total sediment phosphorus was found to vary between catchments, probably as a result of different geological soil parent materials. Figure 2.4 shows mean available Resin-P ± 1 SD from this work. The conclusions from this work are as follows:

- Increasing agricultural intensification within a catchment generally increases Resin-P concentrations.
- There were no consistently significant differences between pools, riffles and separation zones.
- There was a high degree of heterogeneity within the measurements.
- The heterogeneity increased with agricultural intensification.
- However, like the Nene, the mean values of Resin-P were similar for catchments, suggesting that the catchment phosphorus status was an important factor in determining mean phosphorus concentrations.

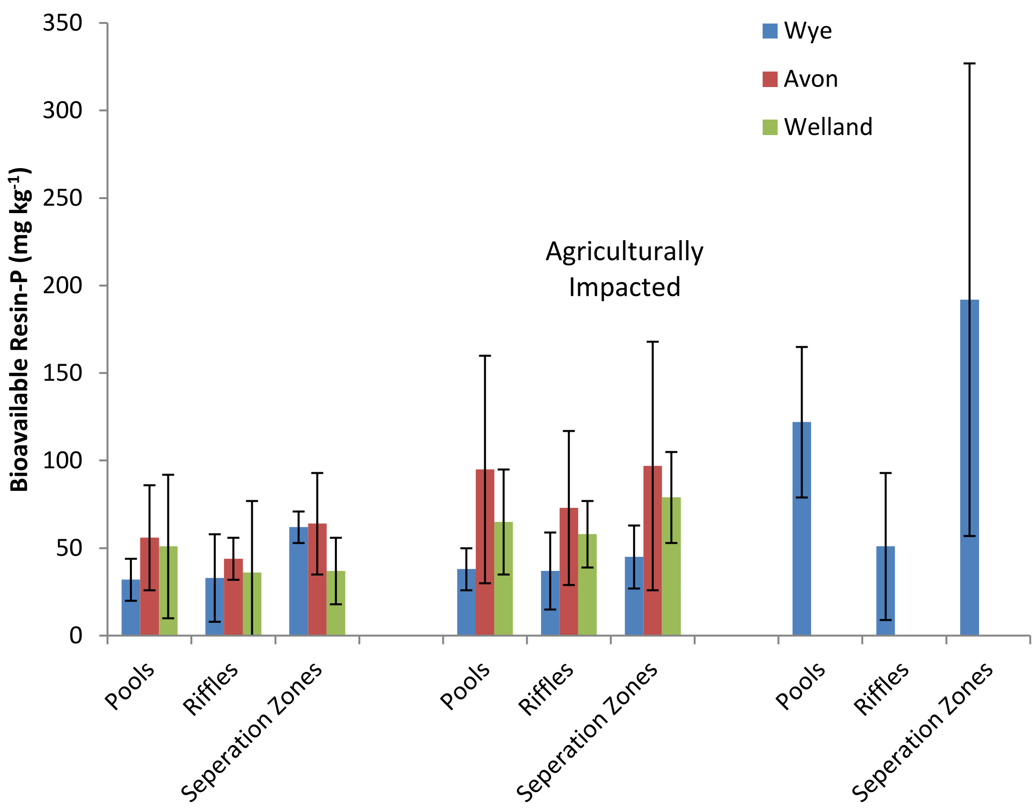

Figure 2.4 Sediment Resin P concentrations in pool, riffles and separation zones in paired catchments with different agricultural intensities [there are two agriculturally impacted rivers for the Wye Catchment]. Data from Palmer-Felgate et al. (2009)

2.4.5 Labile pools and mineralogy

The general lack of information about measurements of labile pools of phosphate in river sediments means that interactions between sorptive surfaces and mineralogy, particle size, organic carbon and labile phosphorus are hard to make. Several authors have described sediment mineralogy but this is usually in relation to total phosphorus pools. For example, Tye et al. (2013) found relationships between total phosphorus and manganese and iron oxides in sediments of the River Nene. However, these relationships were considered to be primarily geologically influenced (that is, as rock sediment was laid down) rather than a result of fertiliser application and erosion of sediment. In another study, House and Denison (2002a) found relationships between total phosphorus, calcium and iron. Mineral phases that have been suggested to precipitate using speciation models and calculation of 'saturation indices' include calcite, octacalcium phosphate, calcium hydroxyapatite and tri-calcium phosphate (House and Denison 1997a). The precipitation of minerals, thereby fixing SRP, will effectively transfer the SRP from a labile to non-labile pool. It is likely that stream and river waters with high calcium and hydrogen carbonate (HCO_3^-) will be more likely to precipitate these minerals (for example, chalk streams). However, mineral precipitation of SRP will probably only account for a small percentage of SRP.

Sorption of SRP to clay and oxide minerals is a likely way in which they are maintained in the labile pool. It is likely that clay minerals will not bind SRP as tightly as oxide minerals, particularly iron. In addition, both these mineralogical components will contribute significant surface area to the sediment for sorption of SRP. It would be expected that high surface area sediments will be able to absorb more SRP than low surface area sediments. Clay mineralogy is important as clay minerals have vastly different surface areas on which to sorb SRP. House and Warwick (1999) described the clay mineralogy for sediments of the River Swale as being ~45% illite, ~45% kaolinite and ~10% expandable clays. Typically, kaolinite will have a surface area of 10–30 $m^2\ g^{-1}$, illite between 70 and 175 $m^2\ g^{-1}$, chlorite between 70 and 100 $m^2\ g^{-1}$, and expandable clays such as smectite between 650 and 800 $m^2\ g^{-1}$. Typically maximum absorption will be at ~pH 6, while there would be a decreasing affinity at pH>6, largely reflecting the increase of negative charge (House and Denison 1997).

Sorption of SRP to oxides may result in the phosphate being fixed over time. However, depending on the sediment architecture, a reversible process may occur if sediment finds itself in reducing conditions. House and Denison (1997) suggested that some release of SRP may occur from sediment in the winter due to low oxygen conditions and dissolution of iron oxyhydroxides.

2.4.6 Labile pools and SRP concentrations

Insufficient data are available to examine these relationships.

2.4.7 Interactions of bioavailable phosphorus with macrophytes and other ecology

Bioavailable phosphate concentrations in sediment are important for the growth of plants. Macrophytes are capable of deriving almost all their phosphorus requirements from bioavailable sediment phosphorus reserves (Mainstone and Parr 2002), although Pelton et al. (1998) suggested that the relative contribution of root uptake to macrophyte phosphorus demand varied on the SRP concentration in the overlying water. The increased growth of aquatic plants where there are high levels of bioavailable phosphorus can lead to related problems. Along with greater plant growth trapping more sediment, Mainstone and Parr (2002) suggested that:

- extra phosphorus increases regrowth after plant management
- the species community structure can be altered, favouring species with high growth rates
- root depth is reduced, potentially increasing the plant's susceptibility to being ripped out at high river flows and associated sediment remobilisation

2.4.8 Use of equilibrium phosphorus concentration (EPC_0) and sediments

EPC_0 calculated for sediments is used in conjunction with water SRP concentrations to indicate whether sediment is likely to act as a source or sink for SRP.

The potential relationship between sorbed and solution SRP is determined in the laboratory by creating isotherms of sediment phosphorus sorption (see, for example, House et al. 1995, Jarvie et al. 2005). Typically EPC_0 is determined on wet sediment (0–5 cm) and within seven days of sampling to minimise sample deterioration (Jarvie et al. 2005). The methodology usually involves placing a measured mass of sediment in six bottles with 200 ml of a synthetic water composition roughly matching the major element chemistry of the river from which the sediment was taken (for example, 2 mmol $CaCl_2$). The bottles are then spiked with different concentrations of KH_2PO_4 and placed in an orbital shaker in the dark at 10°C for 24 hours. Samples are centrifuged and their SRP concentration determined (Murphy and Riley 1962). In addition, the linear portion of the isotherm is often used to derive K_d values (l kg^{-1}) (Jarvie et al. 2005). The isotherm is most often modelled using the Freundlich model (Equation 2.2) which is fitted using the least squares method. The Freundlich model takes the form:

$$\Delta \boldsymbol{N_a} = \boldsymbol{K_f C_i^n} \qquad (2.2)$$

where ΔN_a = change in adsorbed P (µmol g^{-1}), K_f is the Freundlich constant, C_i is the concentration of SRP in solution and n is a constant.

Using the fitted isotherms, EPC_0 is calculated as the point where the isotherm crosses the *y*-axis at 0 (see House et al. 1995, Jarvie et al. 2005). This represents the point where there is no net sorption or release of SRP. When considering the dynamics of the interactions of SRP with river sediment, it is know whether the sediment has the potential to act as a source or a sink. Thus, when SRP concentrations in the overlying water are greater than EPC_0, the sediment has the potential to sorb SRP from the water column and act as a sink. In contrast when SRP concentrations are less than EPC_0, the sediment has the potential to release SRP to the water column and act as a source.

2.4.9 Collation of all EPC_0 values calculated for UK and global temperate river systems

Data collected from a range of UK published data are shown in Figure 2.5 as a cumulative distribution function. In general, the majority of values for EPC_0 are <2 µm P l^{-1} (62 µg l^{-1}). The median value is 0.74 µm l^{-1} (23 µg l^{-1}) and the 75th percentile is 1.75 µm l^{-1} (54 µg l^{-1}).

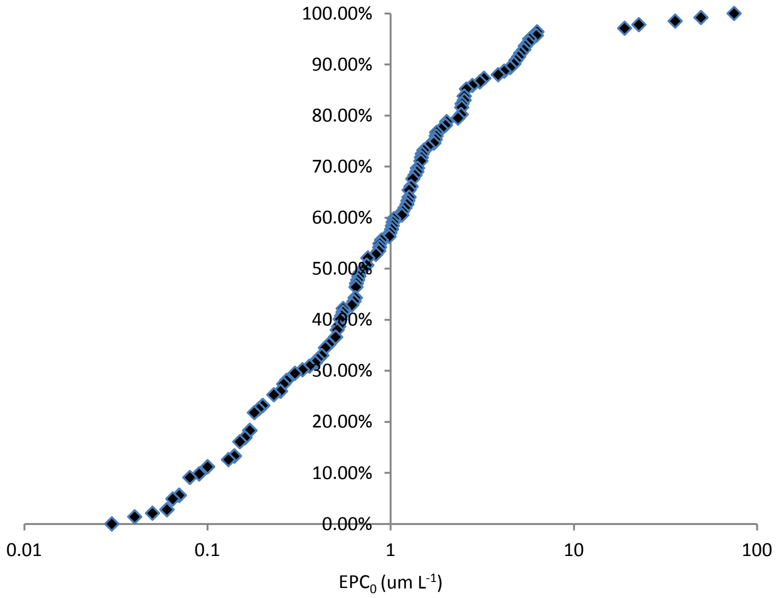

Figure 2.5 Cumulative distribution function of EPC_0 collated from the literature for UK river sediments

Notes: Data for Avon PSYCHIC catchments, Wye PSYCHIC catchments and Wye catchment monitoring sites are from Jarvie et al. (2005).
Data for the Pang and Lambourn catchments are from Jarvie et al. (2006).
Data for the Dee catchments are from Stutter and Lumsden (2008).
Data from the Nene are from Tye et al. (2013).

2.4.10 Primary controls on EPC_0 – labile pools and mineralogy

Theoretically, the EPC_0 concentration is largely determined by:

- ability of sediment to adsorb/desorb phosphate
- concentration of SRP in the river water

It is reasonable to assume that, as labile phosphorus increases in a specific sediment, a higher EPC_0 concentration would be found due to a greater 'capacity' to supply. For example, Withers et al. (2009) examined a soil that had different concentrations of Olsen P as a result of from different applications of phosphorus fertilisers over several years. They found that as Olsen P increased, EPC_0 increased. Figure 2.6 shows the relationship between total phosphorus and Olsen P against EPC_0.

In addition, calculated capacity/intensity relationships in soils have confirmed this as demonstrated by Hartikainen (1991). However, data exploring these relationships are lacking for river sediments, as it is more difficult to set this type of experiment up.

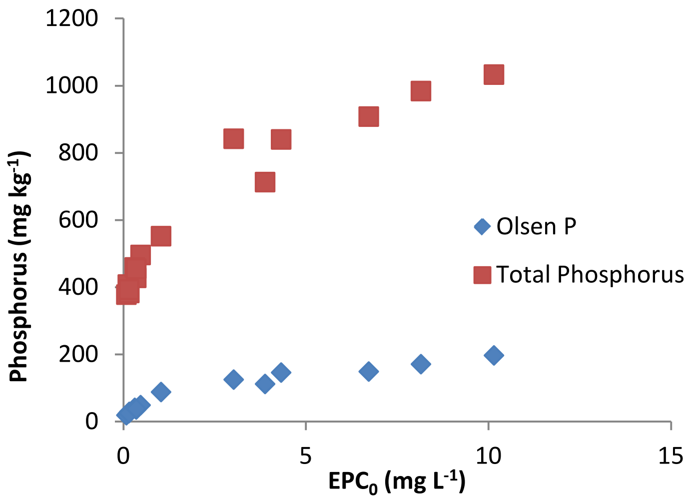

Figure 2.6 Relationships between total P and EPC_0, and Olsen P and EPC_0

Notes: Data from work of Withers et al. (2009)

While soils have demonstrated a fundamental aspect of the behaviour of EPC_0 (that is, as the labile pool increases, EPC_0 increases), not all extractants show this type of response. For example, Hartikainen (1991) compared EPC_0 values with values of labile phosphorus and found poor correlations with the extractions for easily soluble phosphorus.

This project examined the relationship between labile phosphorus and EPC_0 on two sediment datasets where results were available. The first example is from the study by Tye et al. (2013) on sediments from the River Nene. This used Olsen P extractions as an estimate of labile phosphorus and results showed a strong negative relationship between labile phosphorus and EPC_0 (Figure 2.7), which is contrary to expectation, as described previously. These results suggest that there is a considerable labile phosphorus portion that can be extracted with Olsen P but which does not form a large component of the easily available phosphorus, which participates readily in solid–solution equilibria. This could be because the substrate was dominated by iron-rich sand in the upper water bodies with little clay, while at higher EPC_0 values, there was more clay which does not hold phosphate as strongly as do iron oxides.

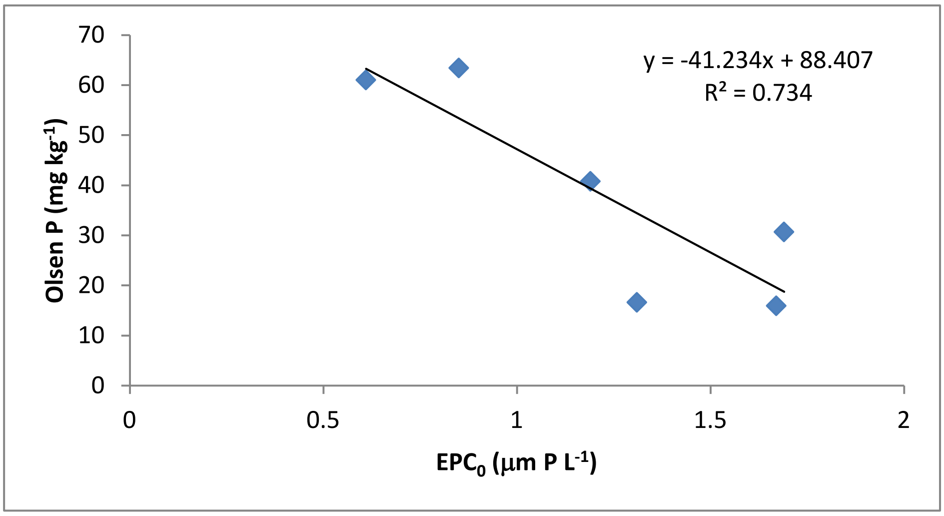

Figure 2.7 Relationship between EPC_0 and labile P as determined by Olsen P extraction for the six non-tidal water bodies of the River Nene

Notes: Data from Tye et al. (2013)

In the second example, using the dataset of Palmer-Felgate et al. (2009), Resin-P was used to obtain concentrations of bioavailable phosphorus and a positive correlation between EPC_0 and Resin-P was found. However, further examination of the dataset suggests that the positive correlation is heavily skewed by the two agriculturally impacted catchments. This suggests that measures of bioavailable phosphorus are generally poor predictors of EPC_0. This is likely to be as a result of many phosphorus extractions being operationally defined and the extracted pool not truly representing the pool of phosphate that is predominately involved in the solid–solution equilibrium or EPC_0 (Logan 1982).

Few authors have examined interactions of EPC_0 with sediment elemental and particle size characteristics and this remains an area where more work is generally required. Jarvie et al. (2008) published mean total Fe_2O_3 and Al_2O_3 results along with mean EPC_0 values for three sites on the Wye, and Tye et al. (2013) published total iron and aluminium results along with EPC_0 values for the Nene.

The Tye et al. (2013) values were converted to Fe_2O_3 and Al_2O_3 concentrations (so to be similar with Jarvie et al. 2008) and are plotted along with EPC_0 values in Figure 2.8. A strong relationship was found between Fe_2O_3 and EPC_0 whereby increasing concentrations of iron oxides resulted in a smaller EPC_0 (Figure 2.8a). However, no relationship was found for Al_2O_3, probably as a result of Al_2O_3 measurement including both clays and oxides (Figure 2.8b). The role of manganese oxide is relatively ignored in the literature, despite its known ability to sorb phosphorus in river waters. Kawashima et al. (1986) found that phosphate is sorbed by MnO_x via the presence of divalent cations (Ba^{2+}, Ca^{2+}, Sr^{2+}, Mg^{2+}) or transition metals (Mn^{2+}, Co^{2+}, Ni^{2+}). Only Tye et al. (2013) have provided data to examine the relationships between MnO_2 and EPC_0 (Figure 2.8c).

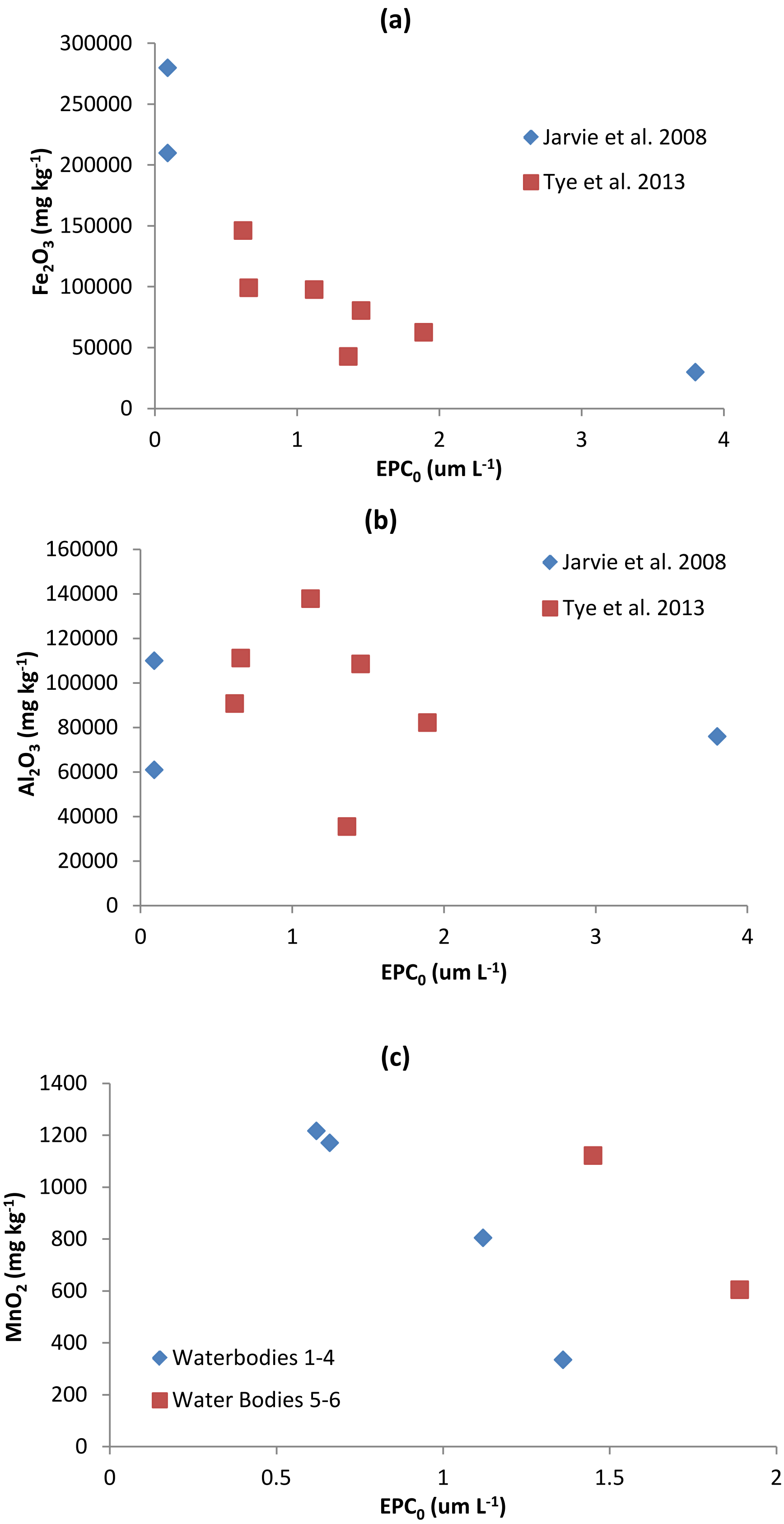

Figure 2.8 Relationships between EPC_0 and (a) Fe_2O_3 and (b) Al_20_3 from the studies of Jarvie et al. (2008) and Tye et al. (2013) and (c) MnO_2 from the study of Tye et al. (2013)

Sediment texture should be a major control on EPC_0 as it is a major control on sediment surface area. The relationship between sediment surface area and EPC_0 has not been studied. However, Rawlins (2011) demonstrated that the surface area of sediments increased with catchment size suggesting that, as the catchment size increases, the water tends to lose velocity, allowing the deposition of finer sediment. This in theory would suggest an increase in surface area as river current decreases.

2.4.11 Relationship between EPC_0 and adsorption affinity

In the calculation of EPC_0 isotherms, the adsorption affinity (K_d) is calculated as the slope of the tangent to the line at EPC_0 (Froelich 1988). K_d provides an estimate of the affinity for sorption of phosphate and is a function of the geochemistry of the sediment and river water. Froelich (1988) suggests that sediments high in natural oxide coatings have a high capacity for phosphorus sorption, and therefore high K_d values and low values of EPC_0 as the phosphorus is less easily desorbed. Although clay minerals have a high surface area and potentially high labile phosphorus, they hold onto phosphorus less tightly and may therefore have higher EPC_0 concentrations.

Figure 2.9 shows an overall trend where a decrease in K_d results in an increase in EPC_0. Sediment properties such as surface area and texture may affect this relationship. Sediments with high clay contents will have higher K_d and lower EPC_0 values than sandy sediments (House and Warwick 1999) because of their higher surface area. Secondly, those sediments with high oxide concentrations, particularly iron oxides, are likely to possess higher K_d and lower EPC_0 values as suggested by (Froelich 1988).

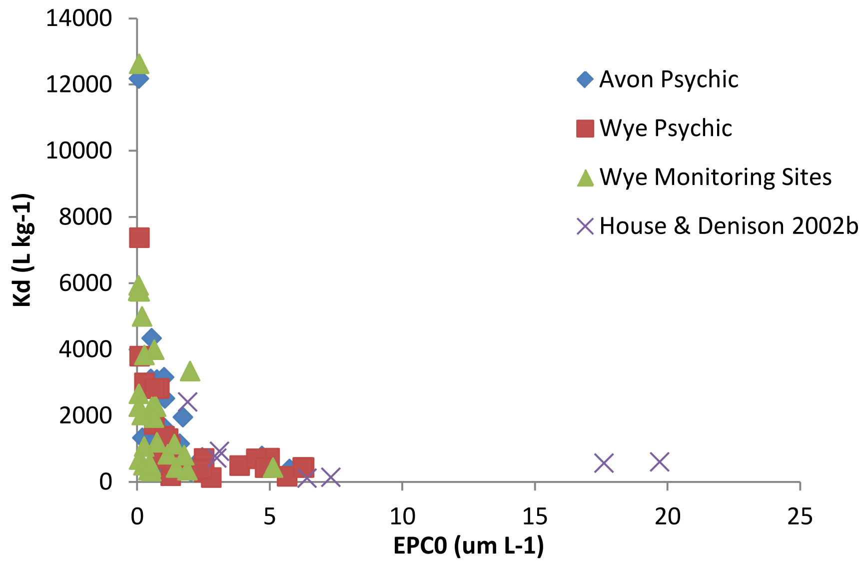

Figure 2.9 Relationship between K_d and EPC_0 for UK rivers

Notes: Data from Jarvie et al. (2005, 2006)

Thus the quantity of phosphate that a sediment can hold is generally related to the geochemical properties of the sediment as well as the properties of the water that interact to determine the surface sorption of phosphate onto clays and oxide minerals. Sediments will often be a heterogeneous mix of oxides and clays with stream velocity determining the sediment architecture.

There was insufficient information from the UK to develop a greater understanding of the influence on EPC_0 values of:

- particle size

- clay type
- organic carbon
- geochemistry (FeO_x, AlO_x, MnO_x)
- geology

2.5 Relationship between EPC_0 and SRP

When EPC_0 measurements are calculated, they are often compared with an SRP value for the water column overlying the sediment. The relationships found for UK rivers shown in Figure 2.10 demonstrate that a positive correlation exists between SRP and EPC_0. This suggests that SRP concentrations in the river water and sediment uptake are related. Values below the 1:1 line represent instances where SRP > EPC_0 and the sediment is likely to act as a sink, whereas those above the 1:1 line represent sediments that may act as a source.

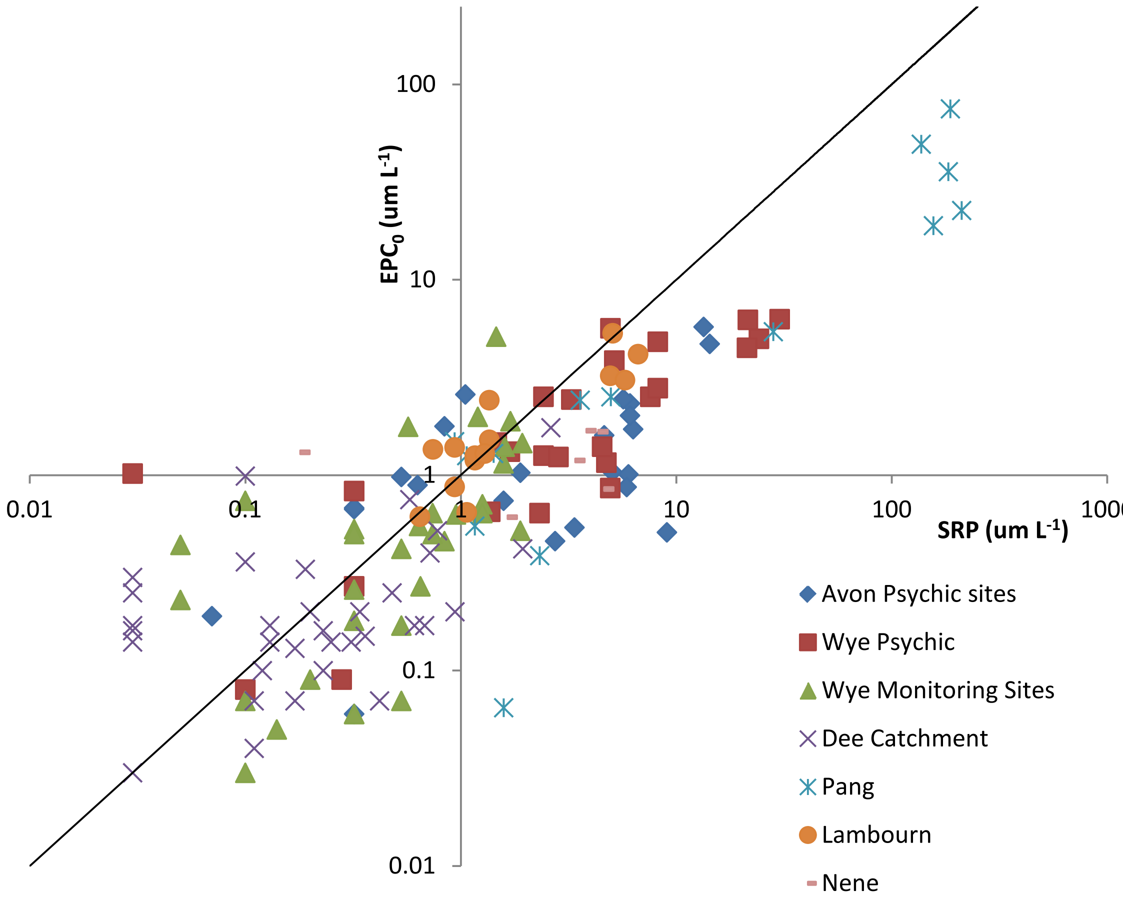

Figure 2.10 Compilation of EPC_0 results plotted against SRP concentrations at the time of sampling

Notes: Solid line represents the 1:1 line where sediments would be at equilibrium.
Data for Avon PSYCHIC catchments, Wye PSYCHIC catchments and Wye catchment monitoring sites are from Jarvie et al. (2005).
Data for the Pang and Lambourn catchments are from Jarvie et al. (2006).
Data for the Dee catchments are from Stutter and Lumsden (2008).
Data from the Nene are from Tye et al. (2013).

2.5.1 Secondary controls on EPC_0

Point sources

The impact of large point source discharges of phosphorus (for example, WTWs) has been found to increase sediment EPC_0 values downstream of the point source. The size of the increase in EPC_0 and the length downstream that EPC_0 values will be affected will depend on:

- the size of the WTW and the quantity of SRP released
- whether phosphorus stripping is utilised

Jarvie et al. (2006) examined interactions between SRP released from WTWs and sediments of the rivers Pang and Lambourn. Important points to be considered in a screening tool were observed in this study. For the River Pang, EPC_0 values up to 75 µm l^{-1} (2.32 mg l^{-1}) were found immediately downstream of the WTW at Compton. The EPC_0 results from various sampling sites downstream of this WTW are plotted against SRP concentrations in Figure 2.10. Results for the Pang show that, when EPC_0 values extend to 75 µm l^{-1} (2.32 mg l^{-1}), river SRP concentrations are still higher, suggesting that the sediments are still acting as a potential sink. This demonstrates that even sediments close to WTWs can act as SRP sinks. However, for the Lambourn, EPC_0 and SRP values are similar in many instances suggesting that the sediment and SRP were close to equilibrium.

The extent to which inputs of SRP from WTWs will interact with sediments can be estimated from changes in SRP concentrations downstream from the point sources. Jarvie et al. (2006) examined SRP concentrations downstream of WTWs on the rivers Pang and Lambourn. On the Pang, after release from the Compton WTW, 80% of SRP loads were lost within 4 km and, on the River Lambourn, 55% of SRP was lost within 1.6 km of East Shefford WTW. Loss of SRP occurs through dilution, sediment or biota uptake.

Treatment and phosphorus stripping

In the study by Jarvie et al. (2006) during the summer (August 2004), release of SRP occurred as EPC_0 exceeded water SRP concentrations. There were a number of reasons why this occurred. First, during the experiment, tertiary phosphorus stripping was introduced which reduced SRP concentrations in the overlying water from 206 to 42 µg l^{-1} with concomitant falls in EPC_0 from 129 to 47 µg l^{-1}, as heavily phosphorus loaded sediment was slowly replaced by phosphorus-poor sediments from upstream. In summer periods, when further uptake of SRP by sediment occurs and a larger biotic phosphorus demand was present, conditions were produced where EPC_0 > SRP, thus releasing SRP.

This case study suggests that sediments close to and within their range of interaction with WTWs where tertiary phosphorus treatment is introduced may be at greatest risk of releasing SRP.

Seasonality

Several authors have examined EPC_0 in relation to seasonal trends. Jarvie et al. (2006) undertook seasonal analysis of EPC_0 on sediments from the Pang and Lambourn as described above. They found that those sediments close to EPC_0–SRP equilibrium are most at risk of changing from being SRP sinks to sources, especially when tertiary phosphorus stripping decreases SRP concentrations and heavily loaded sediment remains.

Annual variations in EPC_0 were calculated for the River Great Ouse between 1.1 and 2.5 µm l^{-1} (34–77 µg l^{-1}) (House and Dension 1997) and between 5.3 and 14.4 µm l^{-1} for the River Wey (House and Dension 1998).

Several factors need to be considered when comparing seasonal EPC_0 changes. One is a seasonal change in EPC_0 caused by changes in sediment particle size distribution and its effect on sediment surface area. The effect particle size has on EPC_0 was examined by House and Warwick (1999) in the River Swale. They found that there were significant differences in the mean EPC_0 values which were 1.02 ± 0.52 µm l^{-1} (31±16 µg l^{-1}) and 0.55 ± 0.44 µm l^{-1} (17± 13.6 µg l^{-1}) for coarse sand and silt, respectively. The adsorption affinities (K_d) also showed large differences with a mean K_d of 434 ± 785 and 1613 ± 1655 for coarse sand and silt, respectively.

Changes in particle size may be controlled by preceding rainfall, channel water velocity and sediment movement between events. For example, House and Denison (2002b) examined changes in particle size distribution through the year at a sampling site on the River Blackwater and found significant variations in the particle size with season. House and Denison (1997a) found large differences, particularly in the fine particle sizes, for sediments at four sites in the Great Ouse.

Changes in redox status

It is likely that a change in redox status to anaerobic conditions could increase the solubility of phosphorus through the dissolution of iron and manganese oxides. This could have significant effects on EPC_0 downstream of WTWs or agricultural inputs where nutrients (carbon, nitrogen, phosphorus) are plentiful and will drive bacterial growth that reduces oxygen concentrations.

House and Denison (2000) demonstrated an increase in EPC_0 with decreasing redox potential. Reddy et al. (1998) also showed increases in EPC_0 as a result of dairy effluent causing anoxic conditions to develop. These types of point sources of phosphorus inputs into rivers and streams should be considered as areas where EPC_0 may increase as a changing redox status. However, the spatial and temporal locations of sediment that may be exposed to redox changes and the extent of change are hard to predict.

2.5.2 How much SRP can sediment adsorb?

The potential for sediment to sorb SRP from river water is often calculated from the determined EPC_0 figure along with the concentration of SRP measured in the water column above the sediment at the time of sampling. This is often called the EPC_0 percentage saturation (EPC_{0sat}) parameter.

$$EPC_{0Sat}\,(\%) = 100 \times (EPC_0 - SRP)/EPC_0) \qquad (2.3)$$

Most studies from the UK suggest that the majority of sediments have the potential for the adsorption of SRP (for example, House and Denison 1997, 1998). Jarvie et al. (2006) reported that >80% of the river bed samples they tested had the potential for net SRP uptake from the water under stable low flow conditions. A compilation of UK results is shown in Figure 2.11. Positive values of EPC_{0sat} indicate that the sediment is likely to be oversaturated with SRP and will release SRP to the water column, while negative values indicate the potential for further uptake, with an increasingly negative percentage indicating a greater potential for uptake.

Figure 2.11 demonstrates that the majority of measured UK sediments have the potential for further SRP uptake – between 0 and 200% more SRP. Sediments in equilibrium are normally considered as those being within ±20% of EPC_{0sat}. The capacity for continued uptake is largely associated with the texture and surface area of the minerals present, with interlayered clays (for example, smectite) and oxides having the greatest surface areas. This may explain why even with the highest SRP concentrations resulting from WTW additions of SRP in the Pang catchment, the sediment still has considerable capacity to take up more SRP.

There appears, in Figure 2.11, to be a tendency for oversaturation to occur slightly more often at the lower SRP concentrations. Insufficient data to assess the effects of texture on EPC_{0Sat} are available, but it is likely that low sediment surface area plays an important role. Thus catchments with high proportion of sandstone geologies and low surface area clays (for example, Kaolin) may be most vulnerable.

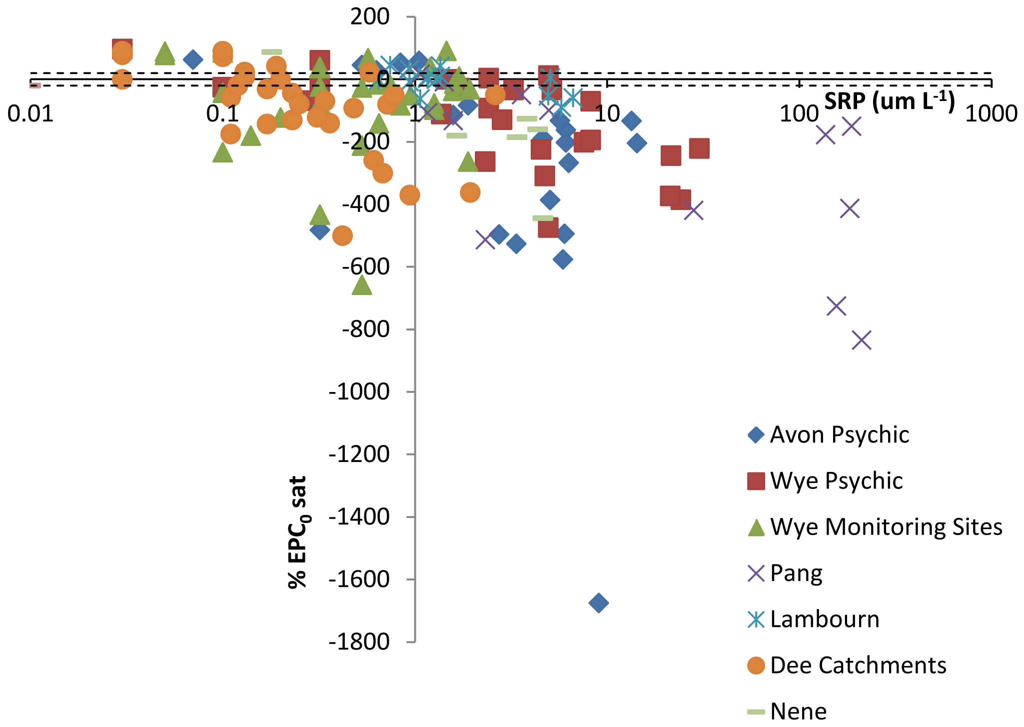

Figure 2.11 Compilation of EPC_{0Sat} results plotted against SRP concentrations at the time of sampling

Notes: Dashed lines represent ±20% of the EPC_{0Sat} where sediments may be close to equilibrium.
Data for Avon PSYCHIC catchments, Wye PSYCHIC catchments and Wye catchment monitoring sites are from Jarvie et al. (2005).
Data for the Pang and Lambourn catchments are from Jarvie et al. (2006).
Data for the Dee catchments are from Stutter and Lumsden (2008).
Data from the Nene are from Tye et al. (2013).

2.5.3 Kinetics of phosphorus uptake

Kinetic measurement of phosphorus uptake and desorption

Kinetic measurement of phosphorus uptake and desorption can be used to assess phosphorus uptake/release from sediments in river channels.

The kinetic methodology described by Jarvie et al. (2005) is often used to calculate the rate of release or sorption of SRP from/to sediments. For SRP release experiments (where EPC_0 > SRP), a measured mass of wet sediment (equivalent to 0.5 g dry sediment) is placed in polypropylene bottles with 200 ml of $CaCl_2$ solution, pre-chilled to 10°C, with no additions of KH_2PO_4. For SRP uptake experiments (where SRP > EPC_0), the synthetic river solution in each bottle is spiked with a similar amount of KH_2PO_4 to an appropriate SRP concentration (greater than the EPC_0 and close to the measured SRP concentration in the water column at the time of sediment sampling). The bottles are placed on an orbital incubator in the dark and shaken at 150 rpm at 10°C. Aliquots are removed after specific time intervals (5 min, 15 min, 30 min, 1 h, 3 h, 6 h, 15 h, 24 h), then centrifuged and analysed for their SRP concentrations. The sorption/desorption rates of SRP (House and Warwick 1999, Jarvie et al. 2005) to/from the sediments were calculated based on the equation:

$$\boldsymbol{R = K_r(C_t - C_0)^n} \qquad (2.4)$$

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

The equation describing SRP uptake and release by bed sediments is based on second-order kinetics represented by a parabolic function (House and Warwick 1999), in which n should approximate to 2. The constants are calculated by minimising the squared difference between the observed concentrations and those predicted by the rate curve. Using the calculated values the quantity of orthophosphate released from the sediment or removed from solution at any time, d_t, is obtained from:

$$\boldsymbol{dM = K_r(C_t - EPC_0)^{\,n} S dt} \qquad (2.5)$$

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

The fine bed-sediment mass S within each water body is taken from the calculation of sediment volumes obtained by probing and the mean bulk density of the sediment. The flux of orthophosphate to/from the bed sediment is calculated by integrating equation 2.2 over the residence time (T_{res}) of river water within the length of the river reach:

$$\boldsymbol{T_{res} = (D_{cs} W_{Cs} L_{riv})/Q} \qquad (2.6)$$

where D_{cs} is the mean cross-sectional depth of the reach, the length of the river reach (L_{riv}), Q is the mean annual discharge of the reach and W_{Cs}.is the average width of the cross section. Bed sediment SRP fluxes to the boundary layer of the river channel are expressed as g P T_{res}^{-1}. The annual flux of orthophosphate to/from the bed sediment into the boundary layer can be estimated by multiplying the flux for this residence time by the number of residence time periods in a calendar year. However, this ignores seasonal effects. Often results for different rivers are normalised by calculating values over a 1 km stretch of water.

Collation of UK river P sorption and release kinetic parameters

Once collated, the variability of these parameters can be assessed with respect to the geochemical, geological and physical attributes of sediment.

Less data are available for the kinetics of SRP uptake or desorption than have been published for EPC_0. Table 2.5 reports on the variation in the kinetic parameter (K_r) found for sorption of SRP to sediments in three UK river systems. There is considerable variation in reported values and these, like EPC_0 values, depend on sediment texture and mineralogy.

Few datasets report both EPC_0 and K_r to enable this comparison. However, Tye et al. (2013) published some data on the River Nene and Figure 2.12 shows this split up into water bodies 1–3 and water bodies 4–6 based on changes in catchment geology, which is the major determinant on texture. Sediment texture is generally coarser in water bodies 1–3 coarser than in water bodies 4–6. Although the relationships are particularly significant, there is a suggestion for each dataset that where a higher K_r is found it has a lower EPC_0, suggesting it may have more affinity for P.

Table 2.5 Collation of kinetic rate constants published in the literature

River system	Uptake/ release	Average K_r ($\mu mol^{1-n}\ l^n\ g^{-1}\ h^{-1}$)	Range K_r ($\mu mol^{1-n}\ l^n\ g^{-1}\ h^{-1}$)	Geology	Reference
Hampshire Avon	Uptake	10.6	0.84–54	Chalk	Jarvie et al. (2005)
Herefordshire Wye	Uptake	4.9	0.54–18.9	Mud/silt stone	Jarvie et al. (2005)
Nene	Uptake	21.8	2.36–51.7	Mud/siltstone	Tye et al. (2013)

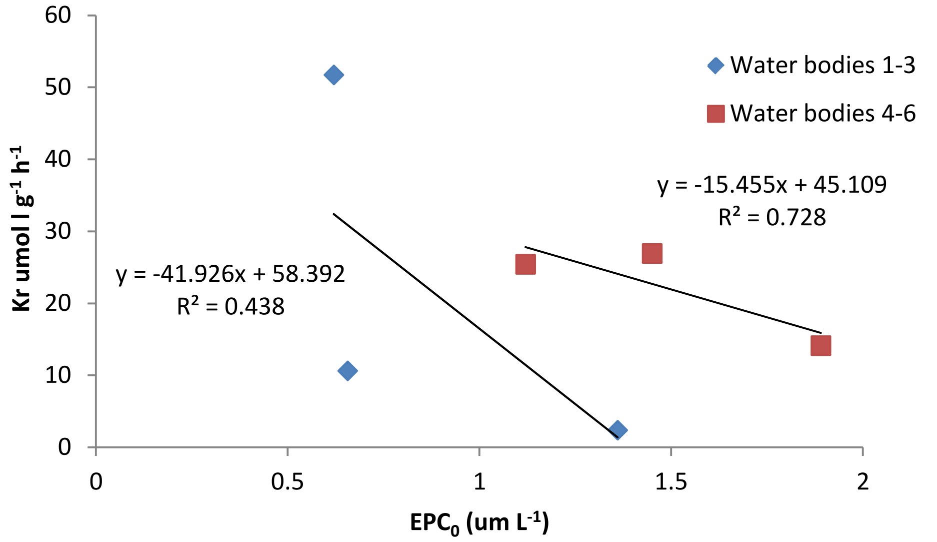

Figure 2.12 Relationship between rate constant for SRP sorption and EPC_0 for River Nene

Notes: Water bodies 1–3 are generally sandier than the siltier sediment from water bodies 4–6.

2.5.4 How much SRP is removed by sediment?

The removal or release of SRP by sediment is considered an important process within river channels. The determination of laboratory rate constants as described above have sometimes been applied for estimating the likely take-up of SRP by sediments by combining with the residence time of water over 1 km. Calculations of the quantity of phosphorus removed from the water are usually based on the interactions between a boundary layer, the 10 cm of water overlying the surface of the sediment. Jarvie et al.

(2005) suggested that ~10% of the SRP in the 10 cm of water overlying the sediment can be taken up. Typically these phosphorus fluxes were around <50 g km^{-1} for the Avon catchment. The greatest uptake fluxes (>100 g P T_{res}^{-1}) have been found in rivers with the highest sewage SRP influence (Jarvie et al. 2005) and at times of highest riverine SRP concentrations.

These calculations provide an estimate of the maximum amount of SRP removal by sediment. However, there are opportunities for errors in the calculation. Jarvie et al. (2005) suggested that the calculation may overestimate SRP removal because:

- the contact time between the boundary layer and bed sediment may be shorter than the crude estimates of water residence time obtained
- the effective boundary layer in intimate contact with the bed sediment may be less than the operationally defined 10 cm boundary layer
- the bed sediment fluxes are based on full mixing of bed sediments and boundary layer
- it is incredibly difficult to estimate the amount of sediment taking part in these interactions

The uptake of SRP by sediments needs to be put into context against the release of SRP via plants and microbes. Seasonal trends in SRP uptake have been found (Jarvie et al. 2005). Figure 2.13 shows the seasonal trends in SRP uptake (as a percentage of SRP entering the river reach) by sediments, the highest uptake being in summer and the lowest in winter in the Avon and Wye catchments. Again this may be because of dilution of SRP concentrations during the winter and less recycling from organic to inorganic forms. However, it may also be related to changes in sediment particle size distribution, with coarser sediment being found in winter as more fine particles are washed away.

Jarvie et al. (2005) calculated how much the reported phosphorus uptake fluxes would decrease water column SRP concentrations in the 10 cm of water over the sediment. Figure 2.14 shows the range of values reported with a median expected decrease in SRP concentrations in the 10 cm above the sediment of 10.3 µg l^{-1} and the 75th percentile being 19 µg l^{-1}.

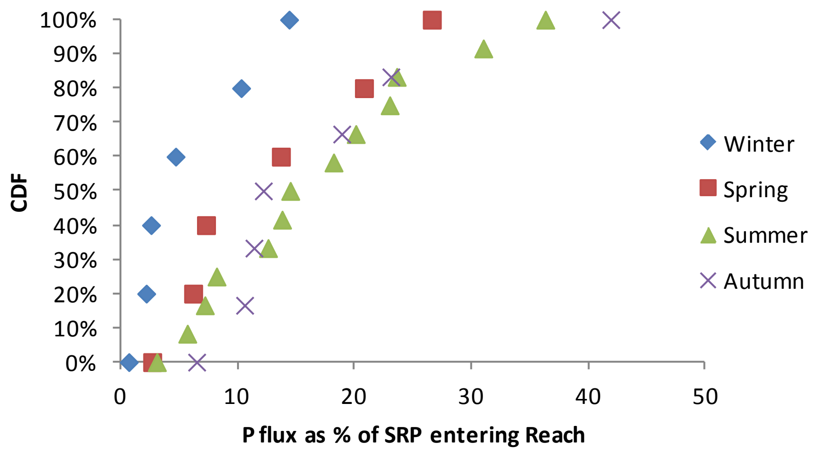

Figure 2.13 Cumulative distribution function for the SRP flux from the 10 cm depth of river water interacting with the sediment as a percentage of SRP in the 10 cm section of the water column entering the reach

Notes: Data calculated over a 1 km stretch of river of rivers in the Wye and Avon catchments (Jarvie et al. 2005).

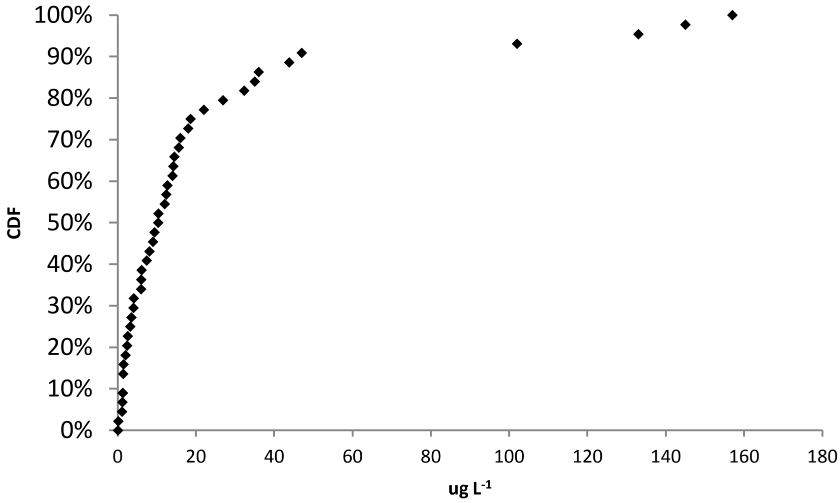

Figure 2.14 Cumulative distribution function showing the range of estimated decreases in SRP concentration (µg l^{-1}) in the 10 cm of water above the sediment as a result of sorption of SRP by the sediment

Notes: Data from Jarvie et al. (2005) for rivers in the Wye and Hampshire Avon catchments and Tye et al. (2013) for the River Nene

2.5.5 Release of SRP from sediments

Available data for assessing the release rates of SRP is limited, partly because the majority of UK river sediments analysed potentially uptake SRP or are considered close to equilibrium. However, Jarvie et al. (2005) calculated the increase in SRP concentration in the 10 cm of water overlying the sediment for rivers in the Wye and Avon catchments (Figure 2.15). Median and 75th percentile values were 3.2 and 6.1 µg l^{-1}, respectively, slightly lower than the equivalent adsorption values. With respect to flux, Jarvie et al. (2005) quoted desorption of up to 20 g km^{-1} for the Avon catchment. This may be a reflection of the smaller dataset or suggestive of the adsorption–desorption hysteresis that is commonly found.

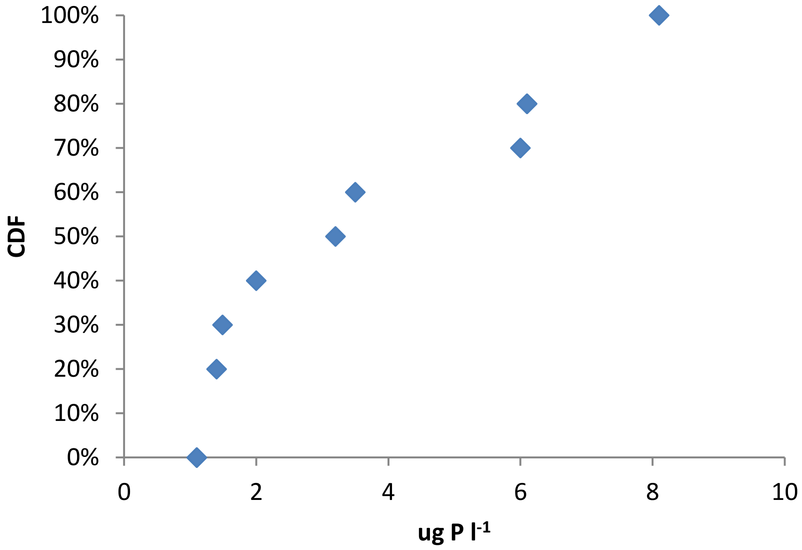

Figure 2.15 Cumulative distribution function (CDF) showing the range of estimated increases in SRP concentration in the 10cm of water above the sediment as a result of desorption of SRP

Notes: Data from Jarvie et al. (2005) from rivers in the Wye and Hampshire Avon catchments.

2.5.6 Relevant points for use in the screening tool

- As a result of sediment mixing within the stream channel, bioavailable or labile phosphorus fractions, while locally highly heterogeneous, generally produce similar mean concentrations between water bodies. This suggests that the concentration of labile phosphorus within a river system is largely determined by the phosphorus load from point and diffuse sources within the catchment. Thus a scale describing the phosphorus load is required for each water body or catchment.

- Reasonable background EPC_0 values are generally below 2 µmol l^{-1} (62 µg l^{-1}). Higher values are normally associated with SRP release from WTWs.

- Measurement of bioavailable phosphorus using extractions such as Olsen P and Resin-P are poor predictors of EPC_0.

- The geology of catchments is important as the soil parent material geochemistry will determine clay and oxide concentrations of sediment entering the river channels. Soils with high total iron, manganese and aluminium concentrations are likely to be able to sorb more SRP and produce lower EPC_0 values and higher K_d (adsorption affinity) values. However, little work has been carried out to explore these relationships to aid the development of a screening tool.

- The texture of sediments is important. Coarser sediments generally have higher EPC_0 and lower K_d values.

- Sediments close to WTWs can still act as sinks for SRP. However, bringing in tertiary phosphorus stripping may make sediments downstream of WTWs vulnerable to SRP release. There will obviously be a crossover period before phosphorus-poor sediment replaces the heavily phosphorus-loaded sediment, but the timescales for this process are unclear.

- SRP and EPC_0 can be very high downstream of WTWs. An estimate of the length of river downstream that could be affected may be obtainable from Environment Agency SRP data for water bodies. Identification of those sediments where SRP and EPC_0 are close to equilibrium will be essential.
- Higher SRP concentrations measured in water are indicative of higher $EPC_{0.}$

2.6 Ecological responses to sediment phosphorus

2.6.1 Where do river plants get their phosphorus from?

Aquatic plants can obtain phosphorus from a variety of sources within rivers. Algae and bryophytes lack root systems and obtain all their nutrients by absorption directly from the water. A number of algae live in direct contact with sediments and will obtain phosphorus from absorption from interstitial waters (water in pore spaces). In principle, this will be the same as absorption directly from the water column except that the micro-environment of the pore spaces might differ from that of the overlying water in a number of respects, potentially leading to greater phosphorus availability than might be suggested by direct measurement of SRP. A further strategy, exhibited by both algae and bryophytes subjected to phosphorus stress, is to release extracellular phosphatase enzymes, which are able to release phosphorus from organic particles (Livingstone and Whitton 1984, Gibson and Whitton 1987). Such sources of phosphorus will, again, be missed by conventional analyses of water column SRP and have the additional complication of being intermittent in nature, detectable only by high resolution sampling (Whitton and Neal 2010).

With the exception of a few free-floating species (for example, *Lemna minor* and *Azolla filliculoides*), all higher plants have root systems that are able to absorb nutrients directly from the sediment. *Potamogeton crispus* obtains most of its nutrients in this way (Chambers et al. 1989), but the relative importance of roots versus shoots in mineral nutrition will vary from species to species. Emergent macrophytes such as *Typha* and *Phragmites*, for example, have a very low surface area of shoots directly exposed to water. Species such as *Elodea canadensis* are often only loosely-attached to the substratum, if not free-floating, while fine-leaved species such as *Myriophyllum spicatum* and *Ranunculus penicillatus* will have large surface areas of submerged shoots in direct contact with the water. Generalisations applicable to all macrophytes are, therefore, impossible, but it is reasonable to assume that many of the taxa which make substantial contributions to both biomass and ecosystem structure within rivers rely on the sediments for a major part of their mineral nutrition.

Carigan (1982) published an empirical relationship to estimate the amount of phosphorus that will be obtained by root uptake by macrophytes. If the concentrations of phosphorus in the sediment pore water was similar to that of the water column only, 27% of phosphorus would be taken through the roots. However, it is likely that sediment pore water SRP is considerably higher than that of the river water. Carignan (1982) reported sediment SRP concentrations in sediments from a range of studies, and these vary between 30 and 3,100 $\mu g\ l^{-1}$.Therefore if the sediment pore water phosphorus was 10 or 100 times greater than the water column, the roots would take up between 72 and ~100% of phosphorus from the sediment. Jarvie et al. (2008) reported that highly phosphorus-enriched sediment pore water (400–5,000 $\mu g\ l^{-1}$) was found in sewage-impacted areas of sediment, whereas sediment pore water values in agricultural (arable) areas and pristine sediments were <70 and 20 $\mu g\ l^{-1}$, respectively.

These results need to be interpreted in light of other findings that indicate that:

- the relationship between macrophyte and phytobenthos assemblages and water column phosphorus is relatively weak (r^2: 0.46; Kelly et al. 2013)
- the most significant ecological changes take place when average concentrations are <100 µg l^{-1} (Mainstone 2010)

Variations in sediment phosphorus may explain some of the unaccounted variation. However, it is also possible that sediment phosphorus is correlated with other factors that control macrophyte composition and abundance, rather than having a significant unique effect.

2.6.2 Other interactions between river sediments and aquatic plants

River sediments play a number of other roles in determining the composition and abundance of the photosynthetic biota. As these associations are often shown along the river continuum, it is important to be able to distinguish the direct effect of alterations to sediment phosphorus from factors that are often correlated with sediment phosphorus but are not actually related.

In particular, sediment architecture and stream power play a major role in determining the size of the sediment available. This, in turn, will determine the range of plants that are able to grow. A high energy stream dominated by boulders and cobbles, for example, will have few fine sediments within which rooted angiosperms are able to grow and will instead be dominated by algae and bryophytes. In contrast, a low energy stream is more likely to be dominated by fine sediments, enabling rooted macrophytes to thrive while mosses and algae will be relatively scarce. In such situations, planktonic algae might also account for a significant part of primary productivity (Hilton et al. 2006). The diversity of organisms present will also be influenced by the range of habitats available within a reach, so that a well-developed pool/riffle system with backwaters will have a mosaic of substrata of different sizes, allowing a wide range of taxa to colonise. This in turn, will correlate with the capacity of the sediments to absorb phosphorus from the water column.

The response of the photosynthetic biota to change in phosphorus will also be influenced by availability of other potentially limiting resources, especially nitrogen. The dynamics of nitrogen will be influenced, in part, by physicochemical relationships of the type described for phosphorus but also by a series of microbial reactions, all of which take place in the sediments and which will be determined by the state of those sediments. Denitrification, for example, can be significant in lowland rivers (García-Ruiz et al. 1998) and varies depending on factors such as substrate composition, organic matter and oxygen supply (Pulou et al. 2012, Tatariw et al. 2013).

Finally, sediments will also act as a reservoir for turions (specialised overwintering buds), stolons (a horizontal branch from the base of a plant that produces new plants from buds at its tip or nodes) and other units of vegetative propagation of aquatic vegetation. In principle, these could ’buffer’ ecological changes as a result of nutrient manipulations by giving the established flora a competitive advantage in the new growing season. In practice, however, production of turions by *Potamogeton crispus* has been shown to decrease at high phosphorus concentrations in the ambient water (Wang et al. 2013), though phosphorus concentrations encountered in UK rivers are unlikely to have a major effect. Generally, there will be species-specific auto-ecological responses to a wide range of factors, some of which may be linked, causally or otherwise, to phosphorus concentrations in river sediments.

2.6.3 Consequences of sediment phosphorus for ecological status

Sediment phosphorus has the potential for influencing all photosynthetic organisms within rivers either as a source of water column phosphorus via remobilisation or from direct uptake by plant roots. This, in turn, has consequences for any efforts to reduce nutrient concentrations and, therefore to move water bodies towards good ecological status. Table 2.6 summarises the major aquatic plant types and where they typically source their phosphorus from.

Table 2.6 Major aquatic plant types and where they typically source their phosphorus from

Aquatic plant type	Source of phosphorus uptake
Macrophyte	Sediment/water column
Periphyton (attached algae)	Intermediate
Epiliths (plants attached to stones)	Water column
Benthic algae	Sediment/water column
Epiphytic algae	Mainly water column

The status of plant and algal communities in rivers is assessed using two tools:

- LEAFPACS – for macrophytes, including larger algae
- DARLEQ – for diatoms

The lower score from these two assessments determines the final status for the WFD quality element 'macrophytes and phytobenthos'. Broadly speaking, DARLEQ should be more responsive to changes in water column phosphorus, while LEAFPACS includes taxa responsive to both water column and sediment phosphorus. In practice, both metrics are most sensitive when SRP is <100 µg l^{-1} (Kelly et al. 2013).

Efforts to reduce inputs of phosphorus in situations where there are significant reserves of sediment phosphorus downstream may not lead to the expected reductions in water column phosphorus. This is due partly to the alteration of equilibria between sediment and water column phosphorus and partly to the remobilisation of phosphorus from sediments. This may occur during high flow events but may also be due to other factors such as navigation (Moss et al. 1986). This would mean that there was unlikely to be a marked change in either DARLEQ or LEAFPACS metrics.

If there were limited reserves of sediment phosphorus, a reduction in water column phosphorus may be expected. This is likely to be accompanied by a change in DARLEQ as long as the final concentrations are <100 µg l^{-1}. Changes in LEAFPACS may also occur, but would depend upon the dominant organisms. A direct effect may be observed where the dominant organisms are macroalgae such as *Cladophora* and *Vaucheria*, though this would depend on the frequency of scouring spates. For macroalgae and diatoms, composition and abundance will depend on non-nutrient controls – availability of suitable substrata, grazing intensity, light – as well as on nutrients.

Many algae are adapted to take advantage of intermittent pulses of nutrients ('luxury consumption'; Stevenson and Stoermer 1982) and established populations often form dense colonies or mats within which nutrients can be rapidly recycled. Rooted macrophytes will have access to sediment phosphorus and, in theory, could persist until these reserves were used up, especially where turions or other means of vegetative propagation are produced. Changes in LEAFPACS, in other words, may take longer to manifest than changes in DARLEQ though there are, to the knowledge of this report's authors, no quantitative studies comparing the dynamics of change of these metrics over time.

More rapid changes may be expected where there were changes in the sediment phosphorus reserves (for example, by dredging), though these may not be wholly attributable to reduced sediment phosphorus. Removal of fine sediments (which will form the major sediment phosphorus reserves) will also remove turions and other propagules and, in theory, create better oxygenated conditions in the coarser sediments that remain. Such factors may themselves favour certain taxa over others and indeed hasten progress towards good status.

2.6.4 Changes in seasonal SRP loads and concentrations and the potential effects on biota

The concentration of SRP in the water body, its sources and its potential for use by river biota varies between seasons. The accumulation of diffuse phosphorus (predominantly via soil erosion) is highest in the autumn and winter due to the autumn/winter rains and low vegetation cover on arable land (Cooper et al. 2002, Mainstone and Parr 2002). However, the period from March to the end of September is when aquatic plants and bacteria have highest demand for SRP. Thus the phosphorus entering watercourses in autumn and winter bound to sediment may accumulate in rivers. If the sediment has high bioavailable phosphorus associated with it, it could lead to an increase in EPC_0 and release of SRP, depending on whether EPC_0 and SRP are close to equilibrium. If the SRP concentration falls below that of the EPC_0 (especially with possible dilution effects on SRP concentrations because of greater rainfall), release may occur. If not, the sediment-bound phosphorus is likely to be available for plant and microbial activity in the spring. Hilton et al. (2006) suggested that, for the River Thames, 75% of the total annual diffuse phosphorus load transported to rivers will be transported in autumn and winter and only ~25% will be transported in the growing season.

However, point sources of SRP, such as WTWs, provide more constant input into the river channel throughout the year in terms of flux. Hilton et al. (2006) suggested that this is a prime reason why the straight line dilution relationship between log(10) river SRP versus log(10) river flow is particularly evident downstream of WTWs (House and Warwick 1998, Jarvie et al. 1998). Thus because of concentration effects, it is likely that concentrations of SRP are highest during low flows of early summer. For the Thames it has been estimated that 57% of the phosphorus derived from WTWs is transported through the growing season (Cooper et al. 2002 as cited by Hilton et al. 2006).

3 Data requirements for a screening tool

3.1 Screening tool development

Findings from the literature review were used to develop an understanding of the main factors influencing sediment accumulation and potential phosphorus release. These points were assessed against data made available as part of this project (Table 3.1). Where data were available for use in the screening tool, a risk score and weighting factor was applied based on the findings from the literature review.

The following important findings and associated datasets were used for the development of the screening tool.

- The phosphorus available to water–sediment equilibrium reactions (that is, the labile pool) is determined by different sources of phosphorus inputs from the catchment. Sources of phosphorus that have been included in the screening tool are (data sources are in brackets):
  - sediment loads from catchment (PSYCHIC model)
  - diffuse sources (SAGIS model)
  - point sources (SAGIS model)
- Accumulation of sediment within a river reach can potentially increase the sediment labile pool of phosphorus. An estimate of where sinks are within a river reach has been included in the screening tool, considering:
  - river velocity data (calculated from digital terrain model (DTM) and SAGIS model)
  - scouring (using Base Flow Index data)
  - the River Macrophyte Hydraulic Index as an indicator of flow based on a plant community’s preference for flow conditions (LEAFPACS)
- Sediments downstream of a WTW act a sink for the digital terrain model. Introducing tertiary digital terrain model removal makes these sediments vulnerable to phosphorus release. An estimate of this phosphate legacy has been included in the screening tool using phosphate load reduction as a result of phosphorus removal at WTWs (SAGIS).

Table 3.1 Summary of project data

Data requirements	Available in SAGIS	Dataset received
River flow statistics (Q_{mean} compared with Q_{95})	✓	
Base Flow Index (BFI)		Centre for Ecology & Hydrology (CEH) National River Flow Archive, for example, BFI data for Anglian region (www.ceh.ac.uk/data/nrfa/data/search_region_anglian.html)
Channel gradient		Not available
Dredging frequency?		Not available
River width		✓
Location of control structures (obstructions)		Data on barriers were made available, but the format of the data prevented their incorporation into the tool at this stage.
Sediment load to the river	Yes and PSYCHIC	
Phosphorus load from the catchment	✓	
Current and historical loads from wastewater	✓	National Urban Waste Water Treatment Directive (UWWTD) and Habitats phosphorus limits Anglian Region UWWTD permits (date the limit comes into force) Anglian Region – all other phosphorus permits
National phosphorus removal scheme implementation dates	✓	WTW with phosphorus stripping
Chemistry and physical properties of sediment (geology)		Data availability from British Geological Society (BGS) through G-BASE (www.bgs.ac.uk/gbase/home.html)
Current phosphorus concentrations	✓	
Macrophyte and diatom community		River macrophyte hydraulic index scores

Notes: SAGIS = Source Apportionment – GIS

4 Risk assessment – sediment-phosphorus release screening tool

This section presents the national GIS layers used to develop a screening tool to quantify risk from sediment phosphorus release. Additional information is shown for the River Nene, the catchment for which more detailed testing is applied in Section 5. The method and approach to calculating an overall risk categorisation is described in Section 4.2.

As discussed in Section 3, the crucial findings from the literature review were used to incorporate available data within the screening tool. The overall risk from sediment phosphorus release was quantified by taking into account the relative importance of the following risk components:

- sediment deposition as indicated by river velocity
- scouring potential as indicated by the Base Flow Index
- River Macrophyte Hydrology Index (RMHI)
- river obstructions
- sediment loading
- orthophosphate loading from diffuse and point sources
- orthophosphate legacy issues from areas with potentially high sediment concentration

4.1 Risk components

4.1.1 Sediment deposition as indicated by river velocity

Options were considered to best estimate the relative balance of scouring and deposition in a river. The calculation of stream power was identified as the most reliable method in the interim report (Atkins 2014a). However, the data for this methodology were not available to provide full national coverage. In particular, bankfull width is required to calculate stream power, whereas the dataset provided by the Environment Agency is for wetted width which is taken during low flow periods; use of these data would lead to underestimations of stream power.

Calculation of stream power remains the best approach for identifying the degree to which a reach is likely to scour or deposit sediment and should be considered if further development of the national screening tool is undertaken. In the meantime, a simpler rapid risk assessment was adopted for this project, based on estimation of river velocities by Guymer (2004).

Reach slope

Equation 4.1 used to calculate slope:

$$S = \frac{T-B}{L} \quad (4.1)$$

where:

S = slope

T = top elevation

B = bottom elevation

L = reach length

The elevation at the start and end of each reach was taken from a 50 m DTM to calculate slope. Slope gradient at a national level is shown in Figure 4.1.

Velocities

Velocities calculated from yearly Q_{mean} derived from SAGIS and the reach slopes are shown in Figure 4.2 using the best-fit approach developed for the Environment Agency Guymer (2004). Equation 4.2 was used to derive velocities:

$$v = 0.671Q^{0.376}S^{0.266} \quad (4.2)$$

where:

V = velocity (m s^{-1})

Q = Q_{mean}

Reaches with the lowest velocities are more likely to accumulate sediment through settlement processes and could therefore pose a risk of phosphate sediment cycling. The lowest velocities are located in south-east England and, in particular, in the Anglian Region.

4.1.2 Scouring potential as indicated by Base Flow Index (BFI)

BFI can be used to identify areas where phosphorus-rich sediments are likely to accumulate. The higher the BFI, the greater the contribution from groundwater and thus the more stable the flow is likely to be with fewer scouring events. Water body level BFI data from water resource GIS have been used for this study. The BFI character has been assigned to each national reach based on the water body in which it is located. Figure 4.3 shows a map of national BFI.

4.1.3 River Macrophyte Hydrology Index (RMHI)

The RMHI describe a plant community's preference for flow conditions on a scale of 1 to 10. Scores of 10 indicates a plant community has a preference for very slow or non-existent flows, while scores of 1 are found in plant communities with a preference for very fast powerful flows. The RMHI forms part of the LEAFPACS suite of indices. Figure 4.4 shows the average scores for national RMHI between 2006 and the present for each reach where monitoring has taken place. The scores provide an indication of flow conditions within a river reach and therefore an indication of sediment deposition.

4.1.4 River obstructions

River obstructions cause sediment deposition where flow is reduced. This could cause large sediment sinks to form and it is therefore important to consider river obstructions.

As noted in Table 3.1, although these data were made available they were not in a suitable format for used in the assessment. This information could be incorporated as part of further development work.

4.1.5 Sediment loading

The contribution from sediment to national reaches was derived from PSYCHIC outputs which are used to populate SAGIS. A map of average yearly national sediment inputs is shown in Figure 4.5. Areas of high sediment input coincide with areas of low velocities in the Anglian Region.

4.1.6 Phosphorus loading from diffuse and point sources

The contribution of phosphorus loads from point and diffuse sources is important in relation to the risk score, as sediment exchange is most important when these inputs are large or after they have been reduced by control measures. The WTW and diffuse contributions to reach orthophosphate concentrations nationally are shown in Figure 4.6 and Figure 4.7, respectively. These data were derived from previous SAGIS modelling for the Environment Agency. Each reach is defined by the concentration at the downstream boundary of the reach.

4.1.7 Phosphorus legacy issues from areas with potentially high sediment concentration

The legacy of phosphorus in sediments is an important consideration in relation to sediment phosphorus release. Across England, approximately 530 WTWs have had phosphorus removal incorporated as part of their treatment processes. Although rivers receiving a reduction in phosphate load would have improved water quality as a result, they may have a legacy of higher phosphate sediment concentrations from periods before treatment was in place. These circumstances may result in higher sediment EPC_0 than the overlying water, which will result in a release of phosphorus from the sediment.

Based on information within SAGIS, Figure 4.8 shows those water bodies that have seen a reduction in phosphate load as a result of phosphorus removal at WTWs. It was assumed that any WTWs with a phosphate effluent concentration < 2 mg l^{-1} has phosphorus removal, which is indicative of effluent having phosphate stripping using iron dosing (Atkins 2014a). The upstream contribution from WTWs was estimated before and after phosphorus removal, and the percentage reduction calculated. It was assumed that effluent concentration before phosphorus removal would be 7 mg l^{-1}, which is the default concentration used by the Environment Agency as a typical effluent concentration without phosphorus removal (Atkins 2014a). The percentage of water bodies in each WFD management catchment (Defra 2013) that are influenced by phosphate load reduction as a result of phosphorus removal at WTWs is given in Appendix A. These data can be used to identify areas where there could be high phosphate sediment concentrations as a result of a legacy from WTWs before phosphorus removal was carried out. If this approach was to be taken further, areas where the agricultural phosphorus load has been reduced through initiatives such as Catchment Sensitive Farming could also be considered.

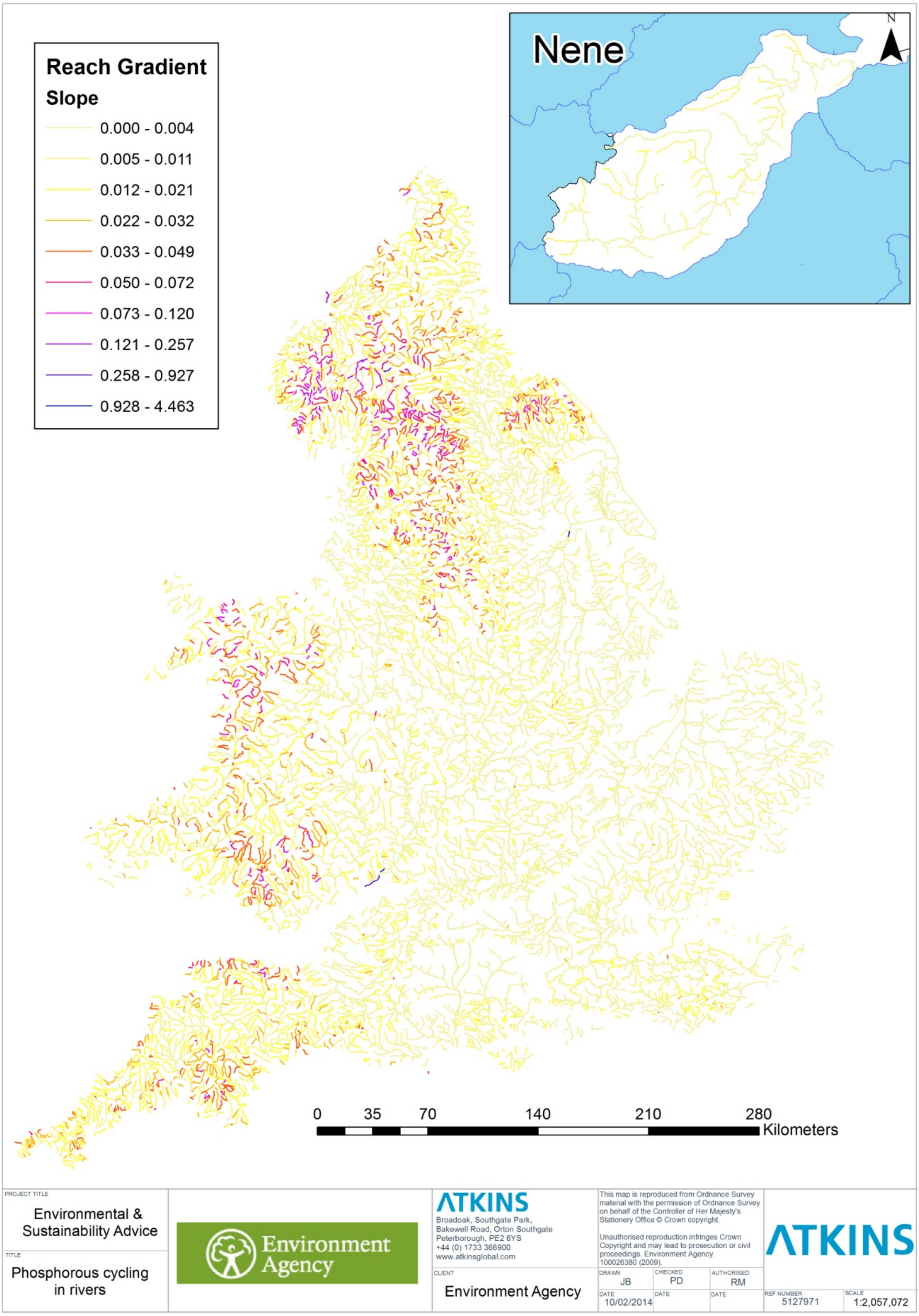

Figure 4.1 Slope determined for individual river reaches

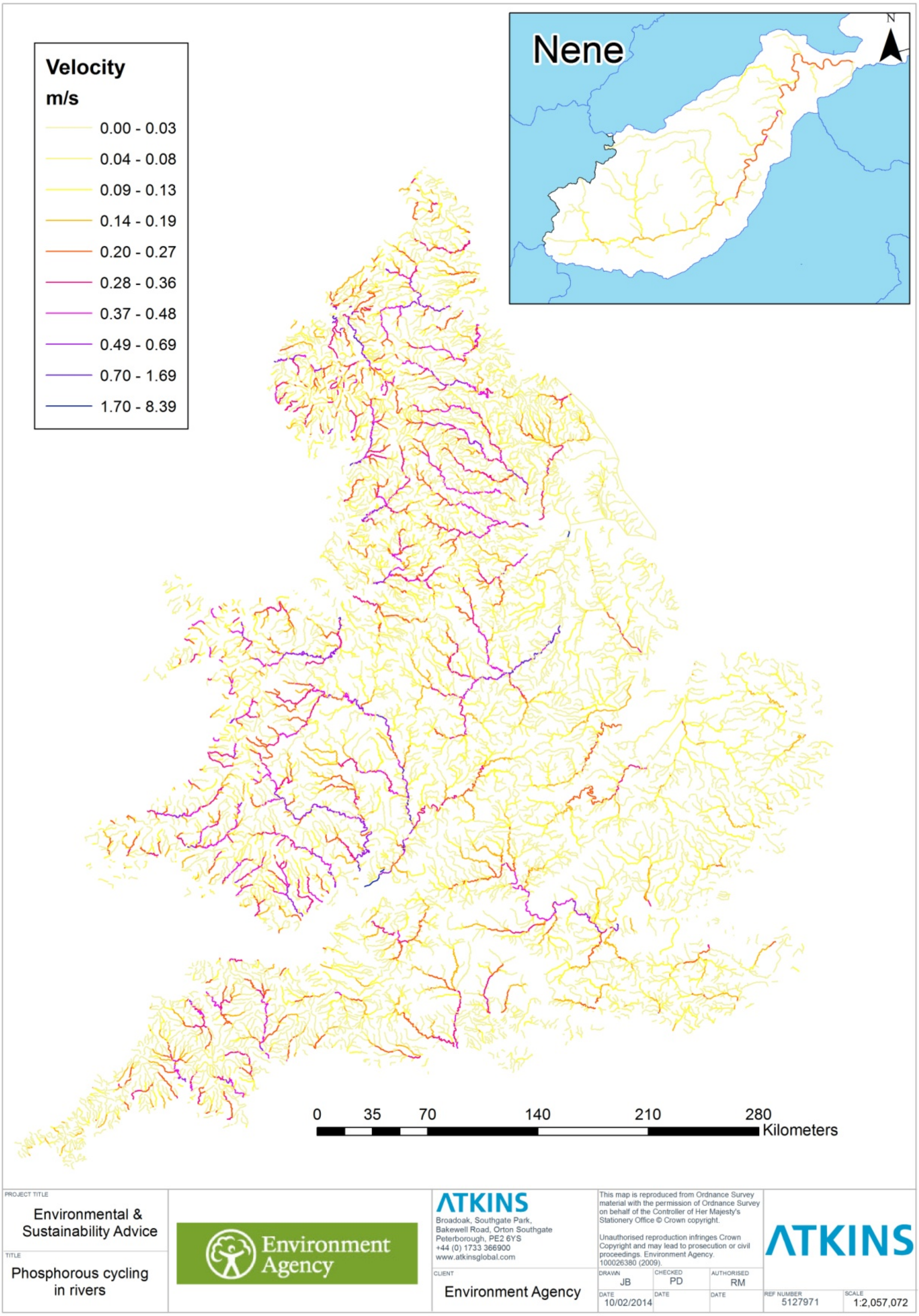

Figure 4.2 Velocity determined for individual river reaches

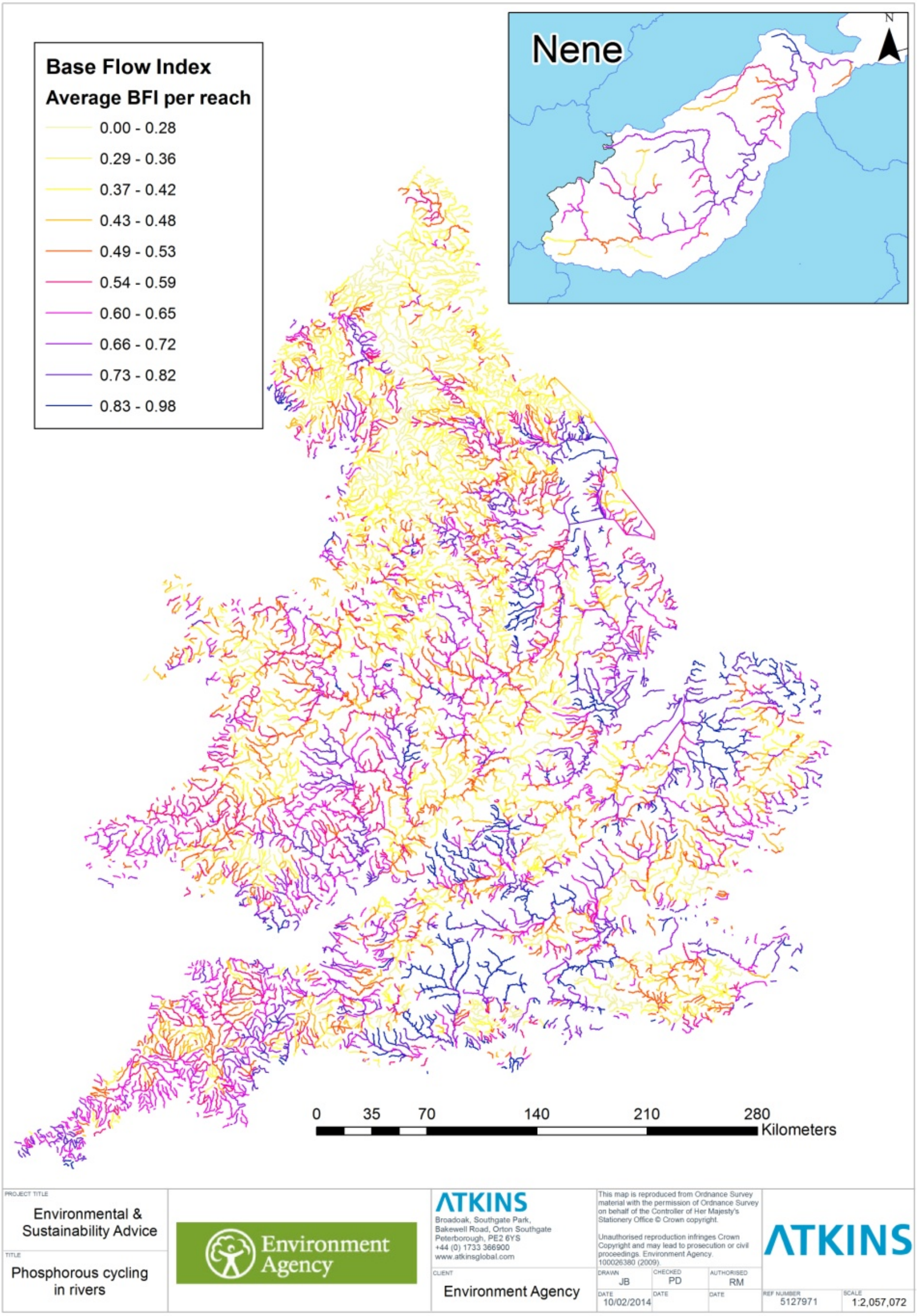

Figure 4.3 National Base Flow Index

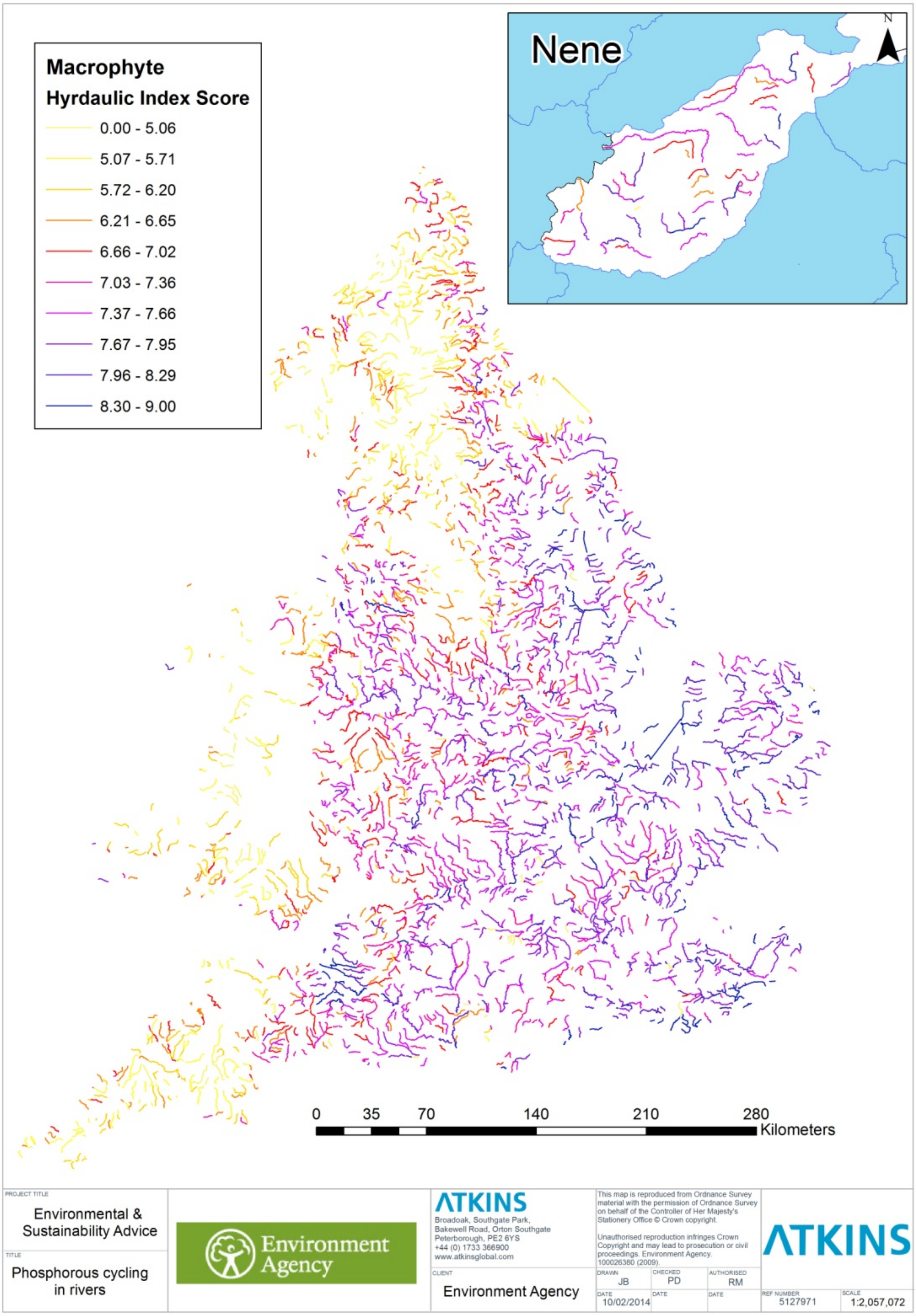

Figure 4.4 National River Macrophyte Hydrology Index

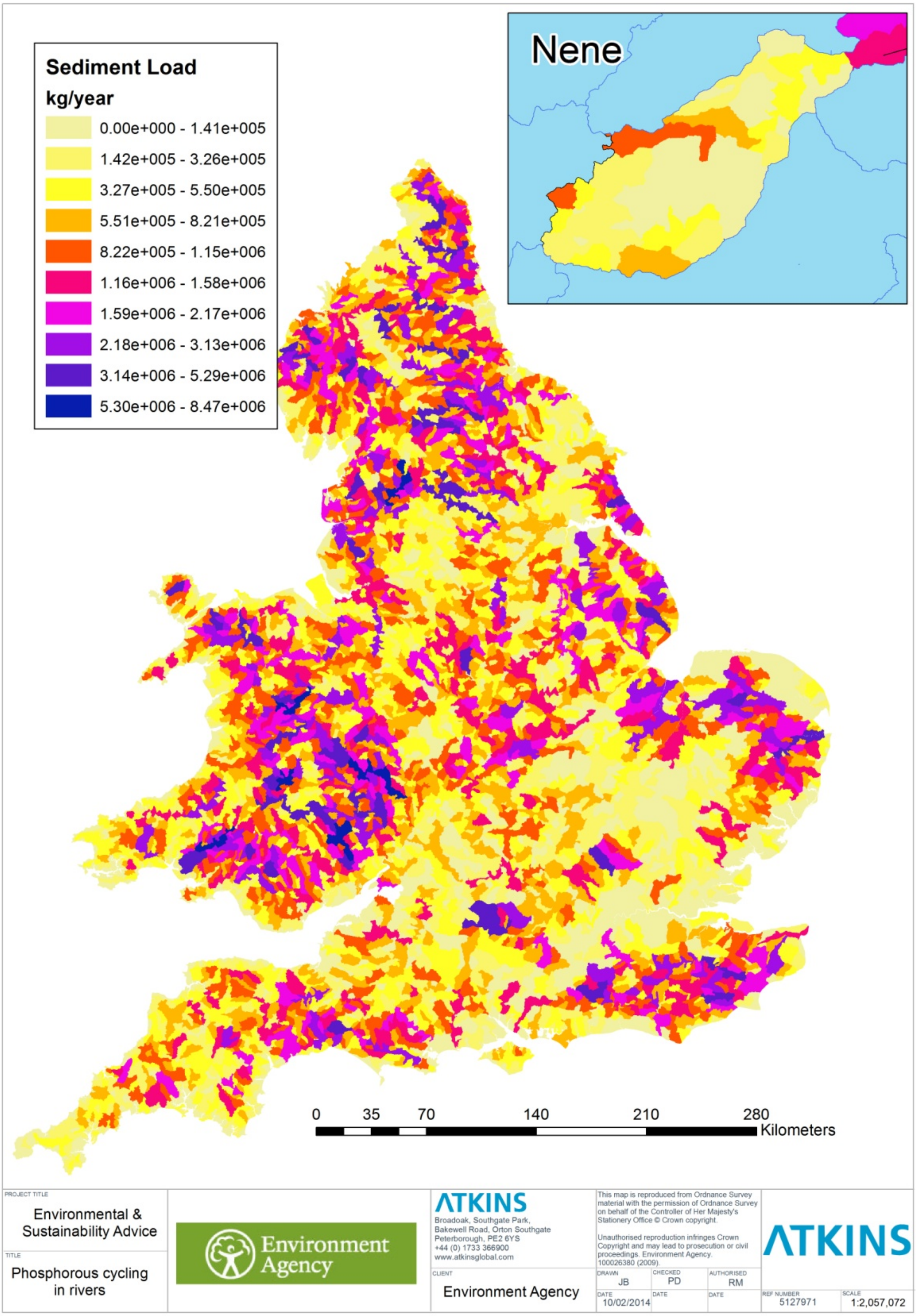

Figure 4.5 National sediment loads

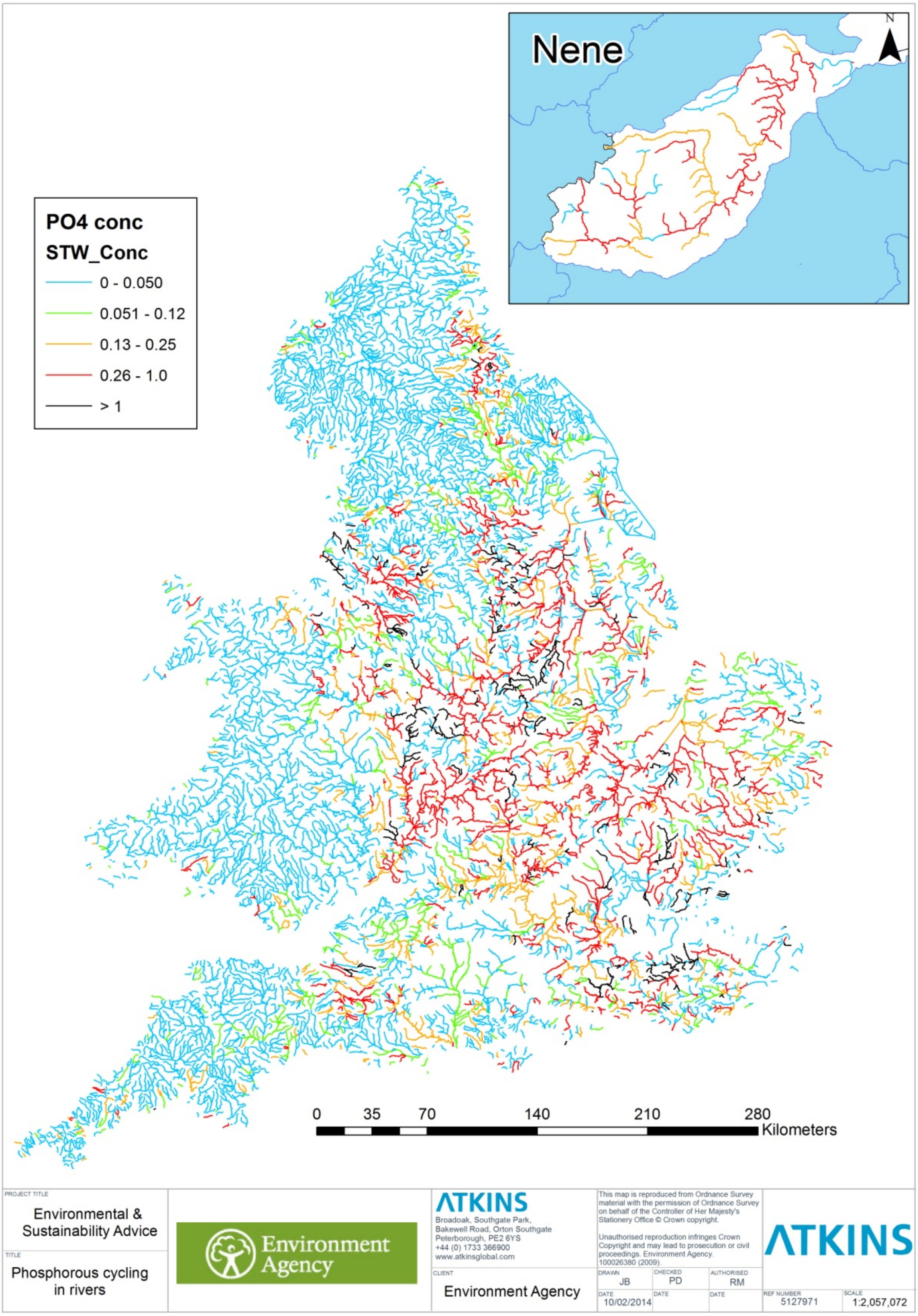

Figure 4.6 WTW contribution of orthophosphate to reach concentrations

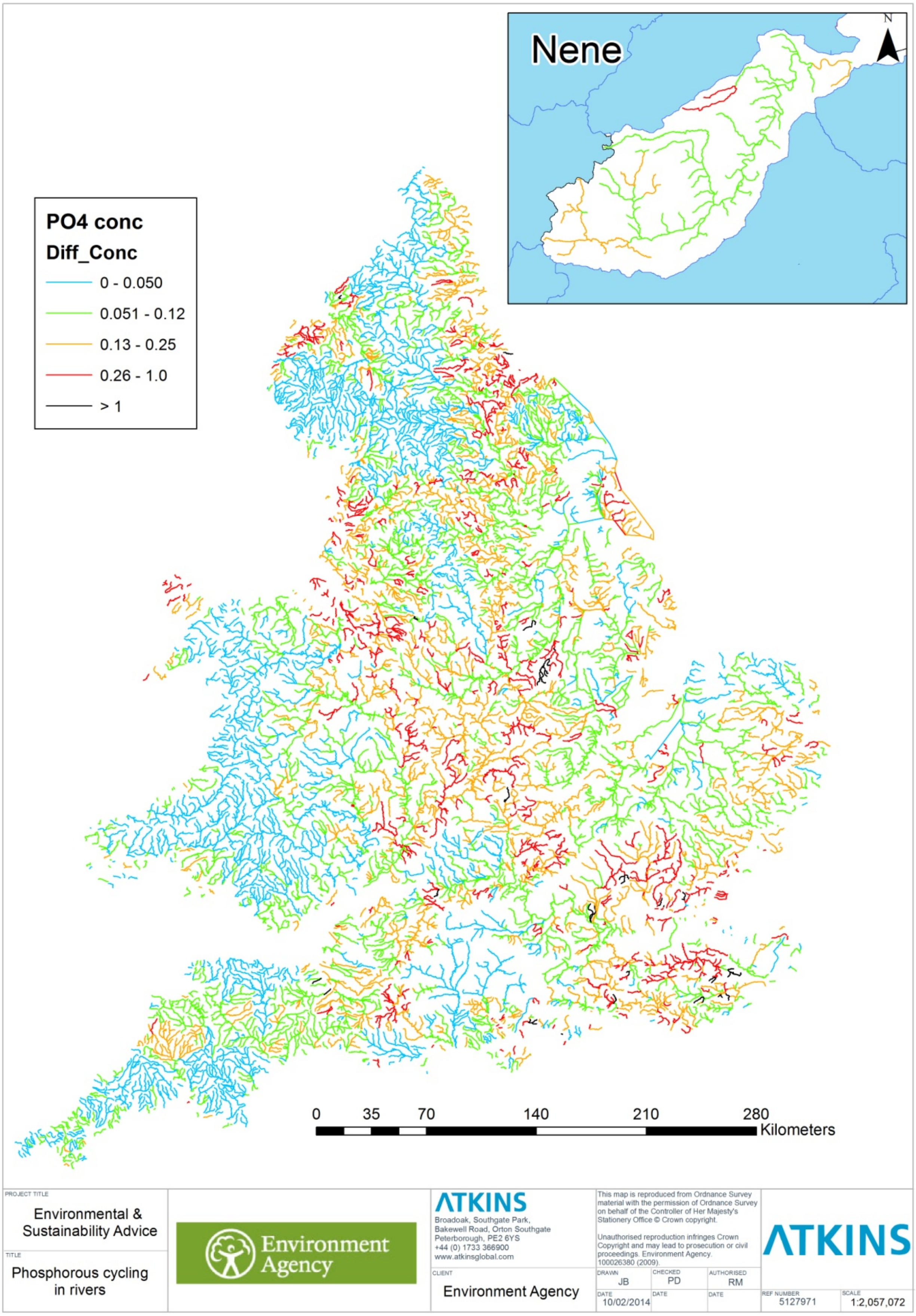

Figure 4.7 Diffuse contribution of orthophosphate to reach concentrations

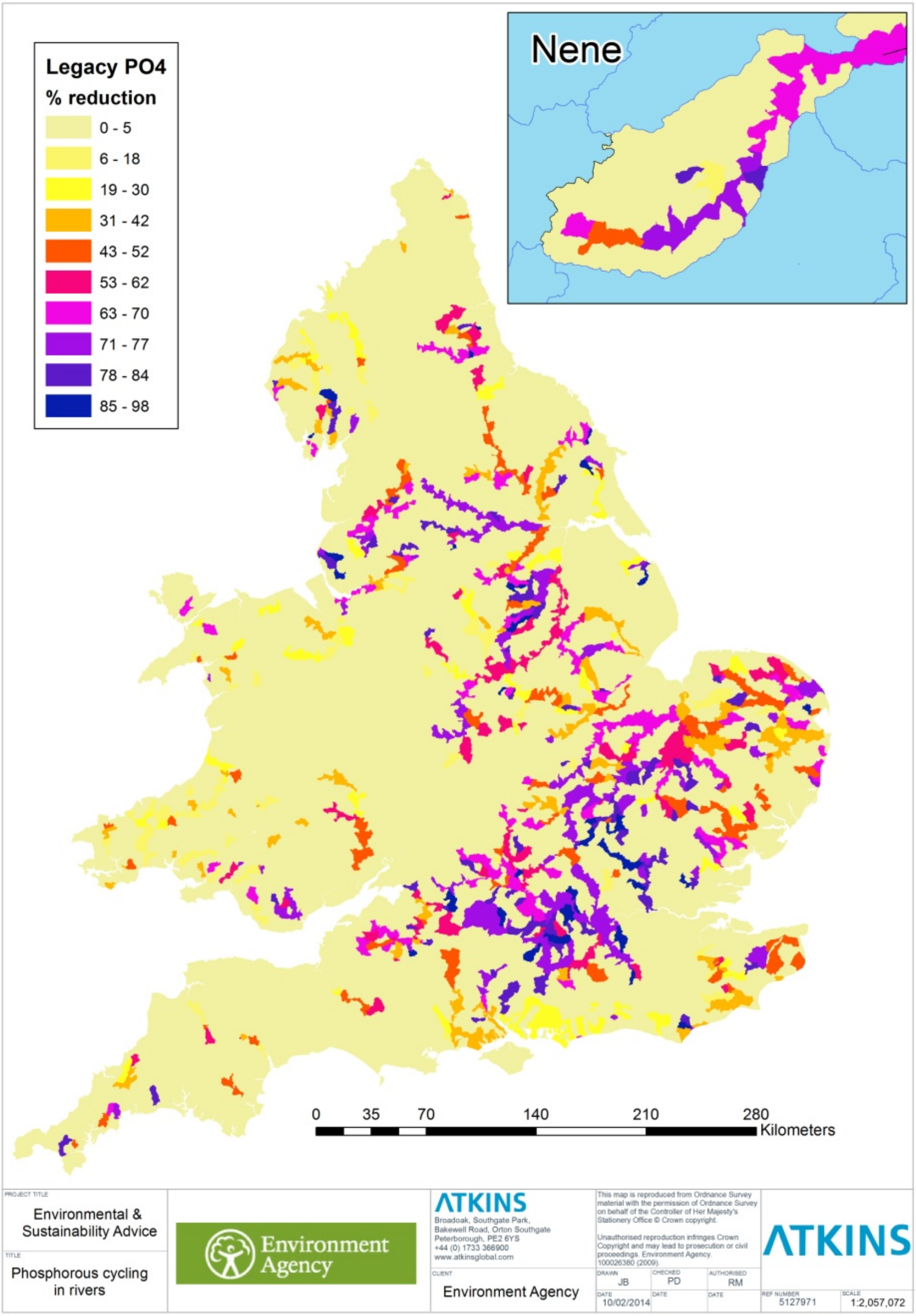

Figure 4.8 Areas where orthophosphate load has fallen as a result of phosphorus stripping at WTWs

4.2 Risk categorisation from phosphorus sediment release

A summary of the data used for the categorisation of risk from P sediment release is given in Table 4.1. Also detailed in the table are the thresholds used to define the risk category for each reach. For example, for point and diffuse sources, a reach was given a low risk for this component if the concentration meant ‘good’ or ‘high’ WFD status.

Each reach was given an overall risk value by applying a weight to each component. The weighting factor was based on the importance of the risk component as determined by the results of the literature review. For the purposes of this investigation, point source concentration, diffuse source concentration and legacy phosphate were given the highest weighting due to their importance as sources of phosphate. The weightings are shown in Table 4.1. The boundaries between the categories and the weightings can be modified and the scores recalculated accordingly.

Table 4.1 Risk categorisation and weighting

Risk component	Description	Low	Medium	High	Weighting
Sediment deposition	Velocity	Lower third percentile[1]	Middle third percentile[1]	Upper third percentile[1]	2
Scouring	BFI	<0.3	0.3–0.6	>0.6	3
Sediment load	Loading of sediment	Lower third percentile[1]	Middle third percentile[1]	Upper third percentile[1]	2
Macrophytes	RMHI	No data or 0–3	3–6	6–10	2
Point source phosphorus (WTWs)	Orthophosphate concentration specifically attributed to WTWs	Poor and bad WFD status[2]	Moderate WFD status[2]	High and good WFD status[2]	5
Diffuse sources	Orthophosphate concentration specifically attributed to diffuse sources	Poor and bad WFD status[3]	Moderate WFD status[3]	High and good WFD status[3]	5
Legacy phosphate	Percentage reduction in phosphorus resulting from phosphate stripping	No reduction or 0–33%	33–66%	66–100%	5

Notes: [1] Across the national dataset.
[2] Orthophosphate concentration attributed to WTWs assessed against current WFD thresholds.
[3] Orthophosphate concentration attributed to diffuse sources assessed against current WFD thresholds.

Risk was calculated for each individual reach. The overall risk categorisation can be defined by:

$$\boldsymbol{R} = \sum \boldsymbol{Ri} \times \boldsymbol{W} \qquad (4.3)$$

where:

R = overall risk for an individual reach

Ri = risk score of a risk component for an individual reach (1 for low risk, 2 for medium risk, 3 for high risk)

W = weighting

The overall risk scores for each reach are shown in Figure 4.9. Natural (Jenks) breaks were used to apportion the overall risk scores between the following categories:

- very high
- high
- moderate
- low
- very low

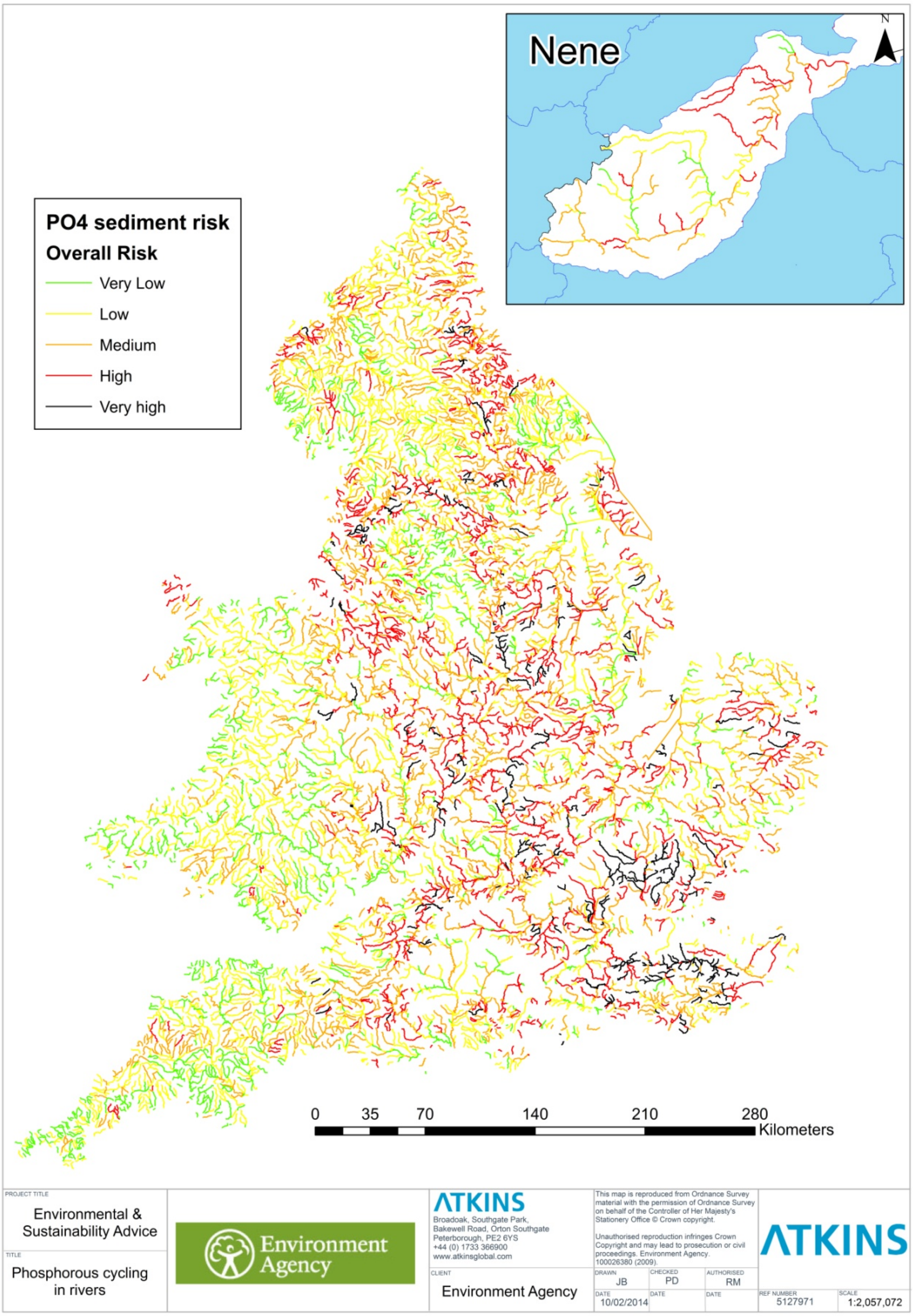

Figure 4.9 Risk categorisation results for orthophosphate sediment risk

5 Sediment release model testing

To test the importance of the in situ cycling processes in relation to other sources of phosphorus, this section tests the sediment flux model based on EPC_0 concentrations (see Section 2) in relation to phosphorus dynamics in the River Nene.

The time series model of the River Nene developed by Daldorph et al. (2001a, 2001b) includes time series data for phosphorus inputs from WTWs and observed river phosphorus concentrations. The model code was modified to incorporate sediment phosphorus equations with the aim of testing the magnitude of modelled sediment phosphorus exchanges compared with other inputs of phosphorus into the river system and the sensitivity of these exchanges to the model parameter settings.

5.1 Model theory

A model for the exchange of orthophosphate from the sediment is described by House and Warwick (1999), based on stream-simulator (fluvarium) experiments. Phosphorus release is estimated using:

$$\frac{dM}{dt} = k_s.A.\left(\frac{(C_t - EPC_0)}{EPC_0}\right)^m \qquad (5.1)$$

where:

M = mass of orthophosphate sorbed (nmol)

C_t = concentration in solution at any time (t)

EPC_0 = equilibrium phosphorus concentration

A = surface area of the sediment in the reach

k_s = rate constant

m = a power term (set to 2)

Values for EPC_0 were estimated for the River Nene catchment by Tye et al. (2013). Phosphorus exchange between the water column and sediment was estimated for the study reaches.

An existing integrated lake and catchment (ILC) model of the Nene catchment is available (Daldorph et al. 2001a, 2001b) that simulates the dynamics of river flow and transport. The 2004 version of the ILC model, for which the model code is available, was modified to incorporate the sediment phosphorus exchange model described by equation 5.1.

Within the existing ILC model, phosphorus inputs to the rivers are a function of:

- phosphorus inputs from the soil zone
- phosphorus loads in base flow
- phosphorus input from discharges (continuous and intermittent)
- phosphorus inputs from water transfers

- phosphorus input from upstream sub-catchments and lakes

Phosphorus inputs from the soil zone are based on disaggregation of annual or monthly export based on Land Use Region export coefficients. Agricultural census data on livestock numbers and cropping areas are combined with export coefficients for six land-use regions (Environment Agency 2000) to calculate loads.

The diffuse phosphorus input is calculated as a function of the annual phosphorus export generated from the export coefficients and run-off from the soil zone. This is based on empirical analysis and literature review of the relationship between phosphorus concentrations and discharge in headwater streams:

$$Load = f(pr.E.x_1) \tag{5.2}$$

where:

pr = phosphorus release factor

E = land use related annual loss (from export coefficients – kg year^{-1})

x_1 = discharge from the soil zone

The default setting for the model (applied for the Nene) is that the daily export of phosphorus is directly proportional to run-off. The average pro rata daily phosphorus load is divided by the average daily run-off to calculate the average run-off concentration. This concentration is used to calculate the daily phosphorus load based on the daily simulated run-off. The phosphorus input to the river is split between dissolved and particulate fractions using a fixed ratio specified by the model user.

Daily phosphorus input from WTWs are input using time series concentrations and flows for individual works or, where time series data are not available, sampled from concentration and flow distributions for individual works defined by mean and standard deviation values.

The concentration of phosphorus in water passing from the soil to the groundwater tank is defined by a ratio to the concentration in run-off to take into account the fact that most phosphorus is removed by adsorption to soil particles before passing into groundwater. Phosphorus in the groundwater is modelled as a conservative substance. However, a flushing rate can be applied to account for the fact that the groundwater is unlikely to be fully mixed (that is, the concentration in water flowing out of the groundwater will be lower than the mixed concentration as defined by equation 5.2). This is calculated from:

$$\frac{dP_{Mass}}{dt} = P_{input} - \frac{GP_{Mass}.Q_{nr}}{G_s} \tag{5.3}$$

where:

GP_{Mass} = mass of phosphorus in the groundwater tank (kg)

P_{input} = the input as defined above

G_s = groundwater volume (m^3)

Q_{nr} = effective outflow to the river (m^3 day^{-1})

The phosphorus river transport model is given by:

$$\frac{dP_{out}}{dt} = \frac{1}{T_4 - \tau}(e^{-k.\tau}.P_i(t-\tau) - P_{out}(t)) - k.P_{out}(t) + \frac{k_r.P_{sed}.D}{D_{sed}} \tag{5.4}$$

where:

P_{out} = phosphorus concentration leaving the sub-catchment

P_i = phosphorus concentration entering the sub-catchment

τ = pure time delay in days

k = phosphorus assimilation rate (day^{-1})

P_{sed} = sediment phosphorus concentration

K_r = sediment release rate (day^{-1})

D = water depth

D_{sed} = sediment depth

T_4 = solute residence time (days)

T_4 is given by:

$$T_4 = \frac{L}{u} \tag{5.5}$$

where u is the mean water velocity calculated using the output of the flow model.

This overall mean solute residence time is split in the same manner as in the aggregate dead zone (ADZ) model (Lees et al. 1998) so that the model accounts for advection and dispersion caused by both Fickian and dead-zone or transient storage processes:

$$\tau = T_4 \times (1 - DF) \tag{5.6}$$

where DF is the dispersive fraction (unitless). This is defined in the ADZ model as the ratio of the volume of the aggregated dead zone to the total volume. Dispersive fraction can also be considered to be a function of the advective time delay (fastest velocity) and the overall residence time (mean velocity).

Phosphorus loss resulting from the decay functions is stored in separate dissolved phosphorus and particulate phosphorus sediment tanks with a fixed volume. Phosphorus is released back into the water column at a specified rate (K_r = sediment release rate; equation 5.4). The sediment release rate can be modified in relation to river flow based on a specified correlation coefficient with river flow that varies the decay rate between 0 and 100% of the specified value.

The sediment release component of the ILC model was disabled and replaced with the EPC_0 based sediment release:

$$\frac{dP_{out}}{dt} = \frac{1}{T_4 - \tau}(e^{-k.\tau}.P_i(t-\tau) - P_{out}(t)) - k.P_{out}(t) - k_s.T_4.A.\left(\frac{(P_{out}(t) - EPC0)}{EPC0}\right)^m \tag{5.7}$$

This equation combines a first order river decay rate defined by k and a separate sediment exchange rate (k_s – as defined in Equation 5.1) which specifies the loss related to the EPC_0 value. A is the surface area of the river bed and m is a power function set at 2 based on House and Warwick (1999).

Inclusion of a first order decay and EPC_0 based sediment exchange could result in double counting of the sediment losses. However, this was corrected by reducing the decay rate so that the overall loss to the sediment retained good calibration with observed data. In reality, loss of phosphorus to the sediment will occur by other processes to those described by EPC_0 based sediment phosphorus exchange. These processes include:

- biological uptake by phytoplanktonic and attached algae
- macrophyte uptake from the water column
- adsorption onto suspended particles

Therefore some of this phosphorus will be transported into the sediment by processes that are not described by equation 5.1 and so need to be accounted for separately.

Outcomes from the formulation of equation 5.1 were explored by considering a 1 km reach of 10 m width with an EPC_0 value of 200 µg l^{-1}. The relationship between P exchange and the river concentration is shown in Figure 5.1. Because of the way equation 5.1 is formulated, phosphorus losses to the sediment when EPC_0 is below the river concentration are greater than releases from the sediment when EPC_0 is greater than the river concentration. The maximum release rate occurs when the river concentration is zero at a rate of $k_s.A$ (see equation 5.1) whereas the losses can be far higher than this. For comparison, the phosphorus load from a WTW works of 500 population equivalent (PE), with and without phosphorus removal, is included in Figure 5.1. Phosphorus losses are comparable with these inputs at high river phosphorus concentrations, whereas phosphorus release is small.

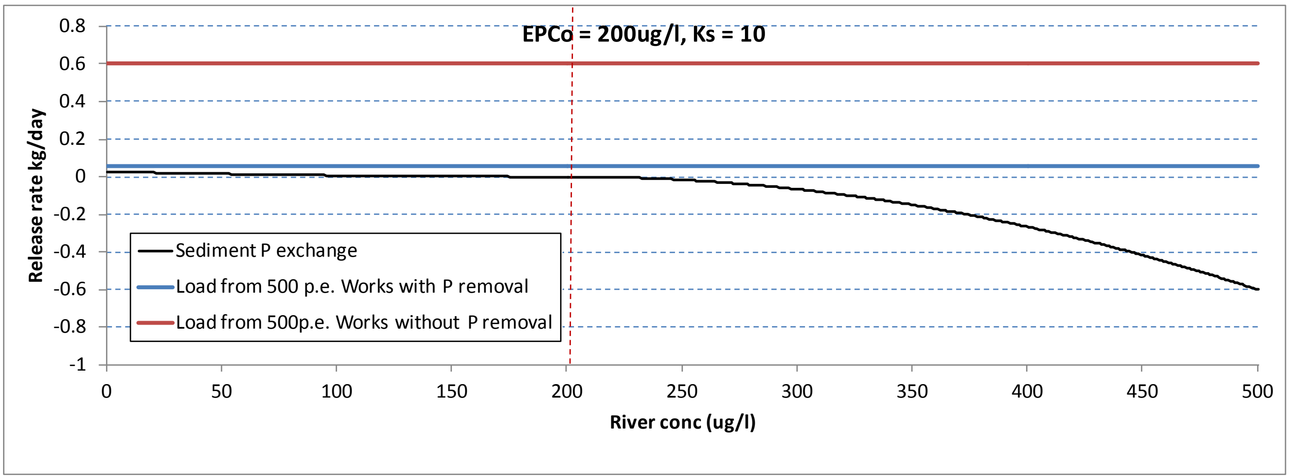

Figure 5.1 Relationship between phosphorus exchange and river concentration and the EPC_0 value

Notes: p.e. = population equivalent

5.2 Model build and calibration

The structure of the ILC model is shown in Figure 5.2. This figure also shows the measured EPC_0 concentrations from Tye et al. (2013) that were added to the model. For the tributaries where no observed EPC_0 values were recorded, average EPC_0 values for all of the measurements were applied.

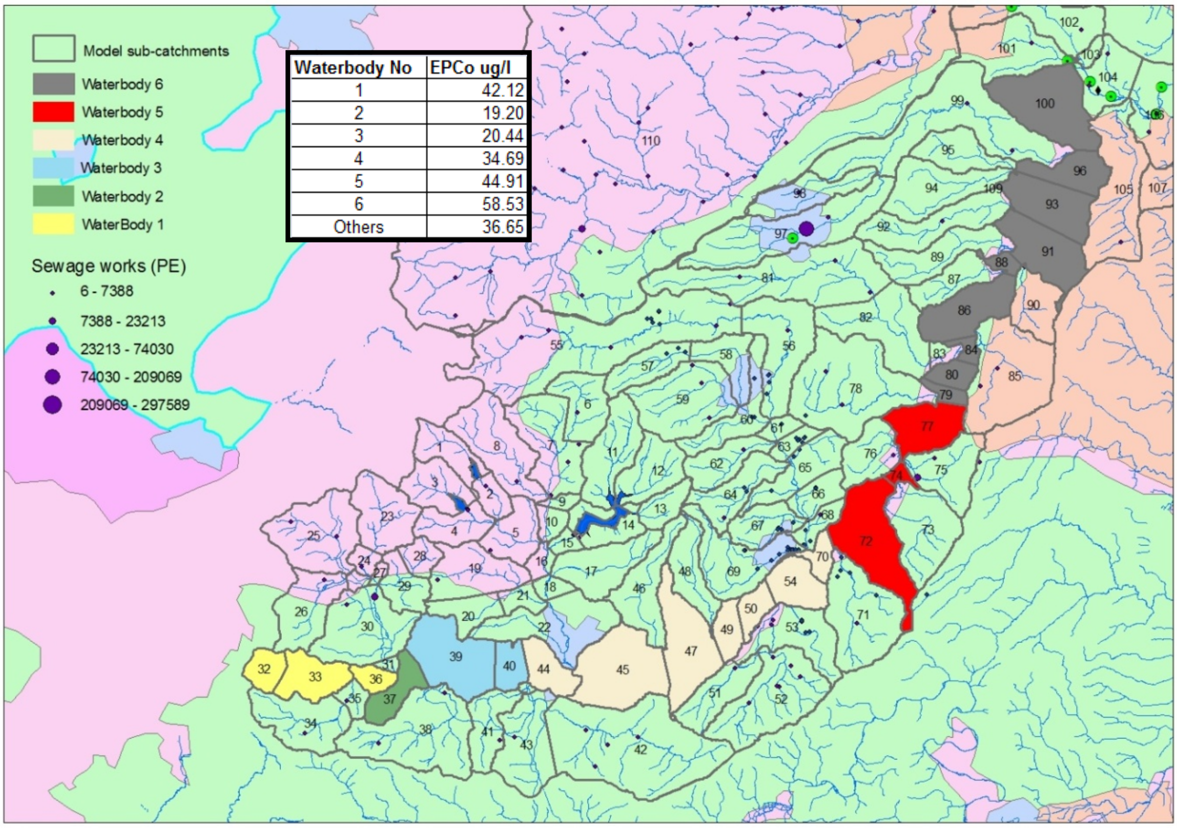

Figure 5.2 Model structure showing water bodies sampled by Tye et al. (2013) and added EPC_0 values

The calibrated model before modification applies a first order phosphorus decay rate of 0.15 day^{-1} for all model sub-catchments.

Once the EPC_0 values were applied it was assumed that a third of the initial first order phosphorus decay rate of 0.15 day^{-1} would apply (that is, 0.05 day^{-1}). Figure 5.3 compares model output with observed data for the original model settings and those applying a k_s value of 0.05 (see equation 5.1) for three of the model sub-catchments downstream of large WTWs. These parameter settings result in a similar model fit to the original unmodified version.

5.3 Simulated sediment phosphorus exchange

Figure 5.4 shows the changes in average simulated orthophosphate in all the model sub-catchments for the period 1996 to 2012 for a k_s value of 0.05 and the observed EPC_0 values shown in Figure 5.2. The EPC_0 values used for this simulation were well below the observed and simulated orthophosphate concentrations in all of the sub-catchments, particularly in the pre-phosphorus removal period and so phosphorus accumulation rather than release occurred throughout. The largest differences were in sub-catchments where orthophosphate concentrations are high. Losses to the sediment increase as a square function of the difference between the river concentration and EPC_0 so increase substantially as the difference between the river concentration and EPC_0 increases. In reality, EPC_0 values are likely to be have been markedly higher downstream of the large WTWs when phosphorus emissions were higher in the late 1990s before phosphorus removal began so these losses are likely to be overestimated.

The modified model was run using the observed EPC_0 values shown in Figure 5.2 for a range of k_s values (equation 5.1). With no k_s value applied (only a first order phosphorus decay of 0.05 day^{-1}), simulated concentrations were well above observed values, particularly during the pre-phosphorus removal period (Figure 5.5). Values of k_s values of 0.05 and 0.1 resulted in a reasonable match between model output and observed data. When k_s values were increased to 0.5, however, the losses to the sediment were too high and model output was well below the observed data. These relatively low k_s values to achieve a good model fit are in line with the values for the River Great Ouse (Table 5.1), which is the river catchment immediately to the south of the River Nene. EPC_0 values for the River Nene and Great Ouse are also similar. In contrast, k_s values from previous research were markedly higher for the rivers Swale and Wey.

Table 5.1 EPC_0 and k_s values reported by House and Warwick (1999)

Comparison of parabolic rate constants [equation 5.1, m = 2], for the net uptake of SRP by reed bed sediments using equation 5.1 as defined by House and Warwick,1999 (equation 2).

River	Month	EPC_0 (mol dm^{-3})	k_s (nmol m^{-2} s^{-1})
Great Ouse[1]	January	2.5	0.26
	March	2.3	0.28
	July	1.9	0.11
	November	1.1	0.02
River Wey[2]	February	9.3	1.9
	May	10.2	1.0
	August	5.3	0.51
	November	14.4	12.7
River Swale (this work)	April	2.1	1.0

Notes: [1] House and Denison (1997)
[2] House and Denison (1998)

5.4 Simulated sediment phosphorus release

The potential for phosphorus release from the sediment occurring following the introduction of phosphorus removal was explored by setting up the model so that the EPC_0 values downstream of the affected WTWs (Whilton, Great Billing, Broadholme and Corby) matched the average simulated river concentrations for the period 1996 to 1997. For sub-catchments not downstream of these works, the EPC_0 values were unchanged. The model was run for the post-phosphorus removal period of 2000 to 2012. This scenario presents a worse case as equilibrium EPC_0 values have generally been found to be well below the average river concentration (see Figure 2.9).

Figures 5.6 and 5.7 show the absolute and percentage change in concentration, respectively, that results from increasing the EPC_0 values compared with the baseline condition of applying the observed values. These differences are primarily a result of a reduction in the loss of phosphorus to the sediment rather than phosphorus release. This reflects the fact that the formulation of equation 5.1 will tend to result in larger deposition than release.

The influence of these processes on river concentrations tends to accumulate downstream as the cumulative contact time between the river water and sediment increases.

Figure 5.8 illustrates the magnitude of phosphorus release from the sediment under conditions when EPC_0 concentrations are elevated, following phosphorus removal, for sub-catchment 54 and the River Nene downstream of the four WTWs with phosphorus removal (Whilton, Corby, Great Billing and Broadholme; Figure 5.4). The average daily release of phosphorus from the sediment for k_s values of 0.05 and 10 is compared with the phosphorus load in the river and the loss to the sediment under sedimenting conditions (that is, when EPC_0 values are not elevated). Rates of phosphorus release from the sediment when EPC_0 values are elevated are very low compared with loads in the river and rates of loss to the sediment when EPC_0 values are low. Even when k_s values are increased to 10, the maximum rates of phosphorus release from the sediment reported by House and Warwick (Table 5.1) are very low. This suggests that sediment phosphorus release is not important in influencing phosphorus dynamics in the River Nene, although the EPC_0 has greater influence on losses to the sediment.

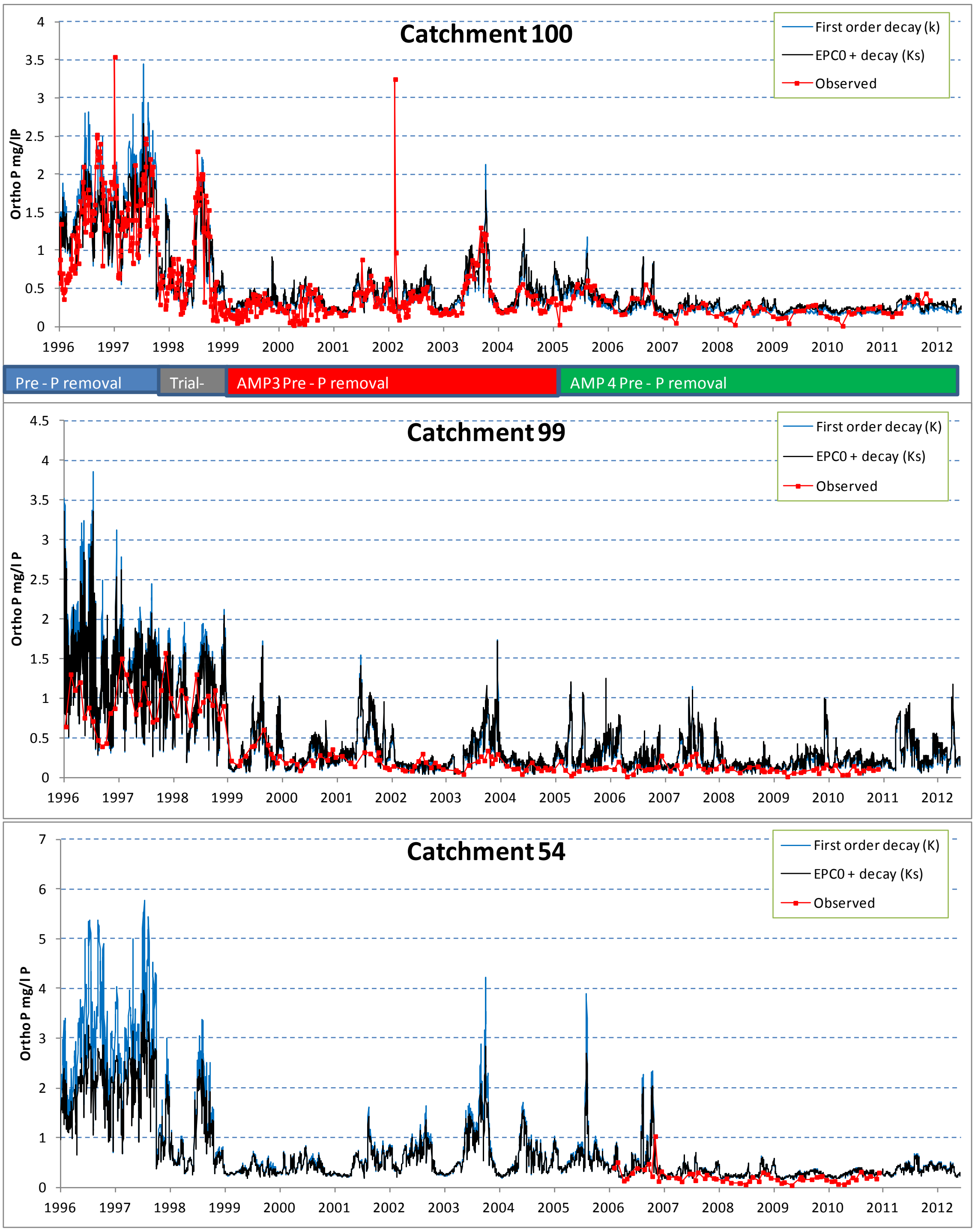

Figure 5.3 Nene model calibration at three sub-catchments downstream of large WTWs

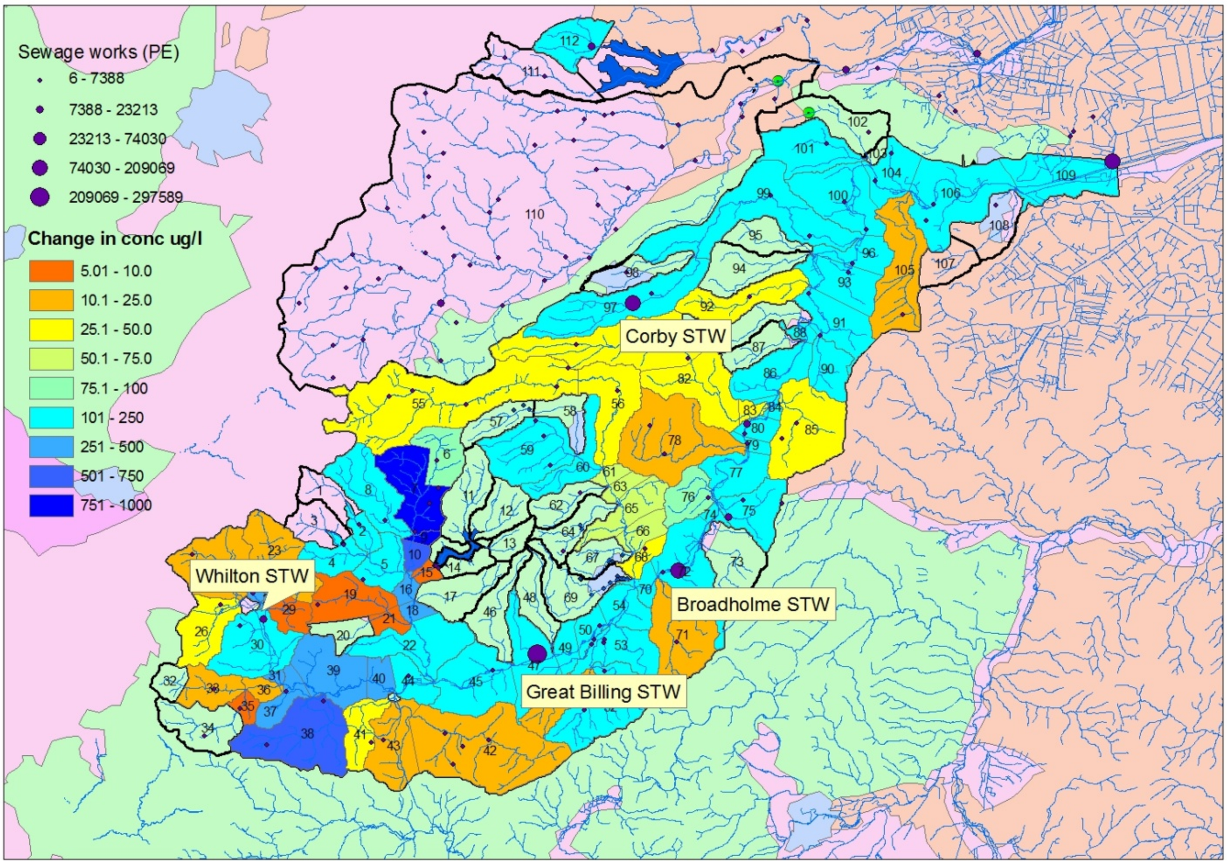

Figure 5.4 Difference in simulated average concentrations after applying EPC_0 equations (k_s = 0.05)

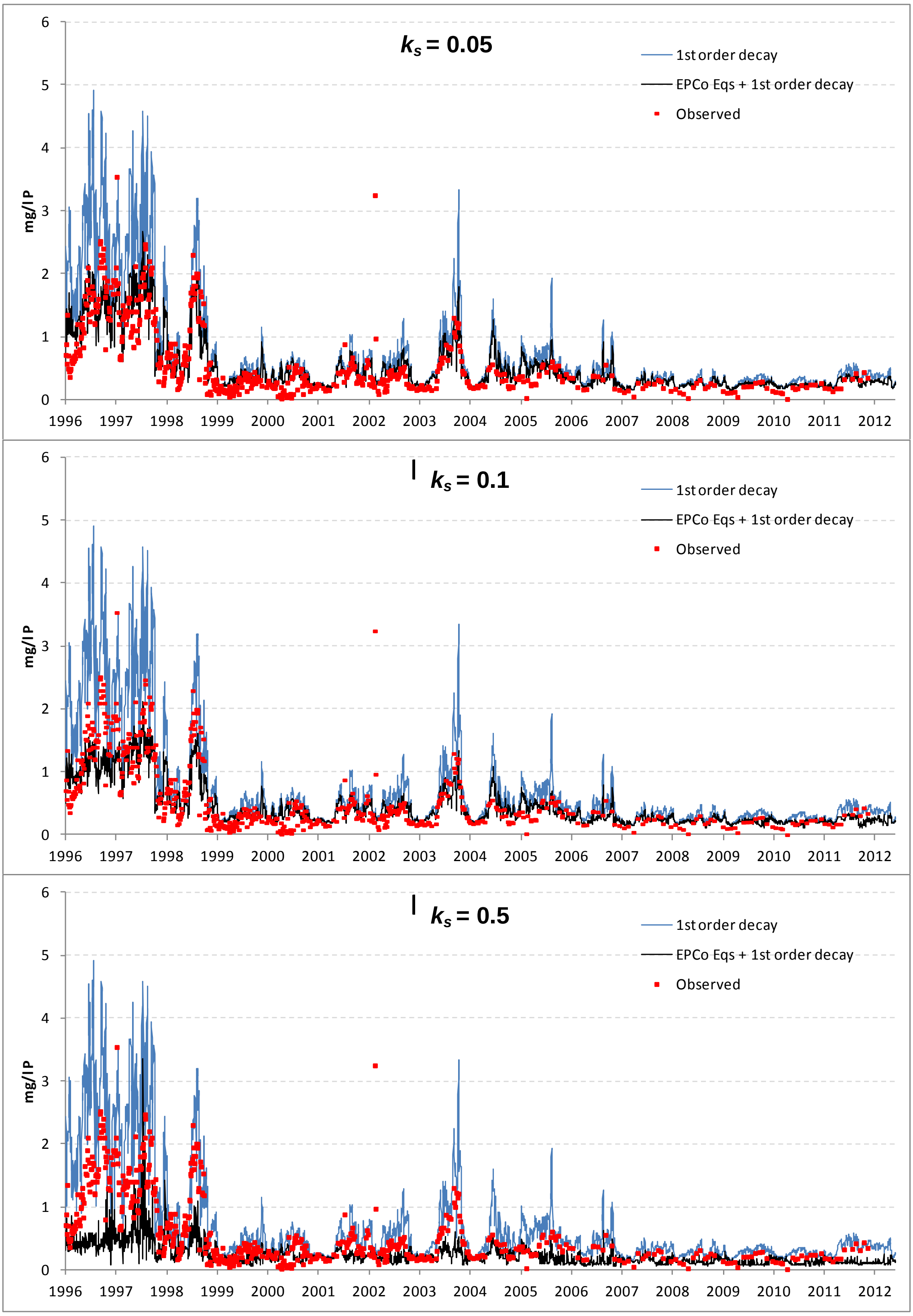

Figure 5.5 Simulated orthophosphate in sub-catchment 100 for a range of k_s values

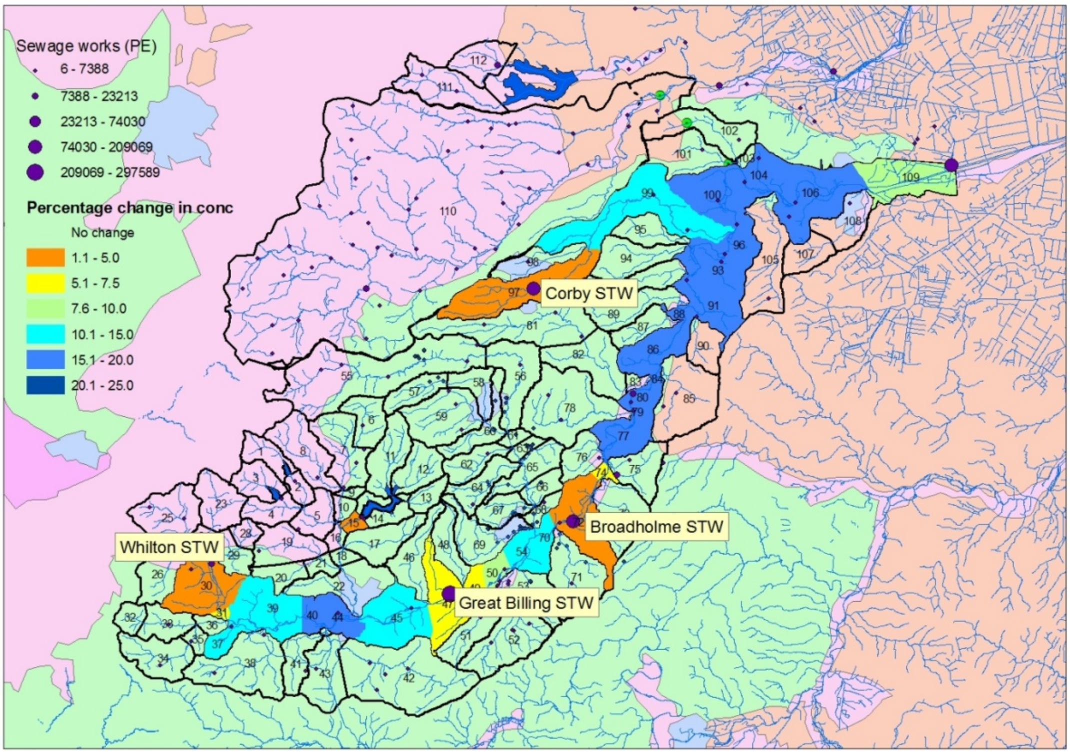

Figure 5.6 Difference between pre 1998 values and average orthophosphate concentrations after elevating EPC_0 values in sub-catchments downstream of works where phosphorus removal has been carried out

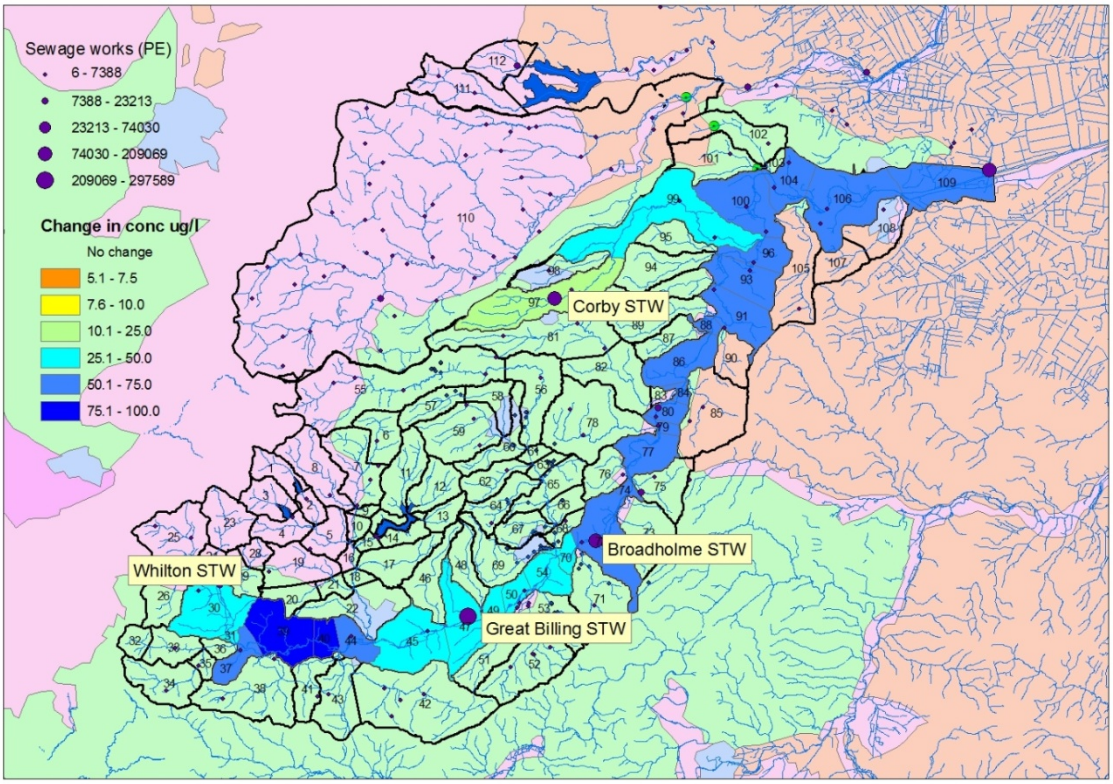

Figure 5.7 Percentage difference between pre 1998 values and average orthophosphate concentrations after elevating EPC_0 values in sub-catchments downstream of works where phosphorus removal has been carried out

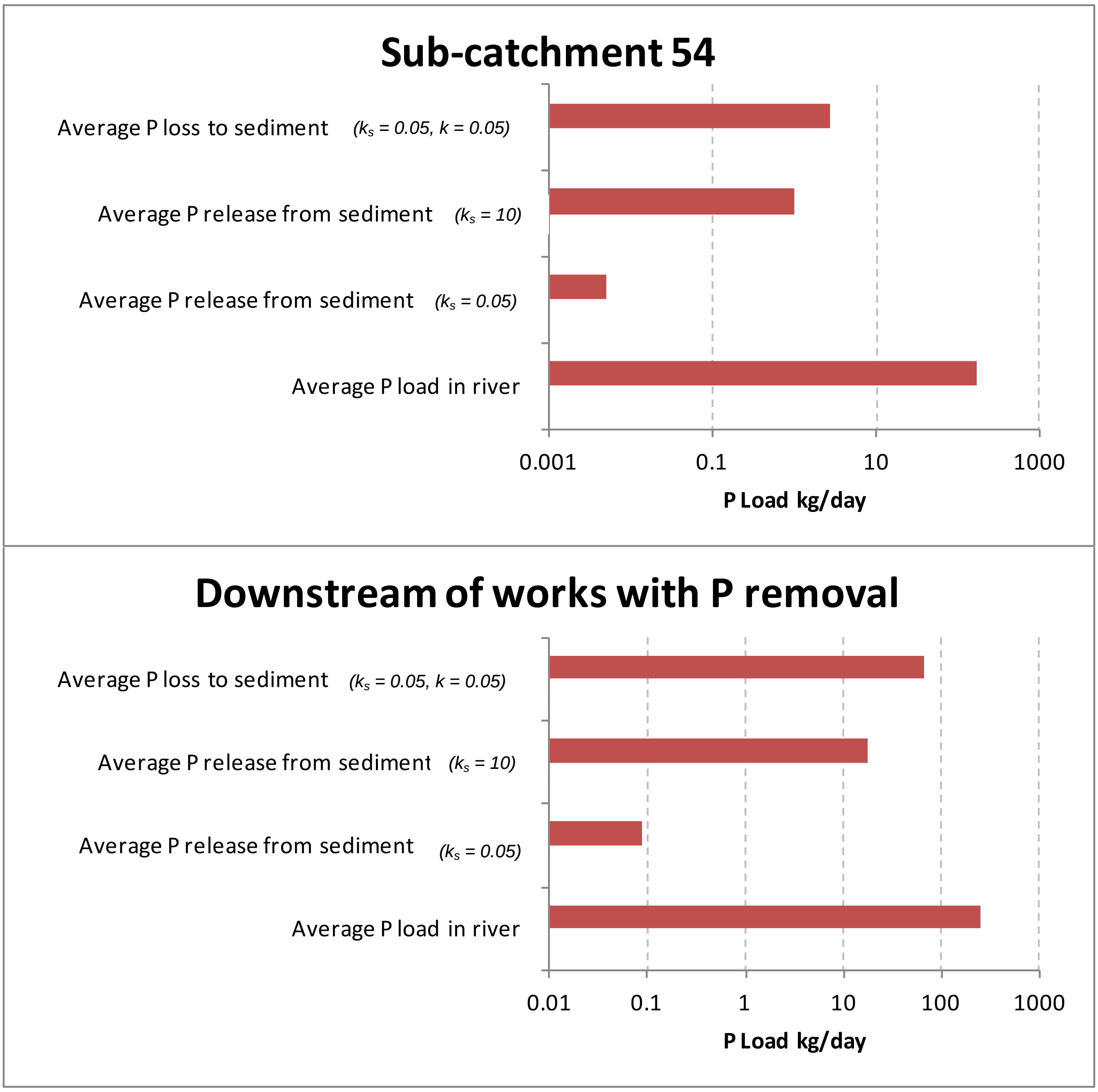

Figure 5.8 Comparison of sediment phosphorus release and losses with river phosphorus loads in the River Nene (*k* = first order decay, k_s = sediment exchange rate as defined in Equation 5.5)

5.5 Discussion

The analysis in this section shows that the sediment model developed by House and Warwick (1999) can be incorporated into a dynamic time series river model. For the River Nene, the model output indicates that, while EPC_0 related phosphorus exchange will reduce losses of phosphorus to the sediment following a reduction in upstream inputs from WTWs, the magnitude of phosphorus release is unlikely to delay improvements in river phosphorus concentrations and ecological status that are linked to river phosphorus concentrations. This does not necessarily mean that accumulated phosphorus is unimportant with regard to ecological status because macrophytes may take up phosphorus directly from the sediment and algae may take up phosphorus from the sediment surface. These are processes that are not represented by the EPC_0 based exchange model.

Phosphorus inputs to the River Nene are very high as the catchment has a high population density and phosphorus loads in the river remain high even after phosphorus removal at the major WTWs. In the River Nene, therefore, phosphorus release from the sediment would need to be very large to substantially change phosphorus dynamics. On the basis of House and Warwick's sediment exchange model, sediment phosphorus exchange is more likely to be significant in rivers with lower phosphorus inputs as similar rates of phosphorus release to those in the Nene will occur as long as the EPC_0 are well above the river concentrations; that is, the following term in equation 5.1 is close to -1.

$$\left(\frac{(C_t - EPCo)}{EPCo}\right)$$

The equations presented by House and Warwick (1999) were developed using fluvarium experiments under particular conditions for sediment and river phosphorus concentrations. The validity of the model under the wider range of conditions represented in a dynamic river model is therefore questionable. It is notable that the range of k_s values reported in Table 5.1 is high, with markedly different values in the same river occurring at different times of year. This suggests that it may not be valid to apply a single constant rate value for phosphorus sediment exchange at all times because the exchange rates are in reality more dynamic.

It is also of interest that the formulation of the equations presented by Jarvie et al. (2005) is somewhat different despite citing House and Warwick (1999) as their source (see equation 2.5, repeated below). In this case, the rate of exchange is dependent on the difference between the river concentrations and EPC_0 rather than the difference divided by the EPC_0 value. This approach, in contrast to equation 5.1, would make the magnitude of phosphorus losses and release equal for the same difference between C_t and EPC_0 (positive rather than negative).

$$\boldsymbol{dM = K_r(C_t - EPC_0)^{n} Sdt}$$

The Jarvie equations were not used in this study because they are based on sediment suspensions that produce much higher exchange rates than the fluvarium experiments of House and Warwick, and so are difficult to apply in a river situation.

The EPC_0 sediment model, developed by House and colleagues, does not provide a representation of how EPC_0 changes over time and the relationship between this measurable and the larger pool of phosphorus in the sediment. The relationship between measured EPC_0 and available phosphorus (measured as Olsen P or Resin-P) is described in Section 2 (Figure 2.5) and shows different relationships for the River Nene and the rivers studies by Jarvie et al. (2005). However, such measurements do not provide information on the dynamics of exchange between the various phosphorus pools in the sediment. Without this information it is not possible to estimate how quickly sediment EPC_0 changes when inputs of phosphorus to the sediment change (for example, following the introduction of phosphorus removal at WTWs upstream) and therefore how long sediment phosphorus exchange is likely to influence river chemistry before equilibrium conditions return.

In addition, information is required on the relationship between phosphorus losses from the river to the sediment and the available phosphorus pool, and the exchange between the available and 'locked up' phosphorus pool in the sediment. If information on these processes can be obtained, this could be incorporated into a dynamic model by simulating the available, unavailable and EPC_0 pools in the sediment separately and parameterising exchange rates that move phosphorus between these pools. The limited amount of scientific research in these areas, however, would make parameterisation problematic. As a consequence, reliable outputs on the dynamics of EPC_0 and the duration of the influence of elevated EPC_0 on river chemistry are unlikely to be forthcoming.

Another important issue in relation to the dynamics of river phosphorus is the process of bulk sediment transport along the river. If sediment is scoured from the bed or transported along the river by other processes, the phosphorus pool in the sediment will be modified accordingly and will control the direction of influence of phosphorus-rich sediment on river chemistry once external phosphorus inputs have been reduced. Modelling of bulk sediment transport does not form part of the existing River Nene model and so substantial changes to this model would be required to simulate these processes. However, a similar type of river model (INCA-Sed) has been developed (Jarritt 2004, Jarritt and Lawrence 2006) and combining the model algorithms from this model and the ILC-P model offers a potential way forward.

A separate line of investigation that would inform these issues would be to carry out an extensive analysis of measured wastewater and river phosphorus concentration downstream of large WTWs where phosphorus stripping has been introduced. By comparing river concentrations immediately after phosphorus removal has been introduced and at later intervals, it should be possible to identify whether phosphorus concentrations were elevated in the early period. This would provide independent evidence on the importance of sediment phosphorus exchange and the duration of these impacts. Because the signal information on both the wastewater emissions and river concentrations tend to be 'noisy', a large dataset would be required. However, this should be available because of the large number of WTWs that have been subject to phosphorus removal in recent years.

In conclusion, there are considerable scientific uncertainties associated with quantifying sediment phosphorus exchange processes. These will, inevitably, constrain the value of further model development at this stage. Development of such models would, however, be valuable to place sediment phosphorus exchange in the context of the wider picture of phosphorus dynamics in rivers and sediment transport processes.

6 Options for integration into existing water quality models

This section considers a number of options that might be considered for integration of the outputs of this study into existing water quality models/tools.

6.1 Screening tool

The screening tool and the scoring system presented in this report have been developed as prototypes but could be relatively easily incorporated into SAGIS. The advantage of this is that it would be immediately available for SAGIS users as required rather than needing a separate analysis. It would also ensure distribution of the tools widely and in a consistent way. The most important GIS layers would be included in the SAGIS databases and an option provided to load these into SAGIS when the models are opened and updated for the model region of interest. In addition to providing the risk scores for phosphorus sediment exchange, the individual layers could provide valuable information to help interpret the outputs from SAGIS (river velocities, presence of barriers and so on).

6.2 Water quality models

6.2.1 SAGIS/SIMCAT

Incorporation of the sediment exchange model into SAGIS/SIMCAT would require modifications to SIMCAT to input EPC_0 values and derived decay rates from the sediment model equations as has been demonstrated in this project for the Nene model. Information would also need to be inputted for the sediment surface area. Sediment release would be inputted as an additional load per km similar to the current representation of diffuse inputs in SIMCAT. The SAGIS interface would also need to be modified to show the proportion of phosphorus derived from the sediment as part of the source apportionment output. Development of SIMCAT would require input from Tony Warn, the model developer, as well as changes to the SAGIS interface.

SIMCAT is suitable to represent the impact of fixed EPC_0 values and exchange rates, following a similar approach to the model modifications to ILC described in Section 5). However, it is not a time series model and so is not suitable to model changes in EPC_0 that might result from bulk sediment transport processes and exchange between EPC_0 and the available phosphorus pool in the sediment.

6.2.2 ILC and other time series models

As developers of the model code for ILC, it was relatively easy for the authors of this report to make the changes to the model to accommodate the EPC_0 based sediment model. This could be extended to represent exchanges with the sediment phosphorus pool. The primary problem with such changes is that the science of phosphorus exchange between the sediment pools is undeveloped and there is little information available to derive process rates. Similar modifications could be made to other time series models such as INCA-P and MIKE 11, but the model code for these is owned by others who would need to be responsible for the task. There are no time series models that have national coverage and so such systems would primarily be used for more detailed local assessments.

As discussed in Section 5, the ILC model does not currently simulate bulk sediment transport. There is the potential to incorporate the algorithms for sediment transport into ILC or to make modifications to INCA-Sed to incorporate phosphorus transport. Similar changes could be made to other existing dynamic river models, but this would require collaboration with the model developers.

Bearing in mind the initial findings of this study (that is, that phosphorus release may be small in the context of overall phosphorus dynamics), large-scale investment in model development is difficult to justify until there is better confidence in the formulation of the EPC_0 sediment exchange model and the interaction between EPC_0 and the available phosphorus pool in the sediment.

7 Conclusions

This project has shown that national datasets are available to generate a risk screening tool for potential sediment phosphorus impacts. No significant intellectual property rights (IPR) issues were encountered in the development of the tool, though it was not possible to incorporate the barriers and stream power values because of issues with the suitability of the data and processing requirements.

An approach has also been developed to test the sediment exchange model within the ILC model framework.

The crucial issue with regard to taking this work forward is that scientific understanding of the key processes of sediment phosphorus dynamics is poor and so quantification of these processes is problematic. While the screening tool provides information on the relative risk of phosphorus sediment impacts, it does not provide a measure of the magnitude of this risk.

In taking the work forward, it is important to bear in mind the scientific uncertainties associated with sediment phosphorus dynamics. These need to be addressed before the influence of sediment phosphorus on river ecology can be assessed with regard to the magnitude of phosphorus inputs and how long these are likely to last. The initial findings suggest the risk is low, but the scientific uncertainties need to be tested before firm conclusions can be drawn.

7.1 Next steps

To take the current work forward, the following steps should be considered.

7.1.1 Task 1: National Screening Tool

The development of the national screening tool should be completed and the tool incorporated into SAGIS. This would allow the tool to be immediately available for SAGIS users rather than requiring a separate analysis. It would also ensure distribution of the tools widely and in a consistent way. The SAGIS databases and functionality would be modified to include the layers generated by this project.

Within the current project it was not possible to incorporate stream power and the barriers layer into the tool because of the format of the information provided and the processing requirements. However, this could be incorporated in the final version of the tool.

7.1.2 Task 2: Data analysis

If sediment exchange has a significant influence on river phosphorus concentrations following a reduction in phosphorus loads from WTWs, this should be evident in monitored river quality data. Because of the large number of sites at which phosphorus removal has been carried out, there is a large amount of relevant data, that is, within the Environment Agency's Water Information Management System (WIMS) database. The approach would be based on comparing the relationship between phosphorus concentrations and river flow immediately after phosphorus removal at upstream WTWs began and later to see if concentrations are elevated in the first period. If elevated concentrations can be demonstrated, this approach might also yield information on how long elevated concentrations occur before a new equilibrium in the river is established; this would help development of the sediment exchange models. If elevated concentrations cannot be demonstrated, this would support the initial findings of the current work that phosphorus release from sediments is small within the context of wider river phosphorus dynamics.

7.1.3 Task 3: Further model development

The ILC model provides a useful basis for testing the implications of variations on the sediment exchange model on river phosphorus concentrations. An important first step would be to understand the different versions of the published sediment exchange models and to establish the current view in the research community of the best approach. The ILC model could also be modified to incorporate the exchange between the available phosphorus pool and EPC_0. However, the only way to test this using existing data would be to compare the modelled rate of change of EPC_0 with the period over which elevated river phosphorus can be demonstrated (see task 2 above).

Before work is carried out to link the phosphorus model with a sediment transport model such as INCA-Sed, a sensible first step would be to set up INCA-Sed on a data-rich catchment such as the River Nene and to simulate sediment transport to test the implications for the build-up of phosphorus in the sediment. This could be followed by further work to modify either INCA-Sed or ILC to link the sediment phosphorus and sediment transport models.

Further testing with dynamic river models is recommended before consideration is given to applying the model to SIMCAT.

7.1.4 Task 4: Research

The magnitude and duration of sediment phosphorus release would be best assessed by:

- identifying a site where phosphorus removal is about to be implemented – as part of Asset Management Programme 6 (AMP6)
- carrying out EPC_0 measures before phosphorus removal begins and at intervals afterwards to test how quickly EPC_0 values change

Ideally the chosen site would be where the WTW is the primary source of phosphorus to the downstream river such that the step change in river phosphorus concentrations is large.

7.2 Timescales and costs

Estimated timescales and costs for the tasks identified in Section 7.1 are outlined in Table 7.1. Detailed costing would be necessary as part of the procurement process before taking these tasks forward.

A phased approach is recommended whereby tasks 1 to 3 are completed to better quantify the magnitude of phosphorus release before a decision is made on investing in model development.

Table 7.1 Estimated timescales and costs for further development work

No.	Task	Timescale	Cost
1	Completion of the national screening tool and incorporation into SAGIS.	Two months	£5,000
2	Data analysis	Six months	£10,000
3a	Further model development:		
	Further testing of sediment model using ILC	Three months	£5,000
3b	Setting up of INCA-Sed on the River Nene[1]	Six months	£20,000
3c	Linking sediment transport model and phosphorus model[1]	12 months	£40,000
4	Monitoring of EPC_0 during phosphorus removal trial	Two years	£30,000 to £60,000

Notes: [1] Would require discussion with developers of INCA-Sed (Reading and Oxford Universities).

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List of abbreviations

ADZ	aggregate dead zone [model]
BFI	Base Flow Index
DTM	digital terrain model
EPC_0	equilibrium phosphorus concentration
EQR	Ecological Quality Ratio
ILC	integrated lake and catchment [model]
MMB	modified Montgomery–Buffington
PE	population equivalent
RMHI	River Macrophyte Hydrology Index
SRP	soluble reactive phosphorus
UKTAG	UK Technical Advisory Group
WFD	Water Framework Directive
WTW	wastewater treatment works

Appendix A: Catchments influenced by phosphorus removal

Table A.1 Percentage of water bodies in each management catchment with load reduction due to phosphorus removal

Catchment	Percentage
Loddon	63
Idle and Torne	61
Maidenhead to Sunbury	57
New Forest	50
Douglas	42
Upper and Bedford Ouse	39
Kennet and Pang	35
Colne	35
Derwent (NW)	35
Broadland Rivers	33
Cam and Ely Ouse (including South Level)	33
Soar	33
Alt/Crossens	31
Wey	31
Cuckmere and Pevensey Levels	29
North Norfolk	29
Rother	28
Thame and South Chilterns	28
East Hampshire	24
Derbyshire Derwent	24
Stour	24
Welland	24
London	23
Dove	22
Old Bedford including the Middle Level	21
Vale of White Horse	21

Catchment	Percentage
Test and Itchen	20
Cotswolds	20
Arun and Western Streams	19
Waver and Wampool	19
Kent/Leven	19
North West Norfolk	17
Bristol Avon and North Somerset Streams	17
Irwell	16
Lower Trent and Erewash	16
Mole	16
Tame Anker and Mease	15
Ribble	15
Adur and Ouse	15
Medway	14
Cherwell	14
Middle Dee	13
South East Valleys	13
Upper Lee	13
Nene	13
Ogmore to Tawe	12
Aire and Calder	12
Wear	12
South West Wales	12
Louth Grimsby and Ancholme	12
Don and Rother	11
Combined Essex	10
Hull and East Riding	10
Upper Dee	10
Derwent (Humber)	9
South West Lakes	9
Usk	9
Staffordshire Trent Valley	9
Loughor to Taf	9

Catchment	Percentage
Eden and Esk	8
Wye	7
Lune	7
Upper Mersey	7
East Suffolk	6
Witham	6
Conwy and Clwyd	5
Swale, Ure, Nidd and Upper Ouse	5
North West Wales	5
Hampshire Avon	5
Wharfe and Lower Ouse	5
Weaver/Gowy	4
Tyne	4
East Devon	4
North Cornwall, Seaton, Looe and Fowey	3
Dorset	3
Northumberland Rivers	3
West Cornwall and the Fal	2
South and West Somerset	2
Tees	2
North Devon	2
South Devon	1
Darent	0
Esk and Coast	0
Isle of Wight	0
Mersey Estuary	0
North Kent	0
Roding, Beam and Ingrebourne	0
Severn Uplands	0
Severn Vale	0
Shropshire Middle Severn	0
South Essex	0
Tamar	0

Catchment	Percentage
Teme	0
Tidal Dee	0
Till	0
Tweed	0
Warwickshire Avon	0
Worcestershire Middle Severn	0
Wyre	0

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