The legacy of industrial pollution in estuarine sediments: spatial and temporal variability implications for ecosystem stress

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Abstract
The direct impacts of anthropogenic pollution are widely known public and environmental health concerns, and details on the indirect impact of these are starting to emerge, for example affecting the environmental microbiome. Anthropogenic activities throughout history, with associated pollution burdens are notable contributors. Focusing on the historically heavily industrialised River Clyde, Scotland, we investigate spatial and temporal contributions to stressful/hostile environments using a geochemical framework e.g. pH, EC, Total organic carbon and potentially toxic elements; As, Co, Cr, Cu, Ni, Pb and Zn and enrichment indicators. With regular breaches of the sediment quality standards in the estuarine system. Multivariate statistical analysis (principle component analysis) identifies 2 dominant components, PC1: As, Cr, Cu, Pb and Zn as well as PC2: Ni, Co and total organic carbon. Our assessment confirms hot spots in the Clyde Estuary indicative of localised inputs n addition there are sites with high variability indicative of excessive mixing. We demonstrate that industrialised areas are dynamic environmental sites dependant on historical anthropogenic activity with short scale variation. This work supports the development of ‘contamination’ mapping to enable an assessment of the impact of historical anthropogenic pollution, identifying specific ‘stressors’ that can impact the microbiome, neglected in estuarine recovery dynamics and potentially supporting the emergence of antimicrobial resistance (AMR) in the environment.

Introduction
Industrial activities, whether contemporary or historical, have often occurred globally along major watercourses, particularly in estuaries where transport hubs and habitation sites have developed over civilization. These features are also naturally chemically and physically important at the interface between terrestrial and marine systems where high flux of natural geochemical transport occurs, stimulating biodiversity and supporting critical ecosystems. The consequence has often been impaired water quality, habitat loss and diminished ecosystem services, which result into deleterious changes in ecosystem structure with risks to human and aquaculture health. These changes could result in toxicologically stressful environments that, in turn, could be relate to changes in microbiome and/or resistance—e.g., development of antimicrobial resistance (AMR) (Rodgers et al., 2018). Recovery of estuaries from long term anthropogenic disruption is understood in some detail for higher trophic levels and within that context shows great variation from months to decades depending on biological species or system components (Borja et al, 2010). Very little understanding exists on the microbiome response to pollution and its impact on other characteristics.

The Clyde estuary, Scotland is an optimal example site to determine environmental “stress”, historically being one of the most contaminated estuarine environments in the UK (Balls et al., 1997). Through its historical development industrial revolution, trade and wider urban development has seen massive anthropogenic disruption over relatively short spatial scales. Despite the recent improvement in water column quality and positive response of higher trophic levels (Whitfield & Elliott, 2002), sediment contamination is retained and slower to recover (Borja et al, 2010). Consequently an extensive list of historical pollutants that has been thoroughly studied (Hursthouse et al., 2003, Edgar et al., 2003, Hursthouse, 2001, Fernandes et al., 2009, Lass-Evans et al., 2012, Rowan, 2002) The River Clyde and its tributaries have been important vectors and sink for contaminated waste from succession of industries located in the conurbation of Glasgow and along the banks of the estuary during the industrial development phase in Western Europe
in the 19th and 20th centuries. Consequently, the river has received pollution from the onset of the Industrial Revolution (18th century) to the present day, changing with urban and industrial development in its catchment (Vane et al., 2010, Vane et al., 2007, Edgar et al., 2006). Metals such as As, Co, Cr, Cu, Ni, Pb and Zn (and other potentially toxic elements – PTEs) can be linked to anthropogenic and natural inputs (Caccia et al., 2003, Rodriguez-Iruretagoiena et al., 2016, Birch et al., 2015, Lenart-Boroń and Boroń, 2014) which are now managed through a range of regulatory instruments e.g. Water Framework Directive (2000/60/EC) (Cuculić et al., 2009, Khan et al., 2017, Larroso et al., 2010). The bioavailability and environmental influence of these pollutants depends on many processes such as i) mobilisation in interstitial water, ii) chemical species, iii) transformation e.g. methylation, iv) sediment compositional e.g. oxides of Fe and organic matter, v) competition with other metal for complexation, vi) spatial distribution and vii) influence of bioturbation, salinity, redox or pH on these processes (Bryan and Langston, 1992, Weil and Brady, 2016, Peng et al., 2008, Konhäuser et al., 2002, Akcil et al., 2015, Zaaboub et al., 2015, Caccia et al., 2003, Berner and Berner, 2012, Petit et al., 2015).

Being able to identify key correlations between physico-chemical and PTE parameters is crucial in order to identify “stressors” within the local environment. With past discharges to the River Clyde being re-worked by estuarine processes and exposure conditions having a dynamic temporal context, there is a unique ecosystem to test the prevalence of pollution-related impacts. For example, the link between AMR and metal content which has previously been identified as a promoter of genetic dissemination by cross and/or co-resistance (Ashbolt et al., 2013, Baker-Austin et al., 2006, Berg et al., 2010, Seiler and Berendonk, 2012, Perry and Wright, 2013, Martinez et al., 2009, Knapp et al., 2017).

In this study, we explore metal levels and other geochemical characteristics along the river Clyde, Glasgow, (Scotland), with an aim to support our baseline hypothesis that specific “stressors” within the environment contribute risks to public health. Through identification of pollution conditions targeting locations with demonstrable exceedances of toxicity screening levels we report the statistical significance of physico-chemical parameters (pH, Ec, OM % and Total organic carbon (TOC)) and key PTEs; As, Co, Cr, Cu, Ni, Pb, and Zn within an industrialised estuary to identify key relationships (components). This research acts as a precursor to a larger study which will incorporate and correlate these results to microbial data.

Analyses
Sample collection
Sediment samples were collected from 19 sites along the inner Clyde Estuary (Figure 1) during sampling campaigns in Autumn 2017 to Spring 2018, to a maximum depth of 30 cm (hand-held coring device; AMS, Inc.). Three cores were collected at each site: one from the high tide line, one from the low tidal front, and one-half way between the two; each core was approximately 5m apart. Four exceptions; Rothesay Dock, King George V Dock, White cart Estuary and the Kelvin Confluence, which were grab samples collected from the centre of the river. Samples were returned to the laboratory and each core was subdivided into 10cm sections, before homogenisation, with sub-samples taken for microbiological analysis. The remaining sample was air dried until constant weight then sieved <500μm for normalisation. This provided nine sub-samples per location.

Figure 1: Location of sample sites along the River Clyde. Code + seaward distance from Glasgow tidal weir (km: HNB: Helensburgh (33.17); GNK: Greenock (37.9); CAR: Cardross (28.47); KBP: Kelburn Park (27.88); DBW: Dumbarton West (25); CYV: Clydeview (23.5); DBC: Dumbarton Castle (22.45); GRB: Gruggies Burn 22.05); PGS: Port Glasgow (22.05); BOW: Bowling (17.42); BSP: Bishopton (16.44); ESK: Erskine Harbour (15.5); NSI: Newshot Island (13.67); RSD: Rothesay Dock; WCB: White Cart Bridge (4.75); WCE: White Cart Estuary; KGD: King George V Dock; KLC: Kelvin Confluence; CUN: Cunningar Loop (-5.4)

Physical and chemical properties
Organic matter (OM) was determined using loss on ignition with total organic carbon (TOC) using van Bemmelen factor (Dean, 1974, Salehi et al., 2011) pH and electrical conductivity were measured using calibrated Mettler Toledo-Five Go meters (Corwin and Rhoades, 1982, Van Reeuwijk, 2002). Moisture content was determined using a Mettler Toledo HB43-5 meter. All analysis was carried out in replicate (n = 5).

Elemental analysis
Replicate aliquots (n = 5) of 0.25g ± 0.05g of sample were treated with 5ml 30% H2O2 overnight to remove organic matter in digestion cups (Environmental Express, USA), then digested using aqua regia at 95°C in a hot block until 5ml in volume. They were then made upto 50ml using UHP water and filtered in-situ using 0.45μm
PTFE filter (FilterMate, Environmental Express, USA). A Certified Reference Material (CRM) was included in the digestion method (BCR667 Estuarine Sediment BCR®; Sigma Aldrich).

Elements were determined by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) (Thermo X-Series II). A calibration series of multi-element standard (BCR320R-40G - channel sediment) was determined regularly (every 60 samples + linearity $r^2 >0.99$) with indium used as the internal standard. Each determination was made in quadruplicate and dilutions were made if necessary. Isotopes used for measurement were $^{75}$As, $^{59}$Co, $^{52}$Cr, $^{63/65}$Cu, $^{60}$Ni, $^{206/207/208}$Pb and $^{66/67}$Zn. Results were subjected to the geoaccumulation index in order to gauge the degree of anthropogenic influence.

Results
Limits of detection were (mg/kg, dry weight): As: 0.10, Co: 0.012, Cr: 0.024, Cu: 0.082, Ni: 0.056, Pb: 0.01 and Zn 0.45 mg/kg with recoveries between 85-110%. Physical properties and PTE concentrations are found in Table 1, with comparable data for sediment quality criteria shown in Table 2. Statistical analysis was carried out using SPSS, with data tested for normal distribution using Kolmogorov-Smirnov and Shapiro-Wilk tests; PTE concentrations were log-transformed for Analysis of Variance (ANOVA) and Principal Component Analysis (PCA).

Table 1: Sediment Characteristics averaged across all sample cores, depths and locations. Concentrations above the Threshold Effect Level (TEL) are italicised and above the Probable Effect Level (PEL) are identified in bold. Values are dry weight mg/kg (95% confidence interval)

Table 2: IUGS/IAGC Global Geochemical Baselines compared to sediment quality guidelines (metal concentrations mg/kg)(Salminen et al., 2005)

Geoaccumulation index ($I_{geo}$)
To provide further indication of combined contamination status the $I_{geo}$ was calculated using the methods of Muller (Muller G, 1979) and Abrahim & Parker (Abraham and Parker, 2008):

$$I_{geo} = \log_2 \left( \frac{C_n}{1.5 B_n} \right)$$

Where $C_n$ is the concentration of the metal of interest in sediment sample, $B_n$ is the background level of the same metal and 1.5 is the factor to minimize the effect of possible variations in the background (Al-Haidarey et al., 2010, Okedeyi et al., 2014, Hasan et al., 2013).

And evaluated against 7 degrees of metal pollution in terms of 7 contamination classes (see figure x), with <-0 demonstrating no contamination and > 5 extremely contaminated.

Figure 2: Heat map showing summary Geoaccumulation data along the River Clyde (downstream from the Tidal Weir in central Glasgow) and various depths (0-10cm, 10-20cm and 20-30cm)

IGO data shows that at all sediment samples (including at varying depths), are contaminated with low to extreme levels of contamination for all PTEs. However, this varied widely between PTE and with distance/depth.

As and Co show low levels of contamination along the hole of the Clyde including historically i.e. with depth. Chromium predominantly shows and increase in contamination throughout history, whereas PTEs Cu, Ni, Pb and Zn show no discernibly trend. Industrial trends throughout history however cannot be discounted without radiometric dating. Zn is seen to be the most extremely contaminated with only moderate levels seen in Port Glasgow. This site shows the lowest level contamination trend for all PTEs. There is varying evidence, which suggests and both an accumulation in PTEs over time, as well as an insight to where contamination may have occurred. We can see the high levels of contamination are seen between 25-33 km from the Weir and again...
16.44km to the weir. These include GNK, CAR, KBP and DBW at the estuaries widest and again BSP, ESK, NSI, WCB and CUN, demonstrating zonal relationships (figure 1).

Analysis of variance (ANOVA) with Kruskal-Wallis testing was used to determine if there were any significant differences in PTE concentration with sample location, depth and distance from the high tide mark (core number) (Table 3). There are significant differences (p<0.001) between the locations for all PTEs but there is no difference in the distance from the high tide line, i.e. tidal influence does not significantly affect PTE concentration. With regards to depth, only Pb showed significant difference with sample depth.

Table 3: ANOVA F-values for PTEs against sample location, depth and (core)

Multiple correlation analysis (Table 4) show a significant positive correlation for most variables with the exception of core number suggesting that the distance to the high tide level does not influence PTE concentrations. Note the negative correlation between location and pH (highlighting the changing salinity of estuarine sediments) and depth with Pb and Zn.

Table 4: physico-chemical and PTE correlation matrix

PCA was carried out using the correlation matrix and varimax rotation to elucidate the principal components(Alexander et al., 2008). Four principal components (PCs) with an Eigenvalue >1 were returned (Table 5) moisture content was not included due the nature of the matrix, i.e. at or near saturation. The dominant facors (41% of total variance) were anthropogenic PTEs: As, Cr, Cu, Pb and Zn which are typical “urban” elements (Fordyce et al., 2012) which were all positively related to each other. The remaining three PCs account for 41.9% of the total variance: PC2 show relationships between Co, Ni and total organic content (19.6%), PC3 is pH (11.8%) and PC4 is conductivity (10.5%). Interestingly, Ni exceeds the G-Base, Threshold Effect Limit and Probable Effect Limits (Table 2) this potentially highlights the importance of their roles as essential nutrients.

Table 3: Principal Component Analysis with varimax rotation of all samples

Discussion
PTE concentrations (Table 1) were compared to a number of previous studies, including the European Geochemical Baseline, Clyde waters and estuary sediments (Jones et al., 2018, Krom et al., 2009), the IUGS/IAGC Global Geochemical Baseline and the FOREGS (Forum of European Geological Survey) (Salminen et al., 2005). The Global Geochemical baselines are the median levels of PTEs we expect to see in stream sediments. FOREGS produced a standardised method of sampling, chemical analysis and data management across 26 countries to produce national baseline datasets for comparable measures. These do not regulate or highlight parameter impact, rather it allows a comparison with broad expected values for terrestrial surface materials (Table 2) (Salminen et al., 2005).

The comparison showed that values from this study exceeded the geochemical baseline values and were more comparable to the Clyde Estuary baseline study results, suggesting that levels exceeding the baseline are likely affected by anthropogenic inputs. As previously reported, estuarine sediments in industrialised regions create environmentally stressful conditions for the sediment microbiome (Rodgers et al., 2018); we therefore focussed on 'stressors' and concentrations above the Threshold Effect Level (TEL) and Probable Effect Level (PEL). The TEL represents the concentration below which adverse effects are unlikely to occur whereas the PEL defines the level in which adverse effects are expected to occur (Macdonald et al., 2000).

It can be seen in Table 1 that As, Co and Cr median values are within the expected geochemical baseline whilst Cu, Ni, Pb and Zn are above typical levels. The physico-chemical parameters (pH and TOC) show that pH sits
within typical baseline values whereas organic carbon content varies greatly. Water content, conductivity and organic matter show a vast variety in concentrations and vary depending on the sampling site.

Newshot Island, Rothesay Dock, King George V Dock and the Kelvin Confluence exceed the TEL for all, if not most, of the PTEs. This could be an artefact of the different sampling techniques employed at the latter three; these were grab samples collected from the centre of the river rather than within the tidal area or it could be due to the heavy industrialised presence at these locations. Newshot Island is on the opposite bank to one of Scotland’s largest Wastewater Treatment Works which is a potential source of pollution in this area (Rodríguez-Irureta et al., 2016, Edgar et al., 2003). The PEL is exceeded at a number of locations: Greenock (Cr, Cu and Pb), Dumbarton Castle (Cr), Newshot Island (As, Pb), Rothesay Dock (As, Cr, Ni, Pb), King George V Dock (Cr, Ni, Zn) and Kelvin Confluence (Ni).

There is no spatial trend in As distribution however there are a number of hotspots e.g. Newshot Island and Rothesay Dock where levels exceed the PEL. Historically, As was used to treat wood at timber and ship yards, both of which are known to have been near these locations (Clydewaterfront, 2014). Elevated Cr levels at Dumbarton Castle (as well as a Igeo level of ‘extremely polluted’), Rothesay Dock and King George V Dock may also be linked to ship and timber yards as well as leather tanning (Muirhead, 2014) particularly associated with known historic pollution levels in the Vale of Leven. Cu is predominantly below the TEL for most sample sites with little variation; the greatest variability is seen at Greenock and Newshot Island, with the former showing up to 13% variability, half of which exceed the PEL.

Elevated levels of Ni at the same site (average of 33.9 mg/kg) can be linked to Cu-Ni alloys typically used in ship building. With Ni there are also hotspots in areas of similar industrial heritage: Rothesay Dock, White Cart Bridge, King George V Dock and Kelvin Confluence. It is also worth noting that the Ni threshold effect level is exceeded at all but five locations, in conjunction with being Moderately – Extremely polluted (Igeo, Figure 2) which will impact the microbiome. There is no clear trend with Co but there is high variability in concentrations (2.3 – 15mg/kg), with only the higher >11.2mg/kg to be considered above the natural baseline. The highest concentration of Zn was found at King George V Dock and this was the only location to exceed the PEL. Zn however has the most polluted Igeo factor suggesting a strong human influence.

There appears to be no pattern in PTE concentration as the locations progress from saline conditions (Helensburgh) to freshwater conditions (Kelvin Confluence). Our control site at Cunningar Loop exceeded the TEL for Ni and three sample sites did not exceed the TEL for any PTE: Helensburgh, Cardross and the White Cart Estuary. These locations are all areas of low current industrial activity compared to other sites. Changes in concentration are also reflected in the minimum and maximum values, with the maximum values exceeding regulatory and typical values. A comparison with a recently published study (Jones et al., 2018) which reported on summary data for samples collected in campaigns nearly 2 decades earlier from the Firth of Clyde (saline conditions) found that their concentrations are higher than our studies however our most comparable site (Greenock) exceeds the TEL for Ni and Zn, and the PEL for Cr, Cu and Pb. Greenock also has the highest concentrations of Cr and Cu in our study (Table 1). A major difference between our study and Jones et al. (2018) is in relation to chromium; Jones et al reported the majority of locations exceeded the PEL and whereas although twelve of our sites exceeded the TEL only four exceeded the PEL.

As the Clyde Estuary is an ‘open system’, it is possible that there has been natural attenuation of historical pollution in the upper sediment column, particularly as Jones et al. (2018) collected samples from a greater depth. A greater column depth would not only reflect an earlier period in time, but also reflect more clay condition and possibly more ‘stable’ conditions i.e. sediments that are not as affected by tidal changes. In our study the uppermost sediments were ‘jelly-like’ in their composition and are constantly being washed which could reduce higher PTE concentrations in areas where there are reduced industrial inputs. This therefore has implications for a potential increase in antimicrobial resistance due to exposure of historical pollution at depth (Rodgers et al., 2018). The time difference between our campaign and previous reports, particularly for Cr, shows the dynamic nature of the system with regards to complexity and elemental movement. It is widely reported that there are localised upstream sources of Cr contamination (Whalley et al., 1999); in the last decade extensive engineering associated with transport infrastructure and international athletics events have transformed some of the most significant sources of Cr pollution with subsequent knock on effect downstream.

PCA analysis highlighted two prominent groupings relating to anthropogenic and natural sources, Component 2 (Co, Ni and TOC) we suggest is the natural and biological requirements within ecosystems because they are less commonly a consequence of anthropogenic causes. However. Co and Ni are typically distributed uniformly
within sediments, their concentration increases with depth and certain locations are likely to be as industrial depositions have accumulated over time (Leyssens et al., 2017, Cempel and Nikel, 2006).

These results suggest that changes in salinity and proximity to high tide level have little impact on concentration however there are a number of pollution hot spots in the Clyde Estuary (Greenock, Newshot Island, Rothesay Dock, King George V Dock and the Kelvin Confluence) suggestive of site-specific inputs. In addition there are sites with high variability which can be attributed to many factors including sediment mixing with historical inputs. Observations of the potential impact of upstream interventions, in particular on the input of chromium highlight the dynamic nature of the system and still the system acts as a net pollution sink.

**Conclusion**
Understanding the distribution of PTEs & geochemical factors in an industrialised estuary is important to elucidate the contributions to stressful/hostile environments. We see levels of PTEs often exceed TEL/PEL levels at various locations and depths along the Clyde, although they are starting to reduce in comparison to historical levels. Our PCA analysis identified 4 components with PC1 and PC2 accounting for the highest variance and associations: As, Cr, Cu, Pb and Zn as well as Ni and Co with TOC. Compared to extensive assessment of sediment quality in the region over more than a decade ago, our data show there has been a gradual reduction in sediment contamination levels, and for example impact of upstream source control (extensive remediation of Cr contamination in Glasgow). However, significant exceedances of sediment quality standards still occur in the estuary and are spatially variable.

It is evident that the estuarine sediments are still a reservoir of contaminants resulting in persistent exposure and disruption to the microbial consortia. Further research is required in order to determine whether these components can be identified as “stressors” within an environmental microbiome. If identified correctly does this subsequently exacerbate the prevalence of genetic mutations and more specifically antimicrobial resistance? The ‘contamination map’ created within this study provides the basis to enable a detailed study of the impact on the microbiome and causes of the emergence of antimicrobial resistance in the environment.

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# Tables

Table 1: Sediment Characteristics averaged across all sample cores, depths and locations. Concentrations above the Threshold Effect Level (TEL) are in shaded cells and above the Probable Effect Level (PEL) are identified in bold. Values are dry weight mg/kg (95% confidence interval)

|                | As  | Co   | Cr   | Cu   | Ni   | Pb   | Zn   |
|----------------|-----|------|------|------|------|------|------|
| TEL            | 5.9 | 37.3 | 36.8 | 18   | 35   | 123  |      |
| PEL            | 17  | 90   | 197  | 35.9 | 91.3 | 315  |      |
| Helensburgh    | 5.1 (0.6) | 4.5 (1.5) | 21.5 (6.5) | 13.9 (4.5) | 17.1 (6.4) | 26.0 (6.5) | 66.4 (12.6) |
| Greenock       | 3.9 (0.8) | 2.9 (0.5) | 164.6 (0.92) | 199.4 (24.0) | 32.1 (4.2) | 103.8 (18.4) | 125.1 (15.7) |
| Cardross       | 2.2 (0.5) | 2.3 (0.05) | 15.6 (1.6) | 6.3 (0.5) | 8.7 (0.6) | 10.8 (1.4) | 40.2 (3.0) |
| Kelburn Park   | 7.8 (0.9) | 8.6 (0.9) | 38.7 (4.0) | 22.4 (1.9) | 23.7 (2.1) | 26.4 (6.1) | 80.9 (12.3) |
| Dumbarton West | 47 (1.6) | 5.8 (0.6) | 32.1 (2.55) | 11.4 (0.7) | 25.3 (1.7) | 28.1 (11.8) | 42.2 (9.8) |
| Clydeview      | 5.6 (0.7) | 8.5 (1.2) | 47.3 (5.0) | 16.3 (1.5) | 27.2 (3.4) | 21.5 (4.3) | 60.3 (3.7) |
| Dumbarton Castle | 13.3 (2.8) | 7.2 (0.6) | 92.0 (24.0) | 25.0 (4.0) | 23.0 (1.5) | 59.0 (15.7) | 105.3 (19.5) |
| Port Glasgow   | 6.8 (0.6) | 10.2 (0.3) | 36.4 (1.4) | 16.7 (0.7) | 32.3 (0.9) | 11.4 (1.8) | 54.0 (4.3) |
| Gruggies Burn  | 10.9 (5.2) | 5.5 (0.8) | 40.7 (7.3) | 18.9 (3.1) | 17.6 (1.1) | 36.1 (9.5) | 82.4 (7.2) |
| Bowling        | 2.0 (0.8) | 7.6 (0.2) | 16.5 (1.2) | 9.9 (2.1) | 18.1 (0.8) | 19.88 (3.1) | 45.6 (12.9) |
| Bishopton      | 4.1 (0.6) | 4.6 (0.2) | 38.0 (1.5) | 10.8 (0.9) | 12.5 (0.7) | 23.3 (1.8) | 51.5 (4.6) |
| Erskine        | 3.5 (1.0) | 5.2 (0.4) | 68.1 (6.4) | 19.9 (2.1) | 17.8 (1.9) | 32.8 (5.0) | (12.0) |
| Newshot Island | 19.5 (3.1) | 5.9 (0.6) | 44.4 (5.9) | 13.66 (29.4) | 22.4 (2.1) | 106.6 (20.9) | 212.5 (37.3) |
| Rothesay Dock | 18.8 (4.2) | 12.0 (2.3) | 158.8 (20.1) | 73.7 (4.1) | 39.5 (3.2) | 122.9 (13.8) | (37.0) |
| White Cart Bridge | 4.7 (0.6) | 17.0 (1.7) | 52.4 (1.3) | 23.3 (1.6) | 46.5 (1.9) | 38.2 (3.9) | 77.7 (4.4) |
| White Cart Estuary | 7.2 | 4.5 | 25.4 | 11.5 | 14.4 | 16.2 | 58.7 |
| King George V Dock | 15.7 (0.3) | 13.8 (2.2) | 153.6 (31.9) | 86.6 (7.4) | 44.9 (1.4) | 91.0 (10.4) | 343.4 (5.4) |
| Kelvin Confluence | 10.2 | 11.6 (1.9) | 57.4 (8.8) | 33.1 (2.5) | 39.1 (3.2) | 60.4 (7.7) | 183.0 (14.4) |
| Cunningar Loop | 3.2 (0.5) | 6.7 (0.2) | 21.1 (1.0) | 13.3 (1.5) | 20.5 (0.3) | 30.6 (4.0) | 75.0 (6.0) |
Table 2: IUGS/IAGC Global Geochemical Baselines compared to sediment quality guidelines (metal concentrations mg/kg)

|                  | G-Baseline*(Salminen et al., 2005) | Clyde(Jones et al., 2018) | Median | Min. | Max. | The Clyde(Krom et al., 2009) | TEL | PEL  |
|------------------|-----------------------------------|---------------------------|--------|------|------|--------------------------------|-----|------|
| pH               | 5.5 – 7.5                         |                           | 6.9    | 4.2  | 7.7  |                                |     |      |
| TOC (%)          | 1.71                              |                           | 3.21   | 0.44 | 12.45|                                |     |      |
| Conductivity (mS)|                                  |                           | 1.41   | 0.41 | 19.95|                                |     |      |
| As               | 6 – 10.1                          | 19                        | 4.7    | 0.00 | 32.53|                                | 5.9 | 17   |
| Co               | 8.0                               |                           | 7.0    | 2.48 | 30.10|                                | 37  | 90   |
| Cr               | 21 – 63                           | 94                        | 50     | 0.0  | 185.44|                                | 37  | 90   |
| Cu               | 14 – 17                           | 19                        | 24     | 3.34 | 314.73| 90 – 137                      | 37  | 197  |
| Ni               | 16 – 21                           | 43                        | 21     | 8.74 | 58.09|                                | 18  | 36   |
| Pb               | 14 – 21                           | 43                        | 21     | 8.74 | 58.09|                                | 18  | 36   |
| Zn               | 60 – 71                           | 83                        | 105    | 10.27| 448.88|                                | 123 | 315  |

**TEL**: Threshold Effect Level; **PEL**: Probable Effect Level. * G-Baseline refers to the median concentrations (mg/kg) measured for European geochemical stream sediment baseline maps (Ccme, 2001).
Table 3: ANOVA F-values for PTEs against sample location, depth and (core) (* p<0.001)

|       | As    | Co    | Cr    | Cu    | Ni    | Pb    | Zn    |
|-------|-------|-------|-------|-------|-------|-------|-------|
| Location | 7.58* | 13.02*| 14.33*| 25.16*| 10.93*| 9.69* | 11.47*|
| Depth  | 0.55  | 2.22  | 0.70  | 0.35  | 2.12  | 3.31* | 1.33  |
| Core   | 0.29  | 0.21  | 1.70  | 0.19  | 0.05  | 0.44  | 0.46  |
Table 4: physico-chemical and PTE correlation matrix

|          | Location | Core  | Depth | Moisture | pH   | EH   | OM   | As   | Co   | Cr   | Cu   | Ni   | Pb   | Zn   | TOC  |
|----------|----------|-------|-------|----------|------|------|------|------|------|------|------|------|------|------|------|
| Location | 1.000    |       |       |          |      |      |      |      |      |      |      |      |      |      |      |
| Core     | -0.047   | 1.000 |       |          |      |      |      |      |      |      |      |      |      |      |      |
| Depth    | -0.123   | 0.087 | 1.000 |          |      |      |      |      |      |      |      |      |      |      |      |
| Moisture | 0.575**  | -0.157| -0.153| 1.000    |      |      |      |      |      |      |      |      |      |      |      |
| pH       | -0.624** | 0.045 | 0.333* | -0.378** | 1.000|      |      |      |      |      |      |      |      |      |      |
| EH       | -0.240** | -0.094| -0.197*| 0.500**  | 0.018| 1.000|      |      |      |      |      |      |      |      |      |
| OM       | 0.439*   | -0.130| 0.004 | 0.834**  | -0.174*| 0.382**| 1.000|      |      |      |      |      |      |      |      |
| As       | 0.104    | 0.018 | 0.065 | 0.287**  | 0.171*| 0.123| 0.322**| 1.000|      |      |      |      |      |      |      |
| Co       | 0.423**  | 0.035 | 0.359* | 0.398*   | 0.029| -0.019| 0.549**| 0.266**| 1.000|      |      |      |      |      |      |
| Cr       | 0.306*   | 0.082 | 0.006 | 0.557**  | -0.232**| 0.219**| 0.481**| 0.469**| 0.463**| 1.000|      |      |      |      |      |
| Cu       | 0.144    | -0.050| 0.021 | 0.233**  | -0.145| 0.119| 0.376**| 0.436**| 0.178* | 0.357**| 1.000|      |      |      |      |
| Ni       | 0.250**  | 0.024 | 0.361* | 0.322**  | 0.086| 0.021| 0.518**| 0.212* | 0.797* | 0.385**| 0.479**| 1.000|      |      |      |
| Pb       | 0.269**  | -0.067| -0.404*| 0.336**  | -0.417**| 0.185*| 0.320**| 0.389**| -0.061| 0.424* | 0.626**| 0.080| 1.000|      |      |
| Zn       | 0.318**  | -0.014| -0.193*| 0.484**  | -0.314**| 0.253**| 0.465**| 0.547**| 0.178* | 0.559**| 0.708**| 0.298**| 0.753**| 1.000|      |
| TOC      | 0.435**  | -0.136| 0.000 | 0.839**  | -0.170| 0.398**| 0.994**| 0.317**| 0.546* | 0.483**| 0.369**| 0.515**| 0.321**| 0.466**| 1.000|

**. Correlation is significant at the 0.01 level (2-tailed). *. Correlation is significant at the 0.05 level (2-tailed). n = 150 for all except Eh n = 141; As n = 144
Table 5: Principal Component Analysis with varimax rotation of all samples

|       | PC1  | PC2  | PC3  | PC4  |
|-------|------|------|------|------|
| pH    | -0.206 | 0.031 | **0.926** | 0.034 |
| EC    | 0.112 | -0.037 | 0.06 | **0.962** |
| As    | **0.769** | 0.084 | 0.478 | 0.024 |
| Co    | 0.108 | **0.943** | 0.061 | -0.061 |
| Cr    | **0.697** | 0.339 | -0.14 | 0.088 |
| Cu    | **0.785** | 0.371 | -0.013 | 0.019 |
| Ni    | 0.133 | **0.951** | 0.091 | -0.043 |
| Pb    | **0.807** | -0.116 | -0.36 | 0.129 |
| Zn    | **0.879** | 0.09 | -0.182 | 0.141 |
| TOC   | 0.285 | **0.646** | -0.206 | 0.463 |
| Variability % | 41.0 | 19.6 | 11.8 | 10.5 |

KMO: 0.703; Bartletts Test of Sphericity: >0.05
| Location | HNB | GNK | CAR | KBP | DBW | CYV | DBC | PGS | GRB | BOW | BSP | ESK | NSI | WCB | CUN |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Depth (cm) | 10  | 20  | 30  | 10  | 20  | 30  | 10  | 20  | 30  | 10  | 20  | 30  | 10  | 20  | 30  |
| Distance from weir (km) | 33.17 | 37.9 | 28.47 | 27.88 | 25 | 23.5 | 22.45 | 22.05 | 22.05 | 17.42 | 16.44 | 15.5 | 13.67 | 4.75 | -5.4 |

### As

| 10 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 1 |
| 20 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 30 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |

### Co

| 10 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 1 |
| 20 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 30 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |

### Cr

| 10 | 1 | 1 | 1 | 4 | 2 | 2 | 6 | 1 | 1 | 1 | 1 | 6 | 3 | 3 | 1 | 1 |
| 20 | 2 | 3 | 3 | 1 | 4 | 5 | 1 | 2 | 2 | 1 | 3 | 6 | 1 | 3 | 2 | 2 |
| 30 | 2 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 1 | 2 | 3 | 3 | 1 | 3 | 2 | 2 |

### Cu

| 10 | 1 | 6 | 1 | 2 | 1 | 1 | 2 | 1 | 1 | 1 | 4 | 1 | 6 | 1 | 1 | 1 |
| 20 | 1 | 6 | 1 | 1 | 2 | 2 | 1 | 1 | 1 | 1 | 4 | 3 | 2 | 2 | 2 | 2 |
| 30 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 3 | 2 | 1 | 1 | 1 |

### Ni

| 10 | 1 | 2 | 1 | 2 | 1 | 1 | 2 | 1 | 1 | 1 | 5 | 2 | 2 | 1 | 1 | 1 |
| 20 | 1 | 4 | 2 | 1 | 3 | 1 | 1 | 2 | 1 | 1 | 1 | 3 | 1 | 3 | 2 | 2 |
| 30 | 2 | 1 | 1 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 1 | 3 | 1 | 1 | 1 | 1 |

### Pb

| 10 | 1 | 4 | 1 | 3 | 3 | 1 | 5 | 1 | 1 | 1 | 6 | 2 | 4 | 1 | 2 | 2 |
| 20 | 1 | 6 | 2 | 1 | 4 | 3 | 1 | 1 | 2 | 1 | 2 | 6 | 2 | 3 | 2 | 2 |
| 30 | 3 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 3 | 2 | 1 | 1 | 2 | 2 |

### Zn

| 10 | 2 | 5 | 2 | 6 | 3 | 2 | 6 | 2 | 3 | 2 | 6 | 4 | 6 | 1 | 4 | 2 |
| 20 | 3 | 6 | 6 | 2 | 6 | 4 | 2 | 2 | 2 | 3 | 2 | 3 | 6 | 4 | 5 | 5 |
| 30 | 4 | 5 | 2 | 1 | 3 | 2 | 2 | 2 | 2 | 5 | 3 | 4 | 3 | 4 | 5 | 5 |