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The phosphorus content of fluvial sediment in rural and industrialized river basins

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Abstract

The phosphorus content of fluvial sediment (suspended sediment and the $<63\ \mu\text{m}$ fraction of floodplain and channel bed sediment) has been examined in contrasting rural (moorland and agricultural) and industrialized catchments in Yorkshire, UK. The River Swale drains a rural catchment with no major urban and industrial areas, and the total phosphorus (TP) content of fluvial sediment is generally within the range $500\text{--}1500\ \mu\text{g g}^{-1}$. There is little evidence of any major downstream increase in TP content. In contrast, fluvial sediment from the industrialized catchments of the Rivers Aire and Calder exhibits both higher levels of TP content and marked downstream increases, with values of TP content ranging from $<2000\ \mu\text{g g}^{-1}$ in headwater areas upstream of the main urban and industrial areas, to values $>7000\ \mu\text{g g}^{-1}$ at downstream sites. These elevated levels reflect P inputs from point sources, such as sewage treatment works (STWs) and combined sewer overflows. The influence of STWs is further demonstrated by the downstream increase in the inorganic P/organic P ratio from <2 in the headwaters to >4 in the lower reaches. Comparison of the P content of suspended sediment with that of the $<63\ \mu\text{m}$ fraction of potential source materials suggests that topsoil from upland moorland/pasture and from cultivated areas, and channel bank material are likely to be the main sources of particulate P (PP) in the River Swale and in the headwaters of the Rivers Aire and Calder. In the middle and lower reaches of the Rivers Aire and Calder, inputs associated with urban and industrial land uses, such as STWs, industrial effluents and street dust, are likely to represent the dominant sources of PP. During high flow events, such urban inputs may be diluted by inputs from moorland and agricultural land in the headwaters. Consequently, for all three rivers, there are inverse relationships between the TP content of suspended sediment and both discharge and suspended sediment concentration, reflecting changes in sediment and P sources during high flow events. Spatial variations in the P contents of the $<63\ \mu\text{m}$ fraction of overbank floodplain deposits and channel bed sediment evidence a similar pattern as those for suspended sediment, with relatively low levels of TP in the River Swale and elevated levels in the middle and downstream reaches of the Rivers Aire and Calder. The PP concentrations associated with floodplain and channel bed sediment are, however, lower than equivalent values for suspended sediment, and this primarily reflects the differences in the particle size composition between the three types of sediments. Rates of floodplain deposition and the amounts of fine-grained sediment stored in the river channels are relatively high, and suggest that such environments may represent important sinks for PP. Based on the sediment samples collected from the study basins, a simple four-fold classification which relates the TP content of suspended sediment to upstream land use has been established. Both the range and the absolute values of TP content tend to increase with an increase in the level of urbanization and industrialization.

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1. Introduction

Many recent studies have shown that a large proportion of the total phosphorus (TP) load transported by rivers is in the form of particulate P (PP) [1–4]. Sources of PP in rivers include both point and diffuse source inputs, and such inputs can be both organic and inorganic in form. Diffuse sources generally represent inputs from both geological sources and land use activities (i.e. fertiliser application). The main point sources are sewage treatment works and industrial effluents. Inorganic PP is generally more important than organic PP in rivers that are dominated by point source inputs [5]. Consequently, the total, inorganic and organic P content of suspended sediment will vary both spatially and temporally, due to variations in the relative importance of point and diffuse sources, variations in land use and other catchment characteristics.

The sediment delivery system plays an important role in the flux of PP through river systems and its delivery to receiving water bodies (cf. [20]). The deposition and storage of sediment on floodplains and channel beds and its subsequent remobilization can exert an important influence on the routing, transport and fate of PP in river basins. Deposition of sediment on floodplains and channel beds can result in conveyance losses and either temporary or longer-term storage of PP (cf. [6,7,26]). Equally, remobilization of channel bed sediment and reworking of floodplain deposits by bank erosion and channel migration can reintroduce PP back into the channel system, even if contributions from other sources have been reduced.

Suspended sediment and sediment deposited on floodplains and channel beds can also exert an important influence on dissolved P (DP) concentrations in river systems. For example, studies reported by Dorioz and Bowes and House [8,9] have shown that, depending on the P concentration gradient between the sediment and water, large amounts of DP may be sorbed onto fluvial sediment. Conversely, P can be released from sediment into the surrounding water.

Information on P fluxes, storage and remobilization is needed in order to plan and implement appropriate basin management strategies. However, despite a growing recognition of the importance of PP to total P fluxes in rivers, sediment-associated P transport in river systems is still relatively poorly understood. There are, for example, relatively few data on the P content ($\mu\text{g g}^{-1}$) of suspended sediment in rivers draining catchments with different land use and catchment characteristics. Such information is needed not only to characterise the P content of suspended sediment, and thus to identify likely sources, but also in order to estimate both total PP and total P loads. Furthermore, there is little information on conveyance losses and storage of PP associated with sediment deposited on

floodplains and channel beds, particularly within large basins. Such components of the delivery system are an important component of the overall P budget of a catchment [8].

This paper reports an investigation of temporal and spatial variations in the P content of fluvial sediment (suspended sediment and the $<63\ \mu\text{m}$ fraction of floodplain and channel bed sediment) within two contrasting large catchments in Yorkshire, UK. The River Aire (1932 km²) drains a highly urbanized and industrialized catchment, whereas the adjacent River Swale (1363 km²) drains a largely rural (moorland and agricultural) catchment of similar size and with similar physiographic characteristics. The main objectives of the study were:

1. To examine the magnitude and downstream trend of the P (total, inorganic and organic) content of suspended sediment in the study rivers.
2. To identify the likely sources of PP.
3. To examine inter- and intra-storm variations in the P content of suspended sediment.
4. To examine the magnitude and downstream trend of the P content of overbank floodplain deposits and channel bed sediment, and to assess the significance of floodplain and channel bed deposition for PP fluxes in the study rivers.

2. Materials and methods

2.1. The study area

The Rivers Aire and Swale are both tributaries of the River Ouse, which drains into the North Sea via the Humber Estuary (Fig. 1). The River Aire has a catchment area of 1932 km² above the UK Environment Agency (EA) gauging station at site 1. The River Calder is the main tributary of the River Aire and has a catchment area of 930 km² upstream of the EA gauging station at site 12. The River Calder contributes about 52% of the flow and about 56% of the suspended sediment load of the River Aire at site 1. The long-term average (LTA) discharges at sites 1 and 12 are $35.8\ \text{m}^3\ \text{s}^{-1}$ (1977–1997) and $18.6\ \text{m}^3\ \text{s}^{-1}$ (1987–1997), respectively. The headwaters of the Aire/Calder system are dominated by rural land use, but the middle and lower reaches drain heavily urbanized and industrialized areas of the catchment, with a population of about 2 million people. Leeds is the largest city in the catchment, with a population of over 0.5 million. The main industries in the catchment include wool, textiles, chemicals, engineering, and food and drink manufacturing. Most of the industrial effluent is treated by sewage treatment works (STWs), although some industries have consents for trade effluent to be discharged directly into the river. There are 69 STWs and 1734 consented

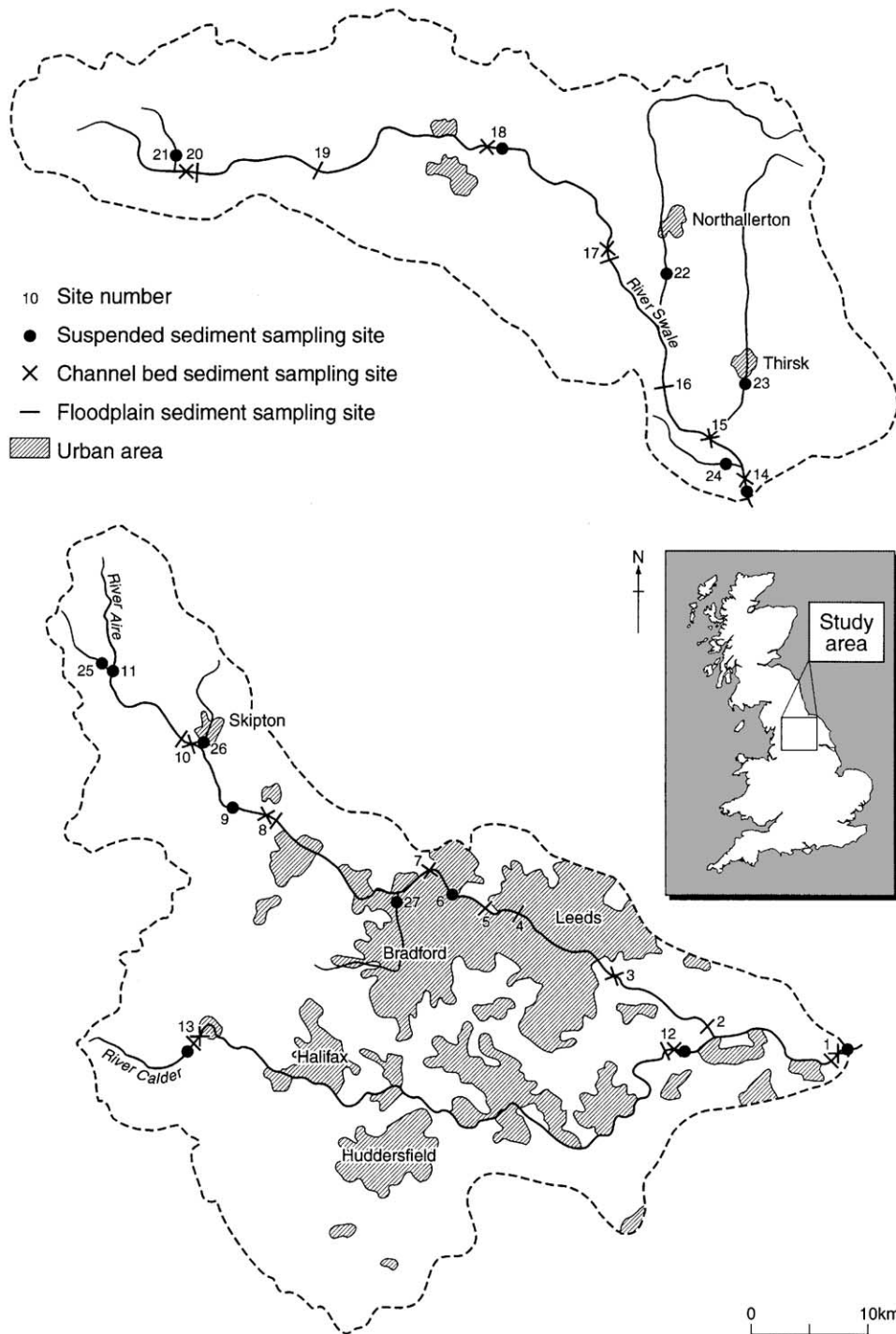


Fig. 1. Location map showing the study catchments and the suspended sediment and floodplain and channel bed sediment sampling sites.

discharges in the Aire/Calder basin [10,11], and most of these are located in the middle and lower reaches of the basin. Consequently, the middle and lower reaches of

the Rivers Aire and Calder are heavily polluted. In contrast, the River Swale is a relatively unpolluted river along its entire length, and drains a predominantly rural

catchment with a low population density. It has a catchment area of 1363 km² at the EA station at site 14 (the LTA discharge is 19.6 m³ s⁻¹ (1955–1990)). The LTA (1961–1990) annual average catchment precipitation for the Aire, Calder and Swale catchments are 973, 1024 and 860 mm, respectively. The headwaters of both the Aire/Calder and the Swale catchments lie in the Pennine uplands to the west and are dominated by moorland and pasture land use. Low-lying land lies to the east of these uplands and is dominated by cultivated land (Swale) and cultivated and urban land use (Aire/Calder). Altitude ranges from >700 m a.m.s.l. in the headwaters to <50 m a.m.s.l. in the lower reaches of the study area. Slopes range from >25° in the headwaters to ca. 2–4° in the lowlands. The underlying geology in the Aire/Calder catchment is Carboniferous limestone and millstone grit, while in the Swale catchment there are also Permian, Triassic and Jurassic strata to the east of site 18. The pH of the water in the Rivers Swale and Aire/Calder is typically ca. 8 and 7.5, respectively.

2.2. Sampling and laboratory methods

Samples of suspended sediment and floodplain and channel bed sediments were collected along the lengths of the Rivers Aire, Calder and Swale (Fig. 1) during the period November 1997–December 1999. Suspended sediment samples ($n = 148$) were collected at eight primary sampling sites (sites 1, 6, 9, 11–14, 18) and seven secondary sampling sites (sites 21–27) (Fig. 1), on occasions that encompassed a range of flow conditions and suspended sediment concentrations. Bulk suspended sediment samples were collected from the centre of the channel during high flow conditions, using a submersible pump, powered by a portable generator, to fill several 25 l acid-washed polyethylene containers. The sediment was recovered from the bulk samples by continuous-flow centrifugation. During low flow conditions, suspended sediment was collected by pumping water from the river through an Alfa Laval field-portable continuous-flow centrifuge. All suspended sediment samples were freeze-dried.

Samples of the fine-grained sediment stored within the upper ca. 5 cm of the channel bed ($n = 120$) were collected at 12 sites (Fig. 1) approximately every two months during the study period. At each site, replicate samples (which were later bulked to form a composite sample) were collected using a simple resuspension technique (cf. [12]) for water depths <1.0 m, and a purpose-built sampler (cf. [13]), operated from an inflatable boat, for water depths >1.0 m. Since the areas of the channel bed surfaces from which the samples were collected were known, these two sampling methods were also used to quantify the amounts of fine-grained sediment stored on the channel bed. In both cases, the bulk water samples collected in the containers

were left to settle-out under controlled conditions and the clear supernatant was siphoned-off. The remaining sediment was recovered by centrifugation and then freeze-dried.

Samples of overbank sediment deposited during individual flood events ($n = 117$) were collected using acid-washed astroturf mats (cf. [14]) of known surface area. These mats were deployed on the river floodplain prior to inundation and removed soon after the floodwaters had receded. The total mass of sediment collected on each mat was recovered using a stainless steel spatula after air-drying.

Samples of potential source materials ($n = 217$) within each catchment were also collected. Bulk samples (>500 g) of topsoil (top ca. 2 cm) from areas of woodland, moorland, permanent pasture and cultivated land, and of channel bank material (from the face of eroding channel banks) were collected using a stainless steel trowel. In the Aire/Calder catchment, samples of street dust were also collected from road surfaces near to drains (i.e. material likely to be transported into the river) using a similar approach. In addition, samples of influent were collected from a large STW near site 7 by filling acid-washed 25 l containers. These samples were left to settle, before the sediment was recovered by siphoning off the supernatant and drying. A single sediment sample was also collected from an outflow pipe emanating from a small industrial facility located on the bank of the River Calder near site 13, which was discharging down the bank into the river.

Prior to analysis for P content, the samples of floodplain and channel bed sediment were screened through a 63 µm sieve in order to facilitate comparison with the suspended sediment samples, where the <63 µm fraction accounted for >95% of the sample mass. The P content (total (TP), inorganic (IP) and organic (OP)) of bulk suspended sediment samples and of the <63 µm fraction of the floodplain and channel bed sediment samples and the source material samples (i.e. µg P g⁻¹), was determined using a Pye Unicam SP6 UV/visible spectrophotometer after chemical extraction (cf. [15]). Organic carbon (C) and nitrogen (N) concentrations were measured using a Carlo Erba ANA 1400 automatic nitrogen analyser. The particle size distribution and specific surface area of samples were determined using a Coulter LS130 laser diffraction granulometer, after the removal of organic matter, and chemical and ultrasonic dispersion.

3. Results and discussion

3.1. The phosphorus content of suspended sediment and associated downstream trends

Table 1 presents information on the P content of suspended sediment collected from the Rivers Aire,

Table 1
Average P and organic matter content and particle size composition of suspended sediment collected from the main sampling sites on the Rivers Aire, Calder and Swale and from tributary rivers in the Swale and Aire basins during the period November 1997–December 1999. Values in parentheses represent 1 standard error of the mean (SE_{mean})

River	Site	n	TP (µg g ⁻¹)	IP (µg g ⁻¹)	OP (µg g ⁻¹)	IP/OP	C (%)	N (%)	d ₅₀ (µm)	SSA ^a (m ² g ⁻¹)
Swale ^b	18	7	1163 (130)	736 (92)	427 (53)	1.8 (0.3)	7.52 (0.52)	0.33 (0.03)	6.81 (0.21)	0.79 (0.03)
	14	48	1385 (69)	955 (44)	430 (28)	2.5 (0.1)	5.48 (0.20)	0.31 (0.03)	7.49 (0.37)	0.73 (0.02)
	11	6	1534 (175)	836 (37)	697 (152)	1.4 (0.2)	8.01 (0.32)	0.57 (0.05)	6.72 (0.56)	0.78 (0.03)
Aire	9	20	2363 (114)	1517 (81)	846 (43)	1.8 (0.1)	9.70 (0.27)	0.82 (0.04)	6.08 (0.42)	0.86 (0.03)
	6	16	4148 (385)	2912 (277)	1236 (114)	2.4 (0.1)	12.0 (0.4)	1.04 (0.08)	6.95 (0.50)	0.76 (0.03)
	1	21	7538 (672)	6303 (513)	1426 (112)	4.6 (0.3)	13.2 (0.4)	1.12 (0.05)	6.50 (0.19)	0.77 (0.01)
Calder	13	1	1663	1193	470	2.5	8.73	0.50	7.20	0.81
	12	6	6644 (1644)	5353 (1411)	1291 (235)	3.9 (0.3)	13.2 (1.22)	1.02 (0.16)	6.20 (0.33)	0.83 (0.02)
Gunnorside Beck	21	1	736	503	233	2.2	4.07	0.17	8.51	0.72
	22	6	2033 (293)	1375 (228)	658 (73)	2.1 (0.2)	5.83 (0.86)	0.57 (0.21)	8.18 (0.61)	0.73 (0.02)
Wiske	23	5	1478 (127)	989 (62)	489 (67)	2.0 (0.2)	5.37 (0.39)	0.37 (0.04)	8.54 (0.59)	0.71 (0.03)
	24	2	949 (0)	691 (0)	258 (0)	2.7 (0.2)	4.78 (0.68)	0.27 (0.01)	8.20 (1.75)	0.72 (0.02)
Thornton Beck	25	5	1829 (120)	1017 (52)	812 (79)	1.3 (0.1)	8.28 (0.26)	0.80 (0.05)	5.20 (0.34)	0.89 (0.04)
	26	3	2321 (321)	1630 (217)	690 (106)	2.4 (0.1)	10.5 (0.9)	0.83 (0.07)	6.62 (1.18)	0.89 (0.01)
Eller Beck	27	1	3663	2214	1449	1.5	14.0	1.02	6.79	0.79

^aSSA = specific surface area.

^bIncludes 25 samples collected from the River Swale during 1994–1997 as a part of the LOIS project (cf. [16]).

Calder and Swale. There is no significant difference (*t*-test, *p* > 0.05) between the TP values for the two sites on the River Swale, which are relatively low (TP < 1500 µg g⁻¹) when compared with values for the Rivers Aire and Calder. These relatively low values of TP reflect the rural nature of the Swale catchment and the dominance of diffuse sources of P. In the case of the River Aire, there is no significant difference (*p* > 0.05) between the average value of TP for site 11 (1534 µg g⁻¹), which lies near the source of the river, and those for the two sites on the River Swale. As with the headwaters of the River Swale, the catchment of the River Aire upstream of site 11 is dominated by Carboniferous rocks and by moorland and pasture land use with no major industrial or urban areas (Fig. 1). The suspended sediment samples collected from the River Aire at site 9 contain elevated levels of TP compared to site 11 (*p* < 0.05), with a mean of 2363 µg g⁻¹, and these probably reflect point source inputs of P (such as from STWs) associated with the town of Skipton (cf. Fig. 1). Downstream of site 9, the TP content of suspended sediment increases further in response to point source inputs from the urban areas, including the cities of Leeds and Bradford (cf. Fig. 1), with a mean value of 7538 µg g⁻¹ at site 1 (tidal limit). In the case of the River Calder, the TP content of a single suspended sediment sample collected at the upstream site 13 is 1663 µg g⁻¹. This is similar to the values for the River Swale and the uppermost site on the River Aire, and is consistent with the rural land use above site 13. The average TP content of suspended sediment from the River Calder at the downstream site 12 is 6644 µg g⁻¹ and this reflects the highly urbanized and industrialized nature of the catchment between sites 13 and 12, including the cities of Halifax and Huddersfield (Fig. 1).

There is also a clear increase in the IP content of the suspended sediment in the River Aire in a downstream direction, from a mean value of 836 µg g⁻¹ at site 11 to a mean of 6303 µg g⁻¹ at site 1. This trend is in keeping with the downstream increase in the importance of point source inputs associated with urban areas. Existing studies (e.g. [5]) have shown that most of the P load in urbanized basins is in inorganic (both dissolved and particulate) form, reflecting discharges from point sources such as STWs and combined sewer overflows (CSOs) (further information for the River Aire is presented later). Although point source inputs of P are generally believed to be predominantly in the dissolved inorganic form (DIP) [17,5], there is evidence to suggest that DIP derived from STWs and other point sources is adsorbed by suspended sediment upon entering the river system [3], thereby elevating the levels of particulate IP. In contrast, organic P (both dissolved and particulate), appears to be related much less to point source inputs, and thus its relative importance increases in rivers with limited point sources [5]. The relative

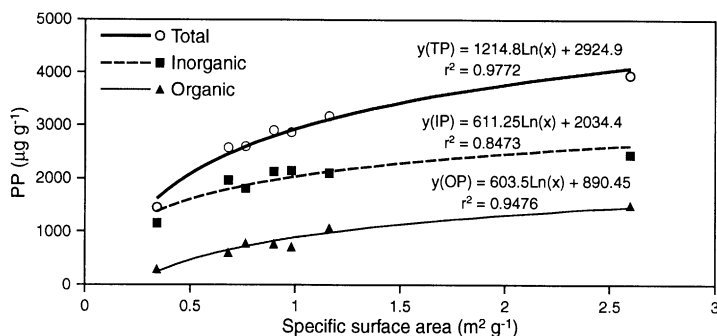


Fig. 2. Relationships between TP, IP and OP and specific surface area for an individual suspended sediment sample collected from site 26 (cf. Fig. 1) which was made progressively finer by a combination of wet sieving and settling.

importance of the IP content of suspended sediment, and thus the importance of point source inputs, is demonstrated by the IP/OP ratio which increases from 1.4 at site 11 to 4.6 at site 1. Values for the River Swale at sites 18 and 14 are 1.8 and 2.5, respectively, and values for the River Calder at sites 13 and 12 are 2.5 and 3.9, respectively.

It is possible that the downstream trends in the magnitude of the TP and IP content of suspended sediment for the Rivers Aire and Calder, described above, could partly reflect P enrichment associated with changes in the particle size composition and organic content of the sediment samples (cf. [2,18,19]), and statistics describing these characteristics are also presented in Table 1. Fig. 2 presents the relationships between specific surface area (SSA) and the TP, IP and OP content for an individual suspended sediment sample collected from site 26. This sample was separated into progressively finer fractions using a combination of wet sieving and settling. Fig. 2 shows a strong positive relationship between SSA and PP content for this sample. However, there are no significant differences ($p > 0.05$) in the particle size composition of the suspended sediment samples between the sites which might explain the spatial patterns in TP and IP. There are significant differences ($p < 0.05$) in the C and N content of the sediment, but these differences alone cannot, however, account for the high values of TP and IP found at the downstream sites, and the five-fold increase in TP observed in the River Aire between sites 11 and 1.

Table 1 also presents information on the P content of suspended sediment samples collected from seven tributary streams. The samples collected from tributaries in the Swale catchment have TP values ranging from 736 to 2033 $\mu\text{g g}^{-1}$, and these values are consistent with those for the main channel of the River Swale, and the land use within their catchments. Thus, Gunnerside Beck, which is located in the headwaters of the Swale and which drains a moorland catchment, has the lowest TP

content ($736 \mu\text{g g}^{-1}$). The River Wiske and Cod Beck both drain larger rural catchments dominated by agricultural land, but which also contain the towns of Northallerton and Thirsk, and suspended sediment samples collected from these tributaries are characterized by average TP values of 2033 and 1478 $\mu\text{g g}^{-1}$, respectively. Similarly, Otterburn Beck drains a small rural (mainly moorland) catchment in the headwaters of the River Aire and the average TP content of suspended sediment samples collected from this stream is 1828 $\mu\text{g g}^{-1}$. Eller Beck drains a catchment with mixed urban and rural land use and the average TP content of the suspended sediment samples collected from this stream is 2321 $\mu\text{g g}^{-1}$. Bradford Beck drains an urban catchment, which includes the city of Bradford, and has very little agricultural land. The single suspended sediment sample collected from this stream has a TP content of 3663 $\mu\text{g g}^{-1}$. Thus, the TP values for these streams are consistent with the relative proportions of rural and urban land use within their catchments and are similar to equivalent samples collected from the main channels of the Rivers Swale and Aire.

3.2. The phosphorus content of source materials

Table 2 provides information on the P content of the $< 63 \mu\text{m}$ fraction of potential source materials. In rural catchments, point source inputs from STWs are unlikely to be major sources of PP, due to the lack of urban and industrial areas, and the most likely sources of sediment and PP are diffuse sources, involving topsoil and channel bank material (cf. [20]). In the Aire/Calder and Swale catchments, the average TP content of these materials ranges from 905 $\mu\text{g g}^{-1}$ (woodland topsoil) to 1499 $\mu\text{g g}^{-1}$ (pasture/moorland topsoil). The values for the TP content of topsoil and channel bank material are similar to the average TP content of the suspended sediment samples collected from sites where the contributing catchment is dominated by rural areas (i.e. sites 14 and 18 on the River Swale, site 11 on the River Aire

Table 2
Average P and organic matter content and particle size composition of the <63 μm fraction of potential source materials collected from the catchments of the Rivers Aire, Calder and Swale. Values in parentheses represent $1 \text{ SE}_{\text{mean}}$

Source type	Source material	n	TP ($\mu\text{g g}^{-1}$)	IP ($\mu\text{g g}^{-1}$)	OP ($\mu\text{g g}^{-1}$)	IP/OP	C (%)	N (%)	d_{50} (μm)	SSA ($\text{m}^2 \text{g}^{-1}$)
Agricultural	Woodland topsoil	56	905 (53)	399 (30)	506 (29)	0.8 (0.1)	14.7 (1.2)	0.85 (0.07)	18.2 (0.9)	0.50 (0.18)
	Pasture/moorland topsoil	49	1499 (101)	831 (86)	668 (45)	1.5 (0.2)	9.4 (0.6)	0.73 (0.03)	14.4 (1.0)	0.60 (0.21)
	Cultivated topsoil	43	1251 (91)	820 (89)	431 (35)	2.8 (0.9)	5.1 (0.3)	0.38 (0.02)	14.8 (1.3)	0.62 (0.16)
Urban/industrial	Channel bank material	53	1138 (255)	837 (224)	301 (44)	2.9 (0.4)	4.8 (0.3)	0.29 (0.04)	15.5 (1.2)	0.56 (0.17)
	Street dust	13	822 (74)	672 (36)	150 (46)	11.0 (3.0)	9.8 (0.8)	0.25 (0.03)	29.4 (2.9)	0.40 (0.26)
	Sewage influent	3	11 520 (3536)	9078 (2896)	2442 (675)	3.6 (0.4)	32.4 (9.1)	2.3 (0.7)	12.5 (0.8)	0.45 (0.04)
	Industrial effluent	1	6083	5814	269	21.6	10.7	0.7	8.2	0.69

and site 13 on the River Calder), which range from ca. 1160 to 1660 $\mu\text{g g}^{-1}$. Differences in TP levels between the <63 μm fraction of topsoil and channel bank material, and suspended sediment are probably due to differences in the particle size composition and organic matter content between the two types of material (see Tables 1 and 2) (cf. [1,2]). The IP/OP ratio for the (rural) suspended sediment samples ranges from 1.5 to 2.7, whereas the ratio ranges from 0.8 to 2.8 for topsoil and is 2.9 for bank material.

The P contents and IP/OP ratios of topsoil and channel bank material are considerably lower than values for suspended sediment samples collected from sites 1, 6, 9 and 12. Since these sampling sites are located within, or downstream of, urban and industrial areas, the elevated values of P content associated with sediment collected from these areas are likely to reflect point source inputs. The average TP content of the <63 μm fraction of street dust material is 822 $\mu\text{g g}^{-1}$ and the IP/OP ratio is 11.0. The street dust is, however, considerably coarser (mean $d_{50} = 29.4 \mu\text{m}$) than the suspended sediment samples (mean $d_{50} = \text{ca. } 7 \mu\text{m}$). Taking account of the elevated IP/OP ratio for street dust and the differences in particle size composition between street dust and suspended sediment, it is clear that street dust could represent a significant source of the suspended sediment collected from sites 1, 6, 9 and 12. Sediment recovered from a single sample of the effluent discharging directly into the River Calder from a small industrial facility near to site 13 had a TP content of 6083 $\mu\text{g g}^{-1}$ and an IP/OP ratio of 21.6. The TP content of this sample is similar to that of the suspended sediment samples collected from sites 1, 6 and 12. The values of d_{50} and C content for this sample are also similar to those documented for suspended sediment from these sites, suggesting that such point source inputs may also represent an important source of the suspended sediment transported through the middle and lower reaches of the Rivers Aire and Calder. The average TP content of the solids recovered from three samples of sewage influent collected from a large STW near to site 7, that serves the city of Bradford, was 11 520 $\mu\text{g g}^{-1}$, with one sample having a TP content of 16 520 $\mu\text{g g}^{-1}$. Most of this PP is in inorganic form and the IP/OP ratio is 3.6. Although the influent to STWs is usually treated prior to being discharged into rivers as effluent, there are times when untreated sewage is discharged directly into the river, such as during large rainfall events, via CSOs and STW bypass channels.

The effect of point sources of PP, and of STWs and CSOs in particular, can be examined further by comparing the P content of suspended sediment samples collected both above (at site 7) and below (at site 6) the sewage effluent discharge pipe of a large STW. The distance between the two sites is ca. 3 km and there are no major inputs of water or sediment between these two

points. On three separate occasions samples were collected from both sites, within a few hours of each other, using a field-portable continuous-flow centrifuge. For samples collected in October 1999 (low flow conditions), the difference in TP content was relatively small, with values for the upstream and downstream sites being 6016 and 6250 $\mu\text{g g}^{-1}$, respectively. For samples collected in July (low flow conditions) and December 1999 (high flow conditions), the difference between the upstream and downstream sites was more pronounced, with values of 5622 and 8765 $\mu\text{g g}^{-1}$ for the July samples, and 2523 and 4349 $\mu\text{g g}^{-1}$ for the December samples. The increase in the TP content of suspended sediment between the two sites suggests that the effluent from the STW represents an important source of the P content of suspended sediment.

There are two important conclusions to be drawn from a comparison of the TP content of solids in sewage influent (Table 2) and of the samples collected upstream and downstream of the STW. Firstly, because previous studies have demonstrated that most of the P discharged from STWs is in the form of DIP, the results presented above indicate that DIP is quickly sorbed onto suspended sediment within the river, thereby elevating the levels of TP associated with suspended sediment downstream of STWs. The precise nature of the interaction between DIP and suspended sediment downstream of STWs will, however, be controlled by river discharge, the DIP concentration in the river and the particle size composition of the suspended sediment. Secondly, the high values of TP associated with the solids recovered from the sewage influent samples suggest that solids discharged from STWs and CSOs may constitute an important source of PP, although their high TP content will subsequently be diluted by mixing with suspended sediment containing lower levels of TP.

3.3. *The relationship between the phosphorus content of suspended sediment and discharge and sediment concentration*

Fig. 3 shows the relationships between the TP content of suspended sediment and both discharge and suspended sediment concentration for samples collected from the downstream sites on the Rivers Swale, Calder and Aire (sites 14, 12 and 1, respectively) and one of the upstream sites on the River Aire (site 9). The relationships for site 14 (rural) are broadly similar to those for site 9 (mixed rural and urbanized) and sites 1 and 12 (urbanized and industrialized), with trends of decreasing TP content with both increasing discharge and increasing suspended sediment concentration. At all of these sites, the relationship between the TP content of suspended sediment and discharge is stronger than that between TP content and suspended sediment concentra-

tion. The observed trend of decreasing TP content with an increasing discharge and sediment concentration suggests that there is a dilution effect associated with changing sediment sources during high discharge events. In the case of sites 1 and 12, point source inputs of both dissolved and particulate P are likely to dominate at times of low flow. It has been estimated that during dry summers more than 66% of the flow of the River Aire downstream of Leeds comprised treated sewage effluent [10]. During higher flows, runoff from the catchment surface and diffuse sources of sediment (e.g. topsoil and channel banks) would assume greater importance. Such sediment inputs would have a lower TP content than those associated with point sources (Table 2), thereby diluting the higher P content of the latter. However, in certain situations there may be increased discharges from STWs during storm events, reflecting increased inputs and operational procedures, and there may also be incidents where STWs and CSOs discharge untreated sewage effluent directly into the river, which would account for the elevated TP content of sediment recovered from some samples collected during high discharge events.

Despite the significant relationships described above, Fig. 3 also demonstrates that there is considerable scatter in the relationships between the TP content of suspended sediment and discharge and suspended sediment concentration at all sites. This is likely to reflect temporal variation in the relative contribution from a range of sediment and PP sources within each upstream catchment, both during individual storm events and through the year. Fig. 4a illustrates the variation of the TP content of suspended sediment demonstrated by five suspended sediment samples collected during a high flow event at site 1 (at the outlet of the Aire catchment) in March 1998. On the rising limb of the hydrograph, the TP content of sediment decreases with an increase in both discharge and suspended sediment concentration, and TP continues to decrease on the falling limb. This trend may reflect the dilution of sediment with a high TP content at the start of the event, by sediment with a lower TP content associated with topsoil and channel bank sources, derived from more distal rural parts of the catchment, as the event progresses. The temporal variation in TP content illustrated in Fig. 4a cannot be explained by variations in the particle size composition and organic content of the sediment, as there were no significant trends in either of these sediment properties during the event.

The temporal variability of TP at site 1 is further illustrated by Fig. 4b, which plots the variation of the TP content of all 21 suspended sediment samples collected from this site through time. Although most samples were collected during the winter months, it can be seen that sediment samples collected during the same

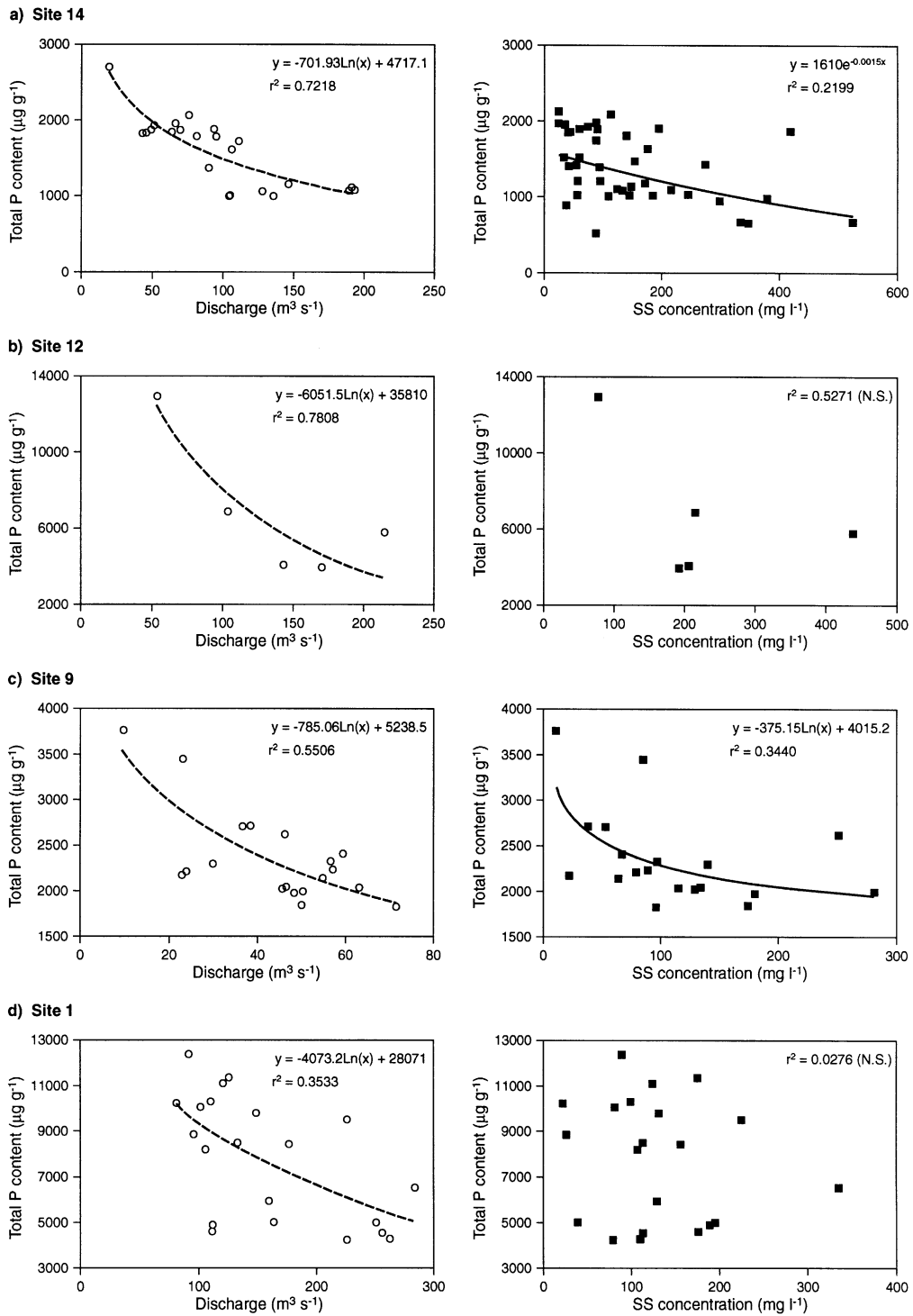


Fig. 3. Relationships between the TP content of suspended sediment and both discharge and suspended sediment (SS) concentration for: (a) River Swale at site 14; (b) River Calder at site 12; (c) River Aire at site 9; and (d) River Aire at site 1. (N.S. = not significant at the 95% confidence level).

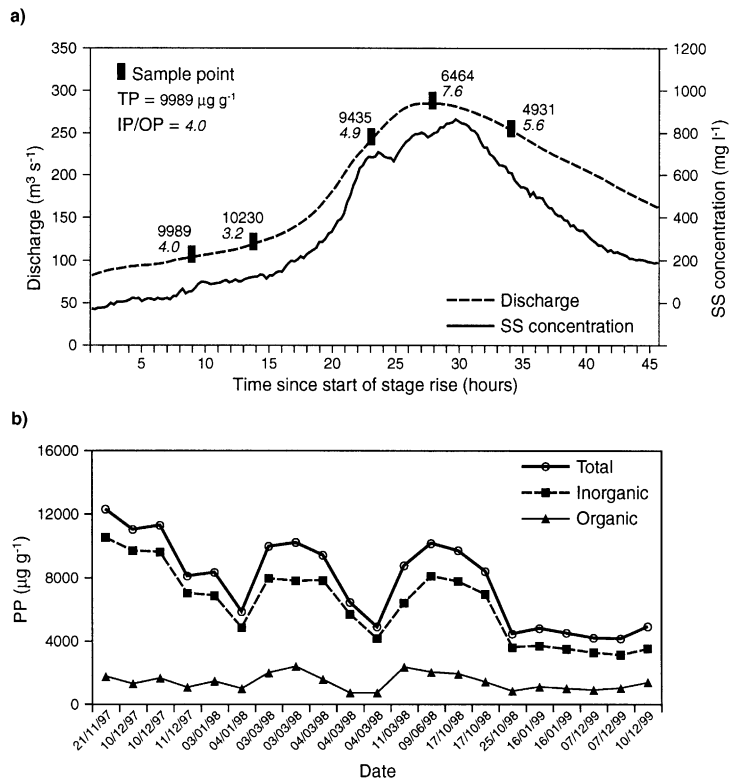


Fig. 4. Temporal variations in the PP content of suspended sediment collected from the River Aire at site 1: (a) the variation of discharge, suspended sediment concentration (SS) and the TP content and IP/OP ratio of suspended sediment samples collected during a high flow event on the 3rd and 4th of March 1998; and (b) the variation in the PP content of all 21 suspended sediment samples collected between November 1997 and December 1999.

season can have markedly different TP contents. For example, three samples collected during a storm event in December 1997 (mean $d_{50} = 6.1 \mu\text{m}$) had TP values ranging between 8126 and 11 293 $\mu\text{g g}^{-1}$, whereas three samples collected during an event in December 1999 (mean $d_{50} = 6.1 \mu\text{m}$) had TP values between 4172 and 4944 $\mu\text{g g}^{-1}$. Conversely, samples collected from different seasons can have similar TP contents. For example, the TP content of the (single) sample collected during June 1998 ($d_{50} = 8.1 \mu\text{m}$) was 10 162 $\mu\text{g g}^{-1}$, whereas samples with TP contents $> 10\,000 \mu\text{g g}^{-1}$ were also collected in November, December and March (d_{50} ranges from 5.2 to 7.0 μm).

The lack of any apparent seasonal trend in the data presented in Fig. 4b, partly reflects the limited number of samples collected during the summer months. However, it may also reflect complex temporal variations in: (i) hydrometeorological controls (such as discharge and antecedent conditions) (cf. [7]); (ii) inputs from various point and non-point sources of sediment and PP (including the timing of peak discharges of sewage effluent, and the timing of fertilizer application

on agricultural land); and (iii) the timing of sample collection relative to the storm hydrograph (see Fig. 4a).

3.4. The phosphorus content of floodplain and channel bed sediment

Table 3 lists values of the average P content of the $< 63 \mu\text{m}$ fraction of samples of overbank floodplain deposits and channel bed sediment collected from the study rivers. In the case of floodplain sediment from the River Swale, TP values range from a minimum of 452 $\mu\text{g g}^{-1}$ at site 20 to a maximum of 695 $\mu\text{g g}^{-1}$ at site 17. Although, the TP content of floodplain sediment from the lower reaches is higher than that of the upper reaches, values are generally similar along the length of the river. Differences between sites may reflect differences in the particle size composition of the sediment (cf. Table 3) and also variations in the locations, relative to the channel, from which samples were collected (cf. [21]). The TP contents of the samples of overbank floodplain deposits collected from the Rivers Aire and Calder are considerably higher than those for the River Swale.

Table 3

Average P content and specific surface area of the <63 μm fraction of floodplain and channel bed sediment collected from the Rivers Aire, Calder and Swale, and estimates of floodplain and channel bed storage of <63 μm sediment and TP. Values in parentheses are 1 SE_{mean}

River	Site	Floodplain sediment								Channel bed sediment								
		n	TP	IP	OP	IP/OP	SSA	Storage ^a (g m ⁻² yr ⁻¹)		n	TP	IP	OP	IP/OP	SSA	Storage ^b (g m ⁻²)		
			(μg g ⁻¹)	(μg g ⁻¹)	(μg g ⁻¹)		(m ² g ⁻¹)	Sed.	TP		(μg g ⁻¹)	(μg g ⁻¹)	(μg g ⁻¹)		(m ² g ⁻¹)	Sed.	TP	
Swale	20	5	452 (21)	383 (24)	69 (18)	8.5 (3.4)	0.48 (0.03)	15 700	7.10	10	1100 (341)	836 (218)	264 (127)	4.6 (1.4)	0.53 (0.01)	39	0.043	
	19	3	470 (55)	403 (11)	67 (45)	17.8 (11.2)	0.54 (0.08)	10 400	4.89									
	18									10	1033 (98)	790 (59)	243 (39)	3.3 (0.3)	0.59 (0.02)	133	0.137	
	17	13	695 (59)	573 (43)	122 (22)	6.4 (1.0)	0.54 (0.04)	10 700	7.44	9	941 (91)	851 (64)	90 (15)	9.5 (2.2)	0.54 (0.02)	339	0.319	
	16	5	566 (23)	507 (20)	59 (11)	10.4 (2.6)	0.58 (0.09)	8630	4.88									
	15									12	1256 (99)	874 (58)	382 (44)	2.5 (0.2)	0.60 (0.06)	91	0.114	
	14									10	1237 (60)	868 (34)	370 (29)	2.4 (0.1)	0.63 (0.03)	329	0.407	
	Aire	10	22	1061 (60)	800 (43)	261 (26)	3.7 (0.4)	0.54 (0.03)	6740	7.15	11	1600 (58)	1183 (40)	417 (27)	2.9 (0.2)	0.67 (0.02)	522	0.835
		8	10	1108 (84)	878 (60)	230 (35)	4.4 (0.6)	0.52 (0.04)	2660	2.95	11	2018 (169)	1603 (100)	415 (71)	4.1 (0.4)	0.60 (0.02)	581	1.17
		7									9	2971 (215)	2351 (199)	620 (188)	3.8 (1.4)	0.61 (0.04)	159	0.472
5		9	1525 (83)	1343 (75)	182 (41)	9.2 (1.8)	0.43 (0.03)	6490	9.90									
4		2	1706 (189)	1568 (122)	139 (67)	14.2 (5.9)	0.50 (0.09)	1010	1.72									
3										10	3421 (497)	2889 (340)	531 (176)	6.8 (2.0)	0.55 (0.02)	112	0.383	
Calder	2	9	3980 (166)	3308 (137)	672 (74)	5.5 (0.7)	0.74 (0.10)	4270	17.0									
	1	25	4657 (373)	4216 (324)	442 (82)	16.0 (2.4)	0.52 (0.03)	3800	17.7	11	5870 (529)	5207 (457)	664 (93)	8.2 (0.8)	0.60 (0.02)	144	0.845	
	13	1	796	701	95	7.4	0.57	4250 ^c	3.38 ^c	9	1002 (96)	800 (31)	202 (18)	4.0 (0.3)	0.54 (0.03)	106	0.106	
	12	12	4708 (353)	4344 (388)	364 (58)	25.0 (8.8)	0.66 (0.08)	9320	43.9	8	4364 (526)	3991 (504)	372 (81)	19.6 (10)	0.54 (0.03)	1448	6.32	

^a Annual values of deposition based on cumulative values for individual overbank events (averaged over two years).

^b Mean values for total storage at the time of sampling (these are not annual values).

^c Values are based on a single floodplain mat.

They also show a marked downstream increase, which cannot be accounted for by changes in the particle size composition or organic matter content of the samples. TP values range from 1061 to 4657 $\mu\text{g g}^{-1}$ for the River Aire and 796 to 4708 $\mu\text{g g}^{-1}$ for the River Calder. In the case of the channel bed sediment, TP values increase in a downstream direction for all three rivers, with the downstream increase in TP content being markedly greater for the Rivers Aire and Calder.

From Tables 1 and 3 it can be seen that the TP values for the $<63\ \mu\text{m}$ fraction of the overbank floodplain deposits and channel bed sediment are similar to those for suspended sediment collected from the same or nearby sites. Some of the differences in the TP values between suspended sediment and the floodplain and channel bed sediment are likely to reflect differences in the particle size composition between the different types of sediment. To take into consideration these differences in particle size composition and to permit a more direct comparison between the TP values for suspended sediment and those for floodplain and channel bed sediment, the TP values for the latter have been “standardized” to those for suspended sediment. Differences in specific surface area between the floodplain and channel bed sediment and suspended sediment collected from the same or nearby site were taken into account, using the relationship between SSA and TP shown in Fig. 2. The resulting data plotted in Fig. 5 indicate that particle size effects account for most of the difference in TP values between the three types of sediment, and for most sites there are no significant differences ($p > 0.05$) in TP content between the three types of sediment. More importantly, Fig. 5 shows that the overall downstream trends shown by the floodplain and channel bed sediments are similar to those for suspended sediment, and highlights the elevated TP content of fluvial sediment in the lower reaches of the Rivers Aire and Calder.

When the IP and OP contents of the floodplain and channel bed sediment (Table 3) are compared with

equivalent values for suspended sediment (Table 1), there are noticeable differences, particularly in the OP values, which are much lower in floodplain and channel bed sediment than suspended sediment. This is likely to reflect post-depositional transformations, or the selective deposition of the mineral fractions, which is commonly characterized by a higher density than the organic fraction. These differences must be recognized and taken into account when comparing and interpreting the patterns exhibited by the P content of the three types of sediments. However, Fig. 5 clearly demonstrates that overbank floodplain deposits and fine-grained channel bed sediment may also be used to elucidate the sources and transport dynamics of PP in river basins.

Table 3 presents mean values for the annual rate of fine-grained ($<63\ \mu\text{m}$ fraction) sediment deposition on the floodplain during overbank events and the associated annual deposition of TP ($\text{g m}^{-2}\text{yr}^{-1}$). These values relate to the amounts of sediment deposited on astroturf mats during individual flood events, which were summed over two separate years in order to estimate the average annual sediment deposition. There is considerable variation in the estimates of sediment deposition rates. Values for the River Swale range from 8630 to 15 700 $\text{g m}^{-2}\text{yr}^{-1}$, and are generally greater than those for the Rivers Aire (range 1010–6740 $\text{g m}^{-2}\text{yr}^{-1}$) and Calder (range 4250–9320 $\text{g m}^{-2}\text{yr}^{-1}$). This situation reflects the higher annual suspended sediment load of the River Swale; i.e. ca. 34 $\text{t km}^{-2}\text{yr}^{-1}$ at site 14 compared to ca. 22 and 26 $\text{t km}^{-2}\text{yr}^{-1}$ at sites 1 and 12, respectively [22]. While rates of sediment deposition for the River Swale decrease downstream, there is no obvious downstream trend in sediment deposition for the River Aire. The apparent downstream increase for the River Calder may reflect the limited number of sites and the fact that only one sample was collected from site 13. The annual deposition of PP on the floodplain (calculated as the product of annual sediment deposition and the mean TP content of this sediment) ranges

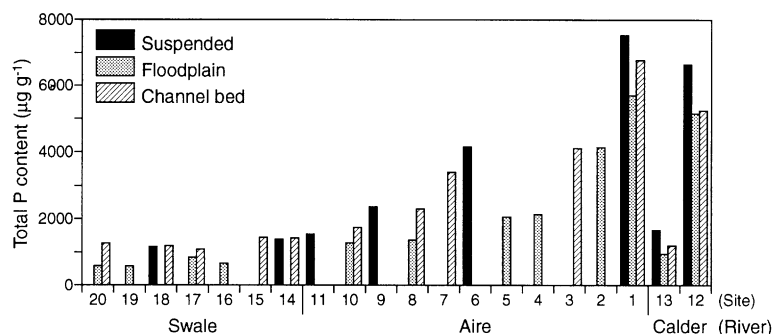


Fig. 5. Downstream trends in the TP content of suspended sediment and the $<63\ \mu\text{m}$ fraction of overbank floodplain deposits and channel bed sediment in the Rivers Swale, Aire and Calder. The values of TP content for floodplain and channel bed sediment were standardized for particle size effects to be directly comparable with those for suspended sediment.

between 1.72 and $43.9 \text{ g m}^{-2} \text{ yr}^{-1}$. Values are greatest at downstream sites on the Rivers Aire and Calder, and this reflects the elevated levels of TP associated with floodplain sediment at these locations.

Table 3 also presents estimates of the storage of $<63 \mu\text{m}$ sediment on, and in, the upper layer of the channel bed, and the associated storage of TP. The estimates of channel bed storage differ in their basis from those reported for annual floodplain deposition and relate to instantaneous measurements of the amount of fine-grained sediment stored (g m^{-2}) in the upper ca. 5 cm of the channel bed, and represent average values of *total* bed storage of fine sediment for the times of sampling (bi-monthly). For the Rivers Swale and Calder, channel bed storage of TP is greatest in the lower reaches, with a maximum of 6.32 g m^{-2} at site 12, reflecting both high storage of sediment $<63 \mu\text{m}$ and high TP content. There is no obvious downstream trend of TP storage in the River Aire, primarily reflecting the limited storage of sediment $<63 \mu\text{m}$ in the lower reaches of this river. Nevertheless, the value of TP storage at site 1 of 0.845 g m^{-2} can still be seen as high when compared to values for the River Swale (range $0.043\text{--}0.407 \text{ g m}^{-2}$) and the upstream site on the River Calder (0.106 g m^{-2}).

3.5. A classification of the P content of suspended sediment in relation to catchment land use

Based on the values of the mean P content of suspended sediment from each individual site, presented above, it is possible to derive a tentative four-fold classification of the P content of suspended sediment for the study area, according to the dominant catchment land use (Fig. 6). The TP content of suspended sediment collected from sites where the contributing catchment is dominated by upland moorland and rough grazing (sites 11, 13, 18, 21 and 25) ranges between ca. 740 and $1830 \mu\text{g g}^{-1}$, and the IP/OP ratio ranges between 1.3 and 2.5 . For sites where the contributing catchment is dominated by pasture and cultivated land use (classified as “agricultural” land use) (sites 14, 22, 23 and 24), the mean TP content of sediment ranges between ca. 950 and $2030 \mu\text{g g}^{-1}$, and the IP/OP ratio ranges between 2.0 and 2.7 . In the case of a sediment collected from sites with either a minor or major proportion of urban and industrial land in the contributing catchment (sites 9, 26 and 27 and sites 1, 6 and 12, respectively), the mean TP content ranges between ca. 2360 and $3660 \mu\text{g g}^{-1}$ and ca. 4150 and $7540 \mu\text{g g}^{-1}$, respectively, and the IP/OP ratio ranges between 1.5 and 2.4 and between 2.4 and 4.6 , respectively. Although there is inevitably some overlap in the type of land use found within each of the four categories, there is, nevertheless, clear evidence of a progressive increase in the absolute magnitude and range of values of the TP content of sediment with the intensification of agricultural land use and, more

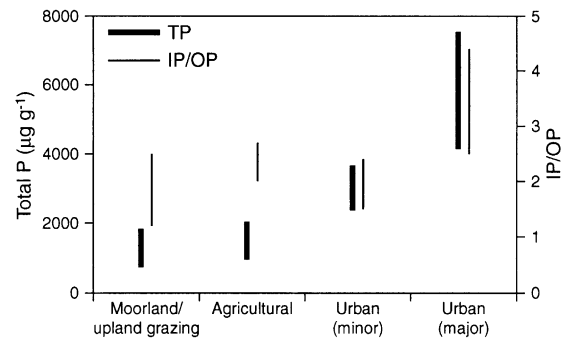


Fig. 6. Variation of the TP content and the IP/OP ratio of suspended sediment in the Aire/Calder and Swale river basins, according to the dominant upstream land use.

particularly, with an increase in the degree of urbanization and industrialization.

3.6. Comparison with PP values reported in other studies

Table 4 lists PP values for other rivers which can be compared with the suspended, floodplain and channel bed sediment samples collected from the Rivers Swale, Aire and Calder. It can be seen that for most rivers the mean TP content of such fluvial sediment generally lies within the range $1000\text{--}2500 \mu\text{g g}^{-1}$, although values for individual samples may be much lower or higher. The TP content of fluvial sediment transported and stored in the River Swale and the upper reaches of the Rivers Aire and Calder are similar to the range of values for other rivers which drain predominantly undisturbed rural catchments. However, the values obtained for the lower reaches of the Rivers Aire (average of $7538 \mu\text{g g}^{-1}$ at site 1) and Calder (average of $6644 \mu\text{g g}^{-1}$ at site 12) must be seen as high when compared to most other rivers, and as reflecting the highly urbanized and industrialized nature of the middle and lower reaches of these catchments and the numerous STWs and other point source inputs located in these reaches (Fig. 1).

Although there is limited information on quality guidelines for the TP content of sediment in aquatic environments, Table 5 reports the guidelines published by the Canadian Province of Ontario. Bulk sediment which has a TP content at or above $2000 \mu\text{g g}^{-1}$ (the severe effect level) is defined as sediment that is considered as heavily polluted and likely to affect the health of sediment-dwelling organisms [42]. Although the P content of the fluvial (suspended, floodplain and channel bed) sediment collected from the catchment of the River Swale (with the exception of the River Wiske) falls below this threshold level, the TP content of fluvial sediment collected from most of the sampling sites in the

Table 4

The TP content ($\mu\text{g g}^{-1}$) of suspended sediment, and floodplain and channel bed sediment reported for other rivers in the UK and worldwide

River	N	Suspended sediment	Floodplain sediment	Channel bed sediment	Reference
Creedy, UK		ca. 900–3000			[23]
Jackmoor Brook, UK		ca. 1000–2500			[24]
Clyst, UK	11	1622 (1183–2126)			[19]
Dart, UK	22	1585 (1012–2874)			[19]
Exe, UK	24	1633 (725–2421)			[19]
Severn, UK	19	1150 (540–1497)			[19]
Avon, UK	13	1637 (567–2299)			[19]
Ouse basin, UK	140	1697 (542–4175)			Walling and Owens (unpublished data)
Tweed basin, UK	36	1327 (756–2326)			Walling and Owens (unpublished data)
Gilwiskaw Brook, UK		1403 ^a			[25]
20 rivers, UK	20		1247 (417–2660) ^b		[7]
Sowe, UK	1		2500 ^c		[26]
Great Stour, UK				241–470	[27]
Adour, France	59	100–13 500 ^d			[6]
Seine and Aube, France	18		1500–3300		[28]
Seine and Marne, France	16			350–4700	[29]
Seine, France (downstream of Paris)					[30]
upstream of Achères STW				2500–3700 ^e	
downstream of Achères STW				2800–5100 ^e	
solids in STW effluent				25 000 ^f	
Kleine Aa, Switzerland		ca. 1000–3500		ca. 400–500	[18]
Gelbæk, Denmark		4091–4507			[20]
Mahantango basin, Pennsylvania, USA	40	897 (670–1114)			[2]
Seven Great Lake rivers, USA		837–1262		424–1007	[31]
Five watersheds, Mississippi, USA		274–1067			[1]
Maumee River, Ohio, USA	5			918 (476–1260)	[32]
Wilton Creek, Ontario, Canada		1175–2790 ^g			Data from [33] given in [34]
Canagagigue Creek, Ontario, Canada	23			858 (520–1800)	[35]
St. Mary's River, Canada/USA	23			548 (200–1300)	[36]
St. Lawrence River, Ontario, Canada	111			430–1500	[37]
Lyons Creek, Ontario, Canada	10			1230 (700–3200)	[38]
Stormwater ponds, Ontario, Canada	15			767 (400–2800) ^h	[39]
Darling-Barwon basin, Australia	96	1210–1960 ⁱ			[40]
Various streams in New Zealand		100–4420			Listed in [41]

^a Time integrated sample collected from two catchments during two winter months.

^b Mean (and range) for uppermost (post-1963) sediment in individual cores collected from 20 different rivers.

^c Content of sediment in a core from a floodplain lake.

^d Range of TP for spot suspended sediment samples collected during low and high flows.

^e IP content of channel bed sediment at a depth of 10 cm collected using cores.

^f The Achères STW receives 90% of the wastewaters from the Paris agglomeration (10 million inhabitants), of which 20% is discharged into the river without treatment [30].

^g Range for spot suspended sediment samples.

^h Surface sediment in urban stormwater ponds in the cities of Guelph and Toronto, which are drained by urban and industrial catchments.

ⁱ Range of mean values for six reaches and six tributaries. Values are for the <10 μm fraction and are weight oxide calculated on an organic-free basis.

Table 5

Quality guidelines for the TP content ($\mu\text{g g}^{-1}$) of bulk sediment in aquatic environments and the values reported for the TP content of bottom sediment in lakes of various trophic status

Location	Sediment quality guidelines		Lake-bottom sediment TP			Reference
	Effect level: Lowest ^a	Severe ^b	N	Mean	Range	
Ontario, Canada	600	2000				[42]
<i>Various lakes world-wide:</i>						[43]
All (oligo- to hypertrophic)			79	2280	500–10 300	
Eutrophic			25	1920	630–4720	
Hypertrophic			20	3130	860–10 300	
Various lakes world-wide			15	1693	662–4700	[44]
Slapton Ley, UK (eutrophic)			1	1200		[45]
Lake Verese, Italy (eutrophic)			1	1700		[46]
Lake Erie, USA/Canada			1	2342		[31]
Wind Lake, USA (eutrophic)			1	644		[47]
Lake George, USA/Canada			1	700		[36]
Various Prairie Lakes, Canada			10	1027	533–1345	[48]
Lake Tabor, Canada (eutrophic)			1	1318		[49]

^aThe sediment is clean to marginally polluted and this level of contamination will have no effect on the majority of sediment-dwelling organisms.

^bThe sediment is considered heavily polluted and likely to affect the health of sediment-dwelling organisms. At this level, a management plan may be required, which may include controlling the source of the contamination and removing the sediment [42].

middle and lower reaches of the Rivers Aire and Calder considerably exceed this level, with maximum values for individual samples collected from the Rivers Aire and Calder exceeding $12\,000\ \mu\text{g g}^{-1}$.

Table 5 also enables the TP content of the fluvial sediment samples collected from the study rivers to be compared with the TP content of sediment collected from the bottom of eutrophic and hypertrophic lakes, where P has often been identified as the limiting nutrient [50]. The average TP content for the 110 lakes given in Table 5 (of which the majority are eutrophic or hypertrophic) is ca. $2000\ \mu\text{g g}^{-1}$ (range is $500\text{--}10\,300\ \mu\text{g g}^{-1}$). Again the TP content of fluvial sediment in the Rivers Aire and Calder must be seen as high compared to that of the sediment from eutrophic and hypertrophic lakes, further emphasizing the elevated levels of TP content in the study rivers.

4. Conclusion

The P content of fluvial sediment has been examined in contrasting rural and industrialized catchments in Yorkshire, UK. The River Swale drains a rural catchment with no major urban and industrial areas, and the TP content of fluvial (suspended and the $<63\ \mu\text{m}$ fraction of overbank floodplain and channel bed) sediment is generally within the range $500\text{--}1500\ \mu\text{g g}^{-1}$. There is little evidence of any major downstream increase in TP content. In contrast, the Rivers Aire and Calder exhibit marked downstream

increases in TP content from $<2000\ \mu\text{g g}^{-1}$ in rural headwater areas upstream of the main urban and industrial areas, to values $>7000\ \mu\text{g g}^{-1}$ at downstream sites. The values of PP for downstream reaches of the Rivers Aire and Calder are considerably higher than those documented for most other rivers in the world. Furthermore, they exceed by a substantial margin the sediment quality guidelines for the “severe effect level” of $2000\ \mu\text{g g}^{-1}$ set by the Canadian Province of Ontario [42], and the TP content of sediment from eutrophic lakes.

The downstream increases in the TP content of fluvial sediment in the Rivers Aire and Calder have important ecological implications, as studies have shown that between 1% and 41% of PP is bioavailable [31,51], although 10–20% is probably a more realistic estimate of bioavailability [40,52]. The downstream increases in the importance of IP is also noteworthy, because a significant proportion of the IP content of sediment may be bioavailable [53], whereas the bioavailability of OP is likely to be more limited [52]. There is a need for further studies to investigate the magnitude, dynamics and fate of PP in river systems, particularly given the detrimental affects associated with elevated levels of P in rivers and receiving water bodies.

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