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Spatio-temporal analysis of the potential toxicological burden of pollutants in a fluvial system, the River Irwell, Manchester, through anthropogenic activities (present and historical) and natural mechanisms.

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Abstract

Anthropogenic addition of trace metals (lead, cadmium, copper, zinc and nickel), metalloids (arsenic) and common polluting ions (phosphate, nitrate, sodium and chlorine) to rivers degrades water quality and affects human, animal and plant health. The River Irwell, Greater Manchester, which has a long history of industrial pollution, was sampled along a rural-urban transect during summer (July) and autumn (November) to assess water quality of the river. Analysis of trace metals, metalloids and ions, via ICP-OES and IC, found concentrations of cadmium, copper, lead, zinc, phosphate and sodium exceeding environmental quality standards. Water quality has improved since the 1980s, but concentrations of copper, zinc and phosphate remain above guidelines and require urgent remediation. Several potential pollution sources were identified, including wastewater treatment plants, agricultural run-off and urban centres.

Keywords

Trace metals; Metalloids; Ions; Pollution; Water security; Toxicity

Introduction

Water security

Water is an essential, finite, natural resource fundamental for producing food, sustaining life and in industrial processes (Liu *et al.*, 2016; Lianos and Pseiridis, 2016; Westall and Brack, 2018). Water security and availability are negatively affected by many factors, including industrialisation, urbanisation, population growth, groundwater extraction and socioeconomic developments, affecting up to five billion people globally (Lianos and Pseiridis, 2016; Rodell *et al.*, 2018; Javeline *et al.*, 2019; Liu *et al.*, 2016; Mhlongo *et al.*, 2018; Westall and Brack, 2018). These stressors can lead to social unrest, deteriorating human and ecosystem health and adverse impacts on the biodiversity and health of aquatic environments (Rodell *et al.*, 2018; Javeline *et al.*, 2019 and Liu *et al.*, 2016).

River water quality issues

Rivers provide economic and ecosystem services as a source of drinking water, a transportation route (Manchester Ship Canal and Elbe River waterway) and a valuable habitat (Prambudy *et al.*, 2019; Berger *et al.*, 2017; Bínová, 2014; Dixit and Witcomb, 1983). Maintaining optimum river water parameters through constant monitoring is crucial in protecting the natural environment and people's livelihoods (Reddy *et al.*, 2015; Martin, 2019; Wang and Yang, 2016). High levels of pollutants can lead to eutrophication and ecological loss, damage to human health and reduced food production (Reddy *et al.*, 2015; Martin, 2019 and Wang and Yang, 2016).

Industrialisation has often been the focus of pollution monitoring and remediation, but in recent years this spotlight has shifted towards agricultural practices, predominantly in high income countries (Wang and Yang, 2016; Evans *et al.*, 2019).

Intensified agricultural practices are increasing pressures on river water quality and water resources globally through the release of pollutants including nitrates (NO_3^-, from synthetic nitrogen fertilisers) and phosphates (PO_4^{3-}, from phosphate fertilisers). Wastewaters can also exacerbate pollutant loads in fluvial systems (Evans *et al.*, 2019; Vrzel *et al.*, 2016; Martin, 2019; Wang *et al.*, 2017; Reddy *et al.*, 2015). High concentrations of NO_3^- can lead to methaemoglobinaemia in humans; high concentrations of PO_4^{3-} and NO_3^- lead to eutrophication in waterways (Gupta *et al.*, 2000; Hashim *et al.*, 2019; Martin, 2019; Gorski *et al.*, 2019; Liu *et al.*, 2017; Li *et al.*, 2017). High sodium

(Na$^+$) and chloride (Cl$^-$) concentrations harm ecosystems by generating osmotic pressure on aquatic inhabitants and affect crop growth (Mainstone and Parr, 2002; Kelly *et al.*, 2019; Khanoranga and Khalid, 2019).

Cadmium (Cd) pollution often comes from mining activity, metal and cement production, batteries and fertiliser, and can enter the body via contaminated water consumption. High bodily Cd levels are linked to kidney damage, bone fractures, cell necrosis, lung function impairment and liver failure (Health Canada, 2019; Rahman and Singh, 2019; Veeshal *et al.*, 2019; Ryan and Shawcross, 2019).

Past mining activities and collieries can be linked to high concentrations of Zn and Cu in fluvial systems (Wright *et al.*, 2018; Gozzard *et al.*, 2011). Copper (Cu) in water supplies can cause short-term gastrointestinal effects and long-term liver and kidney effects (Health Canada, 2019; Morris *et al.*, 2019). Cu-rich waters are also toxic to aquatic life (Morris *et al.*, 2019). High zinc (Zn) levels cause nausea, vomiting, fatigue and epigastric pain (Fosmire, 1990).

Lead (Pb) in water supplies causes haematological effects, affects infant development (behavioural, learning, growth and hearing problems, as well as lowering IQ), affects adults (kidney problems, cardiovascular issues and fertility) and pregnant women (premature births and fetus growth) (Bain, 2014; United States Environmental Protection Agency, 2020). Characteristics of the urban landscape are key in accounting for high Pb concentrations, as well as atmospheric deposition to a lesser extent (Dong *et al.*, 2014; Petrucci *et al.*, 2014; Robertson and Taylor, 2007).

The biological oxygen demand (BOD) is a key characteristic in measuring the degree of organic pollution in rivers, that can result from municipal, industrial and agricultural discharge (Prambudy *et al.*, 2019). Higher amounts of organic matter within the river leads to an increase in decomposition by microorganisms under aerobic conditions, depleting dissolved oxygen (DO) levels and therefore leading to high BOD measurements (United States Geological Survey, 2020).

Historical pollution in Greater Manchester
Technical advancements during the latter half of the 18th century led to rapid industrialisation in and around Manchester, at a time when pollution control was not considered an important issue. Rivers flowing through Greater Manchester were used to dispose of industrial and domestic waste, particularly chemical waste from the textile dying industry (Hurley *et al.*, 2017; Douglas *et al.*, 2002). Although the industrial prowess of Manchester was

centred around its textile industries, Manchester was also home to several different industrial practices from coal mines, engineering works and chemical plants to tanneries, sawmills and paper and printing works (Figure 1; Hurley *et al.*, 2017). Industries that were active during the industrial revolution, such as textiles and textile processing, printing, chemicals and manufacturing, could all still have effects on the concentration of trace metals affecting the water quality.

The River Irwell
The River Irwell flows from the Pennine Moors to the Manchester ship canal, where the river is channelized (Dixit and Witcomb, 1983). The river is 62 km long and has a catchment area of 793 km^2 including Carboniferous Millstone Grit, Coal Measures, Permian Sandstone and Triassic Sandstone (Dixit and Witcomb, 1983; Hurley *et al.*, 2017). There are many sources of pollutants, including former industrial sites as well as modern inputs. A survey in 1983 found Cu, Pb and Zn to be the dominant pollutants in the substrates and invertebrates of the Irwell (Dixit and Witcomb, 1983). Salmon have not been found in the waters of the Irwell since the 1850s (Ikedashi *et al.*, 2012).

Aims
This study focuses on aspects of water security risks related to pollution, industrialisation and urbanisation and assesses the present water quality of the River Irwell, one of the largest rivers flowing through Greater Manchester, by comparing trace metal/metalloid and ionic concentrations to the thresholds above which toxicological effects increase (Hoekstra *et al.*, 2018). The study analyses the spatial and temporal differences in trace metal, metalloid and ionic concentrations by analysing samples taken in different seasons and numerous sites along the Irwell transect, which will help analyse seasonal influences (temporal) and the influence of different land-uses (spatial), and to link each trace metal, metalloid, or ionic concentration, dependent on threshold exceedance, to a potential source (anthropogenic or natural). Results are compared to historical data from the Irwell to test for improvements in water quality (Dixit and Witcomb, 1983).

Methodology
Sample collection
Google Earth Pro and a previous study carried out by Hurley *et al.* (2017), were used to identify existing and historic pollution sources and the land-use change from rural to urban (Figure 1; Al-Omari *et al.*, 2019; Hurley *et al.*, 2017). Water samples were obtained from 7 sites (S1 – S7;

Figure 1, Supplementary Table 1, Supplementary Data File) during the summer season and autumn season. Sites 1 and 4 were located downstream of wastewater treatment plants (WWTPs), sites 2 and 5 were located upstream of an industrial complex and a WWTP, respectively, with sites 6 and 7 located within an urban landscape. At each site two water samples were collected: a one-litre unfiltered bottle and 30 ml filtered *in situ* using a 0.2 μm syringe filter.
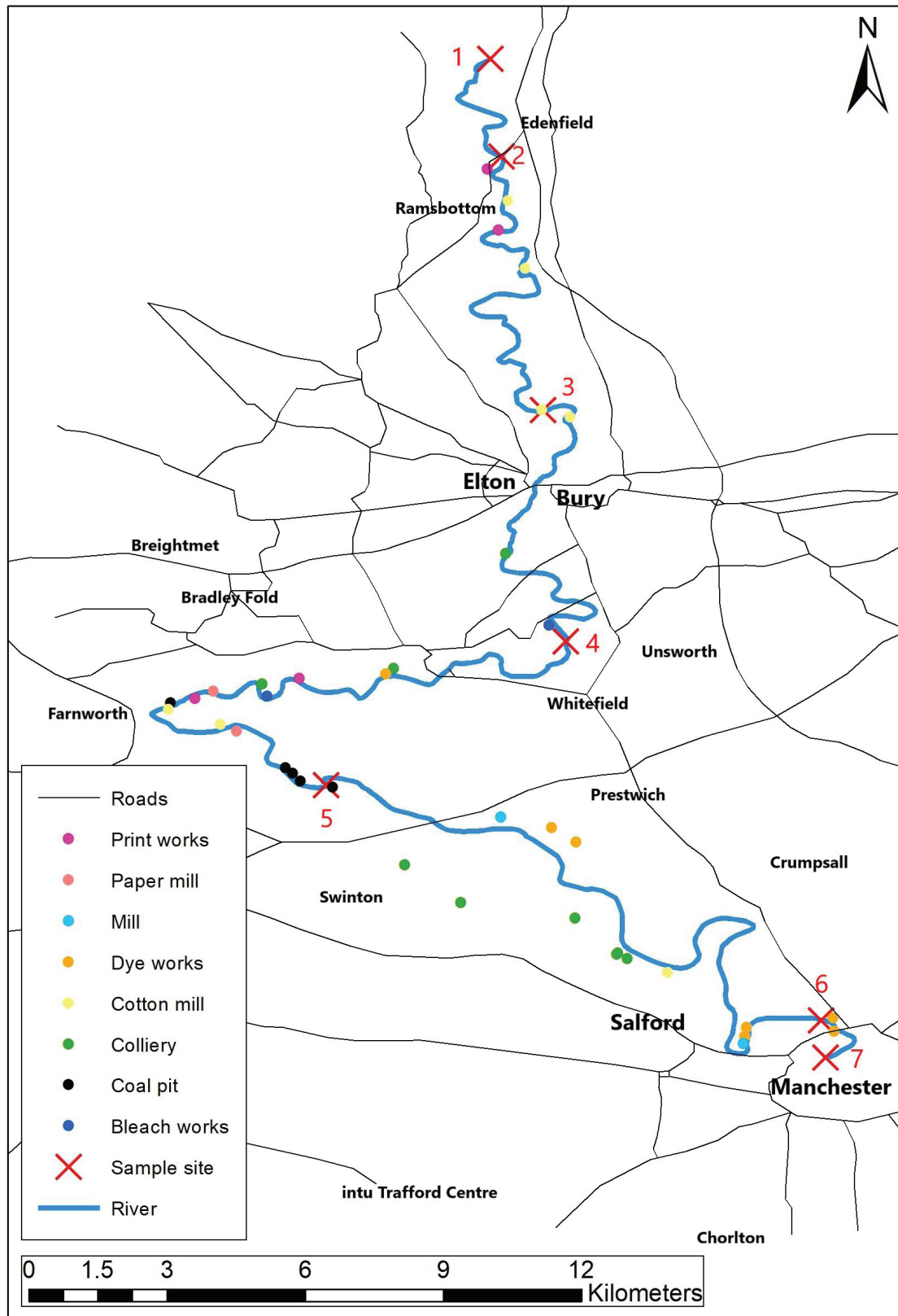

Figure 1: Water sample locations taken along the stretch of the Irwell, Manchester, during the summer and autumn seasons and locations of historic industrial presence in and around Manchester (1850). Data provided by Ordnance Survey archives via old-maps.co.uk (2020) and the Northern Mine Research Society (2020).

Biological Oxygen Demand

The initial dissolved oxygen (DO) reading was taken immediately after the sample was vigorously shaken, to allow for oxygen to be readily available within the sample, by using a Mettler Toledo dissolved oxygen meter. The sample was then filled to the top and a stopper was securely and tightly fixed in place; then the sample was left to incubate in a dark cupboard for 5 days. After five days, secondary DO readings, DO^1, were taken immediately after retrieving the samples.

Equation 1 was used to calculate the biological oxygen demand:

Eq 1: $BOD = DO - DO^1$

Where DO is the initial dissolved oxygen reading and DO^1 is the dissolved oxygen reading after the incubation period.

Trace metals and metalloids in water samples
Automated piston pipettes were used to add 9.5 ml of the filtrate (0.2 μm syringe filter) into 14 ml tubes. A dispensing bottle was utilised to add 0.5 ml of nitric acid (HNO_3) into the 14 ml tubes (Hurley *et al.*, 2017). Samples obtained during the autumn and summer were analysed using a Thermo Scientific iCAP6300 Duo ICP-OES spectrometer and dissolved trace metal and metalloid concentrations were compared against the guidelines provided in Supplementary Table 2.

Trace metals (Cd, Pb, Cu, Zn) were targeted due to their adverse effects on human health. High concentrations of Cd can cause cell necrosis, kidney damage, lung function impairment, liver failure and bone fracturing, with Zn and Cu causing epigastric pain and effecting the liver and kidneys (Fosmire, 1990; Health Canada, 2019; Morris *et al.*, 2019; Rahman and Singh, 2019; Ryan and Shawcross, 2019; Veeshal *et al.*, 2019). High concentrations of Pb have haematological affects and can affect a wide demographic range, from infants to adults and pregnant women (Bain, 2014; Environmental Protection Agency, 2020).

Cations and anions in water samples
Automated piston pipettes were utilised to add 1 ml of filtrate, filtered using a 0.2 μm syringe filter, into small vials and analysed using a Thermo Scientific ICS5000 ion chromatograph. Supplementary Table 3 highlights the guideline values for ionic concentrations in surface waters.

Nitrate, phosphate, sodium and chloride ions were targeted due to their adverse effects on the natural environment at high concentrations. High concentrations of Na^+ and Cl^- can exert osmotic pressure on aquatic life and affect crops, with NO_3^- and PO_4^{3-} leading to eutrophication and methaemoglobinaemia (Gupta *et al.*, 2000; Gorski *et al.*, 2019; Hashim *et al.*, 2019; Kelly *et al.*, 2019; Khanoranga and Khalid, 2019; Liu *et al.*, 2017; Li *et al.*, 2017; Mainstone and Parr, 2002; Martin, 2019).
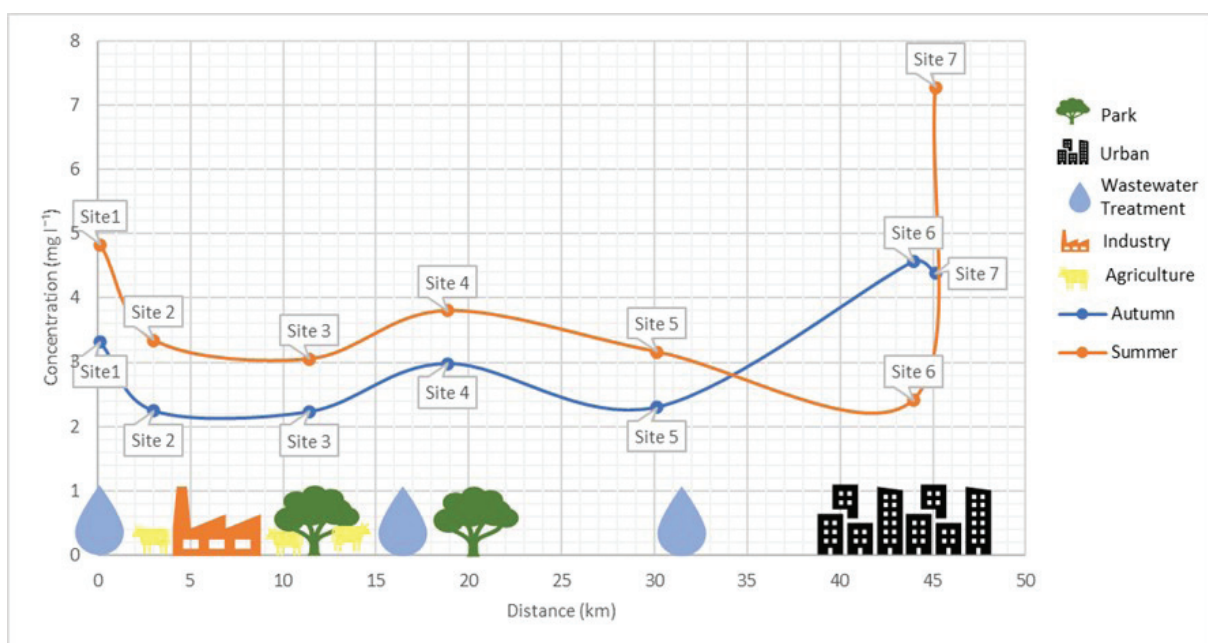

Figure 2: BOD (mg l^{-1}) values from the Irwell, Manchester, showing land use changes along the course of the river.

The sodium absorption ratio (SAR) was calculated using equation 2 to measure the quality of the water for irrigation purposes (Khanoranga and Khalid, 2019).

Eq 2: $$SAR = \frac{Na^+}{\sqrt{\dfrac{Ca^{2+} + Mg^{2+}}{2}}}$$

Where, Na^+, Ca^{2+} and Mg^{2+} are the concentrations of sodium, calcium, and magnesium, respectively.

Equation 3 was used to determine the hardness of the water samples, in mg l^{-1} of $CaCO_3$ (Boyd *et al.*, 2016). This was to allow for the appropriate class value, presented in Supplementary Table 2, to be applied for Cd concentrations.

Eq 3: Hardness = $(Ca^{2+} \times 2.5) + (Mg^{2+} \times 4.12)$

Where, Ca^{2+} is the concentration of calcium, Mg^{2+} is the concentration of magnesium.

Results

Spatio-temporal variation of the BOD in water samples

BOD values ranged from 2.23 mg l^{-1} (Site 3, autumn) to 7.28 mg l^{-1} (Site 7, summer; Figure 2; Supplementary Table 4). High values at sites 1, 4, 6 and 7 are likely due to their location downstream of WWTPs. Sites immediately upstream of these WWTPs (sites 2, 3 and 5) have lower concentrations. BOD concentrations are generally higher during the summer; however, concentrations in sites 6 and 7 in the autumn are higher than in site 6 during the summer.

Trace metal concentrations in water samples

Heavy metal concentrations are reported in Supplementary Table 5. Trace metal and metalloid concentrations followed the order Zn>As>Cu>Pb>Ni>Cd in all locations except sites 4, 6 and 7, where the order was Zn>Pb>As>Cu>Ni>Cd, Zn>As>Cu=Ni>Pb>Cd and Zn>As>Ni>Cu>Pb>Cd, respectively in summer. Autumn concentrations followed the order Zn>Cu>Ni>As>Cd>Pb at sites 1, 2 and 6 and Zn>Cu>Ni>Cd>As=Pb at sites 3, 4 and 7. The order Zn>Cu>Ni>Cd>As>Pb is observed in site 5. Concentrations of As, Pb and Zn were higher during the summer. Concentrations of Cd, Cu and Ni were generally higher during the autumn (Figure 3).

Trace metal and metalloid concentrations were compared to environmental quality standard (EQS) values (Figure 4, Supplementary Tables 2, 6). Following water hardness calculations (equation 3) class 3 of the Cd EQS was applied at site 3, and class 4 was applied at sites 1, 2, 4, 5, 6 and 7 for water samples collected in the summer. Class 3 was applied at sites 1, 2 and 3 and class 4 was applied to sites 4, 5, 6 and 7 for water samples collected during the autumn.

Concentrations of Cd breach the EQS at all sites and by more than 100% at sites 2 and 3 during the autumn. Concentrations of Cu breach the EQS by more than 100% at all sites during summer and autumn. Concentrations of Pb breach EQS at all sites and by more than 100% at site 4 and 7 during summer exclusively. Trace metal and metalloid concentrations breached the EQS in the summer season more frequently than in the autumn season (Supplementary
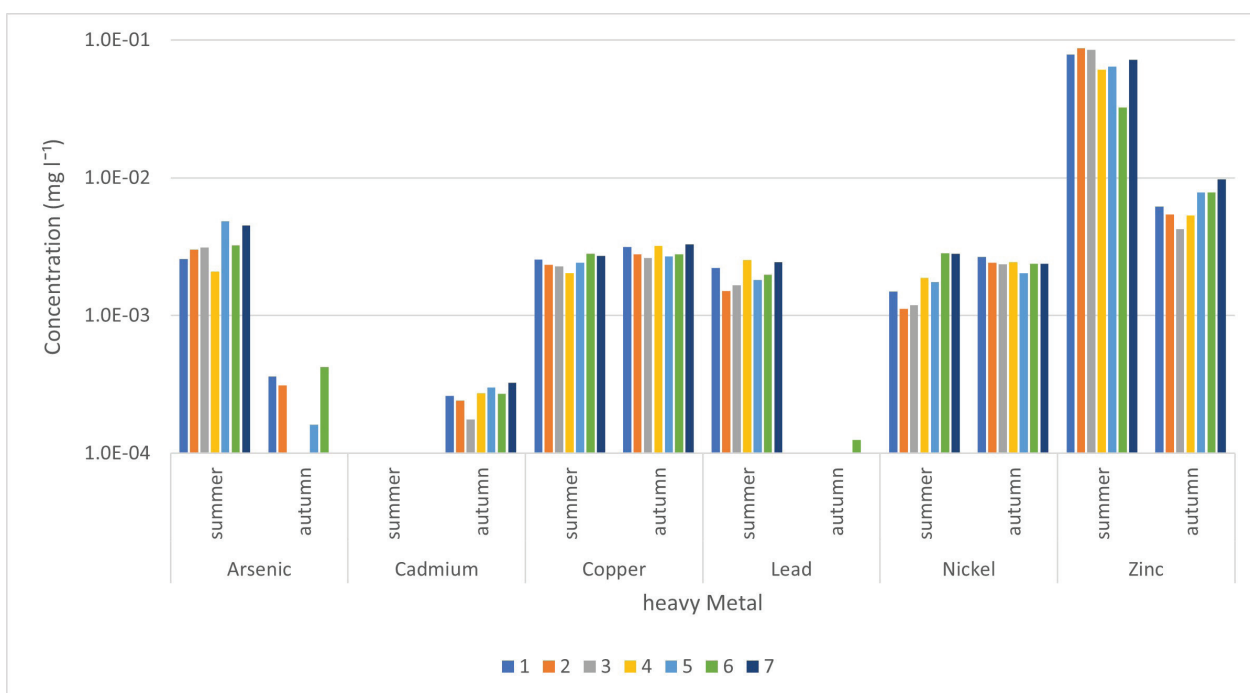

Figure 3: Trace metal and metalloid concentrations ($\mu g\ l^{-1}$) in samples collected from sites 1–7 during the summer and autumn seasons from the Irwell, Manchester.
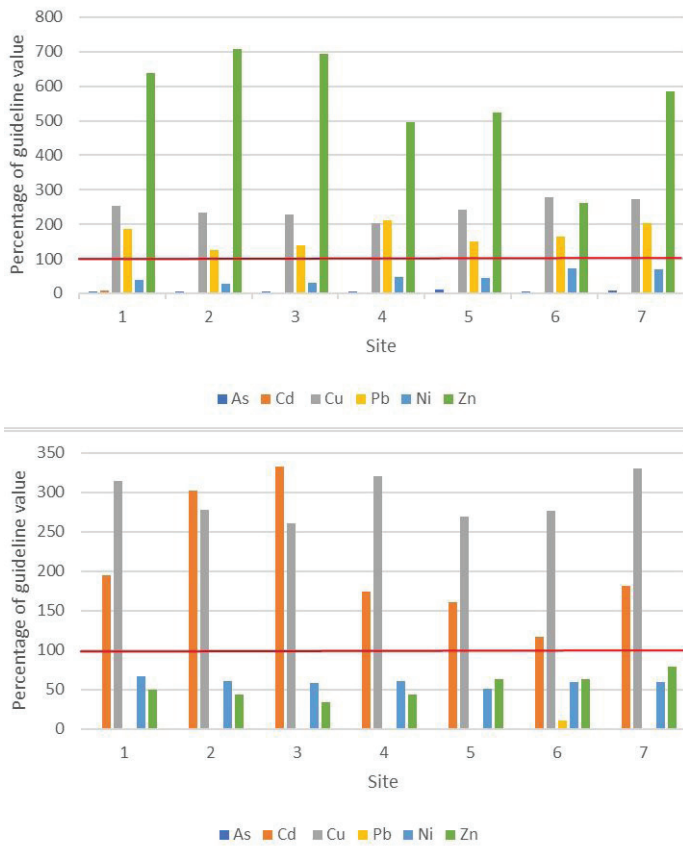
Figure 4: Trace metal and metalloid concentrations in sites 1–7 above/below the EQS (%) highlighted in red. Samples collected in summer (top) and autumn (below).
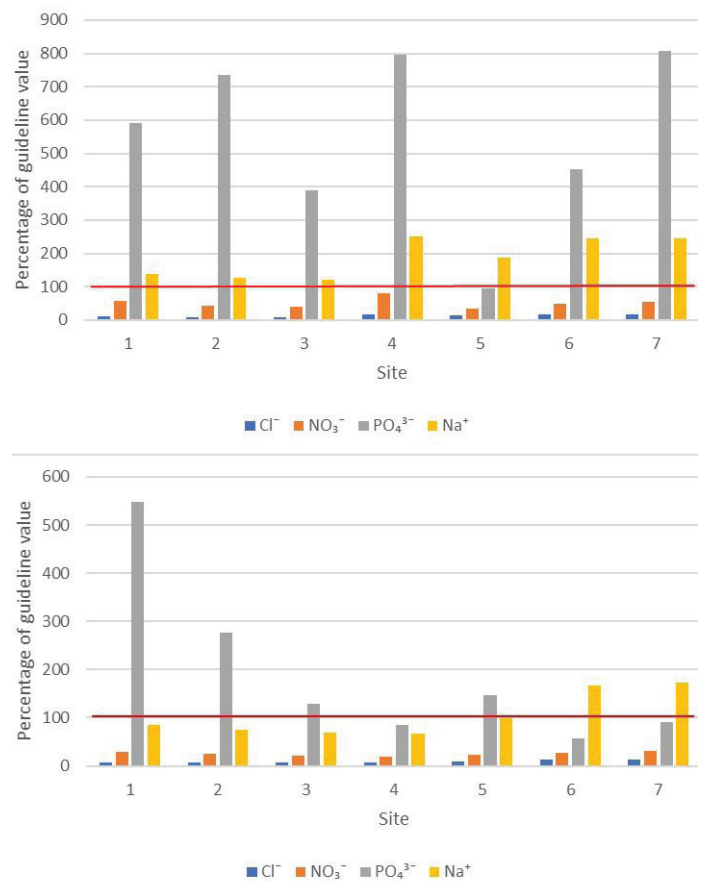
Figure 5: Ionic concentrations in sites 1–7 above/below the EQS (%) highlighted in red. Samples collected in summer (top) and autumn (below).

Tables 6, 9). It can be observed that concentrations of Pb, Cu and Zn are breaching the EQS in the summer season. Concentrations of Cd and Cu are breaching the EQS in the autumn season (Supplementary Table 9).

Ionic concentrations in water samples
Ionic concentrations are reported in Supplementary Table 7. The ion with the highest concentration was sodium (mean 29.16 mg l^{-1}, standard deviation 13.27 mg l^{-1}); phosphate had the lowest concentration (mean 0.37 mg l^{-1}, sd 0.28 mg l^{-1}). Ionic concentrations followed the order $Na^+ > Cl^- > NO_3^- > PO_4^{3-}$ at all sites in summer, $Cl^- > Na^+ > NO_3^- > PO_4^{3-}$ at sites 1, 2, 3, 4 and 5 in autumn and $Na^+ > Cl^- > NO_3^- > PO_4^{3-}$ at sites 6 and 7 in autumn.

Ionic concentrations were compared to EQS values (Figure 5, Supplementary Tables 3, 8). Concentrations of PO_4^{3-} breached the EQS by more than 100% at all sites. Concentrations of Na^+ breached the EQS by more than 100% at sites 6 and 7 and by 11%, 1%, 59% and 43% at sites 1, 2, 4 and 5, respectively. Concentrations of Cl^- and

NO_3^- are consistently below the EQS at all sites with Na^+ concentrations below the EQS by 5% at site 3.

Ionic concentrations, averaged across all seven sites, were higher during the summer (Supplementary Table 7). Concentrations of Na^+ breached the EQS at all sites during the summer and at sites 6 (66%) and 7 (72%) in the autumn. Concentrations of PO_4^{3-} breached the EQS by more than 100% more frequently in the summer season (sites 1, 2, 3, 4, 6 and 7). During the autumn, concentrations of PO_4^{3-} breached the EQS at sites 1, 2, 3 and 5 (Supplementary Table 9).

Discussion
Spatial variation in BOD concentrations
Peaks in BOD were observed in water samples downstream of WWTPs (Figure 2). Rossendale, Bury and Bolton WWTPs are immediately upstream of sites 1, 4 and 6 and 7, respectively. Discharge from these WWTPs could be amongst sources increasing the organic load of the Irwell, increasing bacterial/microorganism activity (Prambudy *et al.*, 2019). This

activity consumes oxygen, hence the lower DO and higher BOD values (Prambudy *et al.*, 2019; United States Geological Survey, 2020). However, there is insufficient evidence from the research presented in this paper to specifically pinpoint sources with a high degree of confidence.

Spatial and temporal trends in heavy metal concentrations
Cd levels peak upstream of the Cuba industrial site and Burrs Country Park (sites 2 and 3) and in Manchester city centre (site 7). Former printworks between sites 2 and 3 (figure 1), a building material supplier (site 7) and the former Kearsley power station (site 5) are possible point sources of Cd (Supplementary Figure 1), as Cd can be released into the environment through the combustion of fossil fuels and the production of cement (Rzymski *et al.*, 2013; Rahman and Singh, 2019). However, the relatively constant downstream Cd concentrations prevents the definitive identification of a source of Cd, hence it cannot not be said with high confidence that this is the source of Cd in the river. Alternatively, Cd concentrations could increase entirely by natural phenomena through processes such as weathering and erosion of the riparian zone (Zhang *et al.*, 2019). The riparian zone is a key regulator of the transfer of sediments and nutrients into the river and can influence the quality of water due to its soil properties, as well as the lithospheric abundance of Cd (generally 0.15 ppm) in forms such as CdS, $CdCO_3$, $Cu_4Cd(SO_4)_2(OH)_6 4H_2O$ and $CdSe$ (Zhang *et al.*, 2019; Rahman and Singh, 2019). Research into the relationship between riparian input and Cd concentrations in the context of the Irwell is needed, through the chemical analysis of soils around the banks of the Irwell.

Copper concentrations are more than 100% above the EQS along the measured Irwell transect, suggesting possible sources of Cu pollution within the catchment. Given the high concentrations at site 1, the sources are likely to be upstream of the transect and it cannot be confidently stated that a single point source has been identified. Multiple mines and collieries operated in the upper Irwell catchment including at Bacup, Lancashire, where historic discharge of mine water into the Irwell is recorded (Coal Authority, 2018). Mines and collieries can release trace metals via acid mine drainage, where the interaction of rainwater and sulfate minerals generates sulfuric acid, which extracts and releases trace metals and metalloids (Wright *et al.*, 2018; Union of Concerned Scientists USA, 2017; Northern Mine Research Society, 2020).

Collieries are also linked to high fluvial Zn concentrations (Gozzard *et al.*, 2011; Wright *et al.*, 2018). However, as is the case with Cd, high concentrations throughout the Irwell transect suggest an upstream source. As well as direct wastewater discharge, surface run-off and groundwater flow can introduce metals into river systems (Gozzard *et al.*, 2011). Zn concentrations were higher in summer than autumn, which correlates with higher regional precipitation (137 mm in July 2019, 101 mm in November 2019) (The National Hydrological Monitoring Programme, 2019a and 2019b). Increased run-off from historical collieries could be a possible explanation for high summer concentrations of Zn; however a definitive point source cannot be derived (Gozzard *et al.*, 2011).

Concentrations of Pb exceed the EQS by more than 100% at sites 4 and 7 in summer. The absence of Pb in autumn could be a result of concentrations being beyond the limit of detection of the machine. These are sites located in highly urbanised areas. The majority of fluvial Pb concentrations can be traced back to watertight joints and roof run-off in urban areas, with exhaust emissions, atmospheric deposition and brake pad wear playing a small part (Petrucci *et al.*, 2014). Road-deposited sediments, including construction material as well as vehicle-derived dust, can contain Cu, Zn and Cd alongside Pb (Robertson and Taylor, 2007).

Upstream of site 4 is an industrial estate including a plumbing merchant (Supplementary Figure 2). Although pipework is no longer pure Pb, plumbing materials can contain up to 8% Pb due to its resistant and malleable characteristics (Lei *et al.*, 2018).

Cations and anions
Sodium and chloride ions are strongly correlated (r^2 = 0.975; Supplementary Figure 3). Road salts are a primary source of these ions in urban areas (Godwin *et al.*, 2003). However, given the timing of sampling dates, this is an unlikely contribution to high Na^+ and Cl^- concentrations in the Irwell. Effluent from WWTPs is a more probable source of Na^+ and Cl^- as the peaks observed in Figure 5 (sites 1, 4 and 6) coincide with sites that were located downstream of Rossendale, Bury and Bolton WWTPs (Panno *et al.*, 2002). However, confidently stating a single point source is beyond the scope of this paper.

Na^+ breaches the EQS at all sites sampled in summer, but only two in autumn (Supplementary Table 9). Sodium absorption ratios (SAR) above 9 SAR can lead to a sodium salinity hazard affecting crop growth due to the relative reduction of the Ca^{2+} and Mg^{2+} ratio (Khanoranga and Khalid, 2019). SAR values in the Irwell are below this (mean 4.6 SAR, range 2 to 8 SAR; Supplementary Table 10), making it suitable for irrigation purposes. Noticeable declines in Na^+ and Cl^- concentrations appear 20–30 years after the

Table 1: Summary of results of BOD, metal/metalloid, and ion concentrations at sample sites along the River Irwell, Manchester.

Site	Location	BOD peak	Metals above EQS	Ions above EQS
1	Downstream of Rossendale WWTP outflow	Summer and Autumn	Cd, Cu, Zn	PO_4^{3-}, Na^+
2	Upstream of Cuba Industrial site	No	Cu, Zn	PO_4^{3-}, Na^+
3	Burrs Country Park	No	Cu, ZN	PO_4^{3-}
4	Downstream of Bury WWTP outflow	Summer and Autumn	Cu, Pb, Zn	PO_4^{3-}, Na^+
5	Upstream of Bolton WWTP outflow	No	Cu, Zn	PO_4^{3-}, Na^+
6	Strangeways, Manchester city centre	Autumn	Cu, Zn	PO_4^{3-}, Na^+
7	The Lowry, Manchester city centre	Summer	Cd, Cu, Pb, Zn	PO_4^{3-}, Na^+

introduction of these ions, to river systems presenting environmental issues for future generations (Kelly *et al.*, 2019).

High fluvial PO_4^{3-} can lead to eutrophication, adversely affecting flora and fauna through CO_2 depletion and lack of sunlight penetration, decreasing the availability of DO and lowering the effectiveness of interventions carried out to remediate other pollutants (Hashim *et al.*, 2019). Sites with increased BOD correlate, albeit weakly ($r^2 = 0.196$), with those that had breached the PO_4^{3-} EQS (Supplementary Figure 4).

There are five main pollutants along the transect of the Irwell which exceed the EQS (Table 1). Site 7 is the most polluted, with five toxic pollutants exceeding the EQS. Site 3 is the least polluted with only three toxic elements exceeding the EQS. The BOD is observed to peak in sites 1, 4, 6 (autumn) and 7 (summer).

Comparison of the modern-day Irwell with other rivers and historical records in the UK

For context, the results from the Irwell were compared to published records from other UK rivers (Dixit and Witcomb, 1983; Armitage *et al.*, 2007). Concentrations of Zn in the Irwell were higher than those found in the South Tyne (measured in 1976 and 2004; Armitage *et al.*, 2007). Present levels of Pb in the Irwell are lower than all comparison rivers (excluding the South Tyne in 1976; Table 2); they are also lower than levels found in an "unpolluted" tributary. Cu levels in the modern-day Irwell are lower than those measured in the same river in 1983. This could be due to the adoption of the EU Water Framework Directive (WFD) in October 2000, which aims to protect the aquatic environment through the reduction of pollution (European Parliament, Council of the European Union, 2000). Lower concentrations could

Table 2: Modern-day Irwell trace metal levels compared to historic trace metal concentrations of the River Irwell and modern-day/historic trace metal concentrations of the River Nent, its tributaries and the River South Tyne.

Sampled areas	Region	Trace metal (mg l^{-1})			Reference
		Cu	Pb	Zn	
River Irwell (2019)	North west England	0.0033[1]	0.0025[2]	0.087[2]	This study
River Irwell (1983)	North west England	0.025 – 0.075	0.01 – 0.09	0.55	Dixit and Witcomb, 1983
River Nent (2004)	North England	–	0.044[3]	1.42[3]	Armitage *et al.*, 2007
River Nent (1976)	North England	–	0.052[3]	1.09[3]	Armitage *et al.*, 2007
River South Tyne (2004)	North England	–	0.006	0.043	Armitage *et al.*, 2007
River South Tyne (1976)	North England	–	0.001	0.06	Armitage *et al.*, 2007
Unpolluted tributary (2004)	North England	–	0.004	0.02	Armitage *et al.*, 2007
Unpolluted tributary (1976)	North England	–	0.004	0.02	Armitage *et al.*, 2007

1: Highest concentration obtained from autumn samples.
2: Highest concentration obtained from summer samples.
3: Mean concentrations in water samples obtained from 10 sites.

also be as a result of the new pipeline directing mine water from the Irwell to a treatment facility, reducing the levels of trace metals and metalloids present in fluvial systems (Coal Authority, 2018). The transition of Greater Manchester from a high level of manufacturing industry to a post-industrial economy during the 1960s and 1970s is another possible explanation for the lower concentrations observed in this study (Madgin, 2010).

Conclusion

Trace metal, metalloid and ion pollution levels were measured along a transect of the Irwell, Greater Manchester, UK, and compared to historical records from the Irwell and similar UK rivers. Local peaks in Pb concentrations could be a result of urban pollution sourced in large towns and cities, such as Bury and Manchester. Increases in Na^+ and Cl^- ionic concentrations in urban locations are likely the result of stormwater run-off and the increases observed during the summer season due to increased precipitation, although above EQS, remained below thresholds of sodium salinity hazard. Increases in PO_4^{3-} and BOD were observed in water samples taken downstream of WWTPs, which could lead to eutrophication and should be monitored further. Cd, Cu and Zn are consistently high throughout the transect, suggesting upstream sources, such as mining and factories. If the sites generating this pollution can be identified, targeted remediation would improve water quality in the Irwell.

Modern metal pollution in the Irwell, as measured in two sample campaigns from 2019, is significantly lower than earlier records, demonstrating that remediation and clean-up efforts are working, likely coupled with effects from the reduction in heavy industry in the region. Concentrations of Cu, Pb and Zn are much lower than in 1983 (Dixit and Witcomb, 1983), with Pb concentrations also lower than the rivers Nent (2004, 1976), South Tyne (2004) and an 'unpolluted' tributary (2004, 1976).

This study provides a snapshot of the quality of water in the Irwell with regards to spatial and temporal variability. Continuous and consistent monitoring and assessment is necessary in order to provide a better insight into the quality of water in the Irwell and to better protect the welfare of society and the natural environment.

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Supplementary information

Water sampling sites: See attachment (Water_sample_sites.kmz) in Google Earth Pro, 2020.

Supplementary Table 1: Water sampling sites along the Irwell, Manchester.

Site	Distance from Rossendale wastewater treatment plant (km)	Latitude (decimal degrees)	Longitude (decimal degrees)	Description
1	0.14	53.68	-2.32	Downstream of Rossendale wastewater treatments works outflow
2	3.03	53.66	-2.31	Upstream of Cuba Industrial Site
3	11.42	53.61	-2.31	Burrs country park
4	18.84	53.56	-2.30	Downstream of Bury wastewater treatments works outflow
5	30.13	53.54	-2.35	Upstream of Bolton wastewater treatment works
6	43.95	53.49	-2.25	Strangeways, Manchester city centre (urban)
7	45.14	53.48	-2.25	The Lowry, Manchester city centre (urban)

Supplementary Table 2: Inland surface water (freshwater) environmental quality standard (EQS) guidelines for trace metals/ metalloids.

Trace metal/metalloid	Concentration guideline (mg l^{-1})	Source
Arsenic (As)	0.05	Cooper and Davies (2015)
Cadmium (Cd) [2,3]	≤ 0.00008 (Class 1) 0.00008 (Class 2) 0.00009 (Class 3) 0.00015 (Class 4) 0.00025 (Class 5)	European Parliament, Council of the European Union (2013) and Cooper and Davies (2015)
Copper (Cu)	0.001	Cooper and Davies (2015)
Lead (Pb) [2]	0.0012	European Parliament, Council of the European Union (2013) and Cooper and Davies (2015)
Nickel (Ni) [2]	0.004	European Parliament, Council of the European Union (2013) and Cooper and Davies (2015)
Zinc (Zn) [1]	0.0123	Cooper and Davies (2015)

1: Concentration guideline based on concentration of Zn and ambient background concentrations (ABC).
2: Annual average guideline.
3: EQS based on the hardness of water in mg l^{-1} as $CaCO_3$, calculated using equation 3. Class 1; <40 mg l^{-1} as $CaCO_3$, Class 2; 40 – 50 mg l^{-1} as $CaCO_3$, Class 3; 50 – 100 mg l^{-1} as $CaCO_3$, Class 4; 100 – 200 mg l^{-1} as $CaCO_3$ and Class 5; ≥200 mg l^{-1} as $CaCO_3$.

Supplementary Table 3: Guideline values for ionic concentrations in surface waters i.e., lakes and rivers.

Ions	Concentration guideline (mg l^{-1})	Sources
Chloride (Cl$^-$)	250	Health Canada (2019)
Nitrate (NO$_3^-$)	45	Health Canada (2019)
Phosphate (PO$_4^{3-}$)	0.1	Mainstone and Parr (2002); Hashim *et al.* (2019).
Sodium (Na$^+$)	20	Godwin *et al.* (2003)

Supplementary Table 4. BOD values in water samples taken along the Irwell, Manchester, during the summer and autumn.

Site	Season	BOD (mg l^{-1})
1	summer	4.83
2	summer	3.34
3	summer	3.05
4	summer	3.8
5	summer	3.16
6	summer	2.41
7	summer	7.28
1	autumn	3.31
2	autumn	2.24
3	autumn	2.23
4	autumn	2.98
5	autumn	2.3
6	autumn	4.57
7	autumn	4.38

Supplementary Table 5: Trace metal and metalloid concentrations in water samples retrieved from the Irwell, Manchester, during the summer and autumn.

Site	Season	Arsenic (mg l^{-1})	Cadmium (mg l^{-1})	Copper (mg l^{-1})	Lead (mg l^{-1})	Nickel (mg l^{-1})	Zinc (mg l^{-1})
1	summer	0.0026	0.0000	0.0025	0.0022	0.0015	0.0783
2	summer	0.0030	0.0000	0.0023	0.0015	0.0011	0.0870
3	summer	0.0031	0.0000	0.0023	0.0017	0.0012	0.0852
4	summer	0.0021	0.0000	0.0020	0.0025	0.0019	0.0611
5	summer	0.0048	0.0000	0.0024	0.0018	0.0017	0.0644
6	summer	0.0032	0.0000	0.0028	0.0020	0.0028	0.0323
7	summer	0.0045	0.0000	0.0027	0.0024	0.0028	0.0719
1	autumn	0.0004	0.0003	0.0031	0.0000	0.0027	0.0062
2	autumn	0.0003	0.0002	0.0028	0.0000	0.0024	0.0054
3	autumn	0.0000	0.0002	0.0026	0.0000	0.0024	0.0042
4	autumn	0.0000	0.0003	0.0032	0.0000	0.0024	0.0053
5	autumn	0.0002	0.0003	0.0027	0.0000	0.0020	0.0079
6	autumn	0.0004	0.0003	0.0028	0.0001	0.0024	0.0078
7	autumn	0.0000	0.0003	0.0033	0.0000	0.0024	0.0097

Supplementary Table 6: Percentage of EQS of trace metal and metalloid concentrations in water samples obtained from the Irwell, Manchester, during the summer and autumn.

Site	Season	Arsenic (%)	Cadmium (%)	Copper (%)	Lead (%)	Nickel (%)	Zinc (%)
1	summer	5	9	254	185	37	637
2	summer	6	0	234	126	28	707
3	summer	6	0	228	138	30	692
4	summer	4	0	203	211	47	497
5	summer	10	0	242	150	44	524
6	summer	6	0	280	165	71	262
7	summer	9	0	272	203	70	584
1	autumn	1	195	315	0	67	50
2	autumn	1	302	278	0	60	44
3	autumn	0	333	261	0	59	34
4	autumn	0	175	321	0	61	43
5	autumn	0	160	270	0	51	64
6	autumn	1	117	277	10	60	64
7	autumn	0	181	330	0	59	79

Supplementary Table 7: Ionic concentrations in water samples retrieved from the Irwell, Manchester, during the summer and autumn.

Site	Season	Chloride (mg l^{-1})	Nitrate (mg l^{-1})	Phosphate (mg l^{-1})	Sodium (mg l^{-1})
1	summer	26.066	25.522	0.591	27.389
2	summer	23.385	18.627	0.736	25.572
3	summer	22.827	17.465	0.388	24.176
4	summer	45.164	35.734	0.797	50.065
5	summer	36.58	15.614	0.095	37.379
6	summer	41.295	22.251	0.453	48.726
7	summer	43.259	24.872	0.808	48.788
1	autumn	18.707	13.357	0.549	16.860
2	autumn	17.445	11.236	0.277	14.836
3	autumn	16.527	9.463	0.128	13.699
4	autumn	16.773	8.462	0.086	13.414
5	autumn	23.447	10.401	0.147	19.760
6	autumn	30.983	12.446	0.056	33.210
7	autumn	33.123	13.965	0.092	34.433

Supplementary Table 8: Percentage of EQS of ionic concentrations in water samples obtained from the Irwell, Manchester, during the summer and autumn.

Site	Season	Chloride (%)	Nitrate (%)	Phosphate (%)	Sodium (%)
1	summer	10	57	591	137
2	summer	9	41	736	128
3	summer	9	39	388	121
4	summer	18	79	797	250
5	summer	15	35	95	187
6	summer	17	49	453	244
7	summer	17	55	808	244
1	autumn	7	30	549	84
2	autumn	7	25	277	74
3	autumn	7	21	128	68
4	autumn	7	19	86	67
5	autumn	9	23	147	99
6	autumn	12	28	56	166
7	autumn	13	31	92	172

Supplementary Table 9: Ionic, trace metal and metalloid concentrations that are exclusively breaching the EQS during the summer and/or autumn seasons in water samples obtained from sites 1 – 7 along the Irwell, Manchester.

Site	Pollutants breaching EQS (%)								
	Copper		Cadmium	Lead	Zinc	Phosphate		Sodium	
	Summer	Autumn	Autumn	Summer	Summer	Summer	Autumn	Summer	Autumn
1	254	315	195	185	637	591	549	137	–
2	234	278	302	126	707	736	277	128	–
3	228	261	333	138	692	388	128	121	–
4	203	321	175	211	497	797	–	250	–
5	242	270	160	150	524	–	147	187	–
6	280	277	117	165	262	453	–	244	166
7	272	330	181	203	584	808	–	244	172

Supplementary Table 10: SAR values of water samples obtained from the Irwell, Manchester, during the summer and autumn.

| Site	Season	SAR value
1	summer	5
2	summer	4
3	summer	4
4	summer	8
5	summer	6
6	summer	7
7	summer	7
1	autumn	3
2	autumn	3
3	autumn	3
4	autumn	2
5	autumn	3
6	autumn	5
7	autumn	5

Supplementary Figure 2: Plumbing merchant recognised to be potential Pb source around site 4. Google Earth Pro, 2020.
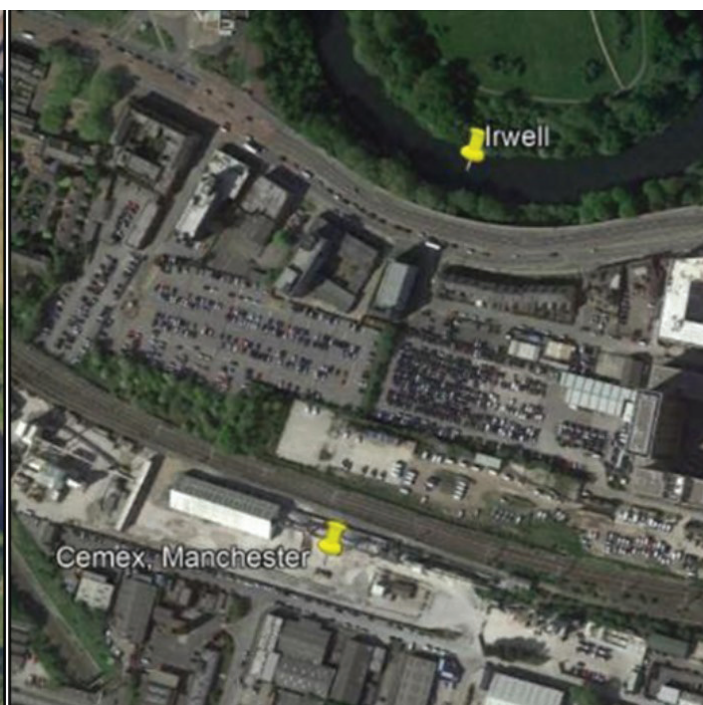
Supplementary Figure 1: Former Kearsley power station and a Cemex plant in Manchester recognised to be potential Cd sources. Google Earth Pro, 2020.
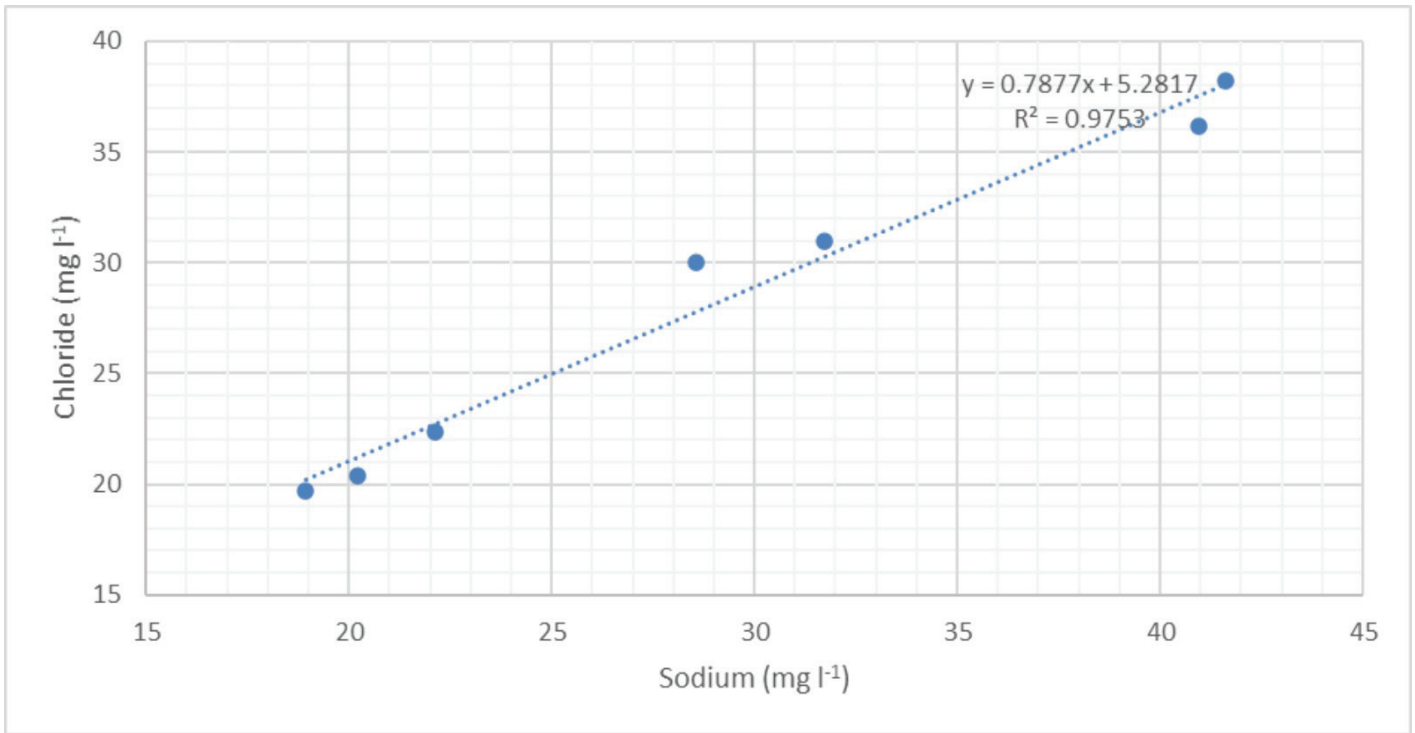
Supplementary Figure 3: Correlation of mean Na$^+$ and Cl$^-$ concentrations in water samples obtained along the Irwell, Manchester, in mg l^{-1}.
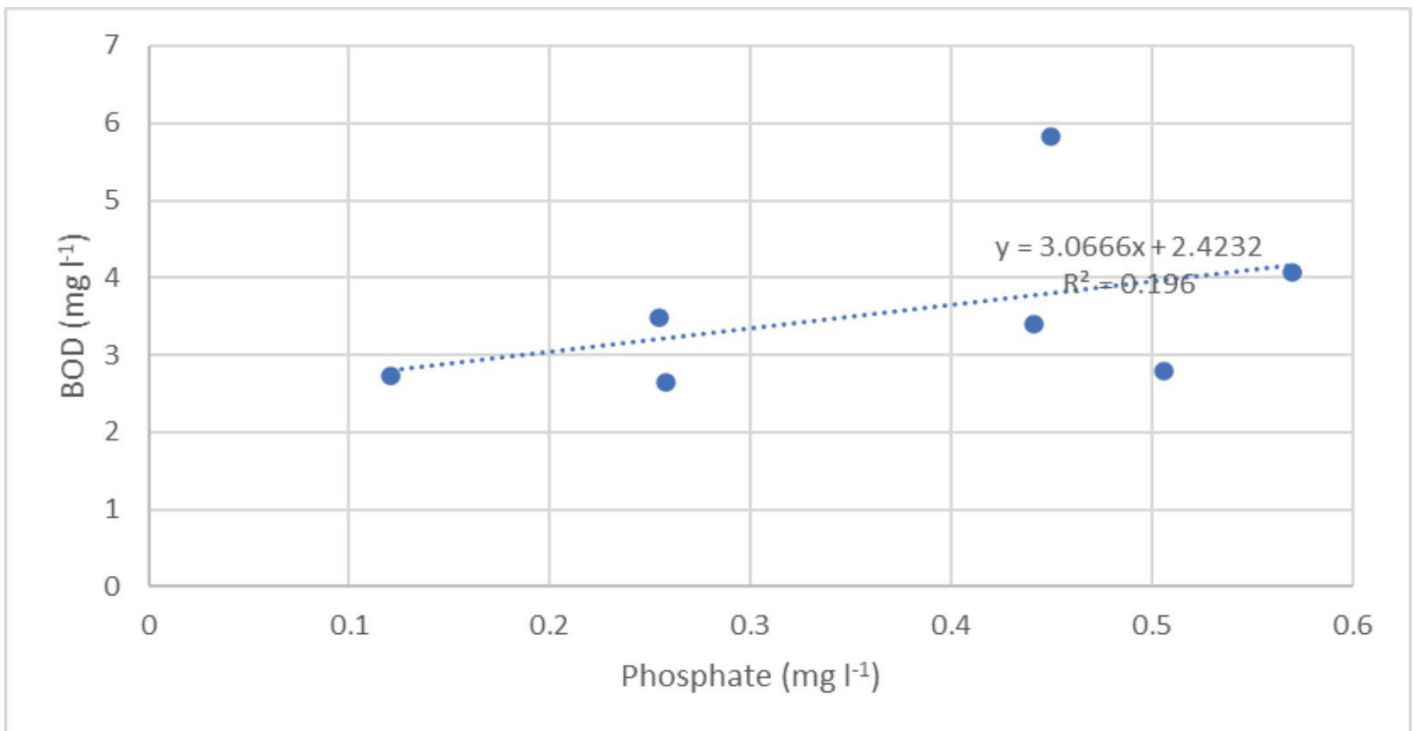
Supplementary Figure 4: Correlation of mean BOD and PO$_4^{3-}$ concentrations in water samples obtained along the Irwell, Manchester, in mg l^{-1}.