Erosion and Sediment Yield: Global and Regional Perspectives (Proceedings of the Exeter Symposium, July 1996). IAHS Publ. no. 236, 1996.

Sediment-associated phosphorus transport in the Warwickshire River Avon, UK

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Abstract This paper examines the partitioning of total P (TP) between dissolved (TDP) and particulate (PP) phases in the 2900 km^2 catchment of the River Avon, Warwickshire, over the period December 1994 to June 1995. Flow, sediment concentration, TP, TDP and PP data are presented for a selection of sites. P erosion potential has been determined by measuring the concentration of P in the < 63 μm particle size fraction of 18 soil types. Results indicate that PP accounts for 52% of the weighted daily TP load at the catchment outlet. Higher PP concentrations occur in rivers with major sewage effluent inputs. The greatest P erosion potential is associated with surface-water gleyed soils. Many soils have as much as 80% of P in bioavailable form.

INTRODUCTION

Increasing phosphorus (P) levels have been recorded in recent years in many UK rivers. Estimates of the contribution of point sources to the transport of soluble reactive phosphorus in UK rivers range from 43% to 36% (SDIA, 1989) but little information currently exists on the dominant forms of phosphorous in runoff. Whilst the EC Urban Waste Water Directive (EC, 1991) has now been implemented in the UK, and some 33 major rivers or river reaches have been designated as Sensitive Areas (Eutrophic) by the DOE (1994), little information currently exists in relation to the partitioning of P between soluble and particulate forms and the potential for various soil types under different land management systems to deliver sediment-associated P to major rivers.

The Warwickshire River Avon is one of the largest single river systems to be designated by the DOE (1994) as Eutrophic Sensitive and this paper presents preliminary results from a sampling and analytical programme established for the Avon and its tributaries in order to address the two issues identified above.

THE WARWICKSHIRE RIVER AVON

The River Avon is located in a lowland (190 m OD to 11 m OD) predominantly agricultural catchment in Midland England (Fig. 1(a)). The total catchment area is

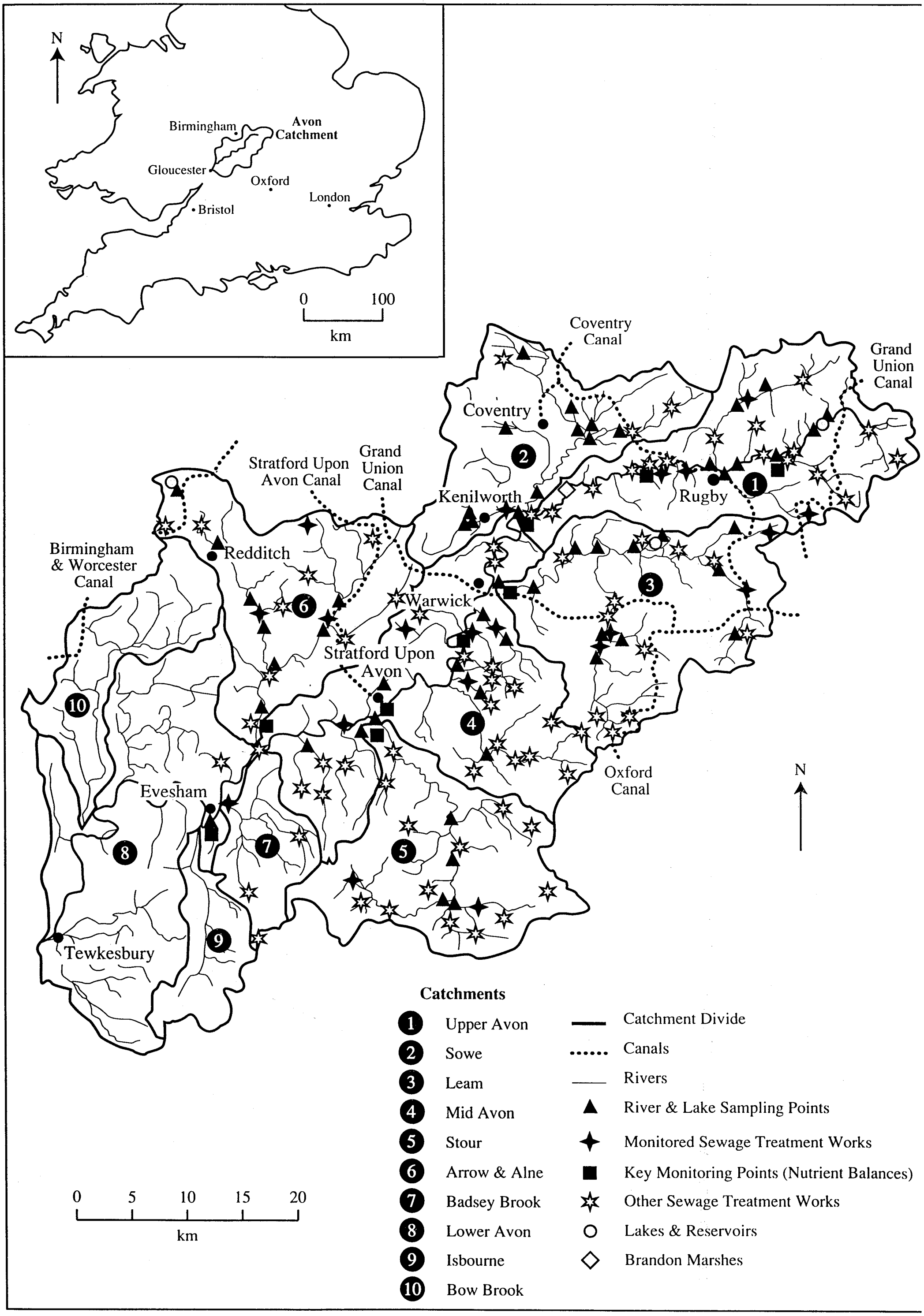

Fig. 1 Location (a) subcatchments and monitoring stations (b) of the Warwickshire River Avon.

c. 2900 km^2, which makes it the tenth largest river in Britain by catchment area. Mean annual discharge is 14.43 $m^3 s^{-1}$ (Ward, 1980). Rainfall ranges from 720 mm in the northeast to 599 mm in the southwest. Effective annual rainfall ranges from *c.* 250 mm to less than 150 mm (NRA, 1991).

Impermeable clays and mudstones cover over 80% of the total catchment area. Small areas of sandstone are to be found in the north and west whilst in the south and east, limestones of the Inferior Oolite series form the high ground of the Cotswold edge. The dominant soil types in the catchment reflect the underlying geology and include brown earths, stagnogleys, pelo-alluvial gleys with calcareous soils located in the southeast (Ragg *et al.*, 1984).

Around 900 000 people live within the Avon catchment, with over half occupying the headwaters of the upper Avon and Sowe subcatchments. Some 7.2% of the total catchment area is classified as urban. There is one major effluent discharge of 120 Ml day^{-1} in the Avon system which is located on the River Sowe (Fig. 1(b)). Other major sewage discharges are at Rugby (20 Ml day^{-1}), Warwick (35 Ml day^{-1}) and Redditch (30 Ml day^{-1}). The total of these discharges (*c.* 205 Ml day^{-1}) accounts for around half of the flow at the 95th percentile on the flow duration curve at Evesham. Of the total catchment area only 4.4% is woodland. Cereals occupy 36% of the catchment area, grassland 30%, root crops 7%, oil seed rape 5% and legumes 2%.

FIELD SAMPLING AND LABORATORY ANALYSIS

In 1994, a field sampling programme was established in order to collect water samples from 79 river, sewage outfall and reservoir sites throughout the Avon catchment at frequencies ranging from weekly to monthly (Fig. 1(b)). A time-based rather than flow-based sampling strategy has been used in this research project due to the size of the catchment, which constrains the sampling schedule, and the limitations imposed by laboratory processing time. Five main river locations were sampled weekly between Rugby (Upper Avon) and Evesham (Lower Avon) (Fig. 1(b)). Whilst a number of field and laboratory determinations are undertaken for each sampling point, only P, flow and suspended sediment data for the period December 1994 to June 1995 are considered here.

Laboratory analysis was undertaken by the Environment Agency (National Laboratory Services) in Nottingham within two days of sample collection. Total Phosphorus (TP) was analysed using an acidic perchlorate digestion on unfiltered homogenized samples. Total Dissolved Phosphorus (TDP) was determined by the same method on field-filtered (<0.45 μm) water samples. The difference between TP and TDP is referred to as the Particulate Phosphorus fraction (PP). Suspended sediment concentrations in each sample were determined gravimetrically on filtered (<0.45 μm) water samples.

In June 1995 18 major soil series were sampled from grassland and cereal fields (Table 1). Five soil samples (0-5 cm depth) were collected from random locations in a 1 m^2 quadrat and bulked for subsequent analysis. Sampling was limited to the upper 5 cm of the soil profile under the assumption that this represented an integrated sample to the maximum depth from which eroded soil was likely to contribute to the suspended sediment load of the rivers. Samples were oven dried at 50°C for 48 h and dry sieved to <63 μm for subsequent chemical analysis. Phosphorus speciation of triplicate sub-

Table 1 Soil series sampled.

Soil type	Soil code	Soil series	Soil type	Soil code	Soil series
Pelo-alluvial gley	813a 813b	Midelney Fladbury 1	Stagnogleyic argillic brown earth	572f 572g 572h	Whimple 3 Dunnington Oxpasture
Pelostagnogley soils	712b	Denchworth	Gleyic brown earth	543	Arrow
Typical stagnogley soils	711b 711c 711f 711m 711t	Brockhurst 1 Brockhurst 2 Wickham 2 Salop Beccles 3	Typical brown earth Typical argillic soils	541r 431	Wick 1 Worcester
Stagnogleyic argillic brown earth	572c 572e	Hodnet Whimple 2	Typical calcareous pelosols	411a 411b	Evesham 1 Evesham 2

Soil descriptions and classification after Ragg *et al.* (1984).

samples was undertaken using the modified Psenner sequential extraction scheme described by Petterson & Istvanovics (1988) and Stone & English (1993) in order to identify the potential for subsequent P release. A threefold functional classification of bioavailable (Non-apatite inorganic-P: NAIP), residual (Apatite inorganic-P: AIP) and organic-P (OP), based on the subdivisions recognized by Stone & English (1993), are used in this paper. Total P is here defined as the sum of NAIP, AIP and OP.

P TRANSPORT IN THE AVON CATCHMENT

The concentrations of TP, TDP, PP and suspended solids for three monitoring stations on the Avon are shown in Fig. 2. The River Sowe (Fig 2(a)), with a major sewage effluent input at Finham, shows a decline in TP concentration with increasing discharge in January and February, low suspended solids concentrations and a dominance of TDP. Concentrations of TP rise to almost 5 mg l^{-1} in late March and early April. On the Leam (Fig. 2(b)), with no major sewage effluent input, TP concentrations are below 0.6 mg l^{-1}, but a significant proportion of TP in storm events in December and January is associated with PP. The early summer rise in TDP concentrations does not occur until May. At Evesham, the total output from the Avon catchment (Fig. 2(c)) shows the integration of the various subcatchment responses. Maximum TP concentrations approach 3 mg l^{-1} in June, but a significant increase in PP concentrations is associated with the January flood events. The PP load in these floods makes a major contribution to the TP transport over the 7 month period (Fig. 3(a)).

Weighted mean daily TP, PP and TDP loads for each site were estimated in two stages. First, the daily load was estimated from the product of instantaneous concentration and discharge. Secondly, the weighted daily load was estimated from:

$$\mathrm{WDL} = \sum_{i=1}^{n} (\mathrm{DL} \times K) \qquad (1)$$

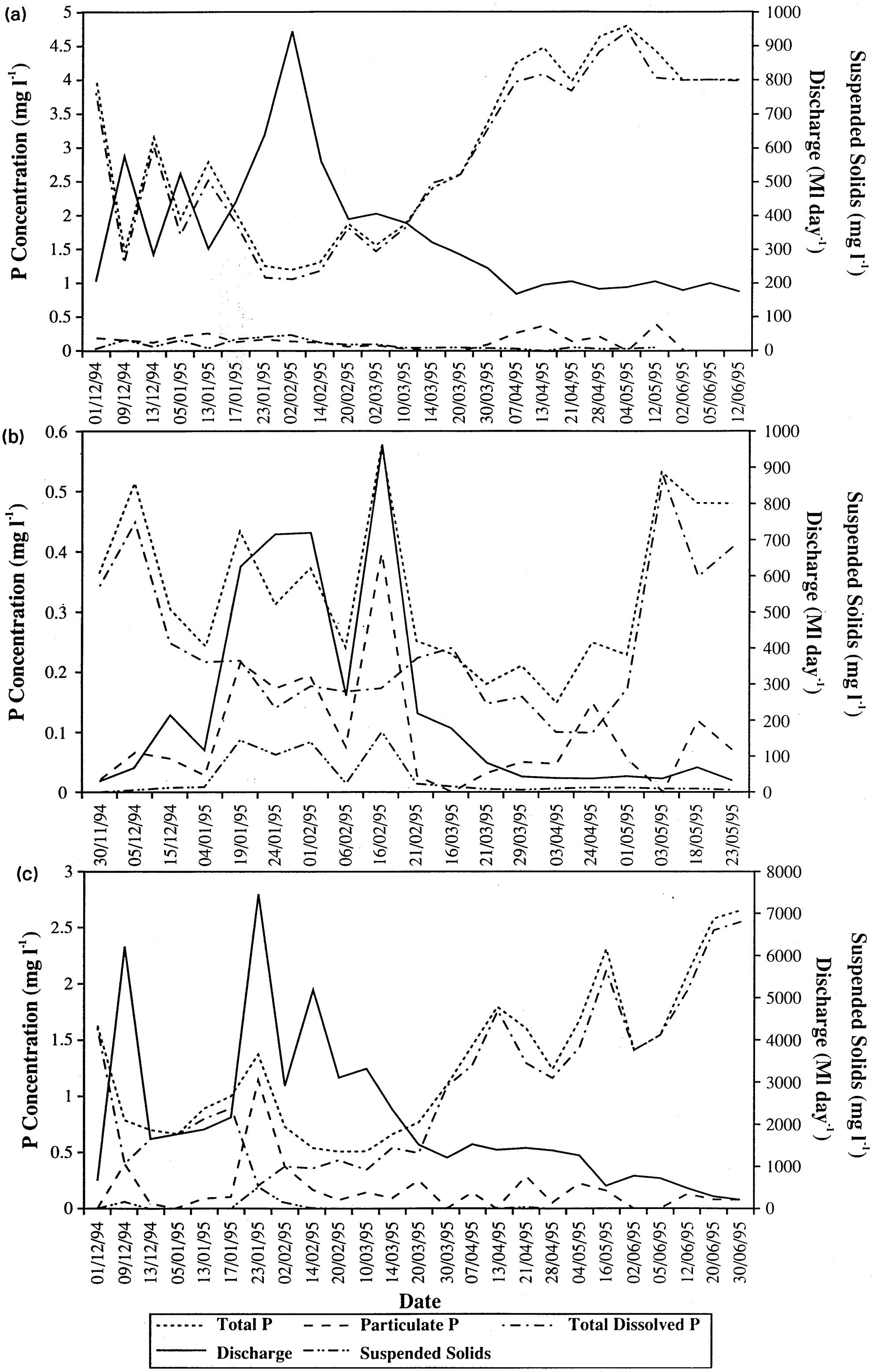

Fig. 2 Temporal trends in TP, TDP, PP, discharge and suspended solids in the Rivers Sowe (a), Leam (b) and Avon at Evesham (c).

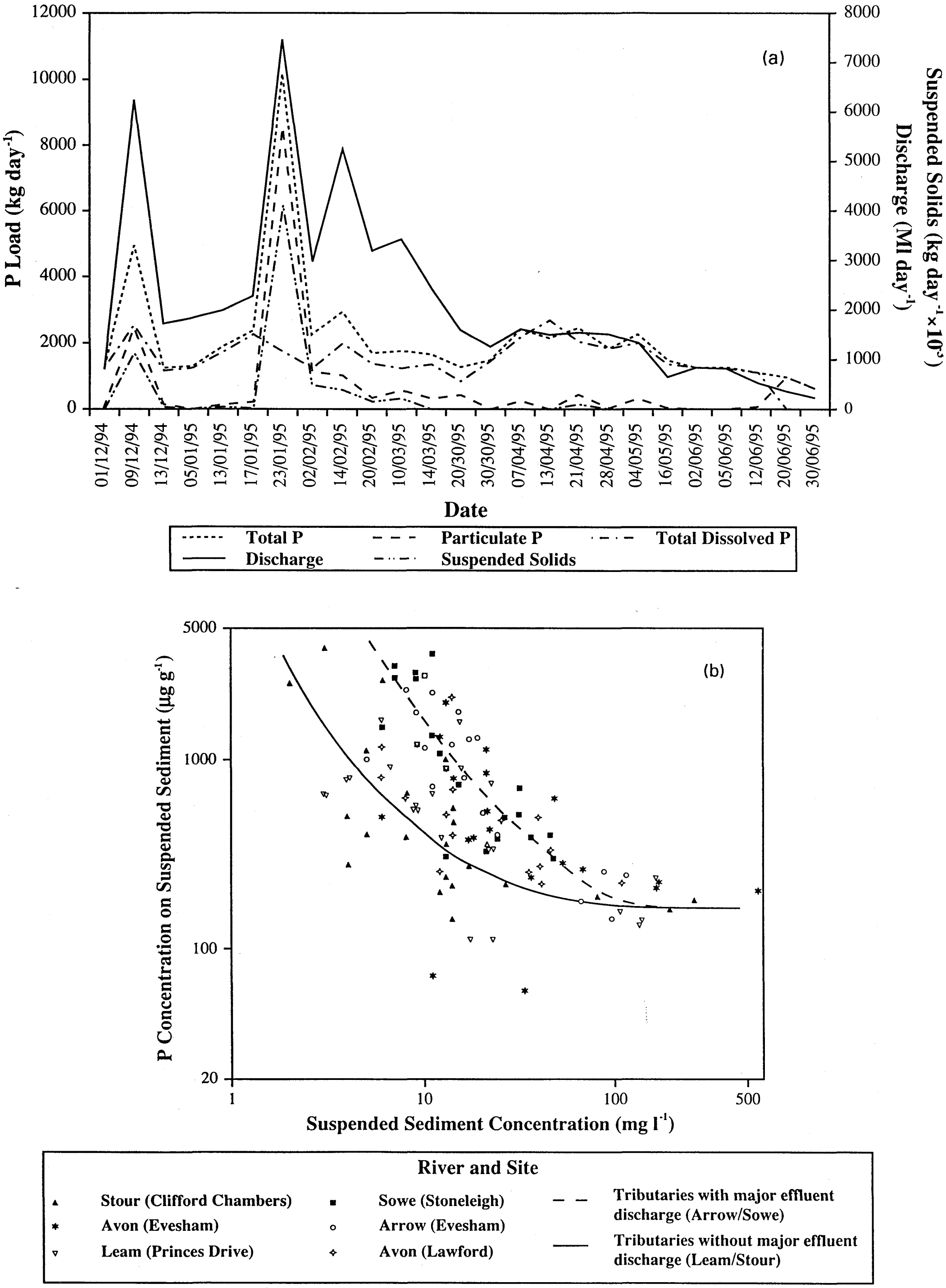

Fig. 3 Load of TP, TDP, PP and suspended solids in the River Avon at Evesham (a) and the relationship between PP concentration and suspended solids concentration at six river monitoring stations (b).

where WDL = weighted daily load; DL = daily load; K = a flow proportional weight; and n = sample size. K, the flow proportional weight, was derived as:

$$K = \frac{Q_i}{\sum_{i=1}^{n} (Q_i)} \tag{2}$$

where Q_i = mean daily discharge.

No attempt has been made in this preliminary analysis to estimate mean daily or annual P loads from extrapolation rather than interpolation procedures (cf. Walling *et al.*, 1992) since only 7 months of data are currently available. The relative contribution of PP and TDP to TP load is expressed as a proportion of WDL (equation (1)).

On the basis of the above calculation procedure, it has been estimated over the seven month monitoring period that the Avon at Evesham transports almost 3500 kg TP day^{-1} of which 52% is PP. However, there are substantial spatial variations in TP loads and in the relative proportion of PP and TDP transported (Table 2). At the monitored sewage works, PP contributes between 7 and 17% of P load.

In rivers with major effluent discharges (Sowe and Arrow) PP contributes less than 20% of TP load. In rivers with no major effluent discharges (Leam and Stour) PP contributes over 40% of the TP load. However, the contribution of PP to TP load at Evesham (Table 2, Fig. 3(a)) is higher than would be expected from the above calculations which would suggest some in-stream adsorption of P to actively transported sediment. The possible significance of in-stream adsorption is supported by the relationship between PP concentration and the concentration of suspended sediment in river water samples (Fig. 3(b)). Two groups of rivers are identified in this diagram. First, rivers with a significant contribution from effluent discharge (Arrow and Sowe) show high concentrations of PP at suspended sediment concentrations below 100 mg l^{-1}. Secondly, rivers with no major effluent inputs (Leam and Stour) have much lower PP concentrations than the Arrow or the Sowe. At low suspended sediment concentrations, the difference between these river types becomes more pronounced. However, there is also a substantial difference between the PP concentrations of rivers receiving no effluent input which may reflect variations in the P concentration of eroded catchment soils. This issue is considered in the next section.

Table 2 P transport in the River Avon and subcatchments.

Site	PP (kg day^{-1})	TDP (kg day^{-1})	PP as % TP
Avon (Lawford)	64.45	126.44	33.8
Sowe (Stoneleigh)	62.75	793.63	7.4
Leam (Princes Drive)	136.51	108.81	55.6
Stour (Clifford Chambers)	83.81	111.58	42.9
Arrow (Broom)	75.03	304.04	19.8
Avon (Evesham)	1794.20	1649.48	52.1

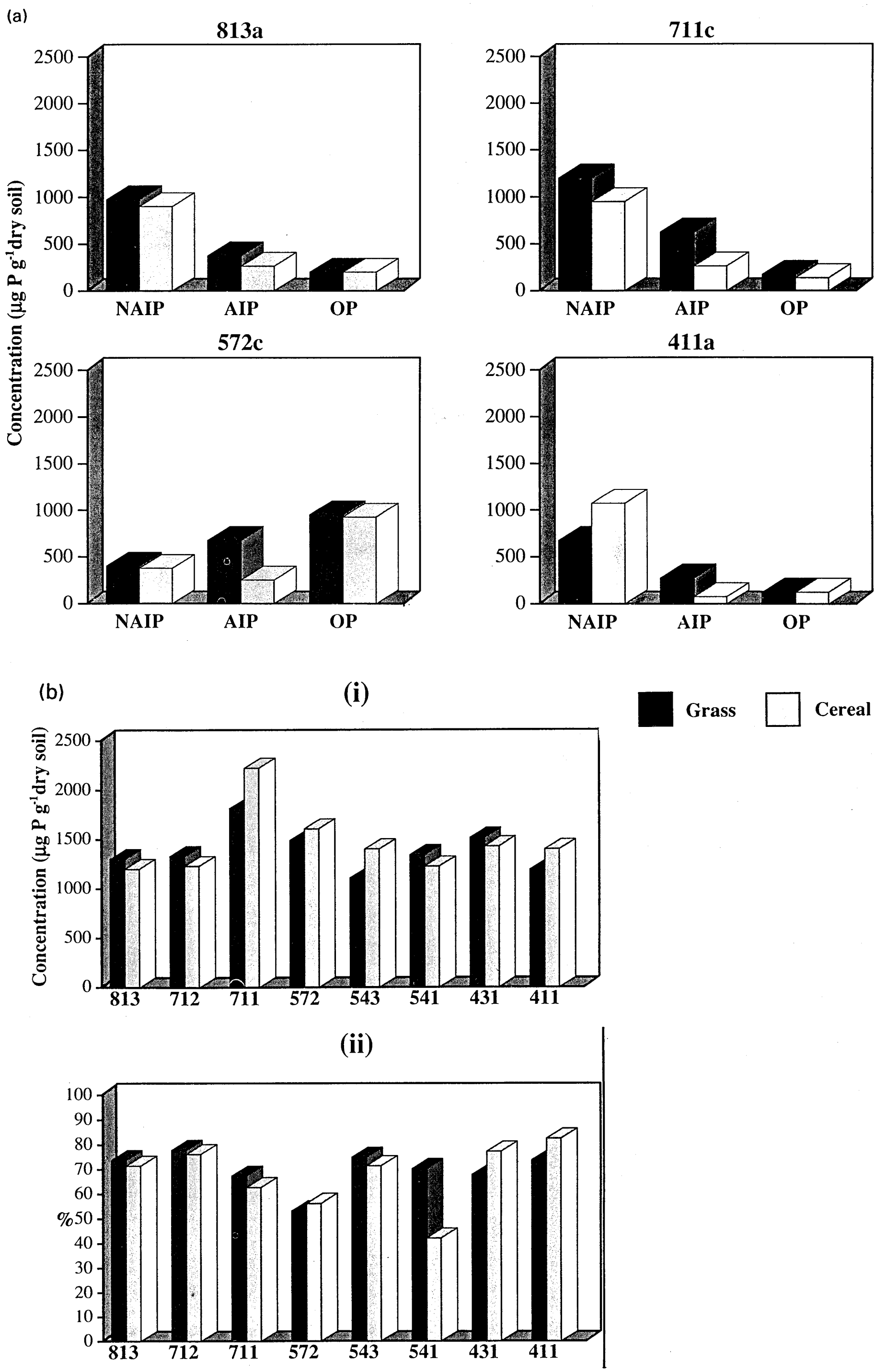

Fig. 4 NAIP, AIP and OP concentrations in the <63 μm particle size fraction of four soil series (a); the total P concentration (NAIP + AIP + OP) of eight soil types (b(i)) and the percentage of bioavailable P in eight soil types (b(ii)).

SOIL P ASSOCIATIONS

Examples of the distribution of the three P fractions in grassland and cultivated soils reveal some complex patterns (Fig. 4(a)). The alluvial gley (813a) is dominated by NAIP, but with significant AIP and OP fractions. A similar pattern, but with higher overall concentrations, is found in many of the stagnogley soils (e.g. 711c). Some of the brown earths (572c) show P to be dominant in the OP and AIP fractions. The calcareous soils have low overall P concentrations and the major components are NAIP and AIP.

Total P concentrations in the 18 soil series are grouped into the eight major soil types of Table 1 and plotted by land-use classes in Fig. 4(b(i)). Total P concentrations range from over 2000 to under 1500 $\mu g\ g^{-1}$. There is no statistically significant difference between P concentrations in soils under grassland and cereal crops for the 18 individual soil series (t test; $p = 0.05$). The greatest sediment-associated P concentrations are found in the $< 63\ \mu m$ fraction of the stagnogley soils (711 and 572) which are widespread throughout the central portion of the Avon catchment. Lowest sediment-associated P concentrations are associated with calcareous soils (411) and alluvial gleys (813). Calcareous soils dominate the Stour subcatchment and this river generally exhibits the lowest PP concentration (Fig. 3(b)).

The patterns shown in Fig. 4 suggest that the highest concentrations of sediment-associated P are found in the heavy surface-water gley soils where runoff might be expected to produce high levels of erosion. Indeed, in Warwickshire, recent estimates suggest that sediment yields from similar soils on mixed agricultural land approach 40 $t\ km^{-2}\ year^{-1}$ (Foster *et al.*, 1990). However, highest losses in this study were shown to be associated with grassland where yields reached 70 $t\ km^{-2}\ year^{-1}$ and only 10 $t\ km^{-2}\ year^{-1}$ from cultivated fields (cereals).

Between 50 and 80% of total P is bioavailable (Fig. 4(b(ii))). This has significant implications for in-stream P adsorption/desorption rates. Furthermore, the OP fraction in some soils may also become available for release depending on the nature and rate of in-stream mineralization processes (Stone & English, 1993).

CONCLUSIONS

These preliminary analyses indicate that PP contributes 52% of the daily TP load at Evesham. In part, the high PP contribution to the TP load appears to be controlled by in-stream adsorption. However, in rivers receiving no effluent input there is a higher PP concentration associated with the suspended sediment of the Leam than the Stour and this appears to reflect the difference in total P concentrations in the local soils. From these preliminary results, the land-use control on soil P concentrations is not evident. Whilst the PP concentration in the lower Avon appears to be dominated by effluent inputs to the upper Avon and Arrow, eroded soils will carry a significant proportion of both bioavailable and organic P. The latter may also make a contribution to P availability depending on the rate of mineralization. The difference in the PP concentration between rivers receiving and not receiving effluent appears to diminish as suspended sediment concentrations increase. This trend may reflect the dominance of diffuse over point sources at high discharges and the shorter residence times of water in the channel to allow P adsorption by the suspended sediment.

Acknowledgements The research reported was funded by the UK Environment Agency. Flow measurements have been provided by the hydrometric unit of the Environment Agency (Solihull) and Severn-Trent plc. Field sampling was undertaken by Paul Andrew, Suzanne Howarth and Sarah Harrison, and laboratory analysis has been undertaken by the Environment Agency (National Laboratory Services), Nottingham, UK. Thanks go to Jason Jordan for the diagrams.

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