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Spatial and temporal variability of the chromium content of suspended and flood-plain sediment in the River Aire, Yorkshire, UK

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Abstract Suspended sediment transported by the River Aire, Yorkshire, UK is characterized by elevated levels of heavy metals relative to other northern rivers, due to its location in a highly urbanized industrial region. An investigation of the spatial variability of heavy metal contamination of fluvial sediment has documented downstream changes in chromium (Cr) concentration from the headwaters, through the city of Leeds and towards the tidal limit. Average Cr concentrations associated with suspended sediment and overbank flood-plain deposits range from *c*. 50–100 mg kg^{-1} in the headwater reaches to *c*. 300 mg kg^{-1} at the tidal limit, with a maximum value of up to 630 mg kg^{-1} in sediment from the River Calder, a tributary of the River Aire. Results from the study also demonstrate how any assessment of spatial variability of sediment contamination must take account of temporal variation of sediment-associated metal concentrations. Chromium concentrations in suspended sediment sampled at a specific location may increase by over 100% during a single storm event and also evidence significant seasonal variation. In 1998, average Cr concentrations associated with recent flood-plain deposits at the tidal limit were found to vary from *c*. 400 mg kg^{-1} in January to *c*. 150 mg kg^{-1} in December.

INTRODUCTION

River sediments frequently act as a sink for heavy metals, which enter the fluvial system from weathering of bedrock, from diffuse agricultural and urban sources, or as point source industrial pollution. Horowitz (1991) argues that suspended sediment commonly contains substantially higher concentrations of trace elements than are found in solution. Studies of channel and flood-plain sediments are therefore important if we are to understand the transport and storage of contaminants within terrestrial and aquatic ecosystems. The River Aire, in Yorkshire, is characterized by elevated levels of many heavy metals in its sediment when compared to other rivers in northern England (Robson & Neal, 1997). This reflects *c*. 250–300 years of industrial and urban development around Leeds and Bradford (Dawson, 1997). Since the River Aire eventually flows into the Humber Estuary, these metals could have an important environmental impact on the North Sea. Many previous studies of the

River Aire have involved sampling at a single site, usually near the tidal limit (e.g. Neal *et al.*, 1999), or have considered only short periods (e.g. Dawson & Macklin, 1998) or very long historical time scales (e.g. Hudson-Edwards *et al.*, 1999). Several of these studies, such as that by Dawson (1997), have failed to consider the impact of the River Calder, a tributary of the River Aire, on its water quality. This study adopts a basin-wide perspective to evaluate both short- and longer-term temporal variability of levels of sediment-associated chromium (Cr) in the River Aire catchment. These are important considerations in establishing patterns of sediment-associated contaminant transport and storage, and also help to evaluate the potential environmental risk. Other heavy metals are also important for sediment quality in this catchment, but are beyond the scope of this paper.

STUDY AREA

The River Aire (Fig. 1) has a total catchment area of 1932 km^2 above the tidal limit at site 1 and a population of 1.9 million. The River Calder is the main tributary of the River Aire and has a catchment area of 930 km^2 upstream of site 11. The River Aire rises in the Pennines, an upland area underlain by Carboniferous limestone, where the land use is predominantly sheep grazing. Its downstream course flows over areas underlain by millstone grit and coal measures, and through the major industrial cities of Leeds and Bradford before passing into the agricultural lowlands, which are underlain by Permian magnesian limestone. Around 1.1 million people live within the Aire sub-catchment and industrial activity is very intense along the river corridors with a total of 887 consented discharges and 37 sewage treatment works discharging a variety of pollutants into the river (Environment Agency, 1998a). In contrast to the River Aire, the River Calder rises on peat moorlands overlying millstone grit. Its catchment area contains a population of *c.* 800 000 (Environment Agency, 1998b) and it has similar numbers of sewage works and consented discharges along its course. The extensive urban areas with much industrial activity, including metal plating, wool, textile and chemical manufacturing industries, make the Aire/Calder catchment an ideal site for studying the transport of contaminants by fluvial sediment.

METHODOLOGY

Bulk suspended sediment samples containing between 100 and 250 l of water were collected from several sites within the study catchment (Fig. 1) during high flow events. The samples were obtained using a submersible pump powered by a portable generator. Samples were returned to the laboratory, where the sediment was recovered by continuous flow centrifugation and then freeze-dried. In total, 65 suspended sediment samples were collected over a 15 month period. An automatic pump sampler (EPIC) that collected 500 ml samples at pre-determined intervals, when threshold stage levels were exceeded, was also used at site 1 to collect suspended sediment throughout a storm event in January 1999. These samples were

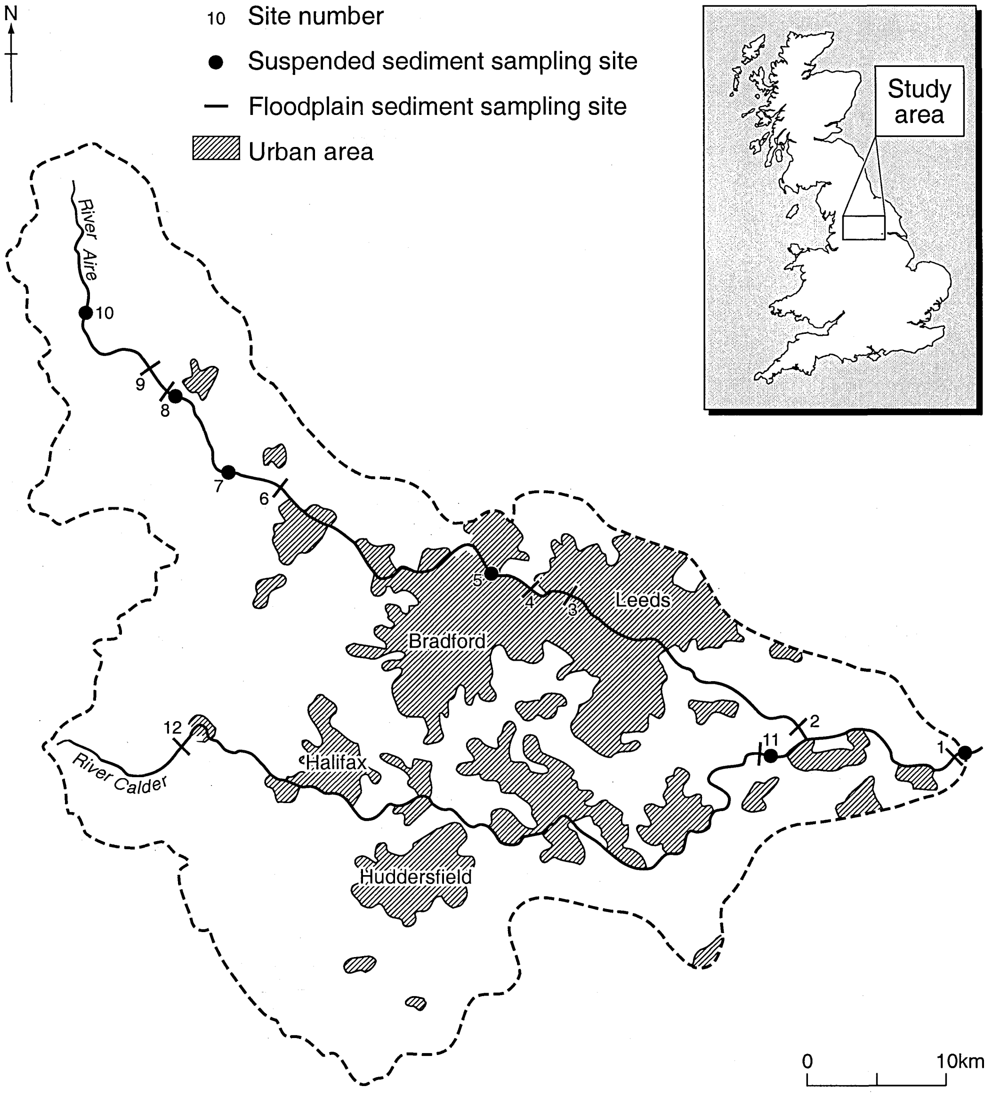

Fig. 1 Location map showing the study area, sampling sites and urban areas.

then filtered and the filter paper retained for analysis. Sediment traps, consisting of *c.* 30 cm × 30 cm pieces of acid-washed plastic "astroturf" were deployed at study sites shown in Fig. 1, in order to collect suspended sediment deposited on flood plains during overbank discharge events. The traps were recovered when water levels receded, then returned to the laboratory and dried. Sediment was brushed off and stored in glass jars prior to analysis. Seventy nine samples of overbank sediment were collected. These were sieved to <63 μm to make them more directly comparable to the suspended sediment. The sediment samples and filter papers were digested using concentrated acids (HF, HCl and HNO_3) (for details see Lum *et al.*, 1982), and the resulting solution was analysed for total Cr by atomic absorption spectrophotometry. Blank samples were included to test for contamination. Absolute particle size distributions were determined using a Coulter LS130 laser diffraction granulometer, after removal of organic matter with H_2O_2, and chemical and ultrasonic dispersion. Organic carbon was measured using a Carlo Erba ANA 1400 automatic analyser.

SPATIAL VARIABILITY OF SEDIMENT-ASSOCIATED CHROMIUM CONCENTRATIONS

Figure 2(a) shows the mean Cr levels in suspended sediment at individual sites within the study catchment. There is a sharp increase in Cr contamination at site 1, where the average Cr content is 308 mg kg^{-1}, and maximum values of 433 mg kg^{-1} have been recorded. Suspended sediment from the River Calder at site 11 exhibits even higher Cr concentrations, with values of up to 627 mg kg^{-1} and this reflects the nature of the industry in the Calder catchment. The background level of Cr in the < 63 µm fraction of soils of the study catchment ranges from 6 to 96 mg kg^{-1}, further suggesting that the Cr input is not from natural sources. Chromium 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. Chromium is regarded as an element of moderate to high toxicity and the average concentrations recorded at sites 1 and 11 are considerably higher than the upper limit of 75 mg kg^{-1} recommended for water supporting aquatic life by the US Environmental Protection Agency (USEPA) (cf. Garbarino *et al.*, 1995) and the "probable effects" level of 160 mg kg^{-1} (USEPA, 1997). Table 1 compares the sediment-associated Cr levels found in this study with those reported by other studies around the world. It is clear that the levels of contamination of sediment in the lower Aire are higher than in many other large rivers, and are within the range of the highly polluted River Rhine.

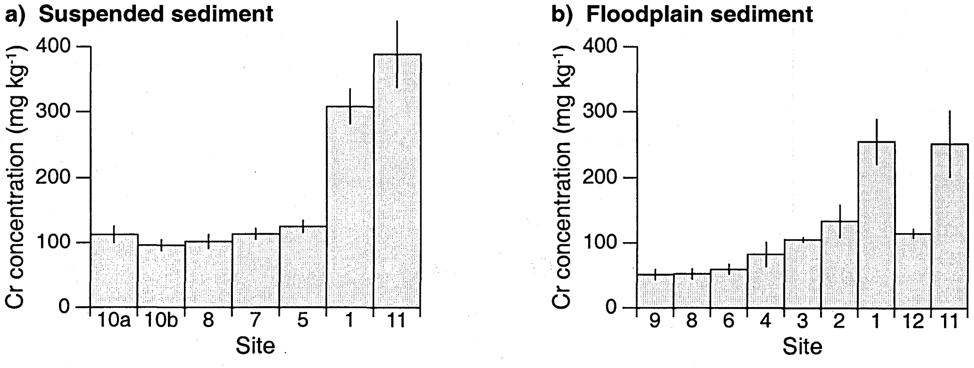

Fig. 2 Downstream variation in (a) mean suspended sediment-associated Cr concentrations and (b) mean overbank sediment-associated Cr concentrations (error bars show the 95% confidence interval of the mean based on the standard error of the mean).

Table 1 Values for the Cr content of fluvial sediment reported from other catchments.

River	Cr concentration (mg kg^{-1})	Study
Swale, Yorkshire, UK	6–50*	Hudson-Edwards *et al.* (1999)
West Fork Blue, USA	80	Horowitz *et al.* (1990)
Rhone, Switzerland	90–114	Burrus *et al.* (1990)
Amazon, Brazil	195	Gibbs (1977)
Yukon, USA	115	Gibbs (1977)
Rhine, Germany	300–1200	Forstner & Wittmann (1981)

* Flood-plain sediment.

The Cr concentrations found in overbank flood-plain deposits are consistently lower than those associated with suspended sediment (Fig. 2(b)). This largely reflects the contrast in particle size between the two sediment types. Most overbank deposits were collected close to the river bank, or from levees, and consequently contain a significant proportion of coarser material. The average D_{50} of the suspended sediment is 6.4 μm, whereas the equivalent value for the <63 μm fraction of the flood-plain sediment is 16.9 μm. However, the spatial trend of the Cr content of overbank deposits parallels that shown by suspended sediment, with a steady increase towards the downstream reaches. Overbank sediment from site 2, immediately above the confluence with the River Calder, has a maximum Cr concentration of 173 mg kg^{-1} compared to a maximum value of 431 mg kg^{-1} for site 1. Site 11, which is located on the River Calder immediately above its confluence with the River Aire, has a similar Cr content to site 1. This emphasizes the major role played by the River Calder in controlling the sediment quality in the lower Aire. Site 12, although located near the headwaters of the Calder catchment and above almost all of the industrial and urban area, is characterized by levels of Cr contamination comparable to overbank sediment collected from central Leeds. This may reflect differences in particle size or organic content between the two rivers. Horowitz (1991) has emphasized the importance of particle size in exerting a fundamental control on the ability of sediment to adsorb ions. As particle size decreases, and specific surface area increases, the amounts of organic matter and iron and manganese oxides that collect on the surface of the sediment, and which act as a surface for the adsorption of heavy metals, also increase. The average D_{50} of overbank deposits from the River Calder is 13 μm, compared to 20 μm for the River Aire. The average organic carbon content of overbank sediment from the Calder and from the Aire upstream of its confluence with the Calder is 9.01% and 6.20%, respectively. While such properties undoubtedly exert some influence over sediment quality, there is no statistically significant relationship between Cr content and either particle size composition or organic carbon content for the overbank sediment samples obtained from this industrial area. This suggests that the downstream increase in Cr is heavily influenced by industrial inputs of the metal. Previous studies which have analysed samples from site 1 (e.g. Neal *et al.*, 1999) and documented high levels of contamination, attributed these to the urban and industrial areas of Leeds and Bradford. However, this more detailed study shows that the sources are more complex, with the highest concentrations being found in the River Calder. This reflects the nature of the industry found throughout the Calder catchment. Such high levels of Cr are of long-term environmental significance as they may be stored within the system and cause long-term pollution problems, for example, through the reworking of flood-plain sediments.

TEMPORAL VARIATION OF SEDIMENT-ASSOCIATED CHROMIUM CONCENTRATIONS

Any assessment of spatial variability of sediment contamination must also take account of temporal variations of sediment-associated metal concentrations, which will reflect both accumulation and remobilization of contaminated sediment according to flow conditions, and variations in sediment and contaminant sources.

Seasonal variation

A total of 18 flood-plain samples were collected at site 1 over a 12 month period and these provide the opportunity to investigate seasonal variations of sediment-associated Cr levels. The flood-plain samples can be seen as being more temporally representative than suspended sediment samples, since they represent composite samples derived from an entire event and are not influenced by the time of sampling during the event. The particle size composition of the samples varied very little and therefore cannot explain the variation in Cr content. The highest Cr levels in the flood-plain deposits were associated with the first two events of the 1997/98 winter season (Fig. 3). This may reflect the storage of Cr in river bed sediment during the preceding dry summer months, that is remobilized during the subsequent flood event and deposited on the flood plain. The Cr levels declined during the winter, before peaking again in May and June 1998, when the longer intervals of drier weather between wet periods would have allowed sediment to accumulate on the river bed. Flow conditions were relatively high

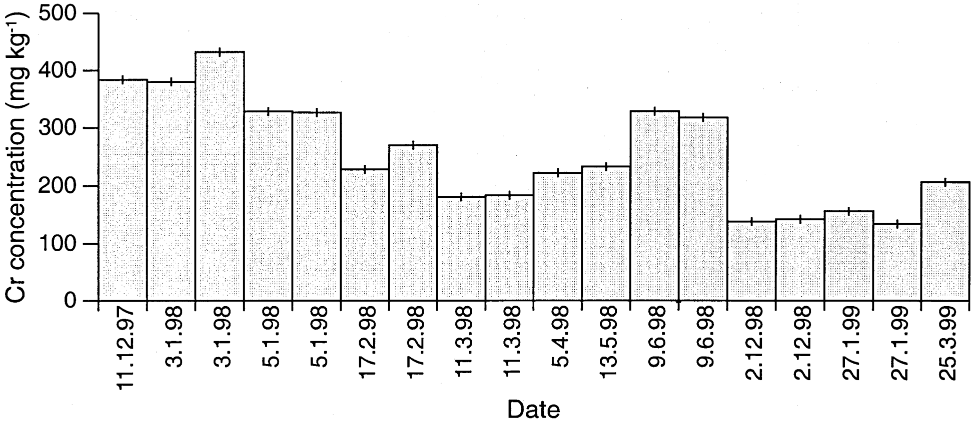

Fig. 3 Seasonal variation in the Cr content of overbank deposits at site 1 (error bars show the 95% confidence interval of the laboratory measurement).

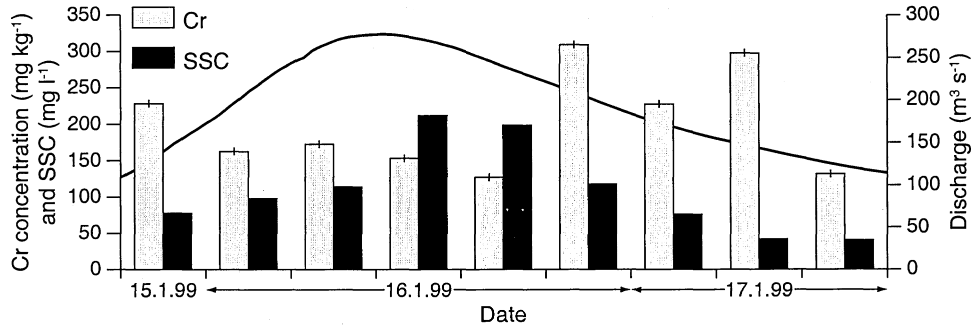

Fig. 4 Storm-period variation in suspended sediment-associated Cr concentrations (error bars show the 95% confidence interval of the laboratory measurement).

during the rest of the summer and very little in-channel storage will have occurred. Chromium concentrations recorded in sediment deposited in December 1998 were therefore much lower than during the previous year.

Storm-period variations

Chromium concentrations in suspended sediment can also vary markedly during storm events, in response to changes in flow conditions and suspended sediment source. During a storm event in January 1999 (Fig. 4), suspended sediment concentrations were highly correlated with discharge (r^2 = 0.82, significant at the 95% confidence level). Figure 4 shows how the Cr content of the suspended sediment varied from 125 mg kg^{-1} to over 300 mg kg^{-1} over a three hour period. Regression analysis showed no significant relationship between levels of sediment-associated Cr and either suspended sediment concentration (SSC) or water discharge. Bradley & Lewin (1982) suggest that a dilution effect may occur during storm events, as coarser particles with lower contaminant concentrations enter the system. This was also noted by Dawson & Macklin (1998) and there is some evidence of this effect during the January storm event. However, shortly after the discharge and sediment peaks there is a marked peak in the level of sediment-associated Cr, suggesting that Cr-rich sediment is washed in at high discharges, either as untreated sewage effluent released by sewer overflows, or from highly contaminated sediment originating from the Calder catchment. 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 and organic carbon content are unable to account for the variations in the Cr content of fluvial sediment in this heavily polluted system.

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REFERENCES

Bradley, S. B. & Lewin, J. (1982) Transport of heavy metals on suspended sediments under high flow conditions in a mineralised region of Wales. *Environ. Pollut.* Series B **4**, 257–267.

Burrus, D., Thomas, R. L., Dominik, B., Vernet, J. P. & Dominik, J. (1990) Characteristics of suspended sediment in the Upper Rhone River, Switzerland, including the particulate forms of phosphorus. *Hydrol. Processes* **4**, 85–98.

Dawson, E. J. (1997) The dispersal, storage and remobilisation of heavy metals in the River Aire contaminated by urban and industrial wastes. PhD Thesis, University of Leeds, UK.

Dawson, E. J. & Macklin, M. G. (1998) Speciation of heavy metals on suspended sediment under high flow conditions in the River Aire, West Yorkshire, UK. *Hydrol. Processes* **12**, 1483–1494.

Environment Agency (1998a) Local Environment Plan (Aire).

Environment Agency (1998b) Local Environment Plan (Calder).

Forstner, U. & Wittmann, G. (1981) *Metal Pollution in the Aquatic Environment.* Springer-Verlag, Berlin, Germany.

Garbarino, J. R., Hayes, H. C., Roth, D. A., Antweiler, R. C., Brinton, T. I. & Taylor, H. E. (1995) Heavy metals in the Mississippi River. In*: Contaminants in the Mississippi River, 1987–1992* (ed. by R. H. Meade), 53–72. US Geological Survey Circular 1133.

Gibbs, R. (1977) Transport phases of transition metals in the Amazon and Yukon Rivers. *Geol. Soc. Am. Bull.* **88**, 829–843.

Horowitz, A. J. (1991) *A Primer on Sediment-Trace Element Chemistry*, second edn. Lewis Publishers, Boca-Raton, Florida, USA.

Horowitz, A. J., Rinella, F., Lamothe, P., Miller, T., Edwards, T., Roche, R. & Rickert, D. (1990) Variations in suspended sediment and associated trace element concentrations in selected riverine cross sections. *Environ. Sci. Technol.* **24**, 1313–1320.

Hudson-Edwards, K. A., Macklin, M. G. & Taylor, M. P. (1999) 2000 years of sediment-borne heavy metal storage in the Yorkshire Ouse Basin, NE England, UK. *Hydrol. Processes* **13**, 1087–1102.

Lum, K. R., Betteridge, J. S. & Macdonald, R. R. (1982) The potential availability of P, Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in urban particulate matter. *Environ. Technol. Lett.* **3**, 57–62.

Neal, C., Jarvie, H. P. & Oguchi, T. (1999) Acid-available particulate trace metals associated with suspended sediment in the Humber rivers: a regional assessment. *Hydrol. Processes* **13**, 1117–1136.

Robson, A. J. & Neal, C. (1997) A summary of regional water quality for eastern UK Rivers. *Sci. Total Environ.* **194/195**, 15–38.

USEPA (1997) *The Incidence and Severity of Sediment Contamination in Surface Waters of the United States*, vol. 1: National Sediment Quality Survey. US Environ. Protection Agency EPA 823-R-97-006.