

Metal contamination of bed sediments in the Irwell and Upper Mersey catchments, northwest England: exploring the legacy of industry and urban growth

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Abstract

Purpose Manchester is often heralded as the first industrial city. Large volumes of physical and liquid contaminants were released into its river network throughout the industrial period up to the latter part of the twentieth century. Water quality has improved dramatically in recent decades, but, given their environmental significance, it is important to ascertain the extent to which a legacy of contamination persists in the modern bed sediments.

Materials and methods Fine-grained bed sediments were sampled at 40 sites in the Mersey and Irwell catchments. Sediments were wet sieved to isolate the <63- μm grain size fraction. Metal concentrations were determined using XRF. Particle size characteristics were also measured. Sediments were subjected to a five-step sequential extraction procedure to ascertain the environmental significance of metal concentrations. Alongside archival research of past industry, enrichment factors, multivariate statistical techniques and conditional inferences trees were used to identify sources of heavy metals.

Results and discussion Bed sediment-associated heavy metal(-loid) concentrations were as follows: As (9.89–110 mg kg^{-1}), Cr (76.5–413 mg kg^{-1}), Cu (53.1–383 mg kg^{-1}), Pb (80.4–442 mg kg^{-1}) and Zn (282–1020 mg kg^{-1}). Enrichment factors ranged from moderate to extremely severe, with Pb showing the greatest enrichment across the catchments. Chemical mobility was generally low, but metal(-loid) partitioning

identified the influence of anthropogenic sources. Statistical analysis highlighted a number of point sources associated with former industrial sites that operated during the industrial period. Conditional inference trees highlighted the role of the textile industry on Cu concentrations in addition to indicating the complexity of sources, fluxes and stores of sediment-associated contamination throughout the system.

Conclusions Fine-grained sediment-associated metal(-loid)s in the Mersey and Irwell catchments are anthropogenically enriched. Concentrations also exceed sediment quality guidelines. A lack of distinct spatial patterning points to a complex network of contaminant inputs across the catchments, even in the headwaters. Whilst potential modern urban sources are likely to be important, spatial patterns and multivariate/data mining techniques also highlighted the importance of releases from former industrial sites as well as the reworking of historically contaminated floodplains and soils.

Keywords Bed sediment · Heavy metals · Historical contamination · Sequential extraction · Enrichment factor

1 Introduction

Due to the timing and speed of industrialisation, Manchester is often heralded as the first industrial city (Marshall 1940; Hoselitz 1955; Hall 1998; Peck and Ward 2002). Beginning in the mid-eighteenth century, and continuing until its eventual decline from the 1920s, the industrial period saw vast quantities of fine-grained particulates (e.g. boiler ash and cinders) and liquid contaminants (e.g. dyes, bleaches and chemicals) discharged into river channels. Whilst environmental legislation to tackle these problems began in the 1890s, the use of the river network as a waste disposal system effectively continued until the 1980s (Burton 2003). Manchester's industrial

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heritage centres upon its textile industries, but paper and printing works, tanneries, saw mills, chemical plants, engineering works, and coal mines were also widespread in this region. Early surveys identified extensive deposition of contaminants into river channels from a variety of industrial sources (Coates 1862; Mersey and Irwell Joint Committee 1892; Douglas et al. 2002). The uninhibited release of contaminants over an extended period added large quantities of heavy metals to the fluvial environment. Although water quality in Manchester has improved in recent decades, there is still a paucity of information regarding sediment quality and the extent to which a legacy of contamination persists within the modern fluvial network.

This paper is part of a wider project assessing the sources, transport pathways and environmental significance of this legacy effect from the Industrial Revolution to the present day. Whilst no formal sediment quality guidelines (SQGs) exist for freshwater bed sediments in the UK, threshold values have been established in Canada and the Netherlands (VROM 2011; CCME 2002), and draft values are under consideration by the UK Environment Agency (EA) (Hudson-Edwards et al. 2008). SQGs provide an assessment of levels beyond which heavy metal contamination may pose a risk to aquatic biota and human health. Furthermore, metal partitioning studies may provide information on mobility and bioavailability. Sequential extractions can be applied to sediments to establish the chemical fractionation of heavy metals and therefore the phases in which metals are bound to sediments. These phases are operationally defined, and a number of methods are used, thus posing potential issues for comparability between studies. The relative proportions for each metal, however, can provide very useful indications regarding the sources and forms of contamination. The various physio-chemical forms of fractionated heavy metals display different behaviours in the wider environment (Tessier and Campbell 1987; Chapman et al. 1998), including changing mobility potential (Calmano et al. 1993; Eggleton and Thomas 2004).

Establishing the relative proportions of modern and historic contaminant sources is not straightforward (Carter et al. 2003; Owens et al. 2016). Principal component analysis (PCA) has been applied to discriminate between natural and anthropogenic sources of contaminants in urban environments (e.g. Manta et al. 2002; Pathak et al. 2015; Wiseman et al. 2015). It is also possible to conceptualise key sources of heavy metals through the grouping of trace elements as geochemical signatures and in mapping factor scores geospatially (e.g. Zhang 2006; Guo et al. 2014; Yuan et al. 2014). Data mining techniques, such as conditional inference trees (CITs), have also been used to identify key explanatory factors influencing heavy metal concentrations (Hu and Cheng 2013, 2016; Guo et al. 2014). This method provides

a hierarchical splitting of possible impact factors to better understand the relative influence of each source type. This study presents the first application of this technique to archival records of catchment contaminant sources.

This study quantifies fine-grained bed sediment-associated contamination across the Greater Manchester river network for the first time. Research has been conducted in other catchments in Northern England, identifying the influence of historic metal mining and modern urban environments upon channel bed contamination (e.g. Macklin et al. 1997; Owens et al. 2001; Walling et al. 2003). The present study explores the contaminant legacy of rapid historical industrialisation and urbanisation within Manchester, the first industry city. Drawing upon historical maps and archival data, we attempt to identify potential contaminant contributions from key industries, as well as those from modern sources. Our primary objectives are to (1) establish total sediment-bound concentrations of key heavy metals and metalloids within the modern river network, (2) utilise a sequential extraction technique and enrichment factors to ascertain the anthropogenic component and wider environmental significance of these contaminants and (3) utilise historical industry data alongside multiple statistical approaches to begin to unravel potential contaminant sources and transport pathways to, and within, the fluvial environment.

2 Materials and methods

2.1 Study site

This study focuses on the Upper Mersey (734 km²) and Irwell (793 km²) catchments in the Greater Manchester region of northwest England. Manchester is a large urban area within a wider regional population of 2.55 million. It is bounded to the north and east by the Pennine uplands. Sampling encompassed all major tributaries in the two catchments including the rivers Roch, Croal, Tonge, Irk, Medlock, Tame, Etherow and Goyt. The underlying geology is dominated by Carboniferous Millstone Grit and Coal Measures, with Permian and Triassic Sandstone in the lower reaches of the Irwell, Medlock and Mersey. Presently, the catchments are dominated by urban and suburban areas, with some more extensive rural land use in the headwaters (Fig. 1).

Figure 1 shows the sample locations. These were selected to be broadly representative of the land uses described above but also to encompass high density areas of both modern and historical industry. Historic surveys demonstrate the widespread and extensive industrialisation along the river network, from headwater catchments to the city centres of Manchester and Salford (Fig. 2).

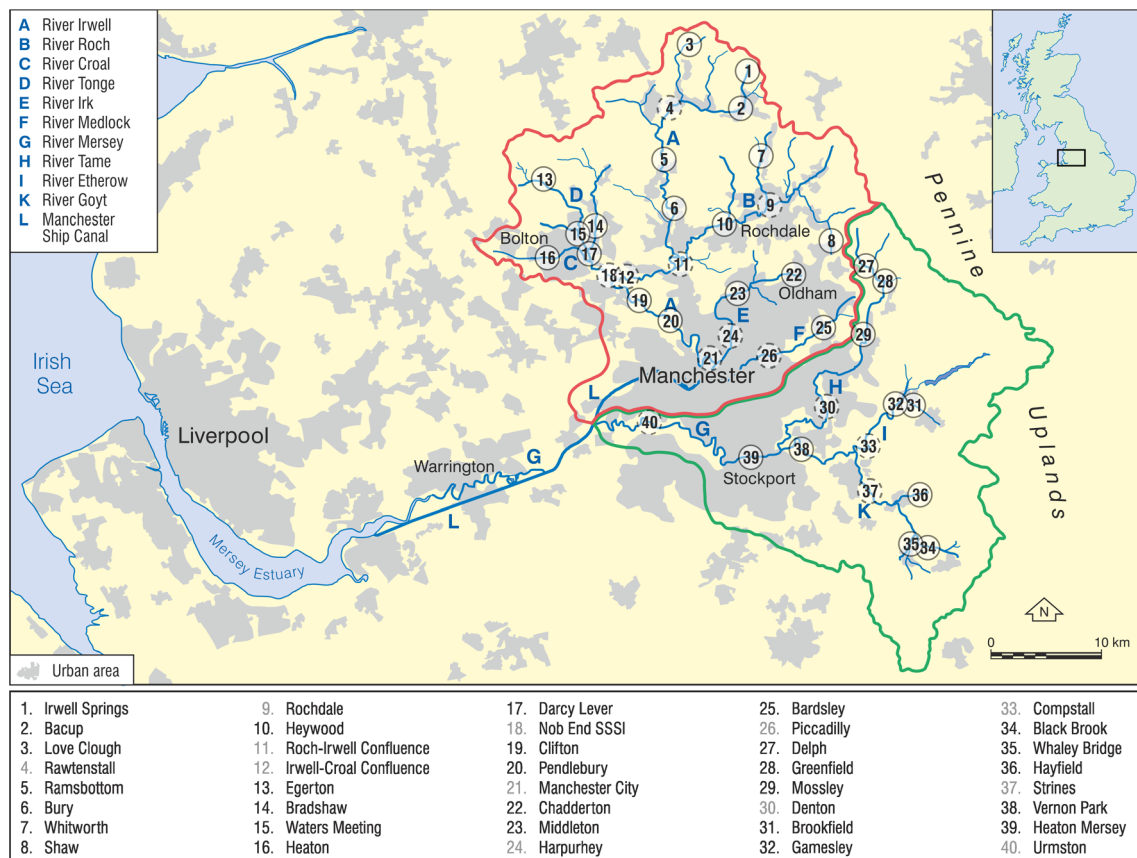


Fig. 1 Map of the Mersey and Irwell catchments, northwest England, UK, represented by the green and red outlines respectively. Urban areas are indicated by the grey shaded areas. Sediment sampling sites are

indicated, where sites selected for sequential extractions are indicated by dashed circles and grey text.

Industrialisation occurred along all tributaries of the Mersey and Irwell but was more concentrated in the upstream Irwell and around the urban centres of Bolton, Rochdale, Manchester and Stalybridge (Coates 1862; Mersey and Irwell Joint Committee 1892; Fig. 2). Anecdotal evidence highlights the poor quality of Manchester's rivers during the height of the industrial period. In 1845, Friedrich Engels commented on the River Irk close to its junction with the Irwell in Manchester city centre:

‘Above the bridge are tanneries, bonemills and gas-works, from which all drains and refuse find their way into the Irk, which receives further the contents of all the neighbouring sewers and privies. It may easily be imagined, therefore, what sort of residue the stream deposits’.

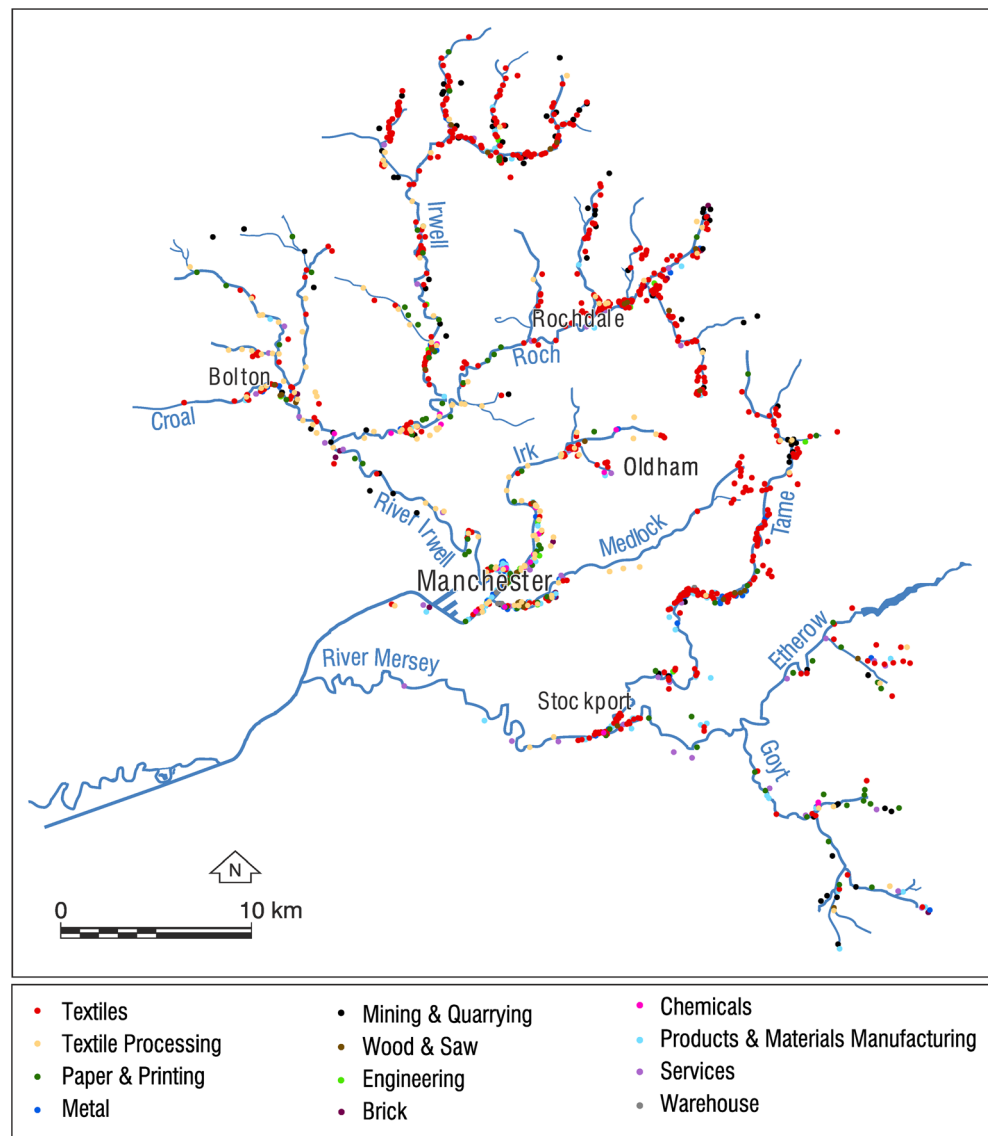
In 1950, the Parliament debated the depositing of physical and chemical waste into the city's river networks and there were reports of the Irwell and Roch as the ‘Rainbow River’ running brightly coloured from discharges of

textile dyeing processes (House of Commons Hansard debates, 18 April 1950; M. Highfield, pers. comm.) By the time the European Community water quality guidance was introduced in the 1970s, the Mersey and Irwell were considered amongst the most polluted rivers in Europe (Jones 2006). Recent efforts have restored water quality to below threshold values (EA 2011), but sediment quality has never been formally assessed on a catchment-wide basis.

2.2 Fine-grained bed sediment sampling

Sediment samples were obtained during low-flow conditions between April and July 2015 across all catchments including headwater reaches. Forty sites were sampled for fine-grained bed sediments following the Lambert and Walling (1988) method. A cylinder of known cross-sectional area (0.14 m^2) was used to isolate a section of river bed and a short depth of bed sediment matrix (5–10 cm). The bed sediments were agitated to bring the surficial and interstitial fine-grained sediment into suspension. During agitation, samples of water and suspended

Fig. 2 Map of historical points of industry within a 1km corridor of river channels for the decade 1890, corresponding with the peak in historical industry in Manchester. Data were obtained from historical Ordnance Survey maps



sediment were decanted into 25 l polyethylene containers. At each site, four points along a cross section were sampled to obtain a representative estimate of contamination and the amount of fine-grained sediment stored on the bed. By isolating a known area of river bed, the use of this cylindrical sampling apparatus permits estimation of fine-grained sediment storage at each site using Eq. (1) (Owens et al. 1999):

$$BS_s = \frac{C_s W_v}{A} \tag{1}$$

where bed sediment storage (BS_s), reported as grams per square metre, is calculated as a function of the sediment concentration associated with the container (C_s , $g\ l^{-1}$) and the volume of water enclosed in the cylinder (W_v , l), divided by the surface area isolated during sampling (A , $0.14\ m^2$).

2.2.1 Sediment analysis

Following settling, sediments were extracted from the containers for analysis. Sediments were wet sieved through a $63\ \mu m$ mesh to isolate the silt and clay fraction, following the technique outlined in Barbanti and Bothner (1993) for preserving sediment-associated metal concentrations. Sediments ($<63\ \mu m$) were freeze-dried and subsampled for subsequent analyses. Grain size analysis was performed using a Malvern 2000G Particle Sizer, following the removal of organic matter using H_2O_2 . Metal(loid) concentrations were obtained from homogenised pressed powder briquettes with a Rigaku CG x-ray fluorescence (XRF) analyser. We have focused on As, Cr, Cu, Pb and Zn as key anthropogenically enriched metal(loid)s. A full XRF suite was obtained for the PCA and for the derivation of enrichment

factors. Samples were analysed in triplicate, and both the variability between analyses and the average errors for all analysed elements were $<\pm 10\%$. Calibration was performed using standard reference materials (SRMs) NIST 2709 and 2780. A library and MCA calibration was performed prior to analysis as recommended by the manufacturer. The 40 sediment samples were also analysed using a PerkinElmer NexION ICP-MS, and in order to ensure comparability between the two analytical approaches, these values were used to calibrate the XRF results. For the targeted trace elements, all samples were within $\pm 10\%$. The ICP-MS analysis was performed using a 7-point calibration procedure. Certified SRMs were run every 10 samples and drift was $<10\%$. Calibration curves all had r^2 values >0.999 .

A five-step sequential extraction procedure was performed on 12 of the sediment samples from sites representing the most downstream locations of each river reach and some key hotspots of heavy metal contamination (Fig. 1). Metal partitioning followed a modified Tessier et al. (1979) scheme. One gram of dried sediment was weighed into 50 ml nitric acid-washed, polyethylene tubes. Metal(loid)s were then extracted in operationally defined phases as follows: (1) exchangeable fraction: 8 ml 1 M MgCl_2 ; (2) bound to carbonate: 8 ml 1 M NaOAc adjusted to pH 5.0 with acetic acid; (3) bound to Fe and Mn oxides: 20 ml 0.4 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% (v/v) HOAc ; (4) bound to organic matter: digested in 3 ml 0.02 M HNO_3 and 5 ml 30% H_2O_2 , followed by a further 3 ml 30% H_2O_2 and finally extracted with 5 ml 3.2 M NH_4OAc in 20% (v/v) HNO_3 ; (5) residual fraction: remaining sediment was digested in a Mars CEM microwave in 10 ml aqua regia (3:1 HCl to HNO_3) for 1 h, before filtering and dilution. Following each extraction (steps 1–4), samples were centrifuged for 25 min at 2000 rpm. The supernatant was decanted and stored for analysis whilst the residue was rinsed in deionised water for 15 min and centrifuged for a further 15 to wash the sediments between stages. All extracts were analysed via ICP-MS. Duplicate samples for the 12 sites were subjected to the sequential extraction procedure, and all results were within $\pm 5\%$.

2.2.2 Water quality analysis

In the laboratory, prior to the sieving of sediment samples, a subsample of river water was retained for each of the sites. These samples were filtered using Whatman 0.45- μm GMF syringe filters and analysed for pH, conductivity and dissolved metals. Duplicate samples were acidified with 2% ultrapure HNO_3 and analysed with ICP-MS for dissolved metal(loid) concentrations.

2.3 Statistical analysis

2.3.1 Enrichment factors

The enrichment of heavy metal(loid)s above background concentrations is calculated as the enrichment factor (EF) using Eq. (2) (Förstner 1984):

$$EF_n = \frac{\left[\frac{C_n \text{ Sample}}{C_{Rb} \text{ Sample}} \right]}{\left[\frac{C_n \text{ Background}}{C_{Rb} \text{ Background}} \right]} \quad (2)$$

where C is the concentration of the sediment-associated metal(loid), n . Background concentrations were obtained using pre-industrial values, sampled from a range of deep channel bank exposures across the Mersey and Irwell catchments. These values were obtained using XRF analysis where ‘pre-industrial’ was defined as persistent low values beneath a sustained peak in heavy metal concentrations. This allowed us to establish the degree of metal(loid) enrichment following the onset of the industrial period. A number of elements have been proposed as the normalisation agent including Al, Cr, Fe, Li, Mn, Sc and Ti (Sutherland 2000). However, due to the degree of contamination observed across the Mersey and Irwell catchments, following Covelli and Fontolan (1997), Rb was used because it is not anthropogenically enriched.

Enrichment factor values are interpreted as follows:

EF < 1	no enrichment
1–3	minor enrichment
3–5	moderate enrichment
5–10	moderately severe enrichment
10–25	severe enrichment
25–50	very severe enrichment
>50	extremely severe enrichment

2.3.2 Maps and documents on past industry and modern land use

In order to explore potential controls on contamination concentrations across the Mersey and Irwell fluvial system, three datasets were compiled. Firstly, historical industry data were obtained from the Ordnance Survey (OS) Edina Digimap collection. All points of industry located within 1 km of the river network were georeferenced and characterised by industry subtype (textile, textile processing, metal working, etc.) and for each decade available from 1840 to 1990. Where maps were not available in a given area for a given decade, archive data were used to verify the persistence of an industry point. This analysis produced a gazetteer of past industry associated with the Mersey and Irwell system. It is important to appreciate, however, that these data do not confirm contaminant

release and can only demonstrate the presence or absence of industry.

To supplement this dataset, additional information was obtained from a historic survey of liquid pollutant inputs across the Manchester river network that was carried out in 1892 (Mersey and Irwell Joint Committee 1892). This provides point data corresponding to registered pollutant releases associated with industry subtypes (printing and dyeing, bleaching, tanning, etc.) which was georeferenced to correspond to the OS data. Whilst this provides some insight into historical inputs, it only covers a snapshot in time and does not offer details on the magnitude of contaminant release from each industry point. Additionally, it does not consider the inputs of physical waste.

In order to evaluate the influence of *modern* contaminant sources, a third dataset was produced for each of the 40 sites. This incorporated modern industry, the proximity to major road networks, proximity to wastewater treatment works and land use for each site.

2.3.3 Statistical analysis

Principal component analysis (PCA) and conditional inference tree (CIT) techniques were applied to the metal(loid) concentrations in order to explore potential sources. Varimax rotation was used to facilitate interpretation of each principal component. Only components with eigenvalues >1 were investigated. Scores were calculated for each site against each component to identify contributions of element groupings to total metal(loid) concentrations.

Conditional inference trees have recently been applied to contaminant concentrations to identify natural and anthropogenic sources (e.g. Zhong et al. 2014; Hu and Cheng 2016). The technique can be performed using a wide range of data considered to possess explanatory potential, whilst also eliminating factors which do not influence the target dataset. This produces, through recursive binary splitting, a tree-based regression model where explanatory variables that exert an influence become ‘branches’ based upon each split and are organised in a hierarchical manner. At the end of each branch, once no further splits are possible, statistically significant groups of values associated with the target variable are presented in terminal nodes. Here, this corresponds to the range of contaminant concentration values associated with each branch. Hence, CITs can indicate the influence of explanatory variables upon metal(loid) concentrations and give reference to their hierarchical significance. The technique can be applied on an element-by-element basis to unpick sources specific to each contaminant. It also resolves issues of overfitting or selection bias which have been highlighted for traditional decision tree models (Hothorn et al. 2006). Full details regarding the CIT methodology can be found in Hothorn et al. (2006).

Existing applications of the CIT approach to unpick contaminant sources have centred on modern explanatory variables such as land use, GDP and population density (Zhong et al. 2014; Hu and Cheng 2016). To identify the influence of industry on metal(loid) concentrations, the three datasets described above were prepared so as to define *total points of industry upstream* produced for each industry subtype and *proximity to industry*, determined by a 1 km radius upstream, for each sediment sampling site. For each industry subtype, two explanatory variables were used, namely total points upstream and number of points in proximity. Due to the distinctive spatial pattern of industry types, two additional variables were included that incorporated *all industry points upstream* and *those in proximity* to a site, irrespective of industry type. CITs were produced in R version 3.1.0 using the ‘party’ package. Trees were produced for each of the selected metal(loid)s and for each of the datasets described above.

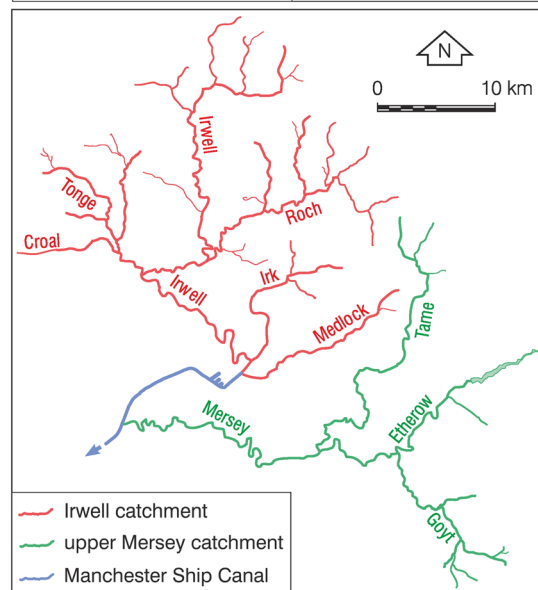
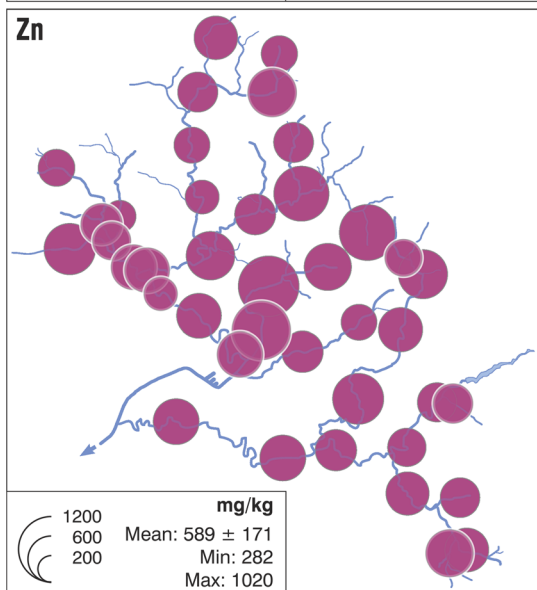
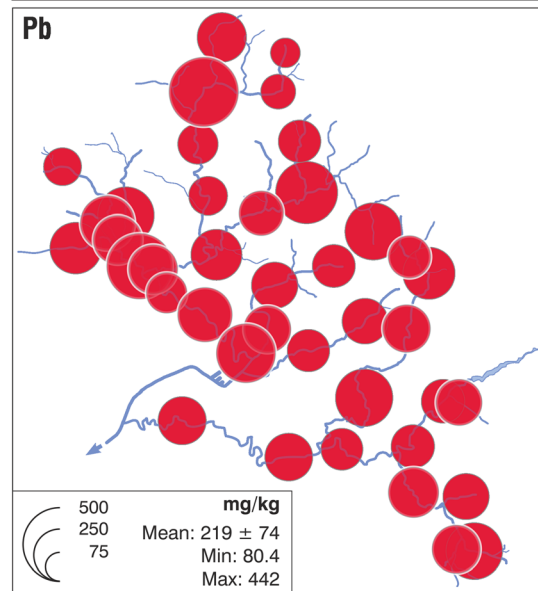
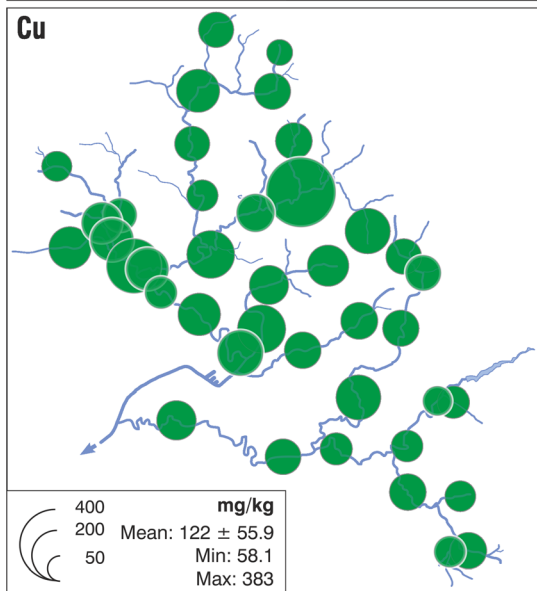
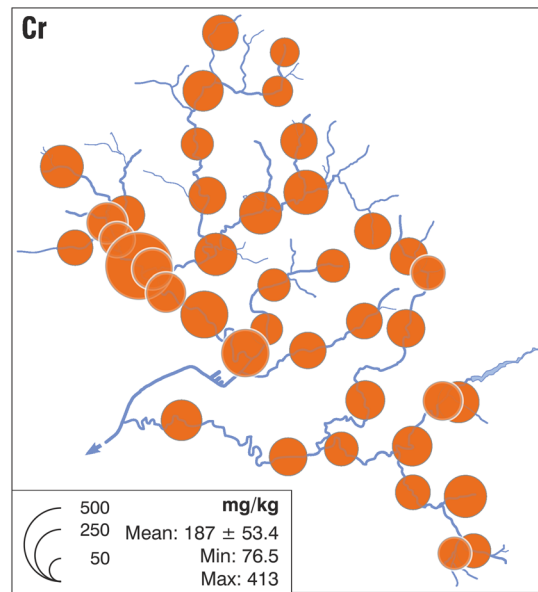
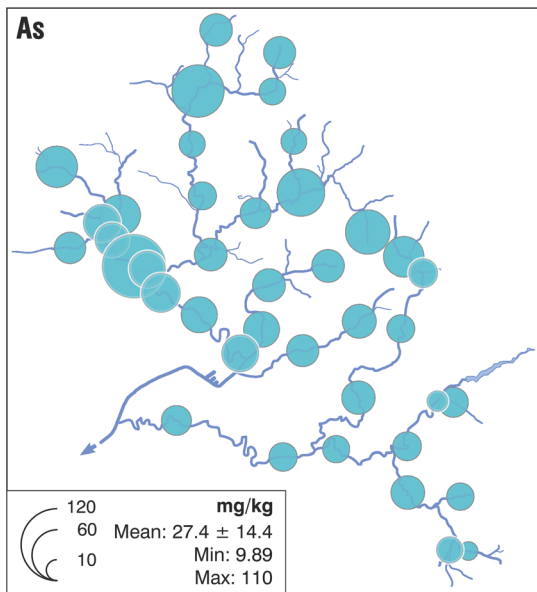
3 Results and discussion

3.1 Fine-grained bed sediment storage and associated metal(loid) concentrations

Figure 3 presents the metal(loid) concentrations of fine-grained bed sediments in the Mersey and Irwell catchments. There is limited spatial variability and no clear downstream trends. Standard deviations for individual metal(loid) concentrations range from 14.4 (As) to 171 (Zn). As, Cr and Cu present some localised hotspots: downstream of Bolton (As, Cr) and Rochdale (Cu). Pb and Zn show even less variability, with persistent high values across much of the two catchments. The Irk is most contaminated by Zn, with values exceeding 1000 mg kg^{-1} , whilst higher Pb concentrations are clustered around Bolton, Rochdale, and Rawtenstall on the upper Irwell.

The most contaminated reaches are in the Irk, Roch, Croal and Tame. These reaches contained numerous historic waste input sites and points of industry (Fig. 2; Coates 1862; Mersey and Irwell Joint Committee 1892), but are also associated with modern industrial and urban areas. Many of the headwater catchments also reveal high concentrations of the metal(loid)s, despite showing very little present-day urban and industrial development. The historical extent of industrialisation, however, reached close to the source of many of Manchester’s rivers (Fig. 2). In these areas, mills utilised the cleaner waters in industrial processes and the higher flow velocity of the steeper gradients to generate water power. Very few, if any,

Fig. 3 Total metal(loid) concentrations (mg kg^{-1}) for As, Cr, Cu, Pb and Zn in fine-grained bed sediments. Values are represented by *proportional circles*. Note that *scales* vary between elements. The standard deviation is provided alongside the mean



sections of the river network, therefore, can be considered pristine.

The absence of any distinctive downstream trends indicates the spatial complexity of contaminant stores and inputs across the Mersey and Irwell system. This suggests that *local* sources play a key role in elevating sediment-associated metal(loid) concentrations. These contaminant sources may be associated with particulate inputs, such as historically contaminated floodplain material, or direct inputs in solution where metal(-loid)s rapidly sorb onto sediment particles within the fluvial system. The nature of the input has implications for the downstream patterns of contaminant transfer. This complexity of sources, stores and fluxes is reflected in the spatial pattern observed in metal(loid) concentrations (Fig. 3). For catchments not heavily influenced by historic metal mining, with the exception of As, the reported concentrations rank amongst the highest urban (non-mining-affected) fluvial systems, as shown in Table 1. It is worth noting that the minimum values observed in the Mersey and Irwell catchments actually exceed, by an order of magnitude, those presented elsewhere,

demonstrating the environmental importance of geographically widespread contaminant release.

All of the metal(loid)s exceed the threshold effect levels (TELs) for the Canadian and draft UK guidelines across all of the sample sites, and the majority also exceed probable effect levels (PELs) (As 37 sites; Cr 28 sites; Cu 33 sites; Pb 39 sites; Zn 37 sites) (CCME 2002; Hudson-Edwards et al. 2008). The maximal concentrations of As, Cr, Cu and Zn exceed the Dutch intervention values (VROM 2011), and a limited number of sites fall below target levels: 1 site for Pb and 14 sites for both Cr and As, demonstrating the low number of sites that evidence ‘acceptable’ levels of contamination. None of the Cu or Zn concentrations fall below the guideline limits. The SQG values represent thresholds beyond which impacts upon ecology are likely to be observed. PELs refer to a higher degree of contamination than TELs and indicate concentrations that regularly result in adverse impacts. Thus, it is of environmental significance that a large majority of sites across the Mersey and Irwell network exceed these values.

Table 1 Comparison of total metal(loid) concentrations in fine-grained bed sediments in catchments around the world

Rivers	Metal(loid)s in bed sediments (mg kg ⁻¹)										References
	As		Cr		Cu		Pb		Zn		
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
Bradford Beck, UK	7.95	20.6	65.8	158	72.4	481	53.9	318	169	5500	Old et al. (2004)
Multiple (Flanders, Belgium)	1	61	1.8	7.5	2.2	189	4	364	14	2380	De Saedeleer et al. (2010)
Rhone, France	1.41	3.12	87	217	59	197	55	122	132	325	Santiago et al. (1994)
Gascogne, France	8.77	27.5	33.5	84.98	11.3	29.6	17	41.94	55.46	140.6	N’guessan et al. (2009)
Po, Italy					31.7	90.1	32	98.5	178	645	Farkas et al. (2007)
	7.4	19.5	148	414	44	102	14.3	63.8	139	398	Camusso et al. (2002)
Yesilirmak, Turkey					13.1	38.7	3.3	17.3	24.7	45.5	Mendil et al. (2010)
Tisza, Serbia			7	23	32	162	11	123	54	567	Sakan et al. (2009)
Kaskaskia, USA			9	328	6	55	10	225	29	528	Rhoads and Cahill (1999)
Manoa, USA					133	267	5	1080	164	512	Sutherland (2000)
Almendares, Cuba			84.4	210	71.6	421	39.3	189	86.1	708.8	Olivares-Rieumont et al. (2005)
Tigris, Iraq					12.15	52	17.5	30.5	19	79.5	Sabri et al. (1993)
Gomti, India			2.4	88.7	3.6	245			8.47	343.5	Singh et al. (1997)
Damodar, India			15	86.8	11.4	125			30.5	134.7	Singh et al. (1999)
Ganges, India			16	134	2	62			22	101	Subramanian et al. (1987)
Jhanli, India			28.5	467	28	69	8.4	30.5	32.2	288.1	Baruah et al. (1996)
Korotoa, Bangladesh	2.6	52	55	183	35	118	36	83			Islam et al. (2015)
Luan, China	2.08	12.9	28.7	153	6.47	179	8.65	38.29	21.09	25.66	Liu et al. (2009)
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
Range of above	1	61	1.8	467	2	481	3.3	1080	8.47	5500	
This study	9.89	110	76.5	413	53.1	383	80.4	442	282	1020	

Catchments impacted by mining were excluded based on the absence of major metal mining in Manchester

Estimations of channel bed sediment storage range from 70 g m^{-2} , at the Egerton site in the headwaters of the River Tonge, to 1240 g m^{-2} , in Rochdale on the River Roch, with a mean of 341 g m^{-2} . These values are broadly similar to those observed in other UK catchments such as the rivers Swale and Calder (Walling et al. 1998, 2003; Owens et al. 2001). The highest sediment storage values are associated with the lower reaches closer to the Manchester city centre, with high values also recorded around the urban centres of Bolton and Rochdale. Owens et al. (2001) identify this degree of channel bed sediment storage as a potentially significant short-term (>1 year) sink for contaminated sediments. Such sinks have the potential to release metal(loid) concentrations under changing environment conditions. Table 2 shows the relationship between the storage of fine-grained sediment and metal(-loid) concentrations across the Mersey and Irwell fluvial system. This indicates the significance of these environments and the potential for channel beds to act as a temporary store of contaminants. Anthropogenic sediment accumulation in the reaches of Irwell was a significant problem in the nineteenth century, and dredging operations were necessary (Douglas et al. 2002).

3.1.1 Particle size controls on sediment-associated metal(loid)s

None of the particle size fractions or the specific surface area (SSA) of the sediments demonstrate a significant relationship with any of the selected metal(loid)s. This is counter to many of the trends reported in the literature where a decrease in particle size is shown to increase contaminant loadings (Förstner and Salomons 1980; Horowitz and Elrick 1987; Walling and Woodward 1992; Borovec et al. 1993; Rhoads and Cahill 1999; Devesa-Rey et al. 2011). Our findings are consistent with those reported by Moore et al. (1989) and Bertin and Bourg (1995). These studies suggest alternative mechanisms—such as the input of contaminants by industrial processes that present a wider range of particle sizes (Moore et al. 1989) or stronger associations with other controls on sediment geochemistry (Bertin and Bourg 1995). In our case, the lack of a relationship could be due to a similarly complex interplay of factors and points to the presence of multiple sources across the catchments.

3.2 Bed sediment-associated metal(loid) enrichment

Calculated as the enrichment above pre-industrial values, the EFs demonstrate the magnitude of the anthropogenic contributions to bed sediment-associated metal(loid) concentrations since the onset of the industrial period. They highlight the role of urban and industrial sources to metal(loid) concentrations across both catchments. Figure 4 shows the EFs calculated for the selected metal(loid)s at each site. Lead shows the greatest

level of enrichment with severe ($\text{EF} = 10\text{--}25$) to extremely severe ($\text{EF} > 50$) enrichment observed across the catchments, including many headwater streams. This demonstrates very clearly the scale of transformation across the two catchments. Cu and Zn show severe enrichment, with extremely severe Zn enrichment evident in the Irk catchment. As and Cr are less heavily enriched, but still display moderate to very severe EFs.

3.3 Sequential extractions

The results of sequential extractions of As, Cr, Cu, Pb and Zn are presented in Fig. 5. The exchangeable fraction is relatively low amongst the metal(loid)s, up to 17.1% for As at Urmston. Proportions are generally higher for Cu, Pb and Zn, demonstrating a greater availability of these metals. The exchangeable fraction is not strongly associated with the pH of the river water, where pH does not vary considerably or fall below the pH threshold values ascertained by Peng et al. (2009): As 5–6; Cr not reported; Cu 4.5; Pb 4; Zn 6–6.5. However, pH is lower at Urmston (6.61) which may explain the higher proportion of exchangeable metals observed at this site. This could be a response to increased mobility through pH control. The exchangeable fraction represents the proportion of total metal(-loid) concentrations most readily available to biota and hence posing the greatest environmental risk (Salomons and Förstner 1980). Low percentages for all the metal(loid)s demonstrate a reduced risk for metal bioavailability at the 12 sites.

The second extract represents metal(loid)s bound to carbonates. Low proportions of this fraction (<10%) are observed for As, Cr and Cu, with a higher percentage of carbonate-bound Pb and Zn (up to 39%). This fraction represents the next highest potential for mobility, given the more aggressive extract used. Commonly applied in mobility factor calculations (Kabala and Singh 2001), this fraction contributes to the higher mobility potential of Pb and Zn. Coupled with higher total concentrations, this factor demonstrates the greater environmental significance of these metals with regard to their potential release from sediments and/or bioavailability.

Iron and Mn oxides represent the dominant fraction for As, Pb and Zn, whilst Cu and Cr show stronger associations with organic material. This indicates that, in the Mersey and Irwell bed sediments, these binding sites show a strong affinity for metal(loid)s. These fractions indicate a lower mobility but represent the potential for metal(loid) release under changing redox conditions.

The residual fraction constitutes a small proportion of Cu, Zn and Pb (3.5–27.2%) but a considerable proportion of As and Cr (9.6–64.1%). The proportion of non-residual fractions for the selected heavy metal(loid)s points to the influence of anthropogenic sources of contamination. Hence, the contribution of *natural* sources, namely lithogenic-derived material, is confined to <30% of Cu, Pb and Zn and to <60% of As and Cr.

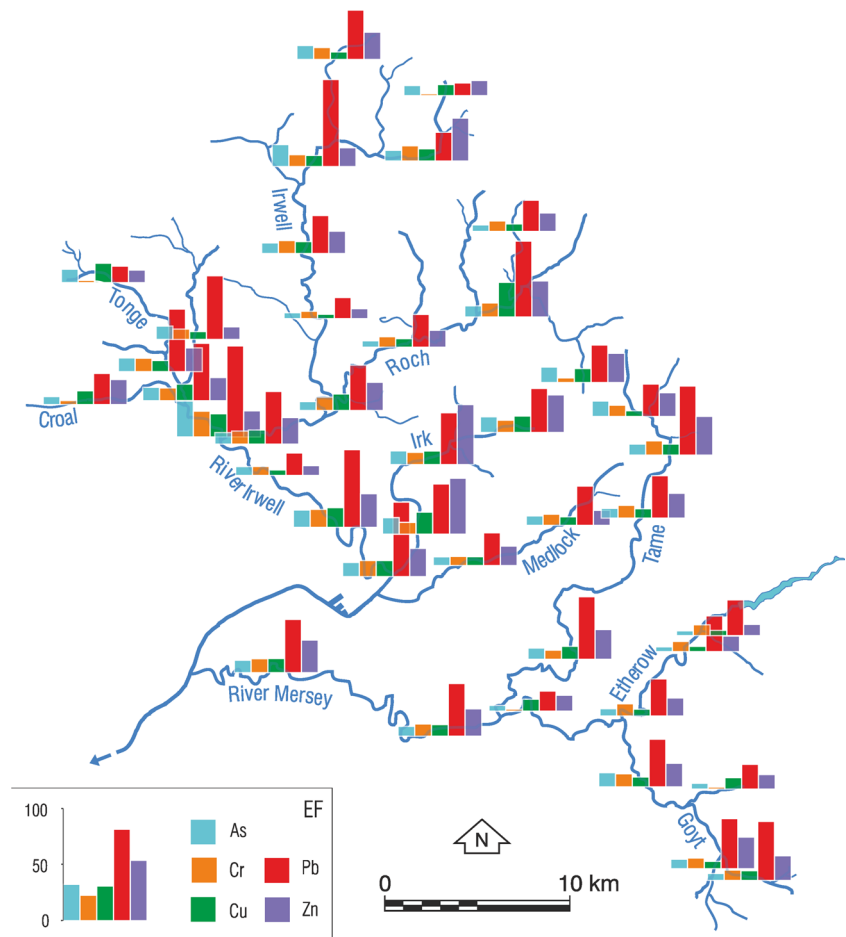
Table 2 Pearson's correlation coefficients for metal(loid)s and particle size characteristics for <63 μm sediments in the Mersey and Irwell catchments

	Mersey catchment <63 μm					Irwell catchment <63 μm					Mersey and Irwell system <63 μm				
	As	Cu	Cr	Pb	Zn	As	Cu	Cr	Pb	Zn	As	Cu	Cr	Pb	Zn
As															
Cu	0.357					0.363					0.740***				
Cr	0.545*	0.182				0.529**	0.610**				0.430***	0.474***			
Pb	0.287	0.042	0.727**			0.762***	0.643**	0.647**			0.623***	0.549***	0.638***		
Zn	0.252	-0.056	0.671*	0.839**		0.245	0.193	0.680***	0.225		0.039	-0.029	0.553***	0.305*	
% <63 μm	0.084	0.189	0.462	0.182	0.385	-0.294	-0.139	-0.092	-0.22	-0.152	-0.138	-0.170	0.119	-0.016	-0.028
% >63 μm	-0.084	-0.189	-0.462	-0.182	-0.385	0.232	0.23	0.177	0.252	0.202	0.154	0.208	0.016	0.070	0.050
SSA	-0.198	-0.332	0.027	0.017	0.047	0.207	-0.070	-0.112	0.104	0.167	0.001	-0.070	-0.112	0.104	0.167
% Coarse silt	0.077	0.182	0.406	0.147	0.315	-0.277	-0.124	-0.23	-0.142	-0.357	-0.140	-0.227	-0.153	-0.217	-0.269
% Medium silt	-0.007	0.203	0.329	0.147	0.364	-0.177	-0.124	-0.163	-0.216	-0.231	-0.076	-0.209	-0.184	-0.185	-0.008
% Fine silt	0.056	0.077	0.455	0.168	0.364	-0.132	-0.194	-0.14	-0.168	-0.128	-0.028	-0.170	-0.095	-0.074	0.078
% Clay	0.035	-0.07	0.385	0.063	0.259	-0.056	-0.286	-0.058	-0.063	-0.178	-0.046	-0.178	-0.070	-0.028	0.099
<63 μm storage	-0.308	-0.077	0.385	0.238	0.427	0.466*	0.194	0.283	0.519*	-0.138	-0.001	0.105	0.567***	0.317**	0.243
Total storage	0	0.063	0.385	0.378	0.231	0.464*	0.174	0.29	0.601**	-0.01	0.049	0.147	0.467***	0.324**	0.333**

Significant relationships are in italics

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$

Fig. 4 Enrichment factors (EFs) for selected bed sediment-associated metal(loid)s



This geological input may be even less for Cr, where residual values can also include unprocessed ore particles from chromate salt works (Evans 1991), which were in operation in the Irwell catchment between 1880 and 1968 (Breeze 1973).

3.4 Identification of potential heavy metal(loid) sources

Spatial associations are apparent between hotspots of contamination and high densities of key industry types and urban areas (Figs. 1, 2, and 3). The enrichment factor and metal(loid) partitioning results demonstrate the influence of anthropogenic sources on fine-grained bed sediment-associated concentrations. Such metal(loid)s have a wide variety of potential sources (Table 3).

Lead and Zn salts were historically utilised in the textile industry to soften and dye fabrics (Choudhury 2006). Cotton mills and dyeing and bleaching works were prominent across both catchments. We see a positive relationship between high metal(loid) concentrations and high densities of textile mills. This may also explain a proportion of the Cu and Cr enrichment observed across the catchment as both are components of dyeing and bleaching effluents (Ademoroti et al. 1992; West et al. 1999). Copper enrichment, known to be

historically linked to blue and green dyes, is highest in Rochdale, which was a hotspot for the dyeing industry.

Zinc is particularly elevated along the Irk and may be associated with former industrial waste tips in operation during the early twentieth century (Douglas et al. 2002). There are also a number of motorway passages over and in close proximity to the Irk, which may contribute Zn from the erosion of vehicle tyres (Charlesworth and Lees 1999). Such road runoff is also associated with high Cu and Pb loadings (Charlesworth and Lees 1999; Sutherland et al. 2012); however, these are not observed in similarly elevated values along the Irk. Moreover, there are additional locations in the catchments where the river is in close proximity to major road networks, but there are no marked increases in Zn concentrations above the mean recorded at these sites. However, the pattern of runoff and its associated metal(loid) concentrations is both spatially and temporally variable (Hoffman et al. 1985), which complicates efforts to identify a clear signature.

It is important to note that contaminant concentrations are likely to be linked to numerous modern inputs that are difficult to characterise. They can, for example, be episodic and difficult to identify at the spatial resolution applied here. This includes combined sewer overflows (CSOs) which release

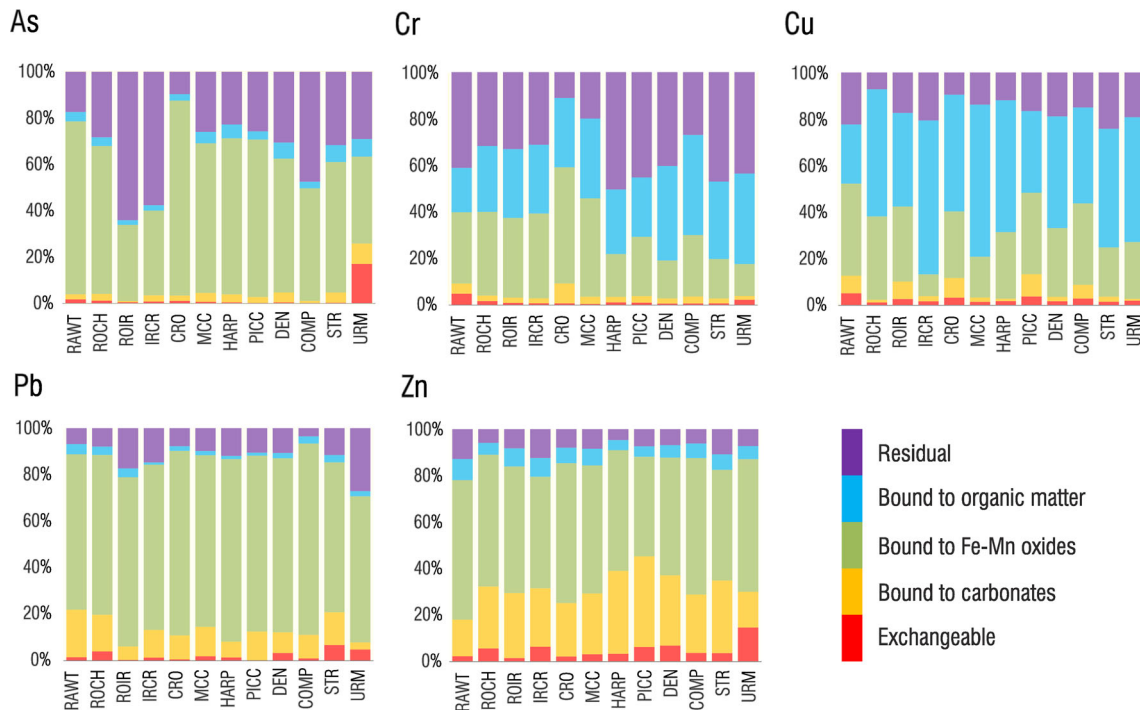


Fig. 5 Five-step sequential extractions of selected bed sediment-associated metal(loid)s. Site abbreviations are as follows: *RAWT* Rawtenstall (4), *ROCH* Rochdale (9), *ROIR* Roch-Irwell confluence (11), *IRCR* Irwell-Croal confluence (12), *CRO* Nob End SSSI (18),

MCC Manchester City Centre (21), *HARP* Harpurhey (24), *PICC* Piccadilly (26), *DEN* Denton (30), *COMP* Compstall (33), *STR* Strines (37), *URM* Urmston (40). Site locations are also demonstrated in Fig. 1, with corresponding site numbers provided above

sediments and wastewater during high precipitation events or at times of lower flow due to mismanagement. Without more detailed CSO data, it is difficult to quantify the contributions from such sources and their influence on modern river bed sediment contamination. In light of the available literature on urban contaminant inputs (Callender and Rice 2000; Sutherland 2000; Taylor and Owens 2009), it is likely that

modern sources do contribute to the observed metal(loid) concentrations across the two catchments.

It is important to recognise that the concentrations observed here exceed many of those recorded in other urbanised (non-mining affected) catchments (Table 1). Whilst sediment-associated metal(loid) concentrations show some spatial association with historical industry, typically the short residence

Table 3 Sources of metal(loid)s from urban and industrial sources

Industry/source	As	Cr	Cu	Pb	Zn	References
Textiles		✓	✓	✓	✓	Deepali and Gangwar (2010)
Coal mining	✓	✓	✓		✓	Querol et al. (1995); West et al. (1999)
Dyeing		✓	✓	✓	✓	Ademoroti et al. (1992); West et al. (1999)
Bleaching					✓	Ademoroti et al. (1992)
Tanning		✓		✓	✓	Möller et al. (2005); West et al. (1999)
Printing		✓	✓		✓	West et al. (1999); Alloway and Ayres (1997)
Paper	✓	✓	✓	✓	✓	Calace et al. (2005); West et al. (1999)
Brick			✓	✓		West et al. (1999)
Wood preservatives	✓	✓	✓		✓	West et al. (1999)
Engineering works			✓	✓	✓	West et al. (1999)
Road deposited sediment (RDS)			✓	✓	✓	Charlesworth and Lees (1999)
Pesticide use	✓		✓	✓	✓	West et al. (1999)
Sewage		✓	✓	✓	✓	West et al. (1999)

time of fine-grained sediment within river channels makes it unlikely that large volumes of contaminated sediments have been stored on channel beds since the industrial period. It is more likely that modern inputs of historically contaminated sediments play a role. Reworking of alluvial material is one possible mechanism (Macklin et al. 2006). Much evidence refers to heaps of physical waste dumped along river banks as it was disposed of directly into the channel (Engels 1944; Coates 1862). The intention was for flood events to cleanse the rivers of this waste. Coates (1862, p.6) described this widespread practice:

“Nevertheless a habit prevails on the banks of all these streams of depositing in the bed of them, ashes, cinders and refuse [...] All this solid matter is carried down by successive floods [...] more than 75,000 tons of cinders are now annually cast into the rivers”.

These considerable volumes of material will have contributed to the river's load, and a significant proportion is likely to have been deposited a short distance downstream as overbank deposition. These environments form a longer-term storage and have the potential to contribute historically contaminated sediment during modern-day flood events, as has been reported for floodplains downstream of former metal mining areas (e.g. Wolfenden and Lewin 1977; Hudson-Edwards et al. 1999; Resongles et al. 2014). The widespread practice of riparian dumping of physical waste across Manchester during the industrial period is likely to have established a complex network of contaminated sediment stores, which reflect the changing industrial and urban environments both locally and upstream. Modification of the network such as channelisation, flood defence and meander removal will have altered the connectivity of these sediment stores, potentially contributing to the highly varied spatial pattern of metal(loid) concentrations observed.

In the Pennine Uplands (Fig. 1), organic-rich soils and peats surrounding Manchester are contaminated with atmospherically deposited heavy metals originating from the industrial period (Rothwell et al. 2010). Erosion of contaminated upland peats can release historical heavy metals into the contemporary headwater river system (Rothwell et al. 2005). This process may explain the elevated level of heavy metals in the Mersey and Irwell headwaters (Fig. 3), but further work is required to quantify this contribution.

3.4.1 Dissolved metal(loid) concentrations

Dissolved metal(loid) concentrations for As, Cr, Cu, Pb and Zn all fall below the threshold values set by the UK Environment Agency (EA 2011). There have been significant improvements in water quality over the past 40 years. Dissolved metal(loid) concentrations do not show a

significant relationship with bed sediment values, suggesting that modern contaminant inputs are *not* the dominant control on the spatial distribution of sediment-associated contamination. Further work is required to better understand the sources of metal(loid)s in the aquatic phase, investigating the role of modern contaminant inputs and sorption and precipitation processes between sediment and water.

3.4.2 Principal component analysis

Table 4 presents the results of PCA of bed sediment-associated metal(loid) concentrations. There are four factors with eigenvalues >1. Factor I represents the lithological contribution with high values obtained for Al, Ti, Ga, Rb, Si and V. These represent geologically derived elements and concentrations (Manta et al. 2002). Calculated scores for this factor are highest for the least contaminated sites, including some headwater reaches and the Etherow subcatchment. It represents the contribution of elements from natural sources and is additional justification for the use of Rb in EF calculations.

Factor II identifies a key anthropogenic component, dominated by Pb, Cu, Sn, As, Cr and Zn. These are common anthropogenically enriched metal(loid)s and have both modern and historical sources (Table 3). Within the Irwell and Mersey catchments, it is not possible to establish the timing of contaminant input from the use of factor analysis alone. In this highly urbanised region, it is likely that contamination derives from a number of modern sources. However, given the scale of past industrialisation and anecdotal evidence of

Table 4 Principal component analysis of bed sediment-associated metal(loid)s

	Factor I	Factor II	Factor III	Factor IV
Pb	0.020	<i>0.867</i>	-0.155	0.199
Cr	0.038	<i>0.539</i>	-0.108	<i>0.695</i>
Cu	-0.108	<i>0.813</i>	-0.017	-0.005
Zn	-0.336	<i>0.534</i>	0.157	-0.522
As	-0.009	<i>0.656</i>	0.177	<i>0.616</i>
Rb	<i>0.822</i>	0.045	-0.405	0.170
Fe	-0.103	0.060	<i>0.904</i>	0.167
Ni	0.048	0.248	<i>0.543</i>	-0.505
Mn	-0.286	-0.167	<i>0.880</i>	-0.123
Sn	0.073	<i>0.776</i>	-0.061	-0.028
Zr	-0.509	0.269	-0.453	0.175
Al	<i>0.936</i>	0.021	-0.139	0.144
Si	<i>0.520</i>	0.189	-0.617	0.144
Ti	<i>0.861</i>	0.118	-0.404	0.111
V	<i>0.419</i>	0.056	-0.005	<i>0.788</i>
Ga	<i>0.857</i>	-0.210	0.112	0.115
% Var	24.75	20.53	18.30	13.89

Factor loadings >0.5 are in italics

historic, very poor river quality, it is very likely that some of this contamination has a longer-term legacy component.

Factor III represents a third group dominated by Fe, Mn and Ni. Analysis of the spatial distribution of calculated scores for factor III identifies the Irwell Springs and Bacup sites (Fig. 1: sites 1 and 2 respectively), in addition to a number of sites in the Tonge and Croal network near Bolton. Irwell Springs has been associated with significant mine water pollution from a disused iron mine. In 2008, for example, a major flood event overwhelmed the mine water treatment plant leading to widespread contamination downstream. The release of iron-rich pollution from abandoned coal mines in Bolton has also been documented (LEAP 2000). This principal component is therefore likely to relate to the contribution of metal-enriched mine water drainage to bed sediment-associated metal(loid)s.

Factor IV identifies an additional anthropogenically-influenced source group, dominated by V, Cr and As. Spatial associations demonstrate a very high calculated score for the Nob End SSSI site (a designated Site of Specific Scientific Interest) on the River Croal (Fig. 1: site 18). This site is linked to well-documented chromium pollution from the leaching of capped waste heaps of a former chromate salt works (Breeze 1973; West et al. 1999). The high value of V within this factor probably relates to the presence of vanadium oxide in chromite ore, which was subsequently released in the smelting process that took place at the plant. The representation of vanadium in both factors I and IV suggests that both lithogenic and anthropogenic sources contribute to the values recorded in the bed sediments. Whilst Fe, Al, Si and Mg are also present in chromite, the much reduced concentration of V of lithogenic origin points to an enhanced proportion derived from the industrial waste.

The high value for As seen in this factor is likely to be associated with the very high As values also recorded at the Nob End SSSI site. This site, at the confluence of the Croal and Irwell, was a former Leblanc waste tip. Galligu, the waste by-product of the Leblanc process, is associated with very high values of As (up to 300 mg kg⁻¹) in contaminated soils (Johnson 2003). This exceeds all values obtained from other industrial processes observed within the catchments, which explains the reduced values for other Galligu contaminants (Cr, Pb, Cu, Ni, Zn) within the factor. They are relatively low compared to other industrial processes observed across the region, suggesting a strong diluting influence.

The PCA factors III and IV represent potential historic sources that have a modern input. This may involve leaching from historical tailings and capped former waste heaps following precipitation events or groundwater seepage. This is one example of the influence of historical industry upon present-day contaminant concentrations at key metal(loid) hotspots across the catchments.

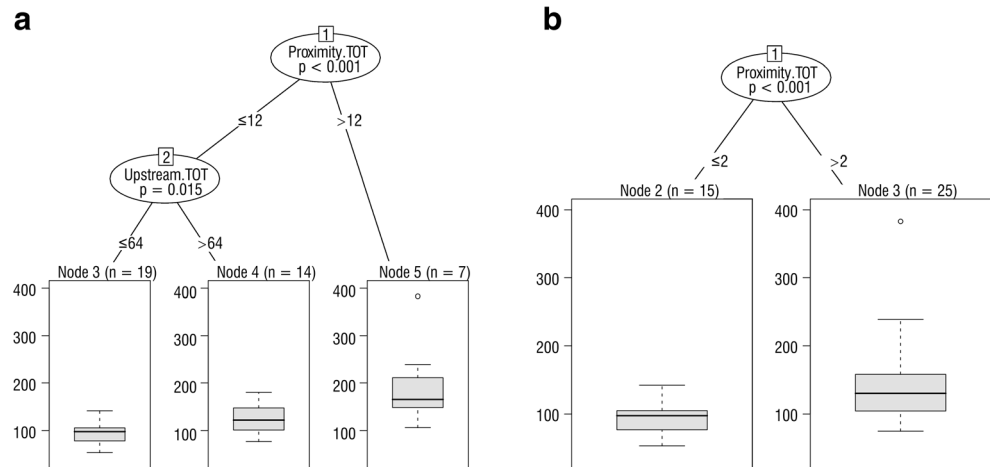
3.4.3 Conditional inference trees

Conditional inference trees were produced for each of the selected metal(loid)s using each of the three datasets of historical industry and potential modern contaminant sources. The nature of the data (in some cases presence/absence of data irrespective of contaminant release) and the extent of blank values (introduced by the temporal and spatial patterns of many industry types across Manchester) limited the efficacy of this analysis. The only outputs achieved were for Cu, representing total industry, for both the OS and 1892 data (Fig. 6). However, the results did provide some valuable insight into historical contributions to modern river bed sediments and the complexity of contamination in Manchester's fluvial system.

For both datasets, proximity exerts the greatest predictor influence, shown in the first hierarchical split. In the OS data (Fig. 6a), higher densities of local industry (>12 sites per 1 km upstream radius) are associated with higher Cu values (node 5). In the second split, the total number of industry points upstream presents mid-range Cu values for counts >64 (node 4), and the lowest Cu concentrations are associated with fewer points of industry upstream (≤64; node 3). In the 1892 data (Fig. 6b), there are only two terminal nodes as a result of a single split, with higher densities of local industry associated with higher Cu concentrations (node 3). In the absence of information regarding the nature and scale of contaminant release, it is not possible to draw direct conclusions regarding the role of particular industries. However, about 40% of the proximal sites in the OS data are associated with textile and textile-processing industries, whilst in the 1892 data approximately 36% are associated with printing and dyeing sources and 35% with woollen industry sources. This suggests that these industry types may contribute to modern bed sediment-associated Cu concentrations, and this is further supported by Table 3 which shows the release of Cu by these industries. Whilst the 'total industry' variable for the OS data incorporates decadal information, the 1892 records represent a useful snapshot in time. The output for Cu provided by these data indicates that historical industry probably does play some role in influencing modern bed sediment-associated Cu concentrations.

For all other selected metal(loid)s, no valid output was obtained using conditional inference trees. This probably reflects the nature of the available data and the great variety of potential sources in both modern and historical contexts. However, indicators of modern contaminant sources also fail to reveal clear associations and provide no significant predictor value or relationship across all of the selected contaminants. Hence, it is unlikely that these modern sources play a significant role in bed sediment metal(loid) concentrations. In other words, individual variables such as land use and proximity to road networks do not strongly control observed

Fig. 6 Conditional inference trees for bed sediment-associated Cubased on **a** decadal OS data and **b** 1892 data



concentrations. Further work is required to interrogate archival records of industry output, employee records and the size and lifespan of mills to augment current datasets with additional information on the scale of potential inputs. Further sources of modern metal(loid) input across the two catchments must also be identified and quantified to establish firmer conclusions on the extent of their influence. This is not straightforward as episodic contaminant inputs can complicate effort to quantify modern sources. Progress in this area will help in establishing more robust associations between contaminants and their modern and historical sources.

The results demonstrated here reflect the complex mosaic of point and diffuse inputs from both modern and historical contamination sources across the fluvial network. Despite recent efforts to significantly reduce modern inputs, it is probable that road-deposited sediments (RDS), municipal and industrial effluents, urban runoff and contributions from CSOs will contribute a range of heavy metal(loid)s across the catchments. Given the varying temporal scale of these inputs and their complex spatial distribution, however, it is difficult to clearly define dominant or discrete sources of fine-grained bed sediment-associated contamination. The reworking of contaminated floodplain sediments is a diffuse historical source (Macklin et al. 2006), whilst capped industrial sites constitute point, albeit in some cases episodic, sources through release of metal(loid)s in leachates or tailings collapses. Modern and historical sources are likely to be distributed widely across all the catchments, whilst the sediments and sorbed contaminants they input become incorporated into a load that is mobilised, stored and reworked across the fluvial environments of Manchester. Fine-grained river sediments represent complex environmental mixtures incorporating material and sorbed contaminants from multiple upstream sources (Walling and Woodward 1995). This hampers any attempt to derive statistically significant controlling factors, particularly in noisy, highly urbanised and formerly industrialised catchments with strong spatial heterogeneity

such as the Mersey and Irwell system. Nonetheless, the approaches presented here have yielded valuable evidence for the legacy of historical contamination within the modern river bed sediments and have raised important new questions.

4 Conclusions

This study presents the first baseline survey of fine-grained bed sediment quality in the Irwell and Mersey catchments. The spatial pattern of metal(loid) concentrations across the system is complex. Sediment-associated concentrations exceed guideline values, highlighting the potential for impacts on ecology and aquatic health. The mobility of the contaminants is generally low, and dissolved concentrations fall well below threshold criteria. Whilst their bioavailability is limited, much of the sediment-associated metal(loid)s are acid-soluble or bound to Fe/Mn oxides or organic matter, and so there is potential for release under changing pH or redox conditions. Enrichment factors, PCA and sequential extractions reveal a significant anthropogenic component to these sediment-associated metal(loid) loadings.

Through the use of multivariate and data mining techniques, this study has examined the extent to which the sources of bed sediment-associated contamination can be identified. Given the rapid and extensive industrialisation observed historically in the Manchester region, and the strong links between this development and the river network, it is very likely that historical contamination plays a role. Statistical analysis highlights inputs from former industrial sites, namely through leaching of metal(loid)s from cappings or release due to failures in remediation strategies. The conditional inference tree models indicate a potential historical signature within Cu concentrations across the catchments, which is linked to the proximity to past industrial sites. This influence is likely to result from the reworking of contaminated floodplains, reintroducing historically contaminated

sediments to the modern channel network. Potential modern inputs to elevated metal(loid) concentrations were not directly identified using these techniques. However, the spatial and temporal patterns of such sources, including from modern municipal or industrial effluents or urban environments, may explain this outcome. These releases are likely to be smaller in magnitude but additive, complicating source identification and quantification. Across the Manchester river network, sediment contamination is a product of the input from sewer networks, urban runoff, modern industrial effluents and potentially discrete contamination events, in addition to the reworking of historical contaminants from multiple sediment stores and former industrial sites. Further work is required to elucidate more fully the origin, storage, flux, and fate of metal(loid)s and other forms of contaminant in this dynamic urban environment.

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