Downstream changes in the transport and storage of sediment-associated contaminants (P, Cr and PCBs) in agricultural and industrialized drainage basins

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Abstract

Samples of suspended, floodplain and channel bed sediment have been used to examine downstream changes in sediment-associated contaminant transport and storage in contrasting rivers in Yorkshire, UK. The concentrations of phosphorus, chromium and selected PCBs associated with sediment in the River Aire and its main tributary, the River Calder, which drain an urbanized and industrialized catchment, are considerably higher than those in the relatively unpolluted River Swale, which drains an agricultural catchment. Concentrations of sediment-associated contaminants in the Aire/Calder system increase downstream, reflecting the location of urban and industrial areas in the middle and lower reaches, and the location of point source inputs, such as sewage treatment works. The contaminant concentrations associated with floodplain and channel bed sediment in the Rivers Aire and Calder are high, particularly in the lower reaches. This, combined with measurements of sediment storage on the floodplain and channel bed, indicate that significant storage of sediment-associated contaminants occurs in the Rivers Aire and Calder. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Suspended sediment; Floodplain sediment; Channel bed sediment; Contaminants; Phosphorus; Chromium; Polychlorinated biphenyls

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1. Introduction

In recent years, there has been an increasing awareness of the important role of suspended sediment in the transport of pollutants and contaminants through fluvial systems (Horowitz, 1995; Meade, 1996; Foster and Charlesworth, 1996; Dawson and Macklin, 1998a). An understanding of the sources, behaviour and storage of sediment-associated contaminants in river systems is therefore needed, so that appropriate strategies may be implemented to reduce and control both contaminant inputs into rivers and the detrimental effects associated with such contaminants within rivers and receiving water bodies. Generally, information on sediment-associated contaminant dynamics in rivers has tended to focus on the use of suspended sediment samples, but increasingly it is being recognised that overbank floodplain deposits and channel bed sediment should also be considered when investigating the temporal and spatial patterns of contaminant behaviour in river systems (Förstner and Salomons, 1980; Horowitz and Elrick, 1988; Macklin and Klimek, 1992; Horowitz, 1995; Dawson and Macklin, 1998b; Horowitz et al., 1999). Furthermore, overbank and channel bed deposits may represent an important sink for contaminants, which could be reintroduced into the river environment, even if direct inputs to the river were to cease (Bradley and Cox, 1990; Lecce and Pavlowsky, 1997).

Currently, there are relatively few data on sediment-associated contaminant transport and storage available for UK river systems, particularly large (i.e. > 1000 km²) systems that drain heavily industrialized and urbanized catchments. This paper describes an investigation into the sediment-associated contaminant dynamics of two contrasting drainage basins in Yorkshire, UK: the River Swale (relatively unpolluted) and the River Aire (heavily polluted). Preliminary results are presented for a nutrient (phosphorus, P), a trace metal (chromium, Cr) and a group of synthetic organic compounds (polychlorinated biphenyls, PCBs). Particular attention is directed towards: (a) the potential for using suspended, floodplain and channel bed sediment to document downstream trends in contaminant concentrations, and thus infer possible sources; and (b) the importance of floodplain and channel bed storage of these contaminants.

2. Study area and methods

2.1. Study area

The Rivers Aire and Swale both drain into the River Ouse, which itself drains into the North Sea via the Humber Estuary (Fig. 1). The River Aire has a catchment area of 1932 km² at the 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, and contributes approximately 50% of the flow of the River Aire at site 1 [the long term average (LTA) discharges at sites 1 and 12 are 35.4 m³ s⁻¹ (1958–1996) and 18.8 m³ s⁻¹ (1988–1996), respectively]. The Aire/Calder system drains a heavily urbanized and industrialized catchment with a population of approximately 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 to the river. Consequently, the Rivers Aire and Calder are both heavily polluted, and receive discharges of sewage effluent from STWs, combined sewer overflows and sewer dykes, and industrial discharges (direct and indirect). In contrast, the River Swale is a relatively unpolluted river, which drains a predominantly agricultural catchment with a low population density and has a catchment area of 1363 km² at the EA station at site 14 [LTA discharge is 19.6 m³ s⁻¹ (1955–1990)]. The headwaters of both the Aire/Calder and Swale catchments lie in the Pennine uplands to the west,
which locally exceed 700 m elevation, and are dominated by moorland and pasture land use. Low-lying land occurs to the east of these uplands, and is dominated by cultivated land (Swale) and cultivated land and urban areas (Aire). The underlying geology in the Aire catchment is Carboniferous limestones and millstone grit, while in the Swale catchment there are also Permian, Triassic and Jurassic strata to the east of site 18.

2.2. Sampling and laboratory methods

Samples of suspended, floodplain and channel bed sediment were collected along the lengths of the Rivers Aire, Calder and Swale (cf. Fig. 1) during the period November 1997 to January 1999. Bulk suspended sediment samples were collected during high flow conditions (when sus-
pended sediment concentrations typically ranged between 50 and 600 mg l⁻¹ from the centre of the channel 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. Samples of the fine-grained sediment stored on and within the channel bed were collected using a resuspension technique (Lambert and Walling, 1988) for water depths < 1.0 m, and a purpose-built sampler (Comerford, 2000) operated from an inflatable boat, for water depths > 1.0 m. In both cases, several 25-l acid-washed polyethylene containers were used to collect the remobilised sediment. These two methods were also used to quantify the amounts of fine-grained sediment stored on the channel beds. The bed sediment collected in the containers was left to settle-out under controlled conditions over a period of 7–10 days and the clear supernatant was siphoned-off (Horowitz, 1988). The sediment was recovered by centrifugation. Samples of overbank sediment deposits were collected using acid-washed astroturf mats (Lambert and Walling, 1987), which were deployed on the river floodplain prior to inundation, and removed soon after the floodwaters had receded. The total amount of sediment on each mat was recovered (estimated to be > 95%) using a stainless steel spatula after air drying.

Bulk subsamples (non-dried and unsieved) of the three types of sediment were analysed for PCBs (PCB 8, 18, 28, 31, 77, 101, 105, 114, 118, 123, 126, 128, 138, 149, 153, 156, 157, 167, 169, 170, 180 and 209) using the procedures described in Meharg et al. (in prep.). Prior to P and Cr analysis, the floodplain sediment samples were air-dried, and the suspended and channel bed sediment samples were freeze-dried, before being passed through a 63 μm sieve (Fürstner and Salomons, 1980; Horowitz and Elrick, 1988). Phosphorus concentrations (total, organic and inorganic) were determined for the < 63 μm fraction of sediment using a Pye Unicam SP6 UV/visible spectrophotometer after chemical extraction (Mehta et al., 1954). Chromium concentrations were determined for the < 63 μm fraction using a Unicam 939 atomic absorption spectrophotometer after acid (HF, HCl and HNO₃) digestion (Lum et al., 1982). Organic carbon (C) and nitrogen (N) concentrations were measured using a Carlo Erba ANA 1400 analyser. Particle size distributions were determined using a Coulter LS130 laser diffraction granulometer, after the removal of organic matter, and chemical and ultrasonic dispersion.

3. Results

3.1. Phosphorus

Table 1 presents information on the P content of the suspended sediment samples collected from the Rivers Aire/Calder and Swale. Values of total P sediment content (TP) for the two sites on the River Swale are similar and relatively low (< 1500 μg g⁻¹), with the value for the downstream site being slightly higher than that for the upstream site. In the case of the River Aire, values of TP increase in a downstream direction, from a mean value of 1534 μg g⁻¹ at site 11, near the source of the river, to a mean of 8276 μg g⁻¹ at site 1. The catchment upstream of the River Aire at site 11 is dominated by moorland and pasture with no major industrial or urban areas. The average TP content of the < 63 μm fraction of natural potential sediment sources (topsoil and channel bank material) in the Aire catchment ranges from approximately 500 to 2500 μg g⁻¹. The suspended sediment samples collected from the River Aire at site 9 have elevated levels of TP, which average 2369 μg g⁻¹, and this probably reflects point source inputs of P associated with the town of Skipton (which lies between sites 9 and 11), as opposed to non-point, diffuse sources of P associated with agricultural land. Downstream of site 9, values of TP increase further in response to point source inputs associated with urban areas, including Bradford and Leeds. During dry summers more than two-thirds of the river’s flow through Leeds may be treated sewage effluent (EA, 1999). In the case of the River Aire at site 1, values of TP also reflect the input from the River Calder which has an average TP value of 6644 μg g⁻¹ at site 12. The River Calder also
Table 1
Average values of the P content, particle size composition and organic matter content of suspended sediment samples collected from the Rivers Aire, Calder and Swale during the period November 1997 to January 1999

<table>
<thead>
<tr>
<th>River</th>
<th>Site</th>
<th>n</th>
<th>TP (µg g⁻¹)</th>
<th>IP (µg g⁻¹)</th>
<th>OP (µg g⁻¹)</th>
<th>IP/OP</th>
<th>C (%)</th>
<th>N (%)</th>
<th>C/N</th>
<th>d₄₃ (µm)</th>
<th>% &lt; 2 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Swale</td>
<td>18</td>
<td>6</td>
<td>1230</td>
<td>777</td>
<td>453</td>
<td>1.7</td>
<td>7.6</td>
<td>0.3</td>
<td>25.3</td>
<td>8.5</td>
<td>17.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(317)</td>
<td>(224)</td>
<td>(129)</td>
<td>(1.3)</td>
<td>(0.1)</td>
<td>(11.5)</td>
<td>(1.5)</td>
<td>(3.1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>11</td>
<td>1486</td>
<td>1050</td>
<td>436</td>
<td>2.4</td>
<td>6.2</td>
<td>0.4</td>
<td>15.3</td>
<td>6.5</td>
<td>23.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(407)</td>
<td>(252)</td>
<td>(162)</td>
<td>(1.1)</td>
<td>(0.1)</td>
<td>(3.5)</td>
<td>(1.2)</td>
<td>(2.6)</td>
<td></td>
</tr>
<tr>
<td>Aire</td>
<td>11</td>
<td>6</td>
<td>1534</td>
<td>836</td>
<td>698</td>
<td>1.2</td>
<td>8.0</td>
<td>0.6</td>
<td>14.4</td>
<td>6.8</td>
<td>22.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(429)</td>
<td>(91)</td>
<td>(375)</td>
<td>(0.8)</td>
<td>(0.1)</td>
<td>(2.3)</td>
<td>(1.5)</td>
<td>(2.7)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>18</td>
<td>2369</td>
<td>1515</td>
<td>854</td>
<td>1.8</td>
<td>9.7</td>
<td>0.8</td>
<td>11.9</td>
<td>6.0</td>
<td>25.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(526)</td>
<td>(382)</td>
<td>(190)</td>
<td>(1.1)</td>
<td>(0.2)</td>
<td>(1.1)</td>
<td>(2.0)</td>
<td>(4.7)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>13</td>
<td>3615</td>
<td>2535</td>
<td>1080</td>
<td>2.3</td>
<td>11.4</td>
<td>0.9</td>
<td>12.4</td>
<td>7.2</td>
<td>21.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(715)</td>
<td>(563)</td>
<td>(207)</td>
<td>(1.1)</td>
<td>(0.2)</td>
<td>(1.2)</td>
<td>(1.8)</td>
<td>(3.4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>18</td>
<td>8276</td>
<td>6799</td>
<td>1477</td>
<td>4.6</td>
<td>13.7</td>
<td>1.1</td>
<td>12.5</td>
<td>6.5</td>
<td>22.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(2516)</td>
<td>(2160)</td>
<td>(530)</td>
<td>(1.7)</td>
<td>(0.2)</td>
<td>(1.1)</td>
<td>(0.9)</td>
<td>(2.3)</td>
<td></td>
</tr>
<tr>
<td>Calder</td>
<td>12</td>
<td>6</td>
<td>6644</td>
<td>5353</td>
<td>1291</td>
<td>4.1</td>
<td>13.2</td>
<td>1.0</td>
<td>13.5</td>
<td>6.2</td>
<td>23.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(3677)</td>
<td>(3155)</td>
<td>(525)</td>
<td>(3.4)</td>
<td>(0.4)</td>
<td>(1.7)</td>
<td>(0.9)</td>
<td>(2.1)</td>
<td></td>
</tr>
</tbody>
</table>

The values in parentheses represent the standard deviations.

Drains a highly urbanized and industrialized catchment, including the cities of Halifax and Huddersfield.

There is also a clear increase in the inorganic P (IP) content of 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 6799 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. Russell et al., 1998) have shown that most of the phosphorus load in urbanized basins is in inorganic form (both dissolved and particulate) reflecting discharges from point sources such as STWs. The relative importance of IP, and thus point source inputs, as opposed to organic P (OP), is demonstrated by the increase in the IP/OP ratio from 1.2 at site 11 to 4.6 at site 1. Values for the River Swale at site 14 and the River Calder at site 12 are 2.4 and 4.1, respectively.

It is possible that the downstream patterns for TP and IP, described above, may be due partly to changes in the particle size composition and organic matter content of the sediment samples, and statistics describing these characteristics are also presented in Table 1. There are, however, no appreciable differences in the particle size composition of the samples between the sites which might explain the spatial pattern in sediment-associated P. There is, however, a substantial increase in the C and N content of the sediment in a downstream direction. However, this increase in C and N alone cannot explain the high values of TP and IP at the downstream sites.

Fig. 2 presents the downstream trend of TP for the < 63 µm fraction of floodplain and channel bed sediment as well as that for suspended sediment described above (see also Table 2). Values
of TP for the floodplain and channel bed sediment are lower than those for equivalent suspended sediment samples. These differences probably reflect differences in the particle size composition of the three types of sediment. Even though the floodplain and channel bed samples were screened through a 63 µm sieve prior to analysis, differences in particle size composition will still exist between the three types of sediment (see Tables 1 and 2) and these will influence their P and other sediment-associated contaminant concentrations (Förstner and Salomons, 1980; Campbell et al., 1988; Horowitz and Elrick, 1988; Horowitz, 1995). Despite these differences, the TP values for the floodplain and channel bed sediment are similar to those of suspended sediment at the same or nearby sites. Although there are only a limited number of channel bed samples from which to infer any trends, the floodplain samples clearly document a downstream increase in TP in the River Aire. When the IP and OP values for channel bed sediment are compared to those of suspended sediment, values for the two types of sediment are similar. However, when the IP and OP data for the floodplain sediment are compared to equivalent values for suspended sediment, there are noticeable differences, particularly in the OP values, which are much lower in floodplain sediment than suspended sediment, possibly due to post-depositional transformations.

3.2. Chromium

Fig. 3 presents results of measurements of the Cr content of suspended sediment and the <63 µm fraction of floodplain and channel bed sediment. As with the results for P, there is a marked downstream increase in the Cr content of the three types of sediment. In the case of the River Swale, Cr values are low (<25 µg g⁻¹) and there is no obvious downstream trend. In the case of the River Aire, there is a threefold increase in the Cr content of suspended sediment, which increases from 98 µg g⁻¹ at site 11 to 306 µg g⁻¹ at site 14.
at site 1. Table 1 indicates that the downstream change in the Cr content of suspended sediment is not simply due to downstream changes in particle size composition. The Cr value for the suspended sediment collected from the downstream site on the River Calder at site 12 is 433 μg g⁻¹, which is noticeably greater than values for the River Aire sediment. This indicates that the high Cr values associated with samples collected at site 1 are likely to reflect inputs from the River Calder. The importance of Cr inputs from the River Calder is reinforced by the channel bed sediment samples, in that the Cr content of bed sediment from the River Aire at site 3 which is located downstream of Leeds and just upstream of the Aire/Calder confluence is only 104 μg g⁻¹, which is less than 50% of the value at site 1. The bed sediment from the upstream site on the River Calder (site 13) already has a high Cr content of 110 μg g⁻¹, and the bed sediment at site 12 has a mean value of 417 μg g⁻¹. Consequently, the River Calder appears to be the main source of sediment-associated Cr in the downstream reaches of the River Aire, and this probably reflects the type of industry located in the River Calder catchment.

When the Cr content of suspended sediment is compared with that of the < 63 μm fraction of floodplain and channel bed sediment, values for floodplain and bed sediment, although similar, are slightly lower than values for suspended sediment at the same, or a nearby, site. Again, this may be due to contrasts in particle size composition among the different types of sediment. Perhaps more importantly, however, the overall trends shown by the three types of sediment are similar.

3.3. Polychlorinated biphenyls

Fig. 4 presents preliminary results for the total (selected 23 congeners) PCB content of suspended sediment and bulk floodplain and channel bed sediment. Although only a limited number of samples have been analysed to date, some important trends are still evident. Total PCB values for the three sites on the River Swale are very low (< 2 ng g⁻¹). Similarly, values for the upper and middle sites on the Rivers Aire and Calder (i.e. sites 3, 4, 5, 7, 8, 10 and 13) are also generally low, although values for suspended sediment at sites 11 and 9 are relatively high, with means of 52 and 31 ng g⁻¹, respectively. The highest values of total PCBs are associated with sediment collected from the middle (site 6) and downstream (sites 1, 2 and 12) sites. The downstream increase in total PCBs is most apparent in the case of the suspended sediment samples collected from the River Aire (i.e. sites 1, 6, 9 and 11). The downstream increase in total PCBs for the Rivers Aire and Calder, shown in Fig. 4, is consistent with a detailed analysis by Meharg et al. (in prep.) of the PCB congener profiles of the sediment samples described above and of bulk (whole) river water samples from the Rivers Aire and Calder, which demonstrated that the major sources of PCBs in the two study rivers are probably point source inputs from STWs associated with the urbanized areas in the middle and lower reaches of the rivers. A similar study of chlorinated microorganic contaminants, such as dieldrin and hexachlorocyclohexane isomers (α + γ), in the Rivers Aire and Calder (Meharg et al., 1998) also identified STWs as primary sources of these contaminants, reflecting the wool, textile and wood industries in the catchment.
Table 3 lists estimates of the storage of fine-grained sediment on the floodplains and channel beds of the study rivers. The floodplain data for each site are average values of overbank deposition for individual flood events, whereas the channel bed data are average values for total bed storage at the times of sampling. Values for bulk sediment deposition on floodplains range from 0.92 to 10.39 kg m\(^{-2}\), whereas values for channel bed storage range from 0.16 to 14.79 kg m\(^{-2}\). For the < 63 \(\mu\)m fraction, estimates of floodplain deposition range from 0.08 to 2.80 kg m\(^{-2}\), and values for channel bed storage range from 0.10 to 2.96 kg m\(^{-2}\). These values of storage indicate that there is significant storage of fine-grained sediment on the floodplains and channel beds of the study rivers. Given the high concentrations of P, Cr and PCBs associated with floodplain and channel bed sediment (Tables 1 and 2 and Figs. 2–4), the floodplains and channel beds clearly represent significant sinks for contaminants, particularly in the middle and lower reaches of the Rivers Aire and Calder.

4. Discussion and conclusion

Samples of suspended, floodplain and channel bed sediment collected along the lengths of the Rivers Aire, Calder and Swale have been used to determine downstream trends in three different sediment-associated contaminants. Comparison of P, Cr and total PCB concentrations for sediment for the River Swale with those for the Rivers Aire and Calder, emphasize the polluted nature of the sediment in the Aire/Calder system. In the Rivers Aire and Calder, there are clear trends of downstream increases in TP, Cr and PCBs. This downstream trend reflects the relatively unpolluted nature of the headwaters and the location of the main urban and industrial areas in the middle and lower parts of the catchment (cf. Fig. 1), and, in particular, point-source inputs associated with the location of certain types of industry and STWs.
Thus, the catchment of the River Calder has been shown to be the main source of Cr to the River Aire, and this reflects the main types of industry found in this catchment.

The magnitude of the contaminant concentrations and overall trends shown by the suspended, floodplain and channel bed sediment samples are similar. This confirms the view that, in addition to suspended sediment, overbank floodplain deposits and fine-grained channel bed sediment may be used to investigate sediment-associated contaminant sources and transport dynamics in river basins. Such floodplain and channel bed sediment are often easier to collect, since sampling does not need to be restricted to a limited number of infrequent high flow events. The absolute concentrations associated with floodplain and channel bed sediment are usually lower than equivalent values for suspended sediment, and this primarily reflects differences in the particle size composition of the different types of sediment, and such effects must be recognised and taken into account when comparing the three types of sediment.

A significant amount of the fine-grained sediment delivered to the study rivers has been shown to be deposited on the floodplain and the channel bed of the main river system. Given the P, Cr and PCB concentrations associated with such sediment, floodplains and channel beds clearly represent significant sinks, particularly in the lower reaches of the Rivers Aire and Calder, where elevated levels of contaminants often coincide with significant values of sediment storage. In the case of channel bed sediment, such storage is short term (i.e. until the next high discharge event remobilizes the deposited sediment), and such deposits probably have a residence time < 1 year. Also, channel bed sediment may represent a net source of P, Cr and PCBs at certain timescales, depending, for example, on the element concentration gradient between the sediment and the overlying river water. In many UK river basins, most of the sediment deposited on floodplains is likely to be stored for time periods between $10^1$ and $10^3$ years, or longer. In situations where lateral channel migration is important, sediment-associated contaminants may be reintroduced back into the channel, and floodplains may represent a net source of contaminants, even if other inputs have ceased (Lecce and Pavlowsky, 1997). The magnitude and residence time of sediment-associated contaminant storage on floodplains and channel beds clearly have important implications for understanding, monitoring and modelling the delivery and fate of sediment-associated contaminants in river systems.

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