Appeared as: Bowes, M.J., Smith, J.T., Jarvie, H.P. and Neal, C. (2008) Modelling of phosphorus inputs to rivers from diffuse and point sources. *Science of the Total Environment* **395** (2-3) 125-138.

Modelling of phosphorus inputs to rivers from diffuse and point sources

Michael J. Bowes [a, *], Jim T. Smith [b], Helen P. Jarvie [a] and Colin Neal [a]

[a] *Centre for Ecology and Hydrology, Maclean Building, Crowmarsh Gifford, Wallingford, Oxfordshire, OX10 8BB, UK*

[b] *School of Earth and Environmental Sciences, Burnaby Building, University of Portsmouth, Portsmouth PO1 3QL, UK*

[*] *Corresponding author. E-mail address: mibo@ceh.ac.uk*

Abstract

The difference in timing of point and diffuse phosphorus (P) delivery to a river produces clear differences in the P concentration – flow relationship. Point inputs decrease in concentration with increasing river flow, due to dilution of a relatively constant input, whereas diffuse (non-point) load usually increases with river flow. This study developed a simple model, based on this fundamental difference, which allowed point and diffuse inputs to be quantified by modelling their contribution to river P concentration as a power law function of flow.

The relationships between total phosphorus (TP) concentration and river flow were investigated for three contrasting UK river catchments; the Swale (Yorkshire), the Frome (Dorset) and the Avon (Warwickshire). A load apportionment model was fitted to this empirical data to give estimates of point and diffuse load inputs at each monitoring site, at high temporal resolution. The model produced TP source apportionments that were similar to those derived from an export coefficient approach. For many diffuse-dominated sites within this study (with up to 75% of the annual TP load derived from diffuse sources), the model showed that reductions of point inputs would be most effective in order to reduce eutrophication risk, due to point source dominance during the plant and algae growing period. This modelling approach should provide simple, robust and rapid TP source apportionment from most concentration – flow datasets. It does not require GIS, information on land use, catchment size, population or livestock density, and could provide a valuable and versatile tool to catchment managers for determining suitable river mitigation options.

Key Words
Eutrophication; Source apportionment; Point source; Diffuse source; Agriculture; Sewage; Nutrient; Load apportionment model

1 Introduction

The effective management and reduction of phosphorus (P) concentrations in rivers requires knowledge of the quantities of P derived from the major sources within the catchment (EEA, 2005). The wide range of nutrient mitigation strategies that are available to catchment managers need to be targeted at those nutrient sources that will produce the greatest improvement to the water quality and ecology of the river. There is currently much research effort focusing on determining the relative contributions from point and diffuse (non-point) source inputs of phosphorus to a wide variety of rivers across Europe, using a whole range of methodologies (EEA, 2005).

Many studies (Bowes et al., 2005a; Hanrahan et al., 2001; Johnes and Heathwaite, 1997; Marchetti and Verna, 1992) have used phosphorus export coefficients that provide annual estimates of phosphorus losses from a range of different land uses, livestock stocking densities and sewage treatment works (STWs). However, such methodologies require detailed data on land use and livestock numbers, knowledge of all point source inputs, and the user can not be certain that the chosen phosphorus export coefficients are appropriate for that particular catchment. Export coefficients usually operate on an annual time step (Burt and Johnes, 1997), and so they can not easily be used to infer seasonal patterns of nutrient delivery, although recent studies have attempted to increase their temporal resolution (May et al., 2001). Such temporal resolution is required to determine phosphorus concentrations during the plant and algae growing season, when eutrophication is most likely to occur.

Other studies have used long term datasets of phosphorus concentrations and flow rates in both the river and the major upstream sewage treatment works to estimate the contribution that point source inputs make to the total P export from the catchment (Cooper et al., 2002; Jarvie et al., 2005). Conservative STW tracers, such as boron, have also been used to infer point source contribution of P (Jarvie et al., 2006; Neal et al., 1998; Neal et al., 2005). One problem with such studies is that phosphorus from STWs can not be assumed to be transported directly to the river monitoring point, due to sediment interactions and bioaccumulation (Bowes and House, 2001; Bowes et al., 2005c; Hill, 1981), particularly during low-flow periods. Therefore, the estimated phosphorus contribution from point sources will be overestimated to some extent during summer periods, and diffuse contribution will be overestimated in winter high-flow periods (due to the remobilisation of stored within-channel P).

The temporal pattern of total phosphorus (TP) load inputs to a river from point and diffuse sources is fundamentally different. Loadings from point sources, such as STWs and industrial effluents, tend to be relatively constant throughout the year, and are generally independent of river flow. Diffuse sources (from agricultural fertiliser, soil erosion, septic tank soak-aways and atmospheric deposition) are principally flow dependent, and should occur intermittently, particularly during the periods of the year with high precipitation. This temporal difference in the mode of P delivery results in clear differences in the relationship between TP concentration and river discharge. In rivers that are point-source dominated, the constant rate of input of phosphorus means that TP concentrations will be highest at low flow, and this concentration will decrease reciprocally with increasing river flow rate, due to dilution. Conversely, rivers that receive phosphorus primarily from diffuse-sources will tend to show an increase in TP load and concentration with increasing river flow. Similar interpretations of P concentration – flow relationships have been made in other studies (Cooper et al., 2002; Jarvie et al., 2006; Jordan et al., 2007; Wood et al., 2005).

This study aims to use this fundamental difference in the mode of phosphorus delivery to develop a simple and rapid method for determining the relative contribution of diffuse and point source phosphorus inputs, using paired TP concentration / river flow datasets. Such data are routinely produced by national environmental agencies and by river nutrient research and monitoring programmes, and are therefore widely available for a broad range of rivers. This proposed load apportionment modelling does not require any knowledge of the land use, catchment size, population or livestock density to estimate TP load contributions derived from point and diffuse sources.

1.1 Study areas and datasets

This study used three datasets, consisting of paired total phosphorus concentration and river discharge, from three UK catchments of varying population density, land use and geology.

River Swale, Yorkshire (catchment area 1457 km^2) The Swale drains the eastern side of the Pennine hills, northern England, before flowing in a south-easterly direction to the confluence with the River Ure (Figure 1a). The dataset used in this study is derived from the 55 km lowland stretch of the river, between Catterick and Crakehill (10 km upstream of the confluence with the River Ure). The underlying bedrock is Triassic New Red Sandstone. The floodplain within this reach consists of high-quality agricultural land, which is mainly used for crop production, and sheep, cattle, pig and poultry farming. The study reach drains the three towns of Catterick, Northallerton and Thirsk, which contribute phosphorus to the river system via their STWs (population equivalents (PE) of 25 800, 25 500 and 17 500 respectively). A more detailed description of the geology, geomorphology and land-use of the River Swale catchment can be found elsewhere (Bowes et al., 2003; Jarvie et al., 1997; Taylor and Macklin, 1997). The dataset used in this study comprised TP and flow data from two sites on the River Swale (Catterick and Crakehill) and its major tributary, Cod Beck. Water samples were taken from the main flow of the river using automatic water samplers (Montec Epic, model 1011). Total phosphorus concentrations (comprising of both dissolved and particulate-bound phosphorus) were determined by digesting unfiltered river water sub-samples with acidic potassium persulphate in an autoclave at 121^{o}C, then reacting with acid ammonium molybdate reagent to produce an molybdenum-phosphorus complex. This intensely coloured compound was then quantified spectrophotometrically at 880 nm (Eisenreich et al., 1975). The data were collected during five two-week monitoring periods between 1998 and 2000, at three-hour sampling interval. These monitoring periods covered all seasons and a full range of flow conditions, described elsewhere (Bowes and House, 2001; Bowes et al., 2005b)

River Frome, Dorset (catchment area 414 km^2) The Frome extends from the village of Evershot on the Dorset – Somerset border, to Poole Harbour (Figure 1b). The dominant rock type for the majority of the study area is Cretaceous Chalk, with an area of Cretaceous Greensand in the River Hooke sub-catchment (Casey et al., 1993). The land use within the catchment is primarily agricultural, mainly grassland and cereals (Casey et al., 1993). The town of Dorchester is the only significant urban area in the study reach, and its STW (PE of 27 000) discharges directly into the River Frome. The locations of the other nine STWs within the catchment are shown in Figure 1b. The dataset used in this study comprised of weekly TP and river flow data from three sites along the River Frome, and five of its major tributaries, between June 1999 and October 2000 (Bowes et al., 2005c). Manual water samples were taken from the main flow of the river, at *ca*. 30 cm depth. These unfiltered samples were analysed for total phosphorus using the method described by Eisenreich et. al. (1975)

River Avon, Warwickshire (catchment area 22000 km^2). The River Avon rises at Naseby in the Northamptonshire uplands of central England, and flows 154 km south-westerly through Stratford-upon-Avon and the Vale of Evesham to its confluence with the River Severn at Tewkesbury. It has a number of large tributaries, including the Rivers Sowe, Leam, Stour and Alne (Figure 1c). The catchment upstream of Evesham consists of 44% arable land and 30% pasture (Hilton et al., 2002), and contains the city of Coventry, and the towns of Stratford-upon-Avon, Warwick, Redditch and Rugby. Urban and semi-urban land use contributed 14% of the total land cover. The catchment is served by *ca.* 100 STWs, seven of which had a population equivalent of > 10 000 during the monitoring period. A more detailed description of the catchment as given elsewhere (Bowes et al., 2005a; Foster et al., 1998). The dataset used in this study was collected from sites throughout the Warwickshire Avon catchment area between December 1994 and September 1996. The water chemistry and flow-gauging data was supplied by the Environment Agency, UK (EA), and had been collected as part of the 'Eutrophication of Controlled Waters in the Warwickshire Avon Catchment' project (Foster et al., 1998; Hilton et al., 2000). All study sites within this project that were monitored at a weekly sampling interval and covered the full range of flow conditions were included in this present study.

2 Methods

2.1 Load apportionment modelling

The phosphorus concentration is modelled as a function of river volumetric flow rate. It is assumed that the load of phosphorus (mg s^{-1}) from point, F_p, and diffuse, F_d, sources can be modelled as a power-law function of the river volumetric flow rate, Q (m^3 s^{-1}):

$$F_p = A.Q^B \quad and \quad F_d = C.Q^D \qquad (1)$$

The total load, F_t (mg s^{-1}) of P at the sampling point is then a linear combination of the loads from diffuse and point-source inputs:

$$F_t = F_p + F_d = A.Q^B + C.Q^D \qquad (2)$$

where A, B, C and D are parameters to be determined empirically.

Since the phosphorus concentration, C_p (mg m^{-3}) at a given sampling point is equal to the load divided by the volumetric flow rate, this can be expressed as:

$$C_p = A.Q^{B-1} + C.Q^{D-1} \quad (3)$$

The first term in Equation (3) ($A.Q^{B-1}$) is interpreted as that part of the P concentration originating from point sources; the second term ($C.Q^{D-1}$) is that part originating from diffuse sources. Equation (3) was evaluated by varying the four fitting parameters, against the empirical data of phosphorus concentration versus volumetric flow rate. In many cases, a simpler model in which *B* was set to zero (i.e. point source load inputs were independent of volumetric flow rate) fitted the data as well as Equation (3) and this model was also tested. Two other special cases of Equation (3) were also examined: firstly for the case of a river dominated by point-source inputs, in which $C = 0$, and, secondly, for a river dominated by diffuse inputs, in which $A = 0$.

A number of constraints were imposed on the model, to provide realistic solutions. Firstly, it was assumed that *B* must always be less than 1, as a *B* value greater than 1 would imply an increase in point-source derived P concentration in the river as flow increases. The model makes the assumption that point source load inputs are continuous, and thereby an increased river flow can only reduce the P concentration, due to dilution. The model was also constrained to only consider *D* values greater than 1, as diffuse inputs must increase with river flow and also tend towards zero at low flow, because the model assumes that these inputs are rainfall and flow dependant.

Equation (3) and its three special cases were fitted to the empirical data using the non-linear least squares regression procedure PROC NLIN in the SAS statistical analysis package (SAS, 2002). In order to test a simpler approach to model fitting, we also fitted the data using the *Solver* function in Microsoft EXCEL©. SAS is able to estimate uncertainty ranges in determined parameter values whereas the *Solver* function does not.

2.2 Physical interpretation of model outputs

Figures 2a to 2d illustrate how each of the model parameters affects the phosphorus concentration – flow relationship. The *A* parameter represents the load of phosphorus entering the river from all 'constant' sources, which will principally include STW, septic tanks connected directly to the river and, in some cases, industrial P inputs. In some catchments, groundwater could also provide a constant load to the river, but this was considered to be a relatively insignificant source of phosphorus input in these study catchments. The relationship between this constant input and river flow describes a simple concentration dilution curve (Figure 2a). For most cases in this study, $B \approx 0$ (i.e. point source load inputs are approximately independent of *Q*), and (by Equation 1) the parameter *A* has units of load (mg s^{-1}), which will be approximately equal to the load of phosphorus entering the river from point sources. For some of the datasets in this study, the *B* parameter did not equal zero. The *B* term assumes that the point-source derived phosphorus is not conservative. A *B* term greater than zero indicates that point-source derived P load is removed from the water column during low flows (Figure 2b), which could represent within-channel storage of point source inputs due to adsorption of soluble P to bed sediments, deposition of particulate P and uptake by biota (Bowes and House, 2001; House, 2003). *A priori*, one would expect that *B* would always be greater than zero, since a negative *B* value would imply a physically implausible increase in point source P inputs with decreasing river flow. Negative *B* values could occasionally occur due to desorption and release of SRP from bed sediments, particularly in nutrient-impacted organic-enriched streams that may become anoxic under low flow conditions. However, over the course of a long term monitoring campaign, it would be expected that a net loss of phosphorus from the water column to the bed sediment would be the most likely process at low flows.

The *C* parameter describes the load of P entering the river from a flow-dependent (and therefore rain-dependent) source (Figure 2c). This will include diffuse P inputs from fertiliser and manure applications, animal faeces, soil erosion and septic tank soak-aways. The *C* parameter also includes within-channel P that is remobilised during storm events, which may originally have been derived from a mixture of diffuse and point sources. The rate of change of P load input with changing flow rate is described by the parameter *D* (Figure 2d), and represents changes in the TP concentration of storm runoff / drain-flow, and the rate of within-channel P remobilisation, with increasing flow rate.

2.3 Model example

An example of how the model apportions the relative contributions of P from different sources is given in Figure 3, showing the flow and TP concentration data observed in the River Leam at Princes Road, and the results from the modelling. This modelled fit is produced from the sum of the 'constant' point source and flow-dependent diffuse load input estimates derived from Equation (3). The intersection of the two lines is the estimated flow rate, Q_e ($m^3\ s^{-1}$), at which the point source and flow-dependent P load inputs are equal. This river flow value was calculated using the equation:

$$Q_e = \left(\frac{A}{C}\right)^{\left(\frac{1}{D-B}\right)} \qquad (4)$$

When Q < Q_e, point sources will dominate the TP load, and diffuse inputs will dominate at river flows > Q_e. Because the River Leam dataset is comprised of samples taken at a uniform sampling interval (i.e. weekly), the percentage of time where point source is the major contributor to the total P inputs throughout the monitoring period can be estimated simply by calculating the percentage of data-points that fall below this Q_e flow value. For the River Leam, point sources dominated the total P input for 21 % of the 20 month study period.

2.4 Phosphorus load apportionment

If high resolution river flow data are available for a particular study site, the model can be used to estimate the total annual load of phosphorus, T_p ($mg\ yr^{-1}$), flowing past the sampling point:

$$T_p = 86400 . \sum_{i=1}^{i=365} A.Q_i^B + C.Q_i^D \qquad (5)$$

Where Q_i is the mean daily volumetric flow rate ($m^3\ s^{-1}$), *A*, *B*, *C* and *D* are the empirically-determined fitting parameters, and 86,400 is the number of seconds in one day.

Equation (5) consists of both a point source ($A.Q_i^B$) and a diffuse source term ($C.Q_i^D$). Therefore, the results of the model fitting can be used to determine the proportion of the total P load that is contributed individually by constant (point) and flow-dependent (diffuse) phosphorus sources.

2.5 Export coefficient modelling

A geographical information system (GIS) approach was adopted to gain a second estimate of point and diffuse TP inputs at each sampling site (Hilton et al., 2002). Digital representations of the Swale, Frome and Avon catchments were entered into the GIS software (ARC INFO version 7.1.2, Environmental Systems Research Inc., USA), using the Centre for Ecology and Hydrology (CEH), River Centre Line Network (CEH Wallingford, UK). The 1993 CEH Land Cover Map of Great Britain (Fuller et al., 1994) was layered over this river network, which gave data on 25 land cover types at 25 m grid resolution. The flow direction and catchment boundaries of the river network were derived from the CEH Wallingford 50 m grid resolution digital terrain map (Morris and Flavin, 1990). The Ministry of Agriculture, Fisheries and Food (MAFF) small area statistics (MAFF, 2000), in conjunction with the Parish-Line Marketeer dataset (Ordnance_Survey, 1991), were used to estimate livestock numbers per hectare, for each animal type.

Estimates of diffuse phosphorus inputs to the rivers from the land cover types present in the catchments were calculated using export coefficients (in kg P ha^{-1} y^{-1}), derived from previous studies (Johnes, 1996; May et al., 1996). The coefficients used are detailed in Hilton et al., (2000) and Bowes *et al.* (2005a) (for the River Avon and River Swale sites) and Hanrahan *et al.* (2001) for the River Frome. The diffuse phosphorus export to the river from livestock excretion was estimated from the animal numbers in each sub-catchment and the relevant export coefficients from cattle (0.22 kg P ca^{-1} yr^{-1}), pigs (0.14 kg P ca^{-1} yr^{-1}), sheep (0.045 kg P ca^{-1} yr^{-1}) and poultry (0.0054 kg P ca^{-1} yr^{-1}) (Johnes, 1996). The annual TP inputs from STW sites were estimated from their population equivalents, assuming an export coefficient of 0.38 kg P $capita^{-1}$ yr^{-1} (Johnes, 1996).

The predicted phosphorus load inputs for each sampling site from the upstream land use, livestock and STW were then summed to produce an estimate of both the annual TP load, and the relative load contribution derived from diffuse and point sources.

3 Results and Discussion

3.1 Total P – flow relationships

The relationships between TP concentration and river volumetric flow for the Swale, Frome and Avon catchments, and their associated model solutions, are shown in Figures 4 and 5. The parameter values produced from the modelling are given in Table 1.

The load apportionment model provided realistic fits to the data for 21 of the 23 study sites. Many sites exhibited a conventional TP dilution relationship with increasing river flow (e.g. all sites on the River Avon and Arrow, and the River Sowe at

Stoneleigh) (Figure 5). All of these sites were located in the River Avon catchment, implying a dominance of point source phosphorus input in the most urbanised catchment in this study. The model described these TP concentration versus flow relationships using only the *A* and *B* parameters, or included a relatively small *C* and *D* component whose errors spanned zero, thereby inferring a complete dominance of point source TP input at these sites (Table 1). Three sites in the River Frome catchment (Sydling Water, South Winterborne and the River Win) (Figure 4) showed an increasing TP concentration with increasing river flow, indicating a lack of any significant point source contribution and a dominance of diffuse P. The model successfully described these relationships using predominantly the *C* and *D* parameters, with the inclusion of a small *A* parameter whose errors spanned zero (and so could not be differentiated from zero) (Table 1). These modelled outputs are plausible, as the River Win and South Winterborne have no STW inputs, and all three rivers are predominantly rural. The majority of the other study sites showed an initial decrease in TP concentration with increasing flow, followed by an increase in concentration, indicating point source dominance at low flow, with increasing diffuse P input as the river flow increased. The load apportionment model was able to successfully fit these relationships using either all four parameters, or just *A*, *C* and *D*.

The model was unable to find a satisfactory solution for two of the study sites; the River Frome at East Stoke and the River Tadnoll at Broomhills, as these sites did not show a clear relationship between P concentration and flow (Figure 4). The load apportionment model produced identical *A C* and *B D* values for these two study sites, when all four parameters were allowed to vary to fit the empirical data. Therefore, the model was unable to distinguish between point and diffuse inputs. The B and D values were ≈1.0 in both cases, meaning that the model was always merely predicting the mean TP concentration for all observed flow rates. Therefore, these model solutions were rejected. These two study sites had the highest TP concentrations during medium flow conditions (Figure 4), which does not fit with our assumption that TP input to the river is either from a constant or a rain-dependent source. This may indicate that the TP input is diffuse dominated, and that this source becomes depleted at higher flows, thereby resulting in reduced TP concentrations at the higher river flow. However, a more likely explanation (due to the poor relationship between TP concentration and flow rate) is that there is a significant input of phosphorus to the river that is neither constant (i.e. STW input) or related to flow (typical of diffuse input). Similar observations have been made by Jordan et al (2007), and attributed to random pollution incidents. Both of these non-conforming sites are downstream of large watercress farms, which may account for these sporadic phosphorus inputs, unrelated to river flow (Casey, 1981) . The river flow at which the diffuse and point source components are equal (Q_e) were calculated for each site, using Equation (4) and are given in Table 1.

3.2 Source apportionment

For each study site, the total phosphorus loads derived from point and diffuse sources were estimated using the model parameter values (Table 1) and the river flow at the time of sampling, using Equation 5. The results are shown in Table 2. The estimated percentage of the annual TP load that was derived from point sources, using this load apportionment modelling approach, agreed with the visual interpretation of the TP versus flow relationships. Much of the River Avon catchment was dominated by

STW inputs, with all sites on the Rivers Avon, Arrow, Stour and Dene having >80% of their annual TP load derived from point source inputs (Table 2). For five of these study sites (Barford, Coughton Ford, Studley, Wellesbourne and Stoneleigh), the point source signal was so strong that the load apportionment model was unable to detect any diffuse signal at all i.e. the TP concentration / flow relationship could be best fitted using only the *A* and *B* parameters of the point source term in Equation 3. In contrast, the more rural catchments of the River Swale and Frome received <30% of their annual TP load from point sources. The model estimated that two of the River Frome catchment sites (the River Win and the South Winterborne) received their entire annual TP load from diffuse sources (Table 2, Figure 4), which is to be expected, as they are the only two rivers in the study that have no upstream STWs.

The estimated percentage point source contributions to the river annual TP load, obtained using the GIS export coefficient approach, are also given in Table 2. These estimates closely agreed with the load apportionment modelling estimates in most cases. The load apportionment modelling produced higher estimates of the percentage point source inputs for STW dominated sites (such as the study sites on the Rivers Avon and Arrow), compared with the export coefficient model estimates. This is probably due to the strength of the point source signal masking any diffuse signal at higher river flow rates. The point source contribution estimates from the study sites in the River Swale and Frome catchments show very close agreement between the load apportionment and export coefficient models.

Three of the River Avon study sites had markedly different estimates from the two models. The export coefficient model estimated only 18, 21 and 38% of the annual TP load was derived from point source inputs (at Clifford Chambers, Wellesbourne and Studley respectively). However, the load apportionment model estimated that point source inputs contributed 75, 100 and 100% respectively. Based upon the dilution patterns observed in the TP concentration versus flow rate relationship (Figure 5), the load apportionment model solutions appear to be more realistic, as there is clearly a constant TP input at these sites. The export coefficient model predicted a total annual TP export of 29.3 and 8.9 t y^{-1} for Clifford Chambers and Wellesbourne, but the actual measured load was *ca.* half these values (16.2 and 3.9 t y^{-1} respectively) (Hilton et al., 2000). This discrepancy is due to a large overestimation of the diffuse input to these sites. The disparities at these sites could be caused by the selection of inappropriate land use export coefficients, or more likely due to the weekly sampling regime missing some short-term high flow events, during which time, a large proportion of the diffuse load may have entered the river (thereby resulting in an underestimation of the annual TP load).

The correlation between the estimated percentage contribution to the annual TP load from point source inputs for the two models is shown in Figure 6. After the removal of the Clifford Chambers, Wellesbourne and Studley sites (due to their questionable modelling estimates), the estimates from the two models showed good agreement, with an R^2 value of 0.92. Therefore, the load apportionment model appears to provide a rapid and robust method for determining the relative contributions from diffuse and point source inputs for most study sites.

3.3 Timing of phosphorus delivery

Previous studies have highlighted that point-source dominated rivers in the UK tend to have their highest phosphorus concentrations during summer low flow periods (Bowes et al., 2005a; Jarvie et al., 2006), when the risk of eutrophication is at its greatest. The major inputs of diffuse phosphorus are expected to occur during high river flows, generally outside the summer growing period in the UK. These diffuse inputs could be large in terms of load, but may only result in a small concentration increase, due to dilution by rainfall / runoff. Therefore, in terms of eutrophication risk, it is important to examine the timing of P delivery from diffuse and point sources, and not just the total annual load.

The load apportionment model was used to investigate this by quantifying the river flow at which the TP contributions from point and diffuse sources were equal (Q_e) (Table 1), using Equation 4. This Q_e value was then used to calculate the percentage of data points that had flows that were less than this value. For long term datasets, consisting of data gathered at a regular sampling interval (i.e. weekly), this will be equivalent to the percentage of time throughout the year that point sources are the dominant contributor to the TP load (Table2). For the sewage dominated study sites (Table 2), these values were similar to the percentage point source load contributions, but for diffuse dominated rivers they were significantly higher. For example, study sites such as Crakehill, Princes Drive, Baginton, Louds Mill, Frampton and Maiden Newton have only 20 to 25% of their annual TP load derived from point source inputs (as calculated by load apportionment modelling). Export coefficient modelling confirmed that the annual TP loads at these sites were dominated by diffuse inputs. However, point source inputs provide the majority of the TP load for between 36 and 77% of the time at these sites, due to the episodic nature of diffuse P delivery (Table 2).

3.4 Using the model for targeting mitigation strategies

It would seem a reasonable assumption that agricultural inputs should be targeted in catchments whose annual TP loading was derived mainly from diffuse inputs. However, due to the seasonality and episodic nature of diffuse TP inputs, this may not be the most effective way of reducing eutrophication risk. To control eutrophication, catchment managers need to introduce mitigation measures that will reduce phosphorus concentrations during the main plant and algae growing period. To test this assumption, the load apportionment model was used to re-examine the TP concentration versus flow relationships for a range of study sites of varying point source contribution. The data points were divided into two equal groups based on the time of sampling; 1st April to 30th September (a six month period roughly equating to the peak plant and algae growing season) and October 1st and March 31st (Figure 7). The flows at which point and diffuse TP inputs were equal (Q_e), derived from Equation 4, are shown by the vertical dashed lines. The sites are plotted in order of increasing point source input.

The River Win (Figure 7a) receives almost no point source input, as there are no STWs on this river. There are very few data points at very low flow that are estimated as being point source dominated, and so diffuse inputs should clearly be targeted to reduce the TP concentration during the plant growing season. Therefore, mitigation options such as riparian buffer strips, soil erosion control, and reducing animal stocking densities and fertiliser applications would be the most appropriate.

The River Sowe at Baginton (Figure 7g) shows approximately equal proportions of data points during the plant growing period lying on either side of the Q_e flow rate, and these data points have relatively similar TP concentrations. This implies that both point and diffuse sources should be targeted equally to improve the water quality at this site, despite only 25% of the annual TP load being derived from point source (or as little as 9%, as estimated by export coefficient modelling). The River Frome at Frampton and Louds Mill, and the River Hooke at Maiden Newton (Figures 7d, e and f) have similar TP concentrations when river flows are greater than or less than the Q_e value during the plant growing period. Therefore both diffuse and point source inputs could be targeted to improve water quality at these sites. However, for these three sites, targeting point source inputs (by improving the rates of phosphorus removal from sewage effluent) would be more effective than reducing diffuse sources, as most of the growth-season data points are point source dominated (i.e. the majority of these data points are at flows that are less than the Q_e value), despite these three sites having only 25 to 30% of their annual TP loads derived from point inputs (Table 2).

The River Swale at Crakehill (Figure 7b) the River Leam (Figure 7c) and Cod Beck (Figure 7h) have the majority (90, 91 and 98% respectively) of growth-season data points occurring during periods of point source domination, and these points also have the highest TP concentrations. For these three sites, estimates of the annual TP load, using both the load apportionment and export coefficient modelling, show that these sites are actually dominated by diffuse inputs, but in order to reduce the spring and summer phosphorus concentrations and the risk of eutrophication, point source input reduction would clearly be the most effective strategy. Sites that receive most of their TP load from point inputs, such as the River Avon at Evesham (Figure 7i) and Lawford (Figure 7j) have the highest TP concentrations during the plant growing season, at a time of point source dominance (i.e. all the growth-period data points occur at flows less than Q_e). Catchment managers clearly need to target point source reductions at these study sites, by the introduction of phosphorus stripping at STWs.

3.5 Model limitations

The load apportionment model appears to produce realistic estimates of the point source and diffuse inputs for most study sites. However, for sites that are point source dominated, the diffuse input signal is difficult to detect. Future work involving point source dominated sites could potentially investigate weighting the data points at high flows, thereby forcing the model to fit to the storm event data. This may allow the model to detect these weak diffuse signals. Another way of improving the detection of diffuse inputs would be to include storm sampling data alongside the routine monitoring, thereby increasing the number of potentially diffuse-dominated data points at high flows.

The model relies on the quality of the paired TP concentration and river flow data. In particular, it is vital that the sampling interval is sufficiently short to be able to capture a representative range of storm events observed at the study site. Without this high flow data, diffuse contributions may be underestimated (Johnes, 2007). The monthly sampling interval monitoring that is typical of the UK Environment Agency and other government agencies may not adequately characterize the high-range TP concentration-flow relationships. Higher sampling frequencies or inclusion of storm sampling data at flashy monitoring sites would greatly increase the robustness of the load apportionment model in terms of diffuse source estimation. It would also capture data points subject to TP concentration / flow hysteresis patterns (Bowes et al., 2005b). This under-representation of high flow events is also a problem with export coefficient modelling (in terms of setting suitable P export coefficients) and phosphorus mass balance studies. However, once the load apportionment model has produced a reasonable fit to the high flow data, this potential bias is actually removed. This is because the empirically-fitted model parameters can be applied to high temporal-resolution flow data from the site (equation 5), thereby fully representing diffuse source inputs at high flows.

The model assumes that TP is relatively conservative. Total phosphorus is clearly subject to processes that can alter its concentration in the water column, such as interactions with sediment and biota, and the suspension / resuspension of particulate P. The model appeared to be able to cope with these perturbations, by fitting the *B* and *D* terms, but may not be applicable to monitoring sites with high rates of internal riverine processing (i.e. sites where within channel TP retention or release forms a large percentage of the total TP load).

The model makes the assumption that all point source inputs are continuous, and all diffuse inputs are flow dependent. While this is generally true, it may not be the case for all study sites and phosphorus input types. For instance, phosphorus outputs from STWs tend to vary diurnally (Neal et al., 2000), and their efficiency can also vary over time (Neal et al., in press). Septic tanks are generally categorised as diffuse inputs (Carpenter et al., 1998). However, in many areas of the UK, septic tanks can be directly connected to the river or land drainage system, and actually operate as numerous small point source sewage inputs (Arnscheidt et al., 2007). The load apportionment model will identify these inputs as point source, rather than the traditional diffuse classification. This ‘limitation’ could actually be a powerful tool for investigating direct septic tank inputs in agricultural catchments with no STW input.

4 Conclusions

The load apportionment model offers a simple, robust and rapid method for determining the relative contributions of diffuse and point source phosphorus to the total annual TP load of the river. It gives good agreement with the more traditional export coefficient modelling approach in most cases, but is much faster to apply, does not require GIS knowledge and software, or access to detailed catchment information. In many cases, it could be argued that it produces more realistic estimates, as it is based directly on actual river monitoring data.

The model can be applied to any long term dataset comprising paired concentration and flow values that cover the full range of river flows typical of the study site. It can be used to both quantify the phosphorus loads derived from each source type, and also the proportion of the year that each source dominates the P budget. The load apportionment model could provide a base for investigating other relatively conservative chemicals that can be derived from constant and flow dependant sources, such as other phosphorus and nitrogen species, major anions and cations, organic pollutants, metals etc.

This first application of the load apportionment model across three catchments of varying size, land use and geology, has highlighted some important catchment management issues. The model showed that for most of the diffuse-dominated sites within this study (in terms of annual TP load), it would still be most effective to reduce point sources, in order to reduce the risk of eutrophication, due to the difference in seasonality of point and diffuse inputs. Due to this ability to estimate point and diffuse inputs for different specific flow conditions, the load apportionment model could provide a valuable and versatile tool to catchment managers for determining river mitigation options to most effectively reduce phosphorus concentrations during the critical plant and algae growing seasons, thereby aiding decision making for the Water Framework Directive.

List of Figures and Tables

References

Arnscheidt J, Jordan P, Li S, McCormick S, McFaul R, McGrogan HJ, Neal M, Sims JT. Defining the sources of low-flow phosphorus transfers in complex catchments. Sci. Total Environ. 2007; 382: 1-13.

Bowes MJ, Hilton J, Irons GP, Hornby DD. The relative contribution of sewage and diffuse phosphorus sources in the River Avon catchment, southern England: Implications for nutrient management. Sci. Total Environ. 2005a; 344: 67-81.

Bowes MJ, House WA. Phosphorus and dissolved silicon dynamics in the River Swale catchment, UK: a mass-balance approach. Hydrol. Process. 2001; 15: 261-280.

Bowes MJ, House WA, Hodgkinson RA. Phosphorus dynamics along a river continuum. Sci. Total Environ. 2003; 313: 199-212.

Bowes MJ, House WA, Hodgkinson RA, Leach DV. Phosphorus-discharge hysteresis during storm events along a river catchment: the River Swale, UK. Water Res. 2005b; 39: 751-762.
Bowes MJ, Leach DV, House WA. Seasonal nutrient dynamics in a chalk stream: the River Frome, Dorset, UK. Sci. Total Environ. 2005c; 336: 225-241.
Burt TP, Johnes PJ. Managing water quality in agricultural catchments. Trans. Inst. Br. Geogr. 1997; 22: 61-68.
Carpenter SR, Caraco NF, Correll DL, Howarth RW, Sharpley AN, Smith VH. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecol. Appl. 1998; 8: 559-568.
Casey H. Discharge and chemical changes in a chalk stream headwater affected by the outflow of a commercial watercress bed. Environ. Pollut. 1981; 2: 373-385.
Casey H, Clarke RT, Smith SM. Increases in nitrate concentrations in the River Frome (Dorset) catchment related to changes in land use, fertiliser applications and sewage input. Chem. and Ecol. 1993; 8: 105-117.
Cooper DM, House WA, May L, Gannon B. The phosphorus budget of the Thame catchment, Oxfordshire, UK: 1. Mass balance. Sci. Total Environ. 2002; 282: 233-251.
EEA. Source apportionment of nitrogen and phosphorus inputs into the aquatic environment. European Environment Agency, Copenhagen, Denmark, 2005, pp. 48.
Eisenreich SJ, Bannerman RT, Armstrong DE. A simplified phosphorus analytical technique. Environmental Letters 1975; 9: 45-53.
Foster I, Sheasby J, Wade S, Harrison S. Eutrophication in controlled waters in the Warwickshire Avon Catchment (Volume 1). Report to Environment Agency., 1998.
Fuller RM, Groom GB, Jones AR. The land-cover map of Great-Britain - an automated classification of Landsat thematic mapper data. Photogramm. Eng. Remote Sens. 1994; 60: 553-562.
Hanrahan G, Gledhill M, House WA, Worsfold PJ. Phosphorus loading in the Frome catchment, UK: Seasonal refinement of the coefficient modeling approach. J. Environ. Qual. 2001; 30: 1738-1746.
Hill AR. Stream phosphorus exports from watersheds with contrasting land uses in southern Ontario. Water Resour. Bull. 1981; 17: 627-634.
Hilton J, Buckland P, Irons GP. An assessment of a simple method for estimating the relative contributions of point and diffuse source phosphorus to in- river phosphorus loads. Hydrobiologia 2002; 472: 77-83.
Hilton J, Irons GP, McNally S. Pilot catchment study of nutrient sources: control options and costs. Environment Agency, 2000, pp. 108.
House WA. Geochemical cycling of phosphorus in rivers. Appl. Geochem. 2003; 18: 739-748.
Jarvie HP, Neal C, Robson AJ. The geography of the Humber catchment. Sci. Total Environ. 1997; 194: 87-99.
Jarvie HP, Neal C, Withers PJA. Sewage-effluent phosphorus: A greater risk to river eutrophication than agricultural phosphorus? Sci. Total Environ. 2006; 360: 246-253.
Jarvie HP, Neal C, Withers PJA, Wescott C, Acornley RA. Nutrient hydrochemistry for a groundwater-dominated catchment: The Hampshire Avon, UK. Sci. Total Environ. 2005; 344: 143-158.

Johnes PJ. Evaluation and management of the impact of land use change on the nitrogen and phosphorus load delivered to surface waters: The export coefficient modelling approach. J. Hydrol. 1996; 183: 323-349.
Johnes PJ. Uncertainties in annual riverine phosphorus load estimation: Impact of load estimation methodology, sampling frequency, baseflow index and catchment population density. J. Hydrol. 2007; 332: 241-258.
Johnes PJ, Heathwaite AL. Modelling the impact of land use change on water quality in agricultural catchments. Hydrol. Process. 1997; 11: 269-286.
Jordan P, Arnscheidt A, McGrogan H, McCormick S. Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser. Hydrol. Earth Syst. Sci. 2007; 11: 372-381.
MAFF. Agricultural and horticultural census database. United Kingdom National Digital Archive of Datasets. Ministry of Agriculture. Fisheries and Food, 2000.
Marchetti R, Verna N. Quantification of the phosphorus and nitrogen loads in the minor rivers of the Emilia-Romagna coast (Italy). A methodological study on the use of theoretical coefficients in calculating the loads. Sci. Total Environ. 1992; Supplement: 315-336.
May L, House WA, Bowes M, McEvoy J. Seasonal export of phosphorus from a lowland catchment: upper River Cherwell in Oxfordshire, England. Sci. Total Environ. 2001; 269: 117-130.
May L, Place CJ, George DG. The effects of soil type on nutrient losses and run-off in the catchment of Bassenthwaite Lake. Report to NRA North West Region,, 1996.
Morris DG, Flavin RW. A digital terrain model for hydrology. 4th International Symposium on Spatial Data Handling 1990; 1: 250-262.
Neal C, Fox KK, Harrow M, Neal M. Boron in the major UK rivers entering the North Sea. Sci. Total Environ. 1998; 210: 41-51.
Neal C, Jarvie HP, Howarth SM, Whitehead PG, Williams RJ, Neal M, Harrow M, Wickham H. The water quality of the River Kennet: initial observations on a lowland chalk stream impacted by sewage inputs and phosphorus remediation. Sci. Total Environ. 2000; 251: 477-495.
Neal C, Jarvie HP, Love A, Neal M, Wickham H, Harman SA. Water quality along a river continuum subject to point and diffuse sources. J. Hydrol. in press.
Neal C, Jarvie HP, Neal M, Love AJ, Hill L, Wickham H. Water quality of treated sewage effluent in a rural area of the upper Thames Basin, southern England, and the impacts of such effluents on riverine phosphorus concentrations. 2005; 304: 103-117.
Ordnance_Survey. ED-LINE Marketeer county boundaries, 1991.
SAS. SAS User Guide. SAS Institute Inc., Cary, North Carolina, USA, 2002.
Taylor MP, Macklin MG. Holocene alluvial sedimentation and valley floor development: the River Swale, Catterick, North Yorkshire, UK. 1997; 51: 317-327.
Wood FL, Heathwaite AL, Haygarth PM. Evaluating diffuse and point phosphorus contributions to river transfers at different scales in the Taw catchment, Devon, UK. J. Hydrol. 2005; 304: 118-138.

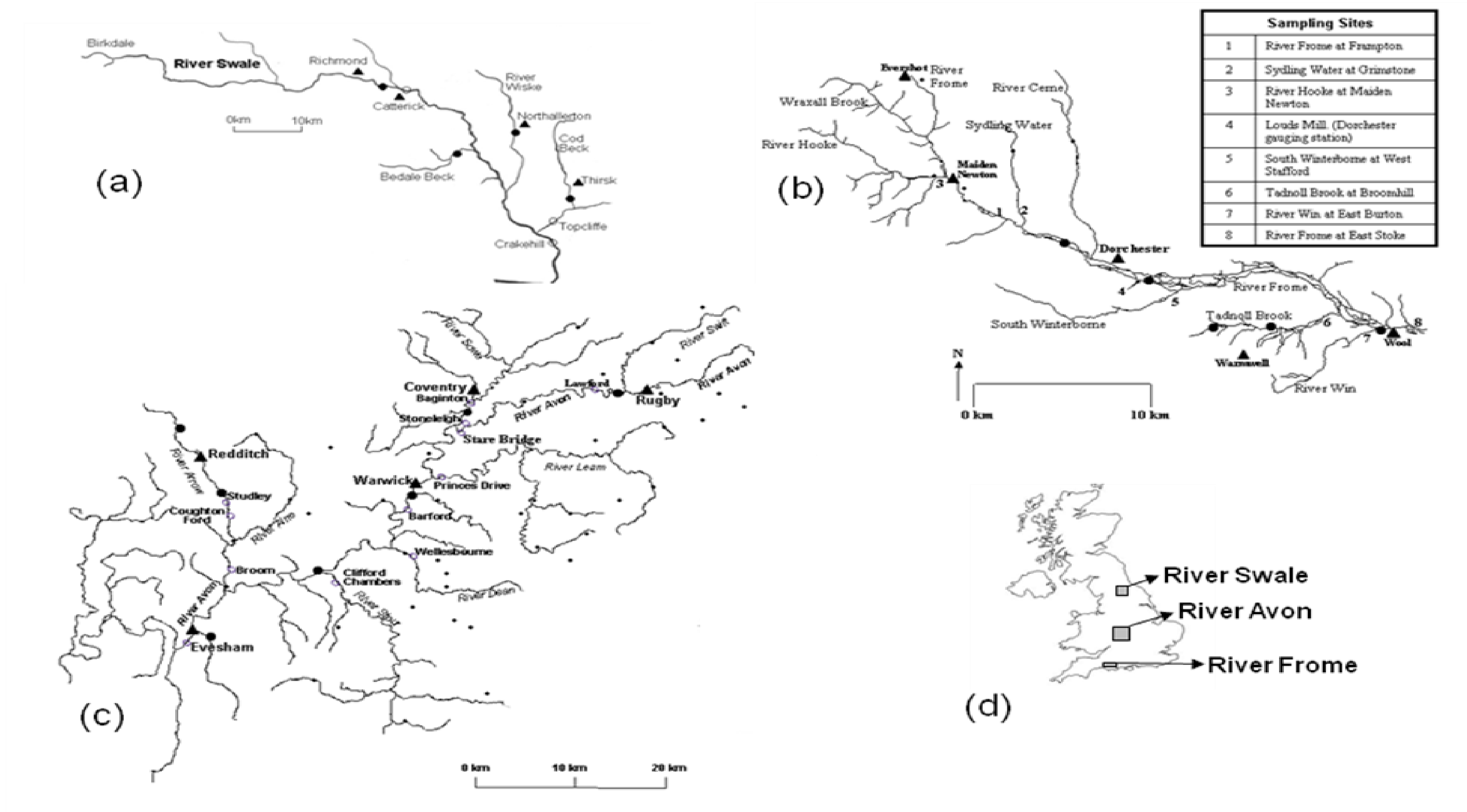
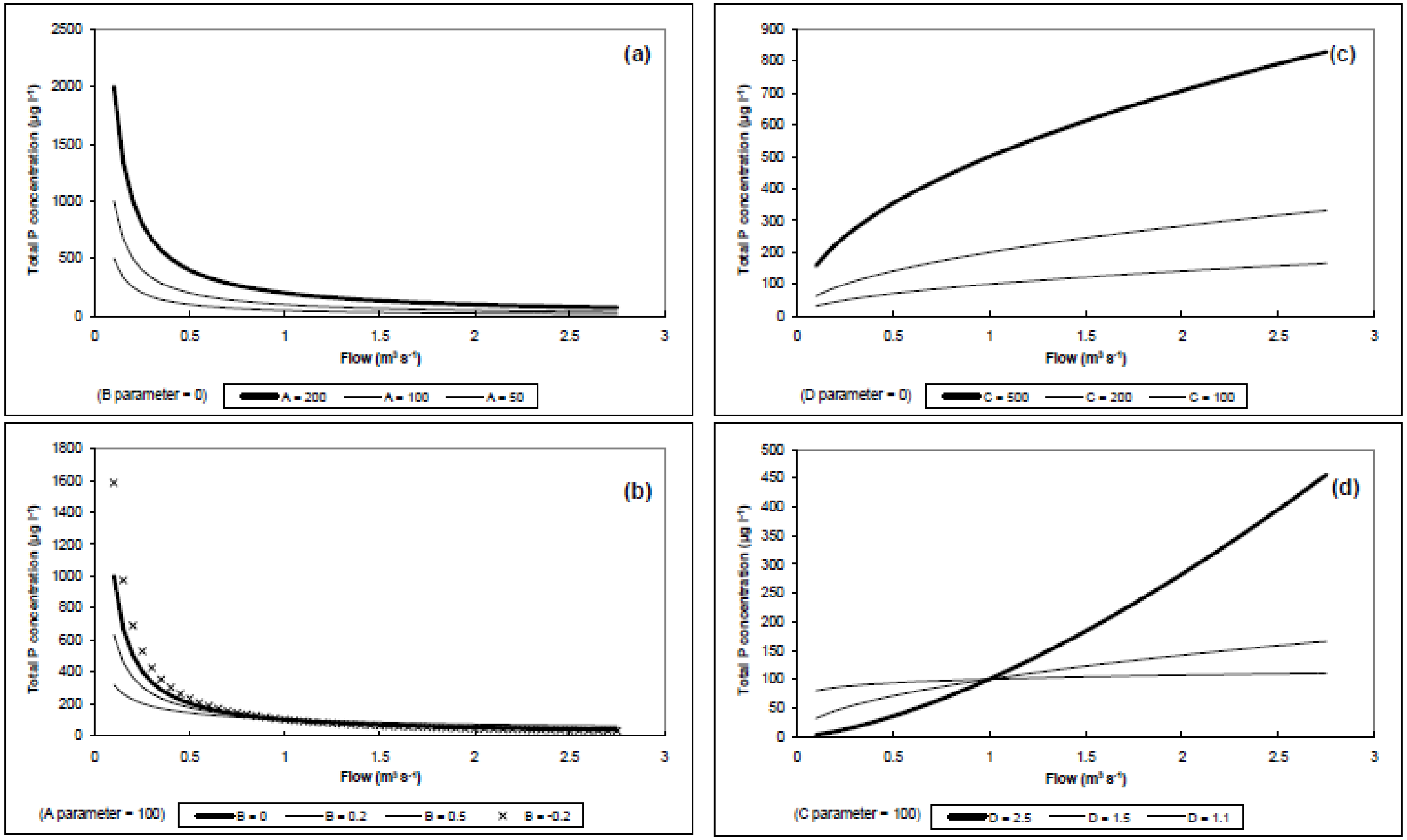


Figure 1. Location map of study areas. (a) The River Swale catchment, Yorkshire. (b) The River Frome catchment, Dorset. The numbers indicate the location of the monitoring points, with site names given in the adjoining table. (c) The River Avon catchment, Warwickshire. (d) Map of the United Kingdom, showing the locations of the study catchments. Monitoring sites = ○; Towns = ▲; Large sewage treatment works = ●; Minor sewage treatment works = •.

Figure 2. The effect of changing parameter values on the total phosphorus concentration versus flow relationship.



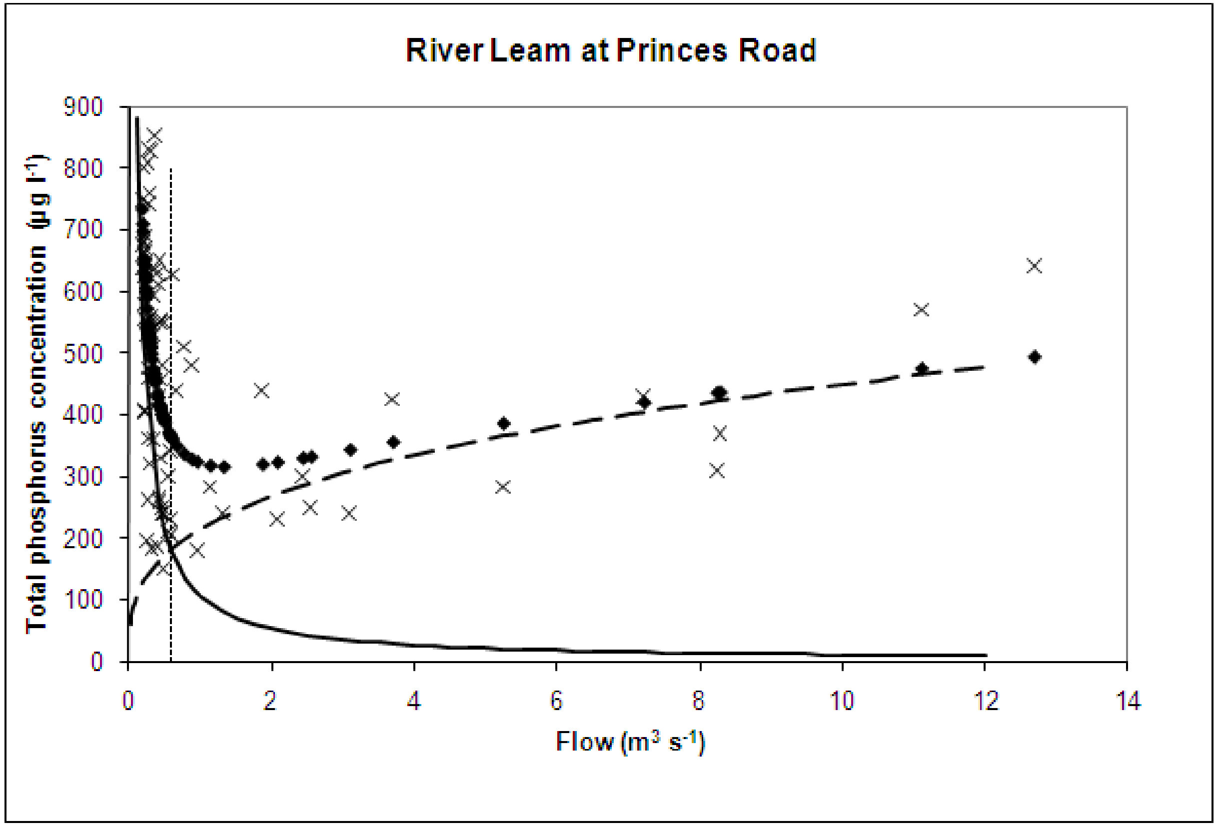


Figure 3. Example of a load apportionment model solution for the River Leam, Avon catchment. x = measured TP concentration data. Solid line = estimated TP concentration from point sources. Dashed line = estimated TP concentration from diffuse sources. ◆ = estimated total input (the sum of estimated point and diffuse inputs). Vertical dotted line = Q_e (the river flow at which the estimated point and diffuse inputs are equal).

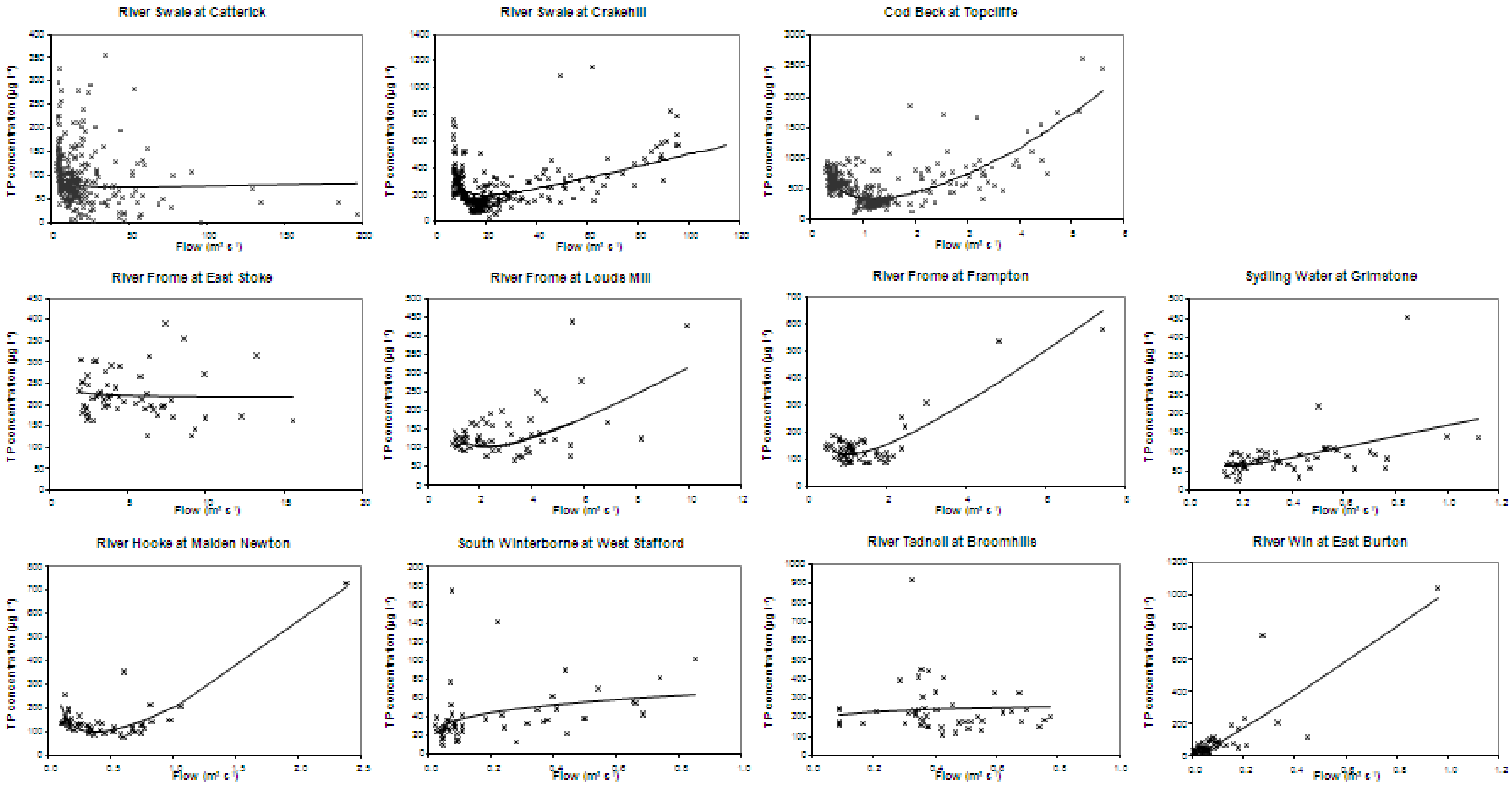


Figure 4. Relationship between total phosphorus (TP) concentration and flow for study sites in the River Swale and River Frome catchments. x = measured river TP concentration data. Solid line = combined TP concentrations from point and diffuse sources, using load apportionment modelling.

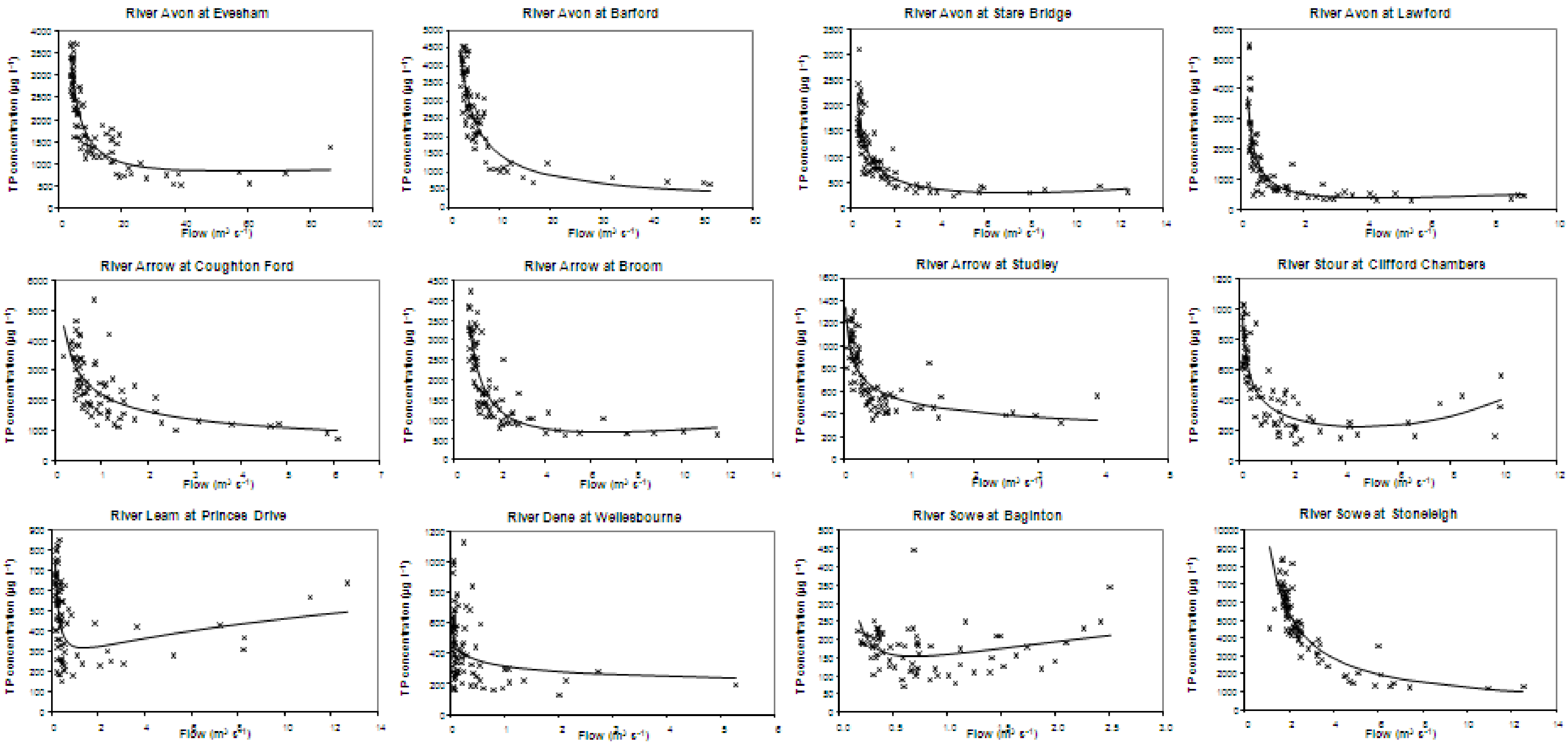


Figure 5. Relationship between TP concentration and flow for study sites in the River Avon catchment. x = raw data. Solid line = combined TP concentrations from point and diffuse sources, using load apportionment modelling.

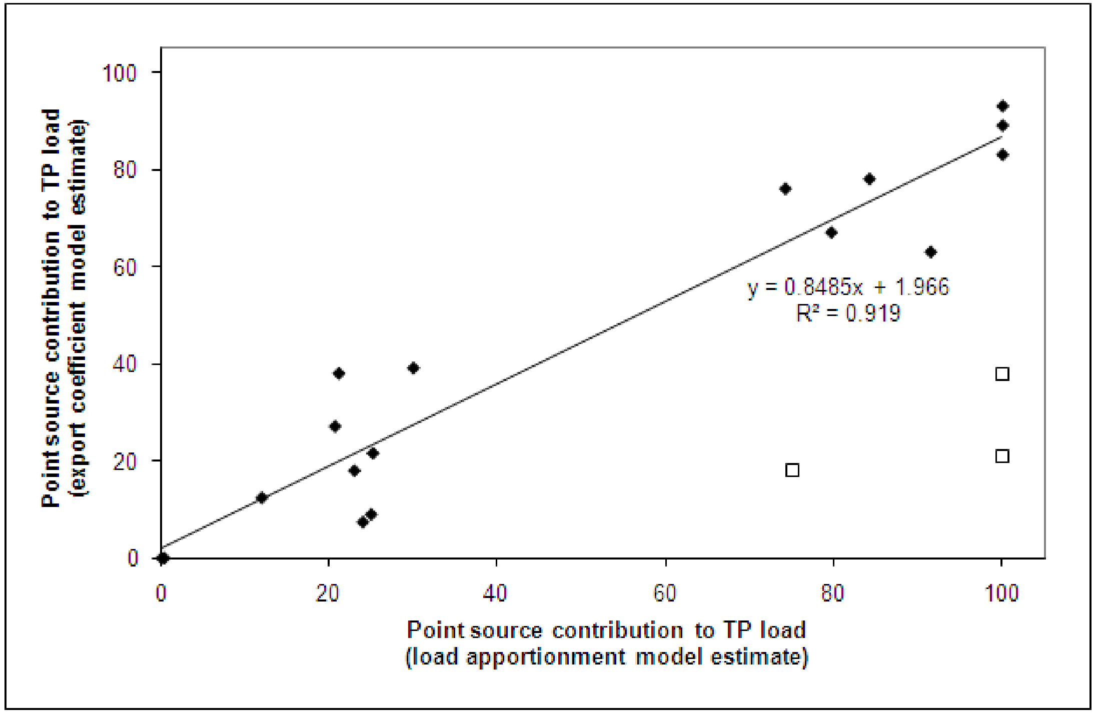


Figure 6. Comparison of the estimated percentage of the TP load contributed by point source inputs, as derived from phosphorus export coefficients and load apportionment modelling. □ = outlying results not included in the correlation equation.

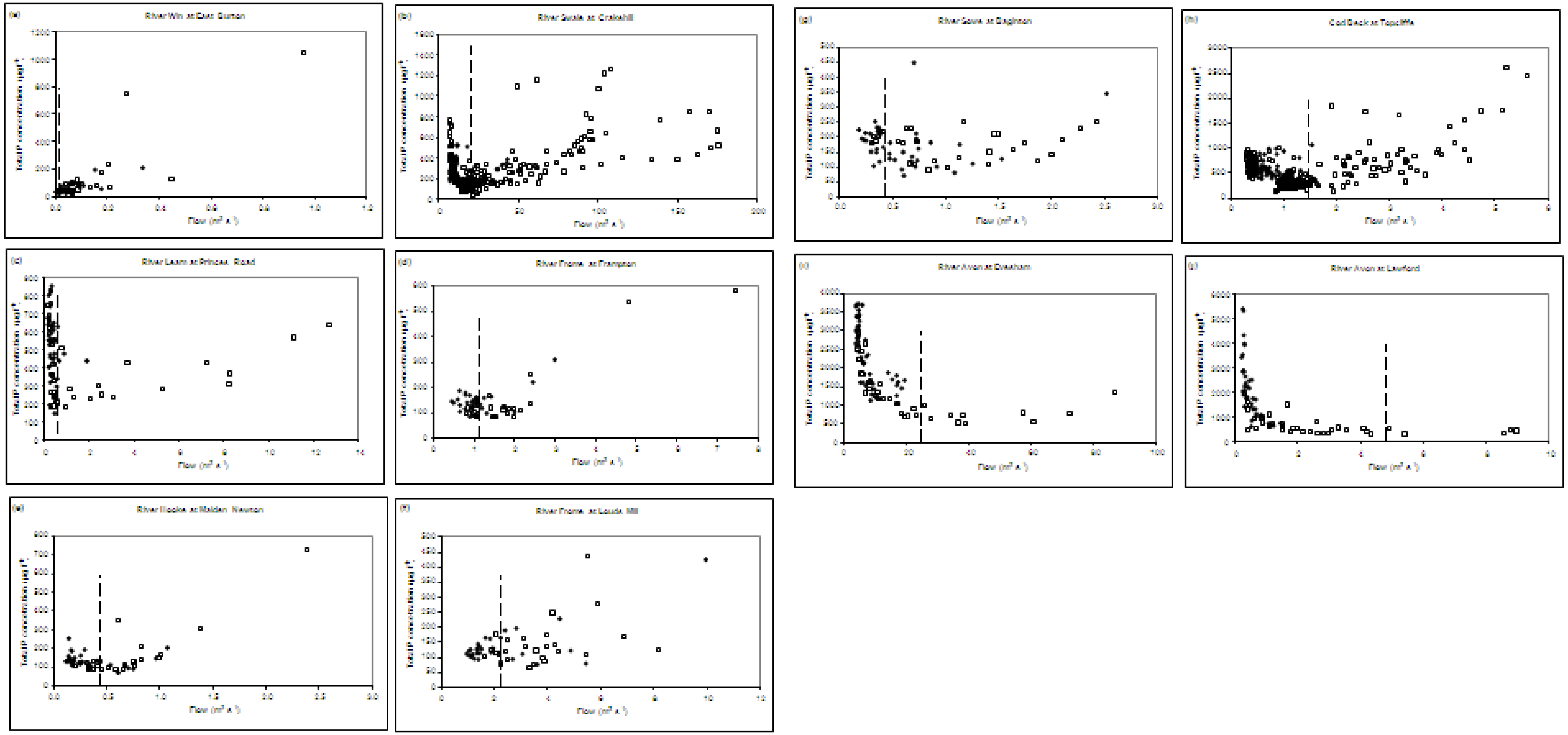


Figure 7. Seasonality of total phosphorus inputs. ◆ = samples taken during the main plant and algae growing season (1st April and 30th September) □ = samples taken between 1st October and 31st March. Dashed line = Q_e (the river flow at which the estimated point and diffuse inputs are equal)

Catchment	River	Sampling site	UK national grid reference	Model parameter values (± 95% confidence interval)				Q_r
				A	*B*	*C*	*D*	($m^3 s^{-1}$)
Swale	Swale	Catterick	42239, 49920	409 (242 - 576)	-	40 (1.6 - 78)	1.14 (0.88 - 1.39)	7.76
	Cod Beck	Topcliffe	44248, 47332	264 (246 - 281)	-	90 (66.8 - 112.7)	2.81 (2.62 - 3.00)	1.46
	Swale	Crakehill	44214, 47661	1975 (1714 - 2235)	-	5.3 (1.8 - 8.8)	1.98 (1.84 - 2.12)	19.9
Avon	Avon	Evesham	40435, 24315	11776 (10009 - 13542)	-	155 (-172 - 481)	1.35 (0.76 - 1.93)	24.9
	Avon	Barford	42680, 26090	8131.7 (6776 - 9487)	0.27 (0.139 - 0.390)	-	-	None
	Avon	Stare Bridge	43300, 27140	929 (818 - 1040)	0.30 (0.14 - 0.46)	0.96 (-20.3 - 22.3)	3.17 (-6.0 - 12.4)	11.0
	Avon	Lawford	44689, 27713	859 (779 - 940)	-	26.1 (-136 - 188)	2.22 (-1.02 - 5.46)	4.81
	Arrow	Coughton Ford	40855, 26035	2218 (2022 - 2413)	0.55 (0.43 - 0.68)	-	-	None
	Arrow	Broom	40868, 25332	2275 (2072 - 2478)	-	49.3 (-105 - 204)	2.02 (0.491 - 3.55)	6.64
	Arrow	Studley	40763, 26393	506 (454 - 559)	0.71 (0.65 - 0.77)	-	-	None
	Stour	Clifford Chambers	41960, 25280	374 (329 - 419)	0.56 (0.47 - 0.64)	0.296 (-2.82 - 3.4)	3.97 (-0.71 - 8.64)	8.12
	Leam	Princes Drive	43080, 26540	106 (77 - 134)	-	215 (128 - 301)	1.32 (1.09 - 1.55)	0.58
	Dene	Wellesbourne	42780, 25520	316 (236 - 395)	0.83 (0.72 - 0.93)	-	-	None
	Sowe	Baginton	43380, 27520	34.6 (18.4 - 50.9)	-	125 (94 - 156)	1.50 (1.11 - 1.88)	0.424
	Sowe	Stoneleigh	43320, 27280	9925 (8810 - 1104)	0.11 (-0.04 - 0.26)	-	-	None
Frome	Frome	East Stoke	38664, 86805	117	0.97	117	0.97	-
	Frome	Louds Mill	37080, 90345	105 (43.4 - 166.5)	-	16.7 (3.50 - 58.7)	2.26 (1.53 - 2.47)	2.25
	Frome	Frampton	36237, 94930	67.8 (48.2 - 87.5)	-	52.4 (35.1 - 69.6)	2.24 (2.05 - 2.44)	1.12
	Sydling	Grimstone	36393, 94720	4.67 (-5.0 - 14.3)	-	164 (116 - 210)	1.87 (1.13 - 2.61)	0.15
	Hooke	Maiden Newton	35951, 97615	21.4 (18.0 - 24.9)	-	181 (152 - 209)	2.57 (2.35 - 2.78)	0.436
	South Winterborne	West Stafford	37237, 89590	0.014 (-1.24 - 1.27)	-	66.2 (39.5 - 92.9)	1.24 (0.87 - 1.62)	0.001
	Tadnoll	Broomhills	38097, 88120	130	1.08	130	1.08	-
	Win	East Burton	38304, 86800	0.115 (-0.181 - 1219)	-	1030 (842 - 1219)	2.09 (1.90 - 2.28)	0.013

Table1. Parameter values from the load apportionment modelling.

Catchment	River	Sampling site	Load apportionment modelling				Export coefficient modelling
			Point source TP load (t y^{-1})	Diffuse source TP load (t y^{-1})	Point source contribution to TP load (%)	% of time that TP load dominated by point sources	Point source contribution to TP load (%)
Swale	Swale	Catterick	13	30	30	36	39
	Cod Beck	Topcliffe	8.3	15	35	80	-
	Swale	Crakehill	62	238	21	68	27
Avon	Avon	Evesham	371	129	74	88	76
	Avon	Barford	402	0	100	100	83
	Avon	Stare Bridge	31	2.9	91	98	63
	Avon	Lawford	27	6.9	80	94	67
	Arrow	Coughton Ford	71	0	100	100	89
	Arrow	Broom	72	13	84	95	78
	Arrow	Studley	9.4	0	100	100	38
	Stour	Clifford Chambers	14	4.6	75	95	18
	Leam	Princes Drive	3.3	12	21	77	38
	Dene	Wellesbourne	3.9	0	100	100	21
	Sowe	Baginton	1.1	3.3	25	36	9
	Sowe	Stoneleigh	347	0	100	100	93
Frome	Frome	Louds Mill	3.3	9.8	25	46	22
	Frome	Frampton	2.1	7.2	23	56	18
	Sydling	Grimstone	0.1	1.1	12	5	12
	Hooke	Maiden Newton	0.7	2.1	24	61	7
	South Winterborne	West Stafford	0.0	0.4	0.1	0	0
	Win	East Burton	0.0	1.0	0.4	13	0

Table 2. Estimated contributions from point and diffuse sources to the total TP load, derived from load apportionment modelling and by using export coefficients.