Spatial and temporal variability in the concentration and speciation of metals in suspended sediment transported by the River Aire, Yorkshire, UK

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Abstract:

In recent years, there has been an increasing awareness of the important role of fine sediment in the transport and storage of metals in fluvial systems. However, there has been little research on the behaviour of contaminated sediment in industrial rivers in the UK. This paper examines spatial and temporal variations in the concentration and speciation of lead, copper and chromium associated with suspended sediment in the River Aire in Yorkshire, UK. An increase in the total concentration of all three metals in sediment was identified in the lower reaches, which reflected inputs of road dust, sewage and industrial effluents. Spatial variations in the chemical speciation of the metals were also identified. The iron–manganese oxides and organic fractions were the most significant for the adsorption of metals by sediment. Both the concentrations and speciation of sediment-associated metals exhibited substantial temporal variation. Such variation reflected the accumulation of metals and organic matter on the river-bed during low flows, the subsequent remobilization of the sediment at high flows and the additional supply of sediment from uncontaminated and contaminated sources, including pulse inputs of road dust, sewage and industrial effluent. The findings presented have important implications for the development of effective catchment management strategies for the control of point- and diffuse-source pollution. Copyright © 2006 John Wiley & Sons, Ltd.

KEY WORDS metals; suspended sediment; urban drainage, speciation; River Aire; spatial and temporal variability; bioavailability

INTRODUCTION

In recent years, there has been an increasing awareness of the important role of suspended sediment in the transport of a number of point- and diffuse-source pollutants, including metals, nutrients (e.g. phosphorus) and pesticides (Horowitz, 1995; Owens and Walling, 2002). For the majority of metals, >90% of the flux through a river system occurs in association with suspended sediment (Gibbs, 1977; Horowitz, 1991). An understanding of the spatial and temporal variability of metal concentrations in sediment therefore represents an essential prerequisite for the design and implementation of appropriate control and remediation strategies.

In addition to total metal concentrations, information on speciation is also required in order to provide both a more detailed understanding of the nature of metal associations with sediment and an indication of the amount of each metal that is potentially available to the environment. There is growing concern that the abnormally high levels of certain metals found in some river sediments may exceed toxic levels for river flora and fauna and, therefore, it is important to assess their bioavailability and the potential for bioaccumulation in the food chain.

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Sediment sources can vary considerably, even within a single storm event (Carter et al., 2003), giving rise to temporal variability in sediment properties, which can strongly influence metal adsorption and partitioning (e.g. Horowitz, 1991, 1995). In order to obtain a comprehensive understanding of the transport of sediment-associated metals through river systems, intensive monitoring, capable of generating detailed information on spatial and temporal variability in the metal content of suspended sediment, is required. To date, few studies have considered temporal variations in the speciation of sediment-associated metals in UK rivers. One exception is the work of Dawson and Macklin (1998a), who documented the temporal variation of both the concentration and the speciation of metals in sediment samples collected during a single storm event from a site on the River Aire, Yorkshire. They found that concentrations and speciation varied throughout the event and were specific to each metal. However, the degree to which their results are representative of all storm events occurring on this river remains uncertain. Similarly, few studies have undertaken detailed investigations of spatial variability in the behaviour of sediment-associated metals. Tessier et al. (1979) investigated spatial variability in the speciation of metals associated with suspended sediment in a single reach and found that iron and manganese (Fe–Mn) oxides scavenged metals introduced into the system. They also identified variations in metal speciation between upstream and downstream reaches, noting the anthropogenic impact in the lower reaches. Gibbs (1973) undertook an investigation within single reaches of the Rivers Amazon and Yukon, but concluded that it was difficult to generalize regarding metal–sediment interactions. Neither of these studies considered the effect of high flow conditions.

There is, therefore, a lack of detailed information on the temporal and spatial variability of both concentrations and the speciation of metals in suspended sediment at the catchment scale, particularly in industrial catchments in the UK. This paper describes an investigation of the spatial and temporal variability of the concentration and speciation of selected sediment-associated metals in the River Aire, Yorkshire, UK. The River Aire is a large catchment, which is dominated by urban and industrial land use in its middle and lower reaches. Sediment samples were analysed for lead (Pb), copper (Cu) and chromium (Cr). Pb and Cu were chosen to represent elements that occur naturally, so that the impact of urban and industrial areas on metals already found within the system could be investigated. In contrast, Cr was chosen because, although occurring naturally in small quantities, it is mainly introduced by industrial processes.

The main objectives of the study were:

1. To examine downstream trends and spatial variability in the concentration and speciation of Pb, Cu, and Cr associated with suspended sediment collected from the River Aire and its main tributary, the River Calder.
2. To examine inter- and intra-storm variability in the concentration and speciation of Pb, Cu and Cr associated with suspended sediment collected from the Rivers Aire and Calder.

The study represents part of a larger project aimed at determining the role of fine-grained sediment in nutrient and contaminant (metals, phosphorus and polychlorinated biphenyls) fluxes within large UK river basins undertaken within the framework of the NERC Environmental Diagnostics Research Programme. Other results from this larger project are presented in Carton et al. (2000), Owens et al. (2001), Owens and Walling (2002, 2003), Carter et al. (2003), Meharg et al. (2003) and Walling et al. (2003).

STUDY AREA AND METHODS

Study area

The River Aire is a tributary of the River Ouse, which drains into the North Sea via the Humber Estuary (Figure 1). It has a total catchment area of 1932 km² above the tidal limit, and a long-term (1977–90) mean annual discharge of 35.8 m³ s⁻¹ (Wass and Leeks, 1999) at the Environment Agency (EA) gauging site at Beal (Figure 1). The River Calder is the main tributary of the River Aire and has a catchment area of 899 km² and a long-term (1987–90) mean annual discharge of 18.6 m³ s⁻¹ at the EA gauging station at
Figure 1. The locations of sampling sites and study area. The EA gauging stations for the Rivers Aire and Calder are located at Beal and Methley respectively (Figure 1), thus contributing nearly half of the discharge of the lower Aire (data from Wass and Leeks (1999)).

The underlying geology of the upper reaches of the Aire–Calder system is Carboniferous limestone and millstone grit. The middle and lower reaches are underlain by Carboniferous coal measures, and this gives way to Permian magnesian limestone below the confluence of the two rivers. The soils in the upper reaches are dominated by raw oligo-fibrous peats and stagnohumic and stagnogley soils. These give way to typical brown earths and pelo-stagnogley soils in the middle and lower reaches. The narrow band of Permian magnesian limestone at the catchment outlet is overlain by typical brown calcareous earths, which are frequently cultivated.

Both the Aire and the Calder rise on land dominated by pasture and rough grazing, where water quality is generally good, except for small discharges of agricultural effluent and some limited diffuse-source pollution. However, in its middle and lower reaches, the Aire–Calder system drains a heavily urbanized and industrialized catchment with a population of approximately 2 million people. The main industries in the catchment include wool, textiles, chemicals, engineering, and food and drink production. 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 middle and lower reaches of both rivers are heavily polluted, receiving discharges of sewage effluent from STWs, combined sewer overflows and sewer dykes (CSOSDs), and industrial discharges (direct and indirect), as well as inputs from roads and other impervious areas.
Sampling and laboratory methods

Samples of suspended sediment were collected along the length of the Aire–Calder river system during the period November 1997 to January 1999. The bulk suspended sediment samples ($n = 74$) were collected from the centre of the channel during high flow conditions (when suspended sediment concentrations (SSCs) typically ranged between 90 and 400 mg l$^{-1}$) 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, freeze-dried and passed through a 63 $\mu$m sieve (Horowitz and Elrick, 1988). An automatic pump sampler (EPIC) was also used at Beal to collect suspended sediment samples throughout four storm events between January and May 1999. This sampler collected 500 ml samples at predetermined intervals, when threshold stage levels were exceeded. The samples collected by the EPIC sampler were then filtered through 0-45 $\mu$m Whatman glass-fibre filter papers and the sediment on the filter paper was retained for analysis.

Potential source materials were collected throughout the study area. Representative samples were collected of: (a) catchment topsoil (top 2 cm from cultivated and uncultivated soils); (b) road dust near to drains in urban areas; and (c) solids from a large STW (Esholt; see Figure 1). All source material samples were dried at 40°C, gently disaggregated and then dry-sieved to <63 $\mu$m to facilitate direct comparison with the fluvial suspended sediment samples. Further information concerning the sampling methods is contained in Carter et al. (2003).

Analyses for Pb, Cu and Cr were carried out on the sediment according to the method originally devised by Tessier et al. (1979) and adapted by Lum et al. (1982). This method partitions sediment-associated metals into five operationally defined fractions: (1) exchangeable metal ions; (2) surface oxide and carbonate-bound metal ions; (3) metals bound to Fe–Mn oxides; (4) organically bound metal ions; and (5) residual metal ions. The extractants were: (1) 1 M magnesium chloride, adjusted to pH 7-0 with 5% sodium hydroxide; (2) 1 M sodium acetate, adjusted to pH 5-0 with acetic acid; (3) 0.04 M hydroxylamine hydrochloride in 25% (v/v) acetic acid; (4) 0.02 M nitric acid, 30% hydrogen peroxide (adjusted to pH 2-0 with nitric acid) and 1-2 M ammonium acetate in 10% (v/v) nitric acid; and (5) concentrated nitric, hydrochloric and hydrofluoric acids. Extractions were conducted in 50 ml high-density polypropylene centrifuge tubes and, after each extraction, separation was effected by centrifuging at 3000 rpm for 40 min. The supernatant was stored in polyethylene bottles, prior to analysis for metals using a Unicam 939 atomic absorption spectrophotometer. All reagents used were AnalR grade or better and prior to use all containers were soaked for 48 h in nitric acid to remove metals from inner surfaces (Massee and Maessen, 1981), rinsed with distilled water and oven dried. Filter papers containing the suspended sediment collected from the EPIC sampler were digested in the same way. A total extraction was also carried out on the bulk suspended sediment samples. This involved performing the fifth stage of the sequential extraction on fresh sediment. As reference materials do not exist for the purposes of sequential extraction, the effectiveness of the extraction procedure can be determined by comparing the sum of the metal concentrations in the individual fractions with the independent measurement of total metal concentration. The recovery achieved by the sequential extraction procedure was found to be $\approx 90\%$. Analytical precision and accuracy were determined using blank duplicates, containing blank filter papers where appropriate, which were run for each matrix and corrections to the analytical results were made where necessary. Organic carbon (C) concentrations were measured using a Carlo Erba ANA 1400 C/N analyser. Particle size distributions were determined using a Coulter LS130 laser diffraction granulometer, after the removal of organic matter, and chemical and ultrasonic dispersion.

RESULTS

Spatial variability

Total concentrations. Figure 2a shows the downstream trend in the mean total concentration (for all the samples collected at each site) and speciation of Pb, Cu and Cr in suspended sediment from individual sites,
Based on the bulk suspended sediment samples. In terms of total concentration, there is a general trend of increasing concentration from upstream to downstream sites (see Figure 1) for all three metals studied. For example, in the case of Pb, mean values were 77 µg g⁻¹ and 291 µg g⁻¹ respectively at Otterburn Beck (upstream; n = 5) and Beal (downstream; n = 18). The maximum Pb concentration for an individual sample, recorded at Beal, was 388 µg g⁻¹. There are no significant differences (Mann–Whitney, p > 0.05) in the Pb content of sediment sampled from adjacent sites, except between Kildwick and Apperley (Mann–Whitney, p = 0.001). This suggests that the main change in sediment geochemistry occurs above Apperley and that the input of contaminated sediment from the River Calder (which is confluent with the River Aire between Apperley and Beal) has a limited effect on the Pb content of suspended sediment in the lower River Aire. Cu concentrations display a similar trend, with the four upstream sites characterized by sediment with low levels of Cu (~100 µg g⁻¹) in comparison with sediment from Apperley, Beal and Methley. Beal exhibits the highest mean Cu concentration, with 188 µg g⁻¹, and the maximum value for an individual sample of 305 µg g⁻¹. The Cu content at Apperley is significantly higher statistically than at all the upstream sites, suggesting that there is an input of this metal between Kildwick and Apperley. However, in contrast to Pb, the Cu content at Beal is significantly higher statistically than at both Apperley and Methley, indicating a further input of the metal below these sites. The sediment from the lower River Calder at Methley exhibits statistically similar
levels of Pb and Cu (Mann–Whitney, $p < 0.05$) to those from Apperley at $\sim 250 \mu g \, g^{-1}$ and $150 \mu g \, g^{-1}$ respectively, indicating the similar levels of Pb and Cu pollution found in the two rivers above the confluence.

The Cr levels at each of the sites in the upper and middle River Aire are similar at $\sim 250 \mu g \, g^{-1}$ and, unlike the Pb and Cu content, do not exhibit a large increase in the middle reaches. There is, however, a significant increase in Cr contamination at Beal (Mann–Whitney, $p < 0.01$), where the mean Cr content is $308 \mu g \, g^{-1}$, and a maximum value for an individual sample of $433 \mu g \, g^{-1}$ has been recorded. Suspended sediment from the River Calder at Methley exhibits even higher Cr concentrations, with a mean of $398 \mu g \, g^{-1}$ and values for individual samples up to $627 \mu g \, g^{-1}$. The difference between the Cr content at Methley and Beal is statistically significant (Mann–Whitney, $p < 0.05$). The higher level of Cr contamination at Methley, compared to Beal, suggests that the River Calder has a significant influence on the Cr content of sediment and is the main source of Cr in the lower River Aire and that less contaminated sediment from the River Aire dilutes the contaminated sediment originating from the River Calder. The general downstream increase in metal levels reflects urban and industrial sources in the middle reaches of the study rivers, as shown in Figure 1 (Carton et al., 2000; Owens et al., 2001; Walling et al., 2003).

The mean Pb, Cu and Cr contents of the suspended sediment collected from the lower reaches of the Rivers Aire and Calder are compared with concentrations of metals associated with catchment soils, road dust and untreated sewage effluent in Table I (collected as part of the larger project; see Carter et al. (2003) for further details). The latter were seen as providing an indication of the potential contribution from STWs and CSOSDs during storm events, when untreated sewage may be discharged directly to the river. Even after accounting for differences in particle size between source materials and suspended sediment, it is unlikely that the high concentrations of metals found in suspended sediment samples collected in the lower reaches of the study rivers are derived from catchment soils, despite the fact that up to 30–40% of suspended sediment in the lower reaches of the Rivers Aire and Calder has been identified as originating from topsoil sources (Carter et al., 2003). The mean Pb and Cu levels in road dust are $303 \mu g \, g^{-1}$ and $503 \mu g \, g^{-1}$ respectively (Table I), and values for individual samples range up to $563 \mu g \, g^{-1}$ for Pb and $1436 \mu g \, g^{-1}$ for Cu. Road dust is, therefore, a potential source of the elevated Pb and Cu levels. This is consistent with the findings of Carter et al. (2003), who reported that road dust may contribute $\sim 20\%$ of the sediment load at Beal and Methley. Conversely, the mean Cr content of road dust is $96 \mu g \, g^{-1}$ and, therefore, is unlikely to be a major source of the Cr contamination in the lower Aire and Calder rivers. Cr is used in many industries, such as metal plating and finishing. It is also a by-product of the extensive textile industry located around Leeds (Dawson, 1997) and is consequently found in many industrial and sewage effluents. The metal contents of three samples of untreated sewage effluent collected from Esholt STW (see Owens and Walling (2002) and Carter et al. (2003)) are shown in Table I. High levels of Pb and Cu are demonstrated, whereas Cr concentrations are lower

![Table I. Mean metal concentrations associated with suspended sediment collected from the lower reaches of the Rivers Aire and Calder compared with concentrations in the <63 μm fraction of catchment soils, road dust and sewage influent](chart)

<table>
<thead>
<tr>
<th></th>
<th>Concentration (μg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>Aire at Beal</td>
<td>18</td>
</tr>
<tr>
<td>Calder at Methley</td>
<td>6</td>
</tr>
<tr>
<td>Catchment topsoil</td>
<td>54</td>
</tr>
<tr>
<td>Road dust</td>
<td>13</td>
</tr>
<tr>
<td>Sewage influent</td>
<td>3</td>
</tr>
</tbody>
</table>

a Represents average value of topsoil from pasture and cultivated fields.
b Collected as part of the larger project (see Carter et al. (2003) for details).
than might be expected. For example, Campbell et al. (1988) measured Cr concentrations of 283 µg g⁻¹ and 1056 µg g⁻¹ in samples of digested sewage sludge from two STWs in London and Manchester respectively. The low Cr concentrations documented for the Aire may reflect the limited number of samples and the impact of the particular industries that supplied the STW at the time of sampling. It is likely that sewage and industrial effluents are highly significant in controlling the metal content of suspended sediment transported by the lower Aire and Calder rivers (Neal et al., 1999). For example, Carter et al. (2003) estimate that solids associated with sewage effluent account for up to 18% of the suspended sediment load of the lower River Aire.

Table II details the variation in particle size characteristics and organic C content of suspended sediment at individual sites throughout the catchment. Metal concentrations commonly reflect variations in the particle size of suspended sediment (Horowitz, 1991), with concentrations increasing as grain size decreases. However, for the samples collected from the Aire–Calder catchment, there are no significant relationships between the Pb, Cu or Cr contents of the suspended sediment and its particle size characteristics (d50 and per cent <2 µm). This reflects the lack of appreciable spatial variability in the particle size composition of suspended sediment and the importance of metal inputs from industrial and urban sources in controlling the metal content of the sediment samples. However, the downstream increases in sediment-associated Pb and Cu are significantly (>95% level) correlated with organic C content (r² = 0.81 and 0.70). This is consistent with an increase in the organic content of suspended sediment from upstream to downstream (Table II). It is likely that the increased organic content of suspended sediment in the downstream reaches reflects an increased contribution from effluent discharges from STWs, as most of the larger STWs occur in the middle and lower reaches (Walling et al., 2003). The mean organic C content of untreated sewage effluent sampled during this study was found to be 32% (n = 3). This value is significantly greater than the mean organic C content of topsoil and road dust, which are both ~10% (Owens and Walling, 2002). However, it remains uncertain whether the organic matter is released from STWs along with Pb and Cu, or whether it acts as an adsorption substrate for Pb and Cu that are already in the water column, having originated from other sources, e.g. from natural sources or industrial effluent. There is no statistically significant relationship between Cr content and the organic C content of the sediment. This suggests that industrial inputs of the metal, rather than changing sediment properties, represent the dominant control on the downstream increase in Cr and that the controls on Cr differ from those for Cu and Pb.

**Speciation.** Figure 2 shows the downstream trend in the mean proportion (%) of Pb, Cu and Cr associated with each chemical fraction for the suspended sediment samples collected from individual sites. For all three metals studied, the proportion transported in exchangeable form is negligible (<6%). Similarly, the carbonate fraction accounts for only small proportions of the total metal content, but is most significant for Pb. The concentrations of exchangeable and carbonate-bound metals are generally <10 µg g⁻¹, and the differences

<table>
<thead>
<tr>
<th>Site</th>
<th>n</th>
<th>d50 (µm)</th>
<th>&lt;2 µm (%)</th>
<th>Organic carbon content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>SE</td>
<td>Mean</td>
</tr>
<tr>
<td>Otterburn Beck</td>
<td>5</td>
<td>5.2</td>
<td>0.2</td>
<td>26.1</td>
</tr>
<tr>
<td>Bell Busk</td>
<td>6</td>
<td>6.7</td>
<td>0.7</td>
<td>22.6</td>
</tr>
<tr>
<td>Eller Beck</td>
<td>3</td>
<td>6.6</td>
<td>0.7</td>
<td>17.5</td>
</tr>
<tr>
<td>Kildwick</td>
<td>19</td>
<td>6.1</td>
<td>0.1</td>
<td>25.1</td>
</tr>
<tr>
<td>Apperley</td>
<td>13</td>
<td>7.3</td>
<td>0.1</td>
<td>24.3</td>
</tr>
<tr>
<td>Beal</td>
<td>21</td>
<td>6.5</td>
<td>&lt;0.1</td>
<td>21.9</td>
</tr>
<tr>
<td>Methley</td>
<td>7</td>
<td>6.2</td>
<td>0.1</td>
<td>23.3</td>
</tr>
</tbody>
</table>

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in these concentrations between individual sites are not statistically significant (Mann–Whitney, \( p > 0.05 \)). The presence of limestone in the headwaters of the River Aire would suggest that the sediment from this portion of the catchment should have a high calcium carbonate content. Indeed, the suspended sediment sampled from the headwater areas has a total Ca content of \( >20000 \mu g/g \) (unpublished data; see also BGS (1996)). Despite this, the carbonate fraction appears to have little influence on the adsorption of metals, and the concentration of Pb associated with this fraction in suspended sediment from the lower River Calder at Methley is similar to that from the headwaters of the River Aire, despite the fact that the River Calder has no limestone in its headwaters.

Particulate Pb and Cu concentrations are dominated by the Fe–Mn oxides fractions (67–85% and 62–73% respectively). Despite the clear downstream increase in total Pb and Cu concentrations, there is no clear change in the percentage contribution of this fraction between upstream and downstream reaches. Conversely, the proportion of Cr associated with the Fe–Mn oxides fractions increases in importance from upstream to downstream, from 19% to 60%. Between Apperley and Beal there is a statistically significant increase in the amount of Cr associated with Fe–Mn oxides (Mann–Whitney, \( p < 0.001 \)), from 38 to 136 µg g\(^{-1}\).

The organic fraction accounts for only a relatively small proportion of all the metals studied. However, there are statistically significant downstream increases in the mean concentration of Pb and Cu associated with the organic fraction, from \( \sim 15 \mu g/g \) at Apperley to levels of 22 µg g\(^{-1}\) and 33 µg g\(^{-1}\), for Pb and Cu respectively, at Beal (Mann–Whitney, \( p < 0.05 \)). The greater downstream increase in the level of organically bound Cu demonstrates the greater affinity of organic matter for Cu compared with Pb and is consistent with other studies (e.g. Salomons and Förstner, 1984; Macklin and Dowsett, 1989; Pardo et al., 1990). Between Apperley and Beal there is also a statistically significant increase in the amount of Cr associated with organic matter (Mann–Whitney, \( p < 0.001 \)), from 18 to 59 µg g\(^{-1}\). This tends to suggest that organic matter exerts a greater influence on Cr adsorption than on Pb or Cu adsorption.

The residual fraction is more significant as a carrier of Cr than of Pb or Cu. However, the downstream increase in the proportion of Cr associated with Fe–Mn oxides is coupled with a decrease in the importance of the residual fraction. There are no significant differences in the concentration of Pb, Cu or Cr associated with the residual fraction between any of the adjacent sites (Mann–Whitney, \( p > 0.05 \)).

The results relating to the speciation of Pb are comparable to those obtained by Tessier et al. (1980) in the Rivers Yamaska and St Francois, Quebec, Canada, by Pardo et al. (1990) in the River Pisuerga in Spain and by Macklin and Dowsett (1989) in the River Tyne in Northumbria, England, who showed that the Fe–Mn oxides fraction is the most important in the transport of particulate Pb (Table III). Other studies (Tessier et al., 1979; Table III. A comparison of the sequential extraction results for Pb, Cu and Cr obtained in this investigation with those from other studies

<table>
<thead>
<tr>
<th>Metal</th>
<th>Contribution from each fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exchangeable</td>
</tr>
<tr>
<td>Pb</td>
<td>This study (mean values from Figure 2a)</td>
</tr>
<tr>
<td></td>
<td>Pardo et al. (1990)</td>
</tr>
<tr>
<td></td>
<td>Tessier et al. (1979)</td>
</tr>
<tr>
<td></td>
<td>Macklin and Dowsett (1989)</td>
</tr>
<tr>
<td>Cu</td>
<td>This study (mean values from Figure 2a)</td>
</tr>
<tr>
<td></td>
<td>Gibbs (1977)</td>
</tr>
<tr>
<td></td>
<td>Tessier et al. (1979)</td>
</tr>
<tr>
<td></td>
<td>Dawson and Macklin (1998a)</td>
</tr>
<tr>
<td>Cr</td>
<td>This study (mean values in upper reaches)</td>
</tr>
<tr>
<td></td>
<td>This study (mean values in lower reaches)</td>
</tr>
<tr>
<td></td>
<td>Gibbs (1977)</td>
</tr>
</tbody>
</table>

Dawson and Macklin, 1998a) have documented the importance of Cu associations with the organic fraction, but this is not particularly evident in the results obtained from the present study. For example, Dawson and Macklin (1998a) found that between 10 and 40% of Cu was associated with the organic fraction, depending on the position in the storm hydrograph. However, the results presented by Gibbs (1977) showed that the organic fraction of sediment in the Rivers Amazon and Yukon only accounted for 8–15% of Cu transport, and Jenne (1968) also argues that organic matter is only of minor importance. This difference may, in part, reflect the relative magnitude of the events sampled, as discussed below. The speciation clearly depends on the conditions in a particular river, but it may also vary over relatively small time-scales. This highlights the need to consider temporal variations in the speciation of metals. There are few other studies that have considered the speciation of Cr in fluvial sediments. One exception is the work of Gibbs (1977), and the results from the present study are compared with his results in Table III. The results from the upstream reaches sampled in this study are similar to the results reported by Gibbs (1977) for a mainly unpolluted catchment. The downstream reduction in the proportion of residual Cr highlights the polluted nature of the River Aire in the lower reaches. This is consistent with the findings of Salomons and Förstner (1984), who, in a study of sediment samples from the estuary of the Rivers Rhine and Ems, noted a decrease in the residual fraction as total metal concentrations increased due to anthropogenic pollution.

Temporal variability

Bulk suspended sediment samples (inter-storm variability). Figures 3 and 4 present information on the temporal variation of the total concentration and speciation of metals in the bulk suspended sediment samples collected from the upper and lower reaches of the study rivers respectively. The samples collected at each site provide evidence of considerable variation both within and between different events, and this is summarized in Table IV. The total concentrations of Pb and Cu are higher in the lower reaches, where there is also decreased variability in the concentrations. In contrast, total Cr concentrations fluctuate considerably more in the lower reaches than in the upper reaches. It is likely that this reflects the impact of discharges from point sources, such as industries, CSOSDs and STWs in the lower reaches, which are potential sources of Cr.

Table V shows the coefficient of variation for metal concentrations in sediment for all chemical fractions. The exchangeable fraction demonstrates the greatest degree of variability for each metal. This is to be expected, as it is this fraction that most readily interacts with metals introduced into the system in solution from urban and industrial sources. This variability will also reflect variations in the relative contributions of natural sediment sources, such as channel banks and catchment soils, which will result in changes in sediment properties. The high variability shown by the exchangeable fraction also reflects the low concentrations of metals associated with it. This fraction is of limited significance in terms of the overall concentration of metals in the sediment. Figures 3 and 4 show that the concentrations of metals associated with the Fe–Mn oxide fraction also exhibit

Table IV. The range of metal concentrations measured in suspended sediment from the upper and lower reaches of the study catchment (coefficient of variation in parentheses)

<table>
<thead>
<tr>
<th>Metal concentration (µg g⁻¹)</th>
<th>Upper reachesᵃ</th>
<th>Lower reachesᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>60–300 (41)</td>
<td>200–380 (16)</td>
</tr>
<tr>
<td>Cu</td>
<td>30–200 (56)</td>
<td>115–300 (26)</td>
</tr>
<tr>
<td>Cr</td>
<td>20–80 (15)</td>
<td>200–620 (28)</td>
</tr>
</tbody>
</table>

ᵃ Otterburn Beck, Bell Busk, Eller Beck, Kildwick and Apperley.
ᵇ Beal and Methley.
considerable variability. It is likely that Fe–Mn oxides are partially responsible for the uptake of metals released from STWs and other industrial sources in the lower reaches. Variations in the concentrations of Pb and Cu associated with the carbonate fraction are relatively low and their occurrence may reflect the arrival of sediment from the limestone headwaters. There are also relatively minor fluctuations in the Pb, Cu and Cr contents associated with the organic fraction.

A ‘dilution’ effect at high flows has been demonstrated by many workers (e.g. Grimshaw et al., 1976; Bradley and Lewin, 1982; Dawson and Macklin, 1998a), who have observed that the concentration of metals in suspended sediment decreases at high flows as a result of inputs of relatively clean sediment. SSC does
appear to have some effect on metal levels in this study. At Kildwick on 15 January 1999, a decrease in SSC, from 174 mg l$^{-1}$ to 115 mg l$^{-1}$, corresponds with an increase in Pb, Cu and Cr contents. Similarly, during the event at Kildwick on 16 October 1998, the concentrations of Pb and Cu rise at the hydrograph peak, as the SSC decreases from 281 mg l$^{-1}$ to 98 mg l$^{-1}$ between samples 2 and 3. However, during the events at Apperley on 10 December 1997 and 16 October 1998, the changes in metal levels and speciation do not relate to changes in SSC, which varied little between the two samples and, therefore, do not reflect a dilution effect. Similarly, at Beal on 10 December 1997, the maximum concentrations of Pb and Cu occur early on the falling limb (middle sample) when the SSC is highest at 193 mg l$^{-1}$. This reflects an increase...
in the contribution from road dust (Carter et al., 2003). Furthermore, for the event of 3–4 January 1998, the concentrations of Pb, Cu and Cr are lower on the falling limb (last sample) than on the rising limb, despite the decrease in SSC from 172 to 142 mg l$^{-1}$. This corresponds to a decrease in the contribution of sediment from STWs and an increase in the contribution from areas of the catchment under pasture on the falling limb (Carter et al., 2003). Therefore, in contrast to the samples taken from Kildwick, dilution by large amounts of cleaner sediment is not evident in the downstream reaches.

Dawson and Macklin (1998a) suggest that lower metal concentrations associated with peak sediment concentrations may also be a result of the accessing of new sediment source areas and a higher percentage of relatively coarse material transported at high discharges. This coarser material will exhibit a lower exchange capacity for metals, and it is well known that particle size composition influences the partitioning and transport of metals (Hart, 1982; Lum et al., 1982). At Kildwick, on 16 October 1998, the particle size of the sediment collected gradually decreased from a $d_{50}$ of 5.75 µm to 4.97 µm (i.e. it gets finer), which could explain the increase in Cu; but alone it does not explain the variation of Pb or Cr. During events at Apperley and Beal, decreases in particle size were not associated with increases in metal levels. For example, at Beal on 3–4 January 1998, the larger particle size ($d_{50} = 8.14$ µm) of the first sample (taken on the rising limb) suggests that metal concentrations should be higher for the subsequent samples, but this is not the case for either Pb, Cu or Cr, where concentrations are lower on the falling limb. If fluctuations in the concentration of metals were related to particle size, then one might also expect each metal to behave in a similar manner, and to increase with decreasing particle size, but this is not the case. It is more likely that, although SSC and particle size composition play a role, changes in source contributions and chemical processes during the storm event will also affect the concentrations of metals and their partitioning.

**EPIC samples (intra-storm variability).** The samples collected by the EPIC sampler at Beal were used for more detailed analysis of storm-period variations in metal levels and speciation. As the sediment on the filter paper was digested, it was not possible to determine any other properties, such as the particle size composition or organic carbon content of the sediment. To evaluate the relationships between the metal content of these sediment samples, river discharge and SSC, the results obtained for four high-flow events that occurred in January, March, April and May 1999 are considered. For two events (March and April), the amount of sediment collected was not sufficient to perform a sequential extraction, so only results from a total extraction are presented. For the January event, insufficient sediment was obtained on the filter papers, so each value considered is a composite of two samples.

The storm hydrographs for each event are plotted in Figures 5–8, and Table VI provides information on the magnitude of the sediment concentration and discharge peaks. The discharge data are from EA flow gauging station at Beal (see Figure 1 for location). The SSC data are derived from continuous turbidity monitoring at the same site. Table VI demonstrates that the timing of the peaks in SSC clearly reflects the timing and magnitude of the peaks in river discharge. Figures 5–8 show how the metal content of the suspended sediment varied during each event, and Table VII presents the Pearson correlation coefficients for...
the relationship between total metal concentration and discharge. Metal concentrations, particularly Cr, appear to show some dependence on discharge and SSC.

During the April event (Figure 7), the concentration of Pb peaks on the falling limb and the correlation of Pb concentrations with discharge is statistically significant (Table VII). As noted previously, this ‘dilution’ effect
has been demonstrated by many workers (e.g. Grimshaw et al., 1976; Bradley and Lewin, 1982; Dawson and Macklin, 1998a) and may relate to inputs of cleaner sediment, which are transported from the upper reaches at high discharges (Carter et al., 2003). Conversely, levels of Cu and Cr tend to be positively correlated with discharge (Table VII). During the April event, Cr is also positively correlated with SSC (Pearson correlation
Figure 7. Temporal variation in the concentration of metals associated with suspended sediment collected from the River Aire at Beal during the storm event of 21 April 1999

coefficient of 0.96, significant at the 95% confidence level). When the rising and falling limbs are considered separately in the March event (Figure 6), the correlation between both Cu and Cr and river discharge is 0.92 on the rising limb (significant at the 99% confidence level), but there is not a significant correlation with discharge on the falling limb. Conversely, during the April event, there is a stronger correlation between both Cu and Cr and discharge (0.93 and 0.92 respectively, significant at the 99% confidence level) on the falling limb compared with the rising limb. Contrasts in the behaviour of Cr and Pb are further highlighted during the second discharge
Figure 8. Temporal variation in the speciation of metals associated with suspended sediment collected from the River Aire at Beal during a storm event on 8 May 1999

peak of the March event, where both metals show a significant correlation with discharge, but Cr exhibits a positive relationship and Pb a negative relationship (0.73 and −0.88 respectively, significant at the 95% confidence level). It is also notable that, during the March event, total Cu correlates with total Cr (0.92, significant at the 99% confidence level). This suggests that these metals originate from the same source (Tessier et al., 1979) and, more importantly, because highly contaminated sediment is likely to be flushed out at higher discharges, it further suggests that this reflects discharges from CSOSDs and from industrial sources. CSOSDs operate at
Table VI. The magnitude of discharge and SSC peaks and their relationships for four storm events at Beal

<table>
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<tr>
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<tbody>
<tr>
<td>Max. Q (m³ s⁻¹)</td>
<td>277</td>
<td>164</td>
<td>239</td>
<td>188</td>
</tr>
<tr>
<td>Max. SSC (mg l⁻¹)</td>
<td>148</td>
<td>130</td>
<td>148</td>
<td>116</td>
</tr>
<tr>
<td>Pearson correlation coefficient Q vs SSC</td>
<td>0.89**</td>
<td>0.95*</td>
<td>0.82*</td>
<td>0.74*</td>
</tr>
</tbody>
</table>

* Significant at the 95% confidence level.
** Significant at the 99% confidence level.

Table VII. Pearson correlation coefficients for the relationship between metal concentration and discharge

<table>
<thead>
<tr>
<th></th>
<th>Pb</th>
<th>Cu</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>January</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>March</td>
<td>—</td>
<td>0.41*</td>
<td>0.57*</td>
</tr>
<tr>
<td>April</td>
<td>—</td>
<td>—</td>
<td>0.98**</td>
</tr>
<tr>
<td>May</td>
<td>—</td>
<td>0.72*</td>
<td>0.80*</td>
</tr>
</tbody>
</table>

* Significant at the 95% confidence level.
** Significant at the 99% confidence level.

high flow, when it is considered that there is sufficient discharge to dilute the effluent to safe levels. Cr levels are not so much controlled by river discharge and SSC as they are by the timing of discharges from CSOSDs and other industrial sources, as illustrated by the correlations with both rising and falling limb discharges. During the April event, Cr concentrations are not correlated with Cu concentrations. This may reflect the reduced magnitude of the event (Table VI), which meant that there was less input from industrial/sewage sources.

During the January storm event (Figure 5), the lack of a statistically significant correlation between Cr and discharge reflects the marked peak in the level of sediment-associated Cr, which occurred several hours after the discharge and sediment peaks, between 20:00 and 23:00 (note also that the lowest Cr concentration occurred at the time of maximum SSC and discharge, in comparison with Pb and Cu). This suggests that Cr-rich sediment is washed into the river from sources unrelated to the discharge peak in the river, e.g. from STWs or industrial sources. This reinforces the concept that industrial sources of Cr represent the dominant influence on sediment quality in the Rivers Aire and Calder and explains why natural sediment properties, such as particle size, are of limited importance in accounting for the variations in the Cr content of fluvial sediment in this heavily polluted system. In a more rural catchment, where a large proportion of the catchment area is occupied by pasture or cultivated land, there is great potential for the accessing of new sediment source areas, which are relatively uncontaminated, during high flows, thus leading to possible dilution effects. However, in catchments such as the Aire–Calder, where a large proportion of the catchment is covered by urban areas, there is less potential for clean sources to be accessed and more potential for contaminated road dust and industrial effluents to be mobilized at high flows. Road dust inputs will dampen any dilution effect and help to maintain the metal content throughout the events (Carter et al., 2003), as demonstrated by Pb, and to some extent by Cu. In addition, contaminated sediment may accumulate on the river-bed during lower flows and be subsequently remobilized during high-flow events (Owens et al., 2001; Walling et al., 2003).

The speciation of the metals varied during events, and this is also depicted in Figures 5 and 8 for the January and May events respectively. During these events, organic matter accounted for, on average, 27% of Cu. This is consistent with findings by Dawson and Macklin (1998a), who found that ~30% of Cu was associated with the organic fraction during a high-flow event on the River Aire in February 1996. The Pearson correlation
coefficients were calculated for the relationships between the element fractions studied, SSC and discharge. During the May event, the amount of Cr that was associated with the organic fraction showed a significant positive correlation with discharge \((r = 0.72, \text{ significant at the } 95\% \text{ confidence level})\). Sewage effluent is commonly characterized by a high organic content (Owens and Walling, 2002), and the positive relationship between the amount of Cr associated with the organic fraction and the increase in discharge again points to the possibility that the increased Cr originates from such a source. It is also possible that releases of organic matter facilitate the uptake of Cr by Fe–Mn oxides (Jenne, 1968), since the concentrations associated with this fraction also increase during the higher flows. During the January event, there is a significant negative correlation between the concentration of Pb associated with the Fe–Mn oxides fraction and SSC, when the whole event is considered \((r = -0.70, \text{ significant at } 95\% \text{ confidence level})\). This highlights the significance of this fraction in controlling the adsorption and desorption of Pb during an event.

In order to present a more detailed view of the May event, flow was divided into the rising and falling limbs. During the rising limb, there was a negative correlation between the amount of Pb associated with the organic fraction and SSC \((-0.98, \text{ significant at the } 99\% \text{ confidence level})\). This is evidence of a dilution effect affecting the organic fraction. This could reflect a decrease in the organic matter content of suspended sediment when concentrations increase during high flows; however, this is unlikely, because high-flow releases from STWs are likely to be enriched in organic matter. It is more likely that changes in stream chemistry during the rising limb of an event lead to desorption of Pb associated with the organic fraction. Unfortunately, the use of filter papers as a source of sediment precluded analysis of pH and organic content, so it is not possible to investigate this further.

There are no further correlations between the chemical fractions of any of the metals and either SSC or discharge. This suggests that the controls on metal levels and speciation are linked to the timing and magnitude of industrial discharges, which are not necessarily in phase with increases in discharge or SSC. This may be a direct influence (i.e. the release of sediment-associated metals from such sources) or a secondary influence, whereby industrial discharges alter the pH or organic content of the sediment, which facilitates the uptake of metal ions already in solution. A combination of the two possibilities is also likely.

**DISCUSSION AND CONCLUSION**

**Spatial variability**

The Pb, Cu and Cr contents of suspended sediment collected from the Rivers Aire and Calder show a clear increase from upstream to downstream. The high levels of metals in the lower reaches are likely to relate to anthropogenic inputs, including road dust, and industrial and sewage effluents. Road dust sources are likely to be more important for Pb and Cu than for Cr, for which sewage and industrial effluents are more likely to represent the key sources, although further research is required to substantiate this.

The Fe–Mn oxides and organic matter fractions have been shown to dominate the transport of metals in the study catchment, especially in the lower reaches. Downstream increases in the concentrations of metals associated with Fe–Mn oxides and/or organic matter emphasize the ability of these fractions to take up inputs of metals to the middle and lower reaches of the river. The important role played by Fe–Mn oxides in the distribution of metals in this catchment may reflect the high levels of extractable Mn in the stream sediments (Carter et al., 2003), and McCallum and Hall (1998) point to the introduction of the gasoline additive methylcyclopentadienyl manganese tricarbonyl (MMT) as a replacement for tetraethyl lead in 1974 as a new source of Mn in the environment. Particulate Mn oxides emitted from fuel combustion could scavenge soluble metals, significantly increasing the levels in suspended sediment. This could explain the higher levels of Pb associated with the Fe–Mn oxides fraction in this urban catchment, compared with studies in less urbanized areas (e.g. Tessier et al., 1979). It has also been argued that increased levels of Fe–Mn oxides may lead to reduced co-precipitation reactions with other phases, further enhancing the elevated levels associated with Fe–Mn oxides (Stone and Droppo, 1996). It is also possible that the high amounts of organic matter
found in sediment in the lower reaches of the river may play a secondary role by producing the reducing conditions that favour adsorption by Fe–Mn oxides. When the total Cr content of suspended sediment was correlated with its organic matter content, the relationship was not significant. However, a more detailed analysis using a sequential extraction procedure has shown that there is a substantially greater downstream increase in the concentration of Cr associated with the organic matter fraction than for Pb and Cu. This highlights the importance of sequential extractions in providing more detailed information on the nature of the association of metals with sediment that could be overlooked when considering data relating only to total metal concentrations.

Tessier et al. (1979) suggested that metals have a unique speciation pattern, which remains unaltered as further ions are introduced. However, the results from this investigation have shown that this is not the case with Cr, and demonstrate that it is not possible to generalize concerning the behaviour of specific metals, especially when dealing with heavily polluted environments. Spatial variations in speciation should not be interpreted solely in terms of the percentage of the total amount of a metal associated with a particular fraction, as previous workers have done (e.g. Dawson and Macklin, 1998a,b). This approach can obscure the existence of changes in concentrations associated with a particular fraction if the percentage changes in proportion to the total pollutant concentrations (Kennedy et al., 1997). Interpretations of spatial variability in metal speciation should, therefore, also consider changes in the actual concentration (µg g⁻¹) of the metal in each fraction.

Sequential extraction data also provide useful information concerning the environmental availability of metals. The Fe–Mn oxides and organic matter fractions constitute the two most important pools of potentially available trace metals, and redox potential and pH are commonly seen as the physicochemical factors most likely to affect the release of trace metals from these sources (Gambrell et al., 1976). The large amounts of metals associated with Fe–Mn oxides in this catchment, therefore, have implications for their potential bioavailability. This is consistent with the findings of Dawson (1997), who showed that metal contaminants introduced into the aquatic system by human activity usually exist in relatively unstable chemical associations and, therefore, are predominantly available for biological uptake. In the UK, there are at present no clear guidelines for determining whether contaminated fluvial sediments represent a risk to the environment. Internationally, there is some controversy over which fractions represent a hazard to the environment, although a number of workers (e.g. Gibbs, 1977; Chen et al., 1989; Stone and Droppo, 1996) have suggested that the first four fractions removed by the Tessier et al. (1979) method represent potentially ‘available’ fractions. Conversely, metals in the residual fraction will only be released by long-term weathering of the sediment. In this context, only the suspended sediment from Beal (Figure 2) exceeded the ‘severe effects’ level of 250 µg g⁻¹ for Pb, as determined for fluvial sediment in the Province of Ontario, Canada (OMOE, 1992), although most sites still exceed the Canadian Sediment Quality Guidelines’ ‘probable effects’ level of 91 µg g⁻¹ (CCME, 1999). The concentration of ‘available’ Cu exceeds the Ontario ‘severe effects’ level of 110 µg g⁻¹ (OMOE, 1992) at Apperley, Beal and Methley, demonstrating that metal inputs have an impact on sediment quality, even above Leeds. The Cr results emphasize the importance of determining which chemical fractions are potentially available to the environment. Although total Cr levels of ~100 µg g⁻¹ in the upper reaches of the River Aire appear to be close to the ‘severe effects’ level of 110 µg g⁻¹ (OMOE, 1992), the values are well below such guidelines when the potentially available fraction is determined. However, Cr levels in the first four chemical fractions of sediment sampled from the downstream sites of Beal and Methley exceeded the Ontario ‘severe effects’ level of 110 µg g⁻¹.

**Temporal variability**

The metal content of suspended sediment and its speciation show considerable inter- and intra-storm variability in both the upper and lower reaches of the study catchment. SSC and particle size composition appear to have little effect on this variability. There is considerable temporal variability in the concentrations of metals associated with the exchangeable fraction, but the concentration of metals associated with the Fe–Mn fraction also shows significant fluctuations. The uptake and release of metals is influenced by chemical
conditions within the river, such as pH and redox potential, and the concentration of the metal and other competing metals. These relationships have not been examined here, and there clearly exists a need for further research into spatial and temporal changes in river water chemistry on metal behaviour and fluxes.

The analysis of sediment samples collected from the upper reaches of the river has permitted inferences on the causes of variability in the lower reaches to be made. This approach has rarely been employed in previous studies. In terms of maximum and minimum values, there is less fluctuation in the total concentration of Pb and Cu in the lower reaches compared with the upper reaches. In contrast, the total concentration of Cr fluctuates more in the lower reaches than upstream, and it is likely that this reflects variable inputs from sewage and industrial sources. Cu and Cr tend to show positive correlations with discharge and with each other, further suggesting that they are released from industrial sources, such as CSOSDs, which function at high discharge. However, industrial releases are not necessarily in phase with changes in discharge and SSC within the river. The high levels of Cr found in sediment at Beal at or around the discharge peak probably reflect the timing of the arrival of contaminated sediment from the River Calder.

Implications for management

A large number of storm events were sampled and the results highlight the fact that it is impossible to generalize regarding the behaviour of metals either during an event or from one event to the next. The concentration of metals at high flow depends on the timing of industrial inputs, the relative proportions of sediment from contaminated and uncontaminated sources, remobilization of contaminated bed sediment and the natural variability in metal levels and speciation that also exists in the system (as demonstrated in the upper reaches, where industrial influences are insignificant). Therefore, variability in metal concentration and speciation will depend on the magnitude of the event, as well as on the magnitude of industrial and sewage discharges that occur, rather than simply on the physical and chemical properties of sediment itself. This has important implications for developing suitable management strategies for controlling the levels of metals in river systems. In addition, the significant spatial and temporal variations demonstrated in both metal concentration and speciation highlight the need for comprehensive and detailed river monitoring and sampling if accurate assessments of potential sediment-associated pollution problems are to be undertaken.

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