# WATER COLUMN AND SEDIMENT PHOSPHORUS IN A CALCAREOUS LOWLAND RIVER AND THEIR DIFFERENTIAL RESPONSE TO POINT SOURCE CONTROL MEASURES

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**Abstract.** Phosphorus control measures at two major (>10000 people equivalent, p.e.) sewage treatment works (STWs) were installed in the lowland calcareous basin of the River Wensum (England). In-stream phosphorus concentrations were monitored seasonally from subcatchments with different levels of phosphorus impacts, as well as before and after phosphorus control, above and below the two major STWs. Point source effluents raised in-stream soluble reactive phosphorus (SRP) concentrations from 9–15 $\mu g\,L^{-1}$ (agricultural sub-catchments) to 580–3270 $\mu g\,L^{-1}$. This was accompanied by an increase of the SRP relative to total phosphorus from 27% to 80–90%. The phosphorus content of the suspended sediment was high (0.2 to 7.7%). Molybdate unreactive phosphorus (1–29 $\mu g\,L^{-1}$) was surprisingly not affected by point source effluents. The river bed sediment bioavailable phosphorus concentrations were higher (4–18 $\mu g\,g^{-1}$ wet weight) downstream from the main effluents, compared to upstream (2–6 $\mu g\,g^{-1}$ wet weight). Phosphorus control at the STWs in 1999 has allowed to reduce in-stream soluble reactive concentrations to 140–280 $\mu g\,L^{-1}$ but has had no significant impact on bioavailable phosphorus in the sediment by 2001, suggesting that either net sediment desorption did not occur or that it is a much slower, longer term response. The relative contribution of the diffuse sources increased from 10% to 27% of the total phosphorus loads at Fakenham. The management of these rivers is therefore problematic.

**Keywords:** eutrophication, reduction of phosphorus loads river sediment phosphorus, source apportionment, suspended solids

## 1. Introduction

The Environment Agency of England and Wales has recently directed a pilot program of phosphorus removal at major sewage treatment works (STWs) in the UK that discharge upstream of stretches of rivers designated as Sensitive Areas (Eutrophic) under the European Urban Waste Water Treatment Directive (91/271/EEC). This management option has long been applied as a first step in the restoration of lake ecosystems (e.g. Moss *et al.*, 1988), but less is known about sediment response to phosphorus stripping in lowland calcareous river systems (e.g. Wade *et al.*, 2002).

The dynamics of phosphorus at the water/sediment interface have been conceptualised as a buffer mechanism involving a dynamic equilibrium between the dissolved and adsorbed or precipitated phosphorus (Froelich, 1988). The solution concentration where the net flux of phosphorus between solid and solution phases is zero is called the Equilibrium Phosphorus Concentration ($EPC_0$, e.g. Klotz, 1988; House and Denison, 2000). The $EPC_0$ therefore reflects both the dissolved phosphate concentrations of the column water and the relative adsorption potential of the sediment (House and Warwick, 1999; Cooper *et al.*, 2002; House and Denison, 2002). In a semi-natural chalk stream such as the upper River Wey, with a mean soluble reactive phosphorus of $59 \pm 22$ SD $\mu$g $L^{-1}$, $EPC_0$ fluctuated around $53 \pm 28$ SD $\mu$g $L^{-1}$ and alternating sorption/desorption of dissolved phosphate by the river bed sediment was observed across the seasons (House and Denison, 1998). However, in most of the lowland rivers of England impacted by major STWs, $EPC_0$ was much lower than the measured dissolved phosphate concentrations (House and Denison, 1997, 1998; House and Warwick, 1999). This implies that there is a constant net sink of phosphorus in the sediment (provided it is not already saturated), i.e. the system is far from the equilibrium expected in natural rivers (Froelich, 1988).

The different forms of phosphorus in the sediment vary in their bioavailability, especially to anchored aquatic macrophytes. Sediment bioavailable phosphorus (BAP) can be determined using the iron oxide-impregnated paper strip test (Chardon *et al.*, 1996) which acts as a sink and may therefore simulate plant root phosphorus absorption from the interstitial water (although the original bioassays were carried out using a phosphorus starved algae – *Selenastrum capricornutum*). This method may have a stronger theoretical basis as a BAP test than methods involving chemical extractants (Sharpley, 1993).

Therefore this study set out to investigate some of the uncertainties over phosphorus dynamics in a river system impacted by sewage discharge. The three objectives were:

1. to quantify the contribution from diffuse, small point sources, and major urban sources, by a catchment-wide analysis of phosphorus concentrations;
2. to quantify the changes of in-stream phosphorus concentrations and loads resulting from phosphorus stripping at two major urban STWs;
3. to evaluate the management implications of phosphorus stripping.

## 2. Study Area

The River Wensum (Norfolk, UK) drains a lowland, rural and agricultural catchment of 570 km$^2$ and is underlain by a chalk aquifer. The catchment area does not rise above 95 metres OD. The rural landscape is dominated by pasture and arable fields, although scattered woodland still remains. River impoundments and weirs were created in the past to operate water mills. These engineering works are still in place but not in use. The consequence is that siltation occurs upstream of the weirs

(Boar *et al.*, 1994). Average annual rainfall is 672 mm year$^{-1}$. The hydrograph displays a damped response to rainfall events due to the catchment permeability and storage in the chalk aquifer. This is reflected by a base flow index of 0.83 at Fakenham where the catchment area is 162 km$^2$ (Institute of Hydrology, 1992). Water abstraction was found to be negligible for the River Wensum (generally <6% and maximum 14% loss of mean weakly flows; Hiscock *et al.*, 2001). It is a prime example of a *Ranunculus*-dominated calcareous lowland river under the European Habitats Directive (92/43/EEC). Although malting and poultry processing industry are present in the catchment, these were situated below the sites investigated in the present study. More details can be found in Boar *et al.* (1994) and Demars and Harper (2002a,b).

Removal of phosphorus by chemical precipitation with an iron salt started at two major STWs in autumn-winter 1999, following the technique adopted in the restoration of the Norfolk Broads (Harper, 1992; Thomas and Slaughter, 1992). The reduction of total phosphorus achieved (outlet/inlet of the STWs) was optimized at 77 ± 9% for Fakenham (13439 people equivalent – p.e.) and 88 ± 4% for East Dereham (17475 p.e., Demars, 2002). Only primary (retention of coarse particles) and secondary (biological oxidation) treatments had previously been conducted at these STWs. Further treatment facilities would be required at these STWs to achieve greater phosphorus stripping efficiency without compromising the existing sanitary consents (Richard Slaughter, personal communication). The catchment areas at these sites are about 162 km$^2$ for the River Wensum at Fakenham and 40 km$^2$ for the Wendling Beck at East Dereham. The River Wensum has several small tributaries not apparently impacted by point discharges although septic tank leakages may occur (Figure 1).

## 3. Material and Methods

### 3.1. Catchment scale: spatial and temporal variation

Temporal variability (3–4 October 2000, 30–31 January 2001, 10–11 April 2001, 28–29 June 2001) of the water and sediment characteristics were investigated at nine selected sites along a cumulative gradient of anthropogenic phosphorus input: four sites impacted only by diffuse sources (site 1 to 4); two sites impacted by distant small point source effluents (site 5 and 6) and three sites impacted by an effluent from a nearby large STW (site 7 to 9) – see Figure 1 and Table I. Additional water samples had also been collected in April and June 2000. The period covered a range of hydrological conditions as illustrated in Figure 2.

The treatment × time field design of the study was analysed as a split plot experimental design with two factors: treatment as main plot and time as subplot. Treatments were the three fixed levels of human impact. Sites within treatments

TABLE I

Summary of the mean solute concentrations and sediment characteristics at the selected sites surveyed in 2000–2001 (after implementation of phosphorus stripping).

| Site codes, NGR, names | | | §People equivalent | †River discharge ($Ls^{-1}$) | ‡Distance (km) | Water column | | | | Suspended sediment | | River bed sediment | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Phosphorus fractions | | | | | | SRP | SUP | PP | TP | SS | PSS | $TP_{SED}$ | BAP |
| Units | | | | | | $\mu g.L^{-1}$ | $\mu g.L^{-1}$ | $\mu g.L^{-1}$ | $\mu g.L^{-1}$ | $mg.L^{-1}$ | $mg.L^{-1}$ | $\mu g.g^{-1}$ | $\mu g.g^{-1}$ |
| Number of samples collected | | | | | | 6 | 6 | 6 | 6 | 4 | 4 | 4 | 4 |
| Sites impacted by diffuse sources only | | | | | | | | | | | | | |
| 1 | 63 089 212 | Tributary of R. Ainse, Whitwell Hall | 0 | 80 | n.a. | 9 | 10 | 30 | 48 | 10.2 | 4.9 | 94 | 2.3 |
| 2 | 53 951 192 | Black Water, East Bilney (South) | 0 | 30 | n.a. | 14 | 10 | 15 | 39 | 2.8 | 19.3 | 186 | 4.1 |
| 3 | 63 035 169 | Penny Spot Beck, Park Farm | 0 | 90 | n.a. | 15 | 13 | 20 | 47 | 7.3 | 3.2 | 285 | 4.0 |
| 4 | 63 107 227 | River Ainse, Booton Bridge | 0 | 130 | n.a. | 14 | 12 | 50 | 77 | 9.6 | 5.8 | 161 | 4.9 |
| Sites impacted by small distant point source effluents | | | | | | | | | | | | | |
| 5 | 53 976 135 | Wendling Beck, East Dereham (above STW) | 184 | 170 | >5.0 | 49 | 12 | 18 | 79 | 4.4 | 9.6 | 183 | 4.2 |
| 6 | 53 921 293 | River Wensum, Fakenham (above STW) | 1855 | 870 | >8.0 | 55 | 11 | 31 | 97 | 5.4 | 6.1 | 152 | 3.6 |
| Sites impacted by large nearby STW effluents | | | | | | | | | | | | | |
| 7 | 53 923 292 | River Wensum, Fakenham (below STW) | 15294* | 900 | 0.1 | 141 | 12 | 56 | 210 | 4.3 | 20.3 | 171 | 5.6 |
| 8 | 53 975 138 | Wendling Beck, East Dereham (below STW) | 17659* | 200 | 0.1 | 282 | 19 | 150 | 451 | 5.1 | 44.9 | 233 | 10.8 |
| 9 | 63 095 213 | River Ainse, Eade's Mill | 4017 | 160 | 2.0 | 384 | 15 | 95 | 493 | 8.3 | 11.0 | 310 | 14.0 |

NGR, National Grid Reference; n.a., not applicable; §cumulated number for all known point source effluents; †long term average estimated from Fakenham gauging station and catchment area pro rata basis; ‡nearest known upstream point source effluent; *before phosphorus stripping at STWs; SRP, soluble reactive phosphorus; SUP, soluble unreactive phosphorus; PP, participate phosphorus; SRP + SUP + PP = TP, total phosphorus; SS, suspended solids; PSS, phosphorus content of the suspended solids; $TP_{SED}$, TP of the sediment; BAP, sediment bioavailable phosphorus.

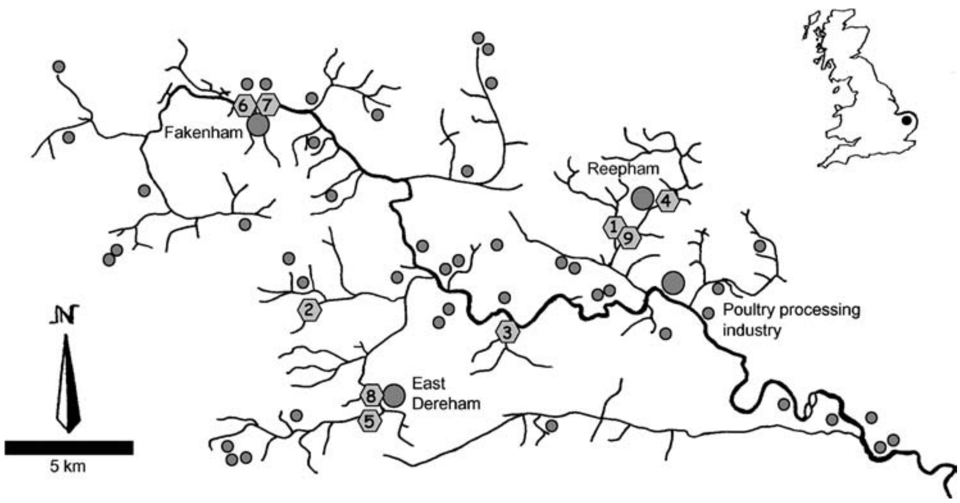


*Figure 1.* The River Wensum catchment area, eastern England. The filled hexagons represent the studied sites (see Table I). The filled circles represent the point source effluents.

were considered as a nested random factor. Two randomly positioned sediment samples were collected within sites and the resulting analyses were averaged to avoid pseudoreplication. Time was a factor with repeated measurements (due to autocorrelation in time series). A two-way anova was used to detect spatio-temporal patterns and investigate the potential interaction of the cumulative human impacts and temporal variability. These statistical analyses follow the recommendations of Sokal and Rohlf (1995) and were performed using SPSS 10.0. Data transformations were applied where necessary. Further analyses (multiple regressions) were carried out to investigate whether discharge or season would explain significant temporal changes. Monte Carlo permutation test were run within the treatments (1000 unrestricted random permutations). These analyses were carried out with CANOCO 4.5 (ter Braak and Šmilauer, 2002).

### 3.2. Localised impact of control measures

To assess the efficiency of phosphorus removal, water samples were collected in 1999 (19/05, 20/08, 12/10), 2000 (18/04, 29/06, 3/10) and 2001 (31/01, 11/04, 29/06), 200 metres above and 100 metres below the major STWs at Fakenham (site 6 and 7) and similarly at East Dereham (site 5 and 8, no data in October 1999). Sediment samples were collected each year during spring at the two pairs of sites.

The compiled data from 1999–2001 at the two major STWs were a classic BACI (Before and After Control Impact) design where BAP, TP and SRP were measured. The statistical analysis was a two-way anova where the null hypothesis (phosphorus

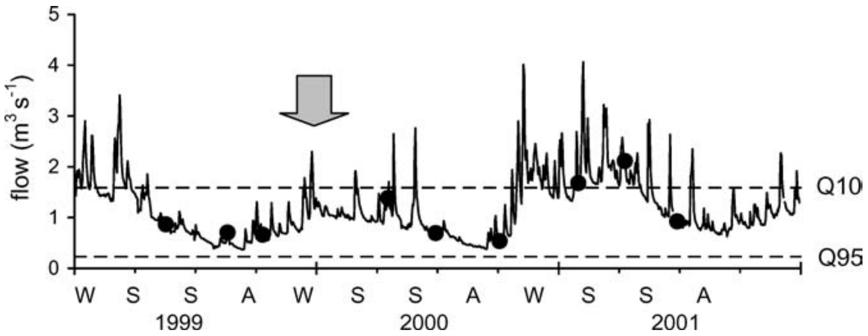


*Figure 2*. Hydrograph (mean daily discharge in $m^3$ $s^{-1}$) at Fakenham (national grid reference TF919294 – 162 $km^2$) with sampling days (black dots). Q95 (low flows) and Q10 (high flows) represent the percentage of time the discharge (dashed line) is exceeded.

removal at STWs has no significant effect on the instream concentration or load of phosphorus) was tested by the interaction of 'site' $\times$ 'year'.

### 3.3. Source apportionment at Fakenham

The diffuse sources of phosphorus were estimated by monitoring streams not impacted by known point source effluents (Figure 1, sites 1–4). The phosphorus concentrations from these four streams monitored at six sampling dates were averaged. The mean daily loads were obtained by multiplying the mean concentration of phosphorus by the mean daily flow (Environment Agency, unpublished data; Figure 2). It was therefore assumed that the concentration of TP in un-impacted (by point discharges, excluding septic tank leakages) streams was constant and that the loads were linearly related to the flow.

The monitoring above (site 6) and below (site 7) Fakenham STW allowed the calculation of the relative contribution of the small distant point source effluents and Fakenham STW. The flow was corrected at site 7 to take into account the inflow from the STW. Errors were propagated through the calculations where necessary.

### 3.4. Data collection

Streamwater samples were collected in the mid-channel by lowering down through the water column a 150 mL plastic bottle. Streamwater samples were filtered through a 0.45 $\mu$m cellulose nitrate filter immediately after collection using a field filtering unit and filter which had been pre-washed with sample.

Two random replicates of sediment (5–7 cm deep) were collected using a plastic hand-scoop, then immediately passed through a 2 mm sieve, and the $<$2 mm fraction stored in plastic containers. Despite the effort to have the same depth for all samples, some small variability occurred due to the heterogeneity of the river bed sediment.

All the water and sediment samples were collected within a period of 30 h and kept in the dark in a cool box (mainly 4–10 °C) while being transported to the laboratory.

### 3.5. Comparability between sites

The geomorphology of the sites had to be comparable. Riffles were selected for ease of sampling during high flows and because they represented semi-natural conditions where *Ranunculus penicillatus* (Dumort.) Bab. or *R. trichophyllus* Chaix were generally growing. The river bed sampled was unvegetated to avoid direct interactions with the primary producers (such as filamentous algae and vascular plants) and to obtain comparable measurements. The river bed was mostly made of pebble, gravel and sand (Figure 3). This type of river bed constitutes a hyporheic zone of the stream due to its coarse granulometry. It was indeed found to be oxic both above and below Fakenham STW (deduced from interstitial water analysis of the redox couple $NO_3/NH_4$ – Demars, unpublished) at the sampled depth of 5–7 cm. The fraction of sediment (<2 mm) retained for analyses had a very sandy texture. The river bed was assumed to be stable. The hydraulic forces and turbulence that could mobilize the sediment are weak due to the moderate spate flows occurring in a flat calcareous catchment and even further reduced by the impact of the weirs above Fakenham (sites 6 and 7).

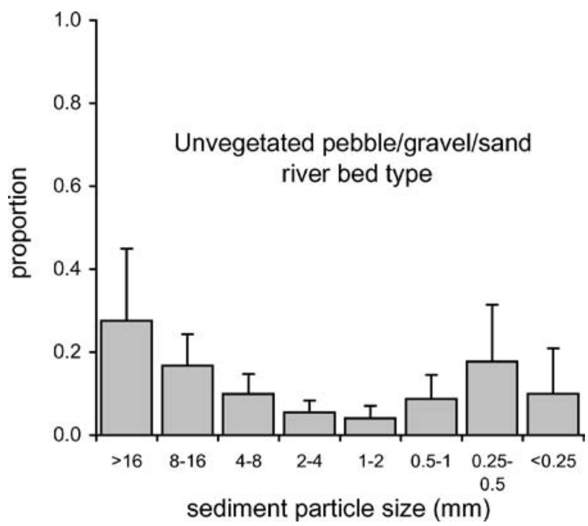


*Figure 3*. Sediment particle size frequency distribution of the unvegetated pebble/gravel/sand river bed type. Average and standard deviation of 51 samples collected across 26 sites in the River Wensum catchment area (1999 data).

### 3.6. Chemical analyses

In the laboratory samples were analysed by manual colorimetry for soluble reactive phosphorus (SRP; Murphy and Riley, 1962) and total dissolved phosphorus (TDP), based on an acid persulphate digestion method (Rowland and Haygarth, 1997). Absorbencies were measured using a HACH DR/2000 spectrophotometer. The total phosphorus (TP) was determined on unfiltered streamwater samples by the same digestion procedure as TDP. Total phosphorus is the sum of SRP, soluble unreactive phosphorus (SUP), and particulate phosphorus (PP). Soluble unreactive phosphorus was calculated as TDP minus SRP and PP as TP minus TDP. Suspended solid (SS) concentrations were measured by the filtration of 500 mL of water through a 0.45 $\mu$m cellulose nitrate membrane filter, air drying and weighing. Particulate phosphorus was used with SS concentrations to calculate the phosphorus content of the suspended solids (PSS).

Two sediment phosphorus fractions were determined: bioavailable phosphorus (BAP; Sharpley, 1993 modified by House and Denison, 1997) and total phosphorus ($TP_{SED}$). The total phosphorus analysis was modified from the ignition method of Andersen (1976), Solorzano and Sharp (1980) and Rose (1995). Sediment samples were dried at 105 °C. Aliquots (0.2 g) were ignited in a muffle furnace in a porcelain crucible (550 °C for 2 h). After cooling the residue was washed into a 10 mL test tube with 5 mL of hydrochloric acid (1 M) and placed in a hot water bath (80 °C for 30 min). Samples were then diluted with deionised water to 100 mL in a volumetric flask. Aliquots were withdrawn for orthophosphate determination using the same method as above. The proportion of organic matter was determined with this ignition step of the total phosphorus analysis.

SRP and BAP analyses were generally started within 48 h of collection and TDP/TP within 62 h. Phosphorus stability trials of SRP (within the range 15–450 $\mu$g L$^{-1}$) and BAP (sandy sediment, see Demars and Harper, 2002b) showed that no significant changes were occurring during storage, after collection and transport (12–48 h). The accuracy of the measurements was good: the coefficients of variation of three replicates of the same sample were on average TP = 4.8%, SRP = 3.8%, $TP_{SED}$ = 15%, and BAP = 17% (Demars and Harper, 2002b).

## 4. Results

### 4.1. Impact of point source effluents on water and sediment phosphorus

Table I summarises the results showing the impact of increasing human pressure on phosphorus concentrations in the water and the sediment. Mean concentrations in agricultural catchments were 13 ± 6 SD $\mu$g L$^{-1}$ for soluble reactive phosphorus and 53 ± 18 SD $\mu$g L$^{-1}$ for total phosphorus. The bioavailable phosphorus in the sediment seemed to be less affected by the point source effluents than the water column concentrations. Sediment total phosphorus did not appear to be affected.

Figure 4 illustrates the impact of treated sewage effluents on the variability of the water characteristics at different sampling dates. Insets give the statistical significance of the observed patterns. Soluble reactive phosphorus and total phosphorus were strongly impacted by the STW (Figures 4A and B). Their concentrations did not change between sampling dates in the agricultural subcatchments, but there was an increasing (see T $\times$ S probabilities) time variability proportional to the size of point source impact. The averaged soluble unreactive phosphorus concentrations were remarkably similar across the three treatments (Table I; Figure 4C) although the STW effluents reduced the temporal amplitude (T $\times$ S , $P < 0.01$). Neither particulate phosphorus (T, $P = 0.07$; Figure 4D) nor suspended solid concentrations (T, $P = 0.67$; T $\times$ S , $P = 0.65$; Figure 4E) were affected by the STWs effluents. The phosphorus content of the suspended solids (PSS, Figure 4F) was inversely related to the suspended solid (SS) concentration (PSS $= 25.508$ SS $^{-0.7593}$, $R^2 = 0.49$, $P < 0.01$) and was not significantly different between treatments ($P = 0.07$). Interestingly, the same temporal variability ($P < 0.01$) in PSS was observed across treatments, independently of changes in SRP concentrations. Finally, note that the sites within each treatments differ significantly from each other – $R(T)$, $P < 0.01$ (Figure 4; Table I). This may be explained by a variety of local factors not investigated (e.g. land use, riparian zone, septic tank leakage, hydrological pathways) between the sub-catchments. Multiple regression analyses showed that the temporal changes associated with SRP, SUP and PSS were all affected by both discharge ($P < 0.01$, $P < 0.01$, $P = 0.05$ respectively) and season ($P < 0.01$, $P < 0.02$, $P < 0.03$ respectively). The seasonnal effect was also significant, after removing the effect of flow for SUP ($P < 0.03$). It was generally not possible however to separate the effect of discharge from season due to the low number of sampling dates.

Figure 5 shows the impact of treated sewage effluents on the variability of the river bed sediment phosphorus characteristics at different sampling dates. Sediment total phosphorus and BAP were very constant over time. Bioavailable phosphorus concentrations were higher downstream from the big STWs, but did not differ significantly between the ‘diffuse’ and ‘distant STW’ treatments (Figure 5). The proportion of organic matter content was low and did not show any significant temporal variability (0.6–2.6% sediment dry weight; Figure 5).

Total phosphorus in the water was linearly related to the sediment bioavailable phosphorus ($R^2 = 0.64$, $P < 0.001$; Figure 6A), but not to the sediment total phosphorus (Figure 7). The river bed sediment bioavailable phosphorus was significantly better predicted when using both river bed sediment and water total phosphorus concentrations as independent variables ($R^2 = 0.73$, $P < 0.001$; Figure 6B).

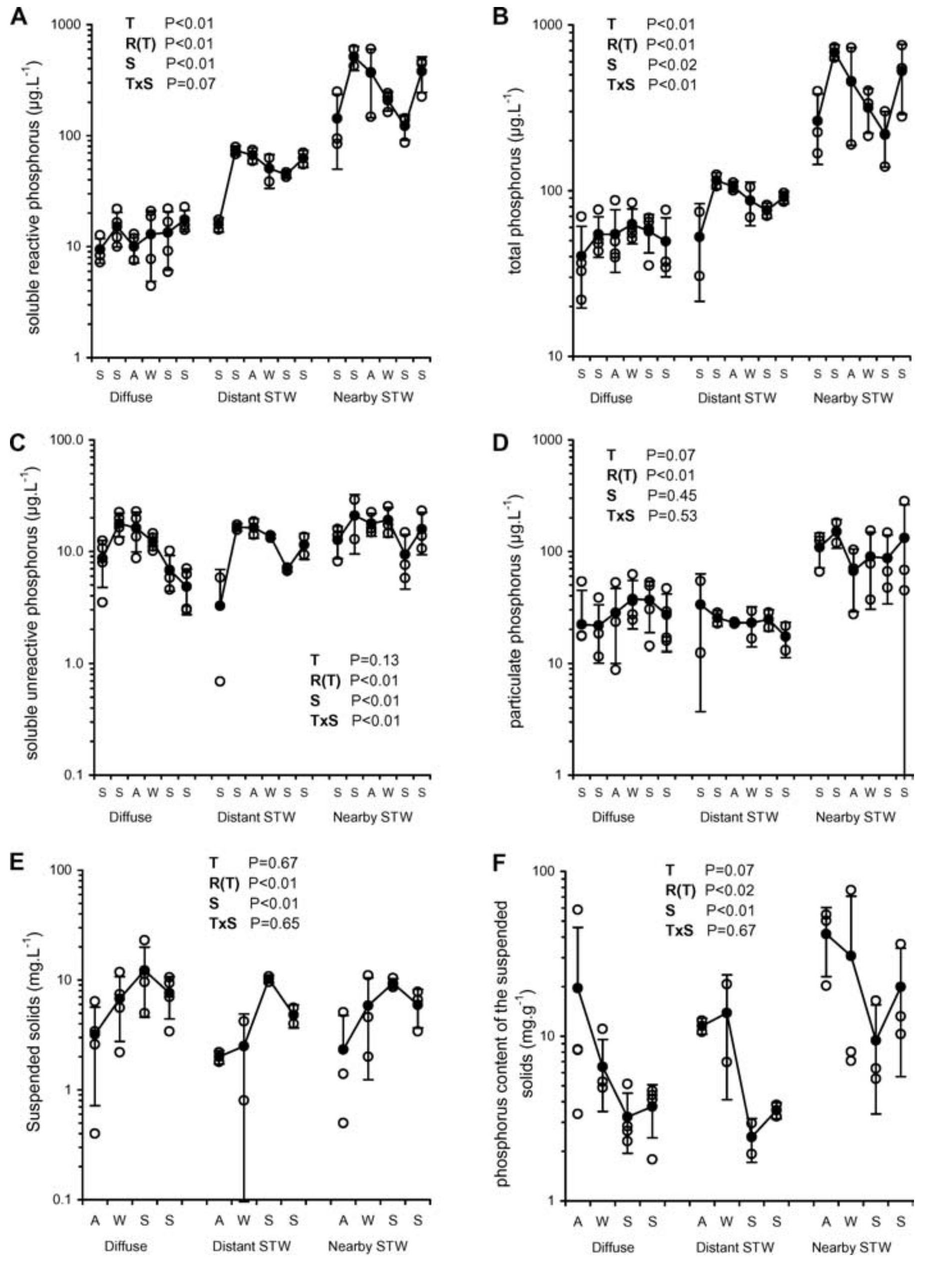


*Figure 4*. Mean ± standard deviation (filled circle with error bar) of water characteristics along a chronological seasonal sequence in year 2000–2001 (after implementation of phosphorus stripping) and across three treatments. A, autumn; W, winter; S, spring; S, summer; Diffuse, sites impacted only by diffuse sources; Distant STW, sites impacted by distant small point sources of pollution; Nearby STW, sites impacted by nearby effluents of large sewage treatment works (see Table I). Open circles represent individual samples. Inset represent the probability that the treatment T, sites within groups $R(T)$, time (S), and interaction factor treatment × time T × S differ.

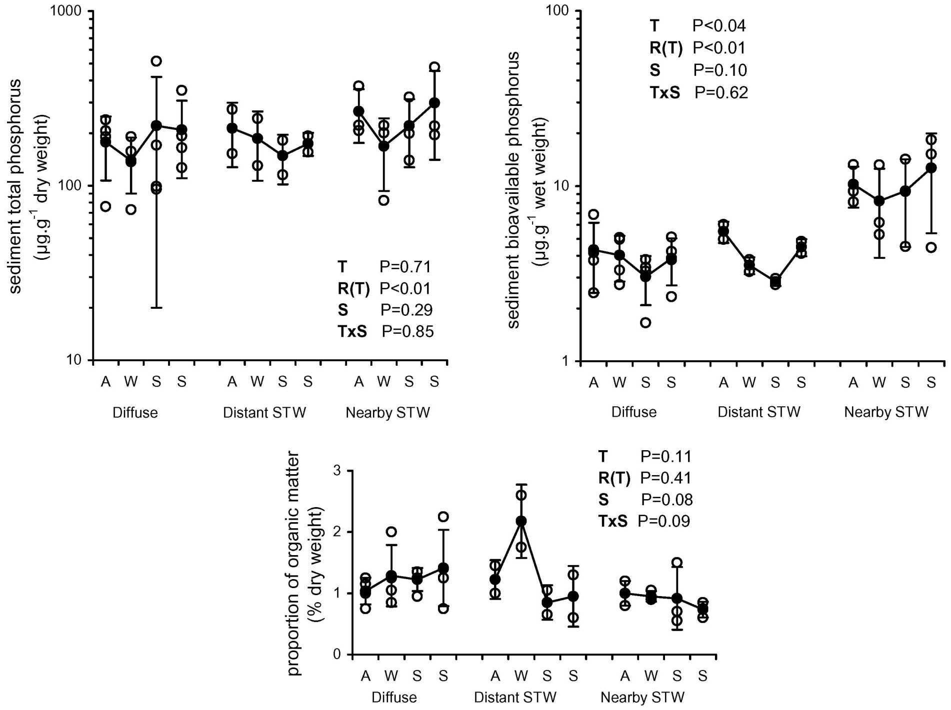


*Figure 5.* Mean ± standard deviation of sediment characteristics along a chronological seasonal sequence in year 2000–2001 (after implementation of phosphorus stripping) for three treatments in pebble/gravel/sand river beds. Same legend as Figure 4.

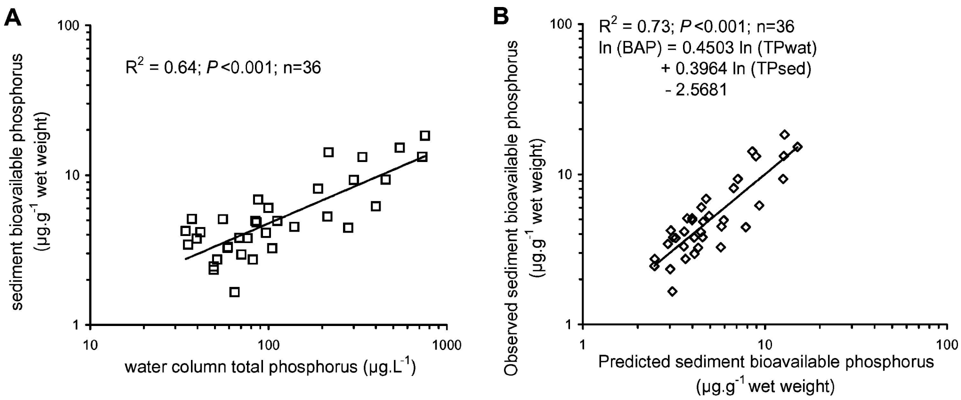


*Figure 6.* Sediment bioavailable phosphorus of pebble/gravel/sand river bed type can be predicted with the water and sediment total phosphorus fractions.

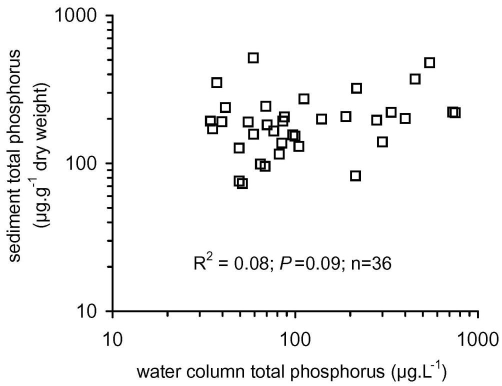


*Figure 7.* Sediment total phosphorus content of pebble/gravel/sand river bed type is not predicted by water total phosphorus concentrations.

### 4.2. Impact of phosphorus removal

The phosphorus stripping programme at the major STWs had a significant impact on the solution concentrations of total phosphorus below the effluent of Fakenham ($P < 0.01$) and East Dereham ($P < 0.04$). Similar results were observed when using phosphorus loads (kg day$^{-1}$ P) at Fakenham: the trend was highly significant ($P < 0.01$) for SRP but only marginally significant for TP ($P = 0.08$). SRP concentrations were still higher than 100 $\mu$g L$^{-1}$ below the STW effluents, after phosphorus stripping (Figure 8A and B). Figure 9 illustrates the change in TP loads expressed in kg day$^{-1}$ $P$ above and below Fakenham STW, before (1999) and after (2000–2001) phosphorus stripping. The control measures at Fakenham STW brought down, on average, the load of phosphorus coming from the STW by 64 $\pm$ 22%, as calculated from the source apportionment. This lead to an increase in proportion of the diffuse sources from $10 \pm 4$% to $27 \pm 7$%, although it was partly due to the high flow events of January and April 2001 (Figures 2 and 9).

In-stream BAP was not reduced at Fakenham ($P = 0.55$; Figure 8C). A trend was observed at East Dereham (Figure 8D) although it was not found to be significant ($P = 0.22$%).

## 5. Discussion

### 5.1. Water phosphorus concentrations

The concentrations of phosphorus in English lowland rivers only impacted by agricultural diffuse sources were not previously very well known. This study finds them to be lower than generally perceived, although existing studies have reported similar findings (e.g. Moss *et al.*, 1988). For comparison, the mean phosphorus

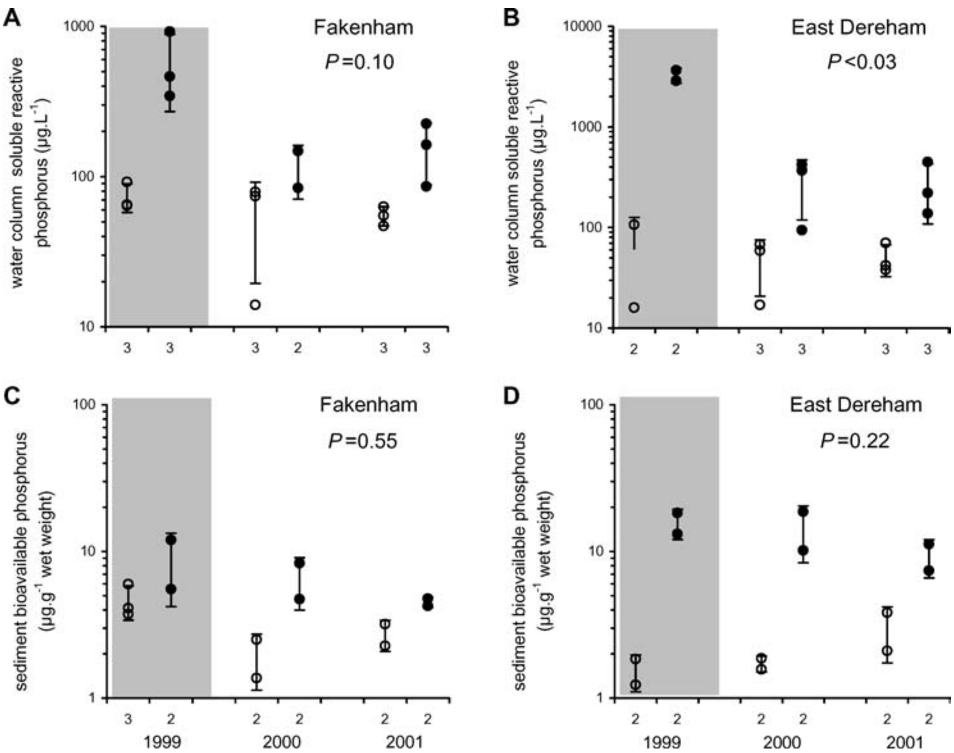


*Figure 8.* Water column soluble reactive phosphorus (A, B) and sediment bioavailable phosphorus (C, D) before (shaded area) and after phosphorus removal, above (open circles) and below (filled circles) Fakenham (A, C) and East Dereham STWs (B, D). The bars represent ± standard deviation. The probability $P$ represent the significance of phosphorus stripping on in-stream phosphorus concentrations. The number below the x-axis represent the number of samples.

concentration found in a catchment entirely of woodland was 4 $\mu$g L$^{-1}$ of soluble reactive phosphorus (SRP) and 40 $\mu$g L$^{-1}$ of total phosphorus (Warren House Stream, Moss *et al*., 1988); and the concentration of SRP from boreholes oscillated around 15 $\mu$g L$^{-1}$ (River Kennet; Neal *et al*., 2002). The source apportionment of the diffuse sources of the River Wensum, such as the different types of land use, remain to be quantified (see Johnes *et al*., 1996; May *et al*., 2001).

The temporal variability of SRP and TP concentrations was not significant for sites not impacted by point sources of pollution, although storm events were not monitored. During storm events a peak of total phosphorus generally occurs (e.g. River Cherwell; May *et al.*, 2001), mostly as particulate phosphorus bound to suspended solids (Harms *et al.*, 1978). But the relationship between PP concentration and discharge can be weak and complex (e.g. Kronvang, 1992; Svendsen and Kronvang, 1993; House *et al.*, 1998). Moreover, suspended solid concentrations were generally under 10 mg L$^{-1}$ and did not exceed about 100 mg L$^{-1}$ even under high flow events in the River Wensum (Edwards, 1971; Environment Agency,

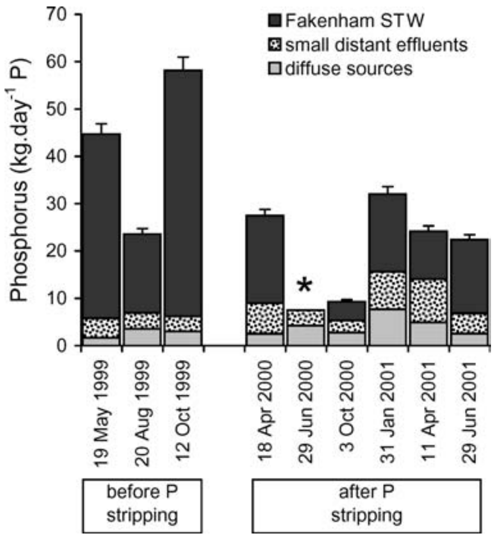


*Figure 9.* Phosphorus source apportionment before (1999) and after (2000–2001) phosphorus stripping at Fakenham STW. Phosphorus loads were based on TP concentrations and mean daily flow (see Figure 2). *Missing data.

unpublished data). This is much lower than other similar rivers (e.g. Kronvang, 1992).

As point source inputs increase, the SRP and TP concentrations are controlled more by discharge variability diluting the relatively constant phosphorus flux from the effluents (Edwards, 1973).

Soluble unreactive phosphorus concentrations were unaffected by the presence of point source effluents but responded strongly to the seasonality and to a less extend to run-off variability. It would suggest that SUP may be of diffuse origin and composed of organic polymers. These organic polymers may be altered by the STW effluents under particular seasonal or discharge conditions (T×S, $P < 0.01$). Further investigations on SUP's nature are required.

## 5.2. Phosphorus content of the suspended solids (PSS)

The PSS may be more related to the nature and structure (e.g. specific surface area, anion exchange capacity, organic material) of the suspended solids and to the origin of the particles (e.g. cultivated soils, river bank erosion) than to the impact of STWs (compare R(T) with T in Figure 4F). This is reinforced by comparing the present set of data with previous studies where the impact of STW effluents was not (or only weakly) detected (e.g. House and Denison, 1997, 1998; Owens and Walling, 2002). The total phosphorus bound onto the particles was generally more variable between sites and between rivers than upstream/downstream STWs (op. cit.). This was confirmed in this study were no substantial evidence of rapid adsorption of phosphorus onto suspended solids below the STWs were found ($P = 0.07$). This was particularly noticeable between sites 2 and 9 (see Table I).

PSS temporal variability may also reflect slow exchange dynamics. Indeed, the first sample collected followed an extended period of low flows and had high PSS; while the other samples, collected after several peak flows, generally had lower PSS. The lowest PSS could reflect the phosphorus content of the original material (derived from soils adjacent to the river) and the highest concentrations could reflect long term saturation under the observed SRP conditions (derived from remobilisation of in-channel particles and river bank erosion). Similar observations were previously reported (see e.g. House *et al.*, 1998). The difference between high and low PSS would therefore reflect the absorption capacity of fine sediment.

Fine suspended sediments are particularly relevant knowing that the phosphorus content of the suspended solids (range 2–77 mg $g^{-1}$) was one order of magnitude higher than the total phosphorus of the river bed sediments (range 73–516 $\mu$g $g^{-1}$, Figure 5) and that there is a 10 times temporal difference between low and high PSS. Sedimentation rates in the river Wensum may be particularly high in the riparian habitats and above the weirs in the impoundments of the old water mills where silt accumulates (Demars and Harper, 2002b). It suggests that fine sediments may play a significant role in river phosphorus dynamics, as found in other studies (e.g. Klotz, 1988) across a wide range of SRP concentrations. Indeed, $EPC_0$ and adsorption affinities of river bed sediment show a higher retention capacity of phosphorus by fine particles (silt and clay) rather than coarse material (Klotz, 1988; House and Warwick, 1999).

PSS temporal variability cannot just reflect differences in particle size mobilisation (hence phosphorus sorption affinity) because PSS in the autumn were much higher than PSS in the summer under similar discharge. The nature of the particles may change between seasons and explain this discrepancy as discussed above.

The highest values for the phosphorus content of the suspended solids seems extremely high (up to 7.7% of $P$). House and Denison (1998) also reported values up to 15–30% of $P$! These high values have been recorded downstream from STW effluents. It is not known what could be the nature of the phosphorus compound. In other studies the highest PSS values recorded did not generally exceed 5% (e.g. House and Denison, 1997; House *et al.*, 1998; Ernstberger *et al.*, 2004).

### 5.3. River bed sediment phosphorus concentrations

It was important that there was no significant differences in organic matter content of the river bed sediment. It showed that sediment samples were comparable. The sediment total phosphorus of this type of river bed (sand/gravel/pebble) was probably already saturated above the STWs as no significant differences were found between treatments. The lack of temporal variability of the phosphorus concentrations contrasts with previous temporal studies (House and Denison, 1997, 1998).

This study focused on a single river bed type with coarse granulometry, whereas House and Denison (1997, 1998) took several samples across the river channel and pooled them all together. The discrepancy is therefore probably due to differences in the type and size of bed sediment. The temporal variability may be observed in other river bed types such as vegetated patches and areas of low flow deposition (pools, riparian habitats) where there are more fine sediments. More samples would have to be collected to test the inter-annual variability of BAP above the STW effluents (Figures 8C and D).

The calcareous nature of the river led to further investigate the calcium content of the sediment at three seasons (autumn 2000, winter and spring 2001). A negative correlation was found between BAP and total calcium content of the sediments ($r = -0.42$, $n = 27$, $P < 0.03$; Demars, 2002). This might have suggested that calcite crystal-growth could be inhibited by high inorganic phosphate content (e.g. House, 1990). However there was no correlation between total phosphorus and total calcium content ($P > 0.3$). House and Denison (1997, 1998) did not detect calcium hydroxyapatite in the sediment of similar rivers, despite highly favorable thermodynamic conditions. Inorganic phosphate co-precipitation with calcite is generally not occuring in UK rivers (e.g. Neal, 2001). Phosphate adsorption onto iron hydroxides was implied in several studies covering a wider range of river bed types (e.g. Svendsen *et al.*, 1995; Demars and Harper, 2002b), however sediment analyses of the total iron (autumn 2000, winter and spring 2001) showed no correlation with sediment total phosphorus ($P > 0.2$; Demars, 2002).

### 5.4. Impact of phosphorus removal

The BACI design would have been strengthened with the addition of a co-variable (e.g. boron measurement – Neal *et al.*, 2000), to partial out the fluctuating phosphorus concentration of the STW effluent (see Harms *et al.*, 1978; Moss *et al.*, 1988), although this was stabilised by the implementation of the phosphorus removal (Demars, 2002, p. 88). The effects of control measures were predicatively more marked at East Dereham compared to Fakenham. East Dereham had a higher phosphorus stripping efficiency at the STW, four times smaller catchment, and a higher population equivalent than Fakenham. Three issues could undermine the sediment BACI study. First, there has been no measurement of in-channel sediment transport (Walling and Amos, 1999). Further, more intensive work using sediment tracer techniques should be undertaken to estimate the effect of sediment transport on BAP variability. Second, the limited number of samples collected weakened the power of the statistical test. However there was less analytical variability (17% for BAP) than differences between treatments (e.g. sediment BAP at East Dereham was 10 times higher below than above the STW effluent in year 1999). Moreover total phosphorus of the column water was alone a good predictor of sediment BAP ($r^2 = 0.64$). Third, hyporheic and groundwater inflows may influence the phosphorus dynamics in riffles (Hendricks and White, 1991).

The assumption that TP concentrations in non point-source impacted streams were constant appeared to be reasonable within the range of sampled flow events (see Figure 5). Despite the low number of samples, the $64 \pm 22\%$ phosphorus reduction calculated from the source apportionment based on in-stream phosphorus concentrations was very similar to the $69 \pm 6\%$ reduction calculated from independent data sets collected by Anglian Water plc. and the Environment Agency (unpublished data) at the outlet of Fakenham STW before and after phosphorus stripping. These give confidence and relevance to the estimation of the phosphorus source apportionment.

The relatively modest reduction of phosphorus at Fakenham STW, as well as the contribution of diffuse and small point sources of phosphorus is the most likely explanation for the lack of BAP decrease below Fakenham STW. The phosphate concentrations are indeed still much higher (Figures 8A and B) than the expected $EPC_0$ (House and Denison 1997, 1998; Cooper *et al.*, 2002) below the STW, and therefore there would have been no net sediment desorption.

## 6. Implications for Management

In the lowland calcareous rivers of Norfolk, average soluble reactive phosphorus concentrations are 4 $\mu$g L$^{-1}$ for a subcatchment entirely covered by woodland (Moss *et al.*, 1988), 9–15 $\mu$g L$^{-1}$ for subcatchments impacted by agriculture, and 577–3267 $\mu$g L$^{-1}$ just below Fakenham and East Dereham STW effluents respectively. The latter was reduced to 141–282 $\mu$g L$^{-1}$ after phosphorus stripping (Figure 8). The considerable increase of phosphorus concentrations with increasing anthropogenic impact is also accompanied by an increase of the SRP/TP ratio from 10% (catchment entirely covered by woodland, Moss *et al.*, 1988), to 27 $\pm$ 12 SD% (agricultural catchment), up to 80–90% (catchment impacted by STWs effluents) – Demars (2002). This means that there is more bioavailable phosphorus exported from the catchment, and a potential increase in the risk of eutrophication downstream, in floodplain standing waters, estuarine and coastal ecosystems. Similar results were reported from Scottish river catchment sampled under low flow conditions (Ernstberger *et al.*, 2004).

The impact of phosphorus stripping on the BAP may only become significant after a few years, although this is relatively improbable, due to the concentrations of SRP below the treated sewage effluents remaining high. Moreover, the coarse materials of the pebble/gravel/sand river bed type did not represent whole stream reaches and even less the catchment of the River Wensum, where aquatic macrophytes, in-stream riparian habitat, and the weirs associated with unused water mills, lead to high levels of siltation in the main channel and high phosphorus storage (Demars and Harper, 2002b). Another major problem is the large impact of small STWs scattered throughout the catchment (Figures 1 and 9; Muscutt and Withers, 1996; Demars, 2002; Demars and Harper, 2002a).

Further studies should now focus on the phosphorus dynamics of different river beds (e.g. silty *versus* gravelly) and apportionment of the phosphorus retention time in the biological and physico-chemical compartments of the ecosystem, and how these can be linked with potential management solutions (e.g. Wilcock *et al.*, 2002).

## 7. Conclusions

Point source effluents raised in-stream soluble reactive phosphorus concentrations from 9–15 $\mu$g L$^{-1}$ (agricultural subcatchments) to 577–3267 $\mu$g L$^{-1}$ (just below major STW effluents). This was also accompanied by an increase of the SRP/TP ratio. The phosphorus content of the suspended sediment (0.2 to 7.7%) was however more likely to be mostly related to slow dynamic processes and to the size and sorption affinity of the particles, rather than the change in soluble reactive phosphorus. Soluble unreactive phosphorus (1–29 $\mu$g L$^{-1}$) was surprisingly not affected by point source effluents. The river bed sediment bioavailable phosphorus concentrations were only higher (4–18 $\mu$g g$^{-1}$ wet weight) downstream from the main effluents, compared to upstream (2–6 $\mu$g g$^{-1}$ wet weight).

Phosphorus control at the STWs in 1999 immediately reduced the phosphorus loads in the column water but has had no significant impact on bioavailable phosphorus in the sediment by 2001. Soluble reactive concentrations below the treated effluents were reduced to 141–282 $\mu$g L$^{-1}$. Phosphorus control and also higher flow events lead to an increase in proportion of the diffuse sources from 10% to 27%.

The contributions from diffuse and numerous small point sources maintain high soluble reactive phosphorus concentrations ($>100$ $\mu$g L$^{-1}$) and so probably prevent net sediment phosphorus desorption and so make phosphorus control at the catchment scale problematic.

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