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Impact of phosphorus control measures on in-river phosphorus retention associated with point source pollution

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Abstract

In-river phosphorus retention alters the quantity and timings of phosphorus delivery to downstream aquatic systems. Many intensive studies of in-river phosphorus retention have been carried out but generally on a short time scale (2–4 years). In this paper, monthly water quality data, collected by the Environment Agency of England and Wales over 12 years (1990–2001), were used to model daily phosphorus fluxes and monthly in-river phosphorus retention in the lowland calcareous River Wensum, Norfolk, UK. The effectiveness of phosphorus stripping at two major sewage treatment works was quantified over different hydrological conditions. The model explained 78% and 88% of the observed variance before and after phosphorus control, respectively. During relatively dry years, there was no net export of phosphorus from the catchment. High retention of phosphorus occurred, particularly during the summer months, which was not compensated for, by subsequent higher flow events. The critical discharge (Q) above which net remobilisation would occur, was only reached during few, high flow events (Q_{25}–Q_{13}). Phosphorus removal from the effluent at two major STWs (Sewage Treatment Works) reduced the phosphorus catchment mass balance variability by 20–24% under the Q_{99}–Q_1 range of flow conditions. Although the absorbing capacity of the catchment against human impact was remarkable, further phosphorus remedial strategies will be necessary to prevent downstream risks of eutrophication occuring independently of the unpredictable variability in weather conditions.

1. Introduction

Many studies have investigated the increase in phosphorus loads with runoff in natural streams (Crisp, 1966; Hobbie and Likens, 1973; McColl et al., 1975; Rigler, 1979; Meyer and Likens, 1979) and in rivers dominated by point source pollution (e.g. Edwards, 1971, 1973; Johnson et al., 1976; Harms et al., 1978). Long term annual mass balance studies of phosphorus have highlighted the great variability of phosphorus retention at catchment scale (Meyer and Likens, 1979; Baker and Richards, 2002). A large proportion of the annual phosphorus loads may be exported during short periods of high flows, particularly after a long period of low flows, during which there is high retention of phosphorus (e.g. Dorioz et al., 1989).

These types of studies, however, are rare (but see Rigler, 1979; Cooke, 1988; Dorioz et al., 1989, 1998; Svendsen and Kronvang, 1993; Jordan-Meille et al., 1998a). Generally the sampling frequency has not been high enough to quantify phosphorus exports during storm events (e.g. Moss et al., 1988; Johnes, 1996a). Government agencies typically collect regular water samples over the long term, but cannot afford to routinely monitor storm events. There are therefore, large uncertainties associated with the calculation of loads (Rigler, 1979; Webb et al., 1997, 2000; Phillips et al., 1999a), unless models are constructed to simulate continuous data (e.g. Verhoff et al., 1982). Calculated phosphorus mass balances may therefore reflect methodological discrepancies rather than true retention (e.g. Moss et al., 1988). Refinements of the export coefficient approach (e.g. Vollenweider, 1968; Johnes, 1996b) have been suggested to allow calculations of monthly mass balances (May et al., 2001), but serious limitations have so far prevented this approach from providing a reliable estimate of phosphorus retention.

Sophisticated models are now being used to simulate daily fluxes of phosphorus from different sources (e.g. Cooper et al., 2002a; Grizzetti et al., 2003). The estimates of phosphorus retention are still reliant, however, on measured TP (Total Phosphorus) loads at the catchment outlet (e.g. Grizzetti et al., 2003). This is because some critical processes such as floodplain sediment deposition during overbank flow events have not yet been modelled adequately. Power laws have been extensively used in geomorphology and hydrology to derive simple models (e.g. Knighton, 1998): these have been explored further to model phosphorus loads (e.g. Edwards, 1973; McColl et al., 1975) and phosphorus retention (e.g. Behrendt and Opitz, 2000). Uncertainties could then easily be propagated throughout the calculations of the loads, something which is seldom reported.

Nearly all european rivers drain populated areas, so the need to understand the contribution from both diffuse and point source pollution has long been recognised (e.g. Owen and Wood, 1968; Edwards, 1971). In England, point source pollution is the major source of phosphorus for most rivers (Muscutt and Withers, 1996). In-channel retention capacity can buffer, to some extent, the impact of point source phosphorus loads (Keup, 1968; Johnson et al., 1976; Harms et al.,1978; Moss et al.,1988; Haggard et al., 2001; Cooper et al., 2002b; Marti et al., 2004). Many published phosphorus budgets showed that annual inputs were higher than annual exports (Owen and Wood, 1968; Edwards, 1971, 1973; Moss et al., 1988; Johnes, 1996a). This is not the case however, in rivers where all the phosphorus retained in the river bed under low flow conditions is flushed during storm events, particularly during the autumn (Harms et al., 1978; Dorioz et al., 1989, 1998; Svendsen and Kronvang, 1993). There is thus an important difference in phosphorus dynamics between river systems, between years (Svendsen and Kronvang, 1993) or even along the longitudinal continuum of a single basin (Bowes et al., 2003). There has been growing pressure in Europe to decrease phosphorus inputs from point sources (Demars and Harper, 2002a) and many phosphorus control measures have been implemented to protect dowstream lake ecosystems (e.g. Harper, 1992, Phillips et al., 1999b). Despite this, the runoff regime has remained a dominant control on phosphorus retention in natural and rural catchments (e.g. Meyer and Likens, 1979; Dorioz et al., 1989) and little effort has been made to estimate the impact of phosphorus control measures on in-river phosphorus retention over a range of flow conditions (but see Cooper et al., 2002a).

The objectives of this study were to develop:

1. a simple model based on power laws to quantify daily phosphorus fluxes from background loads and point sources at the catchment scale,

2. monthly calculations of phosphorus mass balance at catchment outlet with associated uncertainties, and

3. a clear representation of the impact of phosphorus removal over a range of flow conditions.

2. Material and methods

2.1. Study area

The River Wensum (Norfolk, UK) drains a 570 km^2 rural catchment of Upper Chalk solid geology overlain by quaternary deposits (chalk boulder clay; glacial sand and gravel). The catchment area does not rise above 95 m OD. The rural landscape is dominated by pasture and arable fields, although scattered woodland still remains. The dominant industries are malting and poultry processing. The River Wensum is consequently rich in nitrate and phosphorus, but does not seem to be much impacted by other sources of pollution (Robson and Neal, 1997). Average annual rainfall is 672 mm $year^{-1}$. The hydrograph displays a damped response to rainfall events due to the catchment permeability and runoff storage in the chalk aquifer. This is reflected by a base flow index of 0.73 at Costessey Mill (Institute of Hydrology, 1992). The effects of water abstraction on discharge did not exceed a maximum of 14% (generally 2–6%) loss of mean weekly flows in the summers for the period 1971–1992 (Hiscock et al., 2001). The river channel has been substantially modified over the past centuries: impoundments and weirs were created to operate water mills for the grinding of flour. 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). The aquatic flora is very diverse and the river constitutes a prime example of a *Ranunculus*-dominated calcareous lowland river under the European Habitats Directive (92/43/EEC). More information can be found in Baker et al. (1978), Baker and Lambley (1980), Boar et al. (1994), Demars (2002), Demars and Harper (2002a, b).

2.2. Phosphorus loads associated with diffuse sources

The TP concentration of four streams impacted by diffuse sources only, excluding septic tank leakage, were monitored in 2000–2001 (Fig. 1, sites 1–4). Assuming that this would represent a typical concentration for the whole catchment area of the River

Wensum in the absence of point source effluents, this TP concentration was used to calculate the TP loads associated with diffuse sources at Costessey Mill (Fig. 1, site 5 – NGR TG 177 128). The mean TP concentration was 53 (±18) $\mu g\,L^{-1}$ (Demars, 2002).

2.3. Phosphorus loads derived from point source effluents

The spatial distribution of the point source effluents are displayed in Fig. 1. The Environment Agency (EA) monitored the total reactive phosphorus (TRP) of most STWs' final effluents between July 1993 and May 1996 to calculate the mean concentration of total reactive phosphorus (TRP). All the phosphorus analyses carried out for this study were based on Murphy and Riley (1962). The TRP was converted to TP based on a TRP/TP ratio of 0.85 (Anglian Water Services data), which is very similar to previous studies (e.g. Harms et al., 1978). The loads were estimated with the derived mean flow (from the population equivalent or dry weather flow), but if neither was available, from the consented maximum daily flow. The STW effluents from a population equivalent (p.e.) of more than 500 collected the wastewater of 98% of the population connected to treatment plants; the phosphorus load was 1.86±0.36 g capita^{-1} day^{-1}, similar to STW effluents of the Great Ouse and Bure catchments (Owens, 1970; Moss et al., 1988). For the unmonitored STW effluents an estimate per population equivalent (p.e.) was derived from the mean of all discharges from works with a p.e. less than 500, to calculate the loads.

Industrial effluent loads were estimated from the monitored (July 1993 to May 1996) mean TP concentrations (derived from mean TRP) and consented maximum daily flow (first scenario). This was likely to produce an over-estimate, as most discharges do not run at maximum flow. Another scenario based the calculation on 50% consented maximum daily flow. The loads for these point sources were revised from those previously published in Demars and Harper (2002a, p. 36). Table 1 provides the TP load characteristics for STWs (>500 p.e.). Uncertainty of the point source TP loads was estimated as the weighted sum of the uncertainty of the individual effluents.

Removal of phosphorus by chemical precipitation with an iron salt started at two major STWs in autumn-winter 1999, following the technique adopted previously in the restoration of the Norfolk Broads (Harper, 1992; Thomas and Slaughter, 1992). Prior to this only primary (retention of coarse particles) and secondary (biological oxidation) treatments had been in operation at these STWs. The reduction of total phosphorus achieved (outlet/inlet of the STWs) was optimized at 77±9% for Fakenham (13439 p.e.) and 88±4% for East Dereham (17475 p.e., Demars, 2002). Near the outlet of the catchment (Costessey Mill, Fig. 1) the loads from point source effluents consequently decreased from 130 (±29) kg day^{-1} to 82 (±18) kg day^{-1}, assuming that industrial effluents were running at consented maximum flows, or 107 (±23) kg day^{-1} to 60 (±12) kg day^{-1}, with load calculations based on 50% consented maximum flows for industrial effluents. TP concentrations of the final effluent stabilised at about 3.5 mg L^{-1} at Fakenham STWs and 2.0 mg L^{-1} at Dereham, after phosphorus stripping. Further treatment facilities would be required at these STWs to achieve greater phosphorus stripping efficiency without compromising the existing sanitary consents. Anglian Water Services (AWS) provided the phosphorus concentrations (total and soluble) of the crude sewage and final effluent of the two qualifying discharges (Fakenham and East Dereham STWs) before and after phosphorus removal. Further details can be found in Demars (2002) and Demars and Harper (2002a).

2.4. Observed loads at Costessey Mill

River phosphorus has been monitored monthly by the EA since January 1990 and fortnightly since March 2000 at Hellesdon Mill (NGR TG 198 104), about 4 km downstream from Costessey Mill, and above the confluence with the River Tud (Figs. 1–2a). The discrepancy in catchment area between the gauging station (Costessey Mill) and the water quality monitoring station (Hellesdon Mill) was less than 2% and thus was neglected. Observed loads were estimated from the phosphorus concentration and mean discharge at the site on the day of sampling. Different phosphorus determinants were supplied by the Environment Agency over time: TRP from non-filtered samples for the whole period 1990–2001; soluble reactive phosphorus (SRP) from filtered samples for 2000–2001; and also TP for 1995–1996 and 2000–2001. An investigation of the quality of the data revealed that on several occasions TRP concentrations were much higher than TP concentrations. This is likely to be due to analytical problems (see Neal et al., 2000; Jarvie et al., 2003). The relative uncertainty of the observed TRP concentration was about 20%. The TRP concentrations were transformed into TP concentration using the TRP/TP ratio calculated from available data. The TRP/TP ratios were 0.8 and 0.7 before and after phosphorus control, respectively with a 15% relative uncertainty.

2.5. Discharge data at Costessey Mill

The full run of data from the gauging station at Costessey Mill still need to be processed by the EA in order to account for gate movements upstream of the gauging station (EA, personal communication). There are many gaps in the record, particularly in recent years, and anomalous flow sequences. The long term mean daily flow hydrographs at the three gauging stations in the catchment (Fakenham, Swanton Morley and Costessey Mill) however, showed that the flow data at Costessey Mill were of good quality for the period 1990–1994. Costessey mean daily discharge (Q_{571}) for the period 1995–2001 was estimated using Swanton Morley mean daily discharge (Q_{398}) and after correction for differences in catchment area (A) and one day time lag (τ):

$$\frac{\partial Q_{571}}{\partial t} = \frac{\partial Q_{398}}{\partial t-\tau} \cdot \left(\frac{A_{571}}{A_{398}}\right) \tag{1}$$

with numbers in subscript representing the catchment area (km^2).

3. Theory

In-stream TP loads (kg day^{-1}) measured in sub-catchments free from point source pollution were used to calculate background loads (B) representing diffuse source pollution. As the loads were derived from those actual in-stream measurements, they

HESSD

2, 37–72, 2005

Impact of phosphorus control measures

B. O. L. Demars et al.

integrate both the degree of phosphorus pollution in the catchment and the biochemical processes in the floodplain, riparian zone and in-stream affecting these loads. In catchments impacted by point source effluents, in-stream TP loads (kg day^{-1}), were estimated as follows:

$$TP = B + r \sum_j P_j, \qquad (2)$$

where r is a coefficient of TP retention ($r<1$) or remobilisation ($r>1$) representing catchment processes associated with the sum of the point source inputs (P_j in kg day^{-1}). These processes include phosphate adsorption/desorption within the river bed, sedimentation/transport of particles and biological uptake/release. This model allows the assessment of the relative proportion of background (diffuse) loads and point sources contributing to the TP loads. It also allows the study of the impact of point source phosphorus control measures on retention. Assuming that B and r can adequately be estimated with hydrological power laws, then:

$$B = aQ^b \qquad (3)$$

with a and b coefficients representing the background loads under variable discharge (m^3 s^{-1}) conditions; and

$$r = cQ^d, \qquad (4)$$

where c and d are coefficients representing the phosphorus retention/remobilisation associated with P_j under varying discharge (m^3 s^{-1}) conditions. Equation (2) can be re-written as follows, after substition of B and r by Eqs. (3) and (4), respectively:

$$TP = aQ^b + cQ^d \sum_j P_j. \qquad (5)$$

Calculation of the TP mass balance, R (kg), then estimates the phosphorus dynamics of the system associated with the sum of the point source inputs:

$$R = \left(aQ^b + cQ^d \sum_j P_j\right) - \left(aQ^b + \sum_j P_j\right). \quad (6)$$

With $R<0$, there is a net retention of TP. With $R>0$ there is a net remobilisation of TP. At equilibrium, it follows from Eq. (6), that the critical discharge under which there is neither TP retention nor remobilisation is:

$$\Leftrightarrow Q = \left(\frac{1}{c}\right)^{\frac{1}{d}}. \quad (7)$$

The retention parameters (c, d) were calibrated for the periods preceding and following phosphorus control measures at point sources to work out the impact of phosphorus stripping on retention (R). Because the hydrological conditions are unlikely to be identical in these two periods, it was necessary to standardise R with the discharge to make the data comparable. The variability of discharge was best represented by a flow duration curve built using long term data sets of the mean daily discharge. The x-axis represents the percentage of time the discharge is exceeded (e.g. Q_{95} is the flow which was exceeded for 95% of the time) and the y-axis represents Q. R was then calculated for each Q corresponding to a known percentage of time flow exceeded. This allowed the degree of phosphorus retention (or remobilisation) after phosphorus control to be predicted. The impact of phosphorus control, C, on the phosphorus retention variability over the range Q_{99}–Q_1 was then calculated as follows:

$$C = 1 - \frac{R_{Q1}^{\text{after}} - R_{Q99}^{\text{after}}}{R_{Q1}^{\text{before}} - R_{Q99}^{\text{before}}}. \quad (8)$$

4. Results

4.1. Calibration

The mean daily discharges at Costessey Mill predicted from Swanton Morley gauging station were regressed against the observed mean daily discharge data at Costessey Mill for the period 1990–1994. The relationship was very tight (r^2=0.926).

The coefficients of the mass balance model were calibrated against observed data by regressing TP loads (kg day^{-1}) from sub-catchments not polluted by point sources against discharge (m^3 s^{-1}). The regression coefficient, a, was 4.58 (±1.64) linking the background TP concentration (53±18 μg L^{-1}) directly to discharge. The coefficient b was determined by assessing its potential range. The theoretical minimum was 1 and the observed maximum was 1.4 where B slightly exceeded the observed TP export of the highest flow events at the outlet of the catchment. The median value 1.2 (±0.1) was adopted. The background loads were therefore calculated as follows:

$$B = 4.58Q^{1.2}.$$

The coefficients c and d were then determined by iteration so that the regression line between observed and predicted loads at Costessey Mill had a slope equal to one (±0.01) and an intercept equal to zero (±0.01). This process was repeated for each period, i.e. before (c=0.315; d=0.60452) and after (c=0.2248; d=0.76569) phosphorus control assuming that industrial effluent discharge was at the consented maximum. The model explained 78% and 88% of the observed variance before and after phosphorus control, respectively. The coefficients c and d were also determined with load calculations based on 50% consented maximum flows for industrial effluents, again both before (c=0.38; d=0.6036) and after (c=0.307; d=0.7635) phosphorus control.

4.2. Error propagation

Errors have been reported as absolute uncertainties (standard deviation δx) or relative uncertainties ($\delta x/x$). Table 2 reports the error associated with the coefficients and parameters for the period 1990–1999. The uncertainties in c and d only relate to errors derived from calculations. The high error associated with a is largely due to the high variability of the background TP concentrations: 53±18 μg L^{-1}. These errors were then propagated throughout the calculations as follows for additions and subtractions: $\delta(x \pm y)=[(\delta x)^2+(\delta y)^2]^{1/2}$; multiplications: $\delta(xy)/xy=[(\delta x/x)^2+(\delta y/y)^2]^{1/2}$ and power coefficients: $\delta(x^n)/(x^n)=n(\delta x/x)$. The above error propagations for additions and multiplications assumed that the uncertainties of x and y are independent and so may partially cancel each other out. This was not the case when the daily R was summed to provide monthly R (Fig. 2c and 2d) or when monthly TP retention was cumulated over the whole study period (Fig. 3). In these cases the daily errors were simply added.

4.3. Mass balance

The daily input loads dramatically exceeded the daily output loads under low flow conditions, which are a common feature of the summer months. This was true for both scenarios (Figs. 2b, 2c, and 2d). There was therefore an accumulation of phosphorus in the river system and this was not compensated by remobilisation during autumn higher flow conditions under either scenario (Figs. 3a and 3b).

The drop in input loads in early 2000 (Fig. 2b) resulting from phosphorus removal was reflected in the annual loads, although the decrease in point source inputs was compensated by an increase in diffuse sources (Fig. 4). Both scenarios generated similar annual mass balances, although the second scenario (industrial effluent TP loads based on 50% consented maximum daily flow) showed significantly lower phosphorus retention (Fig. 4). From Figs. 2–4, it is therefore not clear what proportion of the resulting mass balance in the period 2000–2001 was due to phosphorus control or to different weather conditions.

Figure 5 shows the change in phosphorus mass balance due to phosphorus control over a range of mean daily flow conditions (Q_{99}–Q_1), based on the flow duration curve derived from the studied period (1990–2001). Phosphorus control reduced the phosphorus retention at Q_{99} from −95 to −67 kg day^{-1} and reduced phosphorus remobilisation at Q_1 from 86 to 70 kg day^{-1} (Fig. 5a). Uncertainties were very large under high flow conditions. The critical discharges above which net remobilisation would occur were 6.77 m^3 s^{-1} (Q_{14}) and 7.02 m^3 s^{-1} (Q_{13}) before and after phosphorus control, respectively, when industrial effluent loads were calculated with consented maximum daily flows (equation 7; Fig. 5a). These represent relatively high flow conditions. The range of variability of phosphorus retention at Q_{99} and Q_1 enabled the impact of phosphorus control C (Eq. 8) to be calculated: C=1-(181/138)=0.241. Phosphorus control therefore buffered the phosphorus mass balance variability by 24% over the Q_{99}–Q_1 range (Fig. 5a).

The critical discharges for the other senario (industrial effluent TP loads based on 50% consented maximum daily flow) were 4.97 m^3 s^{-1} (Q_{25}) and 4.70 m^3 s^{-1} (Q_{27}) before and after phosphorus control, respectively (Fig. 5b). These represented more moderate flow conditions. Under this scenario phosphorus control buffered the phosphorus mass balance variability by 20% over the Q_{99}–Q_1 range (Fig. 5b).

5. Discussion

5.1. Model: assumptions and uncertainties

The determination of TP background concentration in small subcatchment unimpacted by point sources is assumed to represent the background concentrations for the larger catchment. The observed high variability in TP concentrations between subcatchments may be due to differences in land-use (e.g. Vollenweider, 1968), cattle poaching in the riparian zone or undetected small point sources such as septic tank leakage. This approach may not be appropriate when subcatchments unimpacted by point sources are several orders of magnitude smaller than an entire catchment (Kirchner, 1975), when it is heterogeneous (Bowes et al., 2003), or when such subcatchments may not exist in heavily populated areas (Cooper et al., 2002a).

The use of fixed TRP/TP ratios for each period (before and after phosphorus stripping) was a simplification. The concentration of particulate phosphorus (PP) is known to increase during storm events (e.g. Harms et al., 1978), but the relationship between PP and discharge is generally weak and complex (e.g. Meyer and Likens, 1979; 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 (Fig. 6; Edwards, 1971).

It may seem slightly surprising that phosphorus load per capita (1.86±0.36 g capita^{-1} day^{-1}) was similar to STW effluents of the Great Ouse and Bure catchments (Owens, 1970; Moss et al., 1988) given that there has been a general assumption that per capita phosphorus loads have reduced since the 1970s as a result of lower phosphorus detergents. However it is possible that this is negated by industrial sources of phosphorus being treated at these STWs.

During storm events there is an hysteresis of the TP concentration – discharge relationship in rivers, a time lead of the chemograph compared to the hydrograph (e.g. Cahill et al., 1974) or an exhaustion of TP concentrations before the hydrograph peak (Dorioz et al., 1989, Svendsen and Kronvang, 1993). This is the consequence of several related factors (Meyer and Likens, 1979; Rigler, 1979; Jordan-Meille et al., 1998b). It could have been implemented in the model (see Webb et al., 2000) but its impact on monthly TP mass balance is deemed to be negligible. The hydrological conditions preceding the storm events may actually be more important than the magnitude of the storm event itself for TP flux (Dorioz et al., 1989, 1998; Svendsen and Kronvang, 1993; Jordan-Meille et al., 1998a). However, there were not enough data to investigate the impact of peak flows on TP export in different seasons. Since the calibration of the model was good (r^2 ≥0.8), this effect may not be so pronounced in the River Wensum catchment.

Power law relationships have been successfully applied to the calculation of TP loads (e.g. McCall, 1975; Webb et al., 2000), and to relate phosphorus concentrations with discharge (Edwards, 1973; Dorioz et al., 1989; Kronvang, 1992; Demars, 2002). This is not to say that they are always the most appropriate (see e.g. Meyer and Likens, 1979). Rather it was a means in this study to simplify the reality and extract as much information as possible from the monitoring datasets collected by a governmental organisation (EA) and a private water company (AWS) (see Verhoff et al., 1982).

Industrial effluent loads were estimated from consented maximum daily flow and this is likely to produce an over-estimate, as most discharges do not run at maximum flow. The sensitivity of phosphorus retention to industrial phosphorus discharge was investigated using 50% consented maximum daily flows. Further work should therefore quantify the outflow discharge of industrial and small STW effluents to better quantify their contributions to the total budget. This stresses how important it is to quantify uncertainties. Here the model was calibrated but could not be validated against an independent dataset because of lack of data. In more sophisticated models, sensitivity analysis must be carried out (see e.g. Cooper et al., 2002a) and the fit of the model must be reported (see e.g. Grizzetti et al., 2003).

5.2. Phosphorus retention

One of the striking results of this study is that large retention occurred during the dry seasons which was not even slightly compensated by high flow events. There are several processes leading to phosphorus retention in river basins: adsorption onto suspended particles (House et al., 1995) or fine sediments (Klotz, 1988; House and Warwick, 1999), siltation in impoundments above the weirs and in macrophyte patches and riparian habitats (Svendsen and Kronvang, 1993; Demars and Harper, 2002b) and floodplain deposition during overbank flow events (Walling, 1999). Phosphorus co-precipitation with calcium is likely to be negligible (Neal, 2001; Demars and Harper, 2002b). From the numerous studies that have quantified the phosphorus uptake by aquatic plants, it can be concluded that the biological transient storage of phosphorus by these primary producers is negligible (<1% of TP flux) in the Wensum catchment (see Westlake, 1968; Ladle and Casey, 1971; Svendsen and Kronvang, 1993; House et al., 2001). Some phosphorus is removed from the channel when the impoundments above the weirs are dredged or during the EA's weed cutting programme. However these operations are limited to small sections of the main river channel (EA, personal communication). One major sink of phosphorus is likely to be overbank floodplain sedimentation during high flow events (Malanson, 1993; Walling, 1999; Owens et al., 2001; Bowes and House, 2001; Tockner et al., 2002). Walling (1999) estimated that on average 40% of the sediment budget of UK rivers are deposited on the floodplain. Since floodplain retention is a long term sink (10^2–10^4 years) in UK rivers due to low rates of bank erosion (Walling 1999), it would explain the lack of remobilisation observed under high flows at the outlet of the River Wensum catchment. The lack of remobilisation is due to the low water power of lowland rivers further reduced by the reduction of slope by impoundments and the high energy loss at the weirs associated with the water mills. Sedimentation upstream of the weirs may be another significant sink.

Intensive studies have shown that the majority of the total annual phosphorus load is exported out of a catchment during the highest flow events (e.g. Johnson et al., 1976; Meyer and Likens, 1979; Rigler, 1979; Cooke, 1988; Jordan-Meille et al., 1998a). This may not be the case however, in populated lowland rivers. There is generally a large retention of phosphorus (coming from point sources) by the river bed during low flow conditions, as observed in many studies of populated river catchments (e.g. Harms et al., 1978; Dorioz et al., 1989, 1998; Svendsen and Kronvang, 1993), although the sediment adsorption capacity can become saturated (e.g. Marti et al., 2004). Floodplain processes, and net built-up of phosphorus in the sediment above the weirs, are likely to be responsible for the discrepancy in phosphorus export observed in previous studies (e.g. Moss et al., 1988; Johnes, 1996a).

5.3. Climate variability and phosphorus control measures

Many studies have produced graphs to show catchment phosphorus retention variability with increasing discharge (Duffy et al., 1978; Meyer and Likens, 1979). Others have plotted phosphorus export against flow duration curves (Johnson et al., 1976). In this study the TP mass balance was plotted against the flow duration curve before and after phosphorus removal at the two STWs. This had the advantage of clearly illustrating the impact of phosphorus control, after taking into account the impact of discharge variability (see Fig. 5). The critical discharge above which there is a net remobilisation of phosphorus did not change much after phosphorus control. This result was unsurprising because discharge drives the sedimentation and dilution processes that are largely responsible for phosphorus dynamics at the catchment scale. Phosphorus stripping at the STWs has buffered TP retention variability, although the buffering capacity fluctuates with climate variability. The impact of phosphorus control measures on TP retention is greatest under extreme events (long drought or storm events) and least under critical flow conditions (see Fig. 5).

5.4. Management implications

This study indicated that in lowland, low gradient rivers such as the Wensum there is a remarkable degree of phosphorus retention within the catchment, but this does not negate the need to control anthropogenic phosphorus inputs to the system. In the past, biological effects of eutrophication have been particularly pronounced in this river during low flow years. Actions to ensure that designated habitats remain in, or are restored to, favourable condition, need to be taken on a catchment-wide basis, and should ideally be informed by an improved understanding of both the short and long-term dynamics of the system .

Significant financial investment has been required of the water industry, which at Fakenham STW has allowed further phosphorus removal, down to $<1\,\text{mg}\,\text{L}^{-1}$ P in the final effluent, since the completion of the present study. This work now has tertiary phosphorus removal using sand filters with integrated ferric sulphate injection. A similar scheme at East Dereham STW is under construction and will soon be meeting the same levels of phosphorus removal. In a move towards a more catchment-based eutrophication control plan, phosphorus removal has also been initiated at the major industrial input to the river, a poultry processing plant, reducing typical effluent concentrations from ca. 12 mg L^{-1} P to <1 mg L^{-1} P. The impact of these substantial reductions in P inputs from the major point sources in the catchment should now be assessed, alongside the remaining contributions from small STWs and diffuse agricultural inputs, in order to inform future management and investment decisions.

6. Conclusions

High in-channel retention of phosphorus occurred during the summer period under low flow conditions. This retained phosphorus did not appear at the catchment outlet during subsequent high flow events. It was inferred that the floodplain together with impoundments above the weirs associated with water mills constituted long term sinks (and potentially long term sources) of phosphorus coming from point sources. The absorbing capacity (*sensu* Zalewski and Harper, 2001) of the catchment against human impact was remarkable. Further studies should now focus on the quantification of the sedimentation processes.

The TP loads at the outlet of the catchment were not much lower after phosphorus control measures. This was mainly due to an increase in background TP loads during wet years. This study devised a system to calculate the impact of point source phosphorus control measures for any given runoff (climatic condition). The phosphorus removal at two major STWs allowed the reduction of the TP catchment mass balance variability by 20–24% under the Q_{99}–Q_1 range of flow conditions. This study makes it clear that further phosphorus remedial strategies would be necessary to reduce downstream risks of eutrophication.

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Table 1. Summary statistics of the main sewage treatment works (>500 p.e.) of the River Wensum catchment. The relative uncertainties of the total phosphorus (TP) loads are noted $\delta x/x$. * before phosphorus control measures.

STWs effluents	NGR	TP kg day^{-1}	$\delta x/x$ (%)	p.e.	g capita^{-1} day^{-1}
Bylaugh	TG 036 183	5.26	22.5	2913	1.81
East Rudham	TF 835 285	1.15	19.5	560	2.05
East Dereham*	TF 977 135	33.33	21.9	17 475	1.91
Fakenham*	TF 921 289	30.17	15.0	13 439	2.25
Foulsham	TG 026 243	1.57	25.1	998	1.57
North Elmham	TF 998 213	2.06	22.5	1122	1.84
Reepham	TG 104 227	7.58	18.1	4017	1.89
RAF Sculthorpe	TF 833 312	1.78	27.4	1089	1.64
Swanton Morley	TG 013 183	0.90	19.9	502	1.80

Table 2. Relative uncertainties of the coefficients and parameters of the phosphorus mass balance model, with industrial phosphorus load calculations based on consented maximum daily flows.

	$\delta x/x$ (%) 1990–1999	2000–2001
a	35.89	35.89
b	8.33	8.33
c	0.03	0.04
d	0.02	0.01
Q	10.00	10.00
P	22.60	22.07

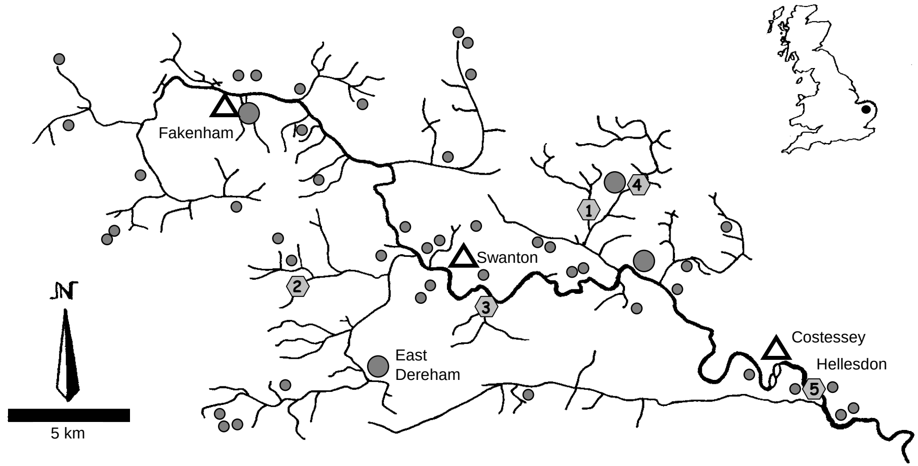

Fig. 1. Water quality monitoring sites (1–5), gauging stations (Δ) and point source effluents (filled circles) of the River Wensum, Norfolk, UK.

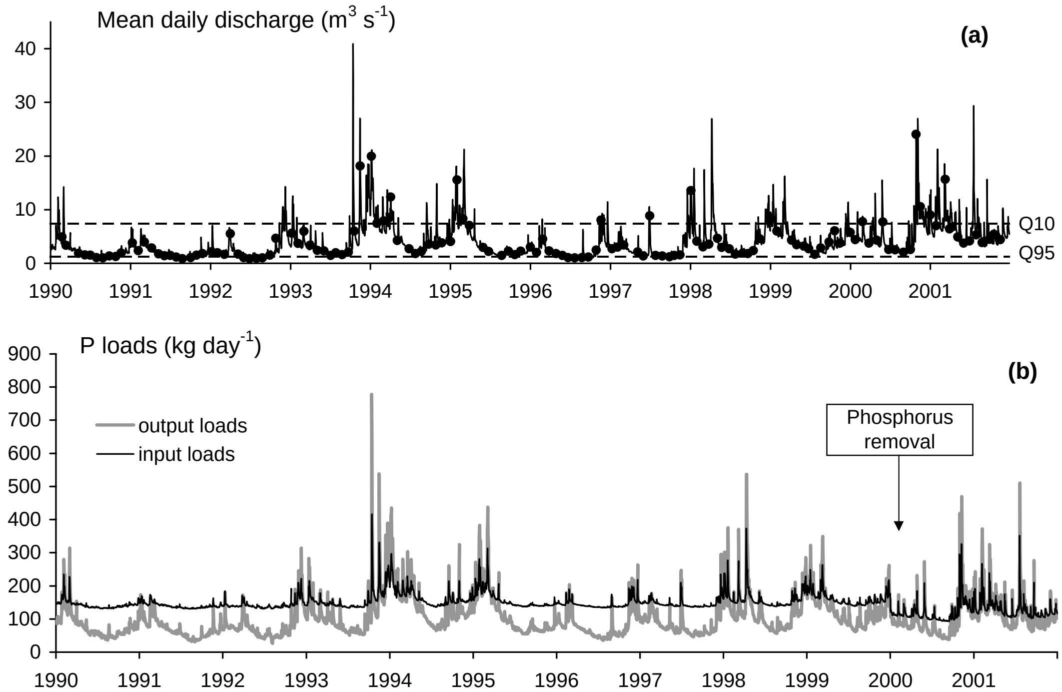

Fig. 2. **(a)** Mean daily discharge and sampling dates, **(b)** modelled daily inputs and outputs of phosphorus loads, **(c)** monthly phosphorus mass balance with industrial phosphorus load calculations based on consented maximum daily flows, and **(d)** monthly phosphorus mass balance with industrial phosphorus load calculations based on 50% consented maximum daily flows. Bars represent uncertainties.

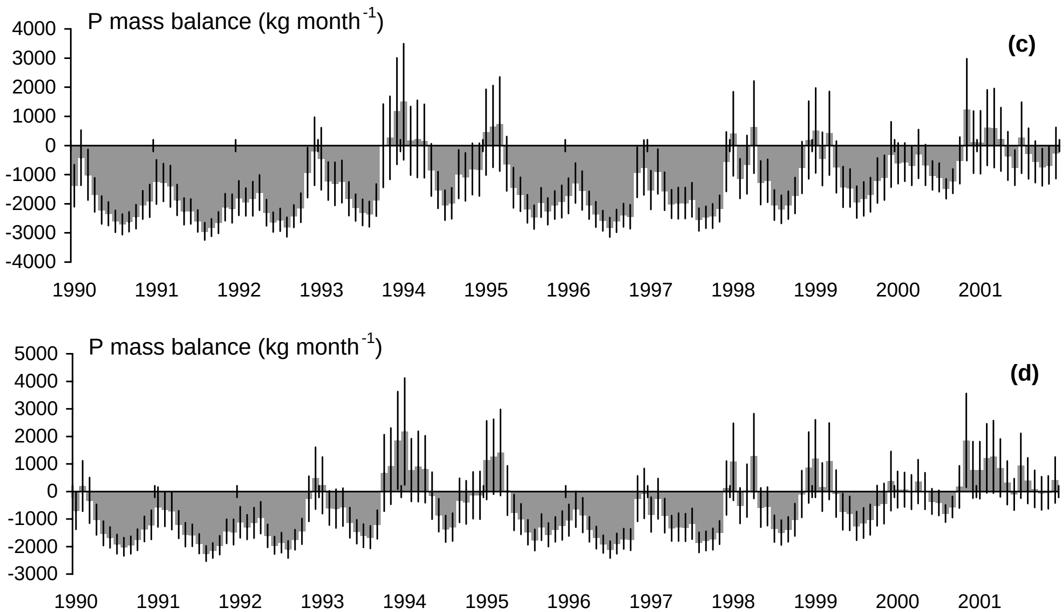

Fig. 2. Continued.

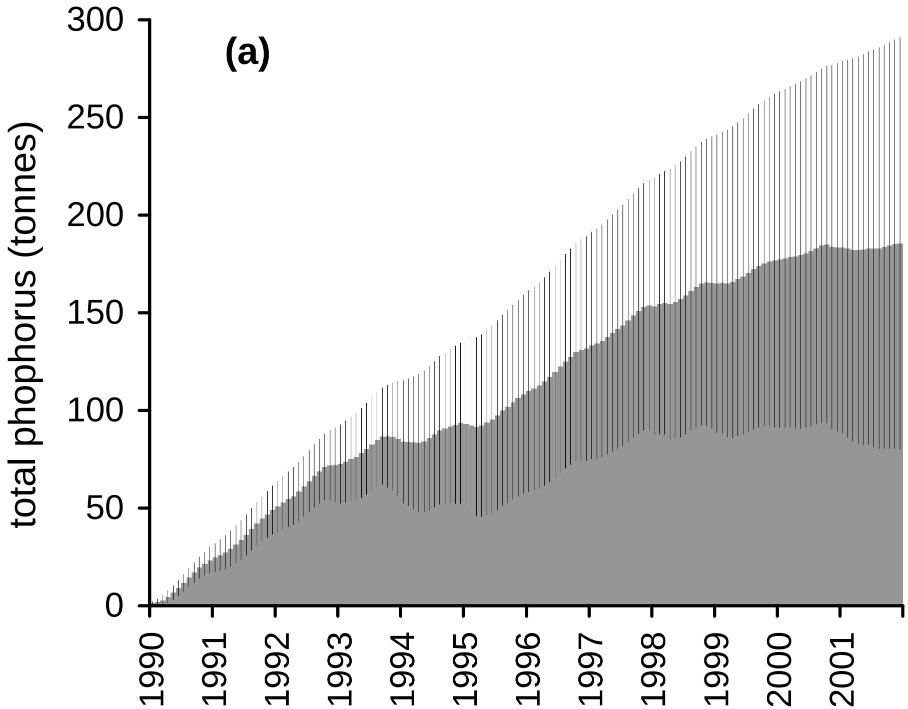

Fig. 3. Cumulative phosphorus retention of the River Wensum catchment area, with **(a)** industrial phosphorus load calculations based on consented maximum daily flows, and **(b)** industrial phosphorus load calculations based on 50% consented maximum daily flows. Bars represent uncertainties.

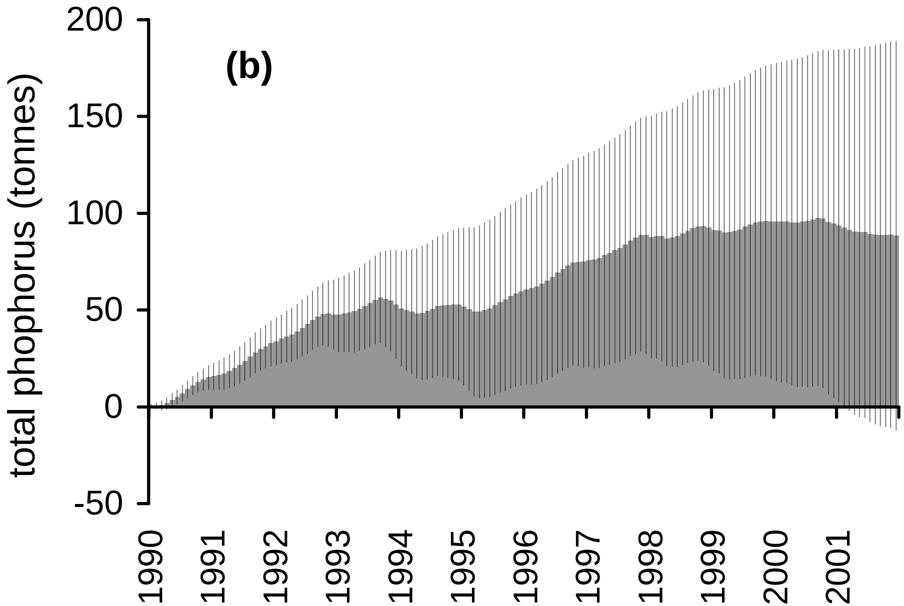

Fig. 3. Continued.

HESSD
2, 37–72, 2005

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◂◂ | ▸▸
◂ | ▸
Back | Close
Full Screen / Esc
Print Version
Interactive Discussion

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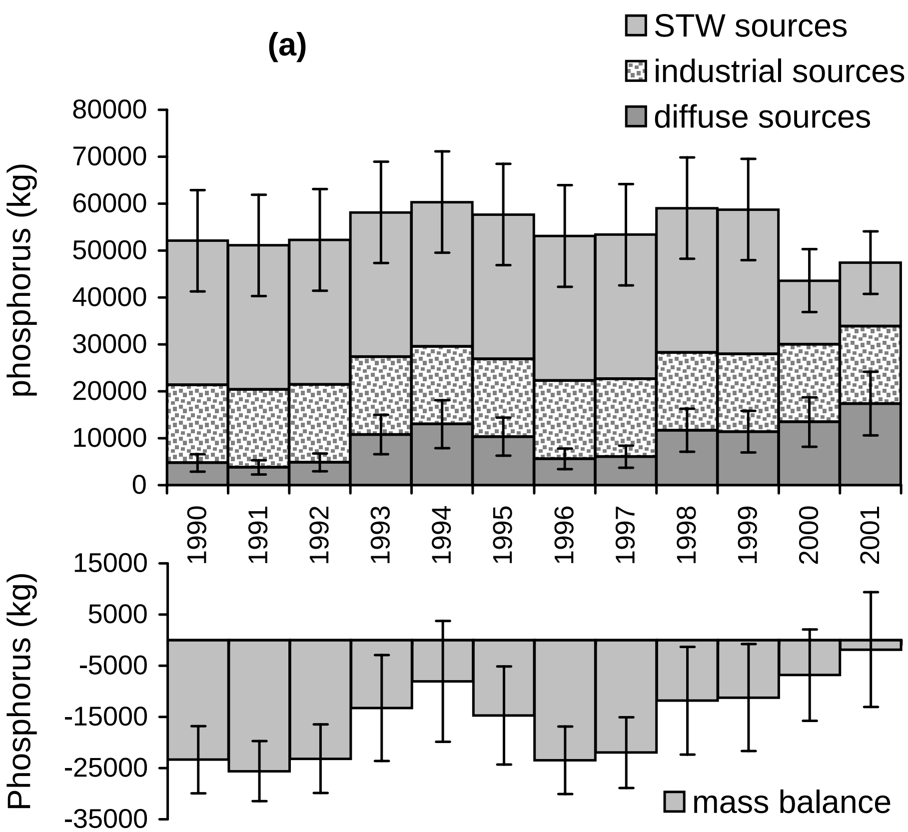
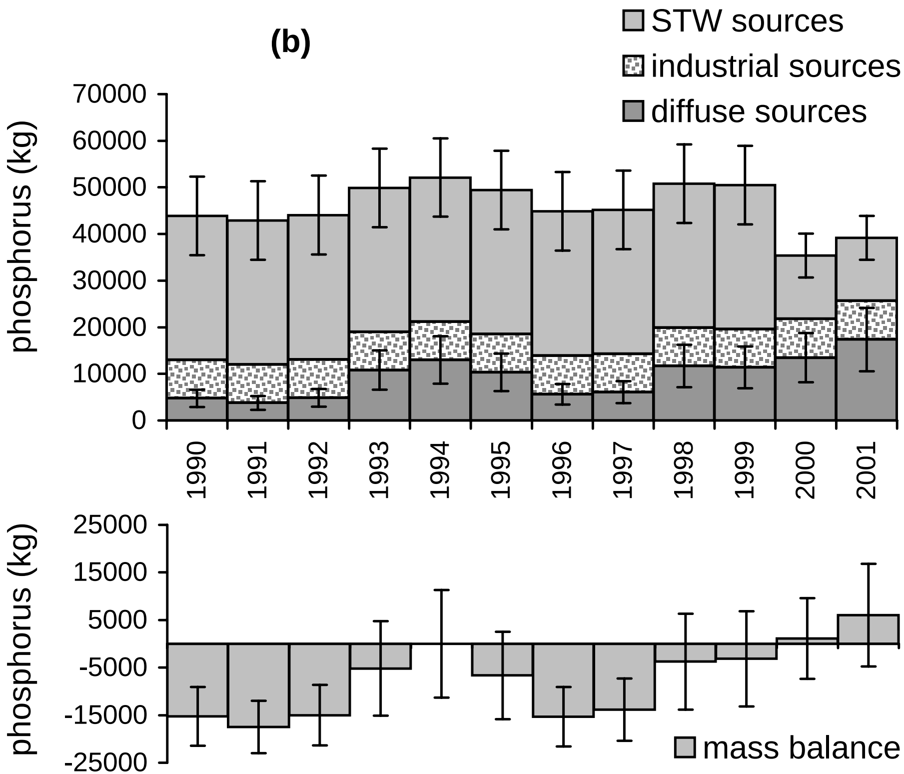


Fig. 4. Mean annual phosphorus loads, source apportionment and mass balance before and after phosphorus control measures, with **(a)** industrial phosphorus load calculations based on consented maximum daily flows, and **(b)** industrial phosphorus load calculations based on 50% consented maximum daily flows. Bars represent uncertainties. Uncertainties of point source loads (from STWs and industry) were pulled together for clarity.



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HESSD
2, 37–72, 2005

Impact of phosphorus control measures

B. O. L. Demars et al.

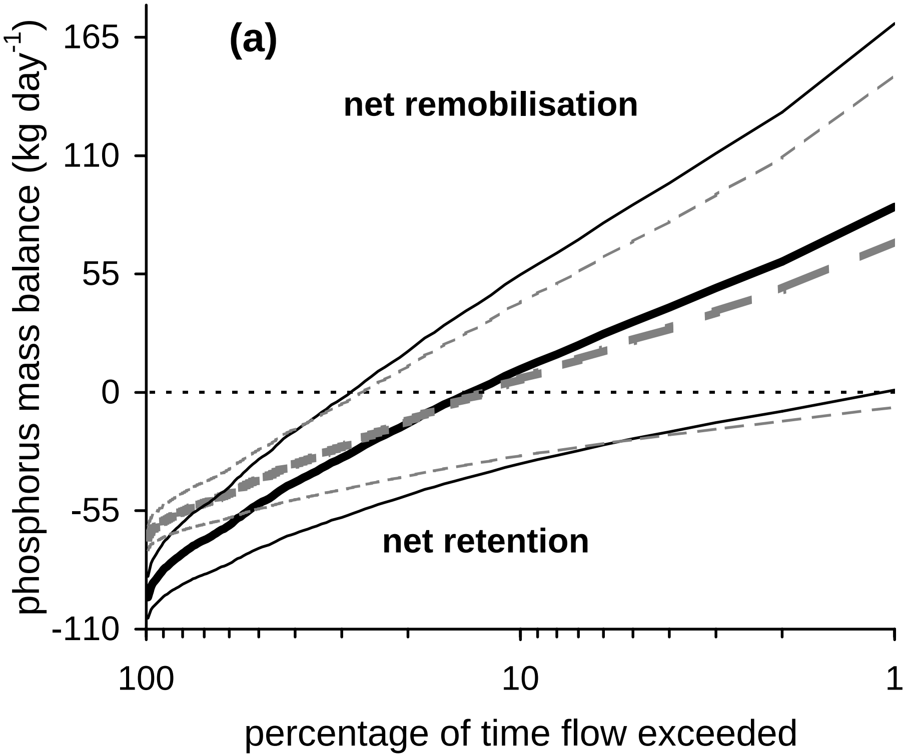
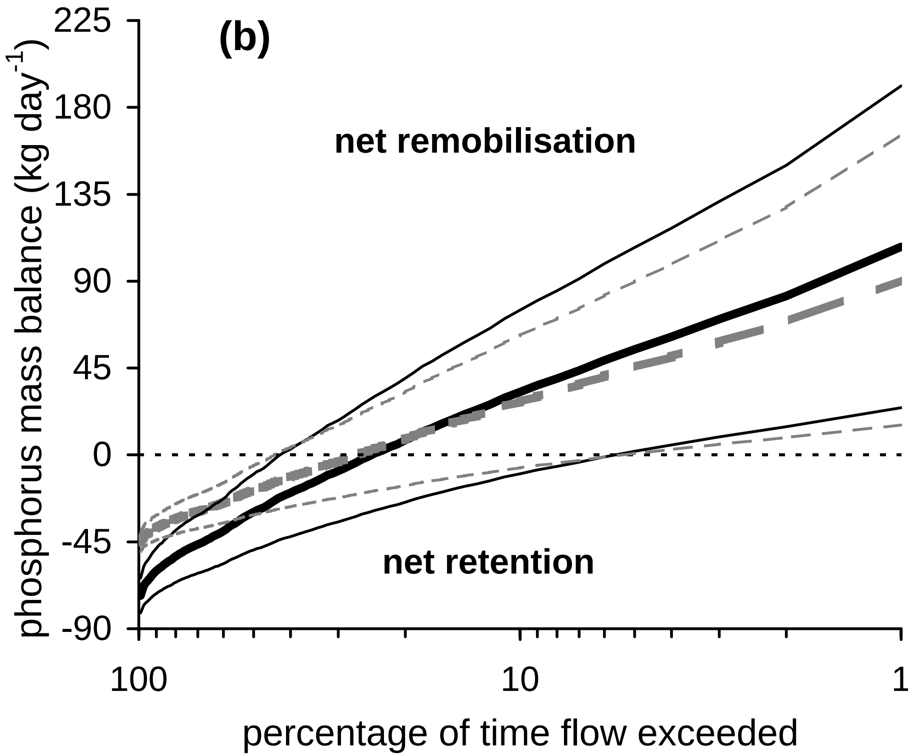


Fig. 5. Phosphorus mass balance before (black lines) and after (grey dashed lines) phosphorus control measures over Q_{99}–Q_1, with **(a)** industrial phosphorus load calculations based on consented maximum daily flows, and **(b)** industrial phosphorus load calculations based on 50% consented maximum daily flows. Thinner lines represent uncertainties.



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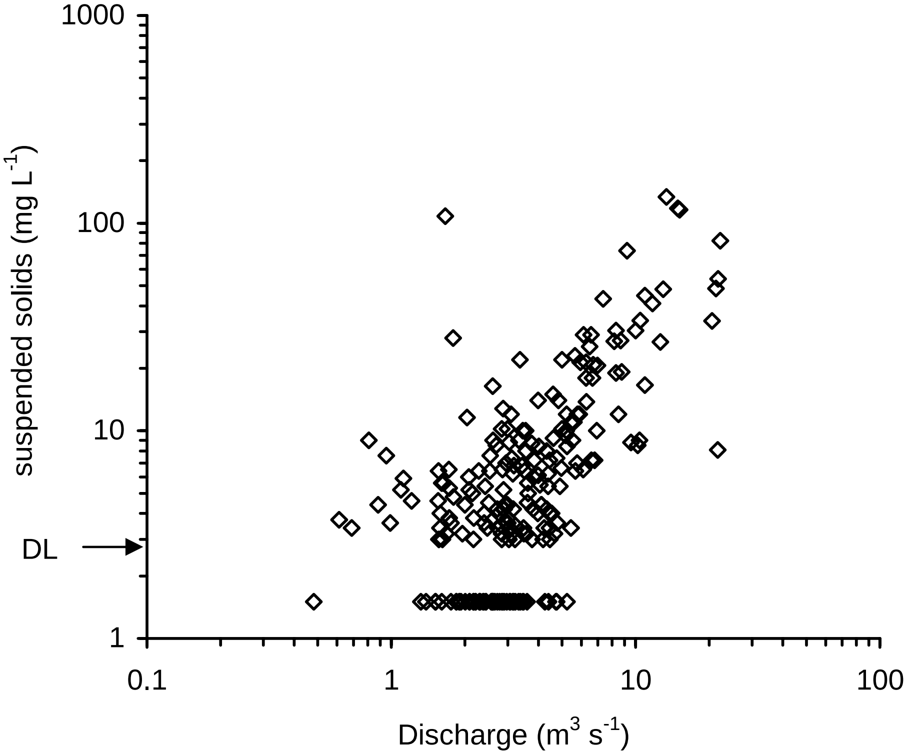

Fig. 6. Suspended solids concentrations increases with discharge (period 1981–1990). DL means analytical detection limit.