Evaluating the Impacts of an Urban Catchment on Water and Sediment Quality of a Receiving River

This thesis is submitted to Middlesex University in partial fulfilment of the requirements for the degree of Doctor of Philosophy

LUCIANA ALVES
M00323413

Supervisors:

Prof Lian Lundy

Prof Mike Revitt

Dr Dirk Wildeboer

Faculty of Science and Technology
Middlesex University

September 2022

DECLARATION

I hereby declare that except where specific reference is made to the work of others, the contents of this thesis are original and have not been submitted in whole or in part for the consideration for any other degree or qualification in this, or any other University. This thesis is the result of my own work and includes nothing which is the outcome of work done in collaboration except where specifically indicated in the text. This thesis contains approximately 99000 words including appendices, references, footnotes, equations and has about 113 figures and tables.

Luciana Alves

September 2022

Signature: Luciana Alves

Date: September 2022

AKNOWLEDGEMENTS

To my beloved son, Manuel Alves, for his unwavering love and support, you gave me strength and motivation, making this experience worthwhile.

I want to express a special thanks to the various academics, PhD students and laboratory technicians in the Faculty of Science and Technology for their expertise, helpful advices, and indicatory hints.

I also want to thank the following persons and institutions for their great cooperation:

- From the Environment Agency (EA): Amanda Maclean, Richard Woodbridge, Pete Rudd, Lucy Shuker, Sandra Spinks and in special, Ross Bissel.
- Chantal Dave from Canal and River Trust (CRT).
- Richard Reeve from Thames Water.
- Victoria from Bureau van Dijk (BvD) – FAME.
- Adel Ibrar and TJ from Phenomenex.

There are yet three people I want to thank in particular; without them I would not have done this PhD, many thanks to my supervisors, Prof Lian Lundy, Prof Mike Revitt and Dr Dirk Wildeboer, who guided me through ups and downs during the development of this thesis.

Finally, I want to say thanks to the Middlesex University for the scholarship granted to me during the first 3 years of this research.

To others who I might have not remembered to acknowledge at the spur of the moment, you are all appreciated.

ABSTRACT

The EU Water Framework Directive requires all water bodies to achieve good ecological and chemical status by 2027. To achieve this a range of measures to improve the quality of water, particularly in urban areas, are required. It is within this context that this thesis uses a combination of field, laboratory and desk-based studies to identify contaminant loadings and their distributions within water bodies located in the Lower Lee catchment (London, United Kingdom). Specifically, water and sediment samples were collected at 11 sites on the River Lee, its' Navigation Channel and main tributaries, over a period of two years. Samples were analysed for a range of metals (cadmium, copper, lead, mercury, nickel, tin and zinc) and 11 polyaromatic hydrocarbons (PAHs) including anthracene, fluoranthene, benzo(b)fluoranthene and benzo(a)pyrene. Laboratory batch test experiments which focused on evaluating the release of metals from field sediments were undertaken to better understand the relationship between sediment and the overlying water column. Substance flow analysis (SFA) was then applied to predict mass loads of selected pollutants entering the receiving waters within 1 km of sampling sites to evaluate the potential use of the approach as a screening tool to identify pollutant hotspots in an urban river catchment. Field sampling data and substance flow analysis outputs were compared to evaluate the use of substance flow analysis as a desk-based approach to predict sediment pollutant hotspots in the field. Use of the approach as a tool to support catchment managers identify locations for interventions to improve water and sediment quality, as well inform the development of policies targeting environmental enhancement, are discussed.

The results show that mean cadmium (2.33 ± 2.79 µg/g), copper (141.07 ± 111.00 µg/g), mercury (0.53 ± 0.45 µg/g), lead (175.70 ± 82.96 µg/g) and zinc (499.92 ± 264.66 µg/g) concentrations in the sediment exceed selected Dutch (Esdat, 2000) and Canadian (CCME, 2001) sediment guidelines. Comparison of mean polyaromatic hydrocarbon concentrations against relevant Canadian and Dutch sediment guidelines also indicates exceedances. With regard to aqueous samples, results reported here refer to total metal concentrations whereas the United Kingdom Technical Advisory Group and European Union Environmental Quality Standard both refer to dissolved and/or bioavailable concentrations. Thus, the exact implications of comparison of results to these standards are unclear as the fraction of each metal in the dissolved phase was not determined. Batch test results indicated that the amount of metal released into the sediment varied between metals and sites with the level of variation generally within an order of magnitude, ranging from a minimum of 0.12 % (tin, site A) to a maximum of 6.12 % (cadmium, site E). Through the use of reported emission factors, the substance flow analysis results predicted that a total of 19,304 kg/year (sum of six metals) and 781 kg/year (sum of five polyaromatic hydrocarbons) were discharged from the identified activities into surface waters within 1 km of each sampling site , with Deephams Sewage Treatment Works associated with a total of 6,715 kg/year for metals and a total of 12 kg/year for PAHs, corresponding to 33.5% of the total discharges for all selected pollutants (metals and PAHs) by mass.

When evaluating trends in substance flow analysis predictions in relation to sediment field data, a very strong correlation ($r \geq 0.94$ and $p \leq 0.05$), was observed for the tributaries for cadmium, copper, mercury, lead and zinc, suggesting that substance flow analysis is a suitable tool to support catchment managers in identifying sediment metal hotspots in relatively smaller water bodies. However, the relationships between field and substance flow analysis data sets for metals at other sites and for PAHs at all sites (with the exception of anthracene) were not statistically significant. This indicates that all PAH predicted loads do not reflect those determined in river sediment. A range of substance flow analysis model limitations were identified, including the inability of the current approach to include emissions from combined sewer overflows and aerial deposition as well as account for in-sediment processes such as remobilisation, transport and degradation and further research in these areas is recommended.

LIST OF ABBREVIATIONS

A	Anthracene
AA	Annual Average
AADT	Annual Average Daily Traffic
ANOVA GLM	Analysis Of Variance General Linear Model
ASE	Accelerated Solvent Extraction
BOD	Biological Oxygen Demand
DOM	Dissolved Organic Matter
Bz(a)A	Benzo(a)Anthracene
Bz(a)Py	Benzo(a)Pyrene
Bz(b)Fl	Benzo(b)Fluoranthene
Bz(g,h,i)Pe	Benzo(g,h,i)Perylene
Bz(k)Fl	Benzo(b)Fluoranthene
C	Chrysene
Cd	Cadmium
CRM	Certified Reference Material
CRT	Canal and River Trust
CSOs	Combined Sewer Overflows
Cu	Copper
DBz(a,h)A	Dbenzo(a,h)Anthracene
DE	diatomaceous earth
Defra	Department for Environment Food and Rural Affairs
DO	Dissolved Oxygen
EA	Environment Agency

EfW	Energy from Waste
EU EQS	European Union Environmental Quality Standard
EU NACE	Statistical classification of economic activities in the European Community derived from the French *__N__omenclature statistique des __a__ctivités économiques dans la __C__ommunauté __e__uropéenne*
EU WFD	European Union Water Framework Directive
E-PRTR	European Pollutant Release and Transfer Register
FAME	Financial Analysis Made Easy
Fl	Fluoranthene
GC-MS	Gas Chromatography Mass Spectrometry
GIS	Geographic Information System
GLUD	Generalised Land Use Database
Hg	Mercury
HSD	Honestly Significant Difference
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
IDL	Instrument Detection Limit
In(1,2,3-cd)Py	Indeno(1,2,3-cd)pyrene
IPPC	Integrated Pollution Prevention and Control
ISQG	Interim Sediment Quality Guideline
IV	Intervention Values
LCA	Life Cycle Assessment
LFC	Lee Flood Relief Channel
MAC	Maximum Allowable Concentration
MFA	Material Flow Analysis

Ni	Nickel
N/A	Not applicable
OECD	Organisation for Economic Cooperation and Development
PAHs	Polycyclic Aromatic Hydrocarbons
Pb	Lead
PE	Population Equivalent
PEL	Probable Effect Level
Ph	Phenanthrene
PHS	Priority Hazardous Substances
PS	Priority Substances
PVC	**P**oly**v**inyl**c**hloride)
Py	Pyrene
REACH	Registration, Evaluation, Authorisation and restriction of CHemicals
RO	Reverse Osmosis
SD	Standard Deviation
SFA	Substance Flow Analysis
Sn	Tin
SPE	Solid Phase Extraction
STW	Sewage Treatment Work
SuDS	Sustainable Drainage Systems
TBT	Tributyltin
TV	Target Values
25 YEP	25 Year Environment Plan
UK SIC	Standard Industrial Classification of economic activities
UK TAG	United Kingdom Technical Advisory Group

US EPA	United States Environmental Protection Agency
Zn	Zinc

TABLE OF CONTENTS

Contents

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1. INTRODUCTION

1.1 Background

1.1.1 Legislative context

The European Union (EU) Water Framework Directive (WFD, 2000) aims to ensure that all European surface and ground waters achieve good chemical and ecological status by 2027 and although the UK has left the EU, a 25 Year Environment Plan (25 YEP) is being developed which incorporates EU environmental laws with the River Basin Management Planning approach still considered to be the main mechanisms utilised to achieve the relevant standards for water quality (House of Lords, 2020; Environment Agency, 2019b; Environment Agency, 2020).

As part of the EU Priority Substances Directive (EU EQS) (2013), 45 substances have been identified as being of particular concern with 24 of them classified as priority substances (PS) and 21 designated as priority hazardous substances (PHS) as presented in Annex X of the Directive. Whilst substances classified as priority substances (PS) were required to meet Environmental Quality Standards (EU EQS) by 2015, PHS designation requires emissions of these substances to water to cease by 2027.

Although under current implementation plans sediment quality plays a relatively minor role in the European Union (EU) Water Framework Directive (WFD), Article 3 of the Environmental Quality Standards Directive (2008) states that standards may be developed for sediment (in addition to water and biota) and calls for the long-term monitoring of priority substances that tend to accumulate in sediment. This demonstrates awareness at policy level that polluted sediments can impact on water quality across Europe. However, whilst sediment Environmental Quality Standards have yet to be developed at an EU level, various sediment quality guidelines have been developed independently by individual Member States and other nations adopting different methodologies. For example, there are guidelines established in Canada (CCME, 2002), The Netherlands (Esdat, 2000) and France (MEDD and Agences de l'eau, 2003) which were developed using a variety of approaches due to a number of open challenges in sediment monitoring, including identification of a suitable sampling technique, selection of the appropriate sediment compartment to sample (bed, bank or suspended sediment), and assurance of the reproducibility of the sampling and analytical techniques (UK TAG 2008a; UK TAG 2008b; Gilbert *et al*., 2005; Crane, 2003; Tokatli, 2019; Hoffman *et al*., 2019).

Several authors have reported concerns that the polluting impacts of humans are causing an accumulation of contaminants in a range of aquatic environments (e.g. Colas *et al*., 2011; Martínez *et al*., 2020; Shah, 2017). There is concern that these may reach critical levels and affect the UK's ability to meet targets set by Defra (2014) based on recommendations from the United Kingdom Technical Advisory Group (UK TAG) for protection of water and aquatic ecology under the European Union (EU) Water Framework Directive (WFD). Contaminated sediments have implications for wildlife habitats and species and the health of ecosystems both in water and on land (Da Costa *et al*., 2012; Lundy and Wade, 2011). Contaminants in sediments may be mobilised by river processes (e.g. storm events, influx from groundwater and bio-turbation) or human activities (e.g. dredging and permitted and unpermitted discharges of effluents and runoff). Remobilisation events can cause contaminants to be re-released into the overlying water column and subsequently re-located many kilometres downstream from the original sources (Turner *et al.*, 2008). Tackling the risks posed by contaminated sediment represents a significant challenge which has implications for the interaction between land-based activities, management of water and protection of the wider environment and human health (Macklin *et al*., 2006; Boelee *et al*., 2019).

Sediments not only constitute an indispensable part of aquatic ecosystems (e.g. as substrate for invertebrates and vegetation), they may also act as a sink and source for many substances. The degree to which pollutants associate with particulate matter is a function of the physico-chemical interactions between them (e.g. organic matter content, solubility) as well as the physico-chemical conditions of the immediate environment (e.g. pH, dissolved oxygen concentration). Sediment layers build-up over time and therefore may provide a reflection of the pollution history of a river basin, as well as acting as a secondary source of pollution when eroded or remobilised (Brils, 2008; Jones *et al.*, 2019; Foster and Charlesworth, 1996). However, surface river bed sediments can hold the most recent contamination (e.g 0-5 cm which are usually accumulated over one-year-period) (IAEA, 2003) and are more dynamic as they are more susceptible to resuspension and transportation and consequently impact even more the quality of surface waters (SedNet, 2004; Environment Agency, 2008a).

Although the introduction and use of chemical substances has provided substantial benefits to society, there have been associated negative effects on human and environmental health. The information available regarding the hazardous nature of many chemical substances is limited, as is knowledge about the impacts of their production and consumption on human health and the environment (European Sediment Network, 2006). To address this, the EU introduced the REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) Regulation (European Commission Regulation 1907/2006/EC, 2006) with the objective of protecting human health and the environment, ensuring chemicals are safely handled and that all necessary information on the properties of substances is provided by the manufacturers and importers to downstream users. Understanding the flow of a substance in a system is crucial in providing information on how a chemical impacts on the environment, associated levels of risk to target receptors and which remediation methods to implement. The implication of evaluating substance flows is that at some stage it will appear in product outflows, either as waste and/or during usage, released to the environment. For risk assessment, strategic environmental planning and waste management, knowledge concerning quantities and flows of hazardous substances is essential. This requires knowledge of the content, lifetime, emission factors and the amounts of products that are entering the market, which is often limited for many substances (Carlsson and Sörme, 2010).

1.1.2 Geographical context

The Lower Lee catchment in North-East London (UK) has a long history of water quality problems. It has been heavily modified over the last 100 years to cope with increasing urbanisation and to reduce the flood risk in the Lee Valley area. Currently, the River Lee receives major discharges of treated sewage effluent at two locations - Hoddesdon and Edmonton - and is also in receipt of multiple discharges from both combined and separate surface water sewer systems, which have been identified as significantly affecting the quality of the lower reaches of the river (Environment Agency, 2012). The chain of 13 reservoirs in the Lee Valley are owned and operated by Thames Water and store raw water for subsequent treatment and supply to Thames Water's London Water Resource Zone. There are a total of five water abstraction locations on the Lower Lee operated by Thames Water, all of which are governed under a single abstraction licence (Licence No. 29/38/08/0194, dated 20 September 1966) (Thames Water, 2015).

The Lower Lee is susceptible to the accumulation of sediments which have been shown to exert a high sediment oxygen demand (i.e. due to microbes breaking down organic matter) thus exacerbating the problem of already low dissolved oxygen levels (Environment Agency, 2015). In 2009, the Environment Agency commissioned the Land and Water Group to dredge years of accumulated sediment from the Tottenham Lock to Lea Bridge stretch of river (3.2 km); around 30,000 tonnes of sediment were removed and disposed of via landfill after bioremediation (Patroncini, 2013; Thames Water, 2012; Environment Agency, 2012; Land and Water Group, 2009). Analysis of the dredged sediment were carried out by Canal and River Trust (CRT) and results were used as comparison to findings reported in this study (Canal and River Trust, 2012). Gob *et al*. (2005a) argue that while dredging can be vital for water and sediment quality it can also have negative impacts such as increased suspended solids concentration and potential release of previously bound contaminants, can impact on the water habitat of native protected species making a channel more vulnerable to invasive non-native species and may only be a short-term solution, (i.e. unless sediment sources are mitigated, levels build up again). For example, despite dredging activities in the River Lee, dissolved oxygen levels continue to drop to zero on occasion, e.g. in response to rainfall events which generate combined sewer overflows. Efforts to mitigate such events include emergency aeration using hydrogen peroxide (Environment Agency, 2012). As an example, in July 2013 following the discovery of thousands of dead fish in the Lower Lee, the Environment Agency (EA) identified the Springfield Marina area as the source of the pollution event. Following a long spell of hot dry weather, there was a short intense storm which led to substantial amounts of silt and debris from the roads and gullies being washed into the river. The dissolved oxygen levels in the River Lee, dropped from 50 % - 70 % saturation before the rainfall event, to approximately 1 % over a seven-hour period causing the fish mortalities (Environment Agency 2013). Low dissolved oxygen levels (down to 0 % saturation) leading to fish kills were also reported in September 1993 between Tottenham and Springfield after a storm event which lasted for 1½ hours (Maddocks, 1993), in 2018 in the River Lee (Thames21, 2019) and again in 2019 taking place in an area running from Tottenham through Hackney (associated with oil spills) (Environment Agency, 2019b). Water quality data from the Environment Agency (2012) show that on 20th July 2007 the biological oxygen demand (BOD) in the Pymmes Brook, a tributary of the River Lee, increased from 4.4 mg/l to 28.2 mg/l over a period of 3 hours with flow data showing an increase from 5.09 m^3/s to 33.3 m^3/s in response to the same rainfall event.

The Environment Agency has also reported that tributyltin (TBT), a WFD priority hazardous substance, exceeded its EQS of 0.0002 µg/l a number of times between 2000 and 2011 in the River Lee at their Carpenters Road sampling site (Figure 1.1). Whilst the use of TBT as an antifouling paint to protect the hulls of boats was banned in 2008, potential sources remain from both the illegal application of old stores of TBT containing antifouling paint, as well as the resuspension/re-release of TBT from historically contaminated sediments. The EA also reported that benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, ideno(1,2,3-cd)pyrene and fluoranthene exceeded their respective EQS in surface water at various sites on the River Lee. These failures were attributed to urban diffuse pollution and re-releases from contaminated sediments (Environment Agency, 2012).

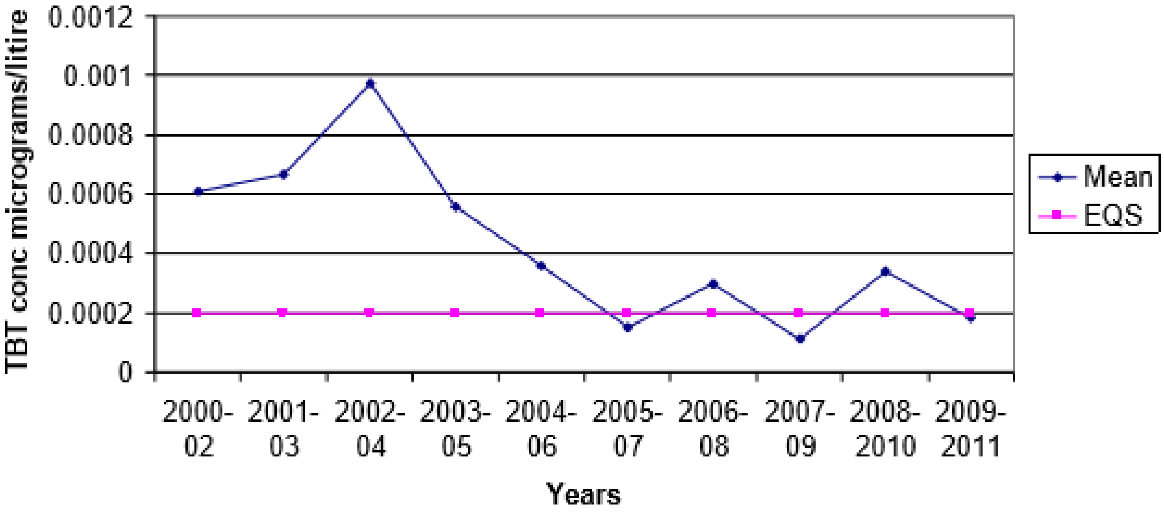


Figure 1.1 Three-year average TBT concentrations at Carpenters Road.
Source: Environment Agency.

1.1.3 Scope of the study

The scope of this work is to explore use of a substance flow approach to predict loads of target pollutants discharged into an urban river through identified activities. The results were ground-truthed through comparison with field monitoring data and used to identify sources of key pollutants and areas of concern for further investigation/mitigation.

The focus of this research is on the impact of an urban catchment on an inland urban river system in terms of its water and sediment quality. The River Lee, its Navigation Channel and major tributaries have been selected to represent such an environment. According to the European Environment Agency water resources are under pressure in many parts of the world with water quality being influenced by point and diffuse pollution due to human activities, posing a threat to the aquatic environment and human health. Therefore, it is essential to investigate water pollution sources in relation to land use processes and to understand the risks posed by *in-situ* contaminated sediment for water quality and ecological organisms. The term 'contaminated sediments' implies the presence of contaminants above pre-industrial or background levels which may or may not pose a risk to the environment or human health at those levels (Crane, 2003). It is also important to consider the potential consequences for the wider environment and the options which are available for their control, remediation or better risk management (Scholes *et al.*, 2008). Target pollutants for this project are the heavy metals (cadmium [Cd], copper [Cu], lead [Pb], mercury [Hg], nickel [Ni], tin [Sn] and zinc [Zn]) and PAHs (phenanthrene [Ph], anthracene [A], fluoranthene [Fl], pyrene [Py], benzo(a)anthracene [Bz(a)A], chrysene [C], benzo(b)fluoranthene [Bz(b)Fl], benzo(k)fluoranthene [Bz(k)Fl], benzo(a)pyrene [Bz(a)Py], dibenzo(a,h)anthracene [DBz(a,h)A], benzo(g,h,i)perylene [Bz(g,h,i)Pe]). These pollutants were selected taking into account the following considerations:

- Being included in the European Quality Standard list.

- Literature review reported previous contamination levels or possible contamination by the selected substances in the area and how likely they can be originated from sources explored in the substance flow analysis model (SFA), such as industrial activities and road runoff.
- Advice from the Environment Agency based on their knowledge and experience.
- Available analytical methods (for the monitoring stage), taking into consideration relevant parameters such as detection limits, sampling size and available storage.

Using substance flow analysis methodology, the research focuses on predicting selected contaminant loads released into surface water at the Lower Lee catchment. The fundamental assumption of SFA is that mass is not lost in physical or chemical processes but only transferred to a new medium or product (Kleijn, 1999; Brunner, 2012). SFA is an evaluation of the movement of a substance within a defined system including identification and quantification of inflows, stocks and outflows (e.g. exports and environmental emissions). It requires the definition of clear physical boundaries to the system under assessment and an identified time frame, normally one year (Revitt *et al.*, 2013). This technique has been previously applied to a range of priority pollutants (PP) in urban stormwater (Björklund *et al.*, 2011). Developing mass balances for specific substance flows within a system can help in identifying and quantifying the key sources of certain pollution problems underpinning the development of appropriate source reduction measures (Baccini and Brunner, 2012).

1.2 Research aim and objectives

This research aimed to explore and evaluate the use of substance flow analysis as tool to predict sediment pollution hotspots in an urban river through a combination of field, laboratory and desk-based studies. To address this aim, the following objectives were undertaken:

a) Completion of a two-year water and sediment sampling programme.

b) Completion of metal and PAH water and sediment analysis to evaluate the impacts of an urban catchment on water and sediment quality of a receiving river.
c) Laboratory batch tests to investigate the release of sediment-associated pollutants under varying physico-chemical conditions.
d) Development of a desk-based substance flow analysis approach as a potential management tool to identify and quantify point and diffuse loads of selected organic and inorganic pollutants originating in the Lower Lee catchment.
e) Implementation of the developed substance flow analysis tool and ground-truthing its predictions through comparison with field data.
f) Consideration of the potential use of the substance flow analysis tool to support catchment managers and policy makers identify locations for the installation of mitigation measures.

CHAPTER 2. LITERATURE REVIEW

2.1 Introduction

In the UK and elsewhere, industrial production increased rapidly after the Second World War and with this came increasing recognition that pollution from industry was of concern in relation to its impacts on the quality of air, soil and water. However, the deterioration of urban rivers, including their biodiversity, due to human actions was an issue largely ignored for many years. The typically held view was that the primary role of urban watercourses was for the disposal of stormwater runoff and effluents. However, recent changes on how the environment is viewed by the public has led to an increase in studies on the damage caused to urban rivers (Paul and Mayer, 2001; Prestes *et al*., 2006). The maintenance of healthy urban waterways is now viewed by the public and stakeholders as highly important and is supported in Europe by legislation such as the Water Framework Directive (Findlay and Taylor, 2006). The Eurobarometer surveys from 2011 and 2020 have shown that public opinion on the environment is shifting towards environmental issues being of more importance to European citizens, with 68 % of UK citizens stating that protecting the environment is very important to them (Eurobarometer survey 501, 2020) compared to 58 % in an earlier Eurobarometer survey held in 2011(Eurobarometer 365, 2011). For example, 95 % of respondents considered environmental change to be an important issue, and although citizens are aware of the importance of the actions of governments, corporations and the EU, 87 % of Europeans believe that they can play a direct role in benefiting the environment as the majority (76 %) state that environmental change has a significant impact upon their daily lives.

Many urban rivers receive significant inputs of contaminated sediments from their catchments and moves to re-habilitate urban rivers often creates slow flow water areas and in-channel vegetation growth where these sediments may accumulate (Gibbs, 2014). While river sediments are also composite products of erosion and weathering representing the source catchment area of a river basin, the role of sediment generation (and its contamination) by anthropogenic activities is also important, especially in lowland areas where population and industrial activities are concentrated (British Geological Survey, 2014). In order to plan and manage urban river rehabilitation schemes and comply with the EU WFD, identification and quantification of organic and inorganic pollutants become essential not only in the overlying water matrix but also in sediments (Gibbs, 2014).

Environmental protection of urban areas includes a wide variety of techniques in order to determine individual factors of pollution and stress to the urban environment (Matějíček *et al.*, 2002). To better visualise and understand natural systems, advances in information technology have been developed and employed with simulation models helping analysts plan, design and operate environmental systems since the 1960s. For example, by predicting the flow and storage of water throughout a system, especially in urban areas, Matrosov and Harou (2010) claim it is possible to evaluate how management systems and infrastructure configurations may react to adverse conditions such as droughts or flooding.

Modelling has become a powerful technique for describing, analysing, operating and evaluating complex systems, providing an efficient means of communication within the scientific community and for policy makers. SFA has become a fast-growing field of research with increasing policy relevance (Balat, 2004; European Environmental Agency, 2007; Brunner 2012). Models are a simplification of reality and have been defined as ‘a description of the essential aspects of a system, which represent knowledge of that system in a usable form’ (Sinha and Kuszta, 1983). Thus, whilst models do not typically attempt to be fully representative of a particular environment, they can nevertheless be very useful in developing management approaches (Meadows, 2001).

Predictive modelling, such as material flow analysis (MFA), has been available for a number of years helping to measure progress with resource productivity and materials use, and provide insight into the economic efficiency and environmental effectiveness of materials used in the production and consumption chain, up to final disposal. MFA-based analyses include approaches such as substance flow analysis, product flow accounts, material balancing, life cycle inventories and bulk material flow accounts. SFA is a specific type of MFA, dealing with the analysis of flows of chemicals of special interest. SFA is defined by the European Environmental Agency (2007) as a detailed level application of the basic MFA concept tracing the flow of selected chemical substances or compounds.

2.2 Water contamination

Palmquist (2001) argues that metal concentrations in urban rivers depend on the type and amount of industrial wastewater discharged into the municipal sewage treatment work (STW) and subsequently discharged to receiving waters, as well as directly discharged road runoff (Davis *et al.,* 2001). According to Lim *et al.* (2012), the spatial variability of metal content in river water and sediment depends on geochemical factors that also influence sediment-water interactions. Various chemical parameters such as DO, pH and temperature strongly influence the behaviour of many constituents present in the water such as heavy metals (Weiner, 2012). For example, in aquatic matrices, a lower pH will increase the solubility of metals such as Cd, Pb and Cr. It is also important to note that toxicity of the metals vary considerably by element and depends on factors such as oxidative stress and reactive oxygen with Cd, Hg and Pb amongst the metals which are most toxic in terms of their potential effects to the environmental and human health as each metal have exclusive physic-chemical properties that confer to its specific toxicity (Tchounwou *et al*., 2012). These metals are harmful to human health even at low concentrations, for example, Cd which is considered a carcinogen and can reach human body through inhalation and ingestion and can cause severe pulmonary and gastrointestinal irritation (Barus *et al*., 2021). Thus, background reference concentrations and toxicity of each metal are taken into consideration when setting quality standards (EU EQS, 2013).

Of the 45 substances identified in the EU Priority Substances Directive (2013), five are metallic, whilst the remaining 40 substances are organic pollutants. However, most water and sediment quality research has focused on pollutants other than organic compounds, such as inorganic nutrients, suspended solids and metals, for which analytical techniques are well established (Wegman *et al*., 1986). Only in recent years, due to rapid improvements in analytical methods for many types of organic pollutants, has the routine monitoring of low levels of a number of organic contaminants become possible (Björklund *et al*., 2011).

PAHs originate from many sources, both petrogenic and pyrogenic. In general, petrogenic substances include crude oil and refined crude oil products such as gasoline, heating oil, asphalt and lubricants, which have been released into urban environments from numerous human activities and industries over the past two centuries. Pyrogenic substances are complex mixtures of primarily hydrocarbon contents produced from organic matter subjected to high temperatures but with insufficient oxygen for complete combustion. Processes such as destructive distillation of coal into coke and coal tar, incomplete combustion of motor fuels and fires are the main sources of pyrogenic PAHs. Coal-tar based products, such as roofing, pavement sealers, waterproofing, pesticides, and some shampoos contain pyrogenic PAHs (a variety of shampoos are made with coal tar and therefore contain PAHs) (Boehm 2006). Lau and Strenstrom (2005) found that both commercial and industrial land uses and roads provided higher concentrations of both metals and PAHs than residential land uses. Steuer *et al*. (1997) found parking lots to be a major contributor of PAH contaminants and Eriksson (2002) also reported that urban runoff is one of the main sources of PAHs, with suspended solids in the water column being carriers of both metals and organic pollutants in urban rivers. Determining the sources of PAHs in urban rivers is a complex process and usually involves evaluating the ratios of individual compounds found in stream sediments. This method, although to be used with caution, is widely used to identify potential PAH sources (Environment Agency, 2015; Jiao *et al.*, 2017). With regard to land use in the Lower Lee catchment, in 2019/20, it was estimated that London population will increase by 70,000 every year, reaching 10.8 million in 2041 and to keep up with this population growth London needs 66,000 new homes each year (GLA, 2021). The developed areas will experience large and rapid changes in their current patterns of land use. The way land is managed has given rise to complex pollution issues with diffuse pollution being a major pressure on the water environment. Defra have identified a number of pressures that need to be addressed in the Thames River Basin District. These include abstraction and other artificial flow regulation; non-native species; organic pollution; pesticides; phosphate; physical modification; sediment; urban and transport pollution; chemicals (including priority hazardous substances, priority substances and specific pollutants). The occurrence of misconnections, surface runoff, discharges from industrial estates and contaminated urban rivers are regarded as the priority areas (Defra, 2009; Defra, 2015b; Environment Agency, 2013b).

According to Defra (2020) there is a need to improve the quality of ‘our water bodies’, reporting that only 16 % of water bodies in England are currently classified as ‘good status’ according to the standards established by the EU WFD (2000) although the 25 Year Environment Plan aims for at least ¾ of the water bodies to reach ‘good status’. Hence, it is necessary to plan for better water quality and protect sensitive local areas such as urban rivers, which can bring many benefits such as safeguarding jobs and businesses which rely on good quality water bodies and making these habitats better places for wildlife.

In England, rivers and bathing waters have become cleaner over the years, mainly due to large scale curtailment of point source discharges and upgrading of many, but not all, combined sewer outflows. For example, England bathing waters have continually improved since 1990 (when 27 % met the EU Bathing Water standards) to 97 % reported as achieving the required standards in 2015. However, much remains to be done with diffuse pollution now identified as a bigger threat to river water quality than point source pollution (Environment Agency, 2007).

It is now well understood that urbanised areas have a major impact on water quality due to current or historical pollution (United Nations, 2011; Weather and Evans, 2009; Royal Commission on Environmental Pollution, 2007; Church *et al.*, 2006). According to the Environment Agency, there are over 300 sites in England and Wales with contaminated land due to their industrial past contributing to 87 % of the rivers being at risk from diffuse pollution. Diffuse pollution sources are extremely variable with common examples being shown in Figure 2.1.

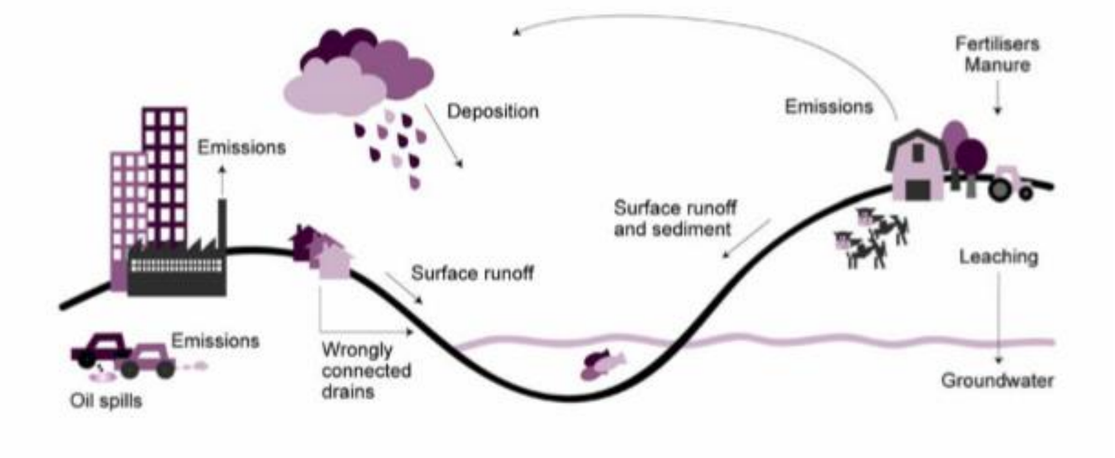


Figure 2.1 Common sources of diffuse pollution.
Source: Environment Agency 2007.

The Environment Agency monitors whether pollution incidents affect air, land or water and classify pollution incidents according to their impact on the environment and people, from category 1 (the most serious) to category 4 (little or no impact). In 2014 (England), most of the incidents affecting water were caused mainly by unidentified activities followed by non-permit activities[1] and permitted activities. From the unidentified activities, the Environment Agency found out that 27 incidents were due to unauthorised activity, such as fly-tipping and unauthorised waste management activities, and 25 were due to natural causes, such as algal activity and no cause was identified for 64 (48 %) of these incidents in 2014. From the 232 incidents, due to non-permitted activities most pollution incidents were associated with agriculture with other sources identified as transport and domestic/residential. Of the 249 incidents caused by activities with permits, most were caused by waste management activities and water companies (Environment Agency, 2015). These results further emphasise the seriousness and complexity of water pollution mitigation in England, although there has been registered a decrease in serious pollution incidents from 2013 (688 incidents) to 2019 (493 incidents) (Environment Agency, 2021).

Data from Defra demonstrated that in regard to water used by industry, approximately half the 12.7 billion cubic metres of water abstracted in 2006-07 in England and Wales was for public water supply, with the remainder largely accounted for by cooling uses in the electricity generation sector and by the agricultural sector. With predictions of warmer summers and wetter winters there will be more pressure on the water supply. Water losses through leakage occur primarily through the public water supply. Therefore, more efficient and sustainable ways of using water in order to have a secure water supply are needed. Water abstraction affects river flows and therefore their ecology. Another important aspect is that lower than average rainfall and low river flows can have an adverse effect on river quality because there is reduced dilution of pollutants. However, periods of intense rainfall can cause transportation of pollutants into rivers from catchments via mobilisation of previously deposited pollutants and

---

[1] Non-permitted sites or activities are sites that do not require a permit under the Environmental Permitting Regulations (EPR) – they may not require a permit, may be regulated by other legislation, or may be sites that are operating illegally.

in-pipe sediments as well as leaching from soils and in river resuspension of previously settled sediments (Defra, 2013; Defra, 2012a).

According to Thames21 one of the biggest single polluters in the Lower Lee catchment is Deephams sewage treatment work (STW) in the form of combined sewer overflows (CSOs) (Thames21, 2012). These occur when STW capacity is exceeded and results in the discharge of a combination of rainwater and raw sewage from businesses and homes in northeast London being discharged into the river to prevent overland flooding. At present, combined sewer systems comprise 40 % of the total network and are designed so that when capacity is reached, excess flow discharging untreated sewage via CSOs to adjacent watercourses (Thames Water 2013a). To meet the new discharge permit, set by the Environment Agency that came into force in 2017, Deephams is undergoing a major upgrading process to address existing capacity problems. It is also reported that in the Lower Lee catchment, up to 10 % of homes are misconnected which means that wastewater from washing machines, showers and/or toilets is entering the surface water sewer system (and thus discharges to local rivers) instead of into the foul or combined sewer pipes (Thames Water, 2015). Further problems in the catchment are the many highways and local roads in the River Lee catchment including the M25. There are more than 2.5 million private cars in London (Transport Statistics Great Britain, 2012), in addition to buses, lorries, taxis and vans. It has been estimated that about 16 % of vehicles leak oil every year which is subsequently washed into the rivers by rainfall events (Thames21, 2012 and 2011). Gardner *et al.*'s (2013) assessment of the treatment performance of 28 STWs across the UK, including Deephams STW, revealed that despite a typical contaminant removal of 80 % to 90 % for many substances, wastewater discharges could still contribute to failed compliance with the EU environmental quality standards (EU EQS) (2013) in surface water quality. This assessment was done through analysis of sewage samples at different treatment stages, which included nine urban catchments across the UK and the principal sources of targeted substances were identified as domestic rather than industrial, with metals such as Ni and Zn having their main sources as domestic sewage (34 % and 64 % respectively) followed by runoff (25 % and 15 % respectively). For Bz(a)Py the main source was industry (37 %) followed by runoff (36 %) then domestic sewage (18 %).

Urban rivers are often contaminated by organic pollutants especially in areas with heavy industrial use, urban traffic, petroleum product leaks and CSOs, all of which have been identified as sources of PAH contamination (Sower, 2008). In previous studies of urban rivers, Brown and Peake (2006) found that stormwater runoff is likely to be a major contributor of anthropogenic PAHs to urban river sediments over time. Sower and Anderson (2008) and Brun *et al.* (2004) reported that PAH deposition is greater during seasons with higher precipitation and lower temperatures due to the presence of increased vapour phase atmospheric PAHs, particularly of lower molecular weight (up to three aromatic rings), which are more volatile PAHs and easily detected in the vapor phase whereas the higher molecular weight (lower vapor pressure PAHs) are sorbed to atmospheric particulates more readily to deposition (Abdel-Shafy and Mansour, 2016).

2.3 Sediment contamination

In polluted waters, many contaminants are predominantly adsorbed to suspended particles in the water column and to sediments settled on the river bed. This identifies sediments not only as pollutant sinks but also as potential sources of contamination as a result of changes in environmental conditions and/or anthropogenic disturbances. Sediments represent a more stable medium for tracing metal sources compared to water (Owens *et al*., 2001). Whereas aqueous phase sampling provides an indication of metal concentrations on a relatively short time scale not exceeding hours, sediments can be representative of pollutant trends over longer periods, usually up to one year (Breault and Granato, 2000; Owens *et al*., 2001 and Taylor *et* *al*., 2008). For this reason, bed sediments have been increasingly employed in the assessment of the contamination of fluvial systems in urban and suburban areas (De Miguel *et al.*, 2005; Blecken *et al*., 2012; De Carlo and Anthony, 2002; Rentz *et al*., 2011; Sebakira *et al*., 2010; Sutherland, 2000).

In aquatic systems, contaminants are mainly found adsorbed onto suspended particles in the water column and bound to sediments settled on the river bed. This identifies sediments not only as pollutant sinks but also as sources of contamination when environmental conditions (driven by natural or anthropogenic disturbances) result in changes in physico-chemical conditions which lead to the remobilization of pollutants to the aqueous phase (Chapman 1992). The particulate matter and retained pollutants will, depending on the river geomorphology and hydrological conditions, be transported within the river system (Viganò, 2000).

Results from studies carried out by Gibbs (2014) highlight the importance of understanding the potential effects of urban river restoration on sediment availability and channel hydraulics and consequently on sediment contaminant dynamics. Taylor and Owens (2009) summarise the sources of sediments and contaminants to urban river basins with the main natural sources of sediments to rivers being atmospheric dust deposition and mass movement events such as landslides and erosion of soil. The major sediment sources associated with anthropogenic activities are from mining, construction, urban road networks, industry and STW.

The Environment Agency reported that 23 % of rivers in England and Wales are at risk from high levels of sediment build-up, physically blocking river-bed gravels and consequently reducing the supply of oxygenated water to aquatic plants and animals. This was exemplified by a study across southern England in 2000 which reported that 28 out of 31 trout spawning beds contained enough fine sediment from soil to kill half its load of eggs and larvae (Environment Agency, 2007).

Along with an increase in global population since the beginning of 20th century there has been a rapid increase in metal production with humanity's sphere of life consisting of a complex system of energy, information and material fluxes. As an example, half of the total world zinc production took place during the last three decades, especially in urban areas. However, the present knowledge of location and mass of accumulated amounts of metals is not certain (Baccini and Brunner, 2012). Metal-containing materials are found in e.g. infrastructure, vehicles and buildings and large surfaces of these materials in contact with air, water or soil can lead to significant amounts of metals being released to the environment over extended time periods (Sörme *et al.*, 2001).

The sediment quality of the River Lee is also affected by anthropogenic activities. In 2008 an analysis of its sediments revealed they were contaminated mainly by heavy metals and (PAHs) (Sodomková, 2009). Such sediment deposits were considered, in part, to be responsible for the low dissolved oxygen levels in overlying waters due to its high sediment oxygen demand (SOD). For this reason, between February and April 2009, dredging operations were undertaken in the reach along a 7 km stretch of waterway from Tottenham Lock downstream to Old Ford Lock (Sodomková, 2009). However, low dissolved oxygen levels continued occurring in the area causing problems such as the incident of dead fish in July 2013 (Environment Agency, 2013a). Dredging activities as such remobilize sediments not only from superficial sediment layers but also from deeper layers resulting in the re-release of historic contamination (Machado *et al.*, 2011; Fonseca *et al.*, 2016).

2.4 Substance Flow Analysis (SFA) approach

Article 3 of the European Commission Environmental Quality Standards Directive (2008) states that “causes of pollution should be identified and emissions should be dealt with at source, in the most economically and environmentally effective manner”. However, by its very nature, diffuse contamination is much more complex than point-source pollution in terms of identifying contributing sources and their mitigation, and while much has been done with regard to investigating sources of metals in urban environments much less work has focussed on identifying and mapping the distribution and sources of organic pollutants. Sörme and Lagerkvist (2002) emphasise that a more robust study of diffuse pollutants is important to make it possible to apply remediation methods to prevent further discharges into the environment. Authors such as Ellis and Mitchell (2006) have addressed the problem of tackling diffuse water pollution in urban environments, using prediction of pollutant loads and impact assessment at a sub-catchment level.

Substance flow analysis (SFA) is used for tracing the flows and stocks of a selected substance or a limited group of substances through a defined system (Brunner, 2012). One of the major contributions of SFA is that it focuses on mass balances of a substance with quantities being the first and most important characterisation aspect in this methodology (Sörme *et al.*, 2001). Lindqvist-Östblom *et al.* (2009) argue that knowledge about the magnitude of stocks and flows of a certain substance contributes to the environmental management process informing about the potential of a future pollution problem. An example of SFA is presented on Figure 2.2 below where the SFA covers PAH flows during one year for an urban catchment area located in the Gothenburg municipality (Sweden). The total amounts of PAHs emitted from traffic and road wear was calculated to be 990 – 3900 µg per driven vehicle kilometre and the total amount of PAHs emitted annually from the studied area may be as high as 32 – 160 kg with the main sources of PAHs include tyre wear, oil leakage, road surface wear. The SFA results were compared to measurements of PAHs in accumulated sediments in the case study area and sources such as exhaust gases and tyre wear were identified as dominant sources (Markiewicz *et al.*, 2017).

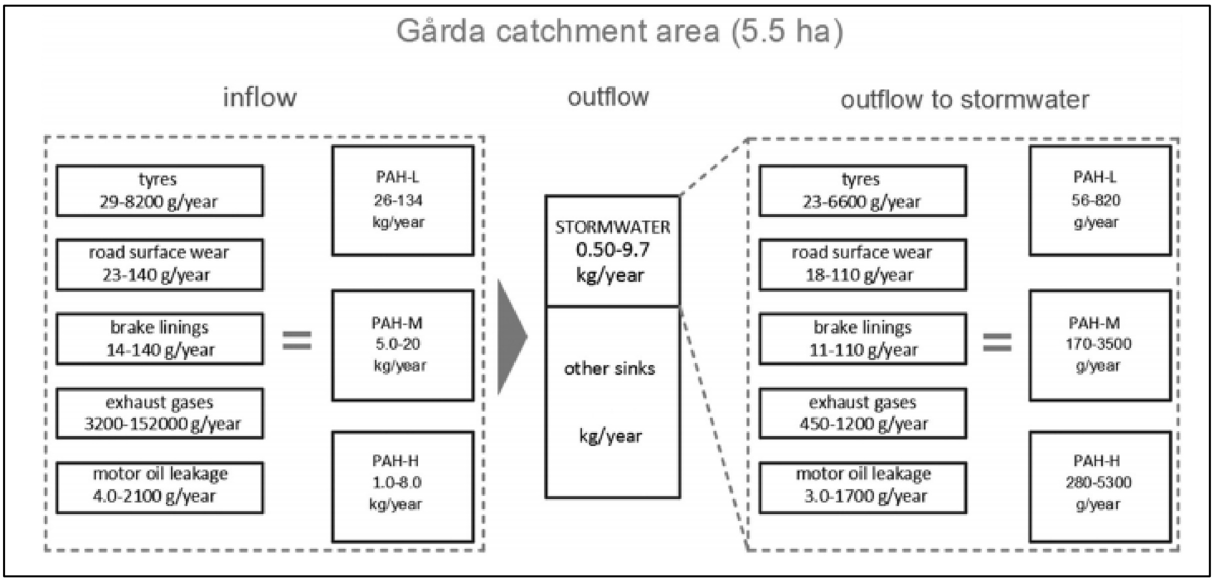


Figure 2.2 Flow chart of the SFA for the Gårda catchment area, with main sources of inflow, outflow to the stormwater facility and other sinks of PAHs identified.
The PAHs have been divided according to their molecular weight as follows: PAH-L (low); PAH-M (medium); and PAH-H (high). Source: Markiewicz *et al.*, 2017.

The SFA approach, provides an alternative methodology for determining the impacts of different strategies for reducing pollutant loads derived from point and diffuse sources as well as recognising the importance of legislation and voluntary controls (Revitt *et al.*, 2013). Brunner and Ma (2009) have pointed out the importance and benefits of the SFA approach especially as a tool to inform waste management decisions through the provision of crucial missing information (e.g. identifying the location of hazardous compounds). It is also useful for modelling and evaluating the fate of crucial substances in contaminated environments at the municipal level. Another opportunity for SFA is to assess the potential constraints on resources and materials in future technologies (Elshkaki, 2007). This will provide scientific support to facilitate the remediation decision-making process by any stakeholder or organisation (Arena and Gregorio 2014) based on the provision of both quantitative and qualitative information (Donner *et al*., 2010).

According to Baccini and Brunner (2012), the flow of pollutants in urban systems can be analysed using techniques such as SFA, providing a more cost-effective tool to contribute to achieving sustainable development objectives. Each study is unique due to influences of parameters specific for each urban area. However, difficulties faced whilst performing an urban water balance are more uniform. The main problem faced by many authors was the lack of the necessary data to enable efficient performance of the used software or the applied model.

Some of the initial SFA studies were undertaken in the 1980s by Brunner *et al.* (1990) and Baccini and Brunner (1991) and for the past thirty years SFA has been applied in various fields such as e-waste management, agriculture, water quality and economics and implemented in a number of software packages e.g. STAN (**s**ubs**t**ance flow **an**alysis) and OMAT (**o**nline **m**aterial flow **a**nalysis **t**ool) (Morf *et al*., 2008), tools which support users to create their SFA models. However, there are limitations, for example, the STAN freeware that supports analysis of substance flows according to the Austrian standard ÖNORM S 2096, cannot identify a missing flow or process; it is not available to be downloaded onto different computer types, for example, Macs and cannot do dynamic modelling. Amongst the different SFA methodologies, Brunner and Rechberger (2016), also highlight the advantages in using Microsoft Excel to perform SFA. Advantages include the fact that many users are already familiar with this software, it offers flexibility and is usually already installed on personal computers, which means that one does not need to acquire additional bespoke software to undertake SFA.

Danius and Burstrom (2001) state that the main benefits and limitations of MFA and SFA are that both methods involve integrating all available data and knowledge relating to material or substance flows to facilitate comparisons and this compilation of data is usually presented as a discrete number i.e. without any indication of associated uncertainty levels. This practice gives a false impression of accuracy. However, in many cases more is known about the data than just the figures as such, and therefore expert estimates can support identification of a single averaged or most certain figure. For example, Antikainen (2005) presented a detailed quantification of the flows and stocks which included a methodology for assessing uncertainties, presenting it as detailed as possible and also giving intervals for variables such as target pollutant concentrations of different products. Hedbrant and Sörme (2001) calculated uncertainty intervals using traditional statistical methods. Antikainen *et al.* (2005) informed that SFAs can be seen as surveys of potentially problematic flows whereas an SFA related to a single substance is usually not sufficient to give any specific recommendations. One reason for this are the uncertainties related to the magnitude of flows. Thus, complementary studies using different kinds of methods are necessary to develop a more robust understanding of the subject (Palm, 2002).

Scarcity of data on chemical content, inaccessible information, and use of data from single references are frequently occurring problems when performing SFA (Eriksson *et al.*, 2008; Månsson *et al.*, 2008) and this is an important restriction on the applicability of SFA for many pollutants. Lack of data availability has been reported as a key limiting factor when performing SFA. In addition, available data can be limited in terms of accuracy and reliability in subsequent decision-making processes (Graedel *et al*., 2004; Chen and Graedel, 2012).

According to Lindqvist-Östblom (2002) SFA are not to be seen as a direct basis for decision-making, even at the micro level, although they concluded that SFA can increase the understanding by municipalities of the complexity of environmental problems. SFA has also been applied in combination with life cycle assessment (LCA) with one of the first studies, combining both techniques, undertaken by Tukker *et al*. (1998) with an analysis related to polyvinylchloride (PVC) and PVC additives in order to influence Swedish policy making to plan and implement measures to further control PVC emissions. In this direction, other research started to take place, such as Azapagic *et al*. (2007) as they combined LCA, SFA, fate and transport modelling of pollutants and geographical information systems (GIS) to integrate and visualise the results from SFA modelling to identify hotspots within an urban environment. Although the combined method focuses on the urban environment, it helps "understand the wider environmental implications of the activities that support urban living but occur elsewhere in the life cycle, often far away from the urban area of interest", thus preventing the shifting of problems to other areas.

Danius (2002) prefers to call the SFA method a tool for learning, rather than a tool for decision-making. Two reasons are given for this. The first is that figures from an SFA study can inevitably be questioned, simply because other input data, other system boundaries, or other variables could have been selected. The second reason is that an MFA/SFA study does not give a single correct answer; rather the final decision is always influenced by personal values and political opinions. However, it is reasonable to ask what exactly the difference is between a tool for learning and a tool for decision-making. The extra information obtained about a subject through the use of a tool for learning by definition is reported to improve the basis for decision-making (Antikainen *et al*., 2005; Ling *et al*., 2009).

The treatment of uncertainty within environment models is widely reported by Beven (2009). The author recognises the role of the EU WFD in promoting the use of a holistic approach and views data as including model predictions. Antikainen *et al*. (2005) point out that SFA normally only considers the total mass of the studied substances flowing in the system and does not discriminate between the fractions that can be harmful versus those that may be relatively inert/not bioavailable. The interpretation of SFA results can consequently be difficult, and their usefulness in decision-making may be limited. Whilst SFA modelling is data and time consuming, it also does not reveal many essential factors behind the sustainable use of natural resources, such as the energy flows and does not cover the links with monetary flows which are often the main driving force behind the socioeconomic system. Work by Rotmans and Van Asselt (2001) suggests an approach that includes assessing uncertainty taking into account the needs of the policy maker and using a range of methods (e.g. standard approaches such as sensitivity analysis, probability-based methods as well as less used approaches such as hedging-oriented methods) to quantify uncertainty. There have also been assessments of uncertainty in a number of models (e.g. Pappenberger *et al*., 2005; Sörme, 2003; Van Gils *et al*., 2020) and the recognition that the increase in numbers of models being evaluated results in a huge increase in the number of simulations undertaken.

Yoshida *et al*. (2015) applied SFA to a municipal wastewater treatment plant to determine the fate of constituents in the main individual treatment processes as well as overall removal rates. In their study, although, results showed evidence that both organic and inorganic contaminants accumulated in the sewage sludge there were a number of uncertainties associated with mass flows as the study was based on gaseous emissions (which are more complex to observe) and not all specific information was available for all the substances investigated. Jamtrot *et al*. (2009) highlight that SFA modelling requires the involvement of several important contributors such as local authorities, industries, businesses and local shop owners, which can be a barrier if they do not wish to communicate the required information. However, SFA is still a useful tool for screening in order to identify areas and pollutants for further and more detailed investigation. For a case study city with 802,600 inhabitants, it has been shown that major sources of Cd are long range transport, traffic and car washes (11, 10 and 8 kg/year respectively), dominant Hg sources are erosion of tyres, erosion of roads and incineration of non-hazardous waste (77, 16 and 8.6 kg/year respectively) and the main sources of benzo(a)pyrene are domestic wood burning, road transport and domestic greywater (8000, 4600 and 526 kg/year respectively) (Jamtrot *et al*., 2009). Chèvre *et al.* (2010 and 2011) report that around 1500 kg/year of Cu, 9.3 kg/year of Cd and 4000 kg/year of Zn enter surface water from urban surfaces (of Lausanne city, which is around 42 km^2 with 130,000 inhabitants) during rain events (considering an average of 1122 mm of rain per year), with the major source of Cu being roofs and major source of Cd and Zn being urban furniture.

Van Gils *et al*. (2020) introduced a computational material flow analysis to predict the occurrence of organic chemicals on a European scale as a complement to surface water monitoring data, but it does not account for substances being released from contaminated sediments.

Denmark provides an example of SFA being used as tool to inform a substance management strategy with the Danish Environmental Protection Agency (Danish EPA) commissioning SFAs, based on substances which have been identified as hazardous to humans and/or the environment the results are used for risk minimisation of the substance in question and for the monitoring of policy success in controlling the substance (Wiedmann *et al*., 2006).

CHAPTER 3. MATERIALS AND METHODS

This chapter describes the materials (including tools and essential chemicals) used in the experiments undertaken in this research. It also details a description of the study area and step-by-step of the monitoring and modelling techniques applied.

3.1 Site Description

Once the Lower Lee area was covered by the Forest of Middlesex which stretched from Brent to Waltham Forest and back in the 13th century the clearing of the forest exposed many of the catchment streams. The Lower Lee catchment stretches for 34 km, from the south of Hoddesdon in Hertfordshire (UK) to Poplar in London where it joins the River Thames. Within this stretch, the River Lee flows through an increasingly urbanised environment as it passes through the London boroughs of Waltham Forest, Enfield, Barnet, Haringey, Hackney, Islington and Newham (Figures 3.1a and 3.1b). The main tributaries in the Lower Lee catchment are the Cobbins Brook, Salmons Brook, Ching Brook, Pymmes Brook, and the waterways in the Lower Lee Valley include the River Lee Navigation, Old River Lee, and the Lee Flood Relief Channel (FRC). Primary uses of the river include:

- water supply for 10 % of London’s population,
- a recipient for treated sewage discharges,
- navigation,
- recreation on and next to the water, and
- environmental interests such as protected areas for wildlife (Environment Agency 2013).

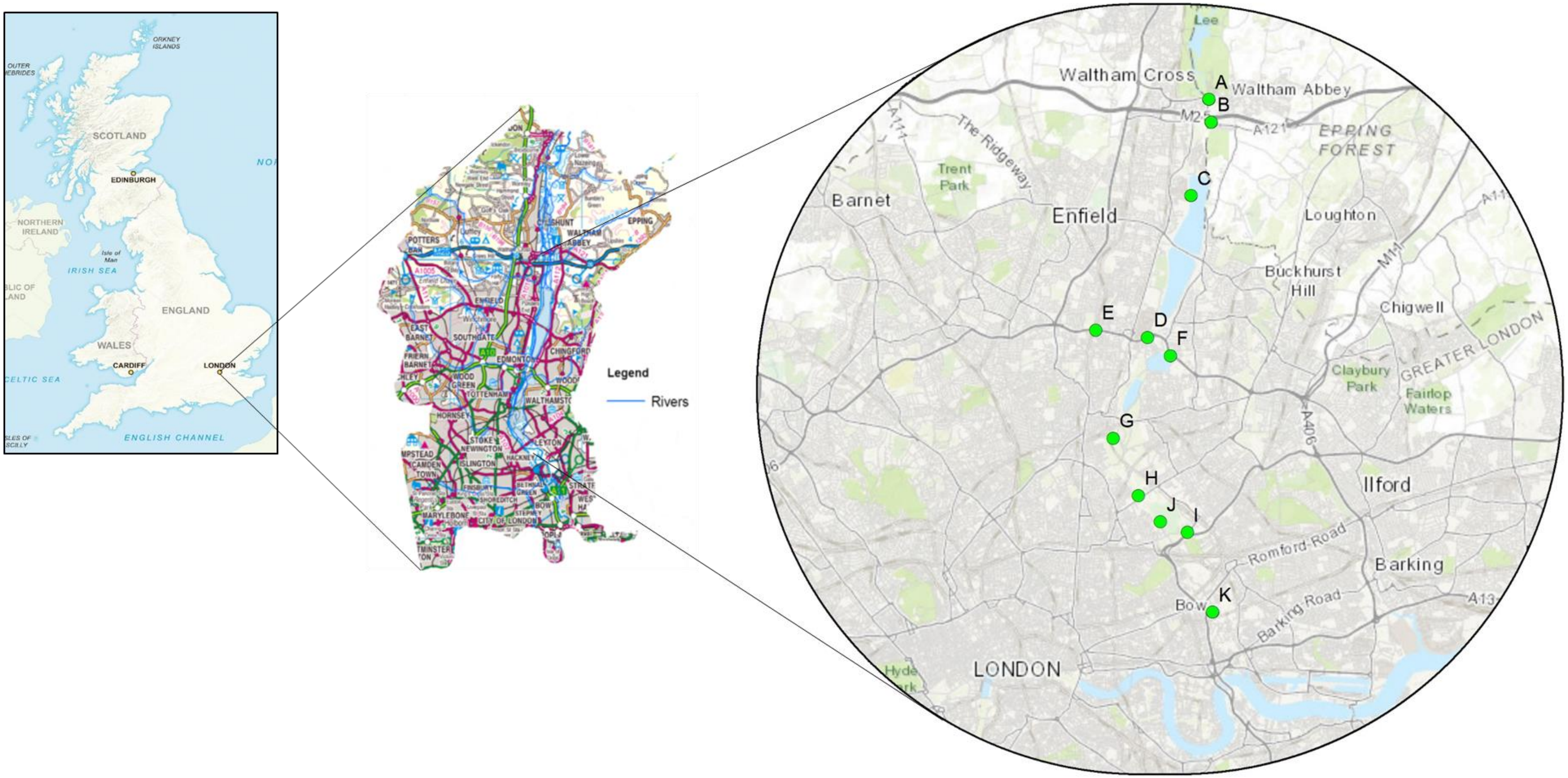


Figure 3.1a. Map of the Lower Lee Catchment and sampling area.
Sources: Environment Agency and Ordnance Survey map.

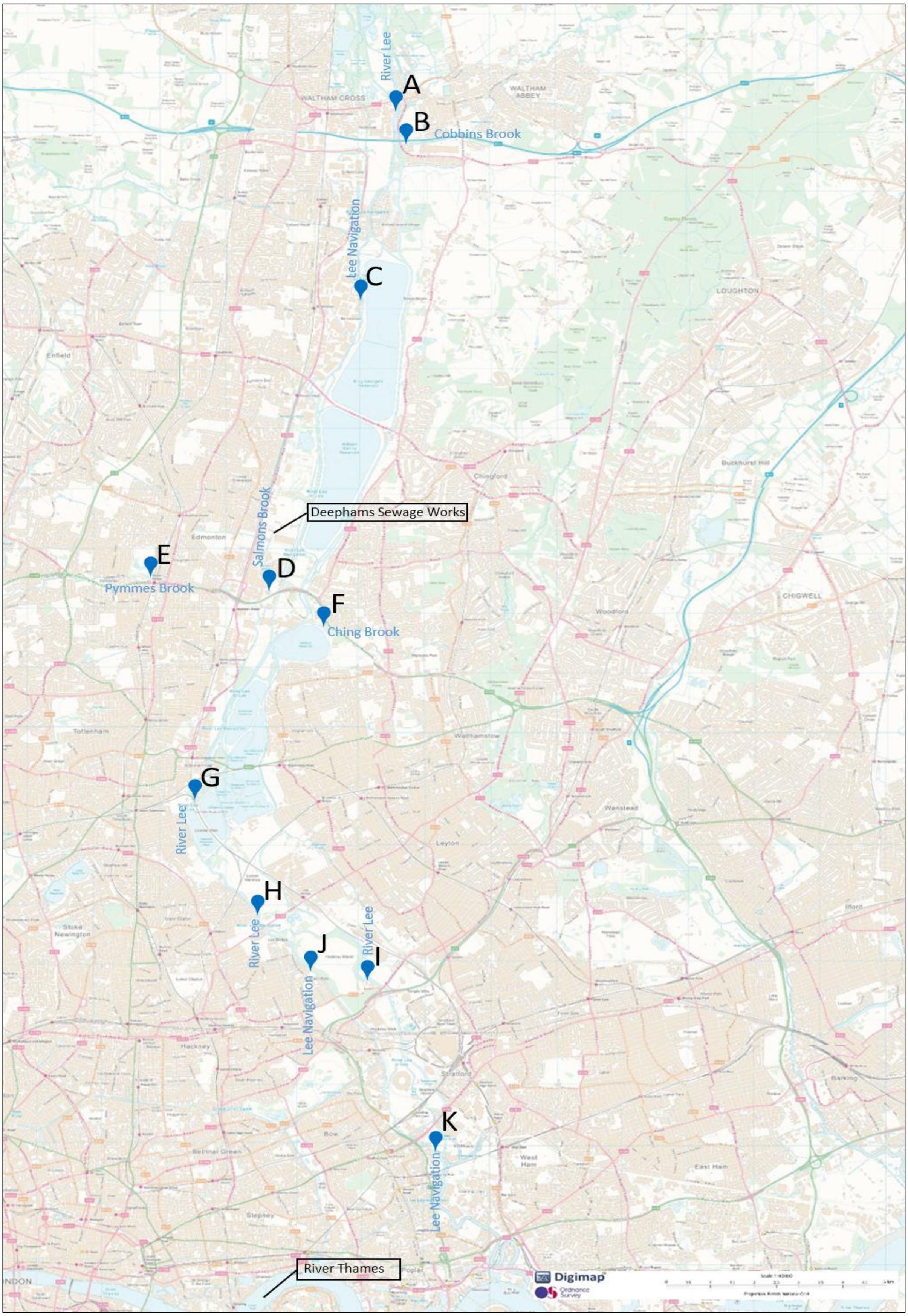


Figure 3.1b. Ordnance Survey map of the Lower Lee sampling area. Source: Edina, 2021.

The catchment area of the Lower Lee from Feildes weir (its upstream marker) to its confluence with the River Thames is around 440 km^2 (Thames21, 2015). The Environment Agency have undertaken extensive work on some of the Lee's tributaries, particularly the Pymmes, Cobbins and Salmons Brooks, where artificial channels or culverts have been installed as part of flood protection initiatives. However, flood risk levels are continuously exacerbated by the building of new housing developments throughout the Lower Lee catchment. The Lower Lee geology comprises London clay with deposits of alluvium and river gravels, overlying chalk. The consequences of this geology and the highly urbanised nature of much of this catchment are that local rivers respond rapidly to rainfall and are liable to sudden flooding after storms. Thus, a high percentage of rainfall runs off directly into the watercourses generating short, high peaks in river levels. The catchment has an annual average rainfall of approximately 637 mm (London RFRA, 2014; Thames21, 2013a and 2013b; Environment Agency, 2012). The rainfall data necessary for this research was provided by the Environment Agency from two different rain gauges located in the Lower Lee catchment (Reference grids: TQ41282 98094 and TQ30557 89795). Therefore, data means for these two rain gauges were used.

Most of the Lower Lee catchment is served by Deephams STW located off Picketts Lock Lane in Edmonton adjacent to the Lee Navigation and its tributaries (including Salmons Brook which receives direct discharges from Deephams STW). It serves a population equivalent (PE) of around 1,000,000 people (Thames Water, 2013). The sewer catchment which Deephams STW serves extends over large parts of northeast London and northwards beyond the M25. According to the Environment Agency (2013), in some areas, rainwater falling on roofs, roads and pavements is collected in surface water sewers which discharge directly to local watercourses. However, in some parts of the Deephams STW sewer catchment, surface water and sewage are carried by combined sewers to the treatment works. Many of these combined sewers were originally watercourses that were turned into pipes or culverts and incorporated into the sewerage system. Raw sewage arising in the Deephams sewerage catchment area arrives at the sewage works via the following three main gravity trunk sewers:

- The Lee Valley Sewer (serving Waltham Abbey, Cheshunt, Cuffley and north

east Enfield),

- The Barnet High Level Sewer (serving east Barnet and south and west Enfield),

and

- The Tottenham Low Level Sewer (serving Tottenham, Wood Green and south

east Enfield).

and a smaller area served by Beckton STW fed by the Northern Outfall Sewer, which is a gravity sewer running from Wick Lane in Hackney to Stratford and is characterised by a mixture of combined and separated sewer network (Thames Water, 2012a). Deephams and Beckton (both owned by Thames Water) receive flow from domestic and commercial premises within the catchment. This includes discharges from toilets, wash hand basins, baths, washing and dish washing machines. These discharges are conveyed from their source to the STW for treatment. The sewage works also receives discharges from industrial premises, though some of these flows require specialist pre-treatment at source as part of their consent to discharge to sewer.

3.2 Sampling site identification and collection and storage of samples

For this study, 11 sampling sites were selected and labelled A to K as presented in Table 3.1 and Figures 3.1a and 3.1b.

Table 3.1 Location of sampling sites.

Sampling Sites	Description	Reference Grid	Nearest address
A	River Lee. Upstream site, above M25. Less urbanised area with a mixture of residential and recreational (e.g. Lee Valley White Water Centre, Waltham Abbey Gardens) areas.	TL37548 00525	Highbridge Street EN9-1BD
B	Cobbins Brook just before confluence with River Lee. Mainly a warehouse area where one of the Sainsbury Supermarket distribution centres is located. Cobbins Brook received direct road runoff discharges from A121.	TQ37650 99743	Meridian Way EN9-1EJ
C	Lee Navigation Channel after confluence with Turkey Brook. Industrial/warehouse area with a number of companies such as Cannon Stell Ldt, Warbutons, BOC Gas etc.	TQ37022 97197	Millmarsh Lane EN3-7UY
D	Salmons Brook before confluence with Pymmes Brook and Lee Navigation Channel. Industrial area where it is also located EcoPark is a waste-to-energy plant which burns waste from several London boroughs to provide electricity for the National Grid.	TQ35647 92283	Advent Way N18-3AG
E	Pymmes Brook before confluence with Salmons Brook. Residential area with local business and parks.	TQ33856 92493	Victoria Road N9-9SU
F	Ching Brook before confluence with River Lee. Mixture of residential area with a number of warehouses such as Costco, B&Q etc.	TQ36466 91678	Harbet Road N18-3QP
G	River Lee below confluence with Lee Navigation Channel, Pymmes Brook and Salmons Brook. Residential area	TQ34562 88790	Yarmouth Crescent N17-9PQ
H	River Lee before splitting into Lee Navigation Channel and River Lee itself. Residential area with growing number in building developments. Constructions of new flats were underway at the time of this research.	TQ35479 86835	Lea Bridge Road E10-7QL
I	River Lee at Hackney Marsh which is an area of public open space for sports and recreational use.	TQ37213 85616	Homerton Road E9-5PF
J	Lee Navigation Channel next to Hackney Marsh which is an area of public open space for sports and recreational use.	TQ36259 85948	Daubeney Road E5-0EP
K	Lee Navigation Subsidiary at Three Mills Lane. Residential area with growing number in building developments. Constructions of new flats were underway at the time of this research.	TQ38150 82890	Hancock Road E3-3DA

The sites were chosen taking into account the following considerations:

- Allowing enough distance between sites to capture different types of land use and water bodies (River Lee, Lee Navigation Channel and main tributaries).
- Results of face-to-face discussions with the Environment Agency who shared their local knowledge and experience of the Lower Lee catchment with regard to flow characteristics, access points and sediment behaviour.
- Accessibility – sites had to be accessible for the samples to be collected.
- Risk assessment – to identify and mitigate risks using safety procedures, protocols and resources from Middlesex University and the Environment Agency.
- Sampling time – all sites had to be sampled in one day, taking into consideration the holding time (samples to be stored at 4° C in laboratory refrigerator the same day).

Site A (an upstream site located in a more rural outer London location) was initially identified as a background site against which the impacts of moving from a rural outer London location to a more intensively urbanised inner London location (i.e. results from sites B to K) could be benchmarked. Whilst inclusion of a site close to the source of the River Lee was initially considered, the source is located outside the study catchment area (in the Upper Lee catchment) and with restricted access. On this basis, Site A was selected as the most upstream site in the Lower Lee catchment located in an accessible, more rural outer London area.

Water and sediment samples were collected at the 11 sites in the Lower River Lee catchment area (Figure 3.1a and 3.1b). A sediment grab (196-B15 Ekman bottom grab from Wildlife Supply Company) was used for sediment collection and a water sampler (183 cm long pole with a 500 ml polypropylene cup from Cole-Parmer UK) for the collection of water samples.

Surface water samples were collected approximately 1.5 m from the river bank and immediately transferred to 500 ml acid washed plastic labelled bottles (for metal analysis) and 500 ml glass bottles (for organic analysis). All water samples were stored in an ice-packed cooler during transfer to the laboratory. Water samples were subsequently stored in a refrigerator at 4 °C until preparation for analysis. Surficial bottom sediments were collected at each site and transferred to labelled plastic bags. All sediment samples were also stored in an ice-packed cooler during transfer to the laboratory. On arrival at the laboratory, sediment samples for metal analysis were dried overnight in an oven at 105 °C and those for organic analysis were dried at 50 °C. Dried samples were ground manually in a porcelain mortar and sieved to ≤ 1 mm, prior to extraction for metals or organic analysis.

3.2.1 Additional field data collection

At the time of sampling, temperature, dissolved oxygen (DO meter: Mettler Toledo Seven Go pro SG6) and pH (pH ATC Pen meter) levels were measured in water samples. However, whilst a wide range of physico-chemical factors are known to influence the behaviour and fate of contaminants in river sediments e.g. organic matter content, sediment pH, dissolved oxygen concentration (Brils, 2008; Jones *et al.*, 2019; Foster and Charlesworth, 1996; Rahm *et al.*, 2005), it was not possible to measure these parameters in the field due to water body depth. As an approach to addressing this limitation, batch laboratory experiments (see Sections 3.8 and 4.4) were undertaken.

3.3 Dates of sample collection

The eight collection dates (see below) span the course of a year and include all four seasons. Samples were collected on the following dates:

- 11th November 2014: Temperature: high = 14ºC and low = 9ºC; cloudy day with sunny spells at times.
- 9th December 2014: Temperature: high = 12ºC and low = 0ºC; cloudy day.

- 11th March 2015: Temperature: high = 14ºC and low = 3ºC; sunny day with clear sky.
- 15th April 2015: Temperature: high = 25ºC and low = 9ºC; hot sunny day with clear sky.
- 20th May 2015: Temperature: high = 16ºC and low = 4ºC; cloudy day.
- 1st July 2015: Temperature: high = 30ºC and low = 13ºC; hot sunny day with clear sky.
- 14th August 2015: Temperature: high = 21ºC and low = 15ºC; storm weather with heavy rain and thunder.
- 23rd March 2016: Temperature: high = 10ºC and low = 6ºC; sunny day with clear sky.

The spread of the sampling dates across the four seasons, targeted both dry and wet weather conditions.

3.4 Preparation of glassware/flasks/vessels

Prior to each use, all glassware was washed in a laboratory dishwasher and then soaked in 10 % nitric acid overnight. Glassware was then rinsed with ultrapure (Reverse Osmosis (RO)) water, oven dried and stored in sealed polyethylene bags until use. For organic analysis, glassware was further rinsed with dichloromethane.

Prior to use modified PTFE-TFM digestion vessels were pre-cleaned with nitric acid (7.5 ml) together with ultrapure (Reverse Osmosis (RO)) water (7.5 ml) and digested in a microwave (MARSpress; CEM Corporation) for 10 minutes at 170 °C followed by a hold time of 10 minutes. The digestion vessels were then emptied and rinsed with DI water before drying in an oven at 110 °C overnight.

3.5 Sample preparation for inorganic analysis

3.5.1 Extraction of trace metals from water

The water samples were acid digested using microwave digestion following an adaptation of United States Environmental Protection Agency (US EPA) method 3015A as recommended by

CEM Corporation (US EPA, 2007). Acid microwave digestion of water samples rapidly breakdowns complex metal form into ionic species which can then be detected by inductively coupled plasma mass spectrometry (ICP-MS) (e.g. Environment Agency, 2008c; Islam *et al.*, 2015; Barros *et al.*, 2015; Maurya *et al.*, 2018; Turek *et al.*, 2019). As a key objective of this research is to ground-truth SFA predictions through comparison with field data, and the SFA draws on metal emissions data which are reported as total metal concentrations, to facilitate comparison between SFA and field data sets, the field analysis focused on determining total metal concentrations only (see Section 6.3 for discussion on the wider implications of analysis of total metal concentrations). The steps undertaken for the water samples preparation were as follows: the water sample (27 ml) was placed in the PTFE-TFM digestion vessel liners followed by the addition of concentrated nitric acid (2 ml) and concentrated hydrochloric acid (1 ml). To act as analytical reagent blank ultrapure (RO) water (27 ml) was placed in the vessel liner and the acids were added. The vessels were sealed and placed into the microwave (MARSpress from CEM Corporation) under the following settings:

Method:	water
Temperature sense:	± 2° C
Temperature:	170° C
Power:	85 %
Time:	10 min
Hold time:	10 min
Method name:	EPA3015A
Reagents:	2HNO 1HCL
Number of vessels:	20

After digestion, each water sample was filtered (Whatman ashless, grade 42) and diluted to 50 ml using ultrapure (RO) water. Extracted water samples were analysed for metals using ICP-MS X-Series 2 from Thermo Scientific.

3.5.2 Extraction of trace metals from sediment

The sediment samples were digested using microwave digestion following an adaptation of US EPA method 3051A (US EPA, 2007) to enable the use of vessels with a 50 ml capacity. Dried sediment samples of approximately 0.5 g each were weighed and placed into the PTFE-TFM digestion vessel liners. Concentrated nitric acid (9 ml) and concentrated hydrochloric acid (3 ml) were added to each vessel. A vessel containing only the acids and no sample was used to provide an analytical reagent blank. Certified reference material [Sigma-Aldrich-SQC001-50 g (Lot 011233)] was extracted following the same procedure. All vessels were sealed and placed in the microwave (MARSpress from CEM Corporation) under the following settings:

Method: inorganic
Temperature sense: ± 2° C
Temperature: 175° C
Power: 85 %
Time: 10 min
Hold time: 10 min
Method name: EPA3051A
Reagents: 9HNO 3HCL
Number of vessels: 20

After digestion, each sediment sample was centrifuged at 4300 rpm for 10 minutes, the supernatant transferred to a volumetric flask and made-up to a volume of 100 ml with ultrapure (RO) water. The metal concentrations of all sediment samples were determined using Inductively coupled plasma optical emission spectroscopy (ICP-OES) iCAP 6000 from Thermo Scientific.

3.5.3 Calibration and quality control measures

The method was validated using certified reference material (CRM) SQC001-50G (lot 011233) and results are reported in Table 3.2. The recovery rates for heavy metals ranged from 81.12 % for Ni to 96.48 % for Zn. Instructions for preparation were followed and the experiment repeated

4 times. With similar results obtained for each sample run, the decision was made to use generated data ‘as is’, rather than use a correction factor based on percentage extracted.

Table 3.2 Total metal concentrations determined in certified reference material (CRM) recovery.

Metal	**CRM SQC001-50G, lot 011233**		**Recovery (%)**
	Certified (µg/g)	**Determined (µg/g)**	
Cd	134.00 ± 2.57	122.78 ± 0.28	91.63
Cu	56.10 ± 1.20	48.37 ± 0.10	86.22
Hg	4.46 ± 0.15	3.82 ± 0.03	85.76
Ni	65.10 ± 1.54	52.81 ± 0.34	81.12
Pb	134.00 ± 3.02	124.14 ± 0.14	92.64
Zn	473.00 ± 9.21	456.35 ± 2.12	96.48

For calibration of the sediment sample analyses, four multi-element standards were prepared by diluting the stock solution (1 ppm) to 0.1, 0.5, 0.75 and 1 ppm in 25 ml volumetric flasks. A blank was prepared using ultrapure (Reverse Osmosis (RO)) water.

For water samples, a blank was prepared using ultrapure (RO) water and the stock solution (1 ppm) was diluted to 2, 4, 6, 8, 10, 12, 20 ppb in 25 ml volumetric flasks and used for instrument calibration.

All analyses were carried out in replicates with the ICP-OES and the ICP-MS generating three readings per analysis. Daily performance checks were run on the ICP-MS at the start of each analysis to ensure the equipment was running at its optimum efficiency. The performance check consisted of looking at a wide range of parameters such as the stability of the mass spectrometer across the mass range and typically being monitored through the selection of, for example, three masses across the mass range (Mg, In, U). Another example of parameter checked through the Performance Test is the ratio of CeO/Ce which had to be < 2 %, it can show possible interferences from diatoms formed in the plasma (e.g. ArO+ (mass 56) interfering with 56Fe (Thomas, 2013).

The instrument calibration was checked every 10 samples throughout the analytical procedure by running one of the calibration solutions as an unknown. Drifts in the calibration measurements were evaluated and when necessary (e.g. when a drift from initial reading was observed to be higher than 10 %) analysis was recalibrated.

3.6 Sample preparation for organic analysis

3.6.1 Solid phase extraction (SPE) of PAH from water

Reverse phase extraction columns, Strata X – 500 mg (Phenomenex UK) were used to isolate target pollutants. The SPE cartridges were first conditioned with 6 ml acetonitrile and equilibrated with 6 ml ultrapure (RO) water. Replicate water samples (250 ml) were loaded onto the SPE columns at a flow rate of 3 ml/min. The washing step was carried out using 6 ml of a solution composed of 10 % (v/v) methanol in water. Columns were dried under full vacuum for 10 minutes and then eluted using 6 ml dichloromethane at a flow rate of 1 ml/min. 12 extractions were performed simultaneously using a 12-port SPE Visi-prep vacuum manifold (Supelco). The eluates were collected in 10 ml glass vials and left to evaporate to dryness in a fume cupboard protected from heat and light. Each eluate was made up to a volume of 0.5 ml for GC analysis. Care was taken to ensure that the surfaces of the adsorbents in the columns did not dry during the conditioning and loading of the sample extracts.

3.6.2 Sediment sample preparation

The procedures described in this method meet the requirements for the extraction of PAHs from solid waste as described in the US EPA method 3545A (US EPA, 2007), which is applicable to soil, sludge and sediment.

The homogenized sediment sample was mixed with 0.5 g of diatomaceous earth (DE)[2] prior to transferring to 11 ml stainless steel extraction cells. Replicates of each sample were prepared following the same steps.

A blank was prepared using 3 g of DE, the amount needed to completely fill the 11 ml extraction cell.

The extraction cells were placed in the Accelerated Solvent Extraction (ASE) 200 unit and following operating conditions applied:

System Pressure:	1500 psi
Oven Temperature:	100 °C
Sample size:	7 g of sediment (10 g for the CRM and 3 g of DE for the blank)
Oven Heat up Time:	5 min
Static Time:	5 min
Solvent:	Dichloromethane/acetone (1:1), (v/v)
Flush Volume:	60 % of extraction cell volume
Nitrogen Purge:	1 MPa (150 psi) for 60 s

The sediment extracts were transferred to 100 ml round bottomed flasks and evaporated to 1 ml using a rotary evaporator. Subsequently, samples were left to evaporate to dryness overnight in a fume cupboard protected from heat and light. After evaporation sediment clean-up procedure was performed as described in Section 3.6.3.

3.6.3 Solid phase extraction (SPE) of PAH from sediment

Reverse phase extraction columns, Strata X – 500 mg (Phenomenex UK) were used to isolate target pollutants. The SPE cartridges were first conditioned with 6 ml acetonitrile and equilibrated with 6 ml ultrapure (RO) water. Dried sediment extracts obtained from the Accelerated Solvent Extraction (ASE 200) extraction were reconstituted using 3 ml acetonitrile and loaded into the SPE columns at a flow rate of 3 ml/min. The washing step was carried out using 6 ml of a solution composed of 20 % (v/v) methanol in water. Columns were dried under

---

[2] The DE was used to prevent sediment particles forming aggregates which can preclude an efficient extraction.

full vacuum for 10 minutes and then eluted using 6 ml dichloromethane at a flow rate of 1 ml/min. 12 extractions were performed simultaneously using a 12-port SPE Visi-prep vacuum manifold (Supelco). The eluates were collected in 10 ml glass vials and left to dry in a fume cupboard protected from heat and light. Each eluate was made up to a volume of 4 ml for GC/MS analysis. Care was taken to ensure that the surfaces of the adsorbents in the columns did not dry during the conditioning and loading of the sample extracts.

3.6.4 Calibration and quality control measures

Certified reference material (Fluka CRM104-50G, lot LRAA1194) was extracted following the same procedure as for PAHs in sediment samples. Results reported in Table 3.3 show the recovery rates for 11 selected PAHs ranged from 91.8 % for C to 114.22 % for Bz(b)Fl.

Table 3.3 Total PAHs concentrations determined in certified reference material (CRM) recovery.

PAH	**CRM104-50G, lot LRAA1194**		**Recovery (%)**
	Certified (µg/g)	**Determined (µg/g)**	
Ph	0.28 ± 0.08	0.30 ± 0.00	106.16
A	0.21 ± 0.07	0.21 ± 0.00	102.16
Fl	0.61 ± 0.24	0.65 ± 0.02	105.62
Py	0.20 ± 0.07	0.20 ± 0.01	101.26
Bz(a)A	0.25 ± 0.08	0.25 ± 0.00	101.02
C	0.30 ± 0.10	0.27 ± 0.00	91.08
Bz(b)Fl	0.22 ± 0.07	0.25 ± 0.01	114.22
Bz(k)Fl	0.30 ± 0.11	0.28 ± 0.02	96.27
Bz(a)Py	0.20 ± 0.05	0.20 ± 0.00	101.00
DBz(a,h)A	0.19 ± 0.07	0.20 ± 0.00	102.84
Bz(g,h,i)Py	0.30 ± 0.03	0.27 ± 0.04	92.42

Calibration was achieved using a 10 µg/ml solution of 16 PAHs in acetonitrile (Sigma-Aldrich-36979). Dilutions to 2, 4 and 6 µg/ml were prepared for calibrating the sediment sample extracts and calibration standards of 0.5, 1.5 and 3 µg/ml were used for the water sample extracts. SPE method was verified using 1 ml of calibration solution (10 µg/ml) and recovery rates ranged from 101.80 % for Bz(b)Fl to 109.80 % for Bz(k)Fl as reported in Table 3.4.

Table 3.4 Total PAHs concentrations determined in calibration solution (10 µg/ml) recovery.

PAH	**Calibration solution (10 µg/ml)**	**Recovery (%)**
	Determined (µg/ml)	
Ph	10.26 ± 0.01	102.60
A	10.24 ± 0.00	102.40
Fl	10.82 ± 0.02	108.20
Py	10.32 ± 0.00	103.20
Bz(a)A	10.56 ± 0.00	105.60
C	10.30 ± 0.01	103.00
Bz(b)Fl	10.18 ± 0.00	101.80
Bz(k)Fl	10.98 ± 0.03	109.80
Bz(a)Py	10.80 ± 0.02	108.00
DBz(a,h)A	10.96 ± 0.00	109.60
Bz(g,h,i)Py	10.24 ± 0.02	102.40

All gas chromatography mass spectrometry (GC-MS) analyses were carried out in duplicates using a Shimadzu QP2010 GC-MS instrument with tuning performed at the commencement of each sample run. Standards were analysed as unknowns after every tenth sample and a solvent run was performed between each sample/standard to avoid any cross contamination.

3.7 Statistical analysis for water and sediment samples analysis results

When summarising data sets, the mean concentration (±SD (standard deviation)) has been selected as the preferred measure of central tendency as it is widely used in the environmental research literature (facilitates comparison between studies) and in setting environmental quality standards (Sultan *et al*., 2011; UK TAG, 2013; EQS, 2013; Medici *et al*., 2011) supporting data interpretation. The inclusion of outliers is also considered as a more robust approach to minimising error in environmental data sets (Garces and Sbarbaro, 2009; Hosseinalizadeh *et al*., 2011).

As some data fell below the instrument detection limit (IDL) and, since less than 15 % of data for each selected substance were non-detects, recommendations by EPA Quality Assessment (2000) were followed meaning non-detects were replaced with the IDL values.

Statistical analyses were performed using the software Minitab 17 package (Minitab, 2017) and the level of significance is ≤ 0.05 used for all tests.

Data were analysed for normality distribution (using the Anderson-Darling statistic test) and for equal variance. Analysis of variance (ANOVA) General Linear Model (GLM) method (Grafen and Hails, 2002) was used to analyse log-transformed data. Post-hoc multiple comparisons were then performed using Tukey's Honest Significance Difference test to identify means with significant differences. Test for relationships between relevant parameters were carried out using correlation analysis when appropriate using the following classification (Minitab, 2017; Owen *et al.*, 2020):

- 0.00 – 0.19 = very weak,
- 0.20 – 0.39 = weak,
- 0.40 – 0.59 = moderate,
- 0.60 – 0.79 = strong,
- 0.80 – 1.00 = very strong

3.7.1 The application of pollution indices to sediment metal concentrations

Several approaches to derive pollution indices to support data interpretation are available including the development of contamination factors (CF), degree of contamination (C_{deg}), pollution load index (PLI), ecological risk factors (E_r) and potential ecological risk index (PERI) (Tomlinson *et al.*, 1980, Purchase *et al.*, 2020). These have been applied to matrices such as soil and river sediment (e.g. Duodu *et al.*, 2016; Karthikeyan *et al.*, 2020; Dash *et al.*, 2021). In this study, these approaches were applied to the mean sediment metal concentrations determined for each site enabling a range of pollution index values to be derived. The following pollution indices calculations were employed:

Contamination factors (CF)

The CF is the ratio between the pollutant concentration in the sample and the background concentrations. Metal specific contamination factors (CF) were calculated using the following equation:

$CF = C_e / C_b$

where,

C_e = the concentration of the pollutant in sediment samples, and

C_b = the soil background values for the contaminant.

In the absence of normal background concentration (NBC) for sediments, data for English soils (Appendix F3), only available for the metals Cd, Cu, Hg, Ni and Pb (from the selected pollutants listed in this research) were used as surrogate values in the calculation of contamination factors (Ander *et al.*, 2013). Håkanson (1980) suggested CF values to be interpreted as follows:

- $CF < 1$ = low contamination,
- $1 \leq CF < 3$ = moderate contamination,
- $3 \leq CF < 6$ = considerable contamination, and
- $CF > 6$ = very high contamination.

Degree of contamination (C_{deg})

The degree of contamination (C_{deg}) is the sum of the CF values (for all pollutants at each site) and is interpreted as follows:

- $C_{deg} < 8$ = low degree of contamination,
- $8 < C_{deg} < 16$ = moderate degree of contamination,
- $16 < C_{deg} < 32$ = considerable degree of contamination, and
- $C_{deg} > 32$ = very high degree of contamination.

Pollution load index (PLI)

The following equation is used for the calculation of PLI (an aggregated total pollution indices):

$PLI = (CF1 \times CF2 \times CF3 \times \ldots\ldots \times CFn)^{1/n}$

where,

CF = contamination factor, and

n = number of metals.

PLI values were interpreted as follows (Håkanson, 1980):

- a value < 1 indicates metal loads are close to background levels, whereas
- an area with value > 1 is considered polluted.

Ecological risk factor (E_r) and potential ecological risk index (PERI)

The ecological risk factor (E_r) is used to quantitatively express the potential risk of the measured metals in the sediment and the potential ecological risk index (PERI) is the sum of the ecological risk factors (E_r) of the individual measured metals (Håkanson, 1980).

The ecological risk factors (E_r) were calculated as follows:

$E_r = T_r \times CF$

where,

T_r = toxic response factor of an individual substance,

CF = the contamination factor, and

E_r = the individual ecological risk factor.

Heavy metal toxic response factors for soils (Appendix F4), which were available for Cd, Cu, Hg, Ni and Pb (Håkanson, 1980; Zhang and Liu, 2014) were used as surrogate in the absence of toxic response factors for sediment.

According to Liu *et al*. (2012) ecological risk levels can be interpreted as follows:

- $E_r < 40$, low potential ecological risk,
- $40 \leq E_r < 80$, moderate potential ecological risk,
- $80 \leq E_r < 160$, considerable potential ecological risk,
- $160 \leq E_r < 320$, high potential ecological risk, and

- $E_r \geq 320$, very high potential ecological risk.

The sum of the ecological risk factors (E_r) of the individual measured metals, called the potential ecological risk index (PERI) was calculated for each sampling site, and interpreted accordingly to Liu *et al*. (2012) as follows:

- PERI < 90, low potential ecological risk,
- 90 < PERI < 180, moderate potential ecological risk,
- 180 < PERI < 360, strong potential ecological risk,
- 360 < PERI < 720, very strong potential ecological risk, and
- PERI ≥ 720, highly-strong potential ecological risk.

Normal background concentrations (NBC) were not available for any of the selected PAHs, thus evaluation of pollution indices could not be applied to the PAHs results.

3.8 Sediment-water Batch Tests

To complement the field studies from the perspective of assessing the environmental behaviour of sediment-associated pollutants under varying physico-chemical conditions, a laboratory batch test was performed involving field collected water and sediment samples from five sites (A, E, F, H and K). The specific aim of this work was to provide an insight into the potential for sediment-associated metals to be released into overlying waters.

The procedures in the batch test method utilised in this study are an adaptation from Organisation for Economic Cooperation and Development (OECD) (2000) guideline and US EPA 835.1230 (US EPA, 2008) which is applicable to soil.

To determine the sediment to water ratio an aliquot of each wet sediment sample was weighed and dried at 105 °C to a constant weight and percentage of moisture content calculated. Based on these results sediment:water ratio was determined as 1:30 a dry weight of sediment equivalent to 30 g and 900 ml of water were used.

For the batch test laboratory experiments, 30 g of field sediment sample was placed inside (on the base) of a sterile 1 L glass bottle followed by the careful addition of 900 ml of field water sample, ensuring minimal disturbance and DO (DO meter: Mettler Toledo Seven Go pro SG6), pH (pH ATC Pen meter) and temperature measured. Bottles were covered with Parafilm and wrapped in foil to protect from light. After leaving it to settle for 24 hours measurements for DO, pH and temperature were taken again. These parameters were measured in the field during sample collection, at the start of each experiment and at the end of the experiment (see Appendices N1, N2 and N3) to determine at which extend these parameters varied over the course of the experiment as previous studies (Li *et al*., 2013; Zhang *et al*., 2018) reported that the DO, pH and temperature can play an important role on the sediment contaminant release as different fractions of different contaminants are highly influenced by such parameters and behave in different ways in river environments when one or all these parameters are modified (e.g. higher pH lead to more Cd release into the water column).

A magnetic stir bar double ended PTFE 55 mm x 8 mm was placed inside each bottle. Samples were stirred for 24 hours using Corning stirring plates (at half speed, approximately 800 rpm), then left to settle for 2 hours and centrifuged at 4300 rpm for 15 minutes and supernatant analysed followed sample preparation for organic and inorganic analysis methods for water.

In addition, TOC and DOC (Shimadzu TOC-VCPH/CPN analysed) were determined before and after batch test to investigate their impacts on contaminant release from sediment to the water column. More details on this procedure in the Section below (3.8.1).

3.8.1 Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC)

The procedures described in this method meet the requirements for the determination of TOC and DOC in water samples as described in the US EPA method 415.3 (US EPA, 2009), which is applicable to source water and drinking water and method US EPA 415.1 (US EPA, 1974) for measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes. The water samples collected for batch test were analysed for TOC and DOC before and after batch test using the Shimadzu TOC-$V_{CPH/CPN}$ analyser, which measures the amount of total carbon (TC), inorganic carbon (IC) and total organic carbon (TOC) in water.

Water samples were measured (20 ml) in duplicates and transferred to 20 ml disposable scintillation vials (Thermo Scientific) and covered with Parafilm M (Sigma-Aldrich). For DOC analysis, water samples were filtered through 0.45 μm syringe filters (Cole-Parmer). Replicates of each sample were prepared following the same steps.

3.8.2 Calibration Standards

Standards for both TC and IC were prepared by the volumetric dilution of a stock solution with carbon concentration of 500 mg/l potassium hydrogen phthalate (TC standard solution) and 500 mg/l of potassium nitrate (IC standard solution) to produce the following series of standards: 20, 40, 60, 80, 100 used for analysis of samples from before batch test and 20, 40, 60, 80, 100, 150, 200 to analyse samples from after batch test. Ultrapure (RO) water was used as blank for all set of standards.

3.9 Substance Flow Analysis (SFA) modelling application

This section explains why using substance flow analysis (SFA) and describes the methodology used to implement the SFA and identifies the various data sources used.

3.9.1 Selection of Substance Flow Analysis (SFA)

SFA was chosen based on a number of criteria. The main aim of this research was to explore and evaluate a cost-effective desk-based approach, requiring a tool which uses existing available data sets and would be flexible enough for implementation on other catchments. Whilst there are a number of predictive models available, these are typically dedicated to a single activity e.g. road runoff (Revitt *et al.*, 2022) or a wastewater treatment plant (Benedetti *et al.*, 2005) and/or a single substance (Yoshida *et al.*, 2015; Kim *et al.*, 2017; Charters *et al.*, 2020) which would not be appropriate for the holistic assessment of catchment activities. Furthermore, these are usually based on monitoring data which require the application of patented software packages. For example, US EPA developed predictive software packages such as PLOAD (Pollutant LOADing) and STEPL (Spreadsheet Tool for Estimating Pollutant Load) are formatted around an established template for specific parameters e.g. N, P and BOD (US EPA, 2001; Tetra Tech, 2011). These US EPA software packages have been criticised for not providing understanding of the exclusive nature of different watersheds and may not produce reliable predictions when estimating long-term pollutant loads and identifying pollutant sources (Meals *et al.*, 2011; Hanson *et al.*, 2022), and therefore not appropriate for a more holistic where flexibility and cost-effectiveness are important for the model to be applied to other urban catchments.

As described in the literature (Section 2.4) SFA was reported as an efficient method to support tracing pollutant sources and quantifying substance loads for various substances at a time (Sörme and Lagerkvist 2002; Chèvre *et al.*, 2011; Baccini and Brunner, 2012; Markiewicz *et al.*, 2017). Whilst there are uncertainties which are inherent to SFA (see Section 3.9.2.8), it is recognised as an important tool for substance flow management (Brunner and Rechberger, 2016) and is used by the European Union as a predictive tool to provide useful information to support policy making at national level (European Environmental Agency, 2007).

3.9.2 Substance Flow Analysis (SFA) methodology applied

SFA characterizes the pathways of a substance or group of substances in, through and out of a specified system, where each study is unique due to influences of parameters specific for each urban area (Brunner, 2012). While there are a variety of SFA approaches and tools, all are framed around the use of a substance mass balance. Analysis of substance flows are often connected to changes in resource availability, for example, where limitations or excess levels of substances are identified as an issue of concern. Over the last two decades, SFA research developments have included developing a standardised SFA methodology available as a toolkit involving a three-step procedure comprising the system definition, inventory, and interpretation (Van der Voet, 2002). Several authors (e.g. Bai *et al.*, 2015; Brunner *et al.*, 2012; Huang *et al*., 2012; Udo de Haes *et al.*, 2000; Sörme, 2003; Månsson *et al.*, 2008) propose a more comprehensive set of actions (see Figure 3.2), to cover limitations identified in previous studies. According to Baccini and Brunner (2012) and Sörme, (2003) a more comprehensive methodology supports identification and evaluation of associated uncertainties, identified as one of the main limitations in earlier SFA studies. These additional steps were incorporated into this research because they have been successfully applied by European countries (such as Austria, Denmark, Germany, the Netherlands, Norway, Sweden and Switzerland) and scientifically reported by a number of authors. The results of these studies have shown that SFA can produce a significant amount of pertinent information for a range of purposes including policy making and tracing flows and understanding the fate of substances (European Environmental Agency, 2007).

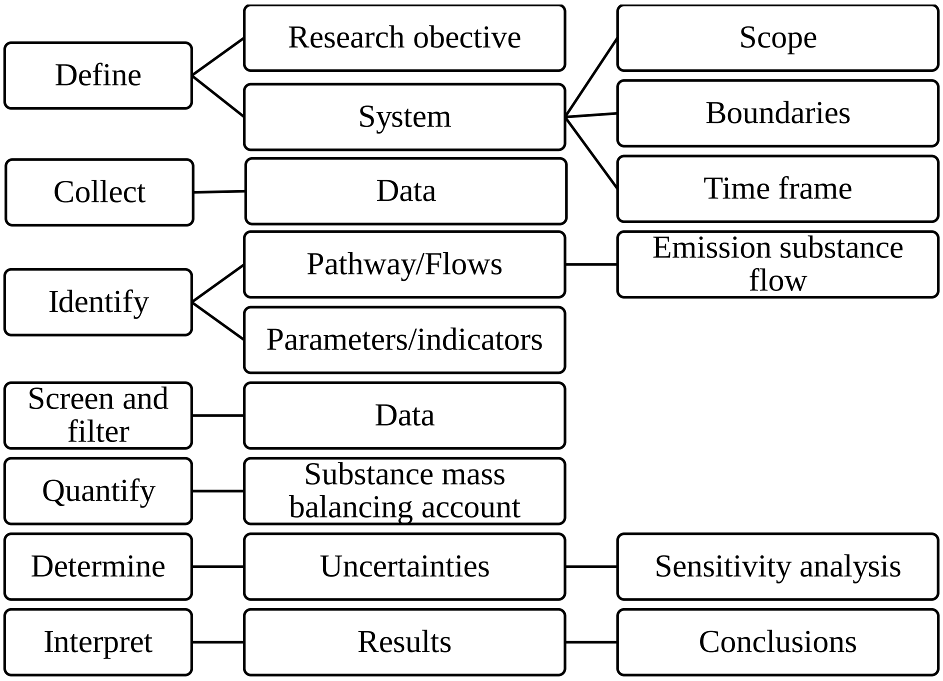


Figure 3.2. Overview of the SFA methodology applied in the Lower Lee catchment (UK).

The following section describes how each step in the Figure 3.2 flowchart was addressed in this study.

3.9.2.1 Definition of research objectives

As presented in Section 1.3, part of evaluating the impacts of an urban catchment on receiving river water and sediment quality involved undertaking a desk-based SFA to address the following objectives:

- Development of a desk-based substance flow analysis approach as a potential management tool to identify and quantify point and diffuse loads of selected organic and inorganic pollutants originating in the Lower Lee catchment.
- Implementation of the developed substance flow analysis tool and ground-truthing its predictions through comparison with field data.

- Consideration of the potential use of the substance flow analysis tool to support catchment managers and policy makers identify locations for the installation of mitigation measures.

3.9.2.2 System definition

The spatial boundary of the SFA is the Lower Lee catchment (London, UK) (see Section 3.1) and the time period in which the analysis was undertaken is the year 2013. The catchment has a total area of 440 km^2, of which around 0.02 Km^2 is covered by surface water bodies (rivers, canals and reservoirs) with a population of approximately 2.3 million people (Thames21, 2015).

3.9.2.3 Data collection

Data on the emission of selected pollutants from different activities were collated from a wide variety of sources including peer-reviewed papers, national/European government reports, local authorities (e.g. outfall maps), water companies (STW characteristics) and the grey literature (e.g. reports from the NGO Thames Water and the charitable trust, Canal and River Trust) through a combination of website searches and face-to-face meetings. Data, at different levels (UK, England and Boroughs) were collated in Microsoft Excel against the following parameters:

- total study catchment area (440 km^2),
- land use types (e.g. residential, industrial estate, green, brownfield etc),
- local authorities' details,
- rainfall average,
- population,
- industries,
- types of transport (e.g. rail, light good vehicles, heavy good vehicles),
- street level transport flows (Annual Average Daily Traffic (AADT)),
- number of STW (with population equivalent (PE)).

Whilst the aim was to collate data for the year of 2013, it was not always possible and where this was the case this is identified in the collated data sheets. Data which related to alternative years include census data (the latest available data set was for 2011), the UK SIC (Standard Industrial Classification of economic activities) and EU NACE (Statistical classification of economic activities in the European Community) codes (most recent data were from 2007 and 2005, respectively).

A list of data collated, and their sources is presented below (Table 3.5).

Table 3.5 List of data sources utilised in the SFA modelling.

Data Source	Data acquired
Office for National Statistics	• UK census data (Office for National Statistics, 2011). • England GLUD (Generalised Land Use Database, 2005). • Measuring material footprint in the UK: 2008 to 2016 (Office for National Statistics, 2016). • Material flow accounts data set for 2013 (Office for National Statistics, 2019a). • Statistical Bulletin - Index of Production for 2013 (Office for National Statistics, 2013). • UK Standard Industrial Classification of Economic Activities (UK SIC of 2007) - used in classifying business establishments and other statistical units by the type of economic activity in which they are engaged. (Office for National Statistics, 2007).
Defra	• Annual Report and accounts for 2013 on the UK Heavy Metals Monitoring Network (Defra, 2014a).
Local authorities	• Outfall discharge points maps. (UK Local Authorities, 2015).
Thames Water	• Deephams STW assessment report and answers to questions, which were sent to Thames Water via emails.
Environment Agency UK	• From Geostore data set: Inventory on pollutants released to air, water, soil and wastewater for England for the year period of 2013 (Environment Agency, 2013d). • Data on Dangerous Substances, River Catchment Water bodies and Locks Location (Environment Agency, 2013b). • Environmental Permit Regulation (industry) (Environment Agency, 2016a). • Substances Discharged of Consented Red List and Outfall Discharge Points. Data acquired through contacts via phone, email and face-to-face. (Environment Agency, 2013c and 2016).
Canal & River Trust	• Outfall discharges information. • Locks location. Both data acquired through contacts via emails. (Canal and River Trust, 2014).
Digimap - Edina	• Ordnance Survey (OS) geographical maps of the study area in shapefile format, which could be used in ArcGIS. (Edina, 2015).

Bureau van Dijk (BvD) – FAME (Financial Analysis Made Easy) website	• Acquired listings of companies, one for the whole UK, and one by local authorities within the research area. (Bureau van Dijk, 2013). The database contains information detailed format, including UK SIC/EU NACE codes, addresses.
Digdat	• Ordnance Survey (OS) underground assets maps - to identify and measure road runoff drainage for each sampling site catchment area (Digdat, 2013).
European Environment Agency	• E-PRTR (European Pollutant Release and Transfer Register) Inventory of activities' reports on pollutants released to wastewater, air, surface water and soil, which provided key environmental data from industrial facilities for the selected substances in the UK for the year period of 2013 (E-PRTR, 2013). • BREFs (Best Available Technique Reference) documents, which are under the Industrial Emissions Directive (IED, 2010/75/EU) (European Union, 2014). • Nomenclature des Activités Économiques dans la Communauté Européenne (EU NACE) - is a European industry standard classification system similar in function to UK SIC code. The UK SIC codes were developed based on the EU NACE codes but without the alphabetical letters' classification; only number were used, which are the same for both code systems (European Union, 2005).
Department for Transport -UK	• Road traffic statistics 2013: AADT (annual average daily traffic) data for major and minor roads. (Department for Transport, 2013).

3.9.2.4 Identification of relevant flows and processes

While information on the composition of specific goods (i.e. furniture, toys, computers, textiles) is abundant, data on the inflow of substances to an area and its stock (i.e. mass that is stored within the process) within the catchment are scarce (Stanisavljevic and Brunner, 2014). Due to this limitation, this thesis focused on emissions (outflows) of selected pollutants into surface water bodies in the Lower Lee catchment. This approach was able to be applied due to the collection of inventory data by relevant authorities for the study area, and their willingness to share. The process for the calculation of outflows is detailed in Section 3.9.2.7.

3.9.2.5 Identification of parameters

The SFA approach was applied to the metals (cadmium [Cd], copper [Cu], lead [Pb], mercury [Hg], nickel [Ni] and zinc [Zn]) and the PAHs (anthracene [A], fluoranthene [Fl], benzo(b)fluoranthene [Bz(b)Fl], benzo(a)pyrene [Bz(a)Py] and benzo(g,h,i)perylene [Bz(g,h,i)Pe]). Whilst field samples were also analysed for tin [Sn], phenanthrene [Ph], pyrene [Py], benzo(a)anthracene [Bz(a)A], chrysene [C], benzo(k)fluoranthene [Bz(k)Fl] and dibenzo(a,h)anthracene [DBz(a,h)] (see Sections 4.1 and 4.4), an SFA was not applied to these substances due to data unavailability for all or some of the required parameters.

Using the approach identified by Brunner and Rechberger (2016) emission loads were calculated (see Section 3.9.2.7) for each selected substance and type of activity for the defined system (see Section 3.9.2.2).

3.9.2.6 Data screening and filtration

In preparation for the quantification of loads of emissions of selected substances by identified activities, collated data on emissions were screened and filtered by undertaking the following steps:

Approximately 900,000 companies were identified (as located in the Boroughs which cover the Lower Lee catchment) using the FAME database. This list was then screened to identify those located in each borough falling in the Lower Lee catchment. Postcodes for this shortlist of approximately 400,000 companies were then converted into geographic coordinates through the UK Grid Reference Finder and Ordnance Survey maps. Using the geographic coordinate system in ArcGIS, it was possible to identify and narrow down those companies located within 1 km radius of the sampling sites (Figure 3.3 and Appendix R1).

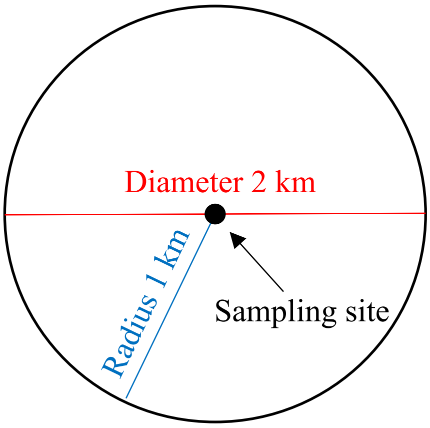


Figure 3.3 Measurement of distance matrix used in ArcGIS to filter companies located in the Lower Lee catchment.

The distance limit was set based on the consideration of the following criteria:

- Study area drainage system: ensure more than one outfall and/or road drain which discharge directly into surface waters were included, to maximise opportunities to capture local emissions.
- Minimise data uncertainties. As stated by Danius (2002) and as with all models, SFA outputs are only as reliable as the input data. The larger the contributing area, greater the associated assumptions and therefore there is a balance between scale and robustness.
- Development of a comprehensive but manageable data set i.e. include relevant companies to trial an approach that can be applicable to other areas.

- Keep research cost and time effective with regard to considering resources available to e.g. environmental protection agencies and catchment basin managers.

The list of companies was then screened for e.g. duplicates (the same company appearing in two site's catchments) leaving only one of the entries under the catchment where the company was closest to a sampling site.

Companies were then grouped by common characteristics using their EU NACE codes (classification system used by Defra to report pollutant emissions as part of EU requirements). Based on the EU NACE codes and data from the literature (see Table 3.5), the emission of pollutants evaluated in this study were matched against each company's activity. As previously reported (e.g. Markiewicz *et al*., 2017; Siopi, 2015; Petrucci *et al*., 2014; Björklund *et al*., 2011; Thames21, 2019), road runoff is considered an important contributor to the degradation of urban rivers, and hence road runoff discharges were also considered in the SFA. Data from the UK Department for Transport were used to calculate the loads of selected pollutants discharged into surface water bodies in the research area through road runoff. The area limitation of 1 km radius distance of each sampling site was also applied for the road runoff quantification.

Using AADT data available on the Department for Transport website and Ordnance Survey (OS) underground assets maps acquired from the Digdat website, length of roads with drainage systems discharging directly into surface water were identified and road runoff substance loads quantified. This quantification process was developed by Revitt *et al*., 2020 and is further explained in Section 3.9.2.7 and Appendix O1.

Application of the data screening processed led to the identification of 14 activities under which a total of 152 companies were identified as located within 1 km radius of the sampling sites (see Tables 3.6, 3.7 and 3.8). All 14 activities were identified in the Environment Agency's pollution inventory (2013) as discharging selected metals to surface water bodies. However, for selected

PAHs, only six activities were reported as PAH sources. Also, it is important to note that for the SFA modelling undertaken in this study, road runoff is not linked to any specific activity or company.

Table 3.6 List of selected activities determined within 1 km radius distance of each sampling site at the Lower Lee catchment (European Union, 2005; Office for National Statistics, 2007).

Activity	EU NACE * code	Code classification description
Wastewater	E37.00	The process comprises treatment of municipal wastewater in the Deephams wastewater treatment plants in the Lower Lee catchment. It contains wastewater from households, some companies as well as from surface runoff.
Waste non-hazardous	E38.11	Collection, treatment and recovery of non-hazardous waste.
Waste treatment	E39.00	Remediation activities and other waste management services This division includes the provision of remediation services, i.e. the clean-up of contaminated buildings and sites, soil, surface or ground water.
Paper/Wood production	C16.00 and C17.00	C16.00 - Manufacture of wood and of products of wood and cork, except furniture; manufacture of articles of straw and plaiting material. C17.00 - Manufacture of paper and paper products, including pulp, corrugate paper, paper stationery, household sanitary and wallpaper).
Refineries	C19.20	Manufacture of refined petroleum products, including motor fuel, fuel oil, white spirits, Vaseline, petroleum briquettes etc.
Production of electricity	D35.11	This class includes operation of generation facilities that produce electric energy, including thermal, nuclear, hydroelectric, gas turbine, diesel and renewable.
Manufacture of basic metals and metal products	C24.10 and C25.00	C24.10 - This division includes the activities of smelting and/or refining ferrous and non-ferrous metals from ore, pig or scrap, using electro metallurgic and other metallurgic techniques. It also includes the manufacture of metal alloys and super-alloys by introducing other chemical elements to pure metals. C25.00 - This division includes the manufacture of “pure” metal products (such as parts, containers and structures).
Manufacture of non-metallic mineral products	C24.40	This class includes precious metals production, aluminium, lead, zinc and tin, copper, chrome, manganese, nickel and nuclear production.

Manufacture of rubber and plastic products	C22.10 and C22.20	C22.10 - This division is characterised by the rubber raw materials used in the manufacturing process, tyres, tubes, bottles, hoses, belts etc. C22.20 - This group comprises processing new or recycled plastics resins into intermediate or final products (bags, packaging, tanks, doors, artificial stone, kitchenware, toilet articles, school/office supplies etc).
Manufacture of chemicals and chemical products	C20.00	This division includes the transformation of organic and inorganic raw materials by a chemical process and the formation of products, such as fertilisers, industrial gases, dyes and pigments, resins, plastics materials, potting soil, pesticides, printing ink, detergents, soap, perfumes, glues, essential oils etc.
Manufacture of cement	C23.51 and C23.60	This class includes manufacture of clinkers and hydraulic cements, including Portland, aluminous cement, slag cement and superphosphate cements, precast concrete, cement or artificial stone articles for use in construction, tiles, flagstones, bricks, boards, sheets, panels, pipes, posts etc.
Food and Drink	C1000 and C1100	Manufacture of food products (includes the processing of the products of agriculture, forestry and fishing into food for humans or animals, and includes the production of various intermediate products that are not directly food products) and beverage (non-alcoholic beverages and mineral water, alcoholic beverages mainly through fermentation, beer and wine, and distilled alcoholic beverages).
Manufacture of textiles	C1300	This division includes preparation and spinning of textile fibres as well as textile weaving, finishing of textiles and wearing apparel, manufacture of made-up textile articles.
Road runoff	N/A**	This class covers load emission (from engine, brake, tyre and road surface), from vehicles such as passenger cars, buses, lorries.

Key: * Activities are classified by groups represented by letters and numbers. Then numbers are added to form subgroups. For example, all Manufacturing activities are classified by letter C, then C10 for manufactures of food products, which contain subgroups such as C10.1 Processing and preserving of meat and production of meat products, C10.2 Processing and preserving of fish, crustaceans and molluscs, and so on.

**Not applicable - Road runoff is not listed under the EU NACE/UK SIC (2007).

Table 3.7 Overview of activities and numbers of companies discharging selected metals at each sampling site in the River Lee, Navigation Channel and tributaries.

	River Lee				**Lee Navigation**			**Tributaries**				**All sites**
Activity	**A**	**G**	**H**	**I**	**C**	**J**	**K**	**B**	**D**	**E**	**F**	
Wastewater									1			1
Waste non-hazardous	4		3	2	1	3	5	2	8	9		37
Waste treatment	2							2	1			5
Paper/Wood production		1	2		1		2		1	4		11
Refineries										1		1
Production of electricity (EfW power plants)	1						4		3		1	9
Manufacture of basic metals and metal products	1	1					2		1	1	2	8
Manufacture of non-metallic mineral products	1											1
Manufacture of rubber and plastic products	6		4		1		6	1	4	5	2	29
Manufacture of chemicals and chemical products					4	1	1		1			7
Manufacture of cement	1						1					2
Food and Drink	1	1	8		1		2	1	3	6	1	24
Manufacture of textiles	1		3		1	1	1		2	4	4	17
Road runoff	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
Total number of activities	10	4	6	2	7	4	10	5	11	8	6	
Total number of companies	18	3	20	2	9	5	24	6	25	30	10	152

Table 3.8 Overview of activities and numbers of companies discharging selected PAHs at each sampling site in the River Lee, Navigation Channel and tributaries.

	River Lee				Lee Navigation			Tributaries				All sites
Activity	**A**	**G**	**H**	**I**	**C**	**J**	**K**	**B**	**D**	**E**	**F**	
Wastewater									1			1
Waste non-hazardous	4		3	2	1	3	5	2	8	9		37
Refineries										1		1
Manufacture of basic metals and metal products	1	1					2		1	1	2	8
Manufacture of chemicals and chemical products					4	1	1		1			7
Road runoff	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
Total number of activities	3	2	2	2	3	3	4	2	5	4	2	
Total number of companies	5	1	3	2	5	4	8	2	11	11	2	54

3.9.2.7 Quantification – mass balancing

As informed by Baccini and Brunner, 2012, SFA is an evaluation of the movement of a substance within a defined system including identification and quantification of inflow, stocks and outflow. However, to keep in line with the research question, this study focused on quantifying stocks of selected pollutants discharges from activities with 1 Km of each sampling site as shown in Figure 3.4. In addition, inflow and outflow data for the Lower Lee catchment for the year of 2013 were not available.

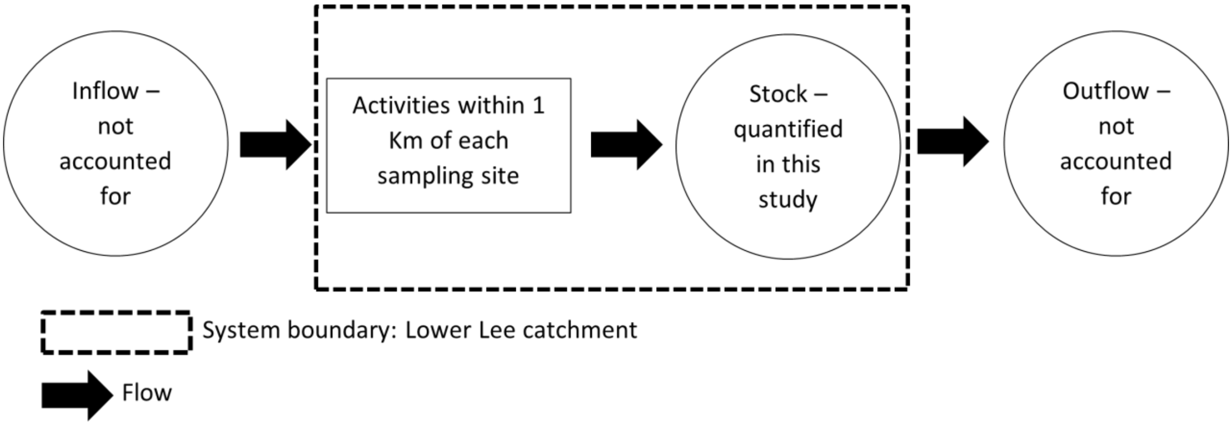


Figure 3.4 Substance flow analysis process applied in this study.

The EA emission data sets for the year 2013 were used to calculate average emissions for each selected activity per substance, based on the number of reported companies (see Table 3.9). This average value was then multiplied by the number of companies under the same activity (as per EU NACE/UK SIC codes) identified in each sampling site sub-catchment. An example of how the calculations were conducted for Cd is shown in Table 3.9.

Table 3.9 Example of calculations for Cd (kg/year) discharged from wastewater activity.

	Number reporting facilities	**Total Cd release to surface water**	**Mean ±SD of Cd released per facility**	**Median of Cd released per facility**	**Cd predicted load for the study area based on the mean***	**Cd predicted load for the study area based on the median***
EA (England)	138	454.11	3.29±1.82	1.34	3.29	1.34

Key: *Calculation is based on one wastewater activity identified in the study area under the wastewater EU NACE code.

The EA emissions data set, some activities reported that emissions were below the reporting threshold. EA emission reporting thresholds are given in Table 3.10, and where a pollutant was identified as emitted below the reporting threshold, the threshold value was utilised as a surrogate.

Table 3.10 Threshold values (kg/year) for the emission of metals and PAHs (Environment Agency, 2013d).

Substance	Threshold value
Cd	1.00
Cu	20.00
Hg	0.10
Ni	20.00
Pb	20.00
Zn	100.00
A	0.10
Fl	0.10
Bz(b)Fl	1.00
Bz(a)Py	1.00
Bz(g,h,i)Pe	0.10

For the wastewater activity, there was only one STW (Deephams) in the identified system boundary. As Deephams STW report their emissions directly to the Environment Agency, the actual reported values were used in this study.

For road runoff emissions, a mathematical model which integrates data on AADT, length of roads (identified from Digdat maps, 2018), and factors for emissions from engine, brake, tyre and road surface wear using the approach developed by Revitt *et al.* (2020). The AADT data from TfL was obtained for 2013 and used as a multiplier to calculate the amount of pollutant deposited on roads. This mass deposited data was combined with catchment rainfall data and a runoff coefficient to produce an annual average concentration which was used to calculate an annual average loading estimate (µg/year) and then converted into kg/year. A summary of the runoff load estimates calculation methodology, including equations and emission factor values, is presented in Appendix O1.

Results of the SFA were then compared with sediment field data (see Sections 4.1 and 4.2) to evaluate if the field data could provide a validation for the SFA results and an indication of sediment hotspots. Comparison of results took place in Sections 6.1.4 and 6.2.4 through use of a statistical approach involving correlation analysis where further details can be found under Section 3.9.2.10.

3.9.2.8 Addressing data uncertainty

Various authors (e.g. Hedbrant and Sörme, 2001; Brunner and Rechberger, 2016; Lindqvist, 2002; Schwab, 2016; Lena, 2002) emphasise that while data uncertainty exists in SFA modelling, valuable information can still be generated as SFA is not only about specific numbers but other processes (e.g. identifying and mapping catchment specific substance flow pathways) which give results and knowledge that are qualitative. In fact, some have argued that the qualitative results of an SFA study are more relevant as a basis for environmental policy making (Hök, 2007;

Kleijn, *et al.*, 2000). Within this setting, this research explores the use of SFA modelling results in different contexts i.e. quantitative, technical, statistical, comparison with field data and geographical information management to further explore the possibilities of SFA as a quantitative and qualitative method.

Uncertainty is defined as a state of having limited knowledge, where it is impossible to exactly describe an existing state or future results (Hubbard, 2014). Approaches to handling uncertainty in SFA modelling has been widely evaluated (DEPA, 2000; Hedbrant and Sörme, 2001; Brunner and Rechberger, 2016; Sörme and Lagerkvist, 2002; Cenčič, 2018). For example, DEPA (2000) and Hedbrant and Sörme (2001) provided a methodological framework to identify and mitigate data uncertainties in SFA modelling involving the use of uncertainty intervals, standard deviation and statistical analysis. It has been argued that all data sets are subject to uncertainty and an assessment of the acquired data is a necessary part of all modelling including SFA (Lassen and Hansen 2000; Danius, 2002; Besseling *et al*., 2014; Baek *et al*., 2018; Antikainen *et al*., 2005).

Considering this setting, Table 3.11 lists identified uncertainties and the steps taken to minimise their impacts.

Table 3.11 List of sources of uncertainties identified in the model applied in this study.

Data set	Data source	Process	Identified uncertainty	Action taken to minimise uncertainty impacts
Substance emissions data set	Environment Agency Inventory	Data collection	Data set relates to the whole of England and average emission factors used in calculations.	Environment Agency data set chosen due to smaller spatial scale (England) and standard deviations when compared to E-PRTR data set. In addition, using a single source minimises uncertainties associated with using different data sources e.g. different ways to gather and report data (Lassen and Hansen, 2000). In addition, using an inventory developed by a Governmental source, data are expected to be authoritative, accurate and validated compared to other sources such as independent research.
			Data only refers to direct discharges to surface water, emissions from other matrices (e.g. soil and air) which could consequently enter the receiving surface water were not included.	The scope of this research was limited to considering emissions directly to surface water as an initial screening tool. Further studies are recommended to enable further sources to be considered.
			Data unavailability re: not all known sources of pollutant emissions to surface water could be considered in this research (e.g. CSOs).	This was unavoidable due to data unavailability, but this aspect was taken into consideration when results were analysed.
		Calculation	Some companies did not have an emission value as they were under the reporting threshold values.	In this case, threshold values were applied as 'worst case scenario' surrogate representing the maximum value it could reach in terms of discharges to surface water.
Companies lists	Bureau van Dijk (BvD) – FAME	Data collection	The provided list of companies was for the whole England.	EU NACE/UK SIC codes were used to identify companies, maintaining reliability. Only companies within 1 km distance from each sampling site were considered, making sure they were in the study area and directly discharging to surface water.

		Data filtration	Data gaps: Some companies were missing EU NACE/UK SIC codes. When identifying companies on ArcGIS within 1 km of each sampling site, some companies were duplicated due to their proximity to different sampling sites.	Companies without EU NACE/UK SIC codes were left out of the research. While this prevented possible errors in classifying them into the incorrect groups, it is possible that not all companies were included in the assessment. Duplications were identified and removed. Only the input which was nearest to a sampling site was considered on the basis it was most likely to drain via the site closest to the river.
SFA results and field data	Results from this study	Results comparison	Different units for SFA (kg/year) and field data (µg/g) results.	Comparison of the relationship and trends between the two data sets were undertaken using correlation and ratios which are dimensionless (Kim, 2018; Sterling and Dekate, 2008).
Road runoff data/calculations	Various (see Appendix O1)	Data collection	Data gathered for the road runoff calculation were available only partially from each data sources, thus various sources were utilised. Due to data availability only emissions from vehicles and asphalt were calculated in relation to road runoff pollution, leaving a gap on emissions from other sources such as roofs, car parks and air deposition etc. The AADT data set is estimated as the total traffic volume passing a point/segment of a road in both directions for a year divided by the number of days in the year. Consequently, as estimates they may contain uncertainties. The AADT data was not available for all the roads in the study area.	A systematic literature review was undertaken utilising data from various data sources. This has been reported and explained in detail in Appendix O1. Identified gaps, are reported in this study and taken into consideration. Future research is encouraged to focus on addressing identified data gaps as well as further understanding of the impact of uncertainties and their implications.
SFA results	Results from this study		Spatial variation in the distribution of selected substances.	This was unavoidable due to the dynamic processes inherent to the study area and although this was taken into consideration when results were analysed, studies would be necessary to further understand these processes and their impacts on data results and provide guidance for future studies.

DEPA (2000) and Hedbrant and Sörme's (2001) frameworks have in common the use of data based on, for example, pollutant content of various goods, derived from different sources providing different data sets which were used to calculate substance flows, meaning that the same item could have more than one value and leaving space for larger uncertainty as different studies/data set will have their own uncertainties according to the methodology used. In both these studies the reported values were used as intervals (for example when three data sets reported different Zn content from roofs), meaning that in the case of wide ranges it would be necessary to discuss the basis for the variation in terms of factors such as data quality and hotspots. In addition, values could be from another area/country and may not serve as best representation for the study area (DEPA, 2000). However, this study focusses on flow of substances within the River Lee catchment and the sources of data used to quantify substances emissions from companies were from one source and from the same country (UK), the Environment Agency pollution inventory (Environment Agency, 2013d), which provided the quantification of substance emissions. Thus, uncertainty intervals were not used in this study.

As stated in the methodology chapter, due to a lack of data, the SFA undertaken in this research does not account for discharges from CSOs (as per Thames Water report (2013)). Most of the combined sewer stock are identified as old and vulnerable to infiltration of groundwater, levels which can vary in response to rainfall events. CSOs in the Lower Lee catchment are reported to account for more than half of the untreated sewage volume discharged in London rivers (Munro *et al*., 2019). For example, the CSOs located at the Abbey Mills Pumping Station were estimated to discharge around 32 million m^3/year of untreated sewage mixed with stormwater into River Lee (Defra, 2015a). Chèvre *et al*. (2011) have reported stormwater and CSOs as the main channels from which metals enter urban surface waters. Another example is that in 2019 it was reported that Thames Water combined sewer overflow (CSO) at Mulberry Court (Olympic Park) discharged untreated sewage 91 times over a period of 1026 hours into the River Lee (Oceanographic Magazine, 2020)

Overall, data used in the SFA modelling were collated from a range of sources including peer-review research papers, official government reports, national and environmental protection agency. With regard to data reliability, only companies listed under EU NACE/UK SIC codes with emissions reported in the EA data set were used for SFA modelling. Whilst the benefit is that as it is an official reporting inventory, the information content is considered authoritative, accurate and validated, a potential downside is that it is possible key companies (in terms of emissions) were left out since companies emitting substances below stated threshold values (see Table 3.10) are not required to report. Thus, the EA data set may not be complete. Since EU NACE codes were used to classify the companies in the study area, following data screening (by sampling site), it was noted that (based on knowledge of the catchment) some companies were registered under what seemed to be an incorrect EU NACE code (e.g. a company coded as manufacture but in reality, was a wholesaler or an office representative of the manufacturing sector). Where noted, companies identified with the ‘incorrect’ code, were removed from the data set.

As previously mentioned, when screening companies with a distance matrix of 1 km radius of each site (Figure 3.3, Appendix R1) using ArcGIS it was observed that some companies were duplicated (e.g. same company was listed under two sites due to some of the sampling sites being located close to each other). In this case, duplication was removed, and one company listed only once under its nearest site on the basis on the basis it was most likely drain via the site closest to the river.

Companies were also filtered on the basis of the matrices they discharged to (e.g. discharge to wastewater, controlled water, air, soil). From the inventories used, there were cases were companies reported emission to one or more matrices. As this research only investigated water and sediment quality in urban rivers, only reported emissions to controlled/surface water were considered in the SFA modelling calculations. Therefore, companies under activities discharging directly to wastewater, air and soil were not considered in this model as, in this study, Deephams STW accounts for companies discharging directly to sewage works. Data requests were sent to relevant authorities regarding companies which had their effluent privately treated (for example, breweries which commissioned private companies to treat their effluent) but no company was willing to provide information citing the General Data Protection Regulation as justification.

Road runoff calculations were applied only for emissions from vehicles and asphalt directly deposited on to roads, leaving a gap on emissions from other sources such as roofs, facades, car parks, air deposition etc. The data set (AADT) used to calculate road runoff were based on extrapolation limited data points as reported by the UK Department of Transport (2013a).

Another source of uncertainty is the spatial variation in the occurrence of selected substances in the field. For example, while substance loads were calculated as releases at a specific site, the model does not have flexibility to account for pollutant degradation, resuspension, transportation and subsequent deposition at other sites. This is an inevitable source of uncertainty due to the dynamics of processes (e.g. land use development, chemical transportation, sedimentation and resuspension) in place at the Lower Lee catchment, which was taken into consideration when results were discussed.

3.9.2.9 Sensitivity analysis

Assessing a model's sensitivity (both to determine its potential utility and to identify possible improvements to the model) is an important step in the model development process (Wagener and Kollat, 2007; Cheng *et al*., 2018). In this study, sensitivity analysis was conducted to assess the robustness of the outcomes and model sensitivities to input uncertainties (Laner *et al*., 2014) and the sensitivity analysis consisted of two steps:

Step one:

To evaluate the most appropriate parameter (mean, median, minimum and maximum) for the ground-truthing process and how these parameters would affect the strength of relationship between SFA and field data, correlation analysis was undertaken between SFA prediction loads and sediment field data output for metals and PAHs as follows:

- Correlation analysis between SFA prediction loads and sediment field utilising the **mean** values for both data set.
- Correlation analysis between SFA prediction loads and sediment field utilising the **median** values for both data set.
- Correlation analysis between SFA prediction loads and sediment field utilising the **minimum** values for both data set.
- Correlation analysis between SFA prediction loads and sediment field utilising the **maximum** values for both data set.

Step two:

In terms of ratios values comparison, to see how/if changing selected parameters (activities and mean, median, minimum and maximum values) could affect the SFA model behaviour, sensitivity analysis was undertaken first through the calculation of ratios after removal and addition of activities. For example, the ratios were calculated with all the activities as reported in this study, then new calculations were applied after the removal of the activities with highest pollutant predicted loads. These activities were wastewater, refineries and production of electricity (EfW – energy from waste power plants) for metals and wastewater, manufacture of chemical and chemical products and manufacture of basic metals and metal products for PAHs.

Those activities were removed and then added back one at a time, to see how the model behaved by the different combinations. Then, the use of median, minimum and maximum were also considered and tested through ratios values comparison between field and substance flow analysis data sets (please see results reported in Section 5.5).

3.9.2.10 Statistical analysis for SFA modelling analysis results

Statistical tools such as correlation have commonly been used to interrogate environmental data sets to support identification of the sources of pollutants including metals and PAHs (Khatoon *et al.*, 2013; Zhang *et al.*, 2018; European Environmental Agency, 2007). Pearson's correlations are simple measures of dependence between two variables (McDonald, 2009) and this statistical analysis was performed using the software Minitab 17 (Minitab, 2017) with the level of significance of ≤ 0.05 used for all tests. The direction and strength of the relationships between field data and SFA modelling were evaluated using correlation analysis with results reported using the following classification (Minitab, 2017; Owen *et al.*, 2020):

- 0.00 – 0.19 = very weak,
- 0.20 – 0.39 = weak,
- 0.40 – 0.59 = moderate,
- 0.60 – 0.79 = strong,
- 0.80 – 1.00 = very strong

As the units from field data set (reported as μg/g) and SFA (reported as kg/year) are different, it was necessary to develop an approach to enable field data and predicted values to be cross-evaluated as part of the ground-truth process. Therefore, ratios and correlation analysis were chosen as they do not consider data units (Kim, 2018; Sterling and Dekate, 2008).

Ratios are commonly used in statistical analysis for reporting research results as they are simple to calculate, simple to understand and can give clear and direct information to researchers

(Andrade, 2015), especially in medical (e.g. comparing two different data groups, usually to find out how effective a specific type of treatment is) (Streiner and Norman, 2012) and environmental studies where, ratios are usually applied between two different pollutants to help identify pollutant sources, and the results are compared to set standards or guidelines which are usually given as range values (Zhao *et al*., 2019; Font *et al*., 2015; Meire *et al*., 2007; Raman and Arellano, 2017; Smith *et al*., 2019). Since ratios are dimensionless, these were applied as an approach which enables data sets with differing specific units to be cross-compared, enabling the relationship between different variables to be compared (Kunes, 2012). The development and use of ratios to combine related but different outcomes is described in the literature (Friedrich *et al*., 2008; Sterling and Dekate, 2008) for medical and computing research and has been used in environmental research studies such as Schneider (2009), which relies on use of units and dimensions for quantification in ecological research and study by Cornelissen *et al*. (2008), where ratios between water and sediment dibenzo-p-dioxin and –furan concentrations were used to investigate contaminants activity between the two matrices. For SFA studies, ratios have been used to analyse flow of substances through different mediums such as in the study by Brunner and Rechberger (2016) where they used ratios to compare substance flows via coal and municipal solid waste and as per Wang *et al*. (2012) to quantify coal, oil and natural gas with a consumption and supply ratio used to better reflect the interactions between population, gross domestic production and fossil fuels. There were few studies which predicted results compared with field data to further support their predictive models (e.g. Huang *et al*., 2015; Van Gils *et al*., 2020; Buser and Morf, 2009;) but comparison was applied directly between results as predicted and measured results were presented in same units. Therefore, this study introduces the use of ratio as an innovative classification system to statistically analyse relationships between SFA results and sediment field data.

The ratio was calculated using the following equation:

Ratio = Pollutant specific SFA result / Pollutant specific sediment field data measurement.

The ratio classification system applied in this study is as follows:

- Ratio in the range of 0.5 to 1.5 (± 50 %) = acceptable level of prediction.
- Ratio of < 0.5 = underprediction (i.e. SFA predicted value is < field value; based on the field data the SFA result is underpredicted).
- Ratio of > 1.5 = overprediction (i.e. SFA predicted value is > field value; based on the field data the SFA result is overpredicted).

For the ratio calculation applied in this research the choice of the numerator and the denominator is important, as is the statistical coherence between the two (OECD, 2008). Thus, values for sediment field data were used as denominator. The ratio classification system applied in this research was based on the fact that whilst a ratio of 1 would be considered a strong relationship between data sets considering SFA uncertainties, contaminant activities in sediment (e.g. deposition, remobilisation) and the complexity of the receiving system an allowance of ± 50 % was applied to the ratios as an initial benchmark to facilitate assessment of the results. In this context, although the selection of a range against which to evaluate data is subjective, a range of 0.5 to 1.5 (i.e. ± 50 %) was selected based on a review of the OECD (2008) guidelines on measuring material flows and the use of a similar approach in several studies e.g. Van Gils *et al*., 2020; Lassen and Hansen, 2000; Danius, 2002. For example, with respect to data accessibility and accuracy, the OECD material flows analysis guidelines (2008) states that when the purpose is communication (as in this study) an order of magnitude is a sufficient level of accuracy. Likewise, Lassen and Hansen (2000) in their guide for substance flow analysis carried out by the Danish EPA state in their section on reliability and level of detail that estimations of emissions can only be considered correct within an order of magnitude. More recently, in a study of material flow analysis of chemicals in European Waters which involved a comparison between predicted concentrations and field measurements, Van Gils *et al*., (2020) discuss levels of uncertainties in terms of orders of magnitude and aim to reduce uncertainty from two to one orders of magnitude, concluding that one order of magnitude is an acceptable level of uncertainty in terms of the prioritisation of substances.

Another reason to use the range of 0.5 to 1.5 was due to the fact that ratios, although being a different measurement compared to correlation, is also a measure of association between data sets and therefore provides information on the strength of relationship between variables (McHugh, 2009) and having the correlation classification as guide, the selected range (0.5 to 1.5 (i.e. ± 50 %)) falls between the 'moderate' to 'very strong' categories (Qwen *et al.*, 2020).

CHAPTER 4. DETERMINATION AND DISCUSSION OF METALS AND PAHs IN WATER AND SEDIMENT

Full details of all metal concentrations determined in water and sediment samples at each sampling site on each sampling date are presented in Appendices A1 to A7. An overview of results and their evaluation are presented in the following sections:

4.1 Concentration of selected metals in surface waters – all sites and sampling dates

The range and mean concentrations of selected metals in various surface water bodies of the Lower Lee catchment are shown in Table 4.1a. The average concentrations of the seven metals in all water samples increase as follows: Hg < Cd < Sn < Pb < Cu < Ni < Zn, which follows a similar order of abundance reported in urban rivers with similar characteristics in previous studies (e.g. Gobeil *et al*., 2005; Goher *et al*., 2014; Magdaleno *et al*., 2014; Raju *et al*., 2013). According to Paul and Meyer (2001) and Faisal *et al*. (2014), both the order of abundance and metal concentrations determined in urban rivers can vary depending on the extent and type of urbanization and also other factors, such as the geological characteristics of the area, land use and weather conditions. The standard deviations for each metal mean concentration, as shown in Table 4.1a, indicate that metal concentrations varied considerably between different sampling locations and sampling dates, this is further explored through ANOVA analysis in Section 4.1.1.

Table 4.1a Overview of maximum, minimum and mean (µg/l ± SD) metal concentrations in surface waters determined at all sites on all sampling dates.

Metal	**Range in concentration**	**Mean concentration (± SD)**	**UK TAG Standards (µg/l)**	**EU EQS (µg/l)**	
				AA*	MAC**
Cd	0.01 – 2.78	0.19 (± 0.38)	---	0.25(c)	1.50(c)
Cu	1.04 – 117.71	11.13 (± 17.78)	1.00(a)	---	---
Hg	0.01 – 3.56	0.17 (± 0.41)	---	---	0.07(d)
Ni	0.11 – 55.05	15.64 (± 11.40)	---	4.00(a)	34.00
Pb	0.02 – 13.25	2.39 (± 2.42)	---	1.20(a)	14.00
Sn	0.01 – 13.90	0.73 (± 1.58)	---	---	---
Zn	0.55 – 62.68	17.16 (± 13.76)	14.20(b)	---	---

Key:
* Annual Average (also referred to as long-term standard)
** Maximum Allowable Concentration (also referred to as short-term standard)
(a) Bioavailable fraction
(b) Bioavailable fraction 10.90 µg/l + Ambient Background Concentration 3.3 µg/l dissolved Zn for River Lee.
(c) For Cd and its compounds, the EQS values here are for Class 5 (≥ 200 mg $CaCO_3$ /l) as per hardness of water in the Lower Lee catchment
(d) Value for Hg and its compounds

Whilst Table 4.1a shows UK TAG (2013) standards which consider an ambient background concentration only for Zn (reported as mean value, 3.3 µg/l), metal background reference concentrations (MBRC) as reported (as median trace metal concentrations for Thames River Basin District categorised as calcareous by EU WFD geological typology) by the WFD-UK TAG Group (2012) and the Environment Agency (2008b) were considered (Table 4.1b) to evaluate if the metal concentrations reflect the background elements of the metals in the Lower Lee catchment or if they are influenced by other sources. Comparison of the relative abundance of metals with water background reference concentrations (MBRC) data (see Table 4.1b) , shows a different trend (Pb < Cu < Zn < Ni for MBRC and Pb < Cu < Ni < Zn for this research), indicating that reported levels are not solely a function of, e.g. underlying geology, but also due to different land use activities which discharge surface runoff – and deposited pollutants - to receiving water bodies (Brils, 2008; Jones *et al.*, 2019; Foster and Charlesworth, 1996; Baccini and Brunner (2012) and Sörme, (2003). Also, when comparing metal background reference concentrations (MBRC) of relevant metals with median metal concentrations, it shows that metals concentrations determined in this research were one to two orders of magnitude higher than the

MBRC values, which indicate anthropogenic activities influencing levels of metal concentrations in the Lower Lee catchment.

Table 4.1b Overview of maximum, minimum, mean and median (µg/l ± SD) metal concentrations in surface waters determined at all sites on all sampling dates in comparison to the MBRC values (µg/l).

Metal	**Range in concentration**	**Mean concentration (± SD)**	**Median concentration**	**MBRC* (µg/l)**
Cd	0.01 – 2.78	0.19 (± 0.38)	0.07	---
Cu	1.04 – 117.71	11.13 (± 17.78)	12.64	0.81
Hg	0.01 – 3.56	0.17 (± 0.41)	0.22	---
Ni	0.11 – 55.05	15.64 (± 11.40)	16.53	3.60
Pb	0.02 – 13.25	2.39 (± 2.42)	2.60	<0.05
Sn	0.01 – 13.90	0.73 (± 1.58)	0.91	---
Zn	0.55 – 62.68	17.16 (± 13.76)	18.19	<1.50

Key:
* MBRC = metal background reference concentrations reported as trace metal median concentrations for Thames River Basin District categorised as calcareous by WFD geological typology (WFD-UK TAG Group, 2012; Environment Agency 2008b).

Results were compared to UK TAG (2013) standards and the EU environmental quality standards (EU EQS) (2013) where available (see Table 4.1a). The results reported for this research are as total metal concentrations in the water column whereas EU EQS standards refer to dissolved concentrations as the proportion of the metal available to interact with biota (Van Leeuwen *et al*., 2005). So, whilst the average concentrations of Ni and Pb reported exceed the respective annual average (AA) concentrations, the exact implications of this are unclear as the fraction of each metal in the dissolved (as opposed to particulate phase) was not determined. Similarly, the UK TAG standards for Cu and Zn target the bioavailable fraction and whilst these were included in Table 4.1a for completeness, direct comparisons between standards and mean metal concentrations cannot be made.

The average concentration of Hg exceeds the maximum allowable concentration (MAC) value as identified in the EU EQS (2013) by an order of magnitude. However, again, further work would be required to enable the implications of this to be understood. With the same caveats, in regard to the MAC value, the variation in the ranges for Cd, Ni and Hg demonstrates that the EU EQS value can be exceeded depending on sampling site and date. The range of metal concentrations also indicates that Cd and Ni exceed the MAC of the European EQS during certain times of the year and/or at some sampling sites, and therefore it is recommended that future studies should focus on determination of the dissolved fraction as opposed to total metals.

The EU EQS list does not include Sn, Cu or Zn. Concentrations of Sn in surface waters have been reported to be generally less than 0.005 µg/l but industrial pollution was reported to increase Sn levels in river water to up to 0.7 µg/l (Yemenicioglu and De Mora, 2009). Ferrante *et al.* (2014) argue that the use of organotin biocides can produce even higher concentrations of inorganic Sn. WHO (2005) report that Sn in surface waters is usually not detected in all sampling sites but it can vary according to land use. For example, a study of US and Canadian rivers detected Sn in only 3 of 59 samples at concentrations ranging from 1.3 to 2.1 µg/l (with the usual sources being from a number of organotin substances used in different manufacturing processes, such as PVC and pesticide manufacture). In contrast to the literature data, the results collected in the current study indicate that Sn was detected on all sampling occasions with a range of 0.01 – 13.90 µg/l, indicating the presence of Sn sources throughout the Lower Lee catchment. Possible sources of Sn include antifouling paints containing tributyltin that are applied as a finish coat to the immersed sections of boats and floating structures as reported by the Environment Agency (2015).

As Cu and Zn are also not included in the EU EQS list, detected concentrations have been compared to the standards recommended by the UK TAG (2013) and approved by Defra (2014). The current standard for Zn is 14.2 µg/l (bioavailable fraction) and this standard includes an ambient background concentration of 3.3 µg/l (dissolved fraction) identified for the Lower Lee catchment based on a 10th percentile of all monitoring data by hydrometric areas (TGD-EQS-EC, 2011) as recommended by the EU EQS. The scope of this research did not include consideration of metal bioavailability fractions, which are influenced by the interactions between metals and a range of water physico-chemical characteristics. An assessment of metal bioavailability through direct measurement (e.g. chemical based extraction and biosensors) or indirect, through the use of bioavailability prediction tool (e.g. biotic ligand model (BIOMET)) would have required substantial further field and laboratory work and – whilst of intrinsic value - would not have developed a data set investigation of further parameters such as water hardness, calcium content, suspended solids and organic matter content (Adams *et al*., 2020; Søberg *et al*., 2019; Zhang *et al*., 2014). So, whilst the average concentrations of results show that the mean concentration of Zn determined can exceed both the background level and the UK standard, the exact implications of this are unclear as the bioavailability fraction of each metal was not determined. As shown in Table 4.1a, the range of Zn concentrations detected in this study indicates considerable variability both throughout the study area and by sampling date. Spatial and temporal distributions of metals in river water is further explored in Section 4.1.1.

With regard to Cu, the concentration ranges indicate Cu is exceeding the UK TAG standard at all sampling locations and dates. The ranges for Cd, Ni and Pb show that these metals can exceed the AA from the EU EQS at certain locations and sampling dates. However, again this is based on a comparison of total concentrations with dissolved fractions and further speciation work is required to enable the impact of metals analysed to be understood. For example, a quick demonstration of the complexity of the dynamics and behaviour of selected metals which influence water quality is shown in Table 4.1c which lists some of the main metals properties which influence solution chemistry and toxic response of each metal in respect to hydrolysis, dissolved organic matter (DOM) and pH.

Table 4.1c Overview of the complexation characteristics of selected metals as reported by Environment Agency, 2008.

Metal	**Characteristics**		
	Hydrolysis	**DOM* complexation**	**Dependence of free ion toxicity on pH**
Cd	negligible	weak	low
Cu	moderate	strong	high
Hg	negligible	moderate	low
Ni	negligible	moderate	low
Pb	moderate	strong	high
Sn	negligible	moderate	low
Zn	negligible	weak	low

Key: *Dissolved Organic Matter

Table 4.1c shows that Cd, Hg, Ni, Sn and Zn have similar chemistries since for each of these metals, large variations of chemical speciation in respect to hydrolysis, pH and DOM are not expected. On the other hand, the hydrolysis and DOM complexation tendencies of Cu and Pb mean that their free ion concentrations will decrease substantially with pH, and will depend strongly upon DOM (Environment Agency, 2008).

Comparing results from this study with other research it was noted that Paul and Meyer (2001) reported elevated concentrations of several metals including Cd, Cu, Ni and Zn as a common feature in urban streams because of their receipt of runoff from wastewater treatment plants, combined sewer overflow, industrial discharges and numerous nonpoint pollution sources (e.g. brake linings, tyres, metal alloys originating from a range of traffic and street furniture sources). Research by Snook and Whitehead (2004) on the lower stretch of the River Lee reported higher average levels of Cd, Cu, Pb and Zn in the water column (see Table 4.2) and it may be that on-going pollution mitigation measures such as modernisation of wastewater treatment plants, installation of sustainable drainage systems (SuDS) and sediment dredging in 2009 along sampling sites G, H and J, implemented to meet EU WFD requirements, have resulted in a decline in metal contamination. However, the same study found lower Hg and Ni in 2004 compared to results in this study, which could be related to changes in specific land use activities (leading to an increase in their discharge over the years), higher sediment resuspension rates of these two metals in comparison to the others or that the mitigation methods put in place have been more effective on certain metals (and their sources) than others. Comparison of the results from this research with those from urban rivers located in various other countries (see Table 4.2), shows that in the Terengganu River basin (Malaysia) Cd and Sn was higher and Hg and Pb lower than results in this study. Results from Reno River in Italy show Cu, Ni and Zn being lower while Hg and Pb are considerably higher. Meanwhile, results from Rudnianský creek in Poland shows Cu, Hg and Zn being lower and only Pb being almost double of the result in this study. Data from the Pardo River in Brazil shows Cd, Cu, Ni, Pb and Zn lower than results in this study. Although compared results were from urban rivers, there is a variability in difference between results and this can be due to factors such as different land uses, geomorphology and geology of each area.

Table 4.2 Comparison of metal concentrations of this study with results from other urban rivers from around the world.

Locations	**Average concentration (µg/l)**							**References**
	Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Sn**	**Zn**	
Lower Lee catchment, London, UK	0.19	11.13	0.17	15.64	2.39	0.73	17.16	This study
River Lee, London, UK*	0.34	13.70	0.04	12.50	15.30	---	42.00	Snook and Whitehead (2004)[1]
Terengganu River basin, Terengganu, Malasya**	4.78	---	0.04	---	0.97	14.68	---	Sultan *et al*. (2011)[1]
Reno River, Emilia-Romagna, Italy*	---	4.40	1.05	1.55	36.30	---	12.30	Ferronato *et al*. (2013)[2]
Rudnianský creek, Rudňany village, Poland***	---	8.00	0.80	---	4.50	---	6.90	Angelovičová and Fazekašová (2014)[2]
Pardo River, Ipuiúna, Brazil****	0.05	2.53	---	5.70	2.54	---	12.45	Alves *et al*. (2014)[2]

Key:
* urban and industrial area
** urban area with a with mixture of mining, industry and agriculture activities
*** urban area with past mining history
**** urban area with sugarcane industry activity

[1] results for dissolved metal concentrations
[2] results for total metal concentrations

Figures 4.1a and 4.1b show the variations in water average metal concentrations at each site over the course of eight sampling trips. The site identification letters are described in Table 3.1. The analysis of the results in Figure 4.1a indicates that there is a considerable variation in metal concentrations in water between the sites. It could be due to the variation of metal composition in sediments from different sites or input of different amounts of heavy metals that have been released from various sources (Lim *et al.*, 2012). Ni and Zn reported the highest mean concentrations at all sites, except for site B where Cu has the highest average concentration as well as the highest standard deviation. This is due to the higher concentrations recorded on two sampling dates (14th August 2015 and 23rd March 2016), which could be due to an unreported incident taken place during this time or related to how it is attached to the particulates (Environment Agency, 2015), although the reason why one metal would leach preferentially to others remains unclear.

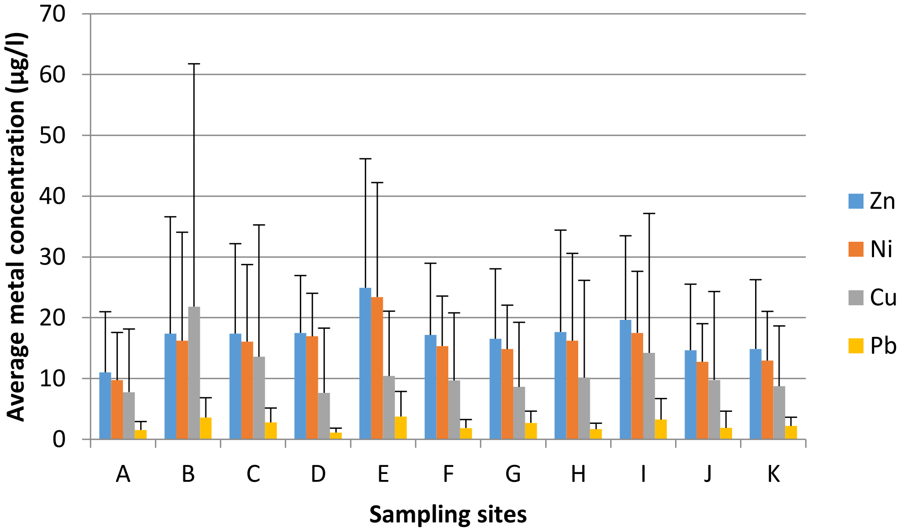


Figure 4.1a Average metal concentrations (±SD) of Zn, Ni, Cu and Pb in surface waters in the River Lee, Navigation Channel and tributaries.

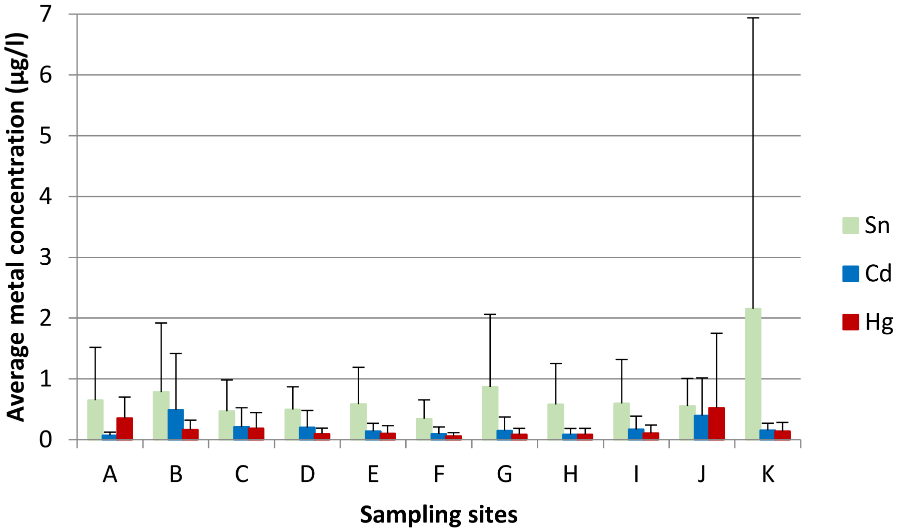


Figure 4.1b Average metal concentrations (±SD) of Sn, Cd and Hg in surface waters in the River Lee, Navigation Channel and tributaries.

Concentrations of Cu generally exceed those of Pb with the concentrations of Sn, Cd and Hg being lower and relatively consistent across sites. Of particular note is the fact that Zn and Ni, and to a lesser extent Cu and Pb, show similar trends in concentration by site potentially indicating a similar source, such as urban runoff, discharge of industrial wastewater and/or effluent from sewage treatment works (Shah *et al*., 2005; Björklund, 2011). Concentrations of Zn, Ni, Cu and Pb in urban rivers have been also reported to be related to sediment resuspension (Wilson *et al*., 2005) and this is further discussed in Section 4.3. The high standard deviation for Cu at site B was due to the detection of an elevated Cu concentration (117.71 ± 0.65 µg/l) at site B on the 23rd March 2016 (Appendix A8), a value one to two orders of magnitude higher in comparison to Cu concentrations recorded on other dates / other sites. The use of process controls and the reproducibility of the sample runs gives confidence this was a robust result The elevated Cu concentration could be due to e.g. the capture of an unreported pollution incident. The fact that only a single metal was elevated on the particular sampling trip suggests a pollutant specific discharge as opposed to e.g. the capture of a sediment resuspension event which would be anticipated to lead to several substances occurring at a greater than usual concentrations.

With regard to Figure 4.1b, Sn was determined with highest concentrations at all sites compared to Cd and Hg and while Hg average concentration was determined higher than Cd at sites A and J, the other sampling sites shows Cd average concentrations higher than Hg, indicating that a variety of sources might be responsible for their occurrence with differentiation in trends between sampling sites (Sultan *et al*., 2011). As for Cu at site B, the average concentration of Sn is associated with a large SD at site K (Figure 4.1b), where a single elevated Sn concentration of 13.90 ± 0.13 µg/l was detected on the 14th August 2015 (Appendix A7), a concentration one order of magnitude higher than Sn concentrations determined at other sites and on other sampling dates. Again, the use of process controls and the reproducibility of the sample runs gives confidence this was a robust result. In addition to the discussion above for the explanation of the elevated Cu concentration on a single sampling date, it is noted that despite a ban on the use of tributyltin as a component of an antifouling agent applied to boats, it is understood to still be in use in antifouling paints applied as a finish coat to the immersed sections of boats and floating structures (Environment Agency, 2015). Thus, the elevated concentration may be a function of a recent application to (or maintenance work of) boats/boating infrastructure. With regard to site A, it was initially selected as background site against which the impacts of an increasing urbanised surface water system could be benchmarked, (see Section 3.2), However, whilst site A showed the lowest surface water concentrations for Cd, Cu, Ni, Pb, and Zn, it was amongst the most contaminated sites in terms of both Hg and Sn (Site A and J reported both the highest Hg concentrations with sites A, B, G and K the highest Sn concentrations). The high levels of pollutant concentrations determined at site A is further discussed in Section 4.1.1 and pollutant sources explored in Chapter 5 through the results of SFA modelling tool.

Appendices B1 and B2 show the distribution of targeted metals throughout the sampling sites in the Lower Lee catchment. As noted in sections 3.1 and 3.2, samples sites are located on:

- The River Lee (sample sites A, G, H and I),

- The Lee Navigation Channel (sample sites C, J and K),
- Four tributaries (from North to South): the Cobbins Brook (B), Salmons Brook (D), Pymmes Brook (E) and Ching Brook (F).

Figures 4.2a and 4.2b present the mean metal concentrations for the water samples collected from sampling sites on the River Lee. Whilst the overall profile of Figures 4.1a and 4.1b indicates increasing metal concentrations as the Lee flows from outer towards inner London, there is considerable variation between the different metals. For example, average concentrations for Cd, Hg, Pb and Sn are generally below 4 µg/l whilst those for Cu, Ni and Zn range over an order of magnitude (from 7.65 µg/l to 24.94 µg/l), which could be explained by a number of factors such as the extent and type of activities in the area and particles binding/release properties in sediment. Highest average concentrations of Cd, Cu, Ni, Pb and Zn were determined at downstream site I. Hg mean concentrations were highest at site A followed by downstream site I, Sn mean concentrations were highest at site G followed by upstream site A.

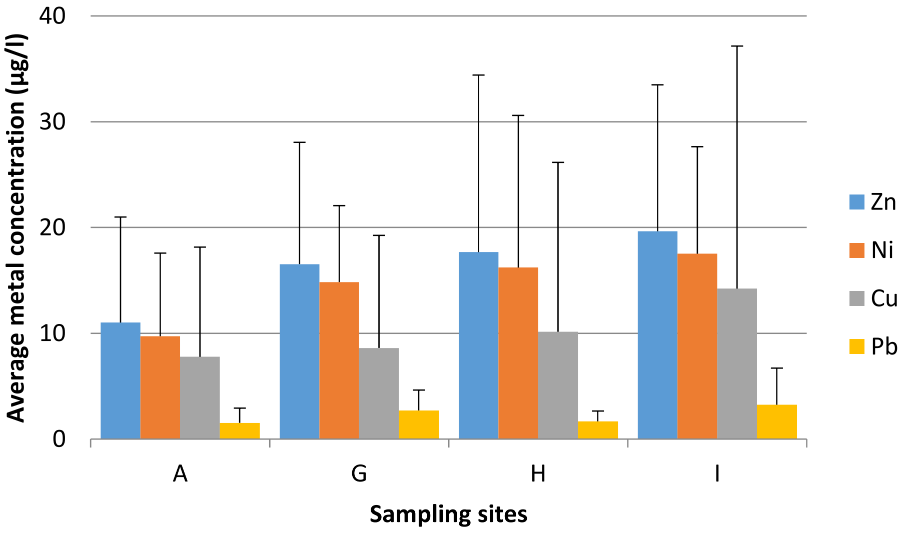


Figure 4.2a Mean concentrations (±SD) of Zn, Ni, Cu and Pb in surface waters of the River Lee.

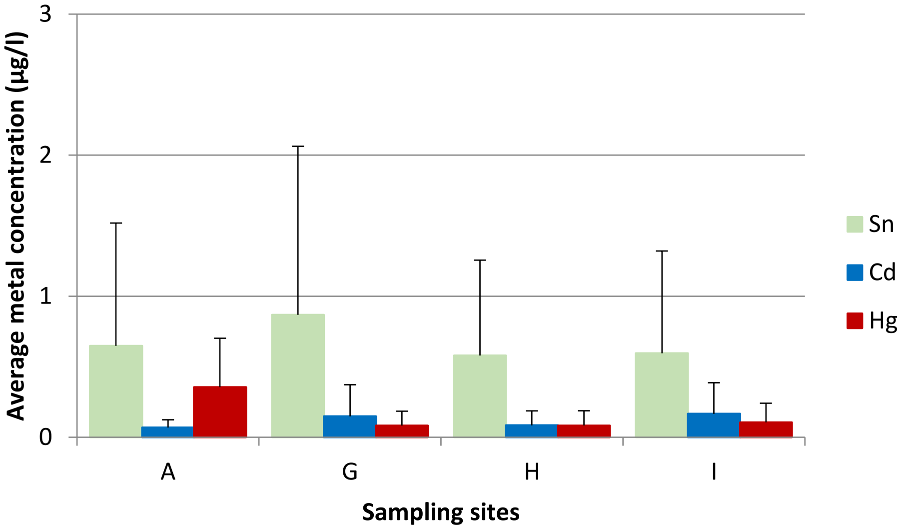


Figure 4.2b Mean concentrations (±SD) of Sn, Cd and Hg in surface waters of the River Lee.

With regard to trends in mean concentrations, Figures 4.2a and 4.2b indicate that only Cu, Ni and Zn in the River Lee occur in the anticipated trend of increasing concentrations as the river flows from less urbanised (upstream site A) areas towards central London (sampling site I). For the other four metals this trend was not present with site G having the highest average concentration of Sn, site I having the highest mean concentration of Cd and Pb and notably for Hg, the highest mean concentration was determined at upstream site A. This lack of increasing trend in metal concentration as the river flows from a relatively rural area to a central city location may be explained by a range of factors including the fact that there are various towns located further upstream on the Lee, variation in flow from various tributaries and changes in land use, highlighting the complexities associated with identifying sources of pollutants in an urban catchment (Sörme and Lagerkvist, 2002; Ellis and Mitchell, 2006; Environment Agency, 2007; Environment Agency, 2006; Baccini and Brunner, 2012). Again, as observed before for the Lower Lee catchment, Zn and Ni were detected at highest concentrations compared to the other metals and exhibit similar trends in behaviour across the sampling sites, followed by Cu and Pb.

The results for the three sampling points (C, J and K) on the Lee Navigation Channel are presented in Figures 4.3a and 4.3b. The concentration ranges are similar to those determined in the main waterway (Sites A, G, H and I) indicating that both river and channel receive similar metal concentrations and/or that the water bodies are well-mixed prior to zones where they diverge into separate channels. A trend of increasing metal concentrations as the Lee Navigation Channel flows downstream was observed only for Sn. In contrast to the trend noted in the River Lee, average concentrations for Zn, Ni, Cu and Pb were determined at upstream site C and mean concentrations of Cd and Hg were highest at site J.

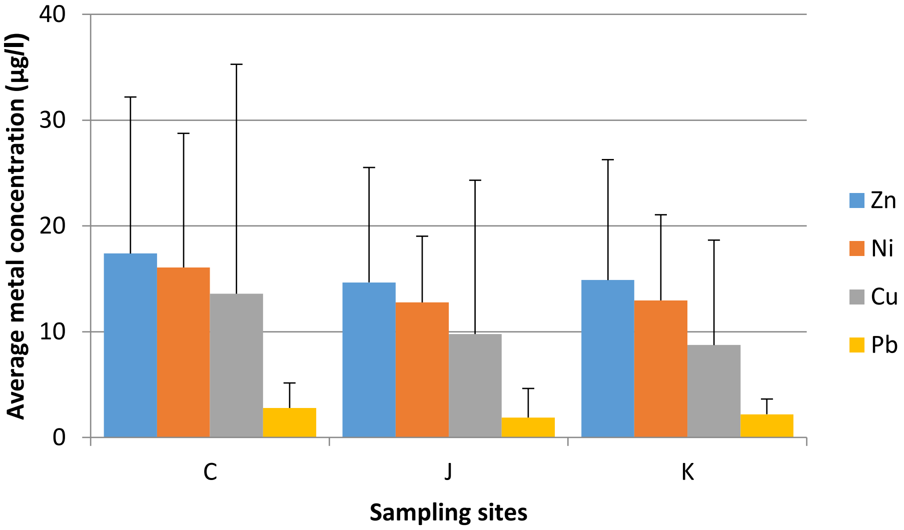


Figure 4.3a Mean concentrations (±SD) of Zn, Ni, Cu and Pb in surface waters in the Lee Navigation Channel.

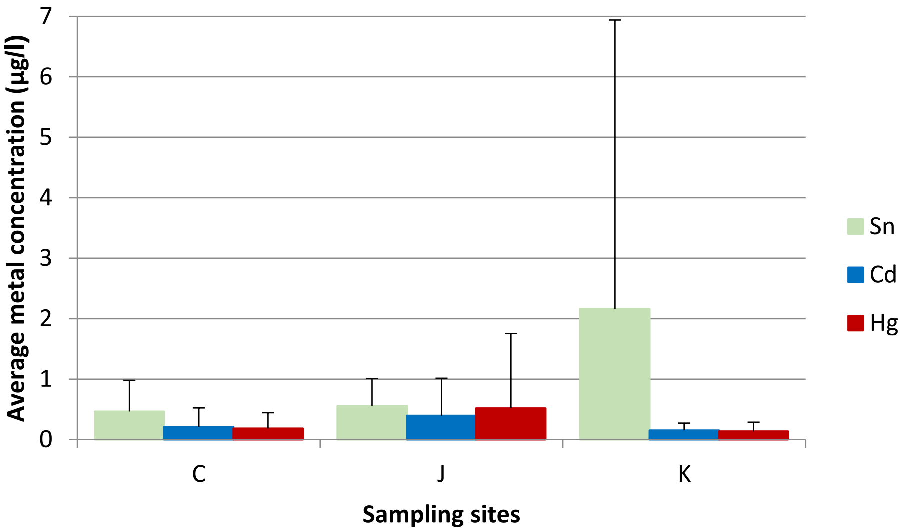


Figure 4.3b Mean concentrations (±SD) of Sn, Cd and Hg in surface waters of the Lee Navigation Channel.

The differences in trends of metals from River Lee to Lee Navigation Channel could also be associated with the fact that, although the River Lee has been heavily modified, the flow in the Lee Navigation Channel is controlled by a number of locks which, can act as a barrier for sediments (and associated pollutants) influencing their occurrence in water and sediment matrices. Again, these results illustrate that aqueous pollutants concentrations do not necessarily increase in a linear manner but are sensitive to internal and external inputs such as sediment resuspension and surface waters drains.

Results of metal concentrations for the tributaries Cobbins Brook (B), Salmons Brook (D), Pymmes Brook (E) and Ching Brook (F) are presented in Figures 4.4a and 4.4b and Appendices B1 and B2. Results indicate that inflow from Cobbins Brook is the most contaminated for Cd, Cu, Hg and Sn although again there is considerable variation. The highest Ni, Pb and Zn average concentrations were determined at Pymmes Brook and Cu and Pb concentrations were lowest in Salmons Brook, with concentrations of Cd, Hg, Ni, Sn and Zn lowest in Ching Brook. Further examination is given in Section 5.1, during substance flow analysis to investigate in more detail the contributions of targeted metals from the tributaries into the River Lee and the Lee Navigation Channel.

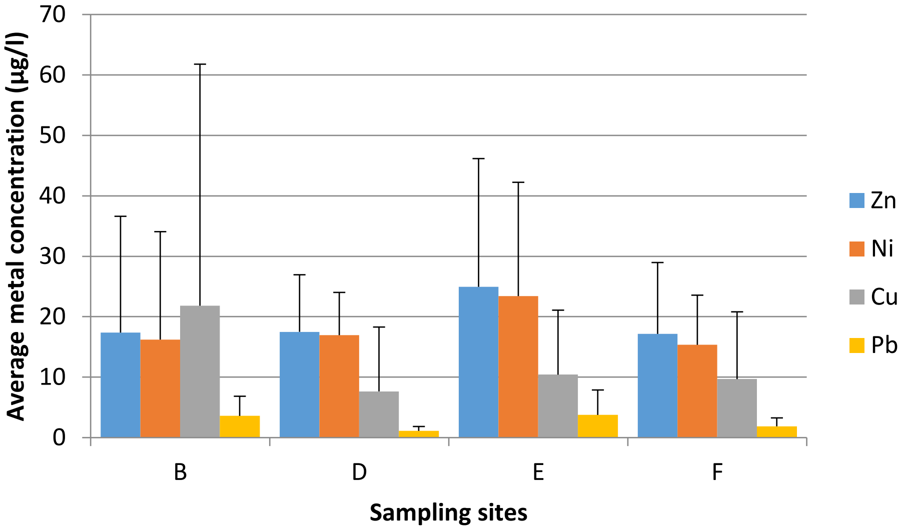


Figure 4.4a Mean concentrations (±SD) of Zn, Ni, Cu and Pb in surface waters of selected River Lee tributaries.

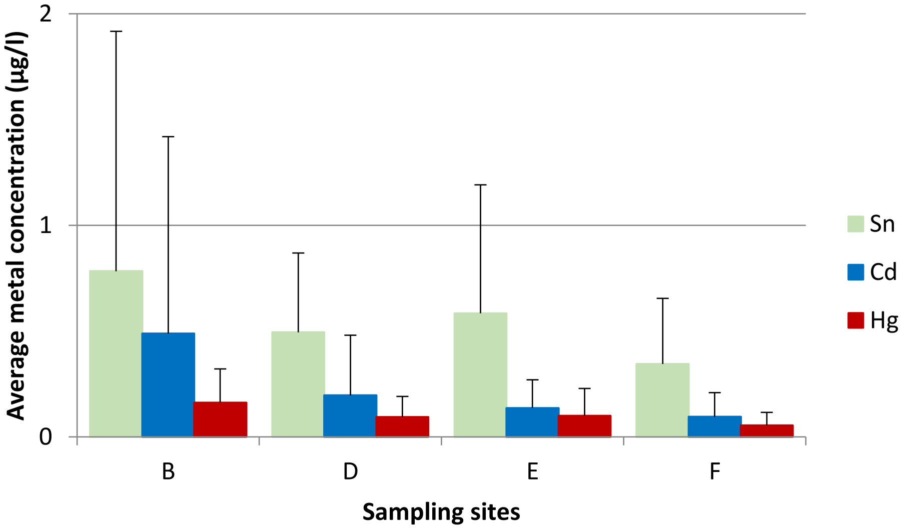


Figure 4.4b Mean concentrations (±SD) of Sn, Cd and Hg in surface waters of selected River Lee tributaries.

The initial descriptive analysis of the data indicated variation of metal concentrations between sampling sites and dates and therefore further analysis was undertaken to identify any significant spatial and/or temporal distribution of targeted metals in river water.

4.1.1 Spatial and temporal distributions of metals in river water

The normality of the data distribution of each parameter was assessed using the Anderson-Darling test (see Table 4.3); as most data sets showed a skewed distribution, variables were log-transformed for the purposes of statistical analysis using the $\log_{10}$ base function. This transformation enabled data sets for some parameters to achieve normality and linearity which are the initial requirements for performing the ANOVA General Linear Model (GLM) analysis which permits the use of more than one factor as predictors. After transformation, results showed data for Cd, Sn, Zn and pH as normally distributed but data for Cu, Hg, Ni, Pb, DO and temperature remained skewed. Equal variance tests for original and transformed data showed P-values < 0.05 indicating unequal variance of the data. However, when checking the conditions of the transformed data through the Minitab Assistant the output report showed that analysis can still be carried out (despite non-normality) as the test is still robust - not only for non-normal distribution data but also for unequal variance of the data in question. Outliers present in samples were kept to maintain integrity of the research and as they may prove interesting in their own right (Weisberg, 2005).

Table 4.3 Results from Anderson-Darling test of normality for data of metals and other parameters in surface waters.

Data sample	**Results from original values**		**Results from $\log_{10}$ values**	
	P-value	**Normal distribution**	**P-value**	**Normal distribution**
Cd	< 0.005	No	0.396	Yes
Cu	< 0.005	No	< 0.005	No
Hg	< 0.005	No	< 0.005	No
Ni	< 0.005	No	< 0.005	No
Pb	< 0.005	No	0.006	No
Sn	< 0.005	No	0.055	Yes
Zn	< 0.005	No	0.125	Yes
DO	< 0.005	No	0.048	No
Temp	< 0.005	No	< 0.005	No
pH	0.280	Yes	0.188	Yes

ANOVA GLM was first performed using metal concentrations as dependent variables and sampling sites and dates as categorical variables to test for site-to-date differences in metal concentrations and to determine whether metal concentrations vary in relation to site at a level which is considered statistically significant (see Table 4.4), it was then repeated using the parameters DO, temperature and pH as dependent variables (see Table 4.16), because these parameters, as observed in the literature review, strongly influence other water quality constituents such as heavy metals (Weiner, 2013).

Table 4.4 Results of the application of ANOVA GLM to the target metal concentrations in surface waters using $\log_{10}$ data.

Sample by metal	**Factor**	**F-test**	**P-value**	**R^2 (%)**	**R^2 Adjusted (%)**
Cd	Sites Dates	1.09 6.15	0.38 < **0.01**	43.52	29.81
Cu	Sites Dates	1.98 79.12	**0.05** < **0.01**	89.12	86.48
Hg	Sites Dates	2.34 21.28	**0.02** < **0.01**	71.13	64.12
Ni	Sites Dates	1.80 11.04	0.08 < **0.01**	57.63	47.35
Pb	Sites Dates	1.28 4.83	0.26 < **0.01**	40.01	25.43
Sn	Sites Dates	0.51 15.87	0.88 < **0.01**	62.40	53.27
Zn	Sites Dates	1.95 18.41	**0.05** < **0.01**	67.95	60.16

Key: Values in bold are for metals that vary significantly by sites and/or dates.

The ANOVA GLM results for metals (Table 4.4) revealed that Cu, Hg and Zn concentrations vary significantly by sampling site and date. The concentrations of the other target metals (Cd, Ni, Pb and Sn) vary significantly in relation to sampling date only. The variation in the metal distribution by sampling dates may be related to land use (i.e. variations in industrial activities) at the Lower Lee catchment and this is further explored in Chapter 5 when discussing results from the substance flow analysis tool. The R^2 adjusted values were over 50 % for Cu, Hg, Sn and Zn meaning that more than 50 % of the variation in these metals can be explained by their relationship with one or more sampling sites and/or sampling dates (Table 4.4). The R^2 values for Cd, Ni and Pb indicate that less than 50 % of their variation explained by their relationship with sampling sites/dates. Therefore, residual plots (Appendices C1 to C10) were obtained in order to check randomness of the data before and after log-transformation. This revealed that log transformed data showed residual plots with more randomness of the residuals vs fit, validating the strength of the model in its accuracy. ANOVA GLM results indicate that Cu, Hg, and Zn concentrations may be more sensitive to variations in land use, for example, resulting from specific discharges at specific locations as described in the Tukey's HSD (honestly significant difference) test results below. As an example, Hg has shown higher concentrations at upstream site A compared to a number of sampling sites, suggesting site A, although less urbanised, it is also located at the downstream end of the Upper Lee catchment and may receive local discharge with higher Hg content or could potentially be influenced by discharges from various towns located further upstream on the Lee (e.g. see Appendix A9 which identifies treated sewage discharge upstream of Site A). Another aspect is that there was a considerable high metal concentration level at a specific date compared to sites and dates, for example, at site A, on 14th August 2015 Hg mean concentration reached a level of 1.00 ± 0.06 µg/l, which was higher than the levels of Hg at most sites and dates (except for site J, which reached the highest Hg level on this same date, 3.56 ± 0.18 µg/l), which could originate from an unreported incident(s) (Environment Agency, 2015). Studies of land use impact on the water quality of urban streams (e.g. Taka *et al.*, 2016 and Silva *et al.*, 2012) suggest that land use directly effects surface water metal concentrations as it can change water chemistry and consequently metal speciation, for example, decreasing dissolved organic carbon, affecting the biota communities and their activities. The temporal variation of metal concentrations, significant for all metals, is not surprising given the variations in rainfall conditions, antecedent dry period, levels of atmospheric deposition and catchment activity factors likely to prevail in association with each sampling trip.

Evidence of significant temporal variations in heavy metal concentrations in surface waters has been reported previously (e.g. Sullivan and Drever, 2001; Kimball *et al*., 2010).

Post-hoc multiple comparisons were then performed using Tukey's Honest Significant Difference (HSD) test (P-value ≤ 0.05) to identify the sources of the significant differences described above. Appendices D1 to D7 show the confidence intervals associated with the mean concentrations per sampling dates for each metal. Due to the large amount of data, comparison Minitab software did not produce confidence interval plots for sampling sites. However, from Tukey's HSD test results available the main findings are:

- With regard to sampling sites, Cu was significantly lower at upstream site A compared to site B, Hg was significantly higher at site A compared to sites F, G and H and Zn was significant lower at site A compared to site E.
- Results for dates showed that Cd was significant higher on 23rd March 2016 compared to all the other sampling dates, except to 14th April 2015; Hg was significantly lower compared to all the other sampling dates; Ni and Zn had similar results being lower on 11th November 2013 compared to 20th May, 14th August 2015 and 23rd March 2016 and significant lower on 9th December 2013 compared to 14th August 2015.

Comparison of results for Hg shows significant difference for site A compared to only sites F, G and H while Figure 4.1b shows other sampling sites with Hg mean concentration higher than sites F, G and H and also site J with Hg average concentration even higher than site A. This discrepancy can be explained by the fact that Figure 4.1b shows Hg mean concentrations by sites while the ANOVA GLM takes into consideration sampling sites and also individual sampling dates. Results in Appendices A1 to A7 shows that Hg average concentrations by sampling date at site A have less variability compared to site J where Hg mean concentration reached a peak of 3.56 ± 0.18 μg/l on 14th August 2015, which is more than 17 times higher than the other sampling dates. The results by dates for Ni and Zn highlight their similar trends not only by sampling sites as previously noted in Figure 4.1a but also by sampling dates strengthening the probability of these two metals being from similar sources.

A number of studies have shown relationships between rainfall and a range of heavy metal concentrations in urban rivers where the increase in metal concentrations correlated with a rise in precipitation (e.g. Chiba *et al*., 2011; Lindsay, 2011). Metal concentration results from this study have been compared to 1-day and 2-day rainfall events[3], where 1-day event corresponds to the daily average rainfall reported for the sampling date and the 2-day event includes the daily average rainfall from the sampling date and the day before the sampling (see Table 4.5).

Table 4.5 Two-day rainfall and river flow for the Lower Lee catchment.

Date	Rainfall (mm)	River flow (m^3/s) by sampling sites				
		B	C	D	E	H
10/11/14	0.10	0.25	0.25	0.15	0.25	7.05
11/11/14	1.20	0.15	0.16	0.09	0.15	6.42
08/12/14	0.00	0.09	0.16	0.07	0.16	5.15
09/12/14	1.60	0.08	0.15	0.06	0.16	4.95
10/03/15	0.00	0.11	0.20	0.05	0.18	5.26
11/03/15	0.00	0.10	0.17	0.05	0.18	5.27
14/04/15	0.00	0.05	0.11	0.03	0.13	4.73
15/04/15	0.00	0.05	0.14	0.03	0.13	5.12
19/05/15	3.90	0.09	0.14	0.13	0.72	5.79
20/05/15	0.10	0.08	0.12	0.07	0.26	5.22
30/06/15	0.00	0.02	0.05	0.02	0.11	3.80
01/07/15	0.00	0.02	0.05	0.02	0.12	3.96
13/08/15	12.30	0.03	0.15	0.18	0.71	5.75
14/08/15	2.00	0.06	0.13	0.07	0.25	4.28
22/03/16	0.00	0.13	0.13	0.04	0.17	4.51
23/03/16	0.00	0.13	0.12	0.04	0.15	4.33

Results were also compared to 1-day and 2-day river flow data as this is expected to respond to precipitation levels and consequently influence accumulation and transport of pollutants (e.g. Environment Agency, 2012; Defra, 2013). Although on initial inspection scatterplots (see Appendix E1) do not appear to show a significant relationship between rainfall and river flow, the results in Table 4.6 do indicate a significant relationship for sites D and E (Salmons and

---

[3] Data provided by the Environment Agency. The location for the rainfall and river flow gauges are described in Chapter 3 (Section 3.1).

Pymmes Brook respectively) with a strong level of correlation. These results with lack of a linear response between rainfall and flow volume for all sites suggests that the rainfall around the sampling dates was not enough to impact the main river or that the drainage system has a buffering effect which was not exceeded by the magnitude of the events recorded. It is important to note that the two tributaries which did show a relationship are heavily influenced by discharges from Deephams sewage treatment works (Thames Water, 2020; CEH, 2016) indicating the STW are both a point source of pollution and flow. Also, data in Table 4.5 suggests that the flows recorded around the sampling dates were not unusually high, e.g. out of the typical range levels determined by the Environmental Agency (2012). These results highlight, as previously mentioned, the complexities associated with predicting the behaviour and identifying sources of pollutants in an urban catchment.

Table 4.6 Results of correlation analysis between rainfall and river flow events.

		B	**C**	**D**	**E**	**H**
Rainfall	**r***	-0.27	0.07	**0.74**	**0.83**	0.26
	P-value	0.32	0.79	**< 0.01**	**< 0.01**	0.33

Key: Values in bold show the pairs of parameters with strong to very strong correlation.

Scatterplots (see Appendices E2 and E3) show that there is no clear relationship between metal concentrations and 1-day rainfall but that a relationship does exist for 2-day rainfall events for Ni, Sn and Zn (Table 4.7). This data is consistent with the highest levels of Ni, Sn and Zn being reported on 14/08/15. Using the 2-day event, this is the only sampling date which is classified as a wet weather event using the MetOffice UK guidelines (a threshold of ≥ 10 mm is used to classify a wet-day) (MetOffice, 2016).

Table 4.7 Pearson correlation analysis of water parameters: Cd, Cu, Hg, Ni, Pb, Sn and Zn with 1-day and 2-day rainfall events.

		Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Sn**	**Zn**
1-day rainfall event	**r***	-0.25	0.05	0.12	0.24	-0.25	0.48	0.40
	P-value	0.55	0.92	0.78	0.57	0.55	0.23	0.34
2-day rainfall event	**r***	-0.14	0.27	0.63	**0.76**	0.17	**0.86**	**0.87**
	P-value	0.74	0.51	0.09	**0.03**	0.70	**0.01**	**0.01**

Key: Values in bold show pairs of parameters with strong to very strong correlation.

The values for pH, DO and temperature are reported in Table 4.8.

Table 4.8 Overview of dissolved oxygen, pH and temperature data by sampling sites.

		Dissolved Oxygen (mg/l)		**Temperature (˚C)**		**pH**	
	Site	**Range**	**Mean (± SD)**	**Range**	**Mean (± SD)**	**Range**	**Mean (± SD)**
River Lee	A	5.65 – 13.34	8.37 (± 2.52)	9.80 – 20.30	13.52 (± 3.97)	8.10 – 8.60	8.36 (± 0.17)
	G	5.04 – 10.55	7.60 (± 1.81)	9.80 – 21.10	15.22 (± 4.02)	7.60 – 8.70	8.01 (± 0.36)
	H	5.20 – 9.28	7.18 (± 1.65)	8.70 – 21.70	14.22 (± 4.97)	7.70 – 8.60	8.13 (± 0.37)
	I	5.04 – 12.40	7.98 (± 2.23)	9.00 – 20.50	13.40 (± 3.98)	7.60 – 8.90	8.25 (± 0.40)
Lee Navigation	C	6.25 – 13.60	8.77 (± 2.43)	10.30 – 19.50	13.22 (± 3.53)	7.90 – 8.90	8.45 (± 0.42)
	J	5.71 – 13.90	7.62 (± 2.75)	9.00 – 19.20	12.37 (± 3.98)	7.50 – 8.60	8.10 (± 0.36)
	K	5.34 – 13.08	8.86 (± 2.48)	9.10 – 21.10	12.93 (± 4.51)	7.80 – 9.50	8.73 (± 0.56)
Tributaries	B	6.07 – 13.79	8.40 (± 2.49)	9.90 – 19.10	13.52 (± 3.33)	8.00 – 8.60	8.44 (± 0.20)
	D	6.49 – 9.39	7.57 (± 1.04)	10.00 – 21.50	15.20 (± 3.96)	6.90 – 8.90	7.63 (± 0.60)
	E	5.42 – 10.93	7.56 (± 2.10)	9.30 – 21.90	15.03 (± 4.31)	7.60 – 8.40	8.09 (± 0.26)
	F	4.71 – 10.21	7.40 (± 2.05)	9.00 – 20.60	12.90 (± 4.19)	8.10 – 8.90	8.29 (± 0.26)
Mean (±SD)		7.97(± 2.14)		13.76(± 3.86)		8.23(± 0.45)	

Water samples from the study area revealed DO measurements in the range of 4.71 mg/l (at Ching Brook) to 13.90 mg/l (in the Lee Navigation Channel at site J) with an overall mean for all monitored water bodies of 7.95 ± 2.14 mg/l (Table 4.8). The River Lee exhibits the lowest average concentration (7.18 ± 1.65 mg/l) and the Lee Navigation Channel the highest average DO concentration (8.86 ± 2.48 mg/l), although this difference is minimal. While no statistically significant differences were noted in the observed DO levels between sampling sites, there was a significant difference with sampling dates as shown by ANOVA GLM analysis (Table 4.9). This is contrary to past studies where significant variation in DO concentrations were shown between sites in the Lower Lee catchment, especially between the River Lee, Pymmes Brook and Salmons Brook, with average DO concentrations at the latter two sites being below 4 mg/l (Davies, 2011; Patroncini, 2013). In this study, although there are individual DO levels that fall below the mandatory value for cyprinid waters (≥ 7.0 mg/l) as set by the European Union Council Directive Freshwater Fish Directive (2006/44/EC) which is now integrated into the EU WFD and used by the EA in the UK, the mean DO levels did not fall below the mandatory value. On the other hand, individual DO levels do not fall below the intervention value (< 4 mg/l), as established by the Directive (2006/44/EC), indicating that the surface waters in the Lower Lee catchment had more than the minimum amount of dissolved oxygen level to sustain fish life at the time of sampling. However, as previously mentioned the study area has had low levels of DO where intervention was necessary as reported by the Maddocks (1993), Environment Agency (2012), Environment Agency (2013), Environment Agency (2019b) and Thames21 (2019), when DO dropped to 1% or less especially after storm events, causing thousands of fish to die.

Temperature trends were consistent with natural seasonal changes: higher in summer and spring, lower in winter and autumn. As shown in Table 4.8, temperatures in the Lower Lee catchment varied from 8.70 ˚C in the River Lee to 21.90 ˚C at Pymmes Brook, which is consistent with previous studies. Patroncini (2013) reported water temperatures in the Lower Lee catchment ranging from 7 ˚C at Chingford to 21 ˚C at Deephams and Pymmes Brook East site (sites which are close to sampling sites D and E respectively from this study). The higher temperatures at Deephams and Pymmes Brook East sites were reported to be influenced by discharges from Deephams STW which can alter natural temperatures of surface waters. Davies (2011) and Environment Agency (2012) also reported similar temperatures for the Lower Lee catchment ranging from 8 ˚C to 22 ˚C. ANOVA GLM analysis (Table 4.9) shows statistically significant variation in temperature by sampling dates and sites with sites D (Salmons Brook) and G (River Lee) presenting highest temperature compared to site J (River Lee). This can be due to a number of factors such as the warming effect of Deephams’ effluent discharges at site D. As noted by

Patroncini (2011), Salmons, Pymmes and Ching Brooks pass through concrete channels and therefore identified variations in temperature at these sites were not due to the presence of vegetation.

Table 4.9 Results of the application of ANOVA GLM to DO, temperature and pH parameters in surface waters using the $\log_{10}$ data.

Parameter	**Factor**	**F-test**	**P-value**	**R^2 (%)**	**R^2 Adjusted (%)**
DO	Sites	2.00	0.06	78.74	73.58
	Dates	34.16	**< 0.01**		
Temp	Sites	2.74	**0.01**	92.08	90.16
	Dates	112.40	**< 0.01**		
pH	Sites	7.71	**< 0.01**	66.05	57.80
	Dates	8.44	**< 0.01**		

Key: Values in bold are for parameters that vary significantly by sites and/or dates.

The catchment water samples exhibited a neutral to alkaline pH in the range of 6.90 to 9.50 with an overall mean of 8.23 ± 0.45. The average pH values for each sampling site were found to be within the 'good' category (pH ≥ 6.00 to ≤ 9.00), according to the European Union Council Directive Freshwater Fish Directive (2006/44/EC) classification. Sites on the River Lee possessed pH values between 7.60 and 8.90. The Lee Navigation possessed pH values between 7.50 and 9.50. The lowest pH value measured during the current study was a pH of 6.90 at the Salmons Brook (D). The highest pH value in the investigation came from the Lee Navigation Channel at the downstream site K with pH of 9.50. The pH values determined in this study are consistent with past results from the Lower Lee catchment (Thames21, 2011; Environment Agency, 2013), but differed in indicating a statistically significant variation between sampling dates and sites (Table 4.8). The temporal and spatial variations are understood to be associated with factors such as variation in temperature and discharge characteristics (Beheim *et al*., 2012).

Temperature can affect both pH (e.g. increasing temperature reduces pH due to more efficient ionisation) and levels of dissolved oxygen (e.g. solubility of oxygen decreases as water temperature increases) (Environment Agency, 2012; Chin, 2006). However, the results from this study show only a relatively limited variation in DO concentration by sampling sites in comparison to a greater level of variation in temperature. This suggests that the relationship between DO and temperature is not linear in the field. The variation in temperature was particularly focused around sites J, D and G, a trend which may not be sufficient to cause significant changes in the DO concentrations across all the sites. Also, the relatively limited variation in DO between sites could be explained by factors such as the limited net movement of DO and the existence of artificial oxygenation activities at several locations throughout the catchment.

Given that their low DO levels are an occurring problem in the study area (Environment Agency, 2012; Thames21, 2012; Patroncini, 2013) and that not only DO but also pH can represent general indicators of water pollution, their relationship with reported metal concentrations was also studied. The results are presented in Figure 4.5 and Table 4.10.

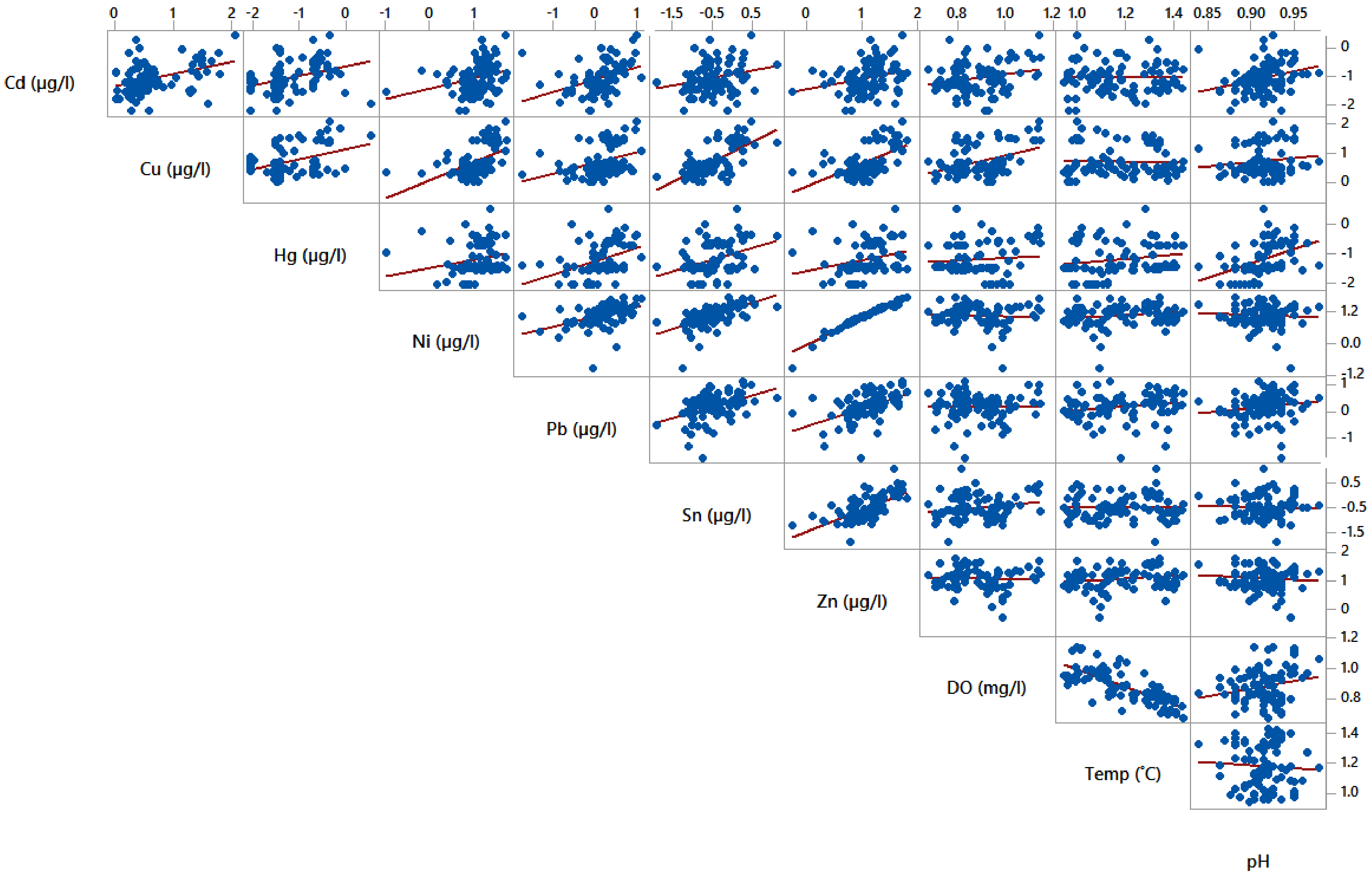


Figure 4.5 Matrix plot of the relationships between Cd, Cu, Hg, Ni, Pb, Sn, Zn, DO, temperature and pH in surface waters.

The matrix plot in Figure 4.5 shows that temperature has a stronger relationship with DO compared to pH. The strongest linear relationship is between Ni and Zn but to investigate other possible significant relationships a Pearson correlation was undertaken as shown in Table 4.10.

Table 4.10 Pearson correlation analysis of water parameters: Cd, Cu, Hg, Ni, Pb, Sn, Zn, DO, temperature and pH.

		Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Sn**	**Zn**	**DO****	**Temp*****
Cu	**r***	**0.40**								
	P-value	**< 0.01**								
Hg	**r***	0.37	0.38							
	P-value	< 0.01	< 0.01							
Ni	**r***	0.28	**0.51**	0.20						
	P-value	0.01	**< 0.01**	0.06						
Pb	**r***	0.39	0.36	0.39	**0.45**					
	P-value	< 0.01	< 0.01	< 0.01	**< 0.01**					
Sn	**r***	0.25	**0.68**	0.36	**0.61**	**0.43**				
	P-value	0.02	**< 0.01**	< 0.01	**< 0.01**	**< 0.01**				
Zn	**r***	0.27	**0.59**	0.26	**0.97**	**0.50**	**0.69**			
	P-value	0.01	**< 0.01**	0.02	**< 0.01**	**< 0.01**	**< 0.01**			
DO	**r***	0.26	**0.42**	0.12	-0.05	0.06	0.21	-0.02		
	P-value	0.02	**< 0.01**	0.28	0.64	0.61	0.05	0.87		
Temp	**r***	-0.02	-0.06	0.20	0.19	0.17	0.00	0.18	**-0.73**	
	P-value	0.89	0.60	0.06	0.08	0.12	0.98	0.09	**< 0.01**	
pH	**r***	0.31	0.14	**0.43**	-0.08	0.16	-0.03	-0.09	0.24	-0.07
	P-value	< 0.01	0.19	**< 0.01**	0.45	0.15	0.79	0.42	0.03	0.56

Key:
* r = Pearson Correlation **DO = Dissolved Oxygen ***Temp = temperature
Values in bold show the pairs of parameters with moderate to very strong correlation.

The P-values (≤ 0.05) for the pairs of variables with moderate to very strong correlation are marked in bold in Table 4.10. Very strong correlations were reported between Zn and Ni, with a positive Pearson correlation of 0.97 indicating that these metals may have come from similar sources; followed by a strong positive correlation between Sn and Cu and an inverse correlation between temperature and DO (r = -0.73) while moderate positive correlations were observed for the following: Cu with Cd, Ni with Cu, Pb with Ni, Ni and Pb, Zn with Cu, Pb and Sn, DO with Cu, pH with Hg. This suggests that despite temporal and spatial variations in many catchment specific factors, there may be some common factors which influence the mobilisation and transportation of the determined pollutants which will be discussed further in context of the relationships of metal concentrations found in sediment (section 4.2). This insight into the relationships between various parameters will inform how they are selected for use in substance flow analysis modelling (see section 2.4).

4.2 Concentrations of selected metals in river sediment – all sites and sampling dates

The concentrations of selected metals in sediments from various water bodies of the Lower Lee catchment are shown in Table 4.11a. The average concentrations of selected metals in all sediment samples increased as follows: Hg < Cd < Sn < Ni < Cu < Pb < Zn, which is a similar order as reported in other studies of urban rivers (e.g. Sabo *et al*., 2013; Suthar *et al*., 2009; Fordyce *et al*., 2013). Results on the Lower Lee catchment from 2012 follows the same pattern with the exception of Sn which was not included in their research (Canal and River Trust, 2012). The analysis of metals in river sediment has been used to identify sources of metals in the aquatic environment as sediment is an essential and dynamic part of a river basin (Islam *et al*., 2015; Eja *et al*., 2003) and metals typically present at a concentration too low to be detected in water samples maybe be identified in sediments (Aderinola *et al*., 2012).

The standard deviations for each metal mean concentration, as shown in Table 4.11a, indicate that metal concentrations varied between different sampling locations and sampling dates. Statistical analysis was undertaken (see section 4.2.1) to further explore this.

Table 4.11a Overview of maximum, minimum and mean (µg/g ± SD) metal concentrations in river sediment determined at all sites on all sampling dates compared to the Dutch and Canadian sediment guidelines.

Metal	**Range in concentration (µg/g)**	**Mean concentration (± SD)**	**Dutch (µg/g)**		**Canadian (µg/g)**	
			TV[1]	**IV[2]**	**ISQG[3]**	**PEL[4]**
Cd	0.18 – 22.53	2.33 ± 2.79	0.80	12.00	0.60	3.50
Cu	32.59 – 642.11	141.07 ± 111.00	36.00	190.00	35.70	197.00
Hg	0.01 – 1.68	0.53 ± 0.45	0.30	10.00	0.17	0.48
Ni	0.01 – 121.74	22.72 ± 17.20	35.00	210.00	---	---
Pb	49.98 – 350.95	175.70 ± 82.96	85.00	530.00	35.00	91.30
Sn	0.53 – 73.95	18.88 ± 15.99	---	---	---	---
Zn	94.12 – 1017.49	499.92 ± 264.66	140.00	720.00	123.00	315.00

Key:

[1] Target Value - indicate the level that has to be achieved to fully recover the functional properties of the soil/sediment for humans, plant and animal life.

[2] Intervention Value - indicate when the functional properties of the soil/sediment for humans, plant and animal life, is seriously impaired or threatened.

[3] Interim Sediment Quality Guideline - represents the concentration below which adverse biological effects are expected to occur rarely.

[4] Probable effect level - defines the level above which adverse biological effects are expected to occur frequently.

Unlike for water quality, there are no UK or EU environmental quality standards for sediments. In the absence of any UK standards, sediment data have been compared against various sediment guideline values to provide an indication of the level of sediment contamination and its potential to cause harm to aquatic life. Table 4.11a presents results in comparison to the Dutch (Esdat, 2000) and Canadian (CCME, 2001) sediment guideline values (where available) which are the guidelines the Environment Agency (2008c) most use as guidance for sediment quality. The aim of the Dutch sediment guideline values is to protect human, plant and animal life whereas the Canadian sediment guideline values have been devised with the aim to prevent biological adverse effects.

The mean concentrations of Cd, Cu, Hg, Pb and Zn exceed both the Dutch target values (TV) and the Canadian Interim Sediment Quality Guideline (ISQG) but do not exceed the Dutch intervention values (IV). However, average concentrations of Hg, Pb and Zn do exceed the Canadian probable effect level (PEL), which indicates the level to be achieved to fully recover the functional properties of the soil/sediment. With regard to maximum levels determined, the range of metal concentrations indicates that Cd, Cu and Zn all exceed the Dutch IV and that Cd, Cu, Hg, Pb and Zn all exceed the Canadian PEL on occasions, indicating exceedances of these more conservative values during certain times of the year and/or at some sampling sites. Ni is only included in the Dutch list and results indicate that while mean Ni concentrations do not exceed any of the Dutch thresholds, on certain sample dates the levels determined were in excess of the Dutch TV.

In addition to the use of sediment guidelines to benchmark sediment quality there are other aspects which could be explored to further assess sediment quality, such as contaminant bioavailability tests, benthic community structure (e.g. ecological functions) and pollution indices (Birch, 2011; Simpson and Batley, 2016). However, to keep in line with the scope of this study and use the available data, only the development and use of pollution indices were applied (see Section 3.7.1).

Table 4.11b provides an overview of the contamination factors (CF), degree of contamination (C_{deg}) and pollution load index (PLI) values derived for five metals at each sampling location. Analysis of CF values indicates only Cd (at site K) and Cu (at sites C, G, H and J) with CF values in the ranges $3 \leq CF < 6$ (considerable contamination) and Cd (at site J) being above 6 (very high contamination), suggesting anthropogenic involvement in the addition to heavy metals in the sediments of the Lower Lee catchment. Whilst almost 50 % of values (Cd at sites C, D, E, G, H and I; Cu at sites D, E F, I and K; Hg at sites C, D, E, G, H, J and K; Ni at site J; Pb at sites C,D, G, H, J and K) fall into the moderate contamination range (i.e. $1 \leq CF < 3$), the CF of 24 of 55 values (Cd for sites A, B and F; Cu at sites A and B; Hg at sites A, B, F and I; Ni at all sites (except at site J); Pb at sites A, B, E, F and I) were < 1, suggesting mean metal concentrations were aligned with natural background levels.

Table 4.11b Contamination Factor (CF) and Pollution Load Index (PLI) by sampling site.

Sampling Site	**CF for each metal**					**C_{deg} for all 5 metals**	**PLI for all 5 metals**
	Cd	**Cu**	**Hg**	**Ni**	**Pb**		
A	0.68	0.74	0.39	0.33	0.38	2.51	0.47
B	0.55	0.88	0.37	0.38	0.48	2.67	0.51
C	2.93	5.17	1.23	0.60	1.11	11.04	1.66
D	1.63	2.33	1.60	0.52	1.14	7.23	1.29
E	1.20	1.28	1.06	0.14	0.95	4.63	0.74
F	0.45	1.47	0.81	0.21	0.53	3.47	0.57
G	2.00	3.34	1.32	0.57	1.50	8.72	1.50
H	2.28	3.35	1.16	0.63	1.47	8.90	1.53
I	1.15	1.33	0.45	0.31	0.65	3.89	0.67
J	7.74	3.07	1.06	1.35	1.41	14.62	2.17
K	5.01	2.05	2.14	0.91	1.09	11.20	1.85
NBC for soil*	1.00	62.00	0.50	42.00	180.00	----	----

Key:
*Normal background levels (NBC) for English soils were used as surrogate for the calculation of contamination factors (CF) (see Section 3.7.1 and Appendix F3).

When adding up the contamination factors for all metals at each sampling site, results for the degree of contamination (C_{deg}) for the study area (Table 4.11b), indicated that the sampling sites A, B, D, E, F and I, typically report a low degree of contamination ($C_{deg} < 8$) with sites C, G, H, J and K reporting a moderate degree of contamination ($8 < C_{deg} < 16$). Degree of contamination (C_{deg}) values for the selected metals did not fall in ranges of ($16 < C_{deg} < 32$) considerable degree of contamination and ($C_{deg} < 32$) very high degree of contamination. This is in contrast to the CF results, which identified a number of sites as considerable contamination and very high contamination, especially site D, which showed CF values for most metals (Cd, Cu, Hg and Pb) in the range of moderate contamination, however, is classified as low degree of contamination (C_{deg}). This highlights that it might not be appropriate to apply national background concentrations for soils when evaluating sediment quality.

Analysis of pollution load index (PLI) values (Table 4.11b) indicate that most of the sites (C, D, G, H, J and K) are polluted, with the highest PLI (2.17) reported for site J followed by site K (PLI = 1.85), where the elevated CFs for Cd (CF of 7.74 at site J and 5.01 at site K) were driving factors. In respect to the tributaries (sites B, D, E and F), the use of PLIs identified Salmons Brook (site D) as the most polluted with a PLI value of 1.66. At Site D most CF values fell in the range of 'moderate contamination' classification, with only one metal (Ni) showing a low contamination, thus indicating the strong influence of anthropogenic discharges in the area. These results are in keeping with the evaluation of mean concentrations which also identified Cd, Cu, Hg, Pb and Zn as exceeding both the Dutch target values (TV) and the Canadian Interim Sediment Quality Guideline (ISQG) while Ni concentrations do not exceed any of the Dutch thresholds (Ni values not available in the Canadian system).

Analysis of ecological risk factors (E_r) shows a slightly different picture (Table 4.11c) with most of the E_r values (42 out of 55) indicating a low potential ecological risk (i.e. $Er < 40$), 9 out of 55 E_r values (Cd at sites D, G and H; Hg at sites C, D, E, G, H and J)) lie in the moderate potential ecological risk range ($40 \leq Er < 80$), whilst 3 out 55 E_r values (Cd at sites C and K; Hg at site K) lie in the considerable potential ecological risk category ($80 \leq Er < 160$) and only 1 out of 55 E_r values (Cd at site J) lie in the high potential ecological risk range ($160 \leq Er < 320$). In terms of metals, these results indicate that mean concentrations of Cu, Ni and Pb represent a low potential ecological risk at all sites, Cd (at sites D, G and H) and Hg (at sites C, D, E, G, H and J) represent a moderate potential ecological risk; Cd (at sites C and K) and Hg (at site K) represent considerable potential ecological risk; and Cd (at site J) represents a high potential ecological risk. Based on the potential ecological risk index (PERI), sampling sites J and K showed highest potential ecological risk. These results indicate the usefulness of the ecological risk factors (E_r) and potential ecological risk index (PERI) when evaluating potential risk of heavy metals contamination further supporting the process of pollutant prioritisation to minimise contamination risk (Liu *et al*., 2021; Purchase *et al*., 2020).

Table 4.11c Ecological Risk Factor (E_r) and potential ecological risk index (PERI) by sampling site.

Sampling Site	**E_r for each metal**					**PERI for all 5 metals**
	Cd	**Cu**	**Hg**	**Ni**	**Pb**	
A	20.26	3.71	15.50	1.96	1.89	43.31
B	16.52	4.42	14.67	2.30	2.42	40.33
C	87.94	25.87	49.02	3.62	5.54	171.99
D	48.95	11.65	64.19	3.10	5.72	133.62
E	35.90	6.42	42.34	0.84	4.76	90.26
F	13.38	7.37	32.23	1.27	2.67	56.91
G	59.91	16.68	52.60	3.43	7.52	140.14
H	68.33	16.77	46.30	3.80	7.37	142.57
I	34.57	6.65	18.00	1.84	3.27	64.33
J	232.17	15.33	42.40	8.09	7.05	305.04
K	150.17	10.27	85.60	5.46	5.47	256.96
T_r *	30.00	5.00	40.00	6.00	5.00	

Key:
*N toxic response factor of an individual substance for soils (Hakanson, 1980) were used as surrogate for the calculation of ecological risk factors (Er) (see Section 3.7.1 and Appendix F4).

In general, results for the pollution indices show that Cd concentrations at site J is the most concern pollutant/site having the highest contamination and ecological risk factors, followed by site K, both sites located downstream of the Lower Lee catchment. The advantage of pollution indices assessment is that they consider the heavy metal toxicity, reflecting the impacts of the different contaminants (Li *et al*., 2022). Thus, it could be assumed that the input of Cd in the sediment within the Lower Lee catchment is of great concern because of its high toxic-response factor and its presence in the environment at concentrations higher than the Dutch target values (TV) and the Canadian Interim Sediment Quality Guideline (ISQG) (Table 4.11a). However as previously mentioned it would be more appropriate to have metal normal background concentrations and toxic response factors for sediment (opposing to soils) to have a more realistic and robust approach.

Comparison of the results from this research with results from urban/industrialised rivers located in various other countries (see Table 4.12) indicate that the average concentrations of Cd, Cu, Ni, Pb, and Zn in fluvial sediments of the Lower Lee catchment are higher than those reported, with the exception of data from the La Marque River (Lafhaj *et al*., 2008) which reported Zn and Cd concentrations an order of magnitude higher than all other studies. Whilst the data provided in Table 4.12 is by no means exhaustive, it is of note that the sediment concentrations determined in this study are at the upper range of values reported in the literature indicating that the Lower Lee catchment is a relatively heavily contaminated site in comparison to other urban catchments. The difference in results between various urban areas is thought to be associated with different land use activities e.g. varying types/intensities of industrial activities in the respective catchment areas, highlighting the importance of considering land use effects on metal concentrations in an urban river (Kuusisto-Hjort, 2009). Results of the analysis of River Lee sediment undertaken by the CRT (2012; second row in Table 4.12) indicate that only Ni concentrations have, on average, decreased overtime, with current Cd, Cu, Hg, Pb and Zn concentrations all showing an increase despite water results indicating that the level of target metals has declined in recent years. However, as noted in section 2.3, sediment results may indicate an historic accumulation of metals in sediment rather than be a recent reflection of aquatic concentrations.

Table 4.12 Comparison of metal concentrations determined in this study with results from other urban rivers from around the world.

Locations	**Average concentrations (µg/g)**							**References**
	Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Sn**	**Zn**	
Lowe Lee catchment, UK	2.33	141.07	0.53	22.72	175.70	18.88	499.92	This study
Lower Lee catchment, London, UK	1.93	97.93	0.34	29.30	161.98	---	297.90	(Canal and River Trust, 2012)
East Tullos Burn, Aberdeen, UK*	---	441.00	---	81.00	85.00	---	407.00	(Wilson *et al*., 2005)
Wantz Stream, London, UK**	5.70	59.00	---	61.00	132.00	---	239.00	(Scholes, 2000)
Flanders' basins, Flemish Region, BE***	1.30	27.60	0.20	13.30	43.90	3.00	252.00	(De Saedeleer *et al*., 2010)
River La Marque, Nord-Pas-de-Calais, FR****	27.40	425.00	---	---	922.00	---	3966.00	(Lafhaj *et al*., 2008)
Basento River, Potenza, IT****	0.24	32.00	---	38.00	30.00	---	193.00	(Medici *et al*., 2011)
Charles River, Massachusetts, USA	---	69.71	0.40	---	142.19	---	328.10	(Luce, 2012)

Key:
* Area within through East Tullos Industrial Estate close to lightly urbanised area in Scotland; ** Heavily urbanized and commercial area in Dagenham, London; ***Urban and industrial rivers from 11 river basins in the Flemish Region; ****Urban and industrial rivers.

Figures 4.6a and 4.6b shows variations in sediment average metal concentrations at each site over the course of 8 sampling trips. The analysis of the results in Figure 4.6a indicates that there is a considerable variation in metal concentrations in sediment between the sites with Zn having the highest mean concentration at all sites followed by Pb and Cu and then to a lesser extent Ni. Only site C differs from this pattern as average Cu concentrations were higher than those determined for Pb. The elevated levels of Zn, Pb and Cu in river sediment reported in this study is consistent with data reported in previous studies (e.g. Reis *et al*., 2013; Rybicka *et al*., 2005). Similar trends in concentration by site for Zn, Pb and Cu potentially indicates that those metals behave in a similar manner in terms of deposition (Salah *et al*., 2015). Figure 4.6b shows Sn with highest concentration at all sites followed by Cd and Hg (Blais *et al*., 2015). Further investigation of the environmental behaviour of each metal would be necessary to further understand the observed trends and identify sources (Prasad *et al*., 2005); batch tests followed by substance flow analysis will be used in the next stage of this work.

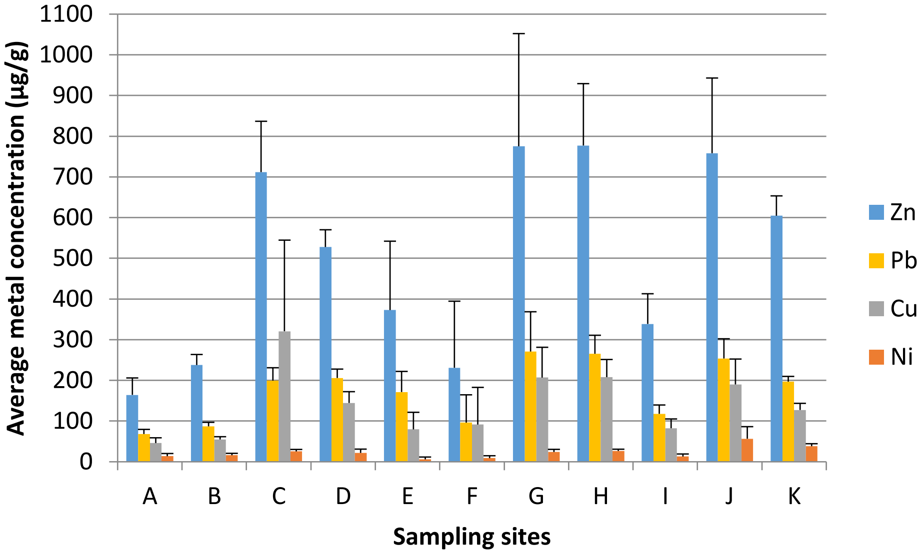


Figure 4.6a Average metal concentrations (±SD) of Zn, Pb, Cu and Ni in sediment in the River Lee, Navigation Channel and tributaries.

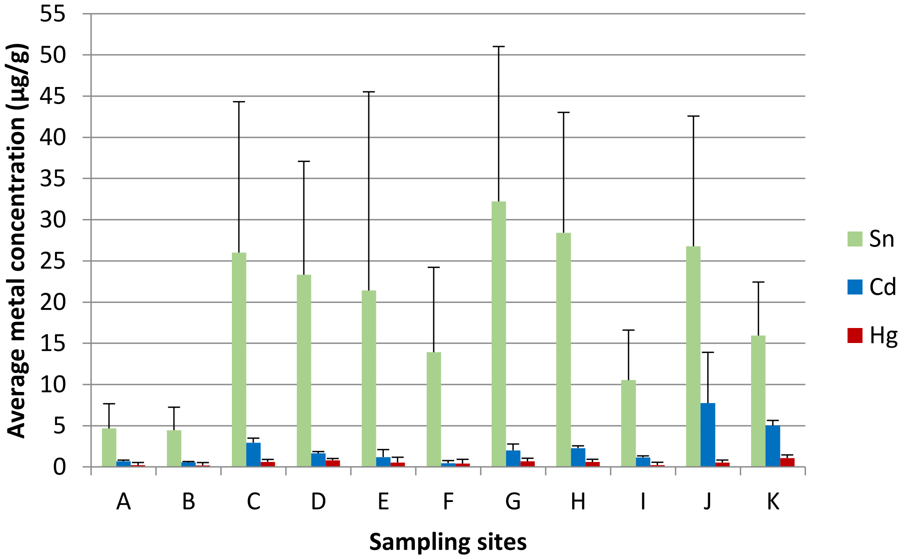


Figure 4.6b Average metal concentrations (±SD) of Sn, Cd and Hg in sediment in the River Lee, Navigation Channel and tributaries.

While Figures 4.6a and 4.6b show metal concentrations for the Lower Lee catchment, the data was separated into components of the catchment (River Lee, Lee Navigation Channel and tributaries) in order to identify and consider trends and tributaries' contributions of target metals. Appendices F1 and F2 show the distribution of targeted metals throughout the sampling sites in the Lower Lee catchment for the River Lee, Lee Navigation Channel and the four tributaries. Figures 4.7a and 4.7b present the mean metal concentrations for the samples collected from sites on the River Lee. Highest concentrations of all metals were found at sites G and H. This is of note, as these two sites were part of the area where sediment was dredged in summer 2009 with a view to reducing metal concentrations as mentioned in Section 1.1.2. For example, according to data (from Lea Bridge sampling site, which correspond to site H in this study) provided by the Environment Agency (2016), Hg dropped from 1.4 µg/g in August 2009 (while dredging was taking place), to 0.47 µg/g in July 2011, Cd dropped from 0.1 µg/g in March 2009, before dredging took place to < 0.01 µg/g in November 2009 maintaining at similar levels up to 2012. Results in this research for site H shows Hg (0.58 µg/g) and Cd (2.28 µg/g) average concentrations higher when compared to after dredging status, suggesting that dredging is likely to prove only a short-term solution until sediment builds up again in case the sources of contamination are not controlled or eradicated.

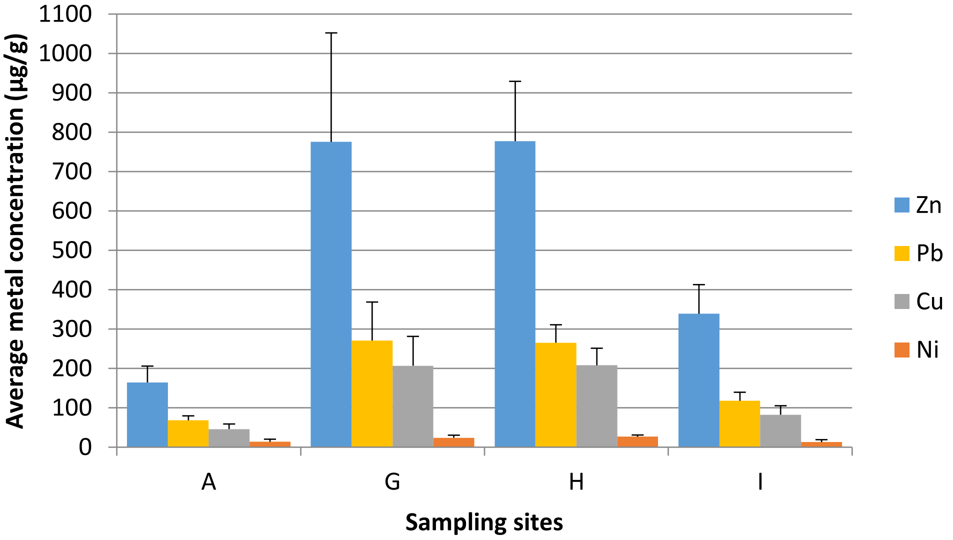


Figure 4.7a Mean concentrations (±SD) of Zn, Pb, Cu and Ni in sediment in the River Lee.

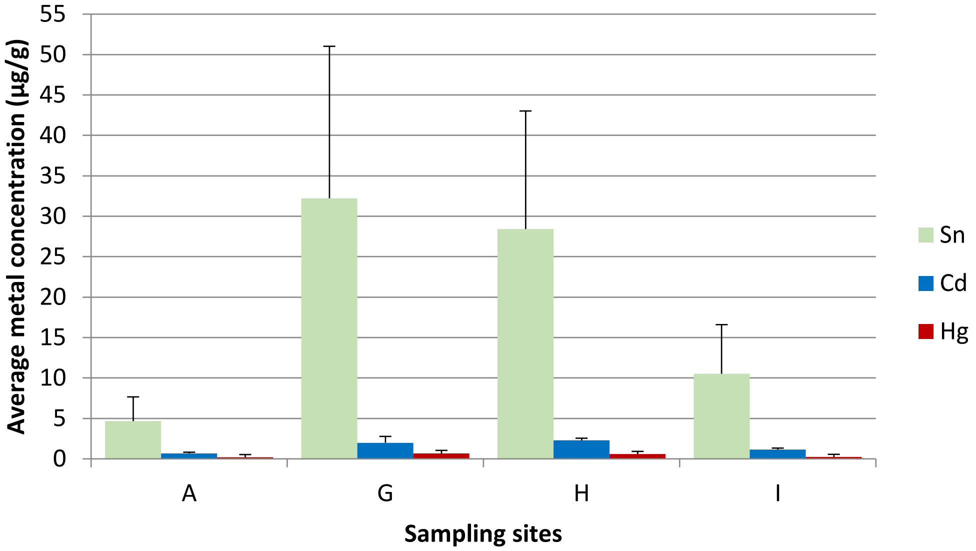


Figure 4.7b Mean concentrations (±SD) of Sn, Cd and Hg in sediment in the River Lee.

Sediment metal concentrations for sampling points in the Lee Navigation Channel (see Figures 4.8a and 4.8b), indicate that average Cd and Ni concentrations tend to be higher than those determined in the River Lee (approximately 3 times higher for Cd and double for Ni). A trend of increasing metal concentrations as the channel flows downstream was only apparent for some metals on same dates for example, Cd, Hg, Ni and Sn on 11th November 2014 as can be seen on Appendices A1 to A8, illustrating that, as with surface waters concentrations, sediment metal concentrations are likely influenced by the complexity of the land uses in the catchment area, sediment resuspension and partition coefficient (Environment Agency, 2012; Lau and Stenstrom, 2005; Crane, 2003).

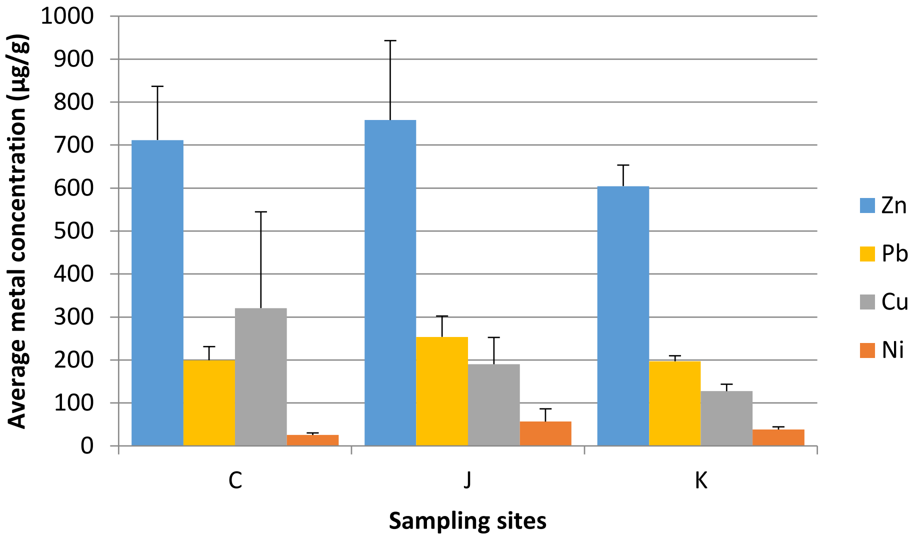


Figure 4.8a Mean concentrations (±SD) of Zn, Pb, Cu and Ni in sediment in the Lee Navigation Channel.

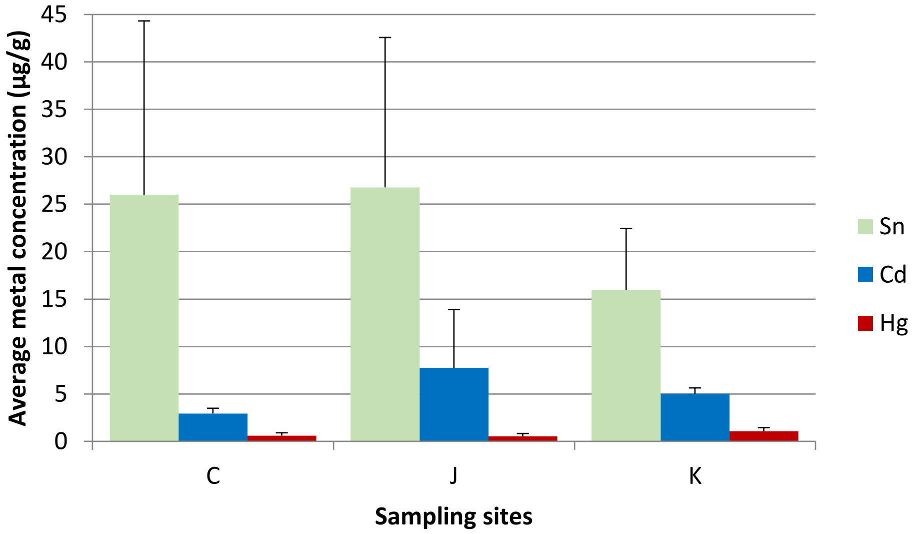


Figure 4.8b Mean concentrations (±SD) of Sn, Cd and Hg in sediment in the Lee Navigation Channel.

Results of sediment metal concentrations in the tributaries Cobbins, Salmons, Pymmes and Ching Brook are presented in Figures 4.9a, 4.9b and Appendices B1and B2. The lowest average concentration for Cu, Hg, Pb and Sn were determined at Cobbins Brook (a site primarily in receipt of road runoff). Lowest average concentrations for Cd and Zn were determined at Ching Brook and lowest mean concentration for Ni was determined at Pymmes Brook. These results suggest that sites receiving effluent from sewage treatment works and road runoff, as in the case of Salmons Brook, can generate higher concentrations of heavy metals in sediment than sites receiving road runoff only (Cobbins Brook).

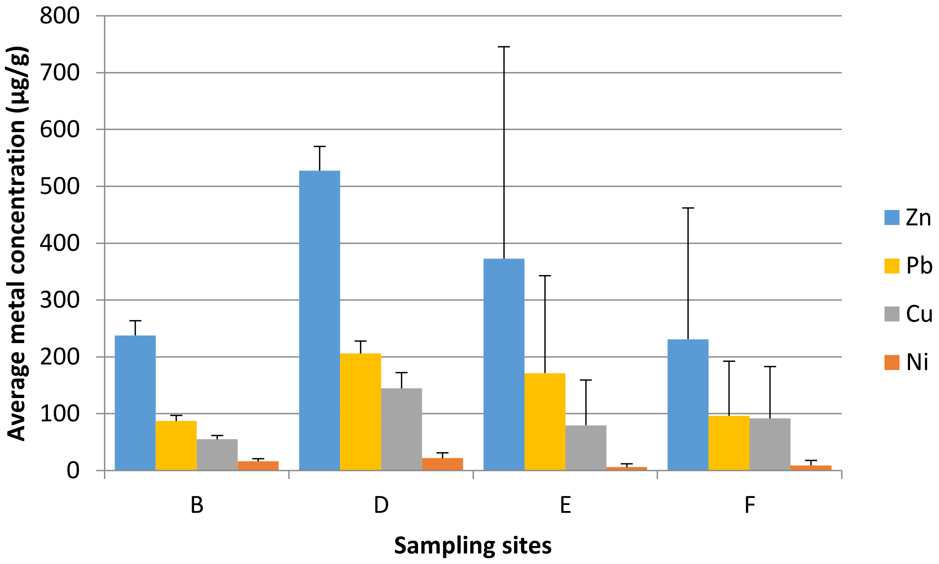


Figure 4.9a Mean concentrations (±SD) of Zn, Pb, Cu and Ni in sediment in the River Lee tributaries.

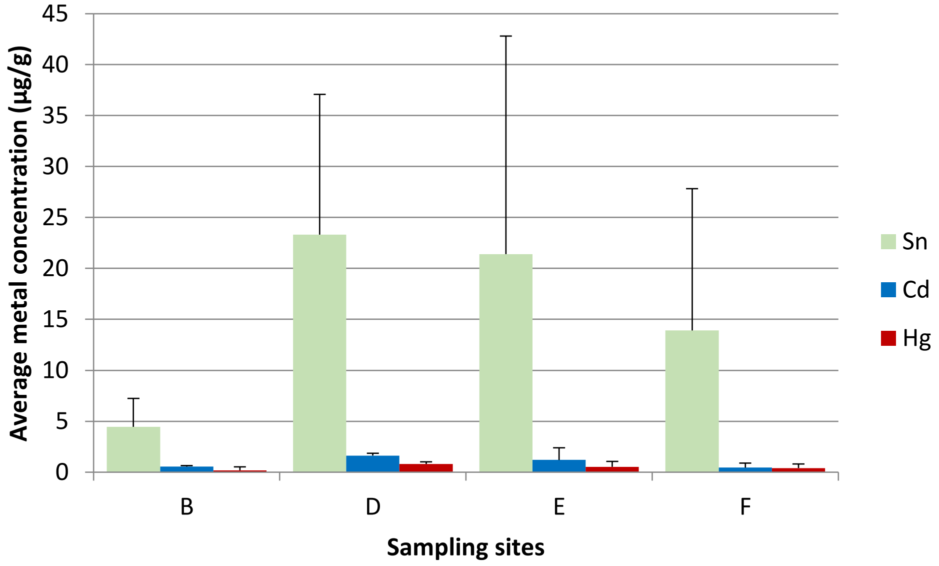


Figure 4.9b Mean concentrations (±SD) of Sn, Cd and Hg in sediment in the River Lee tributaries.

4.2.1 Spatial and temporal distributions of metals in river sediment

The normality of the data distributions of each parameter was assessed using the Anderson-Darling normality test (see Table 4.13). As all metal sediment data sets were skewed, variables were log-transformed for statistical analysis using the $\log_{10}$ base function. After transformation, results showed that only data for Cd became normally distributed. Equal variance tests for original and transformed data showed P-values ≤ 0.05 indicating unequal variance of the data. However, as for water data, the data report from Minitab Assistant indicated that the robustness of the model was maintained irrespective of identified non-normality and unequal variance.

Table 4.13 Results from the Anderson-Darling normality test for metals in river sediment.

Data sample	**Results from original values**		**Results from $\log_{10}$ values**	
	P-value	**Normal distribution**	**P-value**	**Normal distribution**
Cd	< 0.005	No	0.236	Yes
Cu	< 0.005	No	< 0.005	No
Hg	< 0.005	No	< 0.005	No
Ni	< 0.005	No	< 0.005	No
Pb	0.005	No	< 0.005	No
Sn	< 0.005	No	< 0.005	No
Zn	< 0.005	No	< 0.005	No

On this basis, ANOVA GLM was performed, using metal concentrations as dependant variables and sampling sites and dates as categorical variables to test if metal concentrations vary in relation to site and/or date at a level which is considered statistically significant (see Table 4.14).

Table 4.14 Results of the application of the ANOVA GLM to the target metals undertaken using the $\log_{10}$ data from river sediment.

Sample by metal	**Factor**	**F-test**	**P-value**	**R^2 (%)**	**R^2 Adjusted (%)**
Cd	Sites Dates	48.03 1.04	< **0.01** 0.41	87.45	84.40
Cu	Sites Dates	13.25 2.55	< **0.01** **0.02**	68.23	60.51
Hg	Sites Dates	8.43 11.81	< **0.01** < **0.01**	70.46	63.29
Ni	Sites Dates	8.69 3.17	< **0.01** **0.01**	61.91	51.42
Pb	Sites Dates	24.54 2.01	< **0.01** 0.07	73.59	66.42
Sn	Sites Dates	15.65 45.52	< **0.01** < **0.01**	87.16	84.04
Zn	Sites Dates	34.41 4.62	< **0.01** < **0.01**	84.32	80.51

The ANOVA GLM results (Table 4.14) indicate that sediment metal concentrations for Cd and Pb vary significantly in relation to sample site and of Cu, Hg, Ni, Sn and Zn which vary in relation to both, sites and dates. The R^2 adjusted values (see Table 4.14) are higher than 50 % for all, indicating that more than 50 % of the variation in the target metals can be explained by their relationship with sampling sites and/or dates. Evaluation of the residual plots (Appendices G1 to G7) showed more randomness of the log-transformed data compared to residuals from the original data, indicating the strength of the used model. The results from the model may indicate that sediment concentrations of Cu, Hg, Ni, Sn and Zn are affected by land use over time, showing significant temporal and spatial variation, while Cd and Pb show significant spatial variation only. In general, evidence of significant temporal and spatial variations in heavy metal concentrations in sediment are widely reported in the literature in association with factors such as weather and land use (e.g. Kuusisto-Hjort *et al.*, 2013; Luce, 2012; Raulinaitis *et al.*, 2012; Bay *et al.*, 2003). These results can be a reflection of the different environmental behaviour between metals and further investigation would be necessary before drawing any final conclusions. While post-hoc results for sediment show spatial variation for all metals, spatial variation in water was observed only for Cu, Hg and Zn. In relation to temporal variation, it was observed in sediment for Cu, Hg, Ni, Sn and Zn while temporal variation in water was observed for all metals. This could be due to the fact that water samples only give a snapshot representation of metal concentrations at the time of sampling while sediment acting as a sink for pollutants can show a long-term accumulation (Brils, 2008). In this way, as previously mentioned, sediment metal concentrations can be a more reliable representative of metal loadings in a river over time, as opposed to water samples.

Post-hoc multiple comparisons were performed using Tukey's Honest Significant Difference (HSD) test (P-value $\leq$ 0.05) to identify the sources of significant differences in metal concentrations between dates for all metals and between sites for Cu, Hg, Ni, Sn and Zn (see Appendices H1 to H7 for sampling dates). From Tukey's HSD test results, the main findings are:

- In regard to sampling date, it was noted that Hg and Sn were lower on 11th November 2014 compared to all the others sampling dates (with the exception of 9th December 2014).
- With respect to sampling site, it was noted that Cd, Cu, Hg, Pb, Sn and Zn were generally lower at site A in comparison to those further downstream.

Despite the existence of several towns and an STW upstream of site A, the lower concentrations at this site may be due to its location in a relatively rural area in comparison to sites further downstream which receive direct input from more urbanised areas, indicating that Cd, Cu, Hg, Pb, Sn and Zn input into the river is expected to increase as the river shifts from less urbanised areas to heavily urbanised areas. This also corroborates the findings of Sabo *et al*. (2013) and Owens (2008) who concluded that high levels of these metals in sediment from an urban river were due to domestic and industrial waste and road runoff.

In contrast to water metal concentrations, analysis suggests that sediment metal concentrations and rainfall do not appear to have a significant relationship (see Table 4.15), where results from this study are compared to 1-day and 2-day rainfall event data. Whilst it is of note that in most cases, Pearson correlation values shows an inverse correlation, which may indicate metal remobilisation from the sediment to the water column during wet weather, none of these relationships are statistically significant.

Table 4.15 Correlation analysis of sediment parameters: Cd, Cu, Hg, Ni, Pb, Sn and Zn with 1-day and 2-day rainfall events.

		Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Sn**	**Zn**
1-day rainfall event	**r***	-0.40	-0.45	0.00	-0.61	-0.69	-0.71	-0.41
	P-value	0.33	0.26	0.99	0.11	0.06	0.05	0.31
2-day rainfall event	**r***	0.17	0.08	0.65	-0.66	-0.08	-0.05	0.27
	P-value	0.69	0.85	0.08	0.08	0.86	0.91	0.52

Key: *Pearson correlation

The matrix plot in Figure 4.10 shows the relationships between metals in sediments and indicates possible correlations between a number of pairs of metals specifically between Zn and Pb, Zn and Cu and Zn and Cd. To test for the significance of any correlations data were analysed by Pearson's correlation test (see Table 4.16).

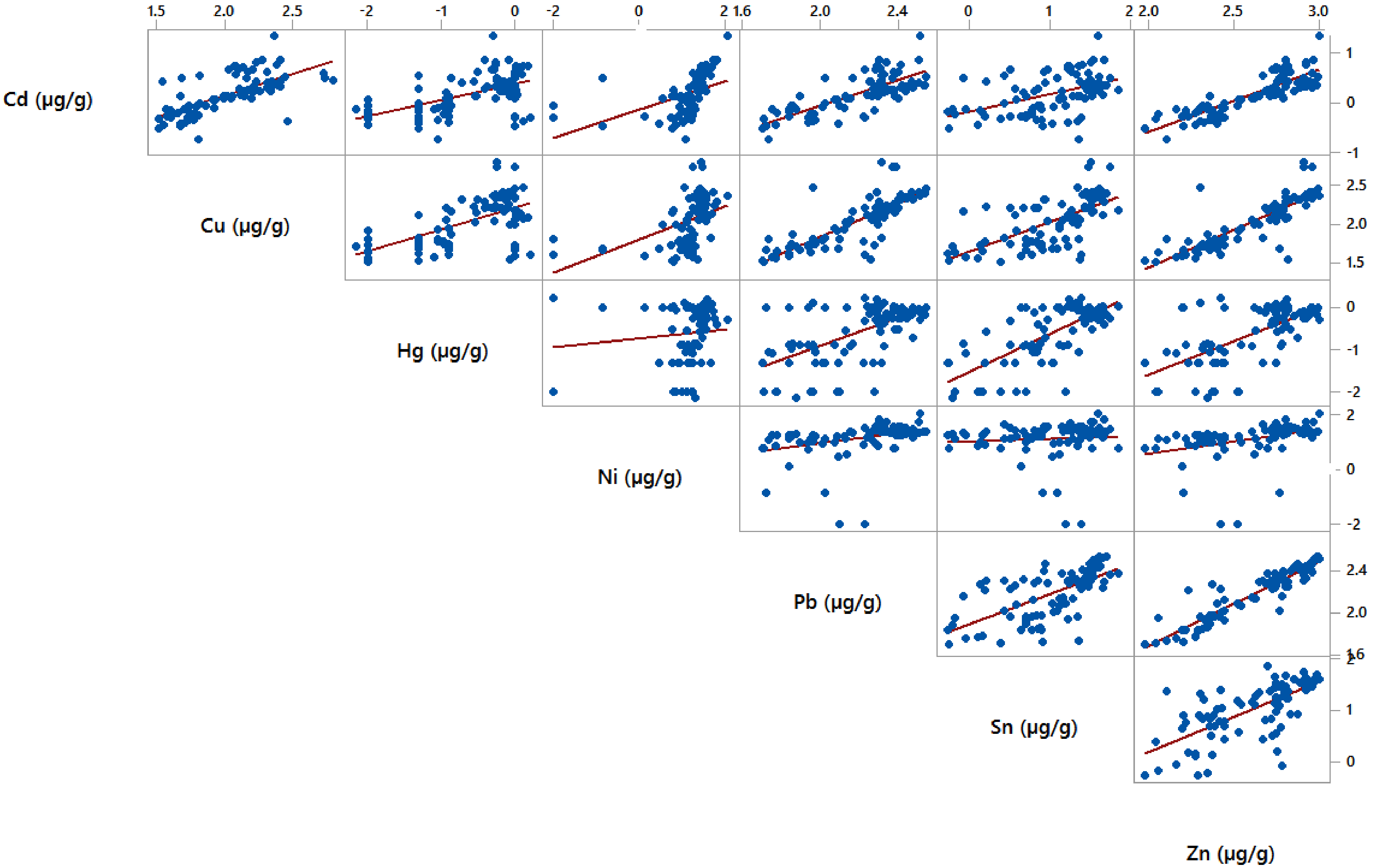


Figure 4.10 Matrix plot of relationship between the concentrations of Cd, Cu, Hg, Ni, Pb, Sn, Zn in sediment.

Table 4.16 Correlation analysis of sediment parameters: Cd, Cu, Hg, Ni, Pb, Sn, Zn in sediment.

		Cd	Cu	Hg	Ni	Pb	Sn
Cu	**r***	**0.68**					
	P-value	**< 0.01**					
Hg	**r***	**0.55**	**0.59**				
	P-value	**< 0.01**	**< 0.01**				
Ni	**r***	**0.47**	**0.45**	0.10			
	P-value	**< 0.01**	**< 0.01**	0.34			
Pb	**r***	**0.76**	**0.81**	**0.60**	0.35		
	P-value	**< 0.01**	**< 0.01**	**< 0.01**	< 0.01		
Sn	**r***	**0.47**	**0.66**	**0.72**	0.08	**0.65**	
	P-value	**< 0.01**	**< 0.01**	**< 0.01**	0.44	**< 0.01**	
Zn	**r***	**0.85**	**0.84**	**0.65**	0.37	**0.93**	**0.69**
	P-value	**< 0.01**	**< 0.01**	**< 0.01**	< 0.01	**< 0.01**	**< 0.01**

Key: *Pearson correlation
Values in bold show the pairs of parameters with moderate to very strong correlation.

The probability (P-value ≤ 0.05) and correlation values for the variable pairs with moderate to very strong correlation are marked in bold in Table 4.16. Correlation results for sediment shows moderate to very strong levels of correlation reported between metals, which could indicate that they may have come from similar polluting sources (Muohi, 2003; Asante, 2005). Results in Table 4.16 show the strongest relationship between Pb and Zn (r = 0.93) which may indicate they could have similar deposition behaviour (Salah *et al.*, 2015).

4.3 Overview: water and sediment results

As expected, metal concentrations in sediment samples were higher than those determined in the overlying waters. This trend was observed at all of the sampling sites and this finding is consistent with a number of other studies reported in the literature (e.g. Salem *et al.*, 2014; Ibrahim and Omar, 2013; Ali and Abdel-Satar, 2005). One factor in this relationship is the environmental behaviour of metals at the pH levels determined. For example, while heavy metals dissociate and come into solution at low pH, at higher pH (such as those determined in the Lee), little or no metals dissociation takes place with metals settling to the bed of the river in the form of a heavy metal complex (Sarpong *et al.*, 2009).

The standard deviations associated with each mean metal concentration, as shown in Tables 4.1 and 4.11a, indicate that metal concentrations varied between different sampling locations and sampling dates. However, sediment concentrations showed less variation in comparison to water metal concentrations. For example, the standard deviations for five metals (Cd, Cu, Hg, Pb and Sn) are higher than the mean values in water whereas only Cd has a standard deviation greater than the mean in sediments. Thus, sediment has been identified as the preferred medium for monitoring the environmental pollution of aquatic systems because it exhibits reduced variation, especially temporally (Agunbiade *et al*., 2010; Taylor *et al*., 2008; Owens *et al*., 2001).

Sediment results, when compared to past research for the Lower Lee catchment, indicate that only Ni concentrations have, on average, decreased overtime, with current Cd, Cu, Hg, Pb and Zn concentrations all showing an increase despite water results indicating that the level of target metals has declined in recent years.

With regard to relating the behaviour of metals in water with those in sediment concentrations, no further consistent trends were apparent. For example, while in water average Ni concentrations were greater than those of Cu and Pb (except for site B), in sediment Pb and Cu concentrations were greater than those of Ni (Figures 4.1a and 4.6a). This may be explained by the fact that in respect to hydrolysis and DOM complexation tendencies, Cu and Pb free ion concentrations will decrease substantially with pH, and will depend strongly upon DOM, thus biding more to particulate matter and deposited in the river bed sediment (Environment Agency, 2008) as shown in Table 4.1c. However, further research on metal bioavailability processes and of the sediment geochemistry would become necessary to better understand metals' behaviour (Zhang *et al*., 2014). With regard to Hg, mean concentrations were higher than Cd at sites A and J in surface water and in sediment mean Hg concentrations were lower than Cd at all sites (Figures 4.1b and 4.6b). For the River Lee the lowest mean Ni sediment concentration was determined at downstream site I, which was also the site of the highest mean Ni water concentrations. Lowest Hg sediment concentrations (site A) was also the site with highest mean water concentrations of the same pollutant, suggesting that the accumulation of heavy metals in sediment maybe not simply be a linear reflection of metal content of the aqueous phase. The lack of an apparent trend in metal behaviour between water and sediment matrices further demonstrates the complexity of the study area and the complex relationship between the two matrices. Whereas water concentrations can vary over short periods of time (minutes to hours), sediment concentrations tend to be much more stable (months to years depending on the system). Several researchers have concluded the need to sample both water and sediment matrices to develop fuller understanding of contamination patterns in an urban river (Taylor, 2009; Taylor *et al*., 2008; Owens *et al*., 2001), and this study supports these findings. Another important factor to note is that whilst analysis of aqueous concentrations indicated a strong relationship between Ni and Zn (Table 4.10), in sediment the strongest relationship was between Pb and Zn (Table 4.16) and while similar behaviour of Ni and Zn in water could be due to derivation of same sources, in sediment the association between Pb and Zn could be due to other factors such as the two metals having a similar deposition behaviour.

Overall, results from matrix plots, presented in Figures 4.5 and 4.10 show a stronger relationship between metals in sediment compared to the water column, which could be due to the fact that water samples only give a snapshot representation of metal concentrations at the time of sampling while sediment acting as a sink for pollutants can show a long-term accumulation (Brils, 2008). The relationship between metal concentrations in water and sediment was then further explored using correlation analysis (Table 4.17) to establish if any statistical relationship was in place. Whilst correlation analysis results show an inverse correlation between same metals between water and sediment, which could indicate deposition/remobilisation process taking place, this relationship was not present at a statistically significant level. Results also indicate that is no statistically significant relationship between different metals in the two matrices (see Table 4.17), indicating that the sources of metals in water can differ from sources of metals in sediment. This may be due to factors previously mentioned, such as historical metal accumulation in sediment (Taylor *et al.*, 2008; Brils, 2008) and differentiations in the environmental behaviour of each metal in different matrices (Evans *et al.,* 2012).

Table 4.17 Correlation analysis of target metals between water and sediment matrices.

			Metals in water						
			Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Sn**	**Zn**
Metals in sediment	**Cd**	**r***	0.29	-0.27	0.39	-0.14	-0.13	0.38	-0.10
		P-value	0.40	0.43	0.24	0.70	0.70	0.25	0.77
	Cu	**r***	0.12	-0.18	-0.07	0.11	-0.15	-0.06	0.12
		P-value	0.73	0.59	0.84	0.74	0.67	0.86	0.73
	Hg	**r***	-0.05	-0.53	-0.25	0.16	-0.28	0.28	0.16
		P-value	0.89	0.10	0.46	0.64	0.40	0.40	0.63
	Ni	**r***	0.38	-0.15	0.47	-0.48	-0.34	0.39	-0.47
		P-value	0.25	0067	0.15	0.13	0.31	0.24	0.14
	Pb	**r***	0.38	-0.15	0.47	-0.48	-0.34	0.39	-0.47
		P-value	0.25	0.66	0.15	0.13	0.31	0.24	0.14
	Sn	**r***	-0.03	-0.40	-0.26	0.35	-0.15	-0.11	0.36
		P-value	0.93	0.22	0.45	0.30	0.67	0.75	0.28
	Zn	**r***	0.22	-0.20	-0.03	0.17	-0.08	0.20	0.18
		P-value	0.53	0.56	0.94	0.62	0.83	0.56	0.59

Key: *Pearson correlation

Correlation analysis was also done by sampling date to check presence of any possible significant correlation of target metals levels between water and sediment. Results with significant correlation are shown in bold in Appendices I1 to I8. From the correlation analysis results the following was observed:

- 11th November 2013 – moderate correlation of Ni in water with Zn and with Sn in sediment.
- 9th December 2013 – moderate correlation of Cu in water with Cu in sediment and Sn in water with Ni in sediment; strong correlation of Cu in water with Sn in sediment.
- 11th March 2015 – moderate correlation of Sn in water with Zn in sediment; moderate inverse correlation of Cd in water with Pb and Sn in sediment; strong inverse correlation of Cd in water with Cu and Zn in sediment; moderate inverse correlation of Hg with Cu

and Hg in sediment; strong inverse correlation of Hg in water with Pb and Zn in sediment; moderate inverse correlation of Pb in water with Sn in sediment; moderate correlation of Sn in water with Zn in sediment.

- 15th April 2015 – strong correlation of Cd in water with Cd and Ni in sediment.
- 20th May 2015 – very strong correlation of Cd in water with Cd and Ni in sediment; moderate correlation of Cu, Ni, Pb and Zn in water with Hg in sediment.
- 1st July 2015 – moderate correlation of Cd in water with Ni in sediment; moderate inverse correlation of Hg in water with Hg, Pb and Zn in sediment; strong inverse correlation of Hg in water with Sn in sediment.
- 14th August 2015 – moderate correlation of Sn in water with Cd in sediment; very strong correlation of Sn in water with Hg in sediment.
- 23rd March 2016 – moderate inverse correlation of Sn in water with Sn in sediment.

No organised pattern was detected for correlation of any particular metal concentration, however, statistically significant correlation between two heavy metals may be an occurrence of strong dependence of both metals on the same causal factor (Ashraf *et al.*, 2012). Inverse correlation of same metal between the water and sediment matrices was more frequent for Hg and Cu which occurred 7 times during the sampling period, followed by Pb which occurred 6 times, then Ni 5 times and Cd, Zn and Sn occurred 3, 2 and 1 time respectively and although only a limited number of those inverse correlations were statistically significant there are maybe an indication of remobilisation process taking place.

The mean concentrations of metals in the water of the River Lee (sites A, G, H and I) shows a general pattern of increase in concentration as the river flows from outer towards inner London. However, for sediment this same trend was not observed (Figures 4.2a-b and 4.7a-b). With regard to the Lee Navigation Channel, this pattern of increasing metal concentration from upstream to downstream was not present in either water or sediment matrices.

This could be due to a number of factors including differences in the geomorphology, point sources discharges and artificial structures. Artificial in-channel structures such as weirs, culverts and bridges are efficient traps for sediments and associated pollutants, interrupting the downstream movement of material, leading to changes in sediment composition, as they act as barriers to the free movement of sediment which can have a direct effect on pollutants distribution throughout the area (Thames Water, 2013). For example, there are a number of locks throughout the study site, including Waltham Town Lock, Enfield Lock (above site C), Tottenham Lock (above site G; located just before Pymmes Brook meets the main channel), Old Ford Lock (above site K) and Bow Locks (downstream of site K). Of particular note is that downstream site K (near the Olympic Park) is sited between two locks (Old Ford and Bow Locks) which may explain the lack of increase of metal concentrations downstream (i.e. metals and associated pollutants are being detained by the upstream lock). However, another important fact is that the River Lee in the Olympic Park area went through an extensive clean-up process (involving dredging, installation of SuDS, a community education/awareness and was the site of project ReedBed, introducing new vegetation in the river, which could also explain the relatively lower concentrations determined at this site.

Another example of different patterns of spatial distributions of metal concentrations between water and sediment matrices was observed in the Lee Navigation Channel. For example, while water results showed Cu, Ni, Pb and Zn highest at site C (Figures 4.3a and 4.3b), in sediment only Cu was determined at highest average concentrations at site C, with mean concentrations of Cd, Ni, Pb, Sn and Zn highest at site J (Figures 4.8a and 4.8b). The spatial variations in metal distributions between water and sediment detected indicate that a variety of sources might be playing an important part in this process, together with other factors such as the presence of historical metal sediment contamination (Shanbehzadeh *et al.*, 2014; Owens *et al.*, 2001). To better understand the type and role of influencing processes, the identification of pollutant sources and land use analysis was undertaken. While some authors argue that temporal and spatial variations in river sediment quality can occur irrespective of industrial or other land use activities (Dowdeswell *et al*., 2010, Crooks *et al*., 2021) other authors support that bottom-sediment metal concentrations have long been considered reliable indicators of the influence of land use on river pollutant loads (Jin *et al.*, 2011; Birch *et al*., 2001; Birch and Olmos, 2008).

For the tributaries, water results showed Cobbins Brook (for Cd, Cu, Hg and Sn) and Pymmes Brook (for Pb, Ni and Zn) were the contributors with highest average concentrations of metals while sediment results indicate Salmons Brook, which receives effluent from the Deephams STW, had the highest mean concentration of all metals amongst the tributaries. In urbanised environments, STW and combined sewer overflows (CSOs) act as major sources of contaminants into river surface waters and bed sediments. Due to increasingly stringent water quality and discharge regulations aqueous concentrations of many parameters have decreased over time and, in association with this, their levels in fluvial sediments are also reported to be declining (Carter *et al*., 2006). Road runoff has also been identified as a major source of urban river sediments and associated metals with, for example, research by Carter *et al*. (2006) showing that around 20 % of contaminants held in sediments of urban rivers were derived from road networks. This study also reported increases of metal concentrations in sediments during storm events, reflecting the connectivity of the road network to the receiving channel system as the storm progressed. Another point to note is that the two components of the catchment, River Lee and Lee Navigation Channel, did not show much difference between levels of metals in water and sediment, whereas much greater differences were found between tributaries with regard to both water and sediment results.

It is important to note that aspects such as river hydrology and hydraulics can directly impact on water and sediment quality and be influenced by rainfall and road runoff. For example, the river bed may be eroded through the river flow or suspended sediment be deposited on the river bed, modifying the river geomorphology, which is affected by sediment transport and consequently impacting on contaminant distribution (Hrissanthou, 2015). Flash flooding is another important aspect, which can contribute to recharging groundwater but can also lead to flooding and combine sewer overflow, overwhelming local drainage systems, disturb aquatic ecosystems and accelerate discharges of industrial and urban toxic materials and nutrients into waterways (Talbot *et al*., 2018; Lintern *et al*., 2018). Understanding these aspects would be important to further account for pollutant distribution, however, they were not included in this study as it would have been necessary to collect additional data and apply further modelling. This knowledge gap should be addressed in future studies to advance the understanding of contaminant transport and distribution.

4.4 Releases of sediment-associated metals to overlying waters

The environmental behaviour of sediment-associated pollutants under varying physico-chemical conditions were assessed through laboratory batch tests. As described in Section 3.8 this was done as part of field studies to look into the potential of sediment metals release into the water column. Measurement of pH, DO, TOC and DOC for selected metals before and after batch tests determined in water samples at sampling sites A, E F, H and K are presented in Appendices N1-N4. The sites were chosen to represent different land use characteristics and components of the river. Site A was included for background, E and F representing tributaries, site H as being on the River Lee and site K on the Lee Navigation Channel.

An overview of the concentrations of selected metals released to surface water during laboratory batch testing is reported in Table 4.18. The average concentrations of the seven metals in the selected water samples increase as follows: Hg < Sn < Cd < Pb < Ni < Cu < Zn, which although follow a similar order of abundance as reported in Section 4.1 for Hg, Pb and Zn, there is a different order for Cd, Cu, Ni and Sn, indicating that sediment resuspension may play an important part impacting the order of abundance of metals in urban rivers (Taylor and Owens, 2009). This is further supported when observing results in Table 4.19, which shows an overview of the concentrations of selected metals in surface waters by sampling sites, before and during batch test experiment. For example, before batch test highest concentration of Cd, Ni and Zn were found at site E, Hg and Sn at site A, Cu at site H and Pb at site F while during batch test highest concentration of selected metals were reported at site K for Cd, Hg, and Ni and at site H for Cu, Pb, Sn and Zn. It is important to highlight that both the order of abundance and metal concentrations determined in urban rivers can vary depending on a myriad of factors such as the extent and type of activities in the area, particles binding properties and heavy metal fractions (Huang *et al*., 2012).

Table 4.18 Overview of mean (µg/l ± SD) metal concentrations in surface waters determined before and during laboratory batch test experiment at different sampling sites.

Site	Cd	Cu	Hg	Ni	Pb	Sn	Zn
A before	0.09 ± 0.00	27.51 ± 0.24	0.45 ± 0.04	9.27 ± 0.10	0.74 ± 0.06	2.38 ± 0.24	11.21 ± 0.10
A after	1.07 ± 0.10	103.25 ± 0.90	0.48 ± 0.09	29.82 ± 2.51	22.10 ± 0.34	2.70 ± 0.28	243.10 ± 1.52
E before	0.44 ± 0.03	28.20 ± 0.20	0.12 ± 0.03	23.78 ± 0.23	1.60 ± 0.11	0.91 ± 0.04	23.94 ± 0.24
E after	2.01 ± 0.32	150.78 ± 0.36	0.13 ± 0.08	47.88 ± 0.86	47.06 ± 0.40	1.97 ± 0.18	461.65 ± 9.21
F before	0.35 ± 0.00	32.46 ± 0.27	0.06 ± 0.00	20.96 ± 0.16	2.24 ± 0.08	0.46 ± 0.07	19.93 ± 0.15
F after	0.59 ± 0.00	74.27 ± 2.61	0.07 ± 0.03	29.46 ± 1.08	11.60 ± 0.98	1.59 ± 0.27	151.73 ± 1.96
H before	0.33 ± 0.02	46.73 ± 0.29	0.29 ± 0.02	16.62 ± 0.15	1.99 ± 0.07	0.45 ± 0.01	16.88 ± 0.17
H after	3.94 ± 0.17	171.90 ± 0.58	0.35 ± 0.07	55.24 ± 1.06	66.08 ± 0.14	3.50 ± 0.72	715.51 ± 1.49
K before	0.39 ± 0.01	26.95 ± 0.24	0.39 ± 0.03	11.81 ± 0.10	2.19 ± 0.00	1.92 ± 0.05	13.47 ± 0.13
K after	7.00 ± 0.18	157.56 ± 1.66	0.50 ± 0.12	67.72 ± 0.79	46.60 ± 0.91	3.49 ± 0.14	638.40 ± 1.06

Table 4.19 Overview of maximum, minimum, median and mean (µg/l ± SD) metal concentrations in surface waters determined during batch test experiment.

Metal	**Range in concentration**	**Mean concentration (± SD)**	**Median concentration**	**UK TAG Standards (µg/l)**	**EU EQS (µg/l)**	
					AA*	MAC**
Cd	0.59 – 7.00	2.92 ± 2.62	2.01	---	0.25^(c)^	1.50^(c)^
Cu	74.27 – 171.90	131.55 ± 41.10	150.78	1.00^(a)^	---	---
Hg	0.07 – 0.50	0.31 ± 0.20	0.34	---	---	0.07^(d)^
Ni	29.46 – 67.72	46.02 ± 16.55	47.88	---	4.00^(a)^	34.00
Pb	11.60 – 66.08	38.69 ± 21.75	46.27	---	1.20^(a)^	14.00
Sn	1.59 – 3.50	2.65 ± 0.87	2.67	---	---	---
Zn	151.73 – 715.51	442.08 ± 243.71	461.65	14.20^(b)^	---	---

Key:
* Annual Average (also referred to as long-term standard)
** Maximum Allowable Concentration (also referred to as short-term standard)
(a) Bioavailable fraction
(b) Bioavailable fraction 10.90 µg/l + Ambient Background Concentration 3.3 µg/l dissolved Zn for River Lee.
(c) For Cd and its compounds, the EQS values here are for Class 5 (≥ 200 mg $CaCO_3$ /l) as per hardness of water in the Lower Lee catchment
(d) Value for Hg and its compounds

Table 4.19 shows the monitored ranges at each site demonstrate considerable, generally with same order of magnitude for Ni, Pb, Sn and Zn and 1 order of magnitude for Cd, Cu and Hg. As previously mentioned, EU EQS (2013) are available for Cd, Hg Ni, and Pb, and UK TAG (2013) standards exist for Cu and Zn (see Table 4.18). A comparison of the determined concentrations (during batch test) with these standards indicate that mean concentrations of all metals exceed the annual average (AA) EQS at all sites. Metal concentrations greater than the maximum allowable concentration (MAC) are indicative of a short-term or acute risk to receiving water health. Mean concentrations of Hg and Pb exceed the corresponding MAC values at sites A, E, H and K with maximum concentrations of Cd mirroring this behaviour at sites E, H and K. Mean concentrations of Cu and Zn exceed the appropriate UK TAG (2013) standards at all sites. As it is well known sediment is an essential, integral and dynamic part of river basins, however, sediment also acts as sink medium for many contaminants (Brils, 2008) and results from this research demonstrated that sediment resuspension further contribute for contaminant levels to UK TAG (2013) and EU EQS (2013) making it clear that there is a link between sediment quality and achieving of this EU WFD objectives, further intensifying the negative impact to the ecological status of these urban rivers.

It is evident that the order of abundance Pb < Cu < Zn < Ni for the metal background reference median concentrations (as reported under Section 4.2, Table 4.1b) does not follow the same trend reported in releases of sediment-associated metals to overlying waters (Pb < Ni < Cu < Zn – trend as per median values on Table 4.19). For example, whilst Zn is the most abundant metal reported in this study, metal background reference concentrations show that Ni is the most abundant, suggesting other pollutant sources (e.g. sediment remobilisation, land use and/or physico-chemical parameters) can contribute to levels of metals in urban rivers. When comparing metal background reference concentrations (MBRC) of relevant metals (Table 4.1b) with median metal concentrations in Table 4.19, it shows that metals concentrations determined in this research were one to three orders of magnitude higher than the MBRC values. Taking into consideration the sediment batch test results which indicated sediment resuspension and the comparison of batch test results with MBRC which suggested the role of anthropogenic activities, it is important to note the necessity of more strictly measures (such as development of sediment quality standards) in order to improve sediment management and minimise impacts on surface water quality (Kwok *et al.*, 2014).

Table 4.20 shows the remobilisation efficiency through the identification of the amount of metal released into the overlying water column during the batch experiment (expressed as the percentage mass of metal released into solution compared to the total amount of metal contained in the sediment). The percentage was calculated to provide an overview of the relative distribution of metals between particulate (K_d) and dissolved phases. Many factors (e.g. organic matter, pH, DO) can influence partitioning and speciation of metals. In addition, during transport of metals in surface water bodies, partition coefficient processes can contribute to a reduction in the dissolved concentration of pollutants and this affects the overall rate of metal transport

(Sedeño-Díaz *et al*., 2019), thus the mobility, fate and bioavailability of metals in surface water bodies can be said to be directly related to their partitioning between suspended solids and water and their speciation (i.e. as they form other compounds) (Filgueiras *et al*., 2004). Further detailed study of metals partition coefficients and speciation behaviour would enable a better understanding about the release of metals from sediment to be generated.

Table 4.20 Percentage metal remobilisation (mean ± SD) at different sites.

Site	Cd	Cu	Hg	Ni	Pb	Sn	Zn
A	3.33 ± 0.36	3.12 ± 0.04	0.64 ± 1.93	3.15 ± 0.39	0.89 ± 0.01	0.12 ± 0.11	3.17 ± 0.02
E	6.12 ± 1.25	4.39 ± 0.01	0.33 ± 2.67	4.47 ± 0.16	1.03 ± 0.01	0.50 ± 0.08	4.73 ± 0.10
F	4.00 ± 0.67	1.95 ± 0.12	0.33 ± 1.00	1.99 ± 0.25	0.52 ± 0.05	0.14 ± 0.03	3.12 ± 0.05
H	4.97 ± 0.26	2.26 ± 0.01	0.42 ± 0.49	3.58 ± 0.10	0.90 ± 0.00	0.33 ± 0.08	3.82 ± 0.01
K	3.84 ± 0.11	2.85 ± 0.04	0.27 ± 0.29	3.28 ± 0.05	0.66 ± 0.01	0.26 ± 0.02	3.33 ± 0.01

Results from Table 4.20 shows a positive metal release into overlying water occurs for sediments collected from all five sites. Although the continual stirring associated with the batch test experiments does not directly simulate the conditions encountered in the field, the results confirm the potential for sediments to release metals and highlight the need for further investigation of the influencing conditions. This is particularly important with respect to the development and implementation of measures to achieve good ecological status under the EU WFD (European Commission, 2000; Crane *et al*., 2007; Comber *et al*., 2008). Whilst the amount of metal released into the sediment varies between metals and sites, the level of variation is generally within an order of magnitude, ranging from 0.12 % (Sn, site A) to a maximum of 6.12 % (Cd, site E). Reported levels of metal release are greatest for Cd (3.33-6.12 %) and Zn (3.12-4.73 %) which is consistent with studies in the literature that identify Cd and Zn as pollutants which typically associate most readily with the dissolved phase (Hem, 1972; Morrison *et al*., 1984) whilst Hg, Pb and Sn showed highest affinity for the particulate bound, as they had remobilisation percentages usually less than 1 % (except for Pb at site E with a remobilisation of 1.03 %). According to Barus *et al*. (2021) different metals have different adsorption capacities with metals such as Pb, Cu and Zn having more affinity with particulate bound phase.

From results in Table 4.20 all metals (with the exception of Hg) show the greatest release at site E indicating that metals stored in sediments at this site are potentially more susceptible to release. Greater potential for the release of metals from sediments at this site could also indicate that sediments are a source of the elevated aqueous metal concentrations also reported at site E (see Section 4.1).

Correlation analysis (Table 4.21) of sediment metal release data with levels of dissolved oxygen (DO), temperature, pH, total organic content (TOC) and dissolved organic content (DOC) determined after the experiment does not suggest that any of these parameters are responsible for the variations in metal release reported from sediments except for Hg where a positive correlation with DO ($p \leq 0.05$; $r = 0.92$) exists. Further examination of the sediments regarding their mineral and total organic content composition, sediment pH and cation exchange capacity may reveal the processes driving this relatively higher release for other metals at this site, which would be interesting to further investigate in future studies.

Table 4.21 Correlation analysis of target metals between batch test results and DO, Temperature, pH, TOC and DOC parameters.

			Metals in water after batch test						
			Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Sn**	**Zn**
Metals in water column	**DO**	**r***	0.43	0.03	**0.92**	0.18	-0.10	0.59	0.08
		P-value	0.47	0.96	**0.02**	0.77	0.86	0.29	0.90
	Temp	**r***	0.29	-0.21	-0.37	0.24	-0.23	-0.23	-0.06
		P-value	0.63	0.74	0.55	0.70	0.71	0.72	0.92
	pH	**r***	-0.06	-0.67	-0.25	-0.24	-0.68	-0.36	-0.50
		P-value	0.92	0.22	0.68	0.70	0.20	0.54	0.38
	TOC	**r***	0.79	0.61	0.29	0.83	0.44	0.57	0.25
		P-value	0.11	0.28	0.63	0.08	0.45	0.31	0.68
	DOC	**r***	0.78	0.64	0.24	0.84	0.49	0.35	0.60
		P-value	0.11	0.24	0.69	0.07	0.40	0.55	0.27

Key: *Pearson correlation
Values in bold show the pairs of parameters with very strong correlation.

DO, pH, temperature, TOC and DOC measurements (Appendices N1-N4) were taken for each water sample on collection at the sampling site, and at the start and completion of the the laboratory batch test experiment. Mean values for the measurements ranged from 2.17 to 4.79 mg/l (for DO), from 8.07 to 8.78 (for pH), from 17.60 to 20.45 ˚C (for temperature), from 18.11 to 24.01 mg/l (for TOC) and from 14.95 to 20.24 mg/l (for DOC) with no parameter showing a consistent trend by site location. Comparisons with UK TAG (2013) water quality guidelines for rivers indicate that samples fall under the 'high/good quality' for pH.

4.5 Concentration of selected polyaromatic hydrocarbons (PAHs) in river water

Although studies of PAHs in surface water using similar method as this research have found concentrations of the target pollutants in water matrix, this study did not detect PAHs in water samples. This could be due to a number of factors such as the relatively lower water solubility of PAHs and high affinity for absorption onto organic matter, they are eventually deposited onto sediments, although some will be degraded in water through photooxidation, chemical oxidation and biodegradation by aquatic microorganisms (Teaf *et al.*, 2010); due to the sample volume utilised in this study (250 ml as recommended by SPE method – Phenomenex UK), although most of the literature used 1 – 2 litres (e.g. Chen *et al.*, 2015; Nawaz *et al.*, 2014;

Kanchanamayoon and Tatrahun, 2008; Li and Lee 2001). Thus, new sampling and analysis would be necessary using higher volumes of water samples to see if PAH concentrations can be detected in the water column.

4.6 Concentration of selected polyaromatic hydrocarbons (PAHs) in river sediment – all sites and sampling dates

Due to their hydrophobic nature, PAHs entering the aquatic environment exhibit a high affinity for suspended particulates in the water column. As PAHs tend to readily sorb to particulate matter, gravitational settling of particles results in their eventual accumulation in bottom sediments (Teaf *et al*., 2010). Whilst all water samples were analysed for a range of PAHs, they were not detected in any samples and therefore, results for PAHs in sediments are reported here only.

Full details of 11 PAHs phenanthrene (Ph), anthracene (A), fluoranthene (Fl), pyrene (Py), benzo(a)anthracene (Bz(a)A), chrysene (C), benzo(b)fluoranthene (Bz(b)Fl), benzo(k)fluoranthene (Bz(k)Fl), benzo(a)pyrene (Bz(a)Py), dibenzo(a,h)anthracene (DBz(a,h)A), benzo(g,h,i)Perylene (Bz(g,h,i)Pe)) concentrations determined in sediment samples at each sampling site on each sampling date are presented in Appendices J1 to J8. An overview of results is presented below.

The average concentrations of the 11 PAHs in all sediment samples increase as follows: A < DBz(a,h)A < Bz(g,h,i)Pe < Ph < Bz(k)Fl < Bz(a)A < Bz(a)Py < C < Bz(b)Fl < Py < Fl with measured concentrations determined ranging from 0.01 to 27.80 µg/g (see Table 4.22). This is consistent with previous research which found that Fl and Py had the highest mean concentrations in urban river sediments (e.g. Kafilzadeh, 2011; Santos, 2018).

Results indicate that the PAH composition pattern is dominated by the presence of 4-ring PAHs (63.50 %) followed by 5-ring PAHs (21.49 %) and 3-ring PAHs (9.60 %), while 6-ring PAHs contribute the least (5.41 %). This is consistent with the work of Kafilzadeh *et al.* (2011) who reported river sediments to be enriched in 4-ring PAHs, with Fl being the most abundant. According to Koh *et al*. (2004), Nasr *et al*. (2010) and Mohammed *et al*. (2009), the composition of PAHs in sediments is primarily dominated by 4-ring PAHs, while in water samples the 3-ring PAHs predominate. This may be attributed to bacterial degradation as lower molecular weight PAHs such as phenanthrene and anthracene are rapidly degraded in sediments (Kafilzadeh *et al*., 2011; European Union, 2011). A 2007 survey of the Lower Lee catchment found that PAHs such as Fl, Bz(b)Fl, Bz(k)Fl were present in surface waters at levels which exceeded the EU EQS (2013) identifying this as being due to urban diffuse pollution inputs and the presence of contaminated sediments (Environment Agency, 2012).

The standard deviations for each PAH mean concentration varies largely between different sampling locations and sampling dates (Table 4.22). An assessment of PAH average concentrations against the Dutch (Esdat, 2000) and Canadian (CCME, 2002) sediment guidelines shows that all selected PAHs exceed the ISQG and the PEL value in the Canadian list. The Dutch TV and the IV values are 1.00 and 40.00 μg/g respectively for the sum of the 10 PAHs identified in Table 4.22 with the 8 PAHs included in this research identified in bold. The average total of these 8 PAHs is 19.79 ± 1.38 μg/g which exceeds the Dutch TV with the sum of the 8 PAHs ranging from 1.46–119.86 μg/g indicating that levels exceed the Dutch IV value on occasions.

Normal background concentrations (NBC) were not available for any of the selected PAHs, thus evaluation of pollution indices could not be applied to the PAHs results.

Table 4.22 Overview of maximum, minimum and mean (± SD) PAHs concentrations determined at all sites on all sampling dates.

PAH	Range in concentration (µg/g)	Mean concentration (± SD)	Dutch (µg/g)	Canadian (µg/g)	
				ISQG[3]	PEL[4]
Ph	0.11 – 17.07	2.12 ± 2.28	Values are for sum of 10 PAHs (N, **Ph, A, Fl, Bz(a)A, C, Bz(a)Py, Bz(k)Fl, Bz(g,h,i)Pe** and In(1,2,3-cd)Py) TV[1] = 1.00 IV[2] = 40.00	0.04	0.52
A	0.09 – 3.28	0.76 ± 0.57		0.05	0.25
Fl	0.41 – 27.80	5.19 ± 4.37		0.11	2.35
Py	0.14 – 24.61	4.54 ± 3.83		0.05	0.88
Bz(a)A	0.20 – 14.90	2.42 ± 2.08		0.03	0.39
C	0.04 – 17.66	2.77 ± 2.41		0.06	0.86
Bz(b)Fl	0.01 – 25.83	4.21 ± 3.87		---	---
Bz(k)Fl	0.28 – 11.50	2.31 ± 2.21		---	---
Bz(a)Py	0.32 – 15.79	2.58 ± 2.25		0.03	0.78
DBz(a,h)A	0.01 – 9.98	1.58 ± 1.61		0.01	0.14
Bz(g,h,i)Pe	0.01 – 11.86	1.63 ± 1.75		---	---
ΣPAHs	1.62 – 180.28	30.11 ± 1.36			

Key: PAHs in bold under the Dutch list identify the PAHs included in this study; [1] Target Value; [2] Intervention Value; [3] Interim Sediment Quality Guideline; [4] Probable Effect Level

Comparing the results from this study with results from urban rivers located in other countries (see Table 4.23) indicates that the average concentrations of the selected PAHs in river sediment of the Lower Lee catchment were within the range of values previously reported although the total PAH concentrations for this study were consistently higher than previous studies. Research by Kafilzadeh *et al*. (2011) on the Kor River in Iran reported average concentrations for Ph and A which were 3 and 4 times higher than those in the current study. Results from Jiang *et al*. (2007) on the Haihe River in China showed Ph and A to be 3 and 2 times higher and Fl slightly higher than those from this study. The difference in results could be due to different land use activities e.g. varying types/intensities of industrial activities in the respective catchment areas, highlighting the importance of considering land use effects on PAH concentrations in an urban river catchment (Stout *et al*., 2004). Results provide by CRT (2012) are lower for all the selected PAHs compared to results in this study with CRT (2012) reporting the sum of the 11 PAHs around 3 times lower than the sum of PAHs from this research. These results may indicate an increase in PAHs accumulation in sediment in the Lower Lee catchment area over time (Environment Agency, 2012).

Table 4.23 Comparison of PAH concentrations determined in this study with results from other urban rivers from around of the world.

PAHs	**Average concentration (µg/g)**			
	This study	**Lower Lee catchment, Canal & River Trust 2012**	**Kor River, Iran – Kafilzadeh *et al.*, 2011**	**Haihe River, China – Bin *et al.*, 2007**
Ph	2.12	0.49	6.11	7.34
A	0.76	0.15	4.95	1.87
Fl	5.19	1.62	0.91	5.92
Py	4.54	2.05	0.78	3.43
Bz(a)A	2.42	0.89	1.34	0.82
C	2.77	0.80	0.75	0.99
Bz(b)Fl	4.21	1.27	0.98	0.60
Bz(k)Fl	2.31	0.45	1.27	0.14
Bz(a)Py	2.58	0.90	1.49	0.32
DBz(a,h)A	1.63	0.14	0.60	0.19
Bz(g,h,i)Pe	1.58	0.69	0.52	0.24
ΣPAHs	30.11	9.45	19.70	21.87

PAH composition in sediments reflects the origin(s) from which they were derived (Yan *et al.*, 2009) and the PAH ratio approach has been widely used for interpreting PAH compositions and inferring possible sources (Tobiszewski and Namieśnik, 2012; Lingle, 2008; Morillo, 2007; Pietari *et al.*, 2016; Costa, 2005). However, it has been suggested that using ratios to determine sources should be used with caution although it can provide a useful starting point for PAH source profile interpretation (Environment Agency, 2015; Yunker *et al.*, 2002). Usually, the PAH ratio is used to differentiate pyrogenic PAHs (incomplete combustion of organic matter, combustion of fossil fuel, vehicular engine combustion, smelting, waste incinerator, forest fire, coal combustion), from petrogenic PAHs (unburned petroleum and its products, gasoline, lubricating oil, kerosene, diesel, asphalt) (Mudge, 2008). The PAH ratios calculated for Ph/A, Fl/Py, Bz(a)A/C and Bz(a)Py/Bz(g,h,i)Pe are shown in Table 4.24 for each sampling site.

Results from Table 4.24 are interpreted as follows: Ph/A ratios less than 10 indicate a pyrogenic (such as the incomplete burning of fossil fuels or wood) PAH source whereas values above 10 indicate a petrogenic source (such as derived from fuel oil or refined petroleum products) (Pietari *et al*., 2016). The Ph/A ratio range of 2.13 – 3.59 (Table 4.24) calculated for this study is therefore consistent with the finding from the Environment Agency (2015) (ranging from 2.00 – 3.75) and identifies the PAH source as predominantly pyrogenic with one of the main sources being from vehicles due to rapid high temperature combustion. Yunker *at al.* (2002) suggest that a Fl/Fl+Py ratio greater than 0.4 indicates a PAH petroleum combustion source and when in excess of 0.5 the source is likely to be due to wood/grass/coal combustion as opposed to petroleum combustion.

Results in Table 4.24 indicate that all sampling sites have Fl/Fl+Py ratios above 0.5 suggesting pollution from wood/grass/coal combustion sources. The Bz(a)A/C ratio is usually used as an indicator of the PAH source from combustion processes when ratio is greater than 0.5 and from petroleum sources when the ratio is less than 0.5 (Yunker *et al*., 2002). Results from Table 4.24 indicate the PAH source is from combustion processes. The ratios of Bz(a)Py and Bz(g,h,i)Pe are an indicator of whether the PAH compounds originate from non-traffic emissions (ratio less than 0.6) or traffic emissions (ratio more than 0.6) (Pietari *et al*., 2016). The values reported in Table 4.24 show that the samples collected at all sites in the Lower Lee catchment probably derive from vehicle emissions and are consistent with the sediment results reported by the Environment Agency (2015).

Table 4.24 Ratios between PAHs means for each sampling site.

	Sampling sites	**PAHs mean ratios**			
		Ph/A	**Fl/Fl+Py**	**Bz(a)A/C**	**Bz(a)Py/Bz(g,h,i)Pe**
River Lee	A	2.25	0.53	0.92	1.28
	G	2.75	0.53	0.80	2.45
	H	2.60	0.52	0.83	3.40
	I	2.41	0.53	0.91	1.40
Lee Navigation	C	2.46	0.51	0.87	1.12
	J	2.85	0.55	0.85	2.19
	K	2.16	0.52	0.71	1.19
Tributaries	B	2.13	0.52	0.88	1.14
	D	3.59	0.54	0.94	1.35
	E	3.10	0.54	1.00	1.43
	F	3.52	1.19	0.95	1.33

Overall, the ratios suggest mixed pyrogenic sources that cannot be solely ascribed to traffic sources. Other potential sources include combustion in power stations, combustion by industry or possibly domestic (Wilcke, 2007) and these possible sources will be explored in the SFA modelling, Section 5.2. The identification of a traffic emission PAH source indicates the existence of a catchment wide problem, as traffic emissions are ubiquitous throughout the urbanised Lower Lee catchment. Van Metre *et al*. (2000) found increasing PAH trends in 10 urban lakes and concluded that this pattern was coincident with urbanization and increases in vehicle traffic in the watersheds. In this context investigation on land use would be necessary to further understand and identify sources of target PAHs.

Figure 4.11 shows the variations in average PAHs concentrations at each site over the course of 8 sampling trips. Analysis of the results indicates that there is considerable variation in PAH concentrations in sediment between the sites with fluoranthene and pyrene demonstrating the highest concentrations at all sites. This is in agreement with previously reported studies (Khazaali *et al*., 2016; Sower, 2008; Brown and Peake, 2006; Brun *et al*., 2004). The highest PAH concentrations are associated with site J where the highest variations also occur. This could be due to high concentrations recorded on 9th December 2014 and could be due to unreported incidents (Environment Agency, 2015). Figure 4.11 shows upstream site A has the lowest mean concentration for all the 11 PAHs. This is also true regarding total concentration for the 11 selected PAHs being lowest at site A (10.66 µg/g) while sampling site J has the highest mean total PAH concentration (67.45 µg/g) followed by sampling site E (43.22 µg/g).

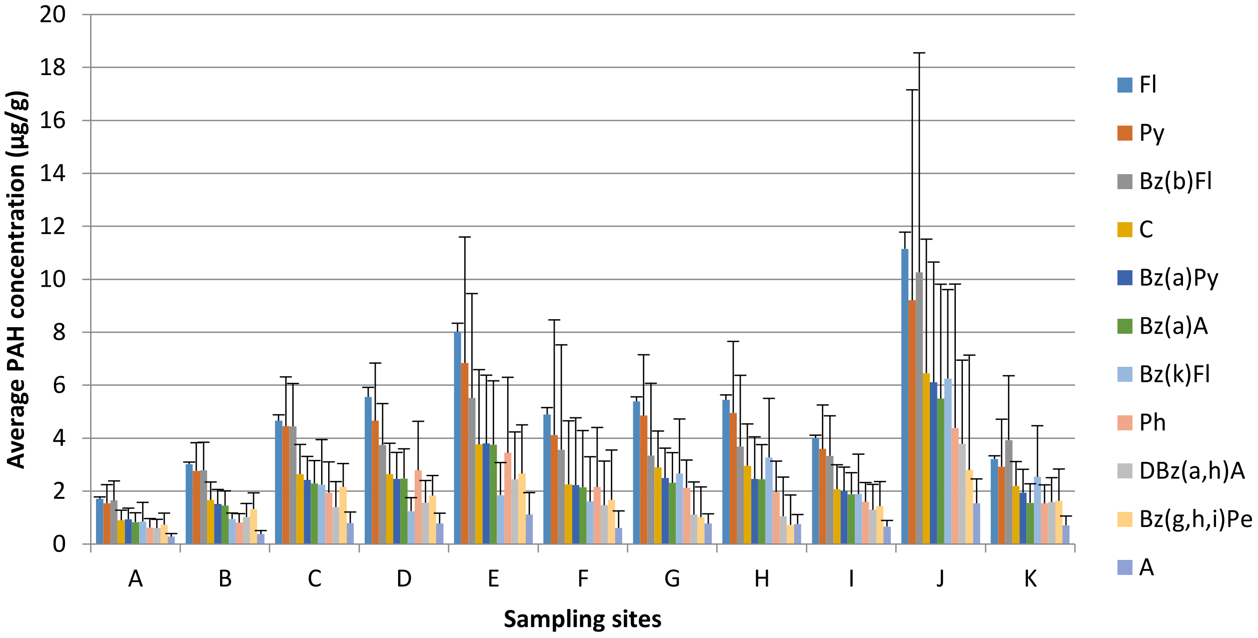


Figure 4.11 Average concentrations (±SD) of selected PAHs in sediment in the River Lee, Navigation Channel and tributaries.

While Figure 4.11 show PAHs mean concentrations for the Lower Lee catchment, the data was divided into components of the catchment (River Lee, Lee Navigation Channel and tributaries), in order to identify and consider any trends and tributary contributions of target PAHs. Appendices K1 and K2 show the distribution of targeted PAHs throughout the sampling sites in the Lower Lee catchment for the River Lee, Lee Navigation Channel and the four tributaries.

Figure 4.12 presents the mean PAH concentrations for the sediment samples collected from sites on the River Lee. Highest mean PAH concentration occurs at sites G and H. As those two sampling sites were part of the area where sediment was dredged in summer 2009 with a view to reducing pollutant concentrations it would be necessary to compare results from this study with data from pre- and post-dredging in order to help identify any possible cause. However, the necessary data was not available. A trend of increasing PAHs concentrations as the river flows downstream was not apparent and further investigation will be necessary to further understand this factor as this lack of trend could be due to a number of circumstances such as variations in land use and the geomorphology of the area.

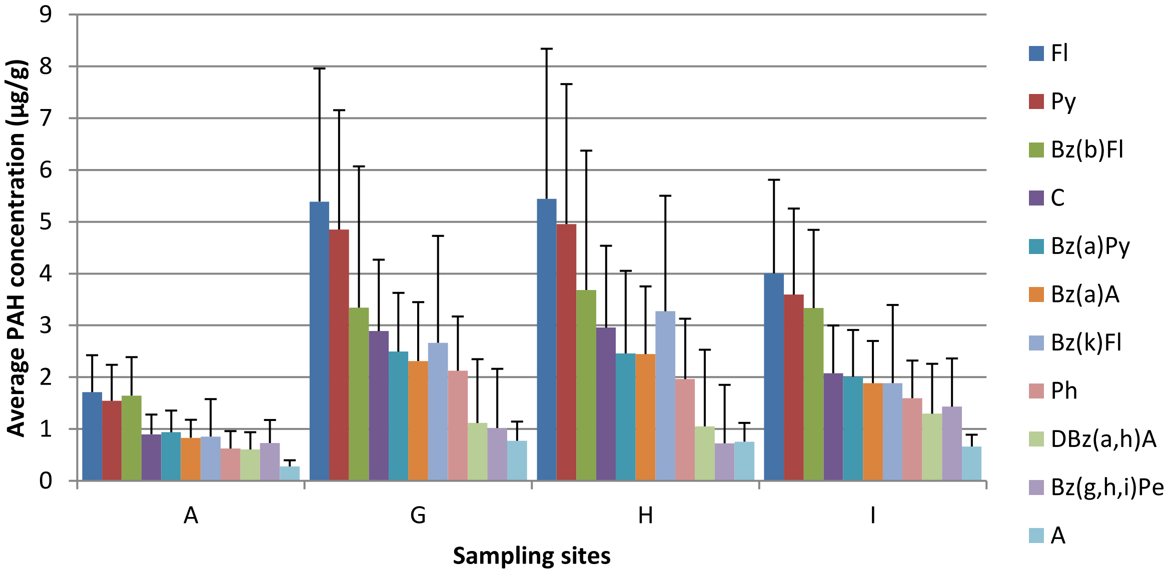


Figure 4.12 Average concentrations (±SD) of selected PAHs in sediment in the River Lee.

The results obtained for the Lee Navigation Channel (Figure 4.13) indicate highest PAH mean concentrations at site J for all selected PAHs (accompanied by high standard deviations). Again, a trend of increasing PAHs concentrations as the channel flows downstream is not apparent. Site J (also dredged in 2009) had the highest average concentration of PAHs. This outcome could be related with intense pressure at this sampling site by specific local activities. A clearer understanding of this may be seen if their source can be traced (Neff *et al.*, 2004). Thus, the necessity to undertake SFA modelling in order to identify sources and predict PAHs load at each sampling site.

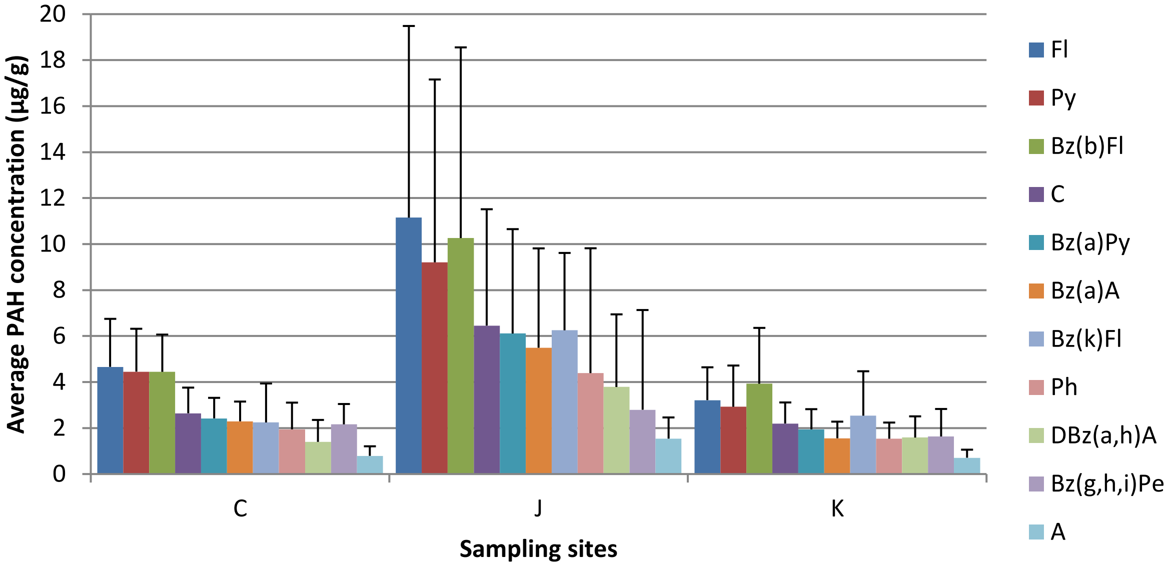


Figure 4.13 Average concentrations (±SD) of selected PAHs in sediment in the Lee Navigation Channel.

The average PAH concentrations for the tributaries Cobbins (B), Salmons (D), Pymmes (E) and Ching Brook (F) are shown in Figure 4.14. Highest average concentrations were determined in the Pymmes Brook for all selected PAHs followed by Salmons Brook. Pymmes Brook is affected by sewage effluents which are discharged into Salmons Brook from Deephams STW. Cobbins Brook represents the sampling site with least average PAHs concentrations. As the ratio diagnostic results showed a pyrogenic source of PAHs for the study area, other studies (Environment Agency, 2019; Brewster *et al.*, 2018; Crane, 2014) argue that the source of PAHs attributed to pyrogenic activities (as most PAHs that are persistent in environmental media) are usually found in various urban settings especially in river sediment, discharges from STW and urban runoff, although petrogenic contribution cannot be ruled out.

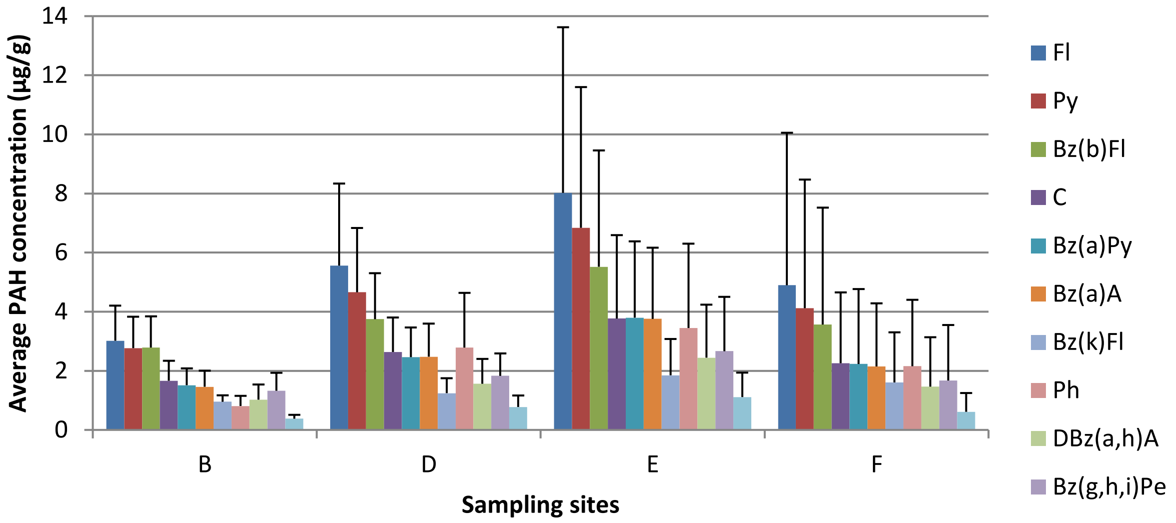


Figure 4.14 Average concentrations (±SD) of selected PAHs in sediment in the River Lee tributaries.

Given the identified variations in PAH concentrations between sampling sites and dates, further analysis was undertaken to identify and better understand these variations.

4.6.1 Spatial and temporal distributions of PAHs in river sediment

The normality of the data distribution for each parameter was checked using the Anderson-Darling statistical test (Table 4.25). As all sediment PAH data sets were skewed, a log-transformation was performed as shown in Table 4.20. This results in the data for most of the PAHs (Ph, A, Fl, Bz(a)A, Bz(k)Fl and Bz(a)Py) being normally distributed but leaving the data for Py, C, Bz(b)Fl, DBz(a,h)A and Bz(g,h,i)Py skewed. Equal variance tests for original and transformed data showed P-values < 0.05 indicating unequal variance of the data. However, when checking the conditions of the transformed data through the Minitab Assistant the output report showed that the analysis can still be carried out (despite non-normality) as the test is still robust - not only for non-normal distribution data but also for unequal variance of the data in question. Outliers present in samples were kept to maintain integrity of the research and since they may prove interesting in their own right (Weisberg, 2005).

Table 4.25 Results from Anderson-Darling test of normality for PAHs in river sediment.

Data sample	**Results from original values**		**Results from $\log_{10}$ values**	
	P-value	**Normal distribution**	**P-value**	**Normal distribution**
Ph	< 0.005	No	0.305	Yes
A	< 0.005	No	0.997	Yes
Fl	< 0.005	No	0.789	Yes
Py	< 0.005	No	0.010	No
Bz(a)A	< 0.005	No	0.750	Yes
C	< 0.005	No	0.006	No
Bz(b)Fl	< 0.005	No	< 0.005	No
Bz(k)Fl	< 0.005	No	0.057	Yes
Bz(a)Py	< 0.005	No	0.844	Yes
DBz(a,h)A	< 0.005	No	< 0.005	No
Bz(g,h,i)Py	< 0.005	No	< 0.005	No

ANOVA GLM analysis was first performed using PAH concentrations as dependent variables and sampling sites and dates as categorical variables to test for sites-to-dates differences in PAH concentrations and to determine whether PAH concentrations vary in relation to site at a level which is considered statistically significant (Table 4.26).

Table 4.26 Results of the application of ANOVA GLM to the target PAHs undertaken using the log$_{10}$ data from river sediment.

PAH	**Factor**	**F-test**	**P-value**	**R^2 (%)**	**R^2 Adjusted (%)**
Ph	Sites	5.10	**< 0.01**	56.94	46.48
	Dates	5.94	**< 0.01**		
A	Sites	6.25	**< 0.01**	62.15	52.95
	Dates	7.49	**< 0.01**		
Fl	Sites	6.14	**< 0.01**	61.77	52.49
	Dates	7.39	**< 0.01**		
Py	Sites	4.74	**< 0.01**	66.86	58.82
	Dates	13.40	**< 0.01**		
Bz(a)A	Sites	6.82	**< 0.01**	62.49	53.38
	Dates	6.91	**< 0.01**		
C	Sites	3.96	**< 0.01**	57.83	47.59
	Dates	8.05	**< 0.01**		
Bz(b)Fl	Sites	1.10	0.38	41.83	27.71
	Dates	5.62	**< 0.01**		
Bz(k)Fl	Sites	6.39	**< 0.01**	53.78	42.55
	Dates	2.51	**0.02**		
Bz(a)Py	Sites	6.86	**< 0.01**	64.15	55.44
	Dates	8.09	**< 0.01**		
DBz(a,h)A	Sites	1.74	0.09	49.81	37.62
	Dates	7.44	**< 0.01**		
Bz(g,h,i)Pe	Sites	3.13	**< 0.01**	43.78	30.13
	Dates	3.32	**< 0.01**		

The ANOVA GLM results for PAHs (Table 4.26) revealed that, with regard to sampling sites, only Bz(b)Fl and DBz(g,h,i)Pe concentrations do not vary significantly ($p > 0.05$) and for sampling dates all selected PAHs concentrations vary in a manner that is statistically significant ($p \leq 0.05$). However, it can be seen from the R^2 adjusted values that the percentage of variation for most of the PAHs is less than 50 %, which means that, for example, only 27.71 % variation in Bz(b)Fl is explained by its relationship with sampling dates and sites, leaving 72.29 % of Bz(a)Fl variation unaccounted for. Residual plots (Appendices L1 to L11) show better randomness of data compared to non-transformed data, validating the strength of the model in its predictions. The spatial and temporal variation results may indicate that most of the PAH concentrations are dependent on land use and weather conditions (Yim *et al.*, 2007).

Tukey's HSD post-hoc multiple comparisons were also performed for the selected PAHs by sampling dates and sites and showed significant variation. Appendices M1 to M11 show figures for the confidence intervals associated with the mean PAH concentrations per sampling dates. From Tukey's HSD test results the main highlights are:

- With regard to sampling dates, it was noted that Ph, A, Fl, Py and Bz(a)A were higher on 11th March 2015, 15th April 2015 and 20th May 2015 compared to sampling dates 14th August 2015 and 23rd March 2016.
- With respect to sampling sites, it was noted that Fl, Py, Bz(a)A and Bz(a)Py were lower at background site A compared to sites C, D, E, G, H and J. Ph was lower at sampling site A compared to sites C, D, E, F, G, H and J.

Comparisons of results indicate that upstream site A has significantly lower average PAH concentration for Fl, Py, Bz(a)A and Bz(a)Py, compared to most of the sampling sites, which is further supported by results from Figure 4.11 which identify site A (located in a less urbanised area) with the lowest mean concentration. PAHs in urban areas are widely reported to be greater than those reported for rural areas, due to the increased levels of vehicular and industrial activities in urban areas. Results also show that PAH average concentrations do not significantly vary in relation to seasons. The significant variation of average PAH concentrations between specific sampling dates may suggest that factors such as types of activities in each area play an important role in variations identified (Ekonomiuk *et al.*, 2006).

To identify possible relationships between PAH average concentrations and 1-day/2-day rainfall depths, a correlation analysis was undertaken. No significant correlation was found suggesting that rainfall did not affect levels of PAHs in river sediment. The matrix plot in Figure 4.15 shows a strong relationship between most PAHs, with Bz(b)Fl, Bz(g,h,i)Pe and DBz(a,h)A showing a much less pronounced relationship with other PAHs. Further correlation analysis was then undertaken to identify the nature and strength of these relationships.

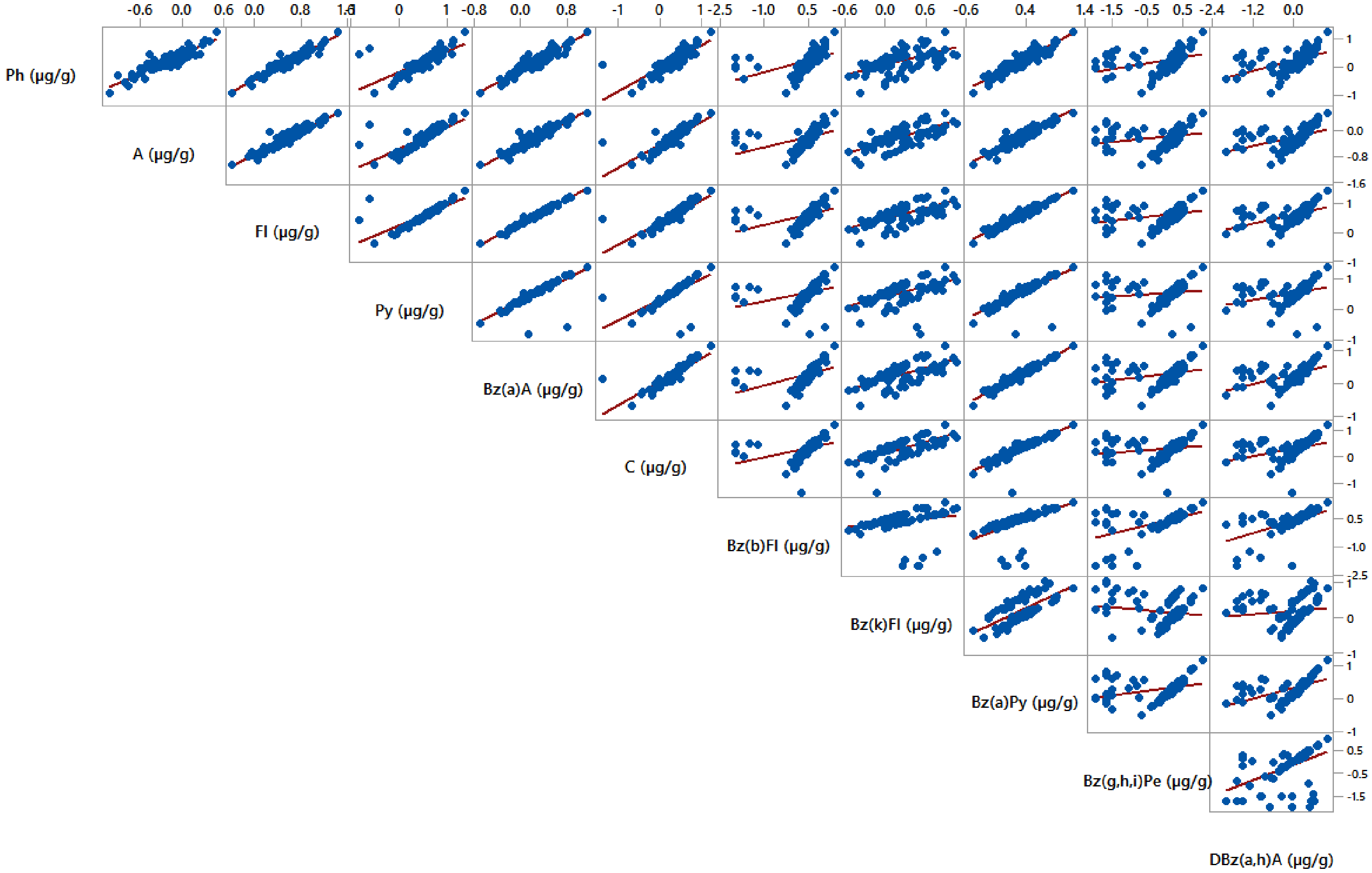


Figure 4.15 Matrix plot of relationship between PAHs in river sediment.

The correlation and probability values of the variable pairs with moderate to very strong correlation are marked in bold in Table 4.27. Very strong correlations exist between most of the PAHs, indicating that they may have come from similar sources or have similar behaviour in the sediment matrix (Liu *et al*, 2017). The existence of these relationships will inform how PAHs are selected for use in substance flow analysis modelling (see Section 2.4).

Table 4.27 Correlation analysis of PAHs in river sediment.

		Ph	**A**	**Fl**	**Py**	**Bz(a)A**	**C**	**Bz(b)Fl**	**Bz(k)Fl**	**Bz(a)Py**	**DBz(a, h)A**
A	**r***	**0.92**									
	P-value	**< 0.01**									
Fl	**r***	**0.96**	**0.95**								
	P-value	**< 0.01**	**< 0.01**								
Py	**r***	**0.73**	**0.80**	**0.80**							
	P-value	**< 0.01**	**< 0.01**	**< 0.01**							
Bz(a)A	**r***	**0.94**	**0.94**	**0.99**	**0.79**						
	P-value	**< 0.01**	**< 0.01**	**< 0.01**	**< 0.01**						
C	**r***	**0.83**	**0.84**	**0.87**	**0.70**	**0.87**					
	P-value	**< 0.01**	**< 0.01**	**< 0.01**	**< 0.01**	**< 0.01**					
Bz(b)Fl	**r***	**0.50**	**0.45**	**0.48**	0.34	**0.50**	**0.41**				
	P-value	**< 0.01**	**< 0.01**	**< 0.01**	< 0.01	**< 0.01**	**< 0.01**				
Bz(k)Fl	**r***	**0.58**	**0.71**	**0.66**	**0.54**	**0.67**	**0.68**	0.21			
	P-value	**< 0.01**	**< 0.01**	**< 0.01**	**< 0.01**	**< 0.01**	**< 0.01**	0.05			
Bz(a)Py	**r***	**0.92**	**0.93**	**0.97**	**0.77**	**0.98**	**0.87**	**0.54**	**0.69**		
	P-value	**< 0.01**	**< 0.01**	**< 0.01**	**< 0.01**	**< 0.01**	**< 0.01**	**< 0.01**	**< 0.01**		
DBz(a,h)A	**r***	**0.51**	**0.47**	**0.50**	0.35	**0.51**	**0.42**	**0.55**	0.14	**0.56**	
	P-value	**< 0.01**	**< 0.01**	**< 0.01**	< 0.01	**< 0.01**	**< 0.01**	**< 0.01**	0.20	**< 0.01**	
Bz(g,h,i)Pe	**r***	0.39	0.25	0.30	0.16	0.32	0.22	**0.53**	-0.18	0.34	**0.48**
	P-value	< 0.01	0.02	< 0.01	0.14	< 0.01	< 0.01	**< 0.01**	0.09	< 0.01	**< 0.01**

Key: * r = Pearson Correlation
Values in bold show the pairs of parameters with moderate to very strong correlation.

4.7 Overview of PAHs and metals behaviour in sediments

PAH river sediment data showed some similarity with the results of metals in sediment. For example, the highest concentrations of most of the targeted pollutants were determined at sampling sites G, H and J which may indicate a possible association of their sources in these areas or similar responses to the in-river fluvial geomorphology processes. Results of the PAH ratio analysis indicate that PAHs in sediment samples in the Lower Lee catchment are primarily from combustion sources of mixed origins which could include petroleum, grass, wood and coal. In work undertaken by Inengite *et al*. (2010) on sediments, PAHs analysis reflected a mixed range of sources and highlighted the role of surface runoff in mobilising and transporting PAHs from various sources generating conflicting results when undertaking analysis of various PAH ratios. Deephams STW can be regarded as potential source of PAHs in river sediments as the highest average PAHs concentrations were determined in tributaries that receive its effluent (Pymmes Brook and Salmons Brook). Salmons Brook and Pymmes Brook also showed highest mean concentration for metals amongst tributaries, suggesting they are a priority source of both organic and inorganic pollutants in the catchment with further critical analysis necessary to understand its overall contribution to pollutant loads in the Lower Lee catchment.

Correlation analysis was undertaken to identify the type and strength of relationships between mean PAH and mean metals sediment concentrations (see Table 4.28).

Table 4.28 Correlation analysis of PAHs and metals in river sediment at the Lower lee catchment.

		Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Sn**	**Zn**
Ph	r*	0.53	0.59	**0.64**	0.17	0.17	**0.84**	**0.63**
	P-value	0.09	0.06	**0.04**	0.61	0.61	**<0.01**	**0.04**
A	r*	**0.70**	**0.65**	**0.65**	0.32	0.32	**0.84**	**0.74**
	P-value	**0.02**	**0.03**	**0.03**	0.34	0.34	**<0.01**	**0.01**
Fl	r*	0.50	0.56	0.50	0.18	0.18	**0.78**	**0.62**
	P-value	0.12	0.08	0.13	0.59	0.59	**0.01**	**0.04**
Py	r*	0.52	**0.60**	0.50	0.21	0.21	**0.80**	**0.66**
	P-value	0.10	**0.05**	0.12	0.54	0.55	**<0.01**	**0.03**
Bz(a)A	r*	0.53	0.55	0.47	0.21	0.21	**0.75**	**0.61**
	P-value	0.10	0.08	0.14	0.53	0.53	**0.01**	**0.05**
C	r*	**0.65**	**0.63**	0.57	0.36	0.36	**0.80**	**0.72**
	P-value	**0.03**	**0.04**	0.07	0.28	0.28	**<0.01**	**0.01**
Bz(b)Fl	r*	**0.68**	0.54	0.50	0.38	0.38	**0.67**	**0.62**
	P-value	**0.02**	0.08	0.12	0.25	0.25	**0.03**	**0.04**
Bz(k)Fl	r*	**0.83**	**0.72**	0.55	**0.62**	**0.62**	**0.75**	**0.80**
	P-value	**<0.01**	**0.01**	0.08	**0.04**	**0.04**	**0.01**	**<0.01**
Bz(a)Py	r*	**0.61**	0.56	0.51	0.28	0.28	**0.75**	**0.64**
	P-value	**0.05**	0.07	0.11	0.40	0.40	**0.01**	**0.03**
DBz(a,h)A	r*	0.57	0.36	0.47	0.23	0.23	0.56	0.46
	P-value	0.07	0.28	0.15	0.50	0.50	0.08	0.16
Bz(g,h,i)Pe	r*	0.35	0.22	0.34	0.02	0.02	0.34	0.22
	P-value	0.30	0.52	0.31	0.96	0.96	0.31	0.51
Σ 11 PAHs	r*	**0.63**	0.46	0.39	0.35	0.35	**0.62**	0.55
	P-value	**0.04**	0.16	0.23	0.29	0.28	**0.04**	0.08

Key: * r = Pearson Correlation.
Values in bold show the pairs of parameters with strong to very strong correlation.

A number of statistically significant positive correlations were recorded (Table 4.28). The result of correlation can prove useful in understanding the relationship of metals with PAHs in sediment. The correlation study revealed strong correlation between Cd and anthracene, chrysene, benzo(b)fluoranthene, benzo(a)pyrene, the total sum of the 11 PAHs; Cu and anthracene, pyrene, chrysene, benzo(k)fluoranthene; Hg and phenanthrene, anthracene; Ni and benzo(k)fluoranthene; Pb and benzo(k)fluoranthene; Sn and fluoranthene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, the total sum of 11 PAHs; Zn and phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(a)pyrene; a very strong correlation between Cd and benzo(k)fluoranthene; Sn and phenanthrene, anthracene, pyrene, chrysene, Zn and benzo(k)fluoranthene. Overall, mean Sn and Zn sediment concentrations show significant positive correlation with 9 PAHs, suggesting these environmental pollutants are emitted from a common source. These results are consistent with results reported by other research such as Wang *et al*. (2010) and Okafor and Opuene (2007), which also found significant correlation between various metals and PAHs in sediments. Results from this analysis identify the need for further research to identify these common pollutant sources so that they may be mitigated with this source identification work undertaken as part of the substance flow analysis modelling.

In summary, the similar trend of variations in occurrence (with majority of metals and PAHs varying by sites and sampling dates), and the correlation found between selected metals and PAHs indicated that source of pollution was the same for both of pollutants and with the tributaries, Salmons Brook and Pymmes Brook amongst the sites with highest mean concentration for metals and PAHs, thus making these two sites as area of concern and possible major pollutant contributors to River Lee and the Navigation Channel in the Lower Lee catchment.

CHAPTER 5. SUBSTANCE FLOW ANALYSIS RESULTS AND DISCUSSION ON METALS AND PAHs IN THE LOWER LEE CATCHMENT

The SFA approach was applied to selected metals (cadmium [Cd], copper [Cu], lead [Pb], mercury [Hg], nickel [Ni] and zinc [Zn]) and PAHs (anthracene [A], fluoranthene [Fl], benzo(b)fluoranthene [Bz(b)Fl], benzo(a)pyrene[Bz(a)Py] and benzo(g,h,i)perylene [Bz(g,h,i)Pe]). The results of SFA are presented and discussed in this chapter, with full data sets given in Appendices P1 to P11.

It is reminded that was not the intention of this research to look into a legacy of contamination at the Lower Lee catchment. Thus, sampling dates were arranged to cover a period of one year, the sediment samples were collected only at the superficial level to make sure it would cover a maximum of one year period and the SFA was also modelled with a one-year period limit. Due to the dynamics of the environment and data availability it was not possible to match exactly the dates/period for the monitoring and modelling stages (SedNet, 2004; Environment Agency, 2008a).

5.1 SFA modelling of selected metals in the Lower Lee catchment – all sites

5.1.1 SFA of metal predicted loads at each sampling site in the Lower Lee catchment

Table 5.1 summarises the predicted loads (kg/year) of selected metals discharged in a 1 km radius from each sampling site to surface water bodies in the Lower Lee catchment. Total loads of the six metals predicted to be discharged to surface water vary between metals and sites and are predicted to increase as follows: Hg < Cd < Pb < Ni < Cu < Zn, with total loads of 11.77, 89.90, 1027.56, 1758.70, 3828.31 and 12587.33 kg/year respectively. The predicted order of abundance follows SFA results reported for urban rivers with similar characteristics in earlier studies (e.g. Gray and Becker, 2002; Månsson, 2008; E-PRTR, 2013; Jamtrot *et al.*, 2009; Sörme, 2008).

Table 5.1 SFA total loads of selected metals predicted to discharge at each sampling site in the Lower Lee catchment.

Sampling site	**SFA metal predicted loads (kg/year)**						**Sum of all metals**
	Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**	
A	13.70	347.78	1.09	201.55	182.97	975.41	1722.50
B	2.06	45.76	0.21	35.05	41.74	203.34	328.17
C	5.51	87.24	0.85	85.33	40.89	409.41	629.22
D	23.11	1921.81	4.31	742.56	243.45	5754.59	8689.83
E	18.60	336.13	1.37	247.56	194.63	2195.30	2993.23
F	4.10	237.22	0.73	74.32	62.28	591.85	970.49
G	1.96	75.71	0.27	28.79	24.03	227.45	358.22
H	5.62	110.20	0.83	96.71	70.58	469.38	753.32
I	0.50	17.51	0.06	6.36	5.20	78.10	107.74
J	1.78	42.72	0.30	27.63	16.92	194.61	283.96
K	12.96	606.22	1.75	213.18	144.87	1487.89	2466.88
Sum of each metal at all sites	89.90	3828.31	11.77	1758.70	1027.56	12587.33	19303.57

Looking across metals, predicted loads of Ni, Cu and Zn generally exceed those of Pb (except for site B where Ni is < Pb) with the predicted loads of Hg and Cd being lower at all sites. Previous studies reported surface runoff as the main source of Zn and Cu, where the use of these metals in building materials results in their emissions to river water via rainwater runoff (Haselbach *et al.*, 2013; Maniquiz-Redillas and Kim, 2014; Sakson *et al.*, 2018; Defra, 2012). Cu and Zn are still traditionally used materials in the buildings sector especially for roofs, guttering and facing materials. Pb in contrast, plays only a subordinate role in current building activities due to its increasingly limited outdoor use (Müller *et al.*, 2020).

When analysing results by sampling site, the highest metal predicted loads were observed at site D, which has greatest number of activities (11, as shown in Table 3.7) and is a direct recipient of discharges from the Deephams STW. The STW is the activity which reported the highest metals emissions: 12.40, 1460.00, 2.82, 573.00, 117.00 and 4550.00 kg/year for Cd, Cu, Hg, Ni, Pb and Zn, respectively, which correspond to a total of 6715.22 kg/year of all selected metals emissions reported as discharging directly to controlled water. In total, Deephams STW accounted for 34.79 % of the total metal predicted loads discharged into the Lower Lee catchment.

In 2013 Deephams STW, served approximately one million PE and reported discharging 232,656 m^3/day of treated effluent into Salmons Brook (Thames Water, 2013). A 2013 EA study reported that this tributary failed standards set by EU EQS (2013) for both ecological and chemical (e.g. dissolved oxygen, phosphate, nonylphenol and tributyltin compounds) standards. The EA stated the reason for this water body failure in achieving the set standards was due to both diffuse (drainage from roads, misconnections and urban development) and point (discharges from Deephams STW and from other industries/manufacturing and business) sources (Environment Agency, 2013b).

Results from this study are in accordance with results presented by other researchers who applied SFAs (Yoshida *et al*. 2015; Gray and Becker, 2002; Sörme, 2008; Angerville *et al*., 2013). A study by Lützhøft *et al*. (2012) which also focussed on water quality in urban areas highlighted that when a single industrial facility is the major source of pollutants in a given river, the introduction or upgrading of on-site industrial wastewater treatment at that facility can be expected to have a major influence on the chemical status of the river system. As in this study Deephams STW was predicted to make a significant contribution to the quality of receiving river water, further investigation is recommended to measure actual discharges and impacts to inform development of more efficient wastewater management to reduce impact. Lowest total loads for all metals were predicted at site I. Only two types of activities (waste non-hazardous and road runoff) where identified as discharging to surface waters. This compares to other sites where 4 – 11 activities were identified, as shown in Table 3.7.

Site A, initially selected as background site (as discussed in Section 3.2), presented a relatively higher metal predicted load (for the sum of all metals) compared to most other sites (i.e. higher that loads predicted at sites B, C, F, G, H, I and J). Both a high number of activities (10) and individual companies (18) are reported to be discharging metals to river water (Table 3.7). Looking at individual metals, from Table 5.1, it can be seen site A reports the third highest load for Cd, Cu, Pb, fourth highest load for Hg, Ni, Zn, and is ranked fourth place in predicted total metal loads after sites D, E and K. Results also showed major sources of metals at site A, as the manufacture of non-metallic mineral products, production of electricity and manufacture of rubber and plastic products, with manufacture of textiles, food and drink and road runoff being the activities predicted to discharge the lowest mass of metals to receiving waters at this site.

Site E (Pymmes Brook) is a residential area with the Environment Agency (2013b) reporting the River Lee at this site which did not achieve the EU EQS (2013) standards in 2013 due to transport drainage, industries and misconnections from domestic houses. In terms of the SFA, Site E reported the second highest predicted loads for Cd, Ni, Pb and Zn, third highest load for Hg and fourth highest for Cu (Table 5.1). Major sources of metal discharges at site E are refineries, waste non-hazardous and paper/wood production with the lowest metal predicted loads (similarly to site A), reported for food and drink, manufacture of textiles and road runoff.

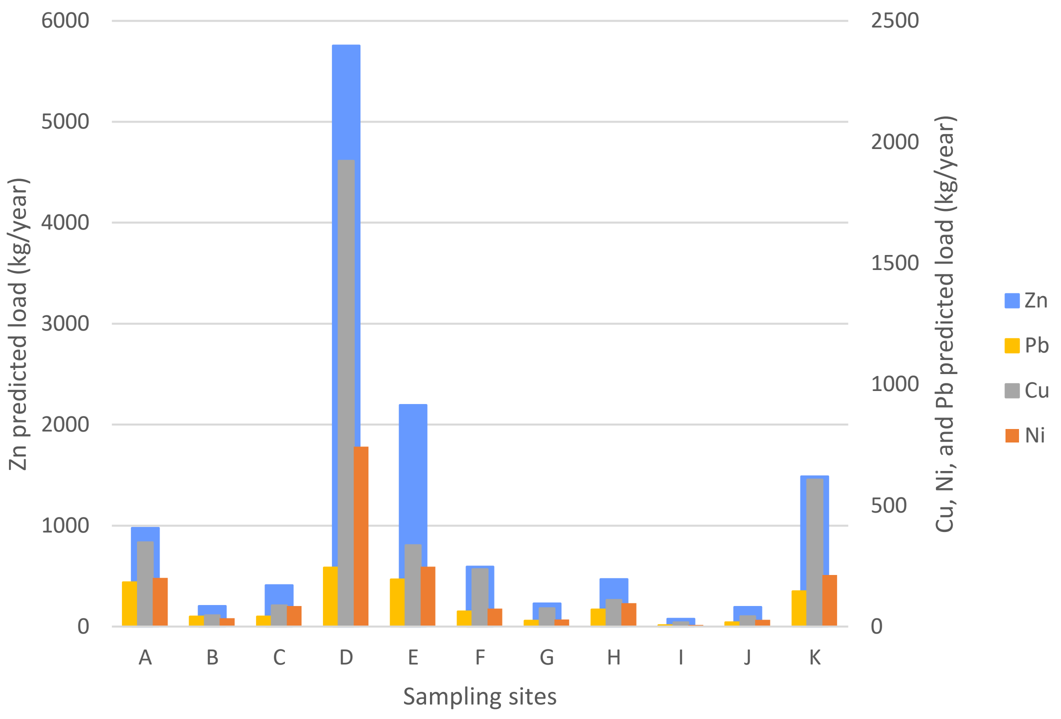


Figure 5.1 Predicted loads of Zn, Cu, Ni and Pb discharged in the Lower Lee catchment.

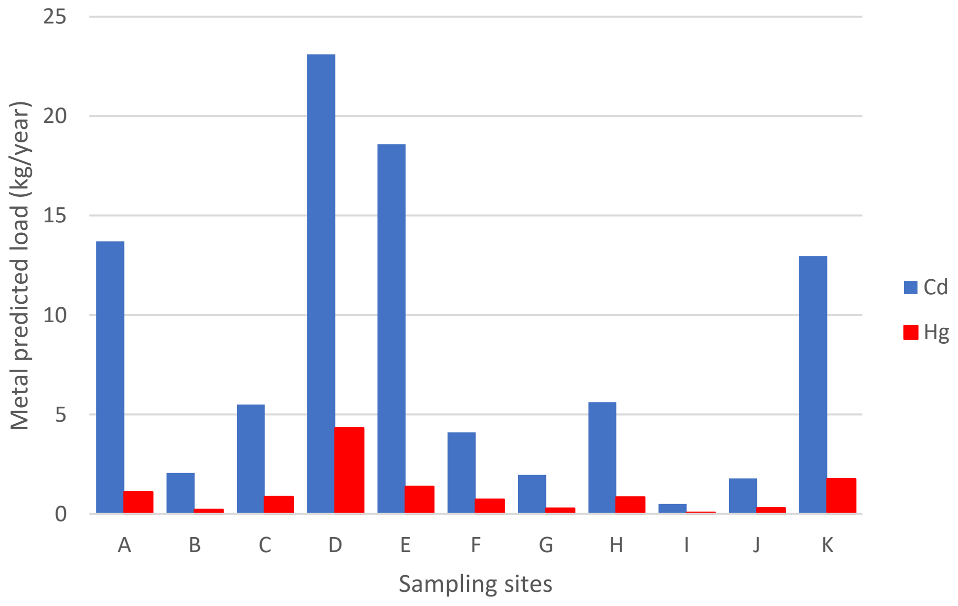


Figure 5.2 Predicted loads of Hg and Cd discharged in the Lower Lee catchment.

In summary, highest metal loads were predicted for sites D, E, K and A which are the sites with highest number of activities and companies. While sites I, J, B and G reported both lower metal predicted loads discharging from the least number of activities and companies. Further discussion on impacts of types and number of activities/companies are under Section 5.1.2.

While Table 5.1 and Figures 5.1 and 5.2 show metal predicted loads for the Lower Lee catchment, Table 5.2 presents metal predicted loads per site by catchment component (River Lee, Lee Navigation Channel and tributaries) to facilitate comparison with the field data with regard to trends and relative contributions of each component of selected metals.

Table 5.2 Overview of predicted loads of selected metals at each sampling site in the River Lee, Navigation Channel and tributaries.

	Sampling site	**SFA metal predicted loads (kg/year)**						**All metals**
		Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**	
River Lee	A	13.70	347.78	1.09	201.55	182.97	975.41	1722.50
	G	1.96	75.71	0.27	28.79	24.03	227.45	358.22
	H	5.62	110.20	0.83	96.71	70.58	469.38	753.32
	I	0.50	17.51	0.06	6.36	5.20	78.10	107.74
Lee Navigation	C	5.51	87.24	0.85	85.33	40.89	409.41	629.22
	J	1.78	42.72	0.30	27.63	16.92	194.61	283.96
	K	12.96	606.22	1.75	213.18	144.87	1487.89	2466.88
Tributaries	B	2.06	45.76	0.21	35.05	41.74	203.34	328.17
	D	23.11	1921.81	4.31	742.56	243.45	5754.59	8689.83
	E	18.60	336.13	1.37	247.56	194.63	2195.30	2993.23
	F	4.10	237.22	0.73	74.32	62.28	591.85	970.49

A total of 2941.79, 3380.05 and 12981.73 kg/year of metals were predicted to be discharged into the River Lee, Lee Navigation and tributaries, respectively, with site D alone, accounting for 34.79 % (6715.22 kg/year) of the total (19303.57 kg/year) (see Section 5.1.3). Also, this result shows that more metals are discharged by Deephams STW alone, than are cumulatively discharged into the River Lee and Lee Navigation components.

Highest predicted loads for of all metals for the River Lee were identified at site A (1722.50 kg/year) and H (753.32 kg/year). These two sites were associated with the highest number of activities and companies. The quantity of activities and companies vary between sites and while some activities are responsible for discharging more metals than others (see table 3.7 and Figure 5.5), the number of companies identified under each activity will also influence the final values. In this case, at site A, 18 companies were identified under 10 different activities, with the manufacture of non-metallic mineral products (a total of 474.54 kg/year metal predicted load) and production of electricity (a total of 269.13 kg/year metal predicted load) being the highest emitters of metals. This calls attention to the fact that the type of activities – and not just the number of activities - play an important role on receiving water quality, as only one company was identified under each of these high emitters, while four companies were listed under waste non-hazardous activity (a total of 185.52 kg/year metal predicted load) and 6 companies under manufacture of rubber and plastic products activity (a total of 232 kg/year metal predicted load).

The influence of activity type is also shown, for example, at site A (10 activities; 18 companies) in comparison to site H (6 activities; 20 companies) (Table 3.7). Although the number of companies identified for sites A and H are relatively close in number, the total metal loads predicted to be discharged at site A is over twice that predicted for Site H (see Table 5.2). Lowest metal loads were predicted at sites G and I, which have lowest number of activities and companies. For site G there were four activities covering three companies and site I with two activities covering two companies. Identified activities include paper/wood production, manufacture of basic metals and metal products, food and drink and road runoff accounting for the discharge of 358.22 kg/year at site G and waste non-hazardous and road runoff accounting for the discharge of 107.74 kg/year at site H.

The total metal loads predicted to be discharged in association with the sampling points on the Lee Navigation Channel (C, J, K) (see Table 5.2), indicate that Cu, Hg and Zn discharges are higher in this component in comparison to the total loads predicted to be discharged to the River Lee component (sites A, G, H, I). In contrast, total metal loads predicted for Cd, Ni and Pb are higher for the River Lee component, indicating that not all metals originate from the same sources. From Table 3.7 it was noted that manufacture of chemicals and chemical products were identified at two sites in the Lee Navigation component but not at any site in the River Lee component. On the other hand, waste treatment and manufacture of non-metallic mineral products were reported for the River Lee sites but not at any of the Lee Navigation sites. This differentiation in occurrence of types of activities and number of companies between the two components are understood to contribute to the differences in metal predicted loads between the two sites. This is because the predicted high emissions of Cu, Hg and Zn are mainly associated with the production of electricity and manufacture of chemicals and chemical products at the Lea Navigation, and the predicted highest discharges of Cd, Ni and Pb from waste treatment and manufacture of non-metallic mineral products at the River Lee sites.

In general, results for the Lee Navigation Channel showed highest metal predicted loads at downstream site K, followed by site C and the lowest metal load occurring at site J. This was due to a total metal load of 2466.88 kg/year predicted to be discharged at site K, with the production of electricity (1076.50 kg/year) and manufacture of basic metals and metal products (457.62 kg/year) identified as the highest emitters. A total of 629.22 kg/year of metals were predicted to be discharged at site C with companies identified under the manufacture of chemicals and chemical products activity (408.26 kg/year) accounting for most of the metal loads predicted. Site J had the lowest predicted total metal load (283.96 kg/year) with companies classified under waste non-hazardous (139.14 kg/year) and manufacture of chemicals and chemical products (102.07 kg/year) accounting for most of the identified metal loads predicted.

Results from the SFA modelling in the tributaries component (i.e. Cobbins, Salmons, Pymmes and Ching Brooks), show highest predicted loads for all metals at Salmons Brook (site D), followed by Pymmes Brook (site E) and Ching Brook (site F). The lowest metal loads were predicted in association with the Cobbins Brook site (B). As previously discussed, site D reported highest metal predicted loads with Deephams STW being the major source of metal discharges into receiving river water. Pymmes Brook followed in second place with the highest number of companies but less types of activities when compared to site D (see Table 3.7). Again, it shows that not only the number of activities/companies but also their type can inform different loads between sites. In this case, a total of 8689.83 kg/year metal load was predicted for site D with wastewater (6715.22 kg/year), production of electricity (807.38 kg/year) and waste non-hazardous activities (371.04 kg/year) accounting for most of the metal loads. At site E, refineries (1556.97 kg/year), waste non-hazardous (417.42 kg/year) and paper/wood production (311.61 kg/year) are the highest emitters contributing to a total of 2993.23 kg/year.

Cobbins Brook shows lowest predicted metal loads for all metals. This is due to a combination of both low numbers of activities and number of companies identified for this site. In contrast to a classification of failure at site D, the EA classified Cobbins and Ching Brook as being of good chemical status in 2013, with the main discharges at Cobbins Brook identified as diffuse sources such as domestic misconnections, agriculture and land management and road runoff, from point source, such as private sewage treatment works; and for Ching Brook, the main contaminant sources were from diffuse pollution such as domestic misconnections, road runoff and physical modifications due to urbanisation.

Broadly translated at the Lower Lee catchment scale, the total mass of metals predicted to be discharged from activities associated with 11 sampling sites was 19303.57 kg/year), of which 65.21 % was Zn (12587.33 kg/year), 19.83 % was Cu (3828.31 kg/year), 9.11 % Ni (1758.70 kg/year), 5.32 % Pb (1027.56 kg/year), 0.47 % Cd (89.56 kg/year) and 0.06 % Hg (11.77

kg/year). In terms of component of the study area, the tributaries are predicted to contribute the highest metal loads (12981.73 kg/year) followed by the Lee Navigation Channel (3380.05 kg/year) and River Lee (2941.35 kg/year) with the highest contribution from the tributaries mainly due to the discharges from the Deephams STW at site D.

More generally, data suggests that both the number and type of activities play an important role on mass discharged to an urban river in comparison to a consideration of the total number of companies alone. The emission data suggests that some activities, such as wastewater treatment plants, refineries and the production of electricity, discharge much greater mass of metals into surface water when compared to activities such as the manufacture of cement and manufacture of textiles. In the event of treatment options being preferred to minimise discharges to receiving water/sediment quality when planning new installations, one should also consider the types of activities and not only their proposed discharge volumes.

5.1.2 SFA overview of the metal predicted loads by activities at the Lower Lee catchment

Figures 5.3 and 5.4 shows selected metal predicted loads discharged by identified activities in the Lower Lee catchment. For the sum of selected metals, the discharge of treated wastewater was predicted to be the major source (6715.22 kg/year), followed by production of electricity (2422.14 kg/year) and waste treatment (430.50 kg/year), manufacture of cement (192.19 kg/year) and road runoff (154.19 kg/year) being the least predicted emitters of selected metal loads.

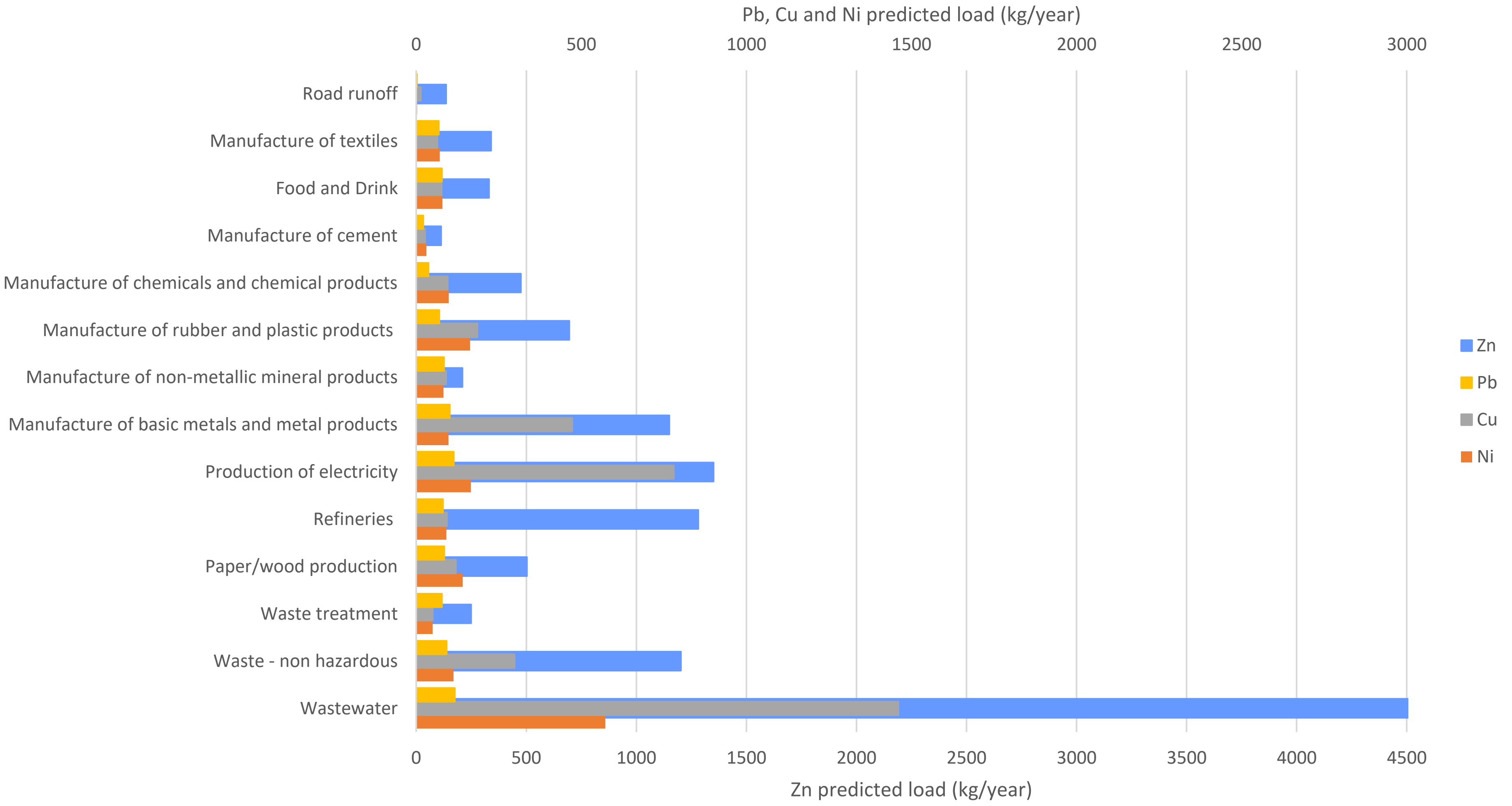


Figure 5.3 Predicted loads of Zn, Pb, Ni and Cu by activities discharged in the Lower Lee catchment.

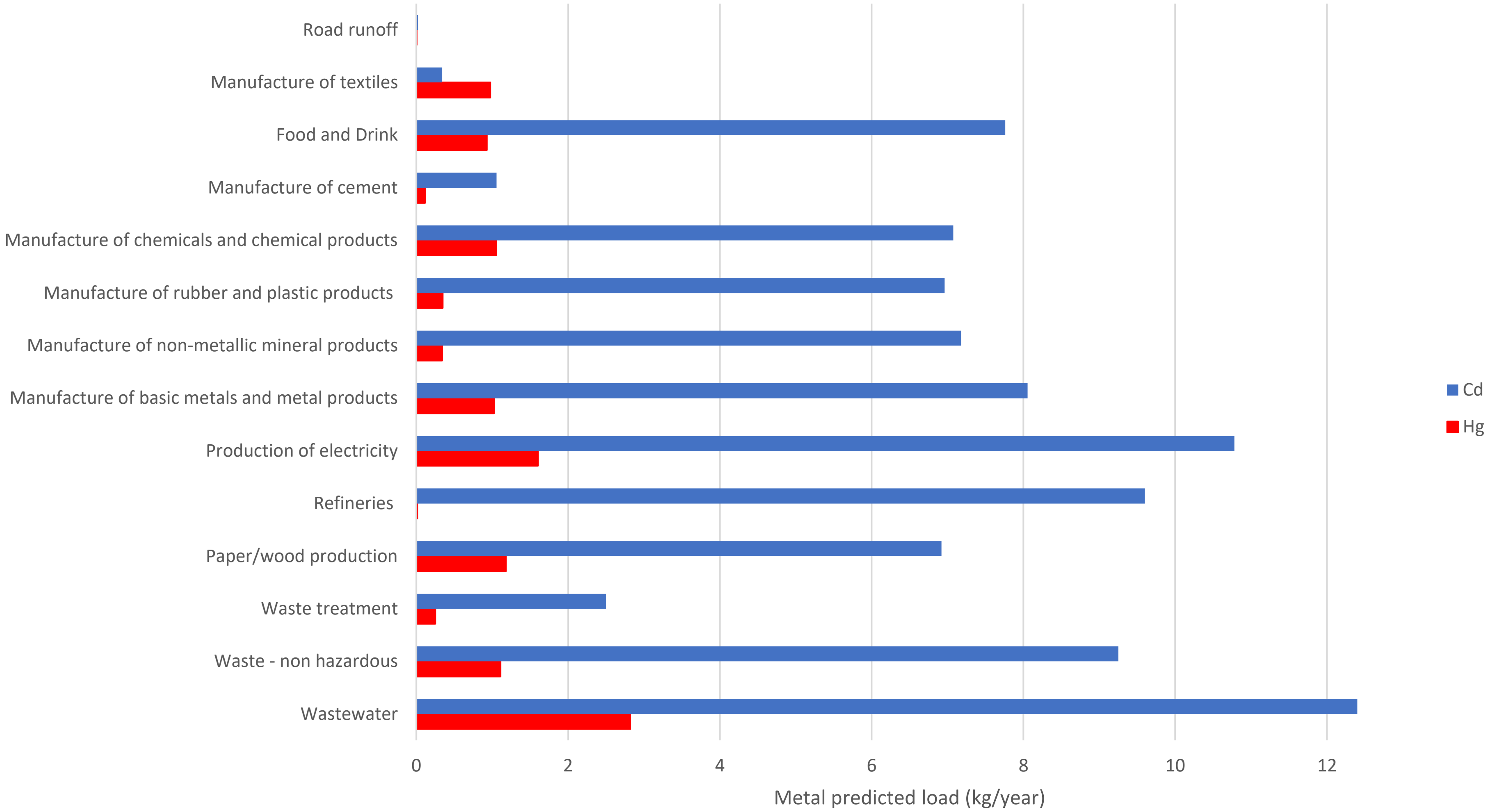


Figure 5.4 Predicted loads of Hg and Cd by activities discharged in the Lower Lee catchment.

In the UK the main types of raw material extracted in 2013 were non-metallic minerals (such as gravel and sand; 58.1 million tonnes extracted), followed by the production of fodder crops (56.5 million tonnes) used not only for animal feed but also for biogas production (Office for National Statistics, 2019) due to the increase of operational biogas plants in UK (from 106 in 2013 to 607 in 2018) with the majority in production and distribution of electricity (Shaw Renewables, 2018), using not only plants but also industrial, commercial, municipal and sewage sludge feedstocks. A total of nine electricity production companies were identified in the Lower Lee catchment (EfW power plants), with the main plants located at Deephams STW and Enfield (the Enfield Power station). Some authors (Baran *et al*, 2016; Waldner *et al*., 2013) argue that this type of electrical generation (EfW power plants) emits less pollution compared to fossil fuels power plants. For example, Font *et al*. (2015) found no evidence of waste incineration emissions in ambient metal concentrations around four UK municipal waste incinerators (which includes EfW plants). However, other authors (Judge *et al*., 2020; Brown, 2015) identify these plants as significant sources of metals loads discharged to air (and consequently to surface waters) compared to fossil fuel power plants. For example, a report commissioned by Zero Emission Europe (2015) investigated five EfW plants located in France, Germany, Slovenia, Spain and the UK and found emissions to air were significantly higher that the safety limits recommended by the World Health Organisation.

From the total predicted loads for each metal, results show treated wastewater as the major source of selected metals discharging to receiving waters, with the highest load contribution percentage being of Cu (38.14 %), followed by Zn (36.15 %), Ni (32.58 %), Pb (11.39 %), Hg (23.96 %) and Cd (13.79 %) when compared to other activities in the study area (see Figure 5.5). This reflects the smaller metals flow from other activities in comparison with that from domestic households and probably runoff entering the wastewater plant. Other studies in the UK (Defra, 2015a; Environment Agency, 2016; Thames21, 2015; Thames Water, 2015), have identified domestic sources of Zn and Ni as major inputs to sewer systems being derived mainly from activities such as car washing, bathing and wastewater (in particular faeces) with the contribution of Pb from domestic sources varying greatly depending on the extend of e.g. use of Pb in plumbing and roof flashings.

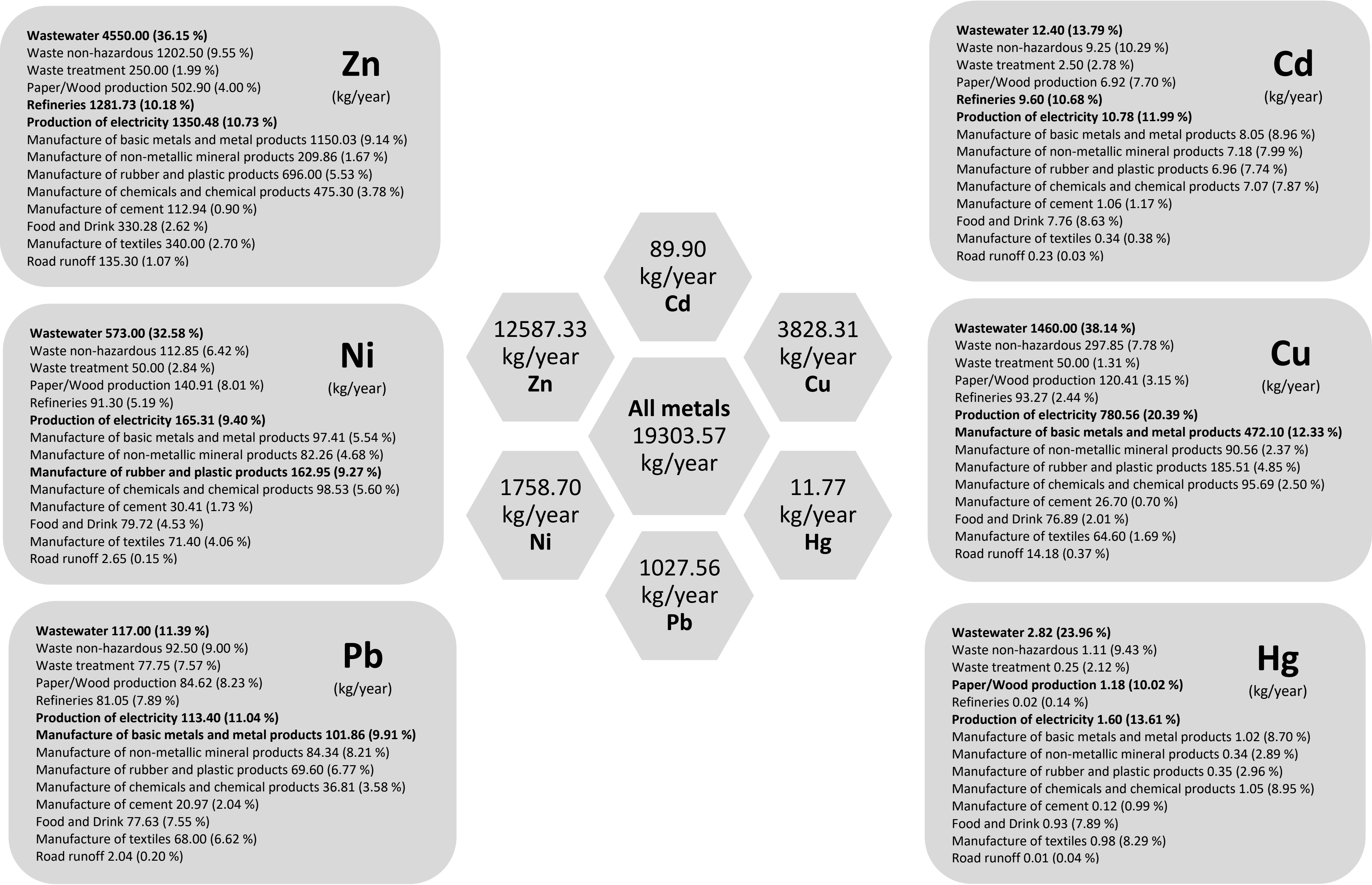
The E-PRTR (2019) reported urban wastewater treatment plants as the largest emission source of Cd, Cu, Hg, Ni, Pb and Zn to surface waters in Europe including the UK. It was also reported that, while there was a decline in Pb emissions over the years (2013-2019), there was an increase in Cd (for example, 28.25 % from road transport) and Hg (for example, 5.89 % from road transport) emissions and even with some of these metals (such as Pb and Hg) being phased out in certain applications, they remained in the environment due to a combination of their historical use and affinity to particulate matter leading to their accumulation in river sediments (E-PRTR, 2019).

As per the Environmental Permitting Regulations 2016 SI 2016/11542, the Environment Agency (2020) reported that certain industries (e.g. milk processing, the manufacture and bottling of soft drinks, breweries, animal feed manufacture etc) discharging wastewater directly to receiving waters must not cause a failure of water quality standards as environmental permits include conditions to ensure receiving waters meet these standards. This research identified food and drink companies at most of the sampling sites (except at I and J), amounting to a predicted total metal load of 573.21 kg/year (Figure 5.5), discharged to receiving waters, indicating that even if they meet their permitting conditions, their permitted discharges contribute a considerable mass of metals at number of sites identified as not achieving good chemical status.

Road runoff (see Figures 5.3, 5.4 and 5.5) was consistently reported to contribute relatively the lowest loads of Cd, Cu, Hg, Pb and Ni. Zn was an exception to this, where the manufacture of cement was identified to contribute less Zn to receiving waters. The fact that road runoff was predicted to contribute relatively the lowest loads, was surprising given that several studies (e.g. Järveläinen *et al.*, 2017; Thames21, 2019; Lützhøft *et al.*, 2012; Lundy and Wade, 2011; Becouze-Lareure *et al.*, 2016; Brown and Peak, 2005) identify road runoff (especially originated from vehicles) as a major contributor of metals to receiving water systems, negatively impacting urban rivers on its water and sediment quality. A factor in the relatively lower importance given to this source in this study was that AADT data in the required format was only available for major roads in the study area. Hence, road runoff emissions from minor and residential roads could not be accounted for.

5.1.3 SFA of the predicted loads by each metal

As previous explained in Section 3.9.2.7 only stock was included in this study as part of the SFA modelling tool. Figure 5.5 identifies the activities contributing metal predicted loads with 1 Km from each sampling site to the Lower Lee catchment, together with the absolute (as kg/year) and as relative contribution (%). Percentages of the total load from each source were based on the total load of each respective metal.



Wastewater 4550.00 (36.15 %)
Waste non-hazardous 1202.50 (9.55 %)
Waste treatment 250.00 (1.99 %)
Paper/Wood production 502.90 (4.00 %)
Refineries 1281.73 (10.18 %)
Production of electricity 1350.48 (10.73 %)
Manufacture of basic metals and metal products 1150.03 (9.14 %)
Manufacture of non-metallic mineral products 209.86 (1.67 %)
Manufacture of rubber and plastic products 696.00 (5.53 %)
Manufacture of chemicals and chemical products 475.30 (3.78 %)
Manufacture of cement 112.94 (0.90 %)
Food and Drink 330.28 (2.62 %)
Manufacture of textiles 340.00 (2.70 %)
Road runoff 135.30 (1.07 %)

Zn
(kg/year)

Wastewater 573.00 (32.58 %)
Waste non-hazardous 112.85 (6.42 %)
Waste treatment 50.00 (2.84 %)
Paper/Wood production 140.91 (8.01 %)
Refineries 91.30 (5.19 %)
Production of electricity 165.31 (9.40 %)
Manufacture of basic metals and metal products 97.41 (5.54 %)
Manufacture of non-metallic mineral products 82.26 (4.68 %)
Manufacture of rubber and plastic products 162.95 (9.27 %)
Manufacture of chemicals and chemical products 98.53 (5.60 %)
Manufacture of cement 30.41 (1.73 %)
Food and Drink 79.72 (4.53 %)
Manufacture of textiles 71.40 (4.06 %)
Road runoff 2.65 (0.15 %)

Ni
(kg/year)

Wastewater 117.00 (11.39 %)
Waste non-hazardous 92.50 (9.00 %)
Waste treatment 77.75 (7.57 %)
Paper/Wood production 84.62 (8.23 %)
Refineries 81.05 (7.89 %)
Production of electricity 113.40 (11.04 %)
Manufacture of basic metals and metal products 101.86 (9.91 %)
Manufacture of non-metallic mineral products 84.34 (8.21 %)
Manufacture of rubber and plastic products 69.60 (6.77 %)
Manufacture of chemicals and chemical products 36.81 (3.58 %)
Manufacture of cement 20.97 (2.04 %)
Food and Drink 77.63 (7.55 %)
Manufacture of textiles 68.00 (6.62 %)
Road runoff 2.04 (0.20 %)

Pb
(kg/year)

89.90
kg/year
Cd

12587.33
kg/year
Zn

3828.31
kg/year
Cu

All metals
19303.57
kg/year

1758.70
kg/year
Ni

11.77
kg/year
Hg

1027.56
kg/year
Pb

Wastewater 12.40 (13.79 %)
Waste non-hazardous 9.25 (10.29 %)
Waste treatment 2.50 (2.78 %)
Paper/Wood production 6.92 (7.70 %)
Refineries 9.60 (10.68 %)
Production of electricity 10.78 (11.99 %)
Manufacture of basic metals and metal products 8.05 (8.96 %)
Manufacture of non-metallic mineral products 7.18 (7.99 %)
Manufacture of rubber and plastic products 6.96 (7.74 %)
Manufacture of chemicals and chemical products 7.07 (7.87 %)
Manufacture of cement 1.06 (1.17 %)
Food and Drink 7.76 (8.63 %)
Manufacture of textiles 0.34 (0.38 %)
Road runoff 0.23 (0.03 %)

Cd
(kg/year)

Wastewater 1460.00 (38.14 %)
Waste non-hazardous 297.85 (7.78 %)
Waste treatment 50.00 (1.31 %)
Paper/Wood production 120.41 (3.15 %)
Refineries 93.27 (2.44 %)
Production of electricity 780.56 (20.39 %)
Manufacture of basic metals and metal products 472.10 (12.33 %)
Manufacture of non-metallic mineral products 90.56 (2.37 %)
Manufacture of rubber and plastic products 185.51 (4.85 %)
Manufacture of chemicals and chemical products 95.69 (2.50 %)
Manufacture of cement 26.70 (0.70 %)
Food and Drink 76.89 (2.01 %)
Manufacture of textiles 64.60 (1.69 %)
Road runoff 14.18 (0.37 %)

Cu
(kg/year)

Wastewater 2.82 (23.96 %)
Waste non-hazardous 1.11 (9.43 %)
Waste treatment 0.25 (2.12 %)
Paper/Wood production 1.18 (10.02 %)
Refineries 0.02 (0.14 %)
Production of electricity 1.60 (13.61 %)
Manufacture of basic metals and metal products 1.02 (8.70 %)
Manufacture of non-metallic mineral products 0.34 (2.89 %)
Manufacture of rubber and plastic products 0.35 (2.96 %)
Manufacture of chemicals and chemical products 1.05 (8.95 %)
Manufacture of cement 0.12 (0.99 %)
Food and Drink 0.93 (7.89 %)
Manufacture of textiles 0.98 (8.29 %)
Road runoff 0.01 (0.04 %)

Hg
(kg/year)

Figure 5.5 Diagram of SFA metal loads (stock flow) predicted to discharge with 1Km of each sampling site into surface water at the Lower Lee catchment.
Three highest values for each metal are marked in bold.

Cadmium (Cd)

Figure 5.5 indicates that the highest Cd predicted loads would be emitted by the wastewater treatment plant, refineries and the production of electricity. These three sources contribute 36.50 % of the total Cd predicted. Waste non-hazards is also a significant contributor of Cd, accounting for 10.29 % of emissions, followed by the manufacture of basic metals and metal products (8.96 %), food and drink (8.63 %) and manufacture of non-metallic mineral products (7.99 %). Similar results were reported by SOCOPSE (2009) with STW, manufacturing processes, metals and primary non-ferrous metal production identified as the major sources of Cd emission to receiving waters in European countries such as the Netherlands and Denmark. In this research the sources with the relatively lowest predicted load of Cd were identified as road runoff (0.03 %) and manufacture of textiles (0.38 %).

Contamination by Cd is caused by both, anthropogenic and natural sources and is recognised to cause adverse health effects on humans, being released to the environment from different sources such as wastewater, combustion of fossil fuels, cement production and incineration of municipal waste (SOCOPSE, 2009). The European Environmental Agency (2019) shows the main anthropogenic sources of Cd in untreated wastewater are primarily associated with human dietary sources e.g. cereals, vegetables, and potatoes, from Zn galvanised pipes and road runoff. In the UK, Cd has previously been used in several consumer and industrial materials, but many of these uses have declined and are now heavily restricted in the EU. Cd is also produced as a by-product from the extraction, smelting and refining of Zn, Pb and Cu and currently, the largest use of Cd is in the production of nickel-cadmium (NiCd) batteries which is diminishing due to tighter regulations, such as the Batteries Directive 2006/66/EC which classify NiCd batteries as hazardous waste because of the Cd content and the 2016 revision of the Directive ended the exemptions for using NiCd in cordless power tools (BIS, 2017). For example, Defra (2015a) reported that Cd emissions have declined by 83 % since 1990. However, despite this downward trend in its use (by mass), Cd is still used in conductors in electronic devices, pigments, stabilisers in plastics, in the electroplating of other metals such as steel, iron and copper and in alloys for coating other materials. In many respects, Cd has continued to be a vital component of modern technology, with applications in the electronics, communications, power generation and aerospace industries (PHE, 2013), and therefore still contributing to environmental impacts. The industrial use of wood and other biomass fuels was estimated to contribute over Cd 50 % of emissions in 2013. European Environmental Agency report (2019) shows that historically emissions from non-ferrous metal activities have declined, primarily due to the closure of a UK's lead-zinc smelting plant in 2003 and a Cu refinery in 1999 and that improved controls at STW and updates on legislation have also played an important role in Cd emission reductions over the years. In 2017, the UK reported a total Cd release of 1035.00 kg/year with 67.25 % (696.00 kg/year) going to surface water compared to a total of 1474.21 kg/year with 69.60 % (1026.21 kg/year) released to water in 2013 (E-PRTR, 2019). Hence Cd emissions to water fell by 330.21 kg (2.35 %) over a four-year time period.

Copper (Cu)

This study the wastewater activity (38.14 %) was identified as the main source for Cu. Production of electricity and manufacture of basic metals and metals products also contribute a high proportion of the Cu load (20.39 % and 12.33 %, respectively) into the system. The relatively lowest Cu predicted loads was reported as road runoff (0.37 %), the manufacture of cement (0.70 %) and waste treatment (1.31 %).

Cu is a naturally occurring chemical and from anthropogenic emissions, including point and diffuse sources and it has been an essential material to humankind since prehistoric times through the use of objects such as arrows, axe heads and saws and in modern times due to its exceptional resistance to corrosion and conductivity it has been used in objects, from classic jam pans, and the blue colour in fireworks to coinage, electrical systems, medical instruments, arts and pipework services (European Copper Institute, 2015 and 2018). Thus, Cu is all around us and makes part of our everyday life, playing a key role in the needs of modern society such as healthcare, transportation and communications. Cu contamination originates from point sources (e.g. mining and smelting operations) and also from diffuse sources such as emission as airborne particles from fossil fuels combustion and break wear, copper roofs and gutters and from copper piping into the water waste stream (Ecology Center, 2021). Elevated Cu concentrations have been widely observed in urban soils and dusts, storm runoff from streets, and discharges from sewage treatment plants (Defra, 2014; Environment Agency, 2007; Gardner *et al*., 2013; Thames21, 2019).

In the UK, there is a continuous decrease in Cu emissions, from 2013 to 2019. For example, in 2017 a total of 123317.61 kg/year was released of which 96.40 % (118877.49 kg/year) was released to water. This compares to 175542.42 kg/year in 2013 of which 96.66 % (169679.83 kg/year) was discharged to surface water, a decrease of 50802.34 kg (28.94 %) over four years (E-PRTR, 2019). It was reported that in the UK, 60 % of total Cu is used in electrical applications, including power networks (Copper Alliance, 2019). To date, about 12 % of known Cu resources have been mined with recycling and reuse paying an important part in meeting the demand and in keeping the flow of Cu in a system. Cu, like all metals, does not break down in the environment, and usually attaches to particles made of organic matter, clay, soil or sand promoting its accumulation in sediments, and impacting on river water quality when resuspended into the water column (Defra, 2015).

One of the challenges in demonstrating contamination from Cu is that pollution from this substance usually occur, in many cases, in conjunction of emissions from many different substances as they are present in same ores and released in same processes, making the environmental damage more complex due to intricate interactions amongst contaminants. Thus, careful testing and analysis are required to determine which contaminants are exerting the most negative effects in each case (Ecology Center, 2021).

Mercury (Hg)

Results from this study showed that treated wastewater discharges, the production of electricity and paper/wood production are the largest sources of Hg, contributing 47.59 % of the total predicted loads (see Figure 5.5). The relatively lowest Hg predicted load was identified for road runoff (0.04 %), followed by refineries (0.14 %) and manufacture of cement (0.99 %). Hg is a natural occurring element but also used in various industries and products commonly used (SOCOPSE, 2009). The United Nations Environment Programme (UNEP, 2020) estimates that 2220 tonnes (~2013950 kg/year) of anthropogenic Hg is emitted to the environment worldwide with production of cement accounting for about 11 % of this globally. With Hg present in the raw materials (e.g. limestone) and/or in the fuel (i.e. coal) used in the cement manufacturing process, the National Atmospheric Emissions Inventory (NAEI) (Dore *et al.*, 2019) predicted UK Hg emission in the range of 13208-36577 kg/year with 9 % being particulate Hg and expected to be deposited on other matrices such as soil and surface water. This issue calls attention to the necessity of further studies on atmospheric emission of Hg and remediation measures, especially with the predicted acceleration of construction activities and consequently the related increase in cement supplies in the next few years, further contributing not only to the global Hg air emissions but also causing pressure on soil and surface water quality.

The Hg predicted load reported in this research for wastewater (2.82 kg/year) is in line with loads of Hg measured in a study by Jamtrot *et al*. (2009) (1.1 – 3.2 kg/year). Sources of Hg in wastewater is varied, ranging from dental practices wastes to paints, domestic waste inputs, groundwater infiltration and stormwater (Hargreaves *et al.*, 2016). Hg is subject to a range of international source control agreements, with the Minamata Convention (2013) for example, stating that efforts must be made to reduce the use of Hg in companies, especially manufacturers who should take measures to restrict the use of Hg or Hg compounds and use alternatives substances (UNEP, 2020). Environment Agency (2015a) estimated that of the total Hg load released to water in England, industrial discharges (128 kg/year) were the largest contributors followed by urban runoff (66 kg/year) and wastewater treatment plants (40 kg/year). Road runoff has also reportedly contributed to the Hg load to river water, since trace concentrations of Hg from motor fuel may be deposited onto urban surfaces such as roads and subsequently washed off during rainfall (Fulkerson *et al*., 2007), showing levels of Hg in urban runoff although the significance of this source appears to vary geographically.

Hg emission to the environment has been growing concern over the years but due to stricter regulations emissions have declined across Europe by 72 % since 1990 (European Environmental Agency, 2019). However, Defra (2015a) is still reporting considerable Hg emissions in UK with the main sources to surface water being effluent from wastewater activities, production of electricity and heat and metal production processes. The European Environment Agency (2019) reported crematories as major source of atmospheric Hg, of which a considerable amount is predicted to be deposited to soil and consequently to surface water.

In 2013, total Hg releases in the UK were 3235.73 kg/year, with 10.51 % (340 kg/year) emitted to water. By 2017, this had decreased to 1734.63 kg/year with 21 % (302 kg/year) discharged to water, a reduction of 38 kg over four years. This was due to tightening of emission controls for the chemical industry under integrated pollution prevention control (IPPC) enforced by the Environment Agency and Defra (E-PRTR, 2019).

Nickel (Ni)

In the current study, sources with the highest Ni emissions were wastewater, production of electricity and manufacture of rubber and plastic products, contributing 51.25 % of the total Ni predicted load discharged to surface water in the Lower Lee catchment (see Figure 5.5). While road runoff (0.15 %), manufacture of cement (1.73 %) and waste treatment (2.84 %) accounted for the relatively lowest Ni predicted loads.

Ni has been reported in water from both point and non-point sources, with major emissions coming from wastewater, power plants and metal industries. According to the European Environmental Agency report (2019), Ni is also applied in nickel-cadmium batteries, in coins, kitchenware, jewellery and turbine production, and is also present in agriculture as phosphate fertilizers contain traces of Ni. Waste separation has proven useful, recovering up to 60 % of Ni which is recycled (European Environmental Agency, 2019).

Ni is an abundant natural occurring substance but also originates form anthropogenic sources and in excessive amounts can adversely impact the environment, thus it is subject to extensive assessments within a number of legislative frameworks (such as EU EQS), which help the reduction/control of Ni anthropogenic emission (Nickel Institute, 2021). Nickel and nickel compounds have many industrial and commercial applications and is used in products such as jewellery, keys, paper clips, clothing fasteners (e.g. zippers and buckles), electrical equipment, coins and medical equipment with the most important end uses being transportation, chemical industry, electrical equipment and construction and the main anthropogenic sources being the burning of residual and fuel oils, Ni mining and refining, and municipal waste incineration (Genchi *et al*, 2020). According to Defra (2015a) Ni emissions in the UK have declined by 68 % since 1990. In 2013 64925.40 kg/year of Ni was emitted to the environment with 77.62 % (50395.93 kg/year) discharged to water compared to 52844.60 kg/year in 2017, where 83.83 % (44299.65 kg/year) was discharged to surface waters, a reduction of 9.38 % in terms of the amount discharged to surface waters (E-PRTR, 2019). However, Ni plays an important role in technology solutions designed to mitigate climate change (Nickel Institute, 2021), which means that its use is expected to continue in the next few years, especially in the UK as the Government has developed plans for the decarbonisation and Ni is one of the elements which will be required to enable this transition (Bloodworth *et al.*, 2019).

Lead (Pb)

SFA results predicted that wastewater, production of electricity and manufacture of basic metals and metal production were the main sources of Pb discharging in the study catchment, contributing to 32.34 %. The lowest Pb predicted loads were reported for road runoff (0.20 %), followed by manufacture of cement (2.04 %) and manufacture of chemicals and chemical products (3.58 %) (see Figure 5.5).

In the UK, wastewater, manufacture of basic metals, urban residential development and stormwater runoff were reported as the largest sources of Pb. In runoff, the major sources of Pb include tyres, brake linings and building roofs. Laundry was also found as large contributor of Pb into stormwater, when discharged into surface water through misconnections. Around 60 % of the used Pb is recycled, most of it is recovered from car batteries (Defra, 2015a). Across the EU, emissions of Pb are reported to have decreased by over 90 % since 1990, with the majority of the decrease occurred by 2004, mainly as a result of the phasing out of leaded petrol (European Environmental Agency, 2019). In 2017, the UK reported a total of 39890 kg/year of Pb emissions, with 24.35 % (9713.41 kg/year) discharged to water in 2017 compared to 51107.16 kg/year 28.63 % (14631.08 kg/year) in water in 2013. This equates to a decrease of 4917.67 kg in a period of four years (E-PRTR, 2019).

Major sources of Pb include iron and steel production, tyres and brakes wear, leaded aviation fuel, wate incinerators and lead-acid battery manufacturers. Pb contamination in households due to degradation of interior painting have been part of our history. In this context, in 1977 the Consumer Product Safety Commission (CPSC) limited the Pb in most paints to 0.06% and further limitation (to 0.009%) was implemented in 2009 and in 2007, the Lead REACH

Consortium (PbRC) was implemented highlighting the vital, safe and sustainable use of Pb in contributing to the EU's decarbonisation aims and industrial strategy (Allen, 2020), meaning that Pb use will continue in the next few years.

Zinc (Zn)

Figure 5.5 shows that the primary sources of Zn emissions are wastewater, refineries and production of electricity contributing 57.06 % with lowest Zn predicted load identified in the manufacture of cement (0.90 %), followed by road runoff (1.07 %) and manufacture of non-metallic minerals products (1.67 %).

Although wastewater has been found as major source of Zn, other research has also identified road transport as one of the main sources of Zn, (Haselbach *et al.*, 2013; Maniquiz-Redillas and Kim, 2014). Sources of Zn emissions arising from road transport include brake and tyre wear (Thames21, 2019; Grigoratos and Martini, 2014), with road runoff an additional key source. Zn is one of the most used metals and in the UK, around 50% of the Zn which is produced is used in galvanizing iron sheets and construction uses at least 2/3 of all these sheets mainly for roofing and cladding and it is present in many items such as communication equipment, street lamp posts, musical instruments, water valves, coins and antifouling paints and widely used in the automotive, electrical, and hardware industries (Defra, 2020; RSC.com, 2021).

As with several other metals, Zn emissions have experienced a reduction of over 50 % since 1990 mainly due to the improvements in abatement measures in the metal industries and the closure of the UK's only primary zinc manufacturing plant (Defra, 2015a). In 2013, Zn emissions were reported as 393718.18 kg/year with 90.06 % (354600.37 kg/year) discharged to water. In 2017, 340782.14 kg were discharged, of which 86.17 % (293637.56 g/year) were emitted to surface water a decrease of 15.48 % over four years.

5.1.4 Comparison of SFA predictions with field data for selected metals

Having developed two distinct data sets (i.e. field sampling of receiving water and sediment samples and SFA modelling of emissions to surface water) which focus on the same catchment, the next stage of the research was to undertake a comparison of the two data sets to determine if, and if so how, the predicted emission data and monitored field values relate to one another. The objective underpinning this component of the research is:

- Implementation of the developed substance flow analysis tool and ground-truthing its predictions through comparison with field data.

Testing this objective involved statistical analysis of relationships between the two data sets through ratios and correlation analysis and the results of this analysis are presented below.

Table 5.3 presents field data results from the sediment sampling analysis and the SFA modelling.

Table 5.3 Overview of data sets for metals determined in sediments with SFA metal loads predicted to be discharged within 1 km of each by sampling site.

	Sampling site	Matrix	Metal concentrations in sediment (µg/g) and SFA predicted loads (kg/year)					
			Cd	Cu	Hg	Ni	Pb	Zn
River Lee	A	Sediment	0.68	45.97	0.19	13.70	68.19	164.39
		SFA	13.70	347.78	1.09	201.55	182.97	975.41
	G	Sediment	2.00	206.84	0.66	24.02	270.84	775.22
		SFA	1.96	75.71	0.27	28.79	24.03	227.45
	H	Sediment	2.28	207.93	0.58	26.60	265.34	777.17
		SFA	5.62	110.20	0.83	96.71	70.58	469.38
	I	Sediment	1.15	82.42	0.23	12.85	117.80	338.69
		SFA	0.50	17.51	0.06	6.36	5.20	78.10
Lee Navigation	C	Sediment	2.93	320.75	0.61	25.37	199.44	711.17
		SFA	5.51	87.24	0.85	85.33	40.89	409.41
	J	Sediment	7.74	190.09	0.53	56.63	253.76	758.23
		SFA	1.78	42.72	0.30	27.63	16.92	194.61
	K	Sediment	5.01	127.33	1.07	38.20	196.95	604.58
		SFA	12.96	606.22	1.75	213.18	144.87	1487.89
Tributaries	B	Sediment	0.55	54.86	0.18	16.07	87.02	237.69
		SFA	2.06	45.76	0.21	35.05	41.74	203.34
	D	Sediment	1.63	144.49	0.80	21.70	205.82	527.61
		SFA	23.11	1921.81	4.31	742.56	243.45	5754.59
	E	Sediment	1.20	79.59	0.53	5.91	171.39	372.78
		SFA	18.60	336.13	1.37	247.56	194.63	2195.30
	F	Sediment	0.45	91.45	0.40	8.88	96.16	230.98
		SFA	4.10	237.22	0.73	74.32	62.28	591.85

For the River Lee (sites A, G, H, I)

While field data showed highest concentrations of Cd, Cu, Ni and Zn were found at site H and Hg and Pb at site G, SFA loads for all metals were predicted highest at site A followed by site H. This may indicate that metals discharges from one site can directly impact other sites, in this case, metal predicted loads at site A could be contributing to metal concentration levels at sites G and H.

For the Lee Navigation (sites (C, J, K)

Highest concentrations of Hg were determined at site K coinciding with the results of SFA modelling which shows highest Hg predicted load at this same site. SFA results showed highest predicted load at site K for all the metals. This indicates that not only land use is responsible for metal concentration levels in urban rivers. Other factors such as river hydrology, sediment dynamics (for example, particles binding/release properties in sediment) need to be taken into consideration.

Comparing the two components, findings of sediment samples analysis (Section 4.2) showed total metal concentrations for Cd, Cu, Hg, Ni and Zn to be higher at the Lee Navigation sampling sites (C, J, K) than those determined in the River Lee (sites A, G, H, I). Cu, Hg and Zn was also observed as highest total metal loads predicted to be discharged at the Lee Navigation Channel compared to River Lee, illustrating that the complexity of land uses is only one of the many factors which impact sediment quality. Meanwhile, total metal concentrations for Pb are higher for the River Lee whilst SFA results showed Cd, Ni and Pb as highest total metal loads predicted to be discharged at the River Lee. These results indicate that highest Cu, Hg and Zn concentrations at the Lee Navigation Channel and highest Pb concentrations at the River Lee could be explained by these metals highest predicted load at each component, further supporting the impact of land use on sediment quality. But concentrations for Cd and Ni could be affected by other factors as previously mentioned.

For the tributaries (sites B, D, E, F)

Sediment results showed Salmons Brook (site D) with highest mean concentration of all metals amongst the tributaries, followed by Pymmes Brook (site E; except for Ni), which is consistent with results of the SFA results which predicted highest loads of all metals at site D (Salmons Brook), followed by site E (Pymmes Brook).

For all the metals in the Lower Lee catchment, results showed lowest metal mean concentrations (except for Hg) were determined in the tributaries compared to other components of the river. In contrast, tributaries were predicted to have the highest total predicted metal loads. This could suggest that they can act as significant pollution contributors to a river catchment. The metal order of abundance in sediment field data closely follows the order of abundance predicted using SFA with only Pb differing in order of appearance, moving from 4th most abundant (in SFA results) to 2nd most abundant (in sediment field data results). This relative greater abundance of Pb may be explained due to historic contamination in the sediment matrix in contrast to SFA methodology which has a time frame of one year. As previously mentioned Pb has been phased out with emissions decreased over 90 % across the EU countries, including the UK (European Environmental Agency, 2019), however, river sediment act as a sink for pollutants showing a long-term accumulation (Brils, 2008; Jones *et al*., 2019). This difference was mainly associated with the metals order of abundance at specific sites. For example, field data results demonstrate that site C differ from the sediment data abundance pattern as Cu average concentrations were higher than those determined for Pb whilst for SFA results, site B is the one which distinguishes from the SFA data abundance pattern when Pb is higher than Ni, suggesting that SFA (with its one-year timeframe) is not sensitive enough to detect longer terms trends.

Overall, results indicate that the two approaches to evaluating metals in the Lower Lee catchment do not behave consistently (by metal, site or water body component).

To further understand this relationship between data sets, ratios between the two approaches were calculated and analysed using the classification system presented in Section 3.9.2.10 (Table 5.4).

Table 5.4 Ratios of predicted metal loads/sediment field data by sampling site.

	Sampling site	**Cd**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
River Lee	A	20.28	7.57	5.64	14.71	2.68	5.93
	G	**0.98**	0.37	0.42	**1.20**	0.09	0.29
	H	2.47	**0.53**	**1.44**	3.64	0.27	**0.60**
	I	0.44	0.21	0.27	**0.50**	0.04	0.23
Lee Navigation	C	1.88	0.27	**1.38**	3.36	0.21	**0.58**
	J	0.23	0.22	**0.56**	0.49	0.07	0.26
	K	2.59	4.76	1.63	5.58	**0.74**	2.46
Tributaries	B	3.75	**0.83**	**1.15**	2.18	0.48	**0.86**
	D	14.16	13.30	5.37	34.21	**1.18**	10.91
	E	15.54	4.22	2.58	41.86	**1.14**	5.89
	F	9.19	2.59	1.80	8.37	**0.65**	2.56

Key: Values in a range of 0.5 to 1.5 (±50 %) are marked in bold.

Table 5.4 shows ratio between SFA predicted load values and sediment field data measurements (see Section 3.9.2.10). The use of ratios (unit-less values) in this study was introduced to facilitate the comparison of data sets. As explained in Section 3.9.2.10, the ratio classification system was applied. It is important to emphasise that ratios are dimensionless and are used to explore variations in trends only i.e. is there a consistent relationship between predicted pollutant emissions to surface water within 1 km of the sample site and the pollutant concentrations determined in sediment samples adjacent to sampling sites to address the question – can SFA be used to predict sediment hotspots in an urban river?

Analysis of the calculated ratios (Table 5.4) showed that most of the values as classified as overpredictions (i.e. 32 values out of 66), where the SFA predictions are typically > field value. This may indicate that either the sediment samples are not a time integrated reflection of the metal predicted loads discharged over the time period of one year and instead there were greater dynamics in sediments including remobilisation (i.e. suspension into water column), subsequent transport (i.e. moving to other sites). On the other hand, another aspect to consider is the robustness of the SFA analysis where, for example, it was noted that some activities were identified under the incorrect EU NACE/UK SIC codes, contributing to the increase or decrease of number of certain types of activities at each sampling site.

Eighteen values (out of 66) were reported as underpredictions, where the SFA predictions are typically < than those reported in the field sampling. This could mean that either the sediment samples are not a time integrated reflection of the metal predicted loads discharged over the time period of one year and instead additionally reflect discharges from previous years (i.e. historic contamination) where metals discharges were higher or also integrate discharges originating from upstream of the study site. Alternatively, the SFA modelling (relying on reported emission data) may not have included all sources. For example, this could include discharges from CSOs (known to occur but data not available) and discharges from numerous smaller companies which are understood to rapidly ‘turnover’ i.e. appear/disappear within larger industrial trading estates as well as indirect discharges to surface water e.g. aerial deposition and groundwater infiltration.

In terms of components of the catchment, six (25 %) ratio values (out of 24) of the River Lee sampling sites were classified as within the prediction range, while eight ratio values are classified as overpredictions and 10 as underpredictions. The ratios for all metals at Site A are > 1.5 i.e. SFA predicted value is > field value. Site A, as previously mentioned, reported the highest predicted loads, which could be also due to the highest number of activities and companies at this site. At Site H, ratios for Cu, Hg and Zn were in the 0.5-1.5 range (and therefore classified as in the prediction range). Ratios between SFA predictions and field data at sampling sites G and I (sites with both the lowest numbers of activities and companies) indicated that the SFA underpredicted metal loadings entering the site. It is worth noting that site G is located just downstream of sites D and E, and therefore also receives contributions from Pymmes and

Salmons Brook (where Deephams STW is located). However, the applied SFA modelling only includes input from local land use as opposed to upstream emissions and this omission could also contribute to the underprediction identified.

At the Lee Navigation only 22.22 % (4 out of 18) of the ratio values were within the prediction range while 7 ratio values indicating that SFA is overpredicted and 7 ratio values indicating that SFA is underpredictions in relation to field sampling data. Of note is that at site K only Pb was within the prediction range, this coincides with ratios for this site showing highest predicted metal loads for Pb. Site J shows most ratios indicating an underprediction with the exception of Hg, which shows a ratio within the prediction range 0.5-1.5. At site C, Hg and Zn fall within the prediction range while Cd and Ni ratios indicate an overprediction and Cu and Pb indicate underpredictions. The underpredictions may be due to the activities which were not accounted for, for example, during visual inspection it was noted that site C was a dock point for cadet's boat storage (Appendix S1) and it may contribute for discharges which were not accounted for in this study modelling; site J was used as a parking space for large boats which seemed to be used as residences and may play an important part on pollutant emission in the area – this was also not accounted for in the SFA model, highlighting the limitations of desk-top studies in isolation of field inspections.

Similar to River Lee, ratios associated with the tributary sampling sites indicate 6 (25 %) ratio values (out of 24) ratios are within the prediction range, but 17 ratios values are classified as overpredictions and only one ratio as an underprediction. Ratios associated with sites D and E indicate SFA overpredicts, i.e. SFA predicted value is typically > field value (Table 5.3). Cobbins Brook is the site with most ratio values within the prediction range and only one ratio as an underprediction. Salmons, Pymmes and Ching Brook show Pb within the prediction range of 0.5-1.5 and ratios for all the other metals are identified as overpredictions. The site D overprediction by SFA is mainly due to the high levels of metal predicted loads in the Deephams

STW's effluent, which as previously mentioned not only impact this site but also potentially the sites downstream, indicating the possible implications of other factors such as sediment dynamics (resuspension, transportation) and land use. For example, the high metals loads predicted to be discharged into the tributaries being mostly classified as overpredicts supports the notion that pollutants discharged do not settle within their immediate environment or – if they do – they are subject to rapid resuspension/transport within a timeframe of one year. This is particularly noted for Site D where discharges to surface water are primarily the emissions from Deephams STW which are monitored by the Environment Agency (2013b). The SFA results indicate that the tributaries were the major contributors of metal predicted loads, calculated to contribute a total of 12981.73 kg of metals/year compared to 2941.79 kg/year for River Lee and 2091.91 kg/year for Lee Navigation, suggesting tributaries may play a big part as contributing sediment contamination in urban rivers.

Reviewing data on a metal-by-metal basis, Hg and Pb were the metals with most values within the prediction range (i.e. 4 out of 11 for each). Cd and Ni were the metals with most overpredicted values in the model (i.e. 8 out of 11 for each one), which could suggest that these metals are more prone to resuspension compared to other metals. This study (see Section 4.4) reported highest levels of metal release for Cd (3.33–6.12 %). Table 5.4 shows Cu with most ratio values classified as underpredicted. It is difficult to know if this is due to the fact that some Cu sources are not fully accounted for or due to other aspects either within the model itself (i.e. it could be due discharges from CSOs which the model does not account for) or the catchment dynamics/complexity, thus, further investigation would be necessary to find more details on the indicated results.

Following the above descriptive analysis of data, correlation analysis was conducted to identify the strength of possible relationships between metal predicted loads discharged to the receiving waters and sediment measurements for each component of the catchment (Table 5.5). Analysis indicated that there was no significant positive relationship between SFA data and field sediment data at sample sites located on the River Lee (Table 5.5). Similarly, Lee Navigation (Table 5.5) also shows no significant correlation with an inverse relationship for all metals, except Hg where analysis indicates that a positive association between metal predicted loads and field sediment concentrations. However, a p-value of 0.15 indicates that despite the strength of the relationship is not statistically significant, the Pearson correlation value of 0.97 may indicate that a relationship between results for Hg and further investigation would be necessary to understand what is underlying this outcome. The inverse correlation further suggest that sediment metal concentrations are not a reflection of the metal predicted loads discharged at the time in the area, maybe due to the factors such as historic contamination, sediment remobilisation and transportation or due to limitations identified for SFA modelling i.e. does not include discharges from CSOs, all roads or aerial deposition, all which can have a significant impact on urban river sediment quality (Defra, 2019; Angerville *et al*., 2013).

Table 5.5 Correlation analysis of metals sediment field data with SFA predicted loads at the River Lee, Lee Navigation and Tributaries.

		Metals in sediment					
		Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
River Lee	**r***	-0.51	-0.52	-0.14	-0,18	-0.52	-0.47
	P-value	0.49	0.49	0.86	0.82	0.48	0.53
Lee Navigation	**r***	-0.40	-0.70	0.97	-0.40	-0.67	-0.99
	P-value	0.74	0.51	0.15	0.74	0.53	0.09
Tributaries	**r***	**0.98**	**0.95**	**0.94**	0.63	**0.99**	**0.99**
	P-value	**0.02**	**0.05**	**0.05**	0.37	**0.00**	**0.01**
		Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
		Metals from SFA					

Key: * r = Pearson Correlation; values in bold show the pairs of parameters with very strong correlation.

In contrast to the relationships between metal predicted loads discharge and field sediment data for sample sites on the River Lee and Navigation Channel, analysis of the relationship between these two data sets in terms of the tributaries (Table 5.5) shows a strong correlation for all metals at a significant level ($p \leq 0.05$), except for Ni. In this way, the very strong relationship observed for Cd, Cu, Hg, Pb and Zn (Table 5.5), not only serve as a strong evidence to support the objective that the pollutant load predictions made through the SFA modelling can be verified using field data but also indicates that SFA can be used as a tool to identify pollutants and areas of concern in smaller water bodies. This stronger relationship may be due to the tributaries having relatively fewer inputs with less complexity in terms of contributing upstream sources when compared to the River Lee and Lee Navigation which are more complex (Stanisavljevic and Brunner, 2014; Sörme and Lagerkvist 2002; Chèvre *et al*., 2011). Further factors are that the river and the navigation channel are also in receipt of activities such as commercial and recreational boating and combined sewer overflows which (due to a scarcity of emission data) could not be accounted for in this research.

As previously mentioned, differentiation between results from SFA modelling and field data could be due not only to modelling limitations but also due to the complexity of the Lower Lee catchment and complexity of metals behaviour in water and sediment matrices. Ratios in the range of 0.5-1, may indicate sediments have not moved i.e. association between SFA results and field data is also a function of river hydrology which informs where sediments deposit, accumulate or scour.

Overall, SFA results show that although there are limitations and uncertainties in the model, SFA can be a valuable tool in predicting metals load in small urban rivers, especially to better understand industrial metabolism as emission sources (European Environmental Agency, 2019). Field results also support the use of SFA modelling as an opportunity to identify and prioritise pollutant sources.

5.2 SFA modelling of selected PAHs in the Lower Lee catchment – all sites

5.2.1 SFA of PAHs predicted loads at each sampling site in the Lower Lee catchment

The results of SFA for selected PAHs emitted by activities identified as occurring in the Lower Lee catchment at each sampling site are compiled in Appendices Q1 to Q11. An overview of results and their assessment is presented in the sections below.

Table 5.6 summarises the predicted loads (mass/year) of selected PAHs in various surface water bodies of the Lower Lee catchment. These results support previous studies wherein Bz(b)Fl was the PAH detected as occurring in the highest concentration in urban rivers (Anyakora and Coker, 2006), industrial areas (Kalugina *et al*., 2018) and steel and iron industries emissions (Yang *et al*., 2002). The SFA load of the five PAHs released to surface water vary between PAHs and sites and increase as follows: A < Bz(g,h,i)Pe < Fl < Bz(a)Py < Bz(b)Fl, with total predicted loads of 20.24, 105.73, 112.60, 226.60, 316.19 kg/year, respectively, a total PAH predicted load of 781.37 kg/year. For example, the load of Bz(b)Fl predicted is three times greater than Bz(g,h,i)Pe, which itself is five times greater than the mass of anthracene predicted to be discharged.

Table 5.6 SFA total loads of selected PAHs predicted to discharge at each sampling sites in the Lower Lee catchment.

Sampling site	**SFA PAHs predicted loads (kg/year)**					**Sum of all PAHs**
	A	**Fl**	**Bz(b)Fl**	**Bz(a)Py**	**Bz(g,h,i)Pe**	
A	1.27	12.45	22.52	14.48	5.75	56.47
B	0.20	0.20	2.00	2.00	0.20	4.61
C	2.62	6.30	73.81	58.60	32.98	174.32
D	6.41	15.25	47.03	36.63	15.70	121.04
E	2.72	13.52	28.54	20.49	6.47	71.74
F	1.74	24.10	37.04	20.96	10.70	94.54
G	0.90	12.10	18.59	10.52	5.38	47.49
H	0.32	0.34	3.05	3.04	0.32	7.08
I	0.22	0.24	2.05	2.03	0.22	4.77
J	0.94	1.88	21.24	17.42	8.54	50.02
K	2.90	26.21	60.32	40.41	19.46	149.29
Sum of each PAH at all sites	20.24	112.60	316.19	226.60	105.73	781.37

The data presented in Figure 5.6, indicates that there is a variation in PAHs predicted loads between the sites with Bz(b)Fl having the highest predicted load at all sites. The 5-ring PAHs (Bz(a)Py and Bz(b)Fl) dominate the load of PAHs discharged into the Lower Lee catchment, suggesting they originate from common sources. This is because of highest predicted emission loads of these PAHs mainly being discharged from two main activities, manufacture of basic metals and metal products and manufacture of chemicals and chemical products (further discussion can be seen in Section 5.2.2). Sediment field data shows the PAH composition pattern is dominated by the presence of 4-ring PAHs (63.50 %) followed by 5-ring PAHs (21.49 %) but for the SFA 4-ring PAHs were not identified as highest discharged predicted load. Further discussion on PAHs sources and comparison of SFA results with field data takes place in Sections 5.2.3 and 5.2.4. Lowest PAH predicted load was predicted for A at all sites while Bz(b)Fl (5-ring PAH) had the largest predicted load at most sites with exception of site C.

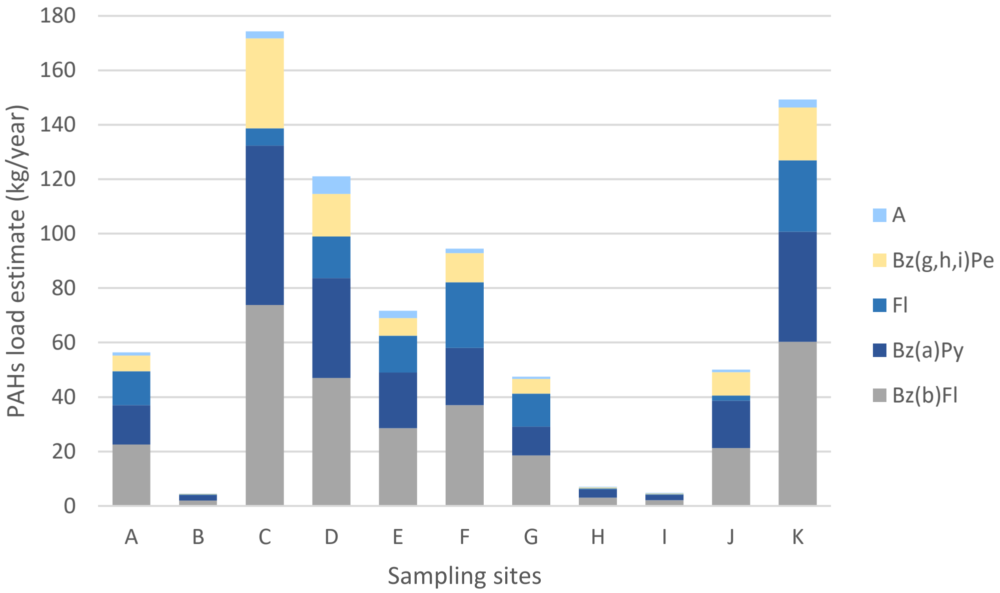


Figure 5.6 PHA predicted loads of A, Bz(g,h,i)Pe, Fl, Bz(a)Py and Bz(b)Fl discharged in the Lower Lee catchment.

When analysing results by each PAH, the highest PAH loads were predicted for site C (for 5 and 6-ring PAHs: Bz(a)Py, Bz(b)Fl and Bz(g,h,i)Pe), site D (for anthracene) and site K (for fluoranthene). The main source of Bz(a)Py, Bz(b)Fl and Bz(g,h,i)Pe is the manufacture of chemicals and chemical products. At site D the large predicted load for anthracene was mainly associated with the emissions of treated effluent from Deephams STW and at site K the main source of fluoranthene was the manufacture of basic metals and metal products. Although site E has the same number of companies as site D (11) most associated with site E are classified under the waste non-hazardous (9) category (see Table 3.8), leading to a relatively lower predicted loading compared to emissions from STW (1 company at site D) and the manufacture of chemicals and chemical products (1 company at site D).

SFA results show that the reported Bz(a)Py predicted loads emissions from Deephams STW (a total of 3.75 kg/year, serving a population of approximately one million inhabitants, treating wastewater generated from households, businesses, public facilities and industries) are greater than those reported by the studies from Sweden, 0.001 kg/year for Bz(a)Py for one STW serving

8,830 inhabitants (Palmquist, 2004). And, although studies from Hong Kong reported a total 1.85 kg/year for 16 PAHs also for one STW (Sha Tin STW) serving 910,000 inhabitants (Man *et al*., 2017), levels for Deephams STW for 5 PAHs still greater, with a total of 12.34 kg/year. Whilst the STW in Sweden only treats wastewater generated from households, businesses and public facilities, the Hong Kong and Deephams STWs also treat wastewater from industries; taking this into consideration it may be that the types of industries at Lower Lee are contributing to the high PAHs predicted emission loads in the study area. It is also important to note that, in the UK, the average person is reported to result in the discharge of 150 litres of wastewater per day (WTE, 2021), an amount which is far more than that reported for many other European countries, e.g. Denmark with an average daily wastewater produce of 80 litres per person/day whilst in Hong Kong it reaches 90 litres per person/day (Office for National Statistics, 2013a and 2019; European Environment Agency, 2013). In a study investigating the effect of different treatment stages on PAH content in wastewater and sewage sludge, Wlodarczyk-Makula (2005) reports that sewage treatment processes remove 83-85 % of PAHs from wastewater effluent. However, other studies report lower removal rates (63 to 69 %) with STW identified as one of the major contributors of PAHs to surface water bodies (Liu *et al*., 2017; Cao *et al*., 2018; Torretta, 2012; Manoli and Samara, 2008; Qi *et al*., 2013).

Reports from the Environment Agency (2013b) identified that tributaries D and E failed good chemical status in 2013 with fluoranthene identified as one of the pollutants which exceeds its respective EU EQS (2013). They identified key sources of Fl as diffuse sources derived from urban development and road runoff. With site such as J, where highest concentration of PAHs (especially for Fl) was found in the sediment matrix (see Figure 4.11) and sites K and F (see Table 5.6), where highest Fl predicted load was identified, demonstrate the potential of sediment enrichment and consequently, through sediment resuspension, possible impacts to water quality with potential of exceedance of the EU EQS. SFA results indicate that at site D, Salmons Brook, while 8 of the 11 companies identified are classified as waste non-hazardous, the companies undertaking the manufacture of basic metals and metal products (1 company), manufacture of chemicals and chemical products (1 company) and Deephams STW are responsible for the majority of discharges. At site E, Pymmes Brook, there are more companies undertaking waste non-hazardous activity (9 companies), compared to site D. However, companies located within 1 km radius of the sampling site E also include refineries (1 company) and manufacture of basic metals and metal products (1 company), contributing to most of the predicted (4.70 kg/year, 48.20 kg/year respectively) PAHs load (Table 3.8).

SFA results predicted the lowest load of PAHs discharged to Site B, followed by site I. This may be because these two sites have the same number and type of activities/companies, waste (non-hazardous) and road runoff and are not home to activities such as STW, refineries, manufacture of basic metals and metal products or manufacture of chemicals and chemical products (Table 3.8).

Table 5.7 presents the PAH loads predicted to discharge to the various sections of the catchment (River Lee vs Lee Navigation Channel vs tributaries). A total of 115.80, 373.64 and 291.93 kg/year PAHs load were predicted to be discharged from the sampling sites to the River Lee, Lee Navigation and tributaries, respectively, with sites C, K, D and F, accounting for most of the PAHs load (22.31, 19.11, 15.49 and 12.10 % of total loads, respectively). Similarly, to the SFA metals results, the River Lee is the component of the study area accounting for the lowest PAH predicted loads. However, while tributaries were found with largest metals load, for PAHs Lee Navigation was the component with largest predicted load, due to sites C and K having more polluting activities (see Table 3.8).

Table 5.7 Overview of predicted loads of selected PAHs at each sampling site in the River Lee, Navigation Channel and tributaries.

	Sampling site	**SFA PAHs predicted loads (kg/year)**					**Sum of all PAHs**
		A	**Fl**	**Bz(b)Fl**	**Bz(a)Py**	**Bz(g,h,i)Pe**	
River Lee	A	1.27	12.45	22.52	14.48	5.75	56.47
	G	0.90	12.10	18.59	10.52	5.38	47.49
	H	0.32	0.34	3.05	3.04	0.32	7.08
	I	0.22	0.24	2.05	2.03	0.22	4.77
Lee Navigation	C	2.62	6.30	73.81	58.60	32.98	174.32
	J	0.94	1.88	21.24	17.42	8.54	50.02
	K	2.90	26.21	60.32	40.41	19.46	149.29
Tributaries	B	0.20	0.20	2.00	2.00	0.20	4.61
	D	6.41	15.25	47.03	36.63	15.70	121.04
	E	2.72	13.52	28.54	20.49	6.47	71.74
	F	1.74	24.10	37.04	20.96	10.70	94.54

For the River Lee, highest loads of all PAHs were predicted at sites A and G. While the SFA for metals predicted highest loads at sites A and H. As noted by Chetty and Pillay (2019), urban rivers are impacted by some types of industrial activities which makes a site more polluted than others even though it may have a smaller number of companies; this is suggested by the SFA results in this research. In this case it can be noted that the activity ‘manufacture of basic metals and metal products’ at site G (although it is a site with the least number of companies) plays an important role in indicating this site as one site with one of the largest PAH loads (Table 3.8). SFA predicted loads showed manufacture of basic metals and metal products as the main source of PAH at site A and consequently to the whole River Lee. As reported for the metals results, lowest PAHs predicted loads were identified at site I and H, which have only two types of activities, waste non-hazardous and road runoff.

SFA predicted PAH loads at sampling sites on the Lee Navigation Channel (see Table 5.7) are predicted to discharge higher loads than the total calculated to discharge to the River Lee. From Table 3.8 it was noted that manufacture of chemicals and chemical products was identified at all sites in the Lee Navigation but not in any site at River Lee. This difference in occurrence of activities between the two components explain the differences in PAH predicted loads between the two. Highest PAH predicted load was reported at upstream site C (for Bz(b)Fl, Bz(a)Py and Bz(g,h,i)Pe), and at downstream site K (for anthracene and fluoranthene). Lowest PAH predicted loads occur at site J for all PAHs.

Results of SFA modelling in the tributaries the Cobbins, Salmons, Pymmes and Ching Brooks, show highest predicted loads for anthracene, Bz(b)Fl, Bz(a)Py and Bz(g,h,i)Pe at Salmons Brook and for fluoranthene at Ching Brook. Again, the activity ‘manufacture of chemicals and chemical products’ seems to be contributing for the largest predicted load of fluoranthene at Ching Brook, while at site D, Deephams STW is the major source of anthracene, Bz(b)Fl, Bz(a)Py and Bz(g,h,i)Pe discharges into the receiving river. Tributaries were the second highest (after Lee Navigation) contributors of selected PAHs predicted load with a total of 291.93 kg/year predicted to be discharged surface waters, further supporting that, as reported for metals, tributaries do play a significant role as contributor in enriching sediments in urban rivers.

In keeping with the metals data, lowest PAH predicted loads were identified at Cobbins Brook. The PAHs values (0.20 kg/year for anthracene, fluoranthene, Bz(g,h,i)Pe and 2.00 kg/year for Bz(b)Fl, Bz(a)Py) at site B (Cobbins Brook) was a function of the need to use the average threshold value (Table 3.10) reported for each PAH for waste non-hazardous activity (this has been explored under Section 3.10.3 Data uncertainty) and the road runoff predicted loads being less that those associated with other sources. Although Pymmes Brook is one of the tributaries with highest number activities and companies within 1 km radius of the sampling site, the type of industries identified at this site do not account for largest PAH predicted loads. This further corroborates the impact of industry type (as opposed to simply the total number) can have on river water and sediment quality.

In summary, at the Lower Lee catchment (781.37 kg/year), a total of 20.24 kg/year has been quantify as load of anthracene being discharged from the selected activities, followed by Bz(g,h,i)Pe (105.73 kg/year), Fl (112.60 kg/year), Bz(a)Py (226.60 kg/year), and Bz(b)Fl (316.19 kg/year). In terms of components of the river, while tributaries were responsible for discharging the highest metal loads, for PAHs the Lee Navigation Channel dominated (373.64 kg/year), followed by the tributaries (291.93 kg/year) with lowest predicted loads of metals and PAHs (115.80 kg/year) associated with the River Lee.

Overall, results suggest that not only the number but especially the type of activities play an important part understanding the discharges of pollutants to urban rivers. Some activities, such as manufacture of basic metals and metal products and manufacture of chemicals and chemical products can discharge much more PAHs into surface water when compared to activities such as wastewater, refineries and waste non-hazardous, and hence provides an opportunity to identify and prioritise sources for the mitigation.

5.2.2 SFA overview of PAH predicted loads by activities at the Lower Lee catchment

Figure 5.7 shows PAH predicted loads by activities at the Lower Lee catchment. For the sum of selected PAHs, manufacture of basic metals and metal production (377.56 kg/year) is the major source followed by manufacture of chemicals and chemical products (301 kg/year), waste non-hazardous (85.10 kg/year), wastewater (12.34 kg/year), refineries (3.70 kg/year) and road runoff (1.67 kg/year).

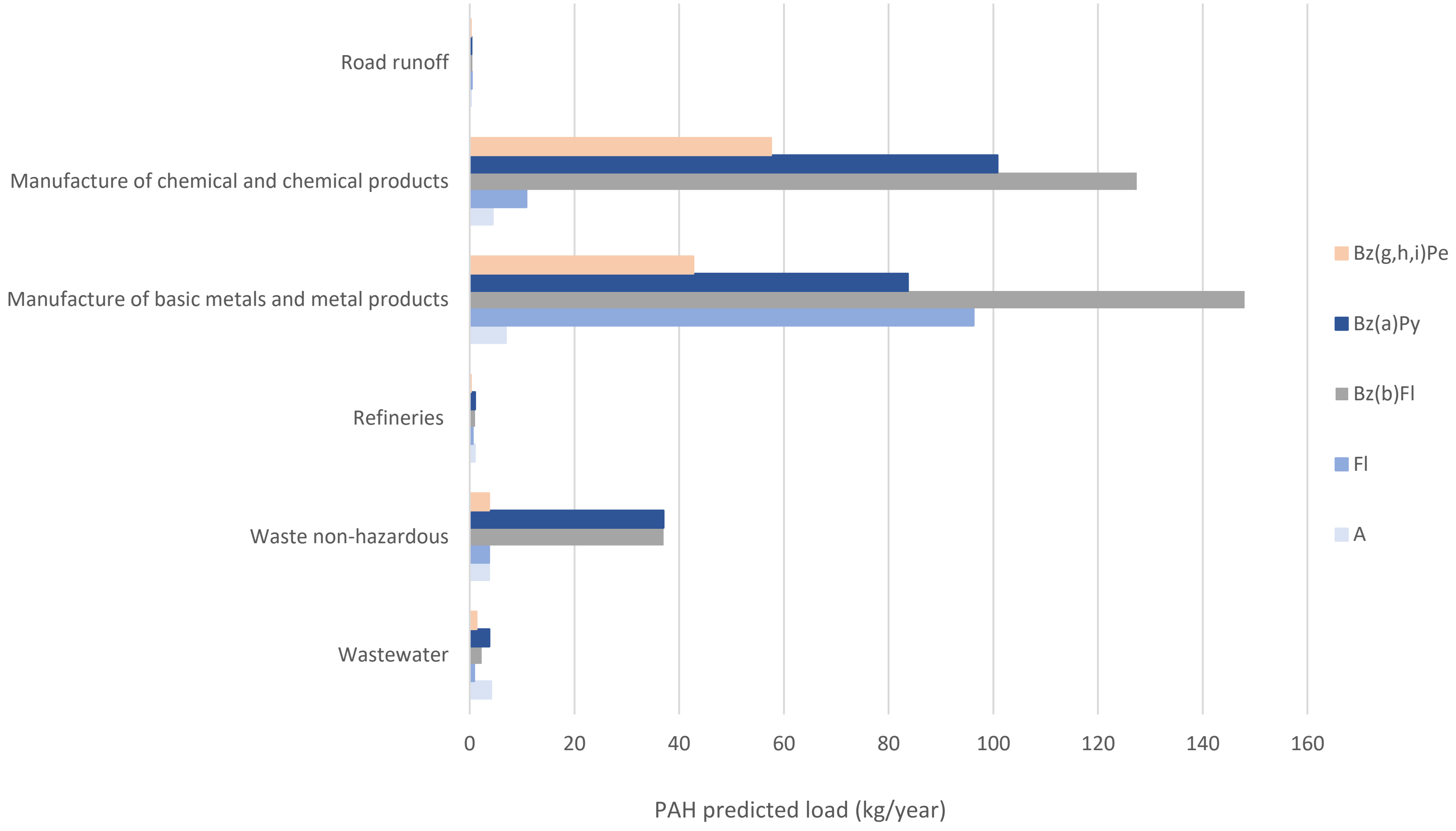


Figure 5.7 Loads of selected PAHs (kg/year) predicted to be discharged by activities located in the Lower Lee catchment.

As per SFA metal results, road runoff was consistently predicted to discharge the lowest mass of PAHs. This finding contradicts several other studies (European Environmental Agency, 2019; Markiewicz, 2017; Watts *et al*., 2010). A factor in this may be the limited data availability as the method used to calculate loads requires AADT data which was available only for a limited number of roads in the study area and limitations of the SFA approach (see Section 3.9.2.8).

Data reported by the Environment Agency (2017) for 2017 identify the wastewater industry as the largest point source of five PAHs (335 kg) (benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene) to water in England, followed by refineries and fuel plants (68 kg for both combined) and iron and steel works (40 kg). As diffuse source, road runoff was identified as a significant contributor to PAHs loads into water (for example, 110 kg/year for benzo(a)pyrene), especially near to industrialised and densely populated urban areas as is the case of the Lower Lee catchment (Environment Agency, 2019). However, for this study although SFA modelling identified treated wastewater effluents as one of the main sources of PAHs, road runoff was approximately three orders of magnitude less than value reported by the Environment Agency (2017) in terms of benzo(a)pyrene.

To summarise, predicted PAH discharges do vary by site and activity but not in a manner consistent to that predicted for metals. In relation to metals results, fourteen activities were identified as discharging metals into the Lower Lee catchment while for PAHs six activities were identified as possible sources. For the Lower Lee catchment, highest PAH predicted load was determined at sites C, D, F and K, with activities such as wastewater, manufacture of basic metals and metal products and manufacture of chemicals and chemical identified as the key sources. Sites B and I reported relatively the lowest PAH predicted loads which originate from two activity types: waste non-hazardous and road runoff. Organic chemicals are very complex and may be volatilized or degraded (for example, through biotic processes) (Abdel-Shafy and Mansour, 2016). Once deposited on soil or sediment particles, PAHs tend to adsorb and therefore accumulate. They are subject to on-going partitioning, degradation and transport processes (Bozlaker *et al*., 2008), originated from various sources, including surface runoff following rainfall, particularly from urban areas where high levels of PAHs may be present (Neff *et al*., 2005; Pies *et al*., 2008), thus, affecting spatial distribution of PAHs in the matrix. Defra (2012) highlighted the possibility of a proportion of PAHs released in the UK can migrate into the oceans making them a global environmental issue. The study also emphasised that surface waters in the UK are not only affected by discharges from industries and CSOs but are also by diffuse pollution from urban runoff from brownfield sites (former industrial sites that often have contaminated soils), road runoff and particularly domestic misconnections. Therefore, activities such CSOs, misconnections and brownfield runoff were not accounted for in this research and is identified as limitation when comparing results from SFA modelling and field data.

5.2.3 SFA of the predicted loads by each PAH

Each PAH was considered separately for further investigation, and Figure 5.8 indicates the quantified load of PAHs predicted to be discharged with 1 Km of each sampling site to the Lower Lee catchment, presenting the absolute (as kg/year) and as relative contribution (%). Presented percentage of the total load from each source is based on the total predicted load of each respective PAH.

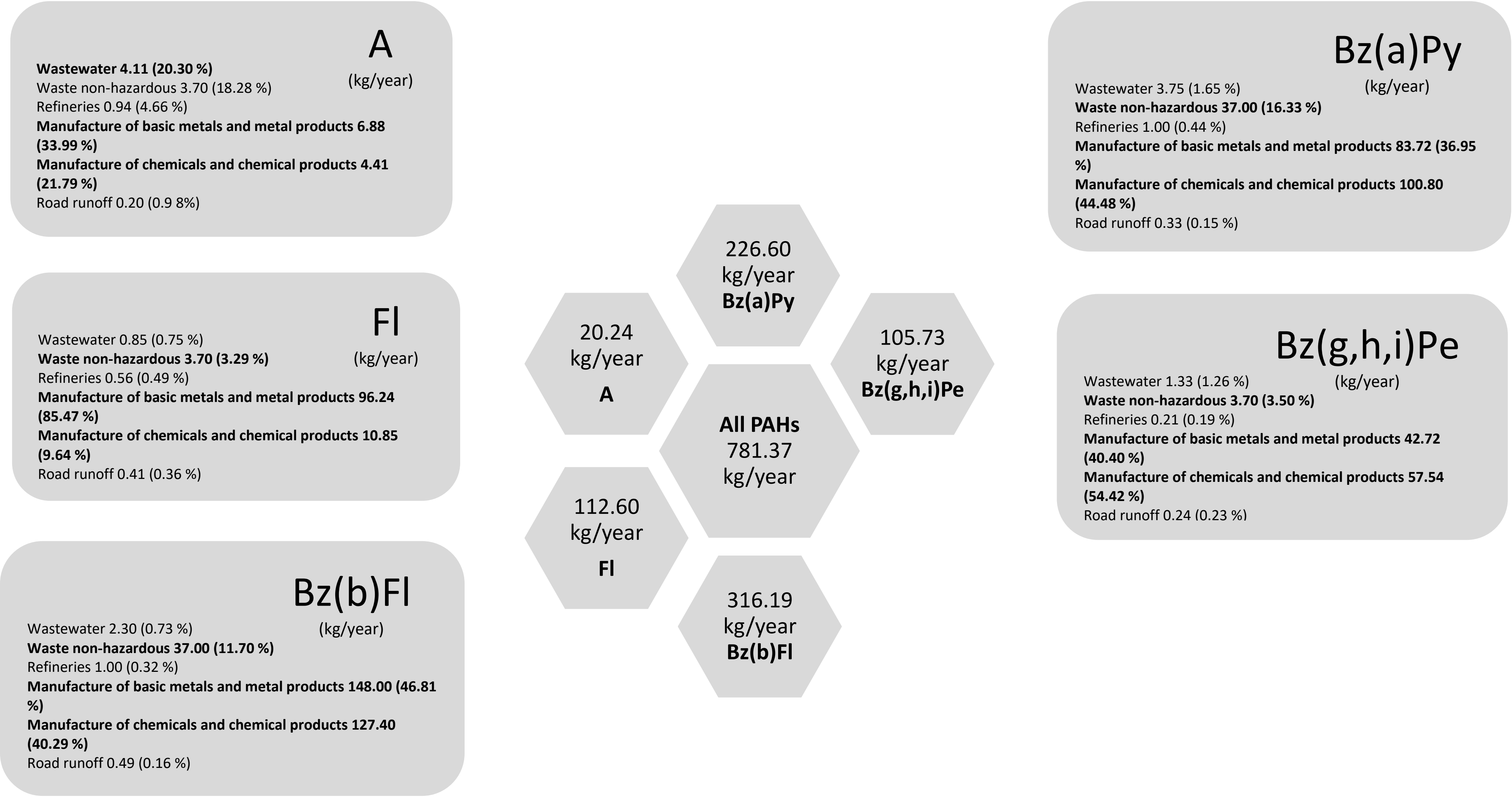


Figure 5.8 Diagram of SFA PAHs loads (stock flows) predicted to discharge with 1Km of each sampling site into surface water at the Lower Lee catchment.
Three highest values for each PAH are marked in bold.

Anthracene (A)

From the SFA results (Figure 5.8), the manufacture of basic metals and metal products is identified as the primary source of A discharging to the Lower Lee system (6.88 kg/year; 33.99 %), Manufacture of chemicals and chemical products are predicted to discharge (4.41 kg/year; 21.79 %) and wastewater (4.11 kg/year; 20.30 %). Road runoff (0.20 kg/year; 0.98 %), refineries (0.94 kg/year; 4.66 %) and waste non-hazardous (3.70 kg/year; 18.28 %) were identified as contributing relatively the lowest masses.

E-PRTR (2019) reported a continuous decrease in A emissions in the UK over a period of four years. As total of 695 kg/year were released in 2017 from all sources of which 79.00 % (549 kg/year) was reported to be released directly to water. This compares with a value of 1654.98 kg/year in 2013 from which 15.89 % (263 kg/year) was discharged to surface water. Although emission of A have reduced, discharge to water has increased from 263 kg/year in 2013 to 549 kg/year in 2017. The increase was mainly due to emissions from the energy sector, production and processing of metals and wastewater industries.

Fluoranthene (Fl)

SFA results (Figure 5.8) identify those activities associated with the manufacture of basic metals and metal products (96.24 kg/year; 85.47 %) as the main source of Fl emissions within the Lower Lee catchment, followed by the manufacture of chemicals and chemical products (10.85 kg/year; 9.64 %) and waste non-hazardous (3.70 kg/year; 3.29 %). As for A, road runoff (0.41 kg/year; 0.36 %), followed by refineries (0.56 kg/year; 0.49 %) and wastewater industry (0.85 kg/year; 0.75 %) contribute relatively the lowest amounts.

The E-PRTR (2019), reported Fl release into surface water in the UK to be 98.4 kg/year in 2013, with emissions over 3-fold to 331 kg/year in 2017. They associated this increase with wastewater industries and chemical production). The relatively low Fl predicted load to be discharged from wastewater activity into the Lower Lee catchment could be explained to the fact that around 90 % of PAH load can be removed from wastewater effluent through treatment as reported by a number of studies (e.g. Gardner *et al*., 2013; UKWIR, 2019).

Benzo(b)fluoranthene (Bz(b)Fl)

Results from the SFA model (Figure 5.8) indicate that Bz(b)Fl contribute the largest proportion of the total selected PAH predicted loads discharged to water. Sources with highest Bz(b)Fl emission within the Lower Lee catchment include the manufacture of basic metals and metal products (148 kg/year; 46.81 %), manufacture of chemicals and chemical products (127.40 kg/year; 40.29 %) and waste non-hazardous (37 kg/year; 11.70 %). While road runoff (0.49 kg/year; 0.16 %), refineries (1 kg/year; 0.32 %) and wastewater (2.30 kg/year; 0.73 %) accounted for the lowest Bz(b)Fl predicted load discharged into surface water in the Lower Lee catchment. Similarly, to this work, Environment Agency (2019) has also reported Bz(b)Fl as one of the PAHs with the highest load discharged into surface waters in urban areas.

Benzo(a)pyrene (Bz(a)Py)

SFA results (Figure 5.8) showed Bz(a)Py as the PAH accounting for the second highest predicted load discharged into the Lower Lee catchment. Manufacture of chemicals and chemical products (100.80 kg/year; 44.48 %), manufacture of basic metals and metal products (83.72 kg/year; 36.95 %) and waste non-hazardous (37 kg/year; 16.33 %) were the main sources of Bz(a)Py. On the other hand, lowest Bz(a)Py predicted load was observed for road runoff (0.33 kg/year; 0.15 %), followed by refineries (1 kg/year; 0.44 %) and wastewater industry (3.75 kg/year; 1.65 %).

Environment Agency (2019) reported an increase of Bz(a)Py emissions over the years (i.e. 872 kg/year in 1990 compared to 5917 kg/year in 2016) associating this with increases in use of wood as a domestic fuel, transport, bonfires, barbecuing and cigarette smoking. The higher molecular weight PAHs such as Bz(a)Py tend to associate with particulate matter (Zheng *et al*., 2012; Živković *et al*., 2015) and in this way increases their chemical stability and resistance to degradation, consequently they are potentially available for transportation over long distances (Rumney *et al*., 2015).

Benzo(g,h,i)Perylene (Bz(g,h,i)Pe)

Figure 5.8 shows that the manufacture of chemicals and chemical products (57.54 kg/year; 54.42 %), manufacture of basic metals and metal products (42.72 kg/years; 40.40 %) and waste non-hazardous (3.70 kg/year; 3.50 %) are the major sources of Bz(g,h,i)Pe predicted load with lowest Bz(g,h,i)Pe predicted load identified in road runoff (0.24 kg/year; 0.23 %), followed by refineries (0.21 kg/year; 0.44 %) and wastewater (1.33 kg/year; 1.65 %). The Environment Agency (2019) reported that in 2013 Bz(g,h,i)Pe emissions to surface waters were reported as 84.10 kg/year, while in 2017 it fell to 68.8 kg/year with a decline in emissions from manufacture of chemicals and chemical products and manufacture of basic metals and metal products over the years.

Overall, in contrast to SFA metals results, this SFA identify PAHs main sources as manufacture of chemicals and chemical products and manufacture of basic metals and metal products, followed by waste non-hazardous (Figure 5.6). However, it seems that minimisation of pollutant release from manufacture of chemicals and chemical products and manufacture of basic metals and metal products has made enough impact to lower PAHs emissions as the decrease has been observed for a number of PAHs from 2013 to 2017 (E-PRTR, 2019; Environment agency, 2019).

Research undertaken by the Environment Agency (2019) suggests that historical contamination significantly contributes to PAHs load to surface waters as much of the PAH contamination in the environment can be considered as from past industrial activities, giving rise to a legacy of contaminants already present in soils and river sediments. Their data suggest an increase of five PAHs (Bz(b)Fl, Bz(a)Py, Bz(g,h,i)Pe, Bz(k)Fl and In(1,2,3-cd)Py) emissions in the Thames River Basin District with Bz(b)Fl continuing having the largest release for 2017. Their data were variable between and within sites, reflecting the high degree of spatial variability in PAH concentrations across the UK with urban and industrial areas having five to eight times more concentrations of PAHs compared to rural areas. A similar pattern was found by Lawal and Fantke (2017), Wang *et al.* (2017) and Bathi (2012) where 16 PAHs showed higher concentrations in urban areas. The Environment Agency (2019) have estimated the main anthropogenic PAH sources in the UK as combustion in industry and at commercial and residential areas and road runoff. When reviewing the literature, it was noted that the data for PAHs varied significantly between studies due to the number of PAHs analysed and the type of catchments. Yet, all studies have suggested road runoff as one of the major contributors of PAH loads in urban water systems.

5.2.4 Comparison SFA predictions with field data for selected PAHs

A key part of this research is to investigate the following objective: ‘Implementation of the developed substance flow analysis tool and ground-truthing its predictions through comparison with field data.’ Testing this objective involved a comparison of pollutant loads predicted to discharge at each sample site (calculated using SFA) with the field data on concentrations determined in sediment at each site with a view to assessing if SFA can act as a screening tool to identify sediment hotspots. This involved statistical analysis of relationships between the two data sets through ratios and correlation analysis and the results of this analysis are presented below.

Table 5.8 displays results from sediment sampling analysis and the SFA modelling.

Table 5.8 Overview of data sets for PAHs determined in sediments with SFA PAH loads predicted to be discharged within 1 km of each sampling site.

	Sampling site	**Matrix**	**PAHs concentrations in sediment (µg/g) and SFA predicted loads (kg/year)**				
			A	**Fl**	**Bz(b)Fl**	**Bz(a)Py**	**Bz(g,h,i)Pe**
River Lee	A	Sediment	0.28	1.71	1.65	0.94	0.73
		SFA	1.27	12.45	22.52	14.48	5.75
	G	Sediment	0.77	5.39	3.34	24.02	1.02
		SFA	0.90	12.10	18.59	10.52	5.38
	H	Sediment	0.76	5.44	3.68	2.46	0.72
		SFA	0.32	0.34	3.05	3.04	0.32
	I	Sediment	0.66	4.00	3.33	2.01	1.43
		SFA	0.22	0.24	2.05	2.03	0.22
Lee Navigation	C	Sediment	0.79	4.66	4.45	2.42	2.16
		SFA	2.62	6.30	73.81	58.60	32.98
	J	Sediment	1.54	11.15	10.26	6.11	2.80
		SFA	0.94	1.88	21.24	17.42	8.54
	K	Sediment	0.71	3.21	3.93	1.94	1.64
		SFA	2.90	26.21	60.32	40.41	19.46
Tributaries	B	Sediment	0.37	2.87	2.58	1.39	1.14
		SFA	0.20	0.20	2.00	2.00	0.20
	D	Sediment	0.78	5.56	3.75	2.46	1.83
		SFA	6.41	15.25	47.03	36.03	15.70
	E	Sediment	1.11	8.02	5.52	3.80	2.66
		SFA	2.72	13.52	28.54	20.49	6.47
	F	Sediment	0.61	4.89	3.57	2.23	1.67
		SFA	1.74	24.10	37.04	20.96	10.70

As an overview of the comparison table (Table 5.8), it was noted the following:

For the River Lee (sites A, G, H, I)

Similar to the SFA metals predictions, results for PAHs show that while field data reported highest PAHs concentrations at site G and H, SFA PAH predicted loads were highest at site A. This further suggest that PAHs discharges from one site may directly impact other sites, in this case, PAH predicted loads discharges at site A could be contributing to PAHs concentration levels in sediment at sites G and H. In addition, results further suggest that PAHs concentrations outcome could be related with intense pressure at these sites by specific activities which are not necessarily local. For example, the activity manufacture of basic metals and metal products being the highest source of

PAHs predicted load at site A could be contributing considerable to highest concentrations of sediment PAHs at sites G and H.

For the Lee Navigation (C, J, K)

Field sediment PAHs concentrations tended to be higher in the Lee Navigation sampling sites in comparison to those determined in the River Lee and tributaries components. Similarly, SFA results shows a higher emission of PAHs at Lee Navigation (373.64 kg/year) compared to other waterway components (115.80 kg/year for River Lee and 291.93 kg/year for tributaries). This could be due to the type of activities discharging at the Lee Navigation channel but also due to the fact that the Lee Navigation is a much more complex area receiving influence of pollutant discharges from the tributaries and the River Lee itself. For sediment, site K was the site with lowest PAHs concentration but for SFA modelling site J (50.02 kg/year) was the one with lowest discharge for PAH predicted loads, while site C (174.32 kg/year) was the site where highest PAH predicted loads was reported and site K was the second highest with a total PAH load of 149.29 kg/year. These results further support suggestion that discharges from one site can impact on concentrations of pollutants on another site and illustrating that the complexity of land uses is only one of the many factors which impact sediment quality. As previously mentioned, other factors such as river hydrology, sediment dynamics (for example, zones of deposition and scour, biodegradation and binding/release of pollutant to sediments) can also play a part in this pollutant distribution in a catchment.

For the tributaries (B, D, E, F)

Sediment results showed Pymmes Brook with highest mean PAHs concentration amongst the tributaries, followed by Salmons Brook, while SFA results showed highest PAH predicted loads at site D (Salmons Brook) (except for Fl), followed by site F (Ching Brook), which may suggest influence of many different factors such as that Pymmes Brook is impacted by PAHs sources originated from other sites or from sources not accounted for in the SFA modelling and that PAH predicted loads discharged at Salmons Brook and Ching Brook could be responsible for contaminating other sites downstream.

For the Lower Lee catchment as a whole, PAHs order of abundance in sediment field data closely follows the order of abundance predicted using SFA, with only Fl differing in order of appearance, moving from 3rd most abundant (in SFA results) to 1st most abundant (in sediment field data results). While sediment PAH field results showed highest PAHs concentrations at site J (Section 4.4), SFA results reported highest PAH predicted loads at site C (Table 5.8). And whilst sediment results showed sites A and I with lowest mean PAHs concentration, PAHs predicted loads were lowest at sites B. These differences on PAHs occurrence between results (SFA and field data) indicates that PAH concentrations may not reflect the PAH predicted loads discharged at the selected sampling sites during the designated period (year 2013) or it may be due to data and/or SFA limitation factors as explained in section 3.10.3, complexity of the study area and PAH behaviour.

As previously discussed in Section 4.4, a 2007 survey of the Lower Lee catchment found that PAHs such as Fl, Bz(b)Fl, Bz(k)Fl were present in surface waters at levels which exceeded the EU EQS (2013). The same report attributed the presence of PAHs as urban diffuse pollution inputs and the presence of contaminated sediments (Environment Agency, 2012). Diffuse pollution sources may also explain the underpredict ratios, suggesting industrial discharges (as identified in this study) together with diffuse pollution can further contribute on urban rivers exceeding the EU EQS (2013). Markiewicz *et al*. (2017) based on Pettersson *et al*. (2005) estimated that approximately 30 % (9.6 to 48 kg/year) of the PAHs loads found in runoff in an urban catchment are retained in the sediments and the remaining 70 % (22.4 to 112 kg/year) is transported through river water to other areas of the catchment, making the situation much more complex in minimising pollutant impacts. Applying this estimation to this study results means that, from a total of 1.67 kg/year of PAHs predicted load originated from road runoff, 0.50 kg/year (30 %) are retained in sediment while 1.17 kg/year are transported by the water matrix. Using this same concept to the predicted total PAH loads identified for the Lower Lee catchment, suggests that from the total of 781.37 kg/year PAH predicted loads, 234.41 kg/year are held in sediment while 546.96 kg/year are transported through the water column.

Diagnostic PAH ratios from the sediment field data measurements suggest that PAHs originate from pyrogenic sources that cannot be solely attributed to traffic (see Section 4.4). Other potential PAH sources in the study area include combustion processes in power stations, industry and/or domestic settings (Wilcke, 2007). The SFA results further complement the field data results, identifying industrial PAHs sources into the Lower Lee catchment, indicating the existence of a catchment wide issue, as pollutant emissions originates from a number of different sources throughout the urbanised Lower Lee catchment.

Overall, as per metals, PAHs results indicate that same PAHs do not behave consistently (by PAH, site and water body) between methods (samples analysis and SFA predictions).

Comparison of the ratios derived for PAHs (Table 5.9) indicate that most of the values as overpredictions for the Lower Lee catchment (35 out of 55) i.e. where the SFA predictions are > field value, indicating that the sediment samples are not a time integrated reflection of the PAH predicted loads discharged over the time period of one year and/or sediments are highly dynamic in terms of remobilisation, transportation (i.e. moving to other sites) and biodegradation. At sites A, D, E and F the PAH ratios are all classified as overpredictions while ratios for A at site G, J and B, for Fl at site C and for Bz(b)Fl and Bz(b)Fl for sites H, I and B fall within the prediction range, suggesting a possible reflection of PAH predicted loads on the PAH concentrations in the sediment matrix.

Table 5.9 shows ratio of SFA predicted loads to sediment field data (see Section 3.9.2.10).

Table 5.9 Ratios of predicted PAH loads/sediment field data by sampling site.

	Sampling site	A	Fl	Bz(b)Fl	Bz(a)Py	Bz(g,h,i)Pe
River Lee	A	4.57	7.27	13.69	15.44	7.88
	G	**1.16**	2.25	5.56	0.44	5.28
	H	0.43	0.06	**0.83**	**1.23**	0.45
	I	0.33	0.06	**0.61**	**1.01**	0.16
Lee Navigation	C	3.31	**1.35**	16.60	24.20	15.26
	J	**0.61**	0.17	2.07	2.85	3.05
	K	4.08	8.16	15.36	20.79	11.90
Tributaries	B	**0.54**	0.07	**0.78**	**1.44**	0.18
	D	8.26	2.74	12.55	14.88	8.59
	E	2.44	1.69	5.17	5.39	2.43
	F	2.84	4.92	10.39	9.40	6.40

Key: Values in a range of 0.5 to 1.5 (±50 %) are marked in bold.

Looking at each individual PAHs, three ratios for anthracene, Bz(b)Fl and Bz(a)Py and one ratio for fluoranthene are identified as in the prediction range. While ratios in prediction range were not identified for Bz(g,h,i)Pe. The absence of a consistent relationship between field sediment data sets and SFA predictions is understood to be a function of a variety of factors such as contaminant historical accumulation, inability to account for all discharges (e.g. CSOs) and the environmental behaviour of PAHs in sediment following their discharge.

In terms of components of the catchment, the River Lee sampling sites showed a total of 4 (20 %) ratio values (out of 20) as prediction range while 8 ratio values are classified as overpredictions and 7 as underpredictions. The ratios for all PAHs at site A are > 1.5 i.e. SFA predicted value is > field value. Site A, reported the highest predicted loads for the River Lee, which could be also due to the highest number of activities and companies at this site in relation sites G, H and I.

The River Lee Navigation component shows two ratios (out of 15) (Table 5.9) fall within the prediction range, and one ratio as underpredicted (for fluoranthene at site J). Most of the ratios are classified as overpredictions particularly evident at site K (site with highest number of activities and companies compared to other sites within this component). As previously mentioned, the underprediction ratios may be due to factors such as limited data sets, activities which were not accounted for (e.g. CSOs), and the on-going occurrence of environmental processes such as PAH remobilisation from the sediment matrix and or loss by e.g. microbial mediated degradation.

For the tributaries, three ratios (out of 20) fall within the prediction range, 15 ratios are classified as overpredictions and two as underpredictions. Only site B shows a mixture of ratios which are underpredictions and within the prediction range. Sites D, E and F have all ratios as overpredictions. It is interesting to note that while Sites D and E have the highest number of activities (5 and 4 respectively) and companies (11 at each site), site F shows same number of activities and companies as site B. However, the type of activities for these two differ, as whilst for site B there are waste non-hazardous and road runoff activities, at site F was identified manufactures of basic metals and metals products and road runoff activities (Table 3.8). This indicates that the type of activity is impacting in terms of impacting sediment quality.

As undertaken for the metals data sets, a correlation analysis was conducted to identify possible relationships between PAH predicted loads and field sediment concentrations for each of the three components of the receiving river system (Table 5.10).

Table 5.10 Correlation analysis of PAHs sediment field data with SFA predicted loads at the River Lee, Lee Navigation and Tributaries.

		PAHs in sediment				
		A	**Fl**	**Bz(b)Fl**	**Bz(a)Py**	**Bz(g,h,i)Pe**
River Lee	**r***	-0.69	-0.40	-0.74	0.28	-0.38
	P-value	0.31	0.59	0.26	0.72	0.62
Lee Navigation	**r***	**-0.99**	-0.76	-0.95	-0.85	-0.50
	P-value	**0.02**	0.44	0.20	0.35	0.67
Tributaries	**r***	0.49	0.45	0.42	0.47	0.30
	P-value	0.51	0.54	0.58	0.53	0.70
		A	**Fl**	**Bz(b)Fl**	**Bz(a)Py**	**Bz(g,h,i)Pe**
		PAHs from SFA				

Key: * r = Pearson Correlation; values in bold show the pairs of parameters with very strong correlation.

No significant correlations were identified in the River Lee component. Results shows an inverse correlation between predicted PAH and field sediment concentrations with the exception of Bz(a)Py which has a weak positive relationship. Analysis suggests that the SFA predicted PAH loads did not reflect actual PAH concentrations found in river sediment. The inverse correlation results suggest that concentrations of PAHs in the sediment matrix are not controlled by the loads of PAHs predicted to be discharged into the River Lee. Similar results are identified for the Lee Navigation component (Table 5.10) where the relationship between data sets is again inverse for all PAHs and not at a level that is statistically significant for any PAH with the exception of anthracene. As above, this data suggests that PAH predicted loads do not reflect those determined in river sediment. Sediment remobilisation and transportation of particulate matter from one place to another could be one of the reasons for that.

In terms of tributaries (Table 5.10), analysis of relationship between data sets similarly, indicates the absence of a relationship between predicted PAHs and field concentrations. Maity and Maiti, 2017 suggest analysis of the r-values (which are independent of sample size) as they can become more important than significance, P-values (which are affected by sample size), especially when showing high degree of association (± 0.50 to ± 1). However, although all the r-values for the Lee Navigation fall within the high degree of association classification but as inverse correlation, the r-values for the tributaries are all below 0.50, which reinforces that the obtained data do not allow to define any conclusions as to the relationships between these data sets.

5.3 Comparison of metals and PAHs SFA modelling results

Whilst for metals results, site D (8689.83 kg/year) was identified with highest metal predicted loads, followed by sites E (2993.23 kg/year) and K (2466.88 kg/year) (see Table 5.1 and Figures 5.1 and 5.2) mainly due to discharges from Deephams STW (at site D), refineries (at site E) and production of electricity (at site K) (see Figures 5.3 and 5.4), for PAHs site C (174.32 kg/year) presented the highest PAH predicted loads followed by site K (149.29 kg/year) and site D (121 kg/Year) (see Table 5.6 and Figure 5.6) mostly due to discharges from manufacture of chemicals and chemical products (at site C), production of electricity (at site K) and Deephams STW (at site D) (Figure 5.7). These results showed some similarity, for example, identifying sites D and K amongst the sites with highest metal and PAH loads predicted to be discharged into the Lower Lee catchment, calling our attention to potential main problematic areas and contaminant sources within the catchment.

Total loads of the six metals predicted to be discharged to surface water increase as follows: River Lee < Lee Navigation < Tributaries, with total loads of 2941.79, 3380.05 and 12981.73 kg/year respectively, whilst total loads of the five PAHs increase as follows: River Lee < Tributaries < Lee Navigation, with total predicted loads of 115.80, 291.93 and 373.64 kg/year, respectively. Results show tributaries with the highest metal load while for PAHs, the Lee Navigation presented highest load, indicating that type of activities at each area plays an important role in level of pollutant load. For example, the four tributaries (sites B, D, E and F) were responsible for discharging the majority of metal load (67.25% of the total metal load for the whole catchment) with Deephams STW (at site D) alone accounting for 34.79% of the total metal load for the whole catchment, making the tributaries highest contributors for metal load within the system, however, the main PAH sources were the manufacture of chemicals and chemical products and manufacture of basic metals and metal products, especially at sites C and K on the channel.

Correlation analysis was undertaken to identify the type and strength of relationships between metal and PAH predicted loads (see Table 5.11).

Table 5.11 shows statistically significant positive correlations were recorded for all metals with the PAH anthracene, suggesting these environmental pollutants are emitted from a common source and in this case the main activity in common for these contaminants is Deephams STW (see Figures 5.5 and 5.8).

Table 5.11 Correlation analysis of metals and PAHs predicted loads at the Lower Lee catchment.

		Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
A	r*	**0.83**	**0.92**	**0.94**	**0.92**	**0.75**	**0.93**
	P-value	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**
Fl	r*	0.50	0.43	0.45	0.38	0.52	0.38
	P-value	0.12	0.18	0.16	0.24	0.10	0.24
Bz(b)Fl	r*	0.42	0.39	0.48	0.38	0.34	0.37
	P-value	0.19	0.22	0.13	0.24	0.30	0.26
Bz(a)Py	r*	0.42	0.40	0.49	0.40	0.32	0.38
	P-value	0.20	0.22	0.12	0.22	0.34	0.24
Bz(g,h,i)Pe	r*	0.27	0.28	0.37	0.27	0.17	0.25
	P-value	0.43	0.40	0.26	0.42	0.62	0.46
Σ 5 PAHs	r*	0.45	0.43	0.51	0.42	0.38	0.40
	P-value	0.16	0.18	0.10	0.20	0.26	0.22

Key: * r = Pearson Correlation; Values in bold show the pairs of parameters with very strong correlation.

According to the Environment Agency (2019) metal and PAH emissions from Deephams STW have declined over the years 2013 to 2018. For example, selected metal loads decreased 19.62 % (from 6715.22 to 5397.92 kg/year) and PAH loads decreased 21.15 % (from 12.34 to 9.73 kg/year). However, there were fluctuations over time (i.e. some years an increase was reported while other years there were a decrease; for example, there was an increase in metal and PAH loads in 2018 compared to 2017) and with the rapid population growth reported contaminant loads are expected to increase (Liyanage and Yamada, 2017). Thus, the necessity of further studies to support impacts identification and water and sediment quality management in urban river catchments.

In terms of measurement ratios, results showed only 18.18 % (i.e. 10 out of 55) of the PAHs ratios and 24.24 % (i.e. 16 out of 66) of the metals ratios were in the predicted range (0.5 to 1.5 (± 50 %)). However, correlation analysis for these two data sets (see Tables 5.5 and 5.10) revealed a very strong positive correlation for all metals at a significant level ($p \leq 0.05$), except for Ni for the tributaries while for PAHs, only Anthracene showed a very strong positive correlation at the Lee Navigation, strongly indicating that SFA can be used as a tool to predict metal loads to identify hotspots in smaller urban rivers and consequently be a useful tool in identifying pollutant sources.

5.4 SFA results uncertainties

Based on the SFA modelling results for selected metals and PAHs, it is important to identify the sources and levels of uncertainties associated with its predictions to ensure its usefulness as an analytical tool for supporting environmental policy and management (Laner *et al*., 2014; Hedbrant and Sörme, 2001).

The classification system used (whereby a value that was within a ± 50 % of the field concentration was classified as 'acceptable level of prediction') identified 50 ratios out of a total of 66 (for metals) and 45 ratios out of a total of 55 (for PAHs) as either underpredictions (i.e. field concentrations exceeded SFA predicted concentrations) or overpredictions (field concentrations were less than SFA predicted values) with correlation analysis indicating that relationships between the two data sets were not significant for the majority of the occasions. A range of limitations and uncertainties were identified (see Table 3.11). These include the fact that activities classified under an EU NACE/UK SIC code and located within 1 km of each sampling site were considered. As previously discussed, (see Section 3.9.2.8), key businesses may have been missed and it is not possible to include known important activities such as CSOs and aerial deposition. Further, the SFA model did not account for historic contamination or the complexity of ongoing processes which may impact on substance occurrence and detection such as bioactivity, physico-chemical transformations, resuspension, transportation and deposition.

Overall, the use of ratios indicates that SFA output may be more predictable for metals in contrast to organic pollutants which can degrade partially or completely on discharge to the environment.

The use of emission factors can also impact SFA results; these are reported as annual emissions and therefore these do not account for temporal variations. It is also, important to note that the results from the field data were from specific sampling sites on a specific date rather than the annual average data value. Therefore, annual variation in flows causes uncertainties (Asmala and Saikku, 2010).

Further factors contributing to the differences between SFA and sediment field data results include the complexity of the study area, with considerations of river hydrology and sediment dynamics.

Further uncertainty is associated with the impact of stormwater runoff. Whilst emissions from vehicles and asphalt were integrated to predict loads carried by road runoff, emissions from other sources such as roofs, building facades, car parks and street furniture etc were not accounted for. The inability to incorporate these sources is identified as a factor in the lower than anticipated contribution of road runoff (e.g. Lützhøft *et al*., 2012; Lundy and Wade, 2011; Becouze-Lareure *et al*., 2016; Brown and Peak, 2005; Järveläinen *et al*., 2017).

From the start, the research focused on the development of a desk-based substance flow analysis approach as a potential management tool to identify and quantify point and diffuse loads of selected organic and inorganic pollutants originating in the Lower Lee catchment, accounting for emissions occurring directly into surface water as per available data which in this case was from data reported by e.g. Environment Agency pollution inventory data set. Thus, despite the fact that a combination of wet and dry deposited materials is (to some extent) addressed by the inclusion of direct discharge of surface runoff from roads, available data sets do not specifically address aerial deposition (let alone support a differentiation between these two modes), consequently the SFA results do not include direct wet/dry deposition into surface water, providing an additional source of uncertainty.

Another important point to note is that, in keeping with the substance flow analysis methodology which requires a time period to be established, the substance flow analysis effectively provided a 'snapshot of activities' (e.g. for the period of one year; 2013). Thus, sediment samples were collected over a one year period from the superficial layer of the river bed and although being only superficial layer, they may covered contamination from over a one-year period, thus impacting on analysis results when comparing the monitoring results with SFA outcome.

In all, SFA results have shown that, although there are limitations and uncertainties, SFA can be a valuable tool in understanding the sources and distribution of selected substances in urban rivers, especially to better understand industrial metabolism of emission sources providing evidence which can influence and support the process of policy making (European Environmental Agency, 2019; Ekvall *et al.*, 2007).

5.5 Sensitivity analysis results

A sensitivity analysis involving correlation analysis utilising mean, median, minimum and maximum values was undertaken when comparing SFA outputs with field data. And the systematic removal and addition of different activities in the SFA data and the use of mean, median, minimum and maximum values when comparing SFA outputs with field data through ratio results was performed to evaluate the robustness of the model.

Correlation analysis was undertaken between pollutant predicted loads and sediment field data using mean, median, minimum and maximum values for each data set, and correlation results from each option were evaluated to see which one perform better (with highest Pearson's coefficient value e.g. a strong 0.60 – 0.79 to very strong 0.80 – 1.00 correlation, at significant level $p \leq 0.05$) for the application of the model (as determined by Ahad *et al*., 2017; Kumar *et al*., 2019; Minitab, 2017).

However, results showed that using median, minimum and maximum values the Pearson's coefficient fell between very weak (0.00 – 0.19) to moderate (0.20 – 0.59) classifications and were not statistically significant ($p \geq 0.05$). Use of mean values of pollutant predicted loads and sediment field data showed Pearson's coefficient varied from very weak (0.00 – 0.19, for 2 metals, Hg and Ni at the River Lee) to very strong (0.80 – 1.00, with statistical significance ($p \leq 0.05$) for 5 metals, Cd, Cu, Hg, Pb and Zn Pearson's coefficient ranging 0.94 to 0.99 at the Tributaries and 1 PAH, anthracene with a Pearson's coefficient of -0.99, at the Lee Navigation). Although for the means correlation analysis showed a weak relationship for two metals, for the median, minimum and maximum this number was higher and utilising the mean was the only option which very strong correlation was present. Hence, these results suggest that SFA utilising mean values is preferred when exploring relationships between pollutant predicted loads and sediment field data.

Table 5.12 shows the outcome of the sensitivity analysis in respect to ratios obtained from SFA results and sediment field data (Appendices T1 to T14) when including/excluding the different activities from the SFA data and then utilising mean, median, minimum and maximum values for SFA and sediment field data. It shows the number of ratios under each classification applied to this research (underprediction, acceptable level of prediction (0.5 to 1.5 (± 50 %) and overprediction (see Section 3.9.2.10). As described in Section 3.9.2.9 polluting activities which reported highest predicted pollutant loads were removed and added back to the model to see how the strength of the relationship responded to different combinations. For metals those activities were the wastewater treatment plant, refineries and production of electricity (EfW power plants) and for PAHs were the wastewater treatment plant, the manufacture of chemical and chemical products and the manufacture of basic metals and metal products for PAHs. The results demonstrated that although in some cases (e.g. after removing the three activities which reported highest predicted pollutant loads from the metals model) the final total predicted load was reduced by over 50 % (e.g. the three activities with metal highest predicted loads represented a total of 10694 kg/year which is 55.40 %

of the total metal load of 19303.57 kg/year reported in Section 5.1.1, Table 5.1), the highest number of ratios fallen within the acceptable prediction range (identified as 0.5 to 1.5 (± 50 %)) was for the model which included all the activities. This indicates the importance of the major emitters in the model to the extension that their exclusion has an impact on the strength of the relationship between predicted and field data and the ratio classifications, suggesting that the model output is sensitive to the inclusion/exclusion of industrial activities with the strength of the correlation with field data sets increasing as further emissions are included. Also, the fact that the relationship between SFA predictions and field data does not completely breakdown when major emitting industries are excluded indicates that multiple sources contribute to sediment pollutant loads. The use of median, minimum and maximum (including all activities) were also considered and tested through sequential comparison of each category of field data with SFA outputs. Use of means to compare with field data showed the best performance of the model as evidenced by the largest number of the ratios results falling within the acceptable prediction range (identified as 0.5 to 1.5 (± 50 %)). The sensitivity analysis also indicates that some parameters result in greater changes (as evidenced by the number of ratios which fall within the range of 0.5-1.5) than others. For example, when using the minimum values, the number of ratios within the acceptable prediction range (0.5 to 1.5 (± 50 %)) for metals and PAHs models, decreased from 16 and 9 to 1 respectively, suggesting that the mean is the most robust measure when summarising data per site.

Table 5.12 Sensitivity analysis of ratios of predicted PAH and metals loads/sediment field data on inclusion/exclusion of activities.

	SFA model	Number of ratios as underprediction	Number of ratios within the acceptable level of prediction (0.5 to 1.5 (± 50 %)	Number of ratios as overprediction
Metals	Model with all activities – Model applied in this research	8	16	42
	Model without wastewater, refineries and production of electricity activities	23	12	31
	Model without wastewater activity	22	11	33
	Model without refineries activity	20	12	34
	Model without production of electricity activity	22	14	30
	Model using median with all activities	49	13	4
	Model using minimum values with all activities	64	1	1
	Model using maximum values with all activities	39	14	13
PAHs	Model with all activities – Model applied in this research	10	10	35
	Model without wastewater, manufacture of chemical and chemical products and manufacture of basic metals and metal products activities	36	9	10
	Model without wastewater activity	11	9	35
	Model without manufacture of chemical and chemical products activity	20	7	28
	Model without manufacture of basic metals and metal products activity	26	8	23
	Model using median with all activities	29	9	17
	Model using minimum values with all activities	46	1	8
	Model using maximum values with all activities	18	9	28

5.6 SFA as potential tool to support decision makers

A number of authors (Stanisavljevic and Brunner, 2014; Sörme and Lagerkvist 2002; Chèvre *et al*., 2011; Ling *et al*., 2009; Comber *et al*., 2013) argue the need to look at smaller urban rivers in a mathematical way to better understand substance flow, identify areas and pollutants of concern. In addition, they highlight the necessity to translate results into practical indicators to further support policy and scientific debates and inform policy making for the monitoring of pollutant discharges. Hence, this study considered the potential use of the substance flow analysis tool to support catchment managers and policy makers identify locations for the installation of mitigation measures.

Allesch and Brunner (2015) argue that for policy making processes it is essential to know the quantity of contaminant accumulated in a system (stock) and its sources and results presented in this study showed that the developed SFA model was able to quantify emission loads and identify pollutant sources in smaller water bodies (see Sections 5.1 and 5.2) highlighting possible pollutant sources as is the case of metal loads results which identified Deephams STW (at site D, Salmons Brook) as highest discharger while for PAH loads manufacture of chemicals and chemical products and manufacture of basic metals and metal products, especially at sites C and K were identified as major dischargers. Additionally, results from this study demonstrated how monitoring pollutant data can be used to ground-truth SFA results, e.g. results from the correlation between predicted metal loads and sediment metal concentrations indicated a very strong correlation ($r > 0.9$) at a significant level ($p < 0.5$) for tributaries for the metals Cd, Cu, Hg, Pb and Zn. This further corroborates the use of SFA as an empirical method to support policy and scientific discussions for identifying locations for the implementation of pollutant emission mitigation measures. Thus, this model is of direct support for decision makers, providing them with vital information through the prediction of pollutant loads and identification of hotspots which present potential to exceed quality standards/guidelines, consequently supporting communication and facilitating transparency between the various groups engaged in river water and sediment quality discussions such as stakeholders from public, industrial and administrative sectors.

The analysis of the model uncertainties can serve as a tool to inform decision makers through the identification of knowledge gaps and guiding stakeholders to identify areas requiring further data collection (e.g. due to scarcity of data, this study directed to possible pollutant sources which were not included in the SFA model (e.g. CSOs activity)) (Brunner and Ma, 2009). This could be used as a guide to identify gaps and facilitate discussion between stakeholders on finding the best way to minimise uncertainties, for example, identifying that CSOs can be one of the missing pollutant source in the model, steps could be taken towards promoting the necessity of continuous monitoring of CSOs pollutant emission (if not yet in place) with the requirement of making data available to support a better development of SFA model for a more efficient management of water and sediment quality in urban rivers. This can further contribute to the knowledge about the magnitude of stocks of specific pollutants and potential sources and increase the understanding of complexity of environmental issues, which can contribute to the environmental management process (Lindqvist-Östblom *et al.*, 2009), e.g. through the understating the implications of transboundary pollution (i.e. when a pollutant which originates in one area is able to impact another area through pathways such as water and sediment).

As a whole, the developed SFA model is identified as an important tool to provide scientific support for stakeholders based on the provision of both quantitative (i.e. quantifying pollutant loads) and qualitative (i.e. identifying hotspots) information (Donner *et al*., 2010) and results used for monitoring and evaluation of pollutants and areas of concern, which can support the guidance of policy development in the field of achieving EU WFD compliance (Wiedmann *et al*., 2006).

CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS

This study set out to evaluate the use of substance flow analysis as a tool to predict sediment pollution hotspots in an urban river catchment. In order to address the aim, the study explores the presence of organic and inorganic contaminants in urban river water and sediment, including a batch test laboratory experiment to evaluate the relationship between sediment and water quality. Substance flow analysis was used as a desk-based approach to identify and quantify point and diffuse loads of selected pollutants within the study area and results ground-truthed through comparison with field sediment data. The use of SFA model outcomes as a tool to inform decisions by catchment managers and policy makers together with implications of the results, limitations and recommendations for future work are presented below.

6.1 Conclusions

With 2027 being the European Union (EU) Water Framework Directive (WFD, 2000) deadline for all European surface and ground waters to achieve good chemical and ecological status, the pressure has grown on EU Member States to demonstrate compliance. Some states are already reporting that it will be unlikely that ecological ambitions will be met by the given date due to factors such as political issues (e.g. lack of legal authority to take necessary measures) or the difficulties surrounding the process of identifying contamination sources, especially in cases of diffuse pollution (Kats *et al.*, 2022). In the UK, Defra (2020) highlighted the need to improve the quality of UK water bodies and the 25 Year Environment Plan aim for at least ¾ of the water bodies to reach ‘good status’ as defined by the Water Framework Directive. In this context, the Environment Act 2021, empowers Ministers to set long-term statutory targets for the improvement of the natural environment, requiring a long-term target for the improvement of surface waters to be established. Hence, this is a great opportunity to inform the legislation to deliver a better water and sediment quality management in both sensitive local areas and heavily modified urban river catchments

(House of Commons, 2022). Many rivers in England and Wales have been significantly contaminated with metals and organic pollutants released from anthropogenic activities such as industry, mining and road runoff (Environment Agency, 2008c; Vane *et al.*, 2022) and the Lower Lee catchment is no exception. This area has been impacted over the years with contamination from sewage discharges from both combined and separate surface water sewer systems which directly (and indirectly via sediment accumulation), are identified as significantly affecting the quality of the catchment surface waters (Maddocks, 1993; Snook and Whitehead, 2004; Davies, 2011; Canal and River Trust, 2012; Environment Agency, 2012; Patroncini, 2013; Thames21, 2019).

This study reports the extent of metal and PAHs contamination in river water and sediment in the Lower Lee catchment by comparing the determined concentrations with reported studies, established guidelines/standards and through the application of different pollution indices. From the monitoring analyses results it is concluded that mean Cd, Cu, Hg, Pb and Zn concentrations in the sediment exceed selected Dutch (Esdat, 2000) and Canadian (CCME, 2001) sediment guidelines. This is further supported by the use of the pollution load index (PLI) which indicates that most of the sampling sites were polluted. In terms of PAHs, results also indicate exceedance of the Dutch (Esdat, 2000) and Canadian (CCME, 2001) sediment guidelines.

The results obtained from the batch test reveal that the amount of metal released into the sediment vary between metals and sites and the level of variation is generally within an order of magnitude, ranging from 0.12 % (Sn, site A) to a maximum of 6.12 % (Cd, site E). This is of particularly importance with respect to the development and implementation of programmes of measures for surface waters to achieve good ecological status. For example, when considering the findings of the batch tests undertaken in this study which show that sediment resuspension can further contribute to aqueous contaminant levels, emphasising the link between sediment quality and achieving EU WFD objectives (Valipour *et al.*, 2017; UK TAG 2008a; UK TAG 2008b; Gilbert *et al.*, 2005; Hoffman *et al.*, 2019). Given the fact that sediments can act as both a sink and a source for contaminants (Brils, 2008; Jones *et al*., 2019; Foster and Charlesworth, 1996) the findings in this study further highlight the need to take into consideration sediment quality when evaluating surface water quality in urban catchments.

Comparison of median metal concentrations with background reference concentrations (MBRC) for surface waters suggests that anthropogenic pollutant sources (e.g. sediment remobilisation, land use and/or physico-chemical parameters), play an important role in levels of metals in surface waters of the Lower Lee catchment. An elevated Sn concentration of 13.90 ± 0.13 μg/l at site K on the sampling date of 14th August 2015 (Appendix A7) and Cu concentration (117.71 ± 0.65 μg/l) detected at site B on 23rd March 2016 (Appendix A8) were identified, suggesting a pollutant specific discharge at specific dates as opposed to e.g. the capture of sediment resuspension event which would be anticipated to lead to several substances occurring at a greater than usual concentration, reinforcing the possibility of anthropogenic pollutant sources.

As SFA has become a fast-growing field of research with increasing policy relevance (Zeng *et al*., 2018; European Environmental Agency, 2007; Brunner 2012), this work explores the use of a substance flow approach as a model to predict target pollutant loads discharged into an urban river through identified activities and ground-truthing the modelling results through field monitoring sediment quality. Through the substance flow analysis modelling approach developed in this study, it was predicted that a total of 19,304 kg/year of metals (sum of six metals) and 781 kg/year of PAH (sum of five polyaromatic hydrocarbons) were discharged into surface waters within the study area. In addition, through the model it was possible to identify areas/pollutants of concern, with Deephams Sewage Treatment Works (located at site D) associated with the highest metal load (6,715 kg/year) and a total of 12 kg/year for PAHs, corresponding to 33.5% of the total discharges for all selected pollutants (metals and PAHs) in the Lower Lee catchment. Results from the SFA modelling in the tributaries component predict highest loads for all metals at Salmons Brook (site

D) supporting the use of the sediment pollution load index (PLI) approach which also identified Salmons Brook as the most metal-polluted sediment site amongst the tributaries.

The above results show that sediment pollutant concentrations pose a risk to good ecological status (i.e. exceedance of relevant standards). SFA results also indicate that whilst tributaries were found to receive the largest metals loads, the Lee Navigation is predicted to receive the highest pollutant load for PAHs. This is associated with the type of activities discharging these pollutants in these areas, for example Deephams STW (at site D, tributary Salmons Brook) is identified as discharging most metals, while the main sources for PAHs are manufacture of chemicals and chemical products and manufacture of basic metals and metal products, especially at sites C and K (at the Lee Navigation). This highlights the fact that the type of activities – and not just the number of activities - play an important role on water and sediment quality and emphasize the benefit of using SFA as a predictive tool to further support the identification of pollution hotspots due to the site-specific influence of land use

The assessment of the strength and significance of correlation between predicted metal loads and sediment metal concentrations indicate the very strong relationship (as per Pearson's correlation coefficient above 0.9) at a significant level ($p < 0.5$)), for the tributaries for the metals Cd, Cu, Hg, Pb and Zn. This indicates that the SFA approach developed in this study has potential for identifying pollutant hotspots in smaller water bodies. Thus, demonstrating that, although SFA is not functional for complex systems such as River Lee and the Navigation Channel due to their physical complexity and unreported pollutant emissions, it is effective for less complex/small rivers such as the tributaries.

A number of authors (Fältström and Anderberg, 2020; Sörme and Lagerkvist 2002; Allesch and Brunner, 2015) concluded that SFA can serve as a tool to understand pollutant flows in urban river system but results from this study, as discussed in Section 5.6, shows that SFA would also be of great value to support stakeholders in decision/policy making processes through the provided quantitative (quantification of pollutant loads) and qualitative (identification of hotspots e.g. Deephams STW as the highest metal load discharger at site D) information. The integrated methodology developed in this study that combines monitoring data with substance flow analysis is not limited to use in the Lower Lee catchment as it is suitable to be applied in other urban river catchments in the UK and internationally.

6.2 Limitations of the study

The identification and evaluation of the implications of research programme limitations are important stages in terms of both contextualising the use of research findings and informing future research agendas (Ross and Zaidi, 2019; Resnik and Shamoo, 2017). Thus, key research limitations are described below.

I. Analysis of water samples in this study determined the total concentration of selected metals and did not consider bioavailability, making it difficult to compare results to the available UK TAG and EU EQS standards and take into consideration metal background reference concentrations as they refer to dissolved phase fraction/bioavailability of each metal. It is important to note that a key objective of this research is to '... ground-truth the SFA predictions through field data', where SFA data draws on information reported as total metal concentrations (kg/year), thus determination of total metal concentrations in field samples is required to facilitate comparison between these approaches. In addition, the focus of environmental quality standards has shifted from the dissolved fraction to the bioavailable fraction (e.g. UK TAG, 2013) in recognition of the fact that the dissolved fraction is itself not homogenous (e.g. see Lindfors *et al*., 2021 for discussion on the relationship between the dissolved, colloidal and truly dissolved bioavailable fractions in urban stormwater samples and how direct analytical measurement of the bioavailable fraction in field samples is extremely challenging.

II. As previously noted, river hydrology and hydraulics can directly impact on water and sediment quality and themselves be influenced by rainfall and surface runoff, affecting sediment transport and consequently impacting on contaminant distribution (Hrissanthou, 2015; Rahman *et al.*, 2021). However, although river flow data was taken into consideration in this study (see Section 4.1.1) further aspects of river (hydrology/hydraulics) were not explored as its collection was out of scope for this study.

III. Although it rained heavily on the 14th August 2015 sampling event, this was the only sampling trip in which rainfall was experienced. It would be necessary to have more dates under such conditions (i.e. wet weather) to enable the differences in pollutant concentrations between wet and dry weather to be evaluated. The fact rainfall was only experienced on a single sampling date may also have had an impact on the SFA model output as wet weather conditions are known to contribute to pollutant enrichment in urban rivers, especially through storms/flash flooding after a long spell of dry weather (Becouze-Lareure *et al*., 2016; Järveläinen *et al*., 2017), which can lead to flooding and combine sewer overflow, overwhelming of local drainage systems, disturbance of aquatic ecosystems and accelerating discharges of industrial and urban toxic materials and nutrients into waterways (Talbot *et al*., 2018; Lintern *et al*., 2018). Hence, developing a more complete understanding of the impact of wet weather events would be important to further account for pollutant distribution (they could not be included in this study as it would be necessary to apply modelling and further data collection which was out of scope for this research).

IV. Wet/dry deposition has been reported as an important parameter to understand how and why water quality differs across space (Lintern *et al*., 2018) and although this study accounted for a combination of wet and dry deposited materials of indirect discharge to surface runoff from roads, this was not enough to cover wet/dry deposition as a whole, thus, the absence of aerial deposition quantification is a limitation in this research. The main objective of this study which is the ‘development of a desk-based substance flow analysis approach as a potential management tool to identify and quantify point and diffuse loads of selected organic and inorganic pollutants originating in the Lower Lee catchment’ accounting for pollutant discharged into surface water as per available data, which in this case was from data reported by e.g. Environment Agency pollution inventory dataset. This EA pollution inventory dataset reported emissions to surface waters only. Hence, wet/dry deposition is not considered in this work. Additionally, whilst data in literature recognise that wet/dry deposition can exert impact on surface water quality (Lintern *et al.*, 2018; Connan *et al.*, 2013) understanding of how important this, still unclear (Pan and Wang, 2015; Totten *et al.*, 2006; Pandey and Singh, 2015).

V. SFA requires a time period to be established and as the aim of this study is to develop a snapshot rather than a legacy of activities, emissions reported for one year period (2013) and field sediment samples taken from the top/superficial layer of the river bed were considered (see Section 3.9.2.2.). This was noted as one of the limitations in this study as, although sediment samples were collected from the superficial layer of the river bed, they have covered contamination from over a one-year period (e.g. sediment resuspension and activities outside this period), thus impacting on analysis results when comparing the monitoring results with SFA outcome. However, this study was still able to keep in with the research question which was to evaluate if there was a relationship between current land use activities and sediment quality as sediment management tool.

6.3 Recommendations for future research

The main product from this study is the substance flow analysis model which enabled a source-based pollution analysis on part of an urban river catchment. The modelling framework was developed to be flexible in order to facilitate future development and adaptation of the model. One of the main overall goals of the UK government is to solve the major environmental problems currently faced and the task of monitoring and evaluating progress towards this goal has been entrusted to governmental departments such as Defra and environmental agencies (e.g. Environment Agency). The Environment Bill, which has been introduced after the withdrawal process of the United Kingdom (UK) from the European Union (EU) (January 2020), to make provision about targets, plans and policies for improving the natural environment and the prospects of reducing the environmental impacts of chemicals in the UK, depend to a very significant degree on the chemicals policy adopted into this Bill (House of Lords, 2020; Environment agency, 2019b). And with the flow of chemicals in the society affecting urban water systems in many ways and from different sources, the SFA model has the potential for being part of such a toolkit for long term and cost-effective evaluation of substance flows of priority pollutants. Therefore, many of the following recommendations below relate to how to reduce uncertainties associated with - and facilitate – the use of SFA.

I. Due to scarcity of data, this study directed to possible pollutant sources which were not included in the SFA model (e.g. commercial and recreational boating and combined sewer overflows activities). In addition, road runoff was consistently the lowest source of pollutant load at all sites, contradicting several other research studies (European Environmental Agency, 2019; Markiewicz, 2017; Watts *et al*., 2010) which suggest it is relatively a much more important contributing source. A factor in this could be that AADT data in the format required was available only for a limited number of roads within the study area. These gaps were important as there are other roads which may had a considerable contribution in road runoff. Thus, in-depth study into these knowledge gaps is recommended.

II. As discussed in Section 6.2, inclusion of metals bioavailability and speciation of metals in the field i.e. its partitioning between particulate, colloidal fractions and their associated implications for bioavailability were out of the scope of this study. However, in terms of supporting stakeholders to further prioritise sites for remediation, inclusion of field sediment physico-chemical parameters would enable knowledge of substance bioavailability to be integrated and thus their inclusion is recommended for future research and sampling campaigns.

III. As explained in Section 6.2 most of the sampling dates occurred during dry weather with only one date covering wet weather conditions, thus it was not possible to evaluate relationship between pollutant level and wet weather conditions. Also, considering the impact of wet weather events on pollutant distribution it is recommended for more wet weather sampling to be covered by future studies.

IV. Batch test result highlighted the pivotal role that sediment resuspension plays in further contributing to aqueous contaminant levels. Thus, making it clear that sediment resuspension can negatively impact urban rivers in achieving EU WFD objectives, highlighting the urgent need for the development of sediment quality standards for a more efficient management of surface water in urban rivers.

V. Various SFA studies (Stanisavljevic and Brunner, 2014; Huang *et al*., 2012; Laner *et al*., 2015) reported the challenges around data scarcity and results from this study was not different. Thus, it is recommended for continuous monitoring of water and sediment quality in urban rivers, especially by stakeholders such as Environment Agency and Thames21 and data to be made available to facilitate future research. This also apply for wastewater companies as through this study it was experienced the challenge in getting hold of data from local water company, where negative responses to data requests were usually justified as ‘data confidentially’ or ‘data unavailability’, even though the Environmental Information Regulations 2004 give people the right of access to environmental information (term referred to as ‘*presumption in favour of disclosure*’).

VI. Through the SFA results presented in this study it was noted that pollutant discharges are not limited to negatively impact a limited area but usually is cross-boundary where a pollutant discharge at one site can directly impact other sites and these can be located at other catchments (as in the case of site A which may receive discharges from Upper Lee catchment). Thus, it is recommended the need for engagement exercises amongst stakeholders from different catchments to work together to facilitate sediment and water pollution mitigation and policy development, especially when different regulatory and mitigations approaches are taken by different groups, hence this engagement work could further contribute for knowledge exchange opportunities and uniformity in regulatory approaches across catchments.

VII. Currently, most water sediment quality strategies largely focus on the environmental aspects (e.g. pollutant emission and physico-chemical properties), leaving out underlying social and economic problems and barriers which could affect decision making (e.g. community and company owners' behaviour and beliefs towards pollution mitigation). Future studies based on a holistic approach for river water and sediment quality evaluation including such aspects (e.g. through application of survey to formal and informal sectors) would be of great value in better understanding and mitigating environmental impacts in water and sediment quality of urban rivers.

VIII. Growing attention to the plastic and pharmaceuticals contamination in urban rivers has shown how these pollutants have an extensive negative impact on water and sediment quality and consequently on human health and environmental ecosystems (Honingh *et al.*, 2020; University of York, 2021; Greenpeace, 2019; Maijer *et al.*, 2021). Thus, although this study focused on some of the toxic metals and PAHs discharged into an urban river catchment, the study of sediment quality coupled with SFA on other contaminants such as plastics and pharmaceuticals is recommended.

6.4 Contribution to knowledge

I. This study adds to the body of knowledge of urban river water and sediment quality and patterns in the types and concentrations of pollutants and associations with land use. The ground-truthing of SFA predicted metal and PAH concentrations with monitoring data has not been previously reported.

II. This study also integrated an approach (See Appendix O1) to predict road runoff loads into an SFA framework. The method utilised (based on the approach developed by Middlesex University in collaboration with Thames21 to estimate the overall pollutant loadings to the road surface) was applied in this study to predict road runoff concentrations discharging into surface waters. The results were integrated into the SFA modelling, showing that other models representing sources not yet included in emission databases can be incorporated into SFA in an effective manner.

III. As described in Section 5.6, this study highlights that SFA results can contribute to informing policy development and implementation for the mitigation of pollutants discharges, e.g. through the quantification of pollutant loads discharged into urban surface waters and the identification of hotspots to support allocation of resources. Thus, coupled with water and sediment monitoring, the use of SFA is supported as a valuable management tool which allows identification and prioritisation of key issues within a system, to guide decision makers on where priorities and facilitating the identification of mitigation measures.

IV. In terms of sediment quality, this study has shown that sediment remobilisation can directly impact negatively on water quality, confirming the need to address sediment quality if urban water bodies are to achieve good chemical and ecological potential by 2027 (as required by European Union (EU) Water Framework Directive for heavily modified water bodies; WFD, 2000). Hence, as previously mentioned, in order to more effectively manage water quality in urban rivers, the development of sediment quality standards is urgently required to support efforts to minimise pollutant contamination and further protect urban surface water bodies.

REFERENCES

Abdel-Shafy, H.I. and Mansour, M.S.M. (2016) A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egyptian Journal of Petroleum*, 25, pp.107-123.

Adams, W., Blust, R., Dwyer, R., Mount, D., Nordheim, E., Rodriguez, H. and Spry, D. (2020) Bioavailability assessment of metals in freshwater environments: A historical review. *Environmental Toxicology and Chemistry*, 39(1), pp.48-59.

Aderinola, O.J., Clarke, E.O., Olarinmoye, O.M., Kusemiju, V., Anatekhai, M.A. (2012) Heavy metals in surface water, sediments, fish and perwinkles of Lagos Lagoon American-Eurasian. *Journal of Agricultural Environmental Sciences*, 5, pp.609-617.

Agunbiade, F.O., Olu-Owolabi, B.I. and Adebowale, K.O. (2010) Seasonal and spatial variations analysis of pollution status of Ondo coastal environment Nigeria using principal component analysis. *Geochemical Journal*, 44, pp.89-98.

Ahad, N.A., Abdullah, S., Zakaria, N.A., Yahaya, S.S.S., and Yuso, N. (2017) Median based robust correlation coefficient. *AIP Conference Proceedings*, 1905, 050002.

Allen, L. (2020) *Lead Matters: The Lead REACH Consortium highlights the essential role of lead in Europe*. Lead REACH Consortium, EU.

Allesch, A. and Brunner, P.H. (2015) Material flow analysis as a decision support tool for waste management: A literature review. *Journal of Industrial Ecology*, 19(5), pp.753-764.

Ali, M. and Abdel-Satar, A. (2005) Studies of some heavy metals in water, sediment, fish and fish diets in some fish farms in El-Fayoum province, Egypt. *Journal of Aquaculture Research*, 31, pp.261 -273.

Alves, R.I.S., Sampaio, C.F., Nadal, M., Schuhmacher, M., Domingo, J.L. and Segura-Muñoz, S.I. (2014) Metal concentrations in surface water and sediments from Pardo River, Brazil: Human health risks. *Environmental Research*, 133, pp.149-155.

Ander, E.L., Cave, M.R. and Johnson, C.C. (2013) *Normal background concentrations (NBCs) of contaminants in English soils: Final project report*. British Geological Survey, Commissioned Report CR/12/107N, 128pp.

Andrade, C. (2015) Understanding relative risk, odds ratio and related terms: as simple as it can be. *Clinical and Prcatical Psychopharmacology*, 76(7), pp.857-861.

Angelovičová, L. and Fazekašová, D. (2014) Contamination of the soil and water environment by heavy metals in the former mining area of Rudňany (Slovakia). *Soil and Water Research*, 9, pp.18-24.

Angerville R., Perrodin Y., Bazin C. and Emmanuel E. (2013) Evaluation of ecotoxicological risks related to the discharge of combined sewer overflows (CSOs) in a Periurban River. *International Journal of Environmental Research and Public Health*, 10(7), pp.2670-2687.

Antikainen, R., Dahlbo, H., Melanen, M. and Ollikainen, M. (2005) Decision support approaches: life cycle assessment (LCA) and substance flow analysis (SFA). *Clean Technologies and Environmental Policy*, 9, pp.32-37.

Anyakora, C. and Coker, H. (2006) Determination of polynuclear aromatic hydrocarbons (PAHs) in selected water bodies in the Niger Delta. *African Journal of Biotechnology,* 5(21), pp.2024-2031.

ArcGIS® (2019) Software version 10.71. ArcGIS® and ArcMap™ by ESRI.

Arena, U. and Gregorio, F.D. (2014) A waste management planning based on substance flow analysis. *Resources, Conservation and Recycling*, 85, pp.54-66.

Asante, K.A. (2005) *Distribution of trace elements in the environment. Case study in the East China Sea and Ghana.* MSc Thesis. Graduate School of Agriculture, Ehime University.

Ashraf, M.A., Maah, M.J. and Yussoff, I. (2012) Chemical speciation and potential mobility of heavy metals in the soil of a former tin mining catchment. *The Scientific World Journal*, 1, pp.1-11.

Asmala, E. and Saikku, L. (2010) Closing a loop: Substance flow analysis of nitrogen and phosphorus in the rainbow trout production and domestic consumption system in Finland. *AMBIO A Journal of the Human Environment*, 39(2), pp.126-135.

Azapagic, A., Pettit, C. and Sinclair, P. (2007) A life cycle approach to mapping the flows of pollutants in the urban environment. *Clean Technologies and Environmental Policy*, 9, pp.199-214.

Baccini, P. and Brunner, P.H. (2012) *Metabolism of the anthroposphere: analysis, evaluation, design*. 2nd edn. Harvard: MIT Press.

Baccini, P. and Brunner, P.H. (1991) *Metabolism of the anthroposphere: analysis, evaluation, design*. 1st edn. Harvard: MIT Press.

Baek, C-Y., Tahara, K. and Park, K-H. (2018) Parameter uncertainty analysis of the life cycle inventory database: Application to greenhouse gas emissions from brown rice production in IDEA. *Sustainability*, 10(4), pp.922-945.

Bai, L., Qiao, Q., Li, Y., Xie, M., Wan, S. and Zhong, Q. (2015) Substance flow analysis of production process: A case study of lead smelting process. *Journal of Cleaner Production*, 104, pp.502-512.

Balat, M. (2004) Material flow analysis and its status in Europe countries. *Energy Exploration and Exploitation*, 22(6), pp.441-455.

Baran, B., Mamis, M.S. and Alagoz, B.B. (2016) Utilization of energy from waste potential in Turkey as distributed secondary renewable energy source. *Renewable Energy*, 90, pp.493-500.

Barros, J.A.V.A., Souza, P.F., Schiavo, D. and Nobrega, J.A. (2015) Microwave-assisted digestion using diluted acid and base solutions for plant analysis by ICP-OES. *Journal of Analytical Atomic Spectrometry*, 31, pp.337-343.

Barus, B.S., Chen, K., Cai, M., Li, R., Chen, H., Li, C., Wang, J. and Cheng, S-Y. (2021) Heavy metal adsorption and release on polystyrene particles at various salinities. Frontiers in Marine Science, doi: org/10.3389/fmars.2021.671802.

Bathi, J.R., Pitt, R.E. and Clark, S.E. (2012) Polycyclic aromatic hydrocarbons in urban stream sediments. *Advances in Civil Engineering*, 34, pp.4064-4070.

Bay, S.M, Zeng, E.Y., Lorenson, T.D., Tran, K. and Alexander, C. (2003) Temporal and spatial distributions of contaminants in sediments of Santa Monica Bay. *Marine Environmental Research*, 56, pp.255-276.

Becouze-Lareure, C., Dembélé, A., Coquery, M., Cren-Olive, C., Barillon, B. and Bertrand-Krajewski, J-L. (2016) Source characterization and loads of metals and pesticides in urban wet weather discharges. *Urban Water Journal*, 13(6), pp.600–617.

Beheim, E., Rajwar, G.S. and Haigh, M. (2012) *Integrated watershed management: Perspectives and Problems*. Oxford (UK): Springer.

Benedetti, L., Blumensaatb, F., Bönischb, G., Krebsb, P. and Vanrolleghema, P.A. (2005) Systems analysis of urban wastewater systems – two systematic approaches to analyse a complex system. *Water Science and Technology*, 52, pp.171–179.

Besseling, E., Quik, J.T.K. and Koelmans, A.A. (2014) Modeling the fate of nano- and microplastics in freshwater systems. In: *Abstract book 24th Annual meeting SETAC Europe: science across bridges, borders and boundaries*.

Beven, K. (2009) *Environmental modelling: An uncertain future*. Abingdon: Routledge Publisher.

Birch, G.F. (2011) Indicators of anthropogenic change and biological risk in coastal aquatic environments. *Treatise on Estuarine and Coastal Science*, 4, pp.235–270.

Birch, G.F. and Olmos, M.A. (2008) Sediment-bound heavy metals as indicators of human influence and biological risk in coastal water bodies – ICES. *Journal of Marine Science*, 65, pp.1407–1413.

Birch, G.F., Taylor, S.E. and Matthai, C. (2001) Small-scale spatial and temporal variance in the concentration of heavy metals in aquatic sediments: a review and some new concepts. *Environmental Pollution*, 113, pp.357-372.

BIS (2017) Department for business, innovation and skills report on *Implementation of the amended batteries directive 2013/56/EU – Impact Assessment*. UK: London.

Björklund, K., Malmqvist, P.A. and Strömvall, A.M. (2011) Simulating organic flows in urban stormwater: development and evaluation of a model for nonylphenols and phthalates. *Water Science and Technology*, 63, pp.508-515.

Blais, J.M, Rosen, M.R. and Smol, J.P. (2015) *Environmental contaminants: Using natural archives to track sources and long-term trends of pollution*. Ontario, Cananda: Springer.

Blecken, G-T., Rentz, R., Malmgren, C., Öhlander, B. and Viklander, M. (2012) Stormwater impact on urban waterways in a cold climate: variations in sediment metal concentrations due to untreated snowmelt discharge. Journal of Soils and Sediments, 12, pp.758-773.

Bloodworth, A., Petavratzi, E. and Gunn, G. (2019) Metals and decarbonisation: A geological perspective. *Science Briefing Paper*: British Geological Survey, UK.

Boehm, P. (2006) Polycyclic Aromatic hydrocarbons (PAHs). In Morrison, R.D. and Murthy, B.L. (eds) *Environmental Forensics Contaminant Specific Guide*. Burlington MA: Academic Press, pp.313-337.

Boelee, E, Geerling, G., van der Zaan, B., Blauw, A. and Vethaak, A.D. (2019) Water and health: From environmental pressures to integrated responses. *Acta Tropica*, 193, pp.217-226.

Boulter, P.G. (2006) *A review of emission factors and models for road vehicle non- exhaust particulate matter*. TRL Report PPR065. Wokingham, UK: TRL Limited.

Bozlaker, A., Muezzinoglu, A. and Odabasi, M. (2008) Atmospheric concentrations, dry deposition and air–soil exchange of polycyclic aromatic hydrocarbons (PAHs) in an industrial region in

Turkey *Journal of Hazardous Materials*, 153, pp.1093-1102 [Online]. Available at: http://www.fbe.deu.edu.tr/all_files/tez_arsivi/2008/dr_p552.pdf. (Accessed: 19 August 2019).

Breault, R.F. and Granato, G.E. (2000) *A synopsis of technical issues of concern for monitoring trace elements in highway and urban runoff: Open-File Report 00-422*. Northborough, Massachusetts: US Department of the Interior and US Geological Survey.

Brewster, C.S., Sharma, V.K., Cizmas, L. and McDonald, T.J. (2018) Occurrence, distribution and composition of aliphatic and polycyclic aromatic hydrocarbons in sediment cores from the Lower Fox River, Wisconsin, US. *Environmental Science Pollution Research*, 25(5), pp.4974-4988.

British Geological Survey - BGS (2014) *Environmental modelling*. UK: British Geological Survey [Online]. Available at: http://www.bgs.ac.uk/research/environmentalmodelling/ home.html. (Accessed: 16 January 2014).

Brils, J. (2008) Sediment monitoring and the European Water Framework Directive. *Annali dell'Istituto Superiore di Sanità*, 44, pp.218-223.

Brown, J.N. and Peake, B.M. (2006) Sources of heavy metals and polycyclic aromatic hydrocarbons in urban stormwater runoff. *Science of the Total Environment*, 359, pp.145–155.

Brown, M. (2015) *Is waste a source of renewable energy?*. Climate, Energy & Air Pollution. Zero Waste Europe.

Brun, G.L., Vaidya, O.M.C. and Leger, M.G. (2004) Atmospheric deposition of polycyclic aromatic hydrocarbons Atlantic Canada: Geographic and temporal distributions and trends 1980–2001. *Environmental Science and Technology*, 38, pp.1941–1948.

Brunner, P.H. (2012) Substance flow analysis: A key tool for effective resource management. *Journal of Industrial Ecology*, 3, pp.293-295.

Brunner, P.H. and Ma, H-W. (2009) Substance flow analysis: An indispensable tool for goal-oriented waste management. *Journal of Industrial Ecology*, 13, pp.11-14.

Brunner, P.H. and Rechberger, H. (2016) *Practical handbook of material flow analysis: Advanced methods in resource and waste management*. New York: Lewis Publisher.

Brunner, P.H., Daxbeck, H., Henseler, G., Von Steiger, B., Beer, B. and Piepke, G. (1990) *Der regionale stoffhaushalt im unteren Bünztal: Entwicklung einer methodik zur erfassung des regionalen Stoffhaushaltes. (Development of a methodology to assess regional material management)*. Dübendorf, ETH Zürich, EAWAG, Abt. Abfallwirtschaft und Stoffhaushalt.

Bureau van Dijk (2013) *FAME website: UK and Ireland company data.* Bureau van Dijk (BvD) [Online] Available at: https://www.bvdinfo.com/en-gb/our-products/data/national/fame. (Accessed 12 January 2013).

Buser, A. and Morf, L. (2009) *Substance flow analysis of PFOS and PFOA: Perfluorinated surfactants perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) in Switzerland*. Environmental studies no. 0922, Federal Office for the Environment, Bern: pp. 144.

Canadian Sediment Quality Guidelines. (2002) *CCME - Canadian council of ministers of the environment, Canadian Sediment Quality Guidelines for the Protection of Aquatic Life*, Canada.

Canal and River Trust - CRT (2012) *Pollutant results for sediment samples numbers 1281546-51*. [E-mail from Chantal Dave]. June 2014.

Canal and River Trust - CRT (2014) *Lowe Lee catchment outfalls and locks locations.* [E-mail from Chantal Dave]. Feb 2015

Cao, W., Qiao, M., Liu, B. and Zhao, X. (2018) Occurrence of parent and substituted polycyclic aromatic hydrocarbons in typical wastewater treatment plants and effluent receiving rivers of Beijing, and risk assessment. *Journal of Environmental Science of Health*, 53(11), pp.992-999.

Carlsson, A. and Sörme, L. (2010) *Domestic inflow of hazardous substances*, Statistika centralbyrån – SCB, Stockholm: Statistics Sweden.

Carter, J., Walling, D.E., Owens, P.N. and Leeks, G.J.L. (2006) Spatial and temporal variability in the concentration and speciation of metals in suspended sediment transported by the River Aire, Yorkshire, UK. *Hydroogical Processes*, 20, pp.3007-3027.

CCME - Canadian council of ministers of the environment. (2001) *Canadian Sediment Quality Guidelines for the Protection of Aquatic Life*, Canada.

CEH - Centre for ecology and hydrology. (2016) UK river and flow regimes. *National river flow archive* [Online]. Available at: http://nrfa.ceh.ac.uk/uk-river-flow-regimes. (Accessed: 20 January 2016).

Cenčič, O. (2018) Webinar on *open material flow analysis with STAN*. April 2018 [Online]. Available at: https://www.youtube.com/watch?v=RxmgYGbpvgo. (Accessed 25 February 2019).

Chapman, P.M., (1992) *Water quality assessments*. New York: Chapman and Hall Press.

Charters, F.J., Cochrane, T.A. and O'Sullivan, A.D. (2020) Predicting event-based sediment and heavy metal loads in untreated urban runoff from impermeable surfaces. *Water*, 12(4), pp.969.

Chen, Y., Jia, R. and Yang, S. (2015) Distribution and source of polycyclic aromatic hydrocarbons (PAHs) in water dissolved phase, suspended particulate matter and sediment from Weihe River in Northwest China. *International Journal for Environmental Research and Public Health*, 12, pp.14148-14163.

Chen, W-Q. and Graedel, T.E. (2012) Anthropogenic cycles of the elements: A critical review. *Environmental Science and Technology*, 46(16), pp.8574-8586.

Cheng, Y. Li, Y., Ji, F. and Wang, Y. (2018) Global sensitivity analysis of a water quality model in the three Gorges Reservoir. *Water*, 10(2), pp.153.

Chetty, S. and Pillay, L. (2019) Assessing the influence of human activities on river health: a case for two South African rivers with differing pollutant sources. *Environmental Monitoring Assessment*, 18(3), pp.168-191.

Chèvre, N., Guignard, C., Rossi, L., Pfeiffer, H-R., Bader, H-P. and Scheidegger, R. (2011) Substance flow analysis as a tool for urban water management. *Water Science and Technology*, 63, pp.1341-1348.

Chèvre, N., Gremaud, D., Guignard, C., Rossi, L., De Alencastro, L-F., Bader, H-P. and Scheidegger, R. (2010) Substance flow analysis: a management tool for heavy metals in urban systems. *7th International Conference on Sustainable Techniques and Strategies for Urban Water Management*. Lyon: Novatech.

Chiba, W.A.C., Passerini, M.D., Baio, J.A.F., Torres, J.C. and Tundisi, J.C. (2011) Seasonal study of contamination by metal in water and sediment in a sub-basin in the Southeast of Brazil. *Brazilian Journal of Biology*, 71, pp.833-843.

Chin, D.A. (2006) *Water-quality engineering in natural systems*. New York (Florida): Wiley and Sons Publication.

Church, T.M., Sommerfield, C.K., Velinsky, D.J., Point, D., Benoit, C., Amouroux, D., Plaa, D. and Donard, O.F.X. (2006) Marsh sediments as record of sedimentation, eutrophication and metal pollution in the urban Delaware estuary. *Marine Chemistry*, 102, pp.72-95.

Colas, F., Archaimbault, V. and Devin, S. (2011) Scale-dependency of micro invertebrate communities: Responses to contaminated sediments within run-of-river dams. *Science of the Total Environment*, 409, pp.1336-1343.

Comber, S.D.W., Merrington, G., Sturdy, L., Delbeke, K. and van Assche, F. (2008) Copper and zinc water quality standards under the EU Water Framework Directive: The use of a tiered approach to estimate the levels of failure. *Science of the Total Environment*, 403, pp.12–22.

Comber, S.D.W., Smith, R., Daldorph, P., Gardner, J.M., Constantino, C. and Ellor, B. (2013) Development of a chemical source apportionment decision support framework for catchment management. *Environmental Science and Technology*, 47(17), pp.9824-9832.

Connan, O., Maro, D., Hébert, D., Roupsard, P., Goujon, R., Letellier, B. and Le Cavelier, S. (2013) Wet and dry deposition of particles associated metals (Cd, Pb, Zn, Ni, Hg) in a rural wetland site, Marais Vernier, France. *Atmospheric Environment*, 63, pp.394-403.

Copper Alliance (2019) *Energy and Renewables*. Copper development association [Online]. Available at: https://copperalliance.org.uk/about-copper/applications/energy-and-renewables/. (Accessed 22 January 2020).

Cornelissen, G., Wilberg, K., Broman, D., Arp, H.P.H., Persson, Y., Sundqvist, K. and Jonsson, P. (2008) Freely Dissolved concentrations and sediment-water activity ratios of PCDD/Fs and PCBs in the open Baltic Sea. *Environmental science and Technology*, 42(23), pp.8733-8739.

Costa, H.J. and Sauer, T.C. (2005) Forensic approaches and considerations in identifying PAH background. *Environmental Forensics*, 6, pp.9-16.

Crane, J. (2014) Source apportionment and distribution of polycyclic aromatic hydrocarbons, risk considerations, and management implications for urban storm water pond sediments in Minnesota, USA. *Archives of Environmental Contamination and Toxicology*, 66, pp.176-200.

Crane, M., Kwok, K.W.H., Wells, C., Whitehouse, P. and Lui, G. (2007) Use of field data to support European Water Framework Directive Quality Standards for dissolved metals. *Environmental Science and Technology*, 41, pp.5014–5021.

Crane, M. (2003) Proposed development of Sediment Quality Guidelines under the European Water Framework Directive: a critique. *Toxicology Letters*, 142, pp.195-206.

Crooks, E.C., Harris, I.M. and Patil, S.D. (2021) Influence of land use land cover on river water quality in rural north Wales, UK. *Journal of the American Water Resources Association*, 57(3), pp.357-373.

Da Costa, T.C., De Brito, K.C.T., Rocha, J.A.V., Leal, K.A., Rodrigues, M.L.K., Minella, J.P.G., Matsumoto, S.T. and Vargas, V.M.F. (2012) Runoff of genotoxic compounds in river basin sediment under the influence of contaminated soils. *Ecotoxicology and Environmental Safety*, 75, pp.63-72.

Danius, L. (2002) *Data uncertainties in material flow analysis. Local case study and literature survey*. Licentiate thesis. Department of Chemical Engineering and Technology, Royal Institute of Technology. Stockholm.

Danius, L. and Burstrom, F. (2001) Regional material flow analysis and data uncertainties: can the results be trusted?. *Proceedings of 15th International Symposium on Informatics for Environmental Protection*, Zurich 10th –12th October.

Dash, S., Borah, S.S. and Kalamdhad, A.S. (2021) Heavy metal pollution and potential ecological risk assessment for surficial sediments of Deepor Beel, India. *Ecological Indicators*, 122, pp. 107265.

Davies, G. (2011) *A water quality analysis of the River Lee and major tributaries within the perimeter of the M25, from Waltham Abbey to Bow Locks*, Thames 21, Unpublished.

Davis, A.P, Shokouhian, M. and Ni, S. (2001) Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources *Chemosphere*, 44, pp.997-1009.

De Carlo, E.H. and Anthony, S.S. (2002) Spatial and temporal variability of trace element concentrations in an urban subtropical watershed, Honolulu, Hawaii. *Applied Geochemistry*, 17, pp.475-492.

De Miguel, E., Charlesworth, S., Ordóñez, A. and Seijas, E. (2005) Geochemical fingerprints and controls in the sediments of an urban river: River Manzanares, Madrid (Spain). *Science of the Total Environment*, 340, pp.137–148.

Defra (2020) *Policy Paper 2016 to 2019: Government policy: water quality*. Department for Environment, Food and Rural Affairs, United Kingdom.

Defra (2019) *National Policy Statement for WasteWater: A Framework Document for Planning Decisions on Nationally Significant Waste Water Infrastructure*, United Kingdom.

Defra (2015) *Policy Paper 2010 to 2015: Government policy: water quality*. Department for Environment, Food and Rural Affairs, United Kingdom, [Online]. Available at: https://www.gov.uk/government/publications/2010-to-2015-government-policy-water-quality/2010-to-2015-government-policy-water-quality. (Accessed: 5 October 2015).

Defra (2015a) *Regulatory impact assessment - sewage collection and treatment for London*. Department for Environment, Food and Rural Affairs, United Kingdom.

Defra (2015b) *In situ contaminated sediments project work package 1A Report*. Department for Environment, Food and Rural Affairs, United Kingdom.

Defra (2014) *Water Framework Directive implementation in England and Wales: new and updated standards to protect the water environment*. Department for Environment, Food and Rural Affairs, United Kingdom. [Online] Available at: https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/307788/river-basin-planning-standards.pdf. (Accessed: 16 January 2016).

Defra (2014a) *Annual report and accounts for 2013 on the UK heavy metals monitoring network*. Department for Environment, Food and Rural Affairs, United Kingdom.

Defra (2013) *Environmental statistics – Key facts.*, Department for Environment, Food and Rural Affairs [Online] Available at: http://data.defra.gov.uk/env/doc/Environmental%20Statistics%20key%20facts%202012.pdf. (Accessed: 12 January 2016).

Defra (2012a) *Tackling water pollution from the urban environment: Consultation on a strategy to address diffuse water pollution from the built environment*, Department for Environment, Food and Rural Affairs, England, UK.

Defra (2012). *Waste water treatment in the United Kingdom - Implementation of the European Union urban waste water treatment directive – 91/271/EEC.*, Department for Environment, Food and Rural Affairs [Online]. Available at:

http://data.defra.gov.uk/env/doc/Environmental%20Statistics%20key%20facts%202012.pdf. (Accessed 12 June 2019).

Defra (2009). *Water for life and livelihoods.* Department for Environment, Food and Rural Affairs. United Kingdom. [Online]. Available at: https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/289937/geth0910bswa-e-e.pdf. (Accessed: 10 January 2016).

Department for Transport (2013) *Fuel consumption (ENV0101 to 0105),* England, UK.

Department for Transport (2013a) *AADT (annual average daily traffic) data for major and minor roads*, England, UK.

DEPA (2000). *Paradigm for substance flow analyses: Guide for SFAs carried out for the Danish EPA.* Environmental Project no. 577, 2000. Danish Environmental Protection Agency, Denmark.

De Saedeleer, A., Cappuyns, V., De Cooman, W. and Rudy Swennen, R. (2010) Influence of major elements on heavy metal composition of river sediments. *Geologica Belgica*, 13, pp.257-268.

Digdat (2013) *Ordnance Survey (OS) Utilities/Assets maps.* Thames Water, UK.

Donner, E., Eriksson, E., Holten-Lützhøft, H-C., Scholes, L., Revitt, M. and Ledin, A. (2010) Identifying and classifying the sources and uses of xenobiotics in urban environments. In: Xenobiotics in the urban water cycle: Mass flows, environmental processes, mitigation and treatment strategies. *Science and Business Media B.V.: Environmental Pollution*, 16, pp.27-50.

Dore, C.J., Watterson, J.D., Murrells, T.P., Passant, N.R., Hobson, M.M., Baggott, S.L., Thistlethwaite, G., Goodwin, J.W.L., King, K.R., Adams, M., Walker, C., Downes, M.K., Coleman, P.J., Stewart, R.A., Wagner, A., Sturman, J., Conolly, C., Lawrence, H. and Cumine, P.R. (2019) *UK emissions of air pollutants 2005-2019. Annual report from the National Atmospheric Emissions Inventory (NAEI)*, Culham, Oxfordshire: Netcen, AEA Technology.

Dowdeswell, J.A., Jakobsson, M., Hogan, K.A., O'Regan, M., Backman, J., Evans, J., Hell, B., Löwemark, L., Marcussen, C., Noormets, R., Ó Cofaigh, C., Sellen, E. and Sölvsten, M. (2010) High-resolution geophysical observations of the Yermak Plateau and northern Svalbard margin: implications for ice-sheet grounding and deep-keeled icebergs. *Quaternary Science Reviews*, 29, pp.3518–3531.

Duodu, G.O., Goonetilleke, A. and Ayoko, G.A. (2016) Comparison of pollution indices for the assessment of heavy metal in Brisbane River sediment. *Environmental Pollution*, 2019, pp.1077-1091.

Ecology Center (2021) *Copper in the environment and copper pollution*. Population Dynamics, USA.

Edina (2021) Ordnance Survey (OS) maps of the Lower Lee catchment in shapefile format, which could be used in ArcGIS platform.

Edina (2015) Ordnance Survey (OS) maps of the Lower Lee catchment in shapefile format, which could be used in ArcGIS platform.

Eja, M.E., Ogri, O.R.A. and Arikpo, G.E. (2003) Bioconcentration of heavy metals in surface sediments from the Great Kwa rivers estuary, Calabar, South Eastern Nigeria. *Journal of Nigerian Environmental Society*, 2, pp.247-256.

Ekonomiuk, A., Malawska, M. and Wilkomirski, B. (2006) Mires and peat PAHs in peat cores from southern Poland: Distribution in stratigraphic profiles as an indicator of PAH sources. *International Mire Conservation Group and International Peat Society*, [Online]. Available at: http://www.mires-and-peat.net/ (Accessed: 14 November 2015).

Ekvall, T., Assefa, G., Björklund, A, Eriksson, O and Finnveden, G. (2007) What life-cycle assessment does and does not do in assessments of waste management. *Waste Management*, 27(8), pp.989-996.

Ellis, J.B. and Mitchell, G. (2006) Urban diffuse pollution: key data information approaches for the Water Framework Directive. *Water and Environment Journal*, 20, pp.19-26.

Elshkaki, A. (2007) *Systems analysis of stock buffering – development of a dynamic substance flow-stock model for the identification and estimation of future resources, waste streams and emissions*. PhD Thesis, Leiden University.

Environment Agency (2021) *Environmental pollution incidents (category 1 and 2) (England and Wales),* 14 January 2021, London, UK.

Environment Agency (2020) *Environmental permitting: Core guidance for the environmental permitting (England and Wales) Regulations 2016 (SI 2016 No 1154),* London, UK.

Environment Agency (2019b) *River basin planning 2021- working together consultation response report for England*, London, UK.

Environment Agency (2019) *Polycyclic aromatic hydrocarbons (PAHs): sources, pathways and environmental data,* London, UK.

Environment Agency (2017) *Inventory on pollutants released to air, water, soil and wastewater for England for the year period of 2017. Geostore data set.* Data acquired with access granted by Ross Bissel, Environment Agency, London, UK.

Environment Agency (2016a) Environmental permitting (England and Wales) Regulations, England, UK.

Environment Agency (2016) Emission inventory *data provided by EA via email.* [E-mail from Ross Bissel]. October 2016.

Environment Agency (2015a) *Mercury and mercury compounds: background data and predicted future emissions*, London, UK.

Environment Agency (2015) *Pollution incidents: 2014 evidence summary,* London, UK.

Environment Agency (2013) *Managing flood risk in the Lower Lee catchment, today and in the future*, London, UK.

Environment Agency (2013a) *Southeast annual fisheries report 2012/2013*, London, UK.

Environment Agency (2013b) Catchment data explorer Lower Lee and lakes. *Environment Agency* [Online]. Available at: https://environment.data.gov.uk/catchment-planning/OperationalCatchment/3275. (Accessed 13 March 2014).

Environment Agency (2013c). Pollution inventory reporting d*ata on pollutant emission: England and Wales*. Data provided by Ross Bissel, Environment Agency.

Environment Agency (2013d) *Inventory on pollutants released to air, water, soil and wastewater for England for the year period of 2013*. *Geostore data set.* Data acquired with access granted by Ross Bissel, Environment Agency, London, UK.

Environment Agency (2012) *Report on water framework investigation: Lee (from Tottenham Locks to the Tideway).* [Email from Ross Bissell]. June 2014.

Environment Agency (2008) *Report on using science to create a better place: Environmental quality standards for trace metals in the aquatic environment*. Science Report SC030194.

Environment Agency (2008a) *Sediment transport and alluvial resistance in rivers*. R&D Technical Report W5i 609.

Environment Agency (2008b) *Report on using science to create a better place: Determination of metal background reference concentrations: Feasibility study*. Science Report SC050063.

Environment Agency (2008c) *Report on using science to create a better place: Assessment of metal mining-contaminated river sediments in England and Wales*. Science Report SC030136/SR4.

Environment Agency (2007) *Report on diffuse water pollution in England and Wales: the unseen threat to water quality*, London, UK.

Environment Agency (2006) *Bringing your rivers back to life: A strategy for restoring rivers in North London*, London, UK.

E-PRTR (2019) *Pollution Inventory reporting* [Online] Available at: https://prtr.eea.europa.eu/#/home. (Accessed 12 January 2014).

E-PRTR (2013) *Pollution inventory reporting* [Online] Available at: https://prtr.eea.europa.eu/#/home. (Accessed 18 January 2020).

Esdat (2000) Dutch target and intervention values - (the New Dutch List). *Environmental Database Management Software*, Netherelands.

Eurobarometer 501 (2020) Attitude of European citizens towards the environment. European Commission [Online]. Available at:

https://ec.europa.eu/commission/presscorner/detail/en/ip_20_331. (Accessed: 7 June 2020).

Eurobarometer 365 (2011) *Attitude of European citizens towards the environment.* European Commission [Online]. Available at: http://ec.europa.eu/environment/pdf/EB_summary_EB752.pdf. (Accessed: 5 January 2016).

European Environment Agency (2019) *Environmental pressures of heavy metal releases from Europe's industry*. Technical report No 1/2019. European Environment Agency.

European Environment Agency (2013) *Water use in Europe — Quantity and quality face big challenges*. WaterPIX / European Environment Agency.

European Environmental Agency (2007) *Feasibility assessment of using the substance flow analysis methodology for chemicals information at macro level. Technical Report No 1/2007*. European Environment Agency *[Online]*. Available at: http://www.eea.europa.eu/publications/technical_report_2007_1. (Accessed: 6 January 2016).

European Commission (2009) *Directive 2009/90/EC of the European Parliament and of the Council of 31 July 2009 'QA/QC directive' technical specifications for chemical analysis and monitoring of water status*, Luxembourg: Office for Official Publications of the European Communities.

European Commission (2008) *Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy*

- *Priority Substances Daughter Directive*, Luxembourg: Office for Official Publications of the European Communities.

European Commission (2006) *Regulation 1907/2006/EC of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)*, Luxembourg: Office for Official Publications of the European Communities.

European Commission (2006) *Directive 2006/44/EC of the European Parliament and of the Council of 06 September 2006 on the quality of fresh waters needing protection or improvement in order to support fish life*. Luxembourg: Office for Official Publications of the European Communities.

European Commission (2000) *Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy*. Luxembourg: Office for Official Publications of the European Communities.

European Copper Institute (2015) *Where, how and why copper is used*. European Union Report on Copper and its Benefits.

European Copper Institute (2018) *Voluntary risk assessment of copper, copper II sulphate pentahydrate, copper(I)oxide, copper(II)oxide, dicopper chloride trihydroxide*. European Union Risk Assessment Report.

European Environment Agency (2019) Cremation: incineration of corpses, EMEP/EEA air pollutant emission inventory guidebook 2019.

European Sediment Network (2006) *Integration of sediment in river basin management*. 2nd SedNet Round Table Discussion - Hamburg [Online]. Available at: http://www.sednet.org/ (Accessed: 15 October 2013).

EU EQS (2013) *Directive 2013/39/EC of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC 2008/105/EC and 2014/101/EC as regards priority* *substances in the field of water policy*, Luxembourg: Office for Official Publications of the European Communities.

European Union (2014) EU best available techniques reference documents (BREFs), under industrial emissions directive (IED, 2010/75/EU).

European Union (2011) *5-6 rings polyaromatic hydrocarbons (PAH) EQS dossier* [Online]. Available at: https://circabc.europa.eu/sd/d/4e13a4c4-07b9-4e55-a43d823e7cd4ce82/PAH%20EQS%20dossier%202011.pdf. (Accessed 12 March 2014).

European Union (2005) Nomenclature des activités économiques dans la communauté européenne (EU NACE) - European industry standard classification system.

European Union (EU) WFD (2000) *Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for community action in the field of water policy*. Luxembourg: Office for Official Publications of the European Communities.

Eriksson, E., Andersen, H.R. and Ledin, A. (2008) Substance flow analysis and source mapping of chemical UV-filters. *Water, Air and Soil Pollution*, 8, pp.473-484.

Eriksson, E. (2002) *Potential and problems related to reuse of water in households*. PhD Thesis. Environment and Resources, Technical University of Denmark.

Evans, R.D., Provini, A., Mattice, J., Hart, B. and Wisniewski, J. (2012) Interactions between sediments and water. *Summary of the 7th International Symposium*, Baveno, Italy.

Faisal, B.M.R, Majumde,r R.K., Uddin, M.J. and Halim M.A. (2014) Studies on heavy metals in industrial effluent, river and groundwater of Savar industrial area, Bangladesh. *International Journal of Geomatics and Geosciences*, 5, pp.182-191.

Fältström, E. and Anderberg, S. (2020) Towards control strategies for microplastics in urban water. *Environmental Science and Pollution Research (international)*, 37(32), pp.40421-40433.

Ferrante, M., Oliveri Conti, G., Rasic-Milutinovic, Z. and Jovanovic, D. (2014) *Health effects of metals and related substances in drinking water - Research report series*. IWA Publishing, London, UK.

Ferronato, C., Modesto, M., Stefanini, I., Vianello, G., Biavati, B. and Antisari, L.V. (2013) Chemical and microbiological parameters in fresh water and sediments to evaluate the pollution risk in the Reno river watershed (North Italy). *Journal of Water Resource and Protection*, 5, pp.458-468

Filgueiras, A.V., Lavilla, I. and Bendicho, C. (2004) Evaluation of distribution, mobility and binding behaviour of heavy metals in surficial sediments of Louro River (Galicia, Spain) using chemometric analysis: a case study. *Science of the Total Environment*, 330(1-3), pp. 115-129.

Findlay, S. and Taylor, M. (2006) Why rehabilitate urban river systems?. *Area*, 38, pp.312-325.

Fonseca, R.M., Araújo, A., Pinho, C., Martins, L. and Dias, N. (2016) Riscos associados à dragagem de materiais sedimentares contaminados por metais pesados. Um caso de estudo em Minas Gerais (Brasil). *XIII Congresso de Geoquímica pos países de Língua Portuguesa*, Fortaleza, Brazil.

Font, A., de Hoogh, K., Leal-Sanchez, M., Ashworth, D.C., Brown, R.J.C., Hansell, A.L. and Fuller, G.W (2015) Using metal ratios to detect emissions from municipal waste incinerators in ambient air pollution data. *Atmospheric Environment*, 113, pp. 177-186.

Fordyce, F.M., Lass-Evans, S. and Ó Dochartaigh, B.É. (2013) A case study to identify urban diffuse pollution in the Light Burn catchment. Glasgow, UK. Stage 3 contribution to: Lundy, L. and Wade, R. (2013) A critical *review of urban diffuse pollution control: methodologies to identify sources, pathways and mitigation measures with multiple benefits*. CREW: the James Hutton Institute. Aberdeen.

Foster, I.D.L. and Charlesworth, S.M. (1996) Heavy metals in the hydrological cycle: trends and explanation. *Hydrological Processes*, 10, pp.227–261.

Friedrich, J.O., Adhikari, N.K. and Beyene, J. (2008) The ratio of means method as an alternative to mean differences for analyzing continuous outcome variables in meta-analysis: A simulation study. *BMC Medical Research Methodology*, 8, pp.32.

Fulkerson, M., Nnadi, F. N. and Chasar, L. S. (2007) Characterizing dry deposition of mercury in urban runoff. *Water, Air, and Soil Pollution*, 185, pp.21-32 [Online]. Available at: https://pubs.er.usgs.gov/publication/70031555 (Accessed 19 May 2018).

Gadd, J. and Kennedy, P. (2000) Preliminary examination of organic compounds present in tyres, brake pads and road bitumen in New Zealand. Prepared for the Ministry of Transport by Kingett Mitchell Limited.

Garces, H. and Sbarbaro, D. (2009) Outliers detection in environmental monitoring data. *IFAC Proceedings Volumes*, 42(23), pp.330-335.

Gardner, M., Jones, V., Comber, S., Scrimshaw, M.D., Garcia, T.C., Cartmell, E., Lester, J. and Ellor, B. (2013) Performance of UK wastewater treatment works with respect to trace contaminants. *Science of Total Environment*, 456, pp.359-369.

Genchi, G., Carocci, A., Lauria, G., Sinicropi, M.S. and Catalano (2020) Nickel: human health and environmental toxicology. *International Journal of Environmental Research and Public Health*, 17(3): pp.679.

Generalised Land Use Database (2005) *GLUD: generalised land use database*. Communities and Local Government. London, UK.

Gibbs, H.M., Gurnell, A.M., Heppell, C. and Spencer, K.L. (2014) The role of vegetation in the retention of fine sediment and associated metal contaminants in London's rivers. *Earth Surface Processes and Landforms*, 39, pp.1115-1127.

Gilbert. R.W., Zedler, E.A., Grilli, S.T. and Street, R.L. (2005) Modelling of wave driven sediment transport over a partially buried cylinder. *Ocean Waves Measurement and Analysis, Fifth International Symposium*, 3rd – 7th July, Madri, Spain.

GLA (2021) The spatial development strategy for Greater London: The London Plan 2021. March, 2021. London, UK.

Gob, F., Houbrechts, G., Hiver, J.M. and Petit, F. (2005a) River dredging, channel dynamics and bedload transport in an incised meandering river (the River Semois, Belgium). *River Research and Applications*, 21, pp.791-804

Gobeil, C., Rondeau, B. and Beaudin, L. (2005) Contribution of municipal effluents to metal fluxes in the St. Lawrence River. *Environmental Science and Technology,* 39, pp.456-464.

Goher, M.E, Hassan, A.M.A., Abdel-Moniem, I.A.I., Fahmy, A.H.A. and El-sayed, S.M.M. (2014) Evaluation of surface water quality and heavy metals indices for Ismailia Canal, Nile River, Egypt. *Egyptian Journal of Aquatic Research,* 40, pp.225–233.

Graedel, T.E., Beers, D-van., Bertram, M., Fuse, K., Gordon, R.B., Gritsinin, A., Kapur, A., Klee, R.J., Lifset, R.J., Memon, L., Rechberger, H., Spatari, S. and Vexler, D. (2004) Multilevel cycle of anthropogenic copper. *Environmental Science and Technology*, 38(4), pp.1242-1252.

Grafen, A. and Hails, R. (2002) *Modern statistics for the life sciences*. Oxford (UK): Oxford University Press.

Gray, S.R. and Becker, N.S.C. (2002) Contaminant flows in urban residential water systems. *Urban Water*, Elsevier, 4, pp.331-346.

Greenpeace (2019) *Upstream: Microplastic in the UK rivers*, London, UK.

Grigoratos, T. and Martini, G. (2014) Non-exhaust traffic related emissions. Brake and tyre wear PM. A Literature Review. JRC Science and Policy Report, European Commission, Joint Research Centre, Institute of Energy and Transport, Ispra, Italy.

Håkanson, L. (1980) An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Research*,14(8), pp.975-1001.

Hanson, R., Hammond, R.J. and Gree, M. (2022) An assessment of 2 watershed models to meet watershed planning needs. *Lake and Reservoir Management*, doi: org/10.1080/10402381.2021.2007181.

Hargreaves, A., Vale, P., Whelan, J., Constantino, C., Dotro, G. and Cartmell, E. (2016) Mercury and antimony in wastewater: fate and treatment. *Water, Air and Soil Pollution*, 227, pp. 89.

Haselbach, L., Poor, C. and Tilson, J. (2013) Dissolved zinc and copper retention from stormwater runoff in ordinary portland cement pervious concrete. *Construction and Building Materials*, 53, pp.652-657.

Hedbrant, J. and Sörme, L. (2001) Data vagueness and uncertainties in urban heavy metal data collection. *Water, Air, and Soil Pollution: Focus*, 1, pp.43–53.

Hem, J.D. (1972) Chemistry and occurrence of cadmium and zinc in surface water and groundwater *Water Resources Research*, 8, pp.661–679.

Hoffman, E., Alimohammadi, M., Lyons, J., Daves, E. and Walker, T.R. (2019) Characterization and spatial distribution of organic-contaminated sediment derived from historical industrial effluents. *Environmental Monitoring and Assessment*, 191, p.590.

Hök, F. (2007) Towels with a dirty past. Swedish Society for Nature Conservation. Technical Report [Online]. Available at: http://www.snf.se/pdf/pdf-ssnc-report-towels-07.pdf (Accessed 2 March 2020).

Honingh, D., Emmerik, T.V., Uijttwall, W., Kardhana, H., Hoes, O. and de Giesen, N.V. (2020) Urban river water level increase through plastic waste accumulation at a rack structure. *Frontiers in Earth Science*, doi: org/10.3389/feart.2020.00028.

Hosseinalizadeh, M., Rivaz, F. and Hedayatizadeh, R. (2011) Importance of outlier detection in spatial analysis of wind erosion. *Biophysical Chemistry*, 7, pp.341-346.

House of Commons (2022) *Environmental audit committee: Water quality in rivers*. Fourth Report of Session 2021-2022, UK.

House of Lords (2020) *Brexit: the revised withdrawal agreement and political declaration,* 1st Report of session 2019-20, European Union Committee [Online] Available at: https://publications.parliament.uk/pa/ld5801/ldselect/ldeucom/4/4.pdf. (Accessed 5 October 2020).

Hrissanthou, V. (2015) *Effects of sediment transport on hydraulic structures*. IntechOpen, University of Thrace.

Hubbard, D.W. (2014), How to measure anything: finding the value of intangibles in business, 3rd Ed. ISBN: 978-1-118-53927-9.

Huang, G., Falconer, R.A. and Lin, B. (2015) Integrated river and coastal flow, sediment and escherichia coli modelling for bathing water quality. *Water*, 7(9), 4752-4777.

Huang, C-L., Vause, J., Ma, H-W. and Yu, C-P. (2012) Using material/substance flow analysis to support sustainable development assessment: A literature review and outlook. *Resources, Conservation and Recycling*, 68, pp.104-116.

IAEA (2003) *Collection and preparation of bottom sediment samples for analysis of radionuclides and trace elements*. International Atomic Energy Agency. Vienna, Austria.

Ibrahim, A.Th.A. and Omar, H.M. (2013) *Seasonal variation of heavy metals accumulation in muscles of the African Catfish Clarias gariepinus and in River Nile water and sediments at Assiut Governorate, Egypt*. Journal of Biology and Earth Sciences, 3, pp.B236-B248.

Inengite, A.K., Oforka, N.C. and Osuji, L.C. (2010). Evaluation of polycyclic aromatic hydrocarbons in sediment of Kolo Creek in the Niger Delta. *International Journal of Applied, Environmental Sciences*. [Online]. Available at: http://www.sid.ir/en/VEWSSID/J_pdf (Accessed: 18 January 2016).

Islam, M.S, Ahmed, M.K., Raknuzzaman, M., Habibullah-Al-Mamun, M. and Islam, M.K. (2015) Heavy metal pollution in surface water and sediment: a preliminary assessment of an urban river in a developing country. *Ecological Indicators*, 48, pp.282-291.

Jiang, B., Zheng, H.L., Huang, G.Q., Ding, B., Li, X.G., Suo, H.T. and Li, R.L. (2007) Characterization and distribution of polycyclic aromatic hydrocarbon in sediments of Haihe River, Tianjin, China *Journal of Environmental Sciences*, 19, pp.306–311.

Jamtrot, A., Seriki, K. and Petterson, M. (2009) *Substance flow analysis for selected priority pollutants in case cities - Source and Control Options for Reducing of Priority Pollutants (ScorePP)*, Sixth Framework Programme, Global Change and Ecosystems [Online]. Available at: https://insynsverige.se/documentHandler.ashx?did=95706. (Accessed 16 January 2016).

Järveläinen, J., Sillanpääb, N. and Koivusalo, H. (2017) Land-use based stormwater pollutant load estimation and monitoring system design. *Urban Water Journal*, 14(3), pp.223–236.

Jiao, H., Wang, Q., Zhao, N., Jin, B., Zhuang, X. and Bai, Z. (2017) Distributions and sources of polycyclic aromatic hydrocarbons (PAHs) in soils around a chemical plant in Shanxi, China. *International Journal of Environmental Research and Public Health*, 14, pp.1198.

Jin, L., Whitehead, P.G., Baulch, H.M., Dillon, P.J., Butterfield, D., Oni, S.K., Flutter, M.N., Crossman, J. and O'Conner, E.M. (2017) Modelling phosphorus in Lake Simcoe and its subcatchments: scenario analysis to assess alternative management strategies. *Inland Waters*, 3(2), pp.207-220.

Jones, B.G., Alyazichi, Y.M., Low, C., Goodfellow, A., Chenhall, B.E. and Morrison, R.J. (2019) Distribution and sources of trace element pollutants in the sediments of the industrialised Port Kembla Harbour, New South Wales, Australia. *Environmental Earth Sciences*, 78, pp.357.

Judge, A., Jonas, C. and Freshwater, S. (2020) *UK Energy from Waste Statistics*. Tolvik Consulting: The Waste and Bioenergy Experts, UK.

Kafilzadeh, F., Houshang, A., Shiva and Malekpour, R. (2011) Determination of polycyclic aromatic hydrocarbons (PAHs) in water and sediments of Kor River, Iran. *Middle-East Journal of Scientific Research*, 10, pp.01-07.

Kalugina, O.V, Mikhailova, T.A and Shergina, O.V. (2018) Contamination of Scots pine forests with polycyclic aromatic hydrocarbons on the territory of industrial city of Siberia, Russia. *Environmental Science Pollution Research International*, 25(21), pp.21176-21184.

Kanchanamayoon, W. and Tatrahun, N. (2008) Determination of polycyclic aromatic hydrocarbons in water samples by solid phase extraction and gas chromatography. *World Journal of Chemistry*, 3, pp.51-54.

Karthikeyan, P., Vennila, G., Nanthakumar, G. and Aswini, M. (2020) Data set for spatial distribution and pollution indices of heavy metals in the surface sediments of Emerald Lake, Tamil Nadu, India. *Data in Brief*, 28, 104877.

Kats, N.V., Dieperink, C., Rijswick, M.V. and Domis, L.S. (2022) Towards a good ecological status? The prospects for the third implementation cycle of the EU Water Framework Directive in The Netherlands. *Water*, 14(3)486, 103390.

Ketzel, M., Omstedtb, G., Johanssonc, C., Düring, I., Pohjolaf, M., Oettlg, D., Gidhagenb, L., Wåhlina, P., Lohmeyere, A., Haakanaf, M. and Berkowicz, R. (2007) Estimation and validation of PM2.5/PM10exhaust and non-exhaust emission factors for practical street pollution modelling. *Atmospheric Environment*, 41, pp.9370-9385.

Khatoon, N., Altaf, H., Khan, S., Rehman, M. and Pathak, V. (2013) Correlation study for the assessment of water quality and its parameters of Ganga river, Kanpur, Uttar Pradesh, India. *IOSR Journal of Applied Chemistry*, 579(3), pp.2278-5736.

Khazaali, A., Kunzmann, A., Bastami, D.K. and Baniamam, M. (2016) Baseline of polycyclic aromatic hydrocarbons in the surface sediment and sea cucumbers (Holothuria leucospilota and Stichopus hermanni) in the northern parts of Persian Gulf *Marine Pollution Bulletim*, 110, pp.539–545.

Kim, H.Y. (2018) Statistical notes for clinical researchers: covariance and correlation *Restorative dentistry and endodontics*, 43(1), pp.4-18.

Kim, H., Jang, Y-C. and Hong, Y-S. (2017) Substance flow analysis of mercury from industrial and municipal wastewater treatment facilities. *International Journal of Applied Engineering Research*, 12(15), pp.5332-5338.

Kimball, B.A, Runkel, R.L. and Walton-Day, K. (2010) An approach to quantify sources, seasonal change, and biogeochemical processes affecting metal loading in streams: Facilitating decisions for remediation of mine drainage. *Applied Geochemistry*, 25, pp.728–740.

Kleijn, R., Huele, R., and van der Voet, E. (2000) Dynamic substance flow analysis: the delaying mechanism of stocks, with the case of PVC in Sweden. *Ecological Economics*, 32(2), pp.241–254.

Kleijn, R. (1999). IN = OUT: The trivial central paradigm of MFA?. *Journal of Industrial Ecology*, 3, pp.8-10.

Klein, J., Molnár-in 't Veld, H., Geilenkirchen, G., Hulskotte, J., Ligterink, N., Dellaert, S., de Boer, R. (2017) Methods for calculating the emissions of transport in the Netherlands. Task Force on Trasportation of the Dutch Pollutant Release and Transfer Register.

Koh, C.H., Khim, J.S., Kannan, K., Villeneuve, D.L., Senthilkumar, K. and Giesy, J.P. (2004) Polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) and 2,3,7,8-TCDD equivalents (TEQs) in sediment from the Hyeongsan River, Korea. *Environmental Pollution*, 132, pp.489-501.

Kumar, V., Pariharb, P.D., Sharma, A., Bakshid, P., Sidhu, G.P.S., Bali, A.S., Karaouzas, I., Bhardwaj, R., Thukral, A.K., Gyasi-Agyeih, Y. and Rodrigo-Cominoi, J. (2019) Global evaluation of heavy metal content in surface water bodies: A meta-analysis using heavy metal pollution indices and multivariate statistical analyses. *Chemosphere*, 236, 124364.

Kunes, J. (2012) *Dimensionless physical quantities in science and engineering*. Czech Republic: Elsevier.

Kuusisto-Hjort, P. (2009) *Controls on trace metals in urban stream sediments – implications for pollution monitoring using sediment chemistry data*. PhD Thesis. University of Helsinki, Finland.

Kwok, K.W.H., Batley, G.E., Wenning, R.J., Zhu, L., Vangheluwe, M. and Lee, S. (2014) Sediment quality guidelines: challenges and opportunities for improving sediment management. Environmental Science and Pollution Research, 21, pp.17-27.

Lafhaj, Z., Samara, M., Agostini, F., Boucard, L., Koczylas F. and Depelsenaire, G. (2008) Polluted river sediments from the North region of France: Treatment with Novosol process and valorization in clay bricks. *Construction and Building Materials*, 22, pp.755–762.

Land and Water Group (2009) Dredging the River Lee: Land and water case study. *Land and Water Group* [Online]. Available at: http://www.land-water.co.uk/dredgingriver-lee-navigation-dredge. (Accessed: 5 June 2014).

Laner, D., Feketitsch, J., Rechberger, H. and Fellner, J. (2015) A novel approach to characterize data uncertainty in material flow analysis and its application to plastics flows in Austria. *Journal of Industrial Ecology*, 20(5), pp.1050-1063.

Laner, D., Rechberger, H., and Astrup, T.F. (2014) Systematic evaluation of uncertainty in material flow analysis. *Journal of Industrial Ecology*, 18(6), pp.859-870.

Lassen, C. and Hansen, E. (2000) *Paradigm for substance flow analyses*. Copenhagen: Danish Environmental Protection Agency.

Lau, S-L. and Stenstrom, M.K. (2005) Metals and PAHs adsorbed to street particles. *Water Research*, 39, pp.4083-4092.

Lawal, A.T. and Fantke, P. (2017) Polycyclic aromatic hydrocarbons: A review. *Cogent Environmental Science*, 3, pp.1-20.

Lena, D. (2002) *Data uncertainties in material flow analysis: Local case study and literature survey*. Licentiate thesis. Royal Institute of Technology, Stockholm.

Li, B., Wang, Q. Haung, B. and Li, S. (2001) Evaluation of the results from a QuasiTessier's Sequential Extraction procedure for heavy metal speciation in soils and sediment by ICP-Ms. *Analytical Science*, 17, pp.1561-1564.

Li, F., Yu, X., Lv, J., Wu, Q. and An, Y. (2022) Assessment of heavy metal pollution in surface sediments of the Chishui River Basin, China. PLos ONE 17(2), doi: org/10.1371/journal.pone.0260901

Li, H., Liu, L., Li, M. and Zhang, X. (2013) Effects of pH, temperature, dissolved oxygen, and flow rate on phosphorus release processes at the sediment and water interface in storm sewer. *Journal of Analytical Methods in Chemistry*, 2013(ID104316), 7 pages, doi: org/10.1155/2013/104316

Li, N. and Lee, H.K. (2001) Solid-phase extraction of polycyclic aromatic hydrocarbons in surface water: negative effect of humic acid. *Journal of Chromatographic Analysis,* 6, pp.255-263.

Lim, W.Y., Aris, A.Z. and Zakaria, M.P. (2012) Spatial variability of metals in surface water and sediment in the Langat River and geochemical factors that influence their water-sediment interactions. *The Scientific World Journal*, 2012, pp.1-14.

Lindfors, S., Österlund, H., Meyn, T., Muthanna, T.M., Lundy, L. and Viklander, M. (2021) Evaluation of measured dissolved and bio-met predicted bioavailable Cu, Ni and Zn concentrations in runoff from three urban catchments. *Journal of Environmental Management*, (287):112263.

Lindgren, A. (1996) Asphalt wear and pollution transport. *Science of the Total Environment*, 189(190), pp. 281–286.

Lindqvist-Östblom, A., Eklund, M. and Roth, L. (2009) *Beyond the inventory - interpretation in substance flow analysis*. workshop on economic growth, material flows and environmental pressure, Stockholm.

Lindqvist-Östblom, A. (2002) *Substance flow analysis for environmental management in local authorities – method development and context. Lindköping Studies in Science and Technology*. PhD Thesis. Lindköping University.

Lindsay, S.J. (2011) *Light metals*. California – USA: Wiley and Sons Publishing.

Ling, Z., Zeng-Wei, Y. and Jun, B. (2009) Substance flow analysis (SFA): A critical review. *Acta Ecologica Sinica*, 29(11), pp.1-10.

Lingle, J. (2008) *Examination of the Sources of polycyclic aromatic hydrocarbon (PAH) in urban background soil*. Eletric Power Research Institute, USA. Interim Report 1015558.

Lintern, A., Webb, J.A., Ryu, Liu, S., Bende-Michl, U., Waters, D., Leahy, P., Wilson, P. and Western, A.W. (2018) Key factors influencing differences in stream water quality across space. *WIREs Water*, 5:e1260.

Liu D., Wang, J., Yu, H., Gao, H. and Xu, Weining (2021) Evaluating ecological risks and tracking potential factors influencing heavy metals in sediments in an urban river. *Environmental Sciences Europe*, 33, 42, doi: org/10.1186/s12302-021-00487-x.

Liu, Z., Li, Q., Wu, Q., Kuo, D.T.F., Chen, S., Hu, X., Deng,M., Zhang, H. and Luo, M. (2017) Removal efficiency and risk assessment of polycyclic aromatic hydrocarbons in a typical municipal wastewater treatment facility in Guangzhou, China. *International Journal of Environmental Research and Public Health*, 14(8), pp.861-881.

Liu, Z.J., Li, P.Y., Zhang, X.L., Li, P, Zhu, L.H. (2012) Regional distribution and ecological risk evaluation of heavy metals in surface sediments from coastal wetlands of the Yellow River Delta. *Environmental Science*, 33(4), pp.1182-1188.

Liyanage, C.P. and Yamada, K. (2017) Impact of population growth on the water quality of natural water bodies. MDPI: Sustainability, 9, pp.1405.

London RFRA (2014) *London regional flood risk appraisal*. Mayor of London [Online]. Available at: https://www.london.gov.uk/sites/default/files/London%20RFRA%20first%20review%20consultation%20draft.pdf. (Accessed: 10 October 2015).

Luce, D.L. (2012) *Sediment metal concentrations as a function of land use in the Charles River, Eastern Massachusetts*. PhD Thesis. University of Massachusetts Boston.

Lundy, L. and Wade, R. (2011) Integrating sciences to sustain urban ecosystem services. *Progress in Physical Geography*, 35, pp.653-669.

Lützhøft, H.H-C., Donner, E., Wickman, T., Eriksson, E., Banovec, P. Mikkelsen, P. S. and Ledin, A. (2012) A source classification framework supporting pollutant source mapping, pollutant release prediction, transport and load forecasting, and source control planning for urban environments. *Environmental Science and Pollution Research*, 19, pp.1119-1130.

Machado, W., Rodrigues, A.P.C., Bidone, E.D., Sella, S.M., Santelli, R.E. (2011) Evaluation of Cu potential bioavailability changes upon coastal sediment resuspension: an example on how to improve the assessment of sediment dredging environmental risks. *Environmental Science and pollution research*, 18, pp.1033-1036.

Macklin, M.G., Brewer, P.A., Hudson-Edwards, K.A., Bird, G., Coulthard, T.J., Dennis, I.A., Lechler, P.J., Miller, J.R. and Turner, J.N. (2006) A geomorphological approach to the management of rivers contaminated by metal mining. *Geomorphology*, 79, pp.423-447.

Maddocks, D. (1993) *Lower Lee fish mortalities associated with rainfall*. Agricultural and environmental data archive – AEDA [Online]. Available at: http://www.environmentdata.org/archive/ealit:3677/OBJ/20001632.pdf. (Accessed: 10 January 2016)

Magdaleno, A., De Cabo, L., Arreghini, S. and Salinas, S. (2014) Assessment of heavy metal contamination and water quality in an urban river from Argentina. *Brazilian Journal of Aquatic Science and Technology*, 18, pp.113-120.

Maijer, L.J.J., Emmerik, T.V., Der Ent, R.V., Schmidt, C. and Lebreton, L. (2021) More than 1000 rivers account for 80% of global riverine plastic emissions into the ocean. Science Advances, 7(18), 5803.

Maity, S.K. and Maiti, R. (2017) *Sedimentation in the Rupnarayan river: estuarine environment of deposition*. Volume 2. Springer.

Man, Y.B., Chow, K.L., Cheng, Z., Mo, W.Y., Chan, Y.H., Lam, J.C.W., Lau, F.T.K., Fung, W.C. and Wong, M.H. (2017) Profiles and removal efficiency of polycyclic aromatic hydrocarbons by two different types of sewage treatment plants in Hong Kong. *Journal of environmental Sciences*, 53, pp.196-206.

Maniquiz-Redillas, M. and Kim, L.H. (2014) Fractionation of heavy metals in runoff and discharge of a stormwater management system and its implications for treatment. *Journal of environmental Sciences*, 26(8), pp.1214-1222.

Manoli, E. and Samara, C. (2008) The removal of polycyclic aromatic hydrocarbons in the wastewater treatment process: experimental calculations and model predictions. *Environmental Pollution*, 151(3), pp.477-485.

Månsson, N. Sörme, L. Wahlberg, C. and Bergbäc, B. (2008) Sources of alkylphenols and alkylphenol ethoxylates in wastewater-a substance flow analysis in Stockholm, Sweden. *Water Air Soil Pollution: Focus*, 8, pp.445–456.

Markiewicz, A., Björklund, K., Eriksson, E., Kalmykova, Y., Strömvall, A-M. and Siopi, A. (2017) Emissions of organic pollutants from traffic and roads: Priority pollutants selection and substance flow analysis. *Science of the Total Environment*, 580, pp.1162–1174.

Martínez, A., Di Cesare, A., Mari-Mena, N., García-Gómez, G., Garcia-Herrero, A., Corno, G., Fontaneto, D. and Eckert, E.M. (2020) Tossed 'good luck' coins as vectors for anthropogenic pollution into aquatic environment. *Environmental Pollution*, 259, p.113800.

Matrosov, E.S. and Harou, J.J. (2010) *Simulating the Thames water resource system using IRAS-2010*. International Environmental Modelling and Software Society (iEMSs). International Congress on Environmental Modelling and Software, Ottawa, Canada.

Matějíček, L., Benešová, L. and Tonika, J. (2002) Environmental modelling in urban Ares with GIS. iEMSs: *The 1st biennial meeting of the International Environmental Modelling and Software Society*, Lugano, Switzerland, pp.61–66.

Maurya, A., Negi, T. and Negi, R.K. (2018) Seasonal assessment of heavy metal pollution in water and sediment of fish pond at Bhagwanpur Roorkee (U.K.), India. *Asian Journal of Animal Sciences*, 12, pp.16-22.

McDonald, J.H. (2009) Handbook of biological statistics. 2nd edition. Sparky House Publishing, Baltimore, US.

McHugh M.L. (2009) The odds ratio: calculation, usage and interpretation. *Biochemia Medica*, 19, pp.120-126.

Meadows, D.L. (2001) Tools for understanding the limits to growth: Comparing a simulation and a game. *Simulation and Gaming*, 32, pp.522-536.

Meals, D.W., J. Spooner, S.A. Dressing, and J.B. Harcum. (2011). *Statistical analysis for monotonic trends*, Tech Notes 6. Developed for U.S. Environmental Protection Agency by Tetra Tech, Inc., Fairfax, VA, 23.

Medici, L., Bellanova, J., Belviso, C., Cavalcante, F., Lettino, A., Ragone, P.P. and Fiore, S. (2011) Trace metals speciation in sediments of the Basento River (Italy) *Applied Clay Science*, 53, pp.414–442.

MEDD and Agences de l’eau (2003) SEQ-eau, Grilles d’évaluation version 2 (TEL).

Meijer, L.J.J., Emmerik, T.V., Van Der Ent, R, Schmidt, C. and Lebreton, L. (2021) More than 1000 rivers account for 80% of global riverine plastic emissions into the ocean. *Science Advances*, 7(18), 101126.

Meire, R.O., Azeredo, A. and Torres, J.P.M. (2007) Aspects ecotoxicologicos de hidrocarbonetos policiclicos aromaticos. *Oecologia Australis*, 11, pp.188-201.

MetOffice (2016) *Available data sets: daily precipitation data set*. Available at: http://www.metoffice.gov.uk/climatechange/science/monitoring/ukcp09/available/daily.html (Accessed: March 2016).

Minitab (2017) *Minitab 17 statistical software*. Minitab Inc., Pennsylvania, USA.

Mohammed, A.B., Al-Taee, M.M.S. and Hassan, F.M. (2009) *The study of some PAH compounds in Euphrates river sediment from Al-Hindiya Barrageto Al-Kifil city, Iraq. 4th Scientific Conference.* College of Science, Babylon University. CSASC English Version, 4, pp.216-230.

Morf, L.S, Busera, A.M., Taverna, R., Baderb, H.P. and Scheideggerb, R. (2008) Dynamic substance flow analysis as a valuable risk evaluation tool – a case study for brominated flame retardants as an example of potential endocrine disrupters. *Chimia*, 62(5), pp.424–431.

Morillo, E., Romero, A.S., Maqueda, C., Madrid, L., Ajmone-Marsan, F., Greman, H., Davidson, C.M., Hursthouse, A.S. and Villaverde, J. (2007) Soil pollution by PAHs in urban soils: a comparison of three European cities. *Journal of Environmental Monitoring*, 9, pp.1001-1008.

Morrison, G.M.P., Revitt, D.M., Ellis, J.B., Svenson, G. and Balmer, P. (1984) Variations of dissolved and suspended solid heavy metals through an urban hydrograph. *Environmental Science and Technology Letters*, 5, pp.313–318.

Mudge, S.M. (2008) *Methods in Environmental Forensics*, USA: CRC Press.

Müller, A., Österlund, H., Marsalek, J. and Viklander, M. (2020) The pollution conveyed by urban runoff: A review of sources. *Science of The Total Environment*, 709, pp.136125.

Munro, K., Martins, C.P.B., Loewenthal, M., Comber, S., Cowan, D.A., Pereira, L. and Barron, L.P. (2019) Evaluation of combined sewer overflow impacts on short-term pharmaceutical and illicit drug occurrence in a heavily urbanised tidal river catchment (London, UK). *Science of The Total Environment*, 657, pp.1099-1111.

Muohi, A.W. (2003) *Heavy metal distribution in surface sediments from Mtwapa and Hirazi Creeks, Kenyan Coast*. New York: Springer-Verlag Inc.

Nasr, I.N., Arief, M.H., Abdel-Aleem, A.H. and Malhat, F.M. (2010) Polycyclic aromatic hydrocarbons (PAHs) in aquatic environment at El Menofiya Governorate, Egypt. *Journal of Applied Sciences Research*, 6, pp.13-21.

Nawaz, S.M., Ferdousi, F.K., Rahma, M.A. and Alam, A.M.S. (2014) Reversed phase SPE and GC-MS study of polycyclic aromatic hydrocarbons in water samples from the River Buriganga, Bangladesh. *International Scholarly Research Notices*, 2014, pp.1-9.

Neff, J.M, Stout, A.S., and Gunstert, D.G. (2004) Ecological risk assessment of polycyclic aromatic hydrocarbons in sediments: identifying sources and ecological hazard. *Integrated Environmental Assessment and Management – SETAC*, 1, pp.22-23.

Nickel Institute (2021) *Nickel and the environment*. Report from Nickel Institute: Technology for a brighter Future.

Oceanographic Magazine (2020) Ocean pollution: Thames Water overflow pipe pumped waste for 1,026 hours into London wetlands in 2019. *Oceanographic Magazine*, Issue 18.

OECD/OCDE (2000) *Adsorption - desorption using a batch equilibrium method*. Organisation for Economic Cooperation and Development [Online]. Available at: http://www.oecd-ilibrary.org/environment/test-no-106-adsorption-desorption-using-a-batch-equilibrium-method_9789264069602-en. (Accessed: 25 February 2015).

OECD/OCDE (2008) *Measuring material flows and resources productivity*. Organisation for Economic Cooperation and Development The OECD Guide, Volume I, USA.

Office for National Statistics (2019) Water withdrawals per capita worldwide, by select country. December 2019. ONS.

Office for National Statistics (2019a) *Material flows account for the United Kingdom*. UK Environmental Accounts [Online]. Available at: https://www.ons.gov.uk/. (Accessed 1 December 2019).

Office for National Statistics (2016) *UK environmental accounts: How much material is the UK consuming?*. UK Environmental Accounts [Online]. Available at: https://www.ons.gov.uk. (Accessed: July 2019).

Office for National Statistics (2013a) Water withdrawals per capita worldwide, by select country. December 2013. ONS.

Office for National Statistics (2013) *Statistical bulletin: Index of production*. December 2013. ONS.

Office for National Statistics (2011) *Census: digitised boundary data (England and Wales)* [Online]. UK Data Service Census Support. Available at: https://borders.ukdataservice.ac.uk/. (Accessed 08 Jnauary 2013).

Office for National Statistics (2007) UK SIC: *Standard industrial classification used in classifying business establishments and other statistical units by the type of economic activity in which they are engaged*. England, UK

Okafor, E.C. and Opuene, K. (2007) Preliminary assessment of trace metals and polycyclic aromatic hydrocarbons in the sediments. *International Journal of Environmental Science and Technology*, 4, pp.233-240.

Owens, P.N. (2008) *Sustainable management of sediment resources: sediment management at the river basin scale*. SedNet. Elsevier.

Owen, A., Marshall, E., Green, D., Croft, T. and Davis, S. (2020) *Statistics support for students* [online]. Available at: www.statstutor.ac.uk (Accessed 11 November 2020).

Owens, P N., Walling, D.E., Carton, J., Meharg, A.A., Wright, J. and Leeks, G.J.L. (2001) Downstream changes in the transport and storage of sediment-associated contaminants (P, Cr and PCBs) in agricultural and industrialised drainage basins. *Science of the Total Environment*, 266, pp.177-186.

Palm, V. (2002). *Material flow analyses in technosphere and biosphere – metals, natural resources and chemical products*. PhD thesis. Department of Civil and Environmental Engineering. Royal Institute of Technology.

Palmquist, H. (2004) Substance flow analysis of hazardous substances in a Swedish municipal wastewater system. *VATTEN*, 60, pp.251-260.

Palmquist, H. (2001) *Hazardous substances in wastewater systems: a delicate issue for wastewater management*. PhD Thesis. Lulea Tekniska University, Sweden.

Pan, Y.P. and Wang, Y.S. (2015) Atmospheric wet and dry deposition of trace elements at 10 sites in Northern China. *Atmospheric Chemistry and Physics*, 15, pp.951-972.

Pandey, J. and Singh R. (2015) Heavy metals in sediments of Ganga River: up- and downstream urban influences. *Water Sciences*, 10.1007.

Pappenberger, F., Beven, K., Hunter N.M., Bates, P.D., Gouleweleeuw, B.T., Thielen, J., and De Roo, A.J.P. (2005) Cascading model uncertainty from medium range weather forecasting (10 days) through rainfall-runoff models to flood inundation predictions using European Flood Forecasting System (EFFS). *Hydrology and Earth System Sciences*, 9, pp.381-393.

Patroncini, D. (2013) *Water quality investigation of the River Lea (NE London)*. PhD Thesis. University of Bedfordshire.

Pettersson, T.J.R., Strömvall, A-M. and Ahlman, S., (2005) Underground sedimentation systems for treatments of highway runoff in dense city areas. *10th International conference on urban drainage*, Copenhagen/Denmark, 21-26 August.

Paul, M., and Meyer, J. (2001). Streams in the urban landscape. *Annual review of Ecology and Systematics*, 32, pp.333-365.

Petrucci, G., Gromaire, M.C. and Chebbo, G. (2014) Substance flow analysis of the primary non-point sources of pollution of urban runoff: a comparative assessment of three catchments. *13th International Conference on Urban Drainage*, Kuching, Sarawak.

Pies, C., Hoffmann, B., Petrowsky, J., Yang, Y., Ternes, T.A. and Hofmann, T. (2008) Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in river bank soils *Chemosphere*, 72, pp.1594-1601.

Pietari, J., O'Reilly, K. and Boehm, P. (2016) A Review of PAHs. *Stormwater Magazine*, July 10.

PHE (2013) *Compendium of chemical hazards: Cadmium general information*. Public Health England, UK.

Prasad, M.N.V. (2008) *Trace elements as contaminants and nutrients: Consequences in Ecosystems and Human Health*, Canada: John Wiley and Sons.

Prestes, E.C., Anjos, V.E., Sodré, F F. and Grassi, M.T. (2006) Copper, lead and cadmium loads and behaviour in urban stormwater runoff in Curitiba, Brazil. *Journal of the Brazilian Chemical Society*, 17(1).

Pulles, T., Denier van der Gon, H., Appelman, W. and Verheul, M. (2012) Emission factors for heavy metals from diesel and petrol used in European vehicles. *Atmospheric Environment*, 61, pp.641-651.

Purchase, D., Abbasi, G., Bisschop, L., Chatterjee, D., Ekberg, C., Ermolin, M., Fedotov, P., Garelick, H., Isimekhai, K., Kandile, N.G., Lundström, M., Matharu, A., Miller, B.W., Pineda, A., Popoola, O.E., Retegan, T., Ruedel, H., Serpe, A., Sheva, Y., Surati, K.R., Walsh, F., Wilson, B.P. and Wong, M.H. (2020) Global occurrence, chemical properties, and ecological impacts of e-wastes (IUPAC Technical Report). *Pure and Applied Chemistry*, 92(11), pp. 1733-1767.

Qi, W., Liu, H., Pernet-Coudrier, B. and Qu, J. (2013) Polycyclic aromatic hydrocarbons in wastewater, WWTPs effluents and in the recipient waters of Beijing, China. *Journal of Environmental Science and Pollution Research*, 20, pp.4254-4260.

Rahm, S., Green, N., Norrgran, J. and Bergman, A. (2005) Hydrolysis of environmental contaminants as an experimental tool for indication of their persistency. *Environmental Science & Technology*, 39(9), pp.3128-3133.

Rahman, M.A., Rahman, S.H. and Chowdhury, M.A.Z. (2021) Role of river-flow in alleviating heavy metal load from a polluted urban river. *Polish Journal of Environmental Studies*, 30, pp.4177-4186.

Raju, K.V, Somashekar, R.K. and Prakash, K.L. (2013) Spatio-temporal variation of heavy metals in Cauvery river basin. *International Academy of Ecology and Environmental Sciences*, 3, pp.59-75.

Raman, A. and Arellano, A.F. (2017) Spatial and temporal variations in characteristic ratios of elemental carbon to carbon monoxide and nitrogen oxides across the United States. *Environmental Science and Technology*, 51(12), pp.6829-6838.

Raulinaitis, M., Ignatavičius, G., Sinkevičius, S. and Oškinis,V. (2012) Assessment of heavy metal contamination and spatial distribution in surface and subsurface sediment layers in the northern part of Lake Babrukas. *Ekologija*, 58, pp.33–43.

Reis, A., Parker, A. and Alencoão, A. (2013) Storage and origin of metals in active stream sediments from mountainous rivers: a case study in the River Douro basin (North Portugal). *Applied Geochemistry*, 44, pp.69–79.

Rentz, R., Widerlund, A., Viklander, M. and Öhlander, B. (2011) Impact of urban stormwater on sediment quality in an enclosed bay of the Lule river, Northern Sweden. *Water, Air and Soil Pollution*, 218, pp.651–666.

Resnik, D.B. and Shamoo, A.E. (2017) Reproducibility and research integrity. *Accountability in Research*, 24, pp.116–123.

Revitt, D.M., Ellis, J.B., Gilbert, N., Bryden, J. and Lundy, L. (2022) Development and application of an innovative approach to predicting pollutant concentrations in highway runoff, Science of the Total Environment, 825, 153815.

Revitt, D.M., Ellis, J.B. and Lundy, L. (2020) Justification of an excel spreadsheet approach for predicting road runoff pollutant concentrations: Report prepared for Thames21, Environment Agency, Greater London Authority and Transport for London, London, UK.

Revitt, D.M., Lundy, L., Eriksson, E. and Viavattene, C. (2013) Comparison of pollutant emission control strategies for cadmium and mercury in urban water systems using substance flow analysis. *Journal of Environmental Management*, 116, pp.172-180.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A and Cass, G.R. (1993) Sources of fine organic aerosol, road dust, tyre debris and organometallic brake lining dust: Roads as sources and sinks. *Environmental Science and Technology*, 27(9), pp.1892-1904.

Ross, P.T. and Zaidi, N.L.B. (2019) Limited by our limitations. *Perspectives on Medical Education*, 8(4), pp. 261-264.

Rotmans, J. and Van Asselt, M.B.A. (2001) Uncertainty in integrated assessment modelling: a labyrinthic path. *Integrated Assessment*, 2, pp.43–55.

Royal Commission on Environmental Pollution (2007) *The urban environment*, 26th Report, London, UK.

RSC.com (2021) Periodic table, element Zinc. RSC. Available at: https://www.rsc.org/periodic-table/element/30/zinc (Accessed: 1 August 2021).

Rumney, H.S., Bolam, S. G. and Law, R.J. (2015) Polycyclic aromatic hydrocarbons in sediments at dredged material disposal sites around England: Concentrations in 2013 and time trend information at selected sites 2008–2013. *Marine pollution bulletin*, 92, pp.180–185.

Rybicka, E.H., Adamiec, E. and Aleksander-Kwaterczak, U. (2005) Distribution of trace metals in the Odra River system: Water-suspended matter-sediment. *Limnologica – Ecology and Management of Inland Waters,* 35, pp.185-198.

Sabo, A., Gani, A.M. and Ibrahim, A.Q. (2013) Pollution status of heavy metals in water and bottom sediment of river Delimi in Jos, Nigeria. *American Journal of Environmental Protection*, 1, pp.47-53.

Sakson, G., Brzezinska, A. and Zawilski, M. (2018) Emission of heavy metals from an urban catchment into receiving water and possibility of its limitation on the example of Lodz city. *Environmental Monitoring and Assessment,* Springer, 190(5) pp.281.

Salah, E.A.M., Zaidan, T.A. and Al-Rawi, A. (2015) Identification of sources of heavy metals pollution in Europhrates river sediments (Iraq) using multivariate statistical analysis. *International Journal of Environment and Water*, 4, pp.50-61.

Salem, Z.B., Capelli, N., Laffray, X., Elise, G., Ayadi, H. and Aleya, L. (2014) Seasonal variation of heavy metals in water, sediment and roach tissues in a landfill draining system pond (Etueffont, France). *Journal of Ecological Engineering*, 69, pp.25-37.

Santos, I.F., Ferreira, S.L.C., Domínguez, C. and Bayona, J.M. (2018) Analytical strategies for determining the sources and ecotoxicological risk of PAHs in river sediment. *Microchemical Journal*, 137, pp.90 – 97.

Sarpong, N.S., Adamafio, N.A. and Obodai, M. (2009) Determination of optimum concentrations of glycerol and metal ions. Proceedings of the 2nd African Conference on Edible and Medicinal Mushrooms, *Noguchi Memorial Institute for Medical Research*, Accra, Ghana.

SedNet (2004) *Contaminated sediment in European river basins*. European Sediment Research Network, European Union.

Schneider, D. (2009) *Quantitative ecology: Measurements, models and scaling*. Second Edition. Science Direct.

Scholes, L., Faulkner, H.P., Tapsell, S. and Downward, S. (2008) ‘Urban rivers as pollutant sinks and sources: a public health concern to recreational river users?. *Water, Air and Soil Pollution Focus*, 8, pp.543-553.

Schwab, O. (2016) *Systematic evaluation of data, system structure and information content in material flow analysis*. PhD Thesis, Technische Universität Wien Vienna.

Sebakira, K., Origa, H.O., Basamba, T.A., Mutumba, G. and Kakudidi, E. (2010) Assessment of heavy metal pollution in the urban stream sediment and its tributaries. *International Journal of Environmental Science Technology*, 7, pp.435-436.

Sedeño-Díaz, J.E., López-López, E., Mendoza-Martínez, E., Rodríguez-Romero, A.J. and Morales-García, S.S. (2019) Distribution coefficient and metal pollution index in water and sediments: Proposal of a new index for ecological risk assessment of metals. *Water*, 12(1), 29.

Shah, M.H., Shaheen, N., and Jaffar, M. (2005) Characterization, source identification and apportionment of selected metals in TSP in urban Islamabad, Pakistan. *Environmental Monitoring and Assessment, 114*, pp.573–787.

Shah, A.I. (2017) Heavy metal impact on aquatic life and human health – an overview, *IAIA17 Conference Proceedings*.

Shanbehzadeh, S., Dastjerdi, M.V., Hassanzadeh, A. and Kiyanizadeh, T. (2014) Heavy metals in water and sediment: A case study of Tembi river. *Journal of Environmental Reserach and Public Health*, 2014, pp.1-5.

Shaw Renewables (2018) *Biogas Plants in the UK.* [Online]. Available at: https://www.shawrenewables.co.uk/biogas-plants-in-the-uk-2018/. (Accessed 22 March 2020).

Silva, D.M.L., Camargo, P.B., Mcdowell, W.H., Vieira, I., Salomao, M.S.M.B. and Martinelli, L.A. (2012) Influence of land use changes on water chemistry in streams in the State of São Paulo, southeast Brazil. *Earth Sciences*, 84(4), pp.919-930.

Simpson, S. and Batley, G. (2016) *Sediment quality assessment: A practical guide*. 2nd edn. Australia: CSIRO Publishing.

Sinha, N.K., and Kuszta, B. (1983) *Modelling and identification of dynamic systems.* New York: Van Nostrand Reinhold Co.

Siopi, A. (2015) Substance flow analysis (SFA) of polycyclic aromatic hydrocarbons (PAHs) in road runoff. *Environmental Science*, ID:130137404.

Smith, M.D., Koerner, S.E, Knapp, A.K., Avolio, M.L., Chaves, F.A., Denton, E.M., Dietrich, J., Gibson, D.J., Gray, J., Hoffman, A.M., Hoover, D.L., Komatsu, K.J, Silletti, A., Wilcox, K.R., Yu, Q, Blair, J.M. (2019) Mass ratio effects underlie ecosystem responses to environmental change. *Journal of Ecology*, 108(3), pp.855-864.

Snook, L. and Whitehead, P.G. (2004) Water quality and ecology of the River Lee: mass balance and a review of temporal and spatial data. *Hydrology and Earth System Sciences*, 8, pp.636-650.

Søberg, L.C., Winston, R., Viklander, M. and Blecken, G-T. (2019) Dissolved metal adsorption capacities and fractionation in filter materials for use in stormwater bioretention facilities. *Water Research X*, 4, 100032.

SOCOPSE (2009) *An inventory and assessment of options for reducing emissions: Cadmium. source control of priority substances in Europe*. Specific Targeted Research Project. INERIS, EU.

Sodomková, K. (2009) *Abnormal diurnal variations of dissolved oxygen in the River Lea Navigation*. Thesis: BSc Environmental Science, Birbeck College, London, UK.

Sörme, L. (2008) *Material flows in Sweden 1998-2005: Data sources, methods and results*. Statistics Sweden, Regions and Environment Department.

Sörme, L. (2003) *Urban heavy metals: stocks and flows*. Linköping Studies in Arts and Science, ISSN 0282-9800, 270. Linköping University, Linköping.

Sörme, L. and Lagerkvist, R. (2002) Sources of heavy metals in urban wastewater in Stockholm. Science of the Total Environment, 298, pp.131-145.

Sörme, L., Bergbäck, B. and Lohm, U. (2001) Goods in the anthroposphere as a metal emission source: A case study of Stockholm *water, air and soil pollution*, 1, pp.213-227.

Sower, G.J. (2008) *Spatial and temporal variations of bioavailable polycyclic aromatic hydrocarbons in the Lower Williamette River*. PhD Thesis. Oregon State University.

Sower, G.J. and Anderson, K.A. (2008) Spatial and temporal variation of freely dissolved PAHs in an urban river undergoing Superfund remediation. *Environment Science and Technology*, 42, pp.9065–9071.

Stanisavljevic, N. and Brunner, P.H. (2014) Combination of material flow analysis and substance flow analysis: A powerful approach for decision support in waste management. *International Solid Waste Association*, 32(8), pp.733-744.

Sterling, T. and Dekate, C. (2008) Productivity in high-performance computing. *Advances in Computers*, 72, pp.101–134.

Steuer, J., Selbig, W., Hornewer, N. and Prey, J. (1997) Sources of contamination in an urban basin in Marquette, Michigan, and an analysis of concentrations, loads, and data quality. *U.S. Geological Survey Water Resources Investigations Report 97-4242,* Denver: U.S. Geological Survey.

Stout, S.A., Uhler, A.D., and Emsbo-Mattingly, S.D. (2004) Comparative evaluation of background anthropogenic hydrocarbons in surficial sediments from nine urban waterways. *Environmental Science and Technology*, 38, pp.2987-2994.

Streiner, D.L. and Norman, G.R. (2012) Mine is bigger than yours: measures of effect size in research. *Chest*, 141(3), pp.595-598.

Sullivan, A.B. and Drever, J.I. (2001) Spatiotemporal variability in stream chemistry in a high-elevation catchment affected by mine drainage. *Journal of Hydrology*, 252, pp.237-250.

Sultan, K., Shazili, N.A. and Peiffer, S. (2011) Distribution of Pb, As, Cd, Sn and Hg in soil, sediment and surface water of the tropical river watershed, Terengganu (Malaysia). *Journal of Hydro-environment Research*, 5, pp.169-176.

Suthar S., Nema, A.K., Chabukdhara, M. and Gupta, S.K. (2009) Assessment of metals in water and sediments of Hindon River, India: Impact of industrial and urban discharges. *Journal of Hazardous Materials,* 171, pp.1088–1095.

Sutherland, R.A. (2000) Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. *Environmental Geology*, 39, pp.611-627.

Taka, M., Aalto, J., Virkanen, J. and Luoto, M. (2016) The direct and indirect effects of watershed land use and soil type on stream water metal concentrations. *Water Resources Research*, 52(10), pp.7711-7725.

Talbot, C.J., Bennett, E.M., Cassell, K., Hanes, D.M., Minor, E.C, Paerl, H., Raymond, P.A., Vargas, R., Vidon, P.G., Wollheim, W. and Xenopoulos, M.A. (2018) The impact of flooding on aquatic ecosystem services. *Biogeochemistry,* 141, pp.439-461.

Taylor, K. and Owens, P.O. (2009) Sediments in urban river basins: a review of sediment-contaminant dynamics in an environmental system conditioned by human activities. *Journal of Soils and Sediments*, 9. pp.281-303.

Taylor, K., Owens, P.O., Batalla, R.J. and Garcia, C. (2008) Sediment and contaminant sources and transfers in rivers basins. *Sustainable Management of Sediment Resources, Sediment Management at the River Basin Scale*, 8, pp.83-135.

Tchounwou, P.B., Yedjou, C.G., Patlolla, A.K. and Sutton, D.J. (2012) Heavy metals toxicity and the environment. PubMed Central, 101, pp.133-164.

Teaf, C.M., Covert, D.J. and Kothur, S.R. (2010) Urban polycyclic aromatic hydrocarbons (PAHs): A Florida perspective. *Soils, Sediments, Water and Energy*, 13, pp.303 – 315.

Tetra Tech (2011) *User's guide spreadsheet tool for the estimation of pollutant load (STEPL)* Version 4.1. Tetra Tech Inc.: Fairfax, VA, USA.

Thames21 (2019) *Spatial quantification of road runoff pollution in Greater London*. London, UK.

Thames21 (2015) *The london management catchment report*. London, UK.

Thames21 (2013a) *Rescuing Pymmes park lake*. Love the Lea News. London, UK.

Thames21 (2013b) *Project reedbed: Existing and potential reedbed sites on the Lea Navigation from Bromley-by-Bow to the M25*. Final report. London, UK.

Thames21 (2012). *Where does pollution come from?*. Thames21 [Online]. Available at: http://www.thames21.org.uk/2012/12/pollutionsources/. (Accessed: 10 January 2016).

Thames21 (2011) *A water quality analysis of the River Lee and major tributaries within the perimeter of the M25, from Waltham Abbey to Bow Locks*. London, UK.

Thames Water Utilities Limited (2020) Deephams sewage treatment works upgrade. Final report. London, UK

Thames Water Utilities Limited (2015) *Lower Lee abstraction investigation programme: Scoping study*. Final report. Cascade Consulting. London, UK.

Thames Water Utilities Limited (2013) *Water resources programme*, London, UK.

Thames Water Utilities Limited (2012a) *Deephams wastewater treatment plant*, London, UK. Information provided via email by Richard Reeve.

Thames Water Utilities Limited (2012) *Water resources management plan: Lower Lee scheme option report*. Phase 1 Assessment. Cascade Consulting. London, UK.

The Technical Guidance for Deriving Environmental Quality Standards - TGD-EQS-EC (2011) *Common implementation strategy for the Water Framework Directive (2000/60/EC)*. Guidance Document No. 27.

Thomas, R. (2013) Practical Guide to ICP-MS: A Tutorial for beginners, USA, CRC Press.

Thorpe, A. and Harrison, R.M. (2008) Sources and properties of non-exhaust particulate matter from road traffic: a review. *Science of the Total Environment*, 400(1-3), pp.270-282.

Tobiszewski, M. and Namieśnik, J. (2012) PAH diagnostic ratios for the identification of pollution emission sources. *Environmental Pollution,* 162, pp.110-119.

Tokatli, C. (2019) Water and sediment quality assessment of the Lifeblood of Thrace region (Turkey): Meric River Basin. *Fresenius Environmental Bulletin*, 28(5), pp.4131-4140.

Tomlinson, D.L., Wilson, J.G., Harris, C.R. and Jeffrey, D.W. (1980) Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. *Helgoläänder Meeresuntersuchungen*, 33, pp.566–575.

Torretta, V. (2012) PAHs in wastewater: removal efficiency in a conventional wastewater treatment plant and comparison with model predictions. *Environmental Technology*, 33(7-9), pp.851-855.

Totten, L.A., Panangadan, M., Eisenreich, S.J., Cavallo, G.J. and Fikslin, T.J. (2006) Direct and indirect atmospheric deposition of PCBs to the Delaware River watershed. Environmental Science & Technology, 40(7), pp.2171-6.

Transport Statistics Great Britain (2012) *Statistical release: Transport statistics Great Britain*, UK: Department for Transport.

Tukker, A., Kleijn, R., van Oers, L. and Smeets, E.R.W. (1998) Combining SFA and LCA: The Swedish PVC analysis. *Journal of Industrial Ecology*, 1, pp.93-116.

Turek, A., Wieczorek, K. and Wolf, W.M. (2019) Digestion procedure and determination of heavy metals in Sewage sludge – analytical problem. Sustainability, 11(6), pp.1753.

Turner, J.N., Brewer, P.A. and Macklin, M.G. (2008) Fluvial-controlled metal and As mobilisation, dispersal and storage in the Rio Guadiamar, SW Spain and implications for long-term contaminant fluxes to the Doñana wetlands. *The Science of the Total Environment*, 394, pp.144-161.

Udo de Haes, H., Heijungs, R., Huppes, G., Voet, E. van der and Hettelingh, J. (2000) Full mode and attribution mode in environmental analysis. *Journal of Industrial ecology*, 4 (1), pp.45-56.

UNEP. (2020) *Mercury negotiations archive: INC5* [Online]. Available at: http://www.unep.org/. (Accessed 27 Mar 2020).

UK Local Authorities (2018) *Outfalls discharge locations through OS maps*, provided by UK local authorities through face-to-face meetings.

UK TAG (2013) *Updated recommendations on environmental standards - river basin management (2015-21): Final Report*. United Kingdom Technical Advisory Group. UK.

UK TAG (2008a) *Proposals for environmental quality standards for annex VIII substances. Final (SR1 – 2007)*. United Kingdom Technical Advisory Group on the Water Framework Directive. UK.

UK TAG (2008b) *Environmental standards and conditions (Phase 1): Final report.* United Kingdom Technical Advisory Group on the Water Framework Directive. (SR1 – 2006).

UKWIR (2019) *The national chemical investigations programme 2015-2020*. Volume 1 Part 3 (2017-2019): monitoring of sewage effluents and surface waters - tranche 3. 14 March 2019. Final report, internal. London: UK Water Industry Research Ltd.

UNEP (2020) *The sustainable development goals report*. United Nations Publications. New York, USA.

United Nations (2011) *Policy brief on water quality. Policy and Analytical Briefs*. March 2011. United Nations. Rome, Italy.

US EPA 415.3 (2009) Determination of total organic carbon and specific UV absorbance at 254 nm in source water and drinking water. United States Environmental Protection Agency [Online]. Available at: https://cfpub.epa.gov/si/si_public_record_report.cfm? dirEntryId=214406 (Accessed: 28 March 2016).

US EPA 835.1230 (2008) *Fate, transport and transformation test guidelines: adsorption/desorption (batch equilibrium)*. United States Environmental Protection Agency [Online]. Available at: https://www.regulations.gov/document?D=EPA-HQ-OPPT-2009-0152-0006. (Accessed: 10 March 2015).

US EPA 3051A (2007) *Microwave assisted acid digestion of sediments, sludges, soils and oils.* United States Environmental Protection Agency [Online]. Available at: http://www3.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3051a.pdf. (Accessed: 5 February 2014).

US EPA 3015A (2007) *Microwave assisted acid digestion for aqueous samples and extracts.* United States Environmental Protection Agency [Online]. Available at: http://www3.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3015a.pdf. (Accessed: 5 February 2014).

US EPA 3545A (2007) *Pressurized fluid extraction – PFE.* United States Environmental Protection Agency [Online]. Available at: http://www3.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3545a.pdf. (Accessed: 20 March 2014).

US EPA (2001) *PLOAD version 3.0 An ArcView GIS tool to calculate nonpoint sources of pollution in watershed and stormwater projects*. User’s Manual. Environmental Protection Agency, USA.

US EPA QA00 (2000) Guidance for data quality assessment practical methods for data analysis. United States Environmental Protection Agency [Online]. Available at: https://www.epa.gov/sites/production/files/2015-06/documents/g9-final.pdf (Accessed: 15 June 2016).

US EPA 415.1 (1974) Measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes. United States Environmental Protection Agency [Online].

Available at: http://www.caslab.com/EPA-Methods/PDF/EPA-Method-4151.pdf (Accessed: 28 March 2016).

University of York (2021) *Global Monitoring of Pharmaceuticals Project*, York, UK.

Utete, B., Nhiwatiwa, T., Barson, M. and Mabika, N. (2013). Metal correlations and mobility in sediment and water from the Gwebi River in the upper Manyame catchment, Zimbabwe. *International Journal of Water Sciences*, 4, pp.1-8.

Valipour, R., Boegman, L., Bouffard, D. and Rao, Y.R. (2017) Sediment resuspension mechanisms and their contributions to high-turbidity events in a large lake. *Limnology and Oceanography*, 62, pp.1045-1065.

Van der Voet, E. (2002) Substance flow analysis methodology. *A handbook of Industrial Ecology*, edited by Ayres, R.U. and Ayres, L.W. The Netherlands, pp.91-101.

Van Gils, J., Posthuma, L., Cousins, I.T., Brack, W., Altenburger, R., Baveco, H., Focks, A., Greskowiak, J., Kühne, R., Kutsarova, S., Lindim, C., Markus, A., Van de Meent, D., Munthe, J., Schueder, R., Schüürmann, G., Slobodnik, J., de Zwart, D. and Van Wezel, A. (2020) Computational material flow analysis for thousands of chemicals of emerging concern in European waters. *Journal of Hazardous Materials*, 397, 122655.

Van Leeuwen, H.P., Town, R.M, Buffle, J., Cleven, R.F.M.J., Davison, W., Puy, J., Van Riemsdijk, W.H. and Sigg, L. (2005) Dynamic speciation analysis and bioavailability of metals in aquatic systems. *Environmental Science and Technology*, 39, pp.8545-8556.

Van Metre, P.C., Mahler, B.J. and Furlong, E.T. (2000) Urban sprawl leaves its PAH signature. *Environmental Science and Technology*, 34, pp.4064–4070.

Vane, C.H., Kim, A.W., Santos, R.A.L. and Moss-Hayes, V. (2022) Contrasting sewage, emerging and persistent organic pollutants in sediment cores from the River Thames estuary, London, England, UK. *Marine Pollution Bulletin*, 175, 113340.

Viganò, L. (2000) Assessment of the toxicity of the river Po sediments with Ceriodaphnia dubia. *Aquatic Toxicology*, 47, pp.191-202.

Wagener, T. and Kollat J. (2007) Numerical and visual evaluation of hydrological and environmental models using the Monte Carlo analysis toolbox. *Environmental Modelling and Software*, 22 (2007), pp.1021-1033.

Waldner, M.H., Halter, R., Sigg, A., Brosh, B., Gehrmann, H.J. and Keunecke, M. (2013) Energy from waste – clean, efficient, renewable: Transitions in combustion efficiency and NOx control. *Waste Management*, 33(2), pp.317-326.

Wang, C., Zhou, S., Wu, S., Song, J., Shi, Y., Li, B. and Chen, H. (2017) Surface water polycyclic aromatic hydrocarbons (PAH) in urban areas of Nanjing, China. *Water Science and Technology*, 76, pp.2150-2157.

Wang, G., Mielke, H.W., Quach, V., Gonzales, C. and Zhang, Q. (2010) Determination of polycyclic aromatic hydrocarbons and trace metals in New Orleans soils and sediments. *Soil and Sediment Contamination: An International Journal*, 1, pp.313-327.

Wang, S., Dai, J. and Su, M. (2012) Material flow analysis of fossil fuels in China during 2000–2010. *Energy Economics and Policy – The scientific World Journal*, 625828.

Watts, A.W., Ballestero, T.P., Roseen, M.R. and Houle, J.P. (2010) Polycyclic aromatic hydrocarbons in stormwater runoff from seal coated pavements. Environmental Science and Technology, 44(23), pp.8849-8854.

Weather, H. and Evans, E. (2009) Land use, water management and future flood risk. *Land Use Policy*, 26, pp.S251-S264.

Weiner, E. (2013) *Applications of environmental aquatic chemistry: a practical guide*. New York, US: CRC Press.

Wegman, R., Melis, P. and Josefsson, B. (1986) Organic pollutants in water. *Critical Reviews in Analytical Chemistry*, 16, pp.281 - 321.

Weisberg, S. (2005) *Outliers and influence, in applied linear regression*. 3rd edn. Hoboken, NJ, US: John Wiley and Sons Inc.

Wiedmann, T., Minx, J., Barrett, J., Vanner, R. and Ekins, P. (2006) *Sustainable consumption and production - development of an evidence base project Ref.: SCP001 Resource Flows*. Stockholm Environment Institute. York, UK.

Wenborn, M.J., Coleman, P.J., Passant, N.R., Lymberidi, E., Sully, J. and Weir, R.A. (1999) *Speciated PAH inventory for the UK*. Prepared by AEA Technology plc for the Department of the Environment, Transport and the Regions. AEAT-3512/REMC/20459131/ISSUE 1.

WFD-UK TAG Group (2012) *Estimation of background reference concentrations for metals in UK freshwaters*. Water Framework Directive - United Kingdom Technical Advisory Group (WFD-UK TAG), England, UK.

WHO (2005) *Tin and inorganic tin compounds. Concise International Chemical Assessment*. World Health Organization. Document 65. Available at: http://www.inchem.org/documents/cicads/cicads/cicad65.htm#6.1.2 (Accessed: 25 January 2016).

Wilcke, W. (2007) Global patterns of polycyclic aromatic hydrocarbons (PAHs) in soil. *Geoderma*, 141, pp.157-166.

Wilson, C., Clarke, R., D'Arcy, B.J., Heal, K.V. and Wright, P.W. (2005) Persistent pollutants urban rivers sediment survey: Implications for pollution control. *Water Science and Technology*, 51, pp.217–224.

Wlodarczyk-Makula, M. (2005) The Loads of PAHs in Wastewater and sewage sludge of municipal treatment plant. *Journal of Polycyclic Aromatic Compounds*, 25(2), pp.183-194.

WTE (2021) *Water technology engineering: Wastewater produced in the home*. WTE Ltd: Sewage Treatment Systems, UK.

Yan, W. Chin, J., Wang, Z., Huang, W. and Zhang, G. (2009) Spatial and temporal distribution of polycyclic aromatic hydrocarbons (PAHs in Sediments from Daya Bay, South China. *Environmental Pollution*, 157, pp.1823-1830.

Yang, H.H., Lai, S.O., Hsieh, L.T., Hsueh, H.J. and Chi, T.W. (2002) Profiles of PAH emission from steel and iron industries. *Chemosphere,* 48(10), pp.1061-1074.

Yemenicioglu, S. and De Mora, S. (2009) Occurrence and seasonal variation of butyltin species along the Mediterranean coast of Turkey. *Marine Pollution Bulletin*, 58, pp.163-166.

Yim, U.H., Hong, S.H. and Shim, W.J. (2007) Distribution and characteristics of PAHs in sediments from the marine environment of Korea. *Chemosphere,* 68, pp.85-92.

Yoshida, H., Christensen, T.H., Guildal, T. and Scheutz, C. (2015) A comprehensive substance flow analysis of a municipal wastewater and sludge treatment plant. *Chemosphere*, 138, pp.874–882.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D. and Sylvestre, S. (2002) PAHs in the Fraser river basin: A critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry*, 33, pp.489-515.

Zeng, X., Zheng, H., Gong, R., Eheliyagoda, D. and Zeng, X. (2018) Uncovering the evolution of substance flow analysis of nickel in China. *Resources, Conservation and Recycling,* 135, pp.210-215.

Zero Emission Europe (2015) *Air pollution from waste disposal: Not for public breath*. Report undertaken by Fundació ENT.

Zhang, C., Yu, Z., Zeng, G., Jiang, M., Yang, Z., Cui, F., Zhu, L., Shen, L. and Hu, L. (2014) Effects of sediment geochemical properties on heavy metal bioavailability. *Environment International*, 73, pp.270-281.

Zhang, L. and Liu, J. (2014) In situ relationships between spatial–temporal variations in potential ecological risk indexes for metals and the short-term effects on periphyton in a macrophytedominated lake: a comparison of structural and functional metrics. *Ecotoxicology*, 23, pp.553-566.

Zhang, X., Liu, Y. and Zhou, L. (2018) Correlation analysis between landscape metrics and water quality under multiple scales. *International Journal of Environmental Research and Public Health*, 15(8), p.1606.

Zhang, Y., Zhang, H., Zhang, Z., Liu, C, Sun, C., Zhang, W. and Marhaba, T. (2018) pH effect on heavy metal release from a polluted sediment. *Journal of Chemistry*, 2018(ID7597640), 7 pages.

Zhao, D., Chen, H., Yu, E. and Lou, T. (2019) $PM_{2.5}/PM_{10}$ ratios in eight economic regions and their relationship with meteorology in China. *Hindawi, Advances in Meteorology* 2019, Article ID 5295726, 15 pages.

Zheng, Y., Luoa, X., Zhangc, W., Wua, B., Hana, F., Lina, Z. and Wangc, X. (2012) Enrichment behavior and transport mechanism of soil-bound PAHs during rainfall-runoff events. *Environmental Pollution*, 171, pp.85-92. [Online]. Available at: http://www.sciencedirect.com/science/article/pii/S0269749112003582. (Accessed 15 March 2020).

Živković, M., Jovasevic-stojanovic, M., Cvetkovic, A., Lazovic, I., Tasic, V., Stevanovic, Z. and Grzetic, I. (2015) PAHs levels in gas and particle-bound phase in schools at different locations in Serbia. *Chemical Industry and Chemical Engineering Quarterly*, 21, pp.159-167.

APPENDICES

APPENDIX A1. Metal concentrations in water (µg/l) and sediment (µg/g) samples collected on 11th November 2014.

Sampling Site	Matrix	Cd	Cu	Hg	Ni	Pb	Sn	Zn
		Mean and standard deviation						
A	Water	0.02 ± 0.00	2.05 ± 0.01	0.02 ± 0.00	3.25 ± 0.01	0.21 ± 0.00	0.24 ± 0.00	3.66 ± 0.00
	Sediment	0.53 ± 0.04	42.22 ± 0.23	0.01 ± 0.00	13.66 ± 0.14	88.84 ± 7.09	0.67 ± 0.04	113.56 ± 4.65
B	Water	0.06 ± 0.00	5.27 ± 0.14	0.01 ± 0.00	2.49 ± 0.07	0.69 ± 0.01	0.42 ± 0.00	2.73 ± 0.07
	Sediment	0.71 ± 0.04	51.89 ± 1.20	0.01 ± 0.00	21.47 ± 0.25	75.33 ± 0.65	0.62 ± 0.11	219.77 ± 2.69
C	Water	0.12 ± 0.00	4.24 ± 0.09	0.01 ± 0.00	1.53 ± 0.04	0.14 ± 0.01	0.10 ± 0.00	1.95 ± 0.06
	Sediment	2.71 ± 0.09	170.66 ± 8.26	0.28 ± 0.01	26.52 ± 0.81	204.07 ± 2.63	1.60 ± 0.46	573.17 ± 12.59
D	Water	0.03 ± 0.00	3.42 ± 0.32	0.01 ± 0.00	10.72 ± 0.38	0.94 ± 0.09	0.10 ± 0.00	10.44 ± 0.29
	Sediment	1.95 ± 0.30	160.43 ± 11.70	0.40 ±0.28	26.57 ± 0.34	207.03 ± 2.69	7.14 ± 0.03	527.87 ± 22.91
E	Water	0.04 ± 0.00	6.92 ± 0.07	0.01 ± 0.00	7.37 ± 0.11	1.20 ± 0.02	0.42 ± 0.00	7.85 ± 0.11
	Sediment	0.69 ± 0.07	53.66 ± 2.40	0.01 ± 0.00	9.99 ± 0.65	191.09 ± 2.43	1.36 ± 0.11	235.77 ± 0.14
F	Water	0.06 ± 0.00	5.51 ±0.18	0.01 ± 0.00	5.89 ± 0.25	0.72 ± 0.01	0.09 ± 0.00	6.25 ± 0.25
	Sediment	0.35 ± 0.01	35.57 ± 1.97	0.01 ± 0.00	7.52 ± 0.72	58.57 ± 8.65	1.29 ± 0.09	187.20 ± 3.55
G	Water	0.07 ± 0.00	4.03 ± 0.12	0.01 ± 0.00	5.86 ± 0.07	3.25 ± 0.02	0.15 ± 0.00	5.94 ± 0.08
	Sediment	0.60 ± 0.00	45.04 ± 1.33	0.01 ± 0.00	17.96 ± 0.90	59.27 ± 2.23	1.47 ± 0.15	187.59 ± 4.50
H	Water	0.06 ± 0.00	2.87 ± 0.08	0.01 ± 0.00	8.38 ± 0.10	0.66 ± 0.01	0.18 ± 0.00	8.36 ± 0.08
	Sediment	2.57 ± 0.18	205.60 ± 2.97	0.19 ± 0.03	30.07 ± 1.44	299.13 ± 18.10	8.76 ± 1.55	755.07 ± 14.99
I	Water	0.03 ± 0.00	2.41 ± 0.00	0.01 ± 0.00	5.84 ± 0.00	0.29 ± 0.01	0.14 ± 0.00	6.07 ± 0.00
	Sediment	1.15 ± 0.04	81.73 ± 5.47	0.01 ± 0.00	17.13 ± 0.24	121.78 ± 7.54	3.84 ± 0.50	337.37 ± 14.28
J	Water	0.01 ± 0.00	3.86 ± 0.14	0.01 ± 0.00	6.51 ± 0.02	0.75 ± 0.02	0.76 ± 0.01	6.56 ± 0.05
	Sediment	4.16 ± 0.05	206.40 ± 7.78	0.31 ± 0.27	37.06 ± 0.58	251.93 ± 4.81	8.58 ± 0.47	684.67 ± 13.58
K	Water	0.08 ± 0.00	3.08 ± 0.14	0.01 ± 0.00	7.05 ± 0.18	0.33 ± 0.00	0.10 ± 0.00	7.13 ± 0.16
	Sediment	4.82 ± 0.05	107.92 ± 3.87	0.53 ± 0.05	37.59 ± 0.31	192.82 ± 1.00	9.42 ± 0.04	565.17 ± 0.14

APPENDIX A2. Metal concentrations in water (μg/l) and sediment (μg/g) samples collected on 9th December 2014.

Sampling Site	Matrix	Cd	Cu	Hg	Ni	Pb	Sn	Zn
		Mean and standard deviation						
A	Water	0.02 ± 0.00	1.04 ± 0.24	0.03 ± 0.00	10.14 ± 0.38	0.92 ± 0.00	0.19 ± 0.00	10.70 ± 0.40
	Sediment	0.74 ± 0.01	37.38 ± 0.23	0.08 ± 0.01	18.50 ± 0.96	56.07 ± 0.68	0.89 ± 0.07	145.52 ± 0.76
B	Water	0.16 ± 0.00	2.10 ± 0.13	0.03 ± 0.00	3.58 ± 0.17	1.70 ± 0.03	0.17 ± 0.00	4.09 ± 0.22
	Sediment	0.66 ± 0.00	41.29 ± 0.18	0.05 ± 0.00	18.01 ± 0.06	68.41 ± 1.36	0.53 ± 0.08	193.06 ± 2.18
C	Water	0.97 ± 0.01	2.65 ± 0.07	0.03 ± 0.00	16.13 ± 0.22	1.48 ± 0.02	0.12 ± 0.01	17.12 ± 0.23
	Sediment	3.16 ± 0.02	146.46 ± 9.22	0.14 ± 0.00	22.34 ± 0.18	146.44 ± 1.88	0.83 ± 0.01	611.86 ± 0.14
D	Water	0.16 ± 0.00	4.14 ± 0.46	0.03 ± 0.00	16.56 ± 0.31	1.79 ± 0.04	0.21 ± 0.00	16.31 ± 0.31
	Sediment	1.70 ± 0.04	159.41 ± 5.73	0.80 ±0.01	27.03 ± 0.20	193.73 ± 3.22	6.54 ± 0.15	489.06 ± 12.59
E	Water	0.14 ± 0.01	1.06 ± 0.16	0.03 ± 0.00	12.83 ± 0.60	1.68 ± 0.05	0.14 ± 0.00	13.43 ± 0.64
	Sediment	0.52 ± 0.04	59.25 ± 0.04	0.05 ± 0.00	8.38 ± 0.00	167.47 ± 11.57	1.55 ± 0.06	169.85 ± 13.08
F	Water	0.01 ± 0.00	1.87 ± 0.12	0.03 ± 0.00	8.16 ± 0.52	0.95 ± 0.02	0.09 ± 0.00	8.60 ± 0.54
	Sediment	0.30 ± 0.02	35.90 ± 3.79	0.05 ± 0.00	6.22 ± 0.06	49.98 ± 3.89	0.55 ± 0.11	94.12 ± 2.29
G	Water	0.05 ± 0.00	4.38 ± 0.01	0.03 ± 0.00	11.54 ± 0.13	1.77 ± 0.01	0.25 ± 0.00	11.79 ± 0.10
	Sediment	1.65 ± 0.00	160.62 ± 0.48	0.12 ± 0.03	24.65 ± 1.05	212.71 ± 4.10	4.82 ± 0.11	597.96 ± 4.24
H	Water	0.06 ± 0.00	2.25 ± 0.02	0.03 ± 0.00	7.19 ± 0.01	1.05 ± 0.00	0.31 ± 0.00	7.26 ± 0.00
	Sediment	1.90 ± 0.12	128.39 ± 8.30	0.05 ± 0.00	28.88 ± 0.07	186.35 ± 4.61	3.71 ± 0.06	558.56 ± 4.24
I	Water	0.09 ± 0.00	2.82 ± 0.06	0.03 ± 0.00	15.94 ± 0.17	2.76 ± 0.01	0.24 ± 0.00	16.33 ± 0.21
	Sediment	0.99 ± 0.04	65.43 ± 2.79	0.05 ± 0.00	14.36 ± 0.19	105.28 ± 3.07	2.69 ± 0.04	278.06 ± 15.41
J	Water	0.13 ± 0.00	1.06 ± 0.01	0.03 ± 0.00	6.80 ± 0.18	0.78 ± 0.01	0.77 ± 0.02	6.91 ± 0.19
	Sediment	3.63 ± 0.02	65.09 ± 2.25	0.05 ± 0.00	48.99 ± 1.78	208.41 ± 18.10	2.70 ± 0.04	469.96 ± 8.49
K	Water	0.01 ± 0.00	1.92 ± 0.06	0.03 ± 0.00	4.81 ± 0.04	0.82 ± 0.01	0.06 ± 0.00	5.12 ± 0.02
	Sediment	4.75 ± 0.09	161.50 ± 1.30	0.49 ± 0.04	35.78 ± 0.86	169.46 ± 6.83	3.30 ± 0.02	534.56 ± 5.09

APPENDIX A3. Metal concentrations in water (µg/l) and sediment (µg/g) samples collected on 11th March 2015.

Sampling Site	Matrix	Cd	Cu	Hg	Ni	Pb	Sn	Zn
		Mean and standard deviation						
A	Water	0.15 ± 0.00	1.93 ± 0.38	0.62 ± 0.27	0.66 ± 0.59	3.34 ± 0.01	0.15 ± 0.06	1.25 ± 0.63
	Sediment	0.84 ± 0.00	54.84 ± 0.55	0.11 ± 0.00	17.51 ± 0.02	71.07 ± 0.04	7.07 ± 0.04	206.96 ± 0.14
B	Water	0.12 ± 0.00	1.72 ± 0.13	0.27 ± 0.11	2.98 ± 0.11	2.26 ± 0.01	0.07 ± 0.00	3.63 ± 0.07
	Sediment	0.58 ± 0.01	58.78 ± 0.47	0.11 ± 0.00	15.92 ± 0.24	92.93 ± 1.12	6.08 ± 0.07	261.36 ± 2.12
C	Water	0.03 ± 0.00	2.23 ± 0.00	0.12 ± 0.01	0.11 ± 0.03	0.90 ± 0.02	0.06 ± 0.01	0.55 ± 0.09
	Sediment	2.74 ± 0.04	226.21 ± 4.24	0.73 ± 0.00	21.82 ± 0.20	179.96 ± 2.60	30.89 ± 0.28	641.26 ± 0.85
D	Water	0.03 ± 0.00	1.52 ± 0.01	0.09 ± 0.00	9.26 ± 0.09	1.19 ± 0.02	0.56 ± 0.01	9.15 ± 0.10
	Sediment	1.40 ± 0.03	131.04 ± 1.17	1.08 ±0.07	14.84 ± 0.46	175.08 ± 3.56	45.74 ± 2.31	550.76 ± 0.14
E	Water	0.04 ± 0.00	3.84 ± 0.04	0.08 ± 0.11	13.72 ± 0.12	0.92 ± 0.02	0.07 ± 0.03	14.47 ± 0.12
	Sediment	1.78 ± 0.03	149.53 ± 3.82	1.07 ± 0.03	6.38 ± 0.06	239.32 ± 1.13	73.95 ± 5.32	499.86 ± 1.70
F	Water	0.06 ± 0.00	4.73 ± 0.37	0.03 ± 0.00	15.63 ± 0.51	1.28 ± 0.07	0.26 ± 0.06	16.21 ± 0.51
	Sediment	1.21 ± 0.01	159.54 ± 2.16	0.55 ± 0.00	18.94 ± 0.26	253.02 ± 0.14	27.60 ± 0.16	616.56 ± 2.40
G	Water	0.02 ± 0.00	1.74 ± 0.05	0.03 ± 0.00	11.34 ± 0.03	0.76 ± 0.02	0.98 ± 0.02	11.62 ± 0.17
	Sediment	2.30 ± 0.02	254.51 ± 1.27	0.92 ± 0.01	24.50 ± 0.48	344.02 ± 2.12	46.10 ± 0.24	974.76 ± 1.27
H	Water	0.01 ± 0.00	1.21 ± 0.01	0.03 ± 0.00	5.25 ± 0.04	0.51 ± 0.00	0.11 ± 0.01	5.45 ± 0.08
	Sediment	2.00 ± 0.05	207.91 ± 2.40	0.76 ± 0.00	24.17 ± 0.55	258.82 ± 0.71	35.83 ± 0.37	773.86 ± 10.18
I	Water	0.04 ± 0.00	2.59 ± 0.04	0.03 ± 0.00	24.34 ± 0.89	2.07 ± 0.00	0.23 ± 0.02	24.92 ± 0.85
	Sediment	1.33 ± 0.00	104.92 ± 0.92	0.29 ± 0.01	13.45 ± 0.12	135.72 ± 0.17	19.75 ± 0.34	428.66 ± 1.70
J	Water	0.05 ± 0.02	2.68 ± 0.23	0.03 ± 0.00	15.89 ± 0.82	0.69 ± 0.17	0.82 ± 0.26	16.33 ± 0.68
	Sediment	6.65 ± 0.07	173.52 ± 0.35	0.55 ± 0.00	58.96 ± 1.19	218.52 ± 0.85	32.94 ± 0.58	848.26 ± 11.31
K	Water	0.11 ± 0.01	3.62 ± 0.48	0.03 ± 0.00	5.65 ± 1.11	1.27 ± 0.13	0.34 ± 0.13	6.03 ± 1.16
	Sediment	3.72 ± 0.04	120.64 ± 1.77	1.29 ± 0.01	35.87 ± 0.41	213.92 ± 0.00	21.40 ± 0.64	635.26 ± 4.24

APPENDIX A4. Metal concentrations in water (µg/l) and sediment (µg/g) samples collected on 15th April 2015.

Sampling Site	Matrix	Cd	Cu	Hg	Ni	Pb	Sn	Zn
		Mean and standard deviation						
A	Water	0.04 ± 0.00	2.85 ± 0.03	0.20 ± 0.00	14.91 ± 0.17	1.79 ± 0.01	0.25 ± 0.01	14.76 ± 0.17
	Sediment	0.67 ± 0.00	40.07 ± 0.10	0.13 ± 0.00	13.90 ± 0.01	68.52 ± 0.78	6.01 ± 0.14	163.65 ± 0.28
B	Water	0.30 ± 0.10	3.20 ± 0.05	0.20 ± 0.00	13.53 ± 0.10	5.13 ± 0.51	0.21 ± 0.03	13.27 ± 0.24
	Sediment	0.53 ± 0.00	54.88 ± 0.00	0.13 ± 0.00	14.42 ± 0.10	91.97 ± 0.25	3.25 ± 0.06	234.21 ± 7.35
C	Water	0.26 ± 0.10	2.74 ± 0.10	0.20 ± 0.00	21.62 ± 0.79	7.31 ± 0.34	0.28 ± 0.02	21.76 ± 0.88
	Sediment	2.73 ± 0.02	35.00 ± 0.85	0.87 ± 0.00	23.13 ± 0.47	182.10 ± 0.13	23.89 ± 0.08	660.81 ± 1.41
D	Water	0.05 ± 0.00	1.73 ± 0.07	0.20 ± 0.00	17.56 ± 0.48	0.96 ± 0.10	0.59 ± 0.03	16.64 ± 0.43
	Sediment	1.37 ± 0.00	99.72 ± 0.31	0.89 ±0.01	7.23 ± 0.02	198.58 ± 0.18	22.62 ± 0.52	447.11 ± 2.12
E	Water	0.18 ± 0.01	2.58 ± 0.05	0.41 ± 0.04	12.12 ± 0.10	4.28 ± 0.00	0.23 ± 0.00	11.65 ± 0.09
	Sediment	1.33 ± 0.01	139.01 ± 0.27	0.31 ± 0.00	6.15 ± 0.01	241.51 ± 0.42	34.28 ± 0.24	606.21 ± 2.83
F	Water	0.17 ± 0.01	4.76 ± 0.05	0.20 ± 0.00	16.66 ± 0.18	4.87 ± 0.07	0.44 ± 0.01	16.39 ± 0.35
	Sediment	0.40 ± 0.00	50.99 ± 0.72	0.13 ± 0.00	10.60 ± 0.09	86.11 ± 0.79	17.01 ± 1.25	209.93 ± 2.15
G	Water	0.28 ± 0.00	3.20 ± 0.07	0.20 ± 0.00	16.41 ± 0.20	6.98 ± 0.10	0.83 ± 0.02	15.76 ± 0.21
	Sediment	2.11 ± 0.00	220.60 ± 0.28	0.84 ± 0.01	20.98 ± 0.06	276.71 ± 0.14	38.87 ± 0.11	814.51 ± 0.42
H	Water	0.06 ± 0.01	2.02 ± 0.03	0.20 ± 0.00	8.27 ± 0.13	1.93 ± 0.02	0.23 ± 0.01	7.51 ± 0.14
	Sediment	2.58 ± 0.01	254.10 ± 0.14	0.93 ± 0.01	24.22 ± 0.00	322.01 ± 0.28	41.92 ± 0.04	945.81 ± 0.28
I	Water	0.33 ± 0.00	2.27 ± 0.00	0.20 ± 0.00	11.62 ± 0.03	8.00 ± 0.02	0.30 ± 0.00	11.07 ± 0.03
	Sediment	1.37 ± 0.00	46.99 ± 0.58	0.13 ± 0.00	9.83 ± 0.01	78.43 ± 0.06	5.02 ± 0.07	230.01 ± 6.22
J	Water	1.82 ± 0.01	2.29 ± 0.04	0.20 ± 0.00	14.84 ± 0.10	8.44 ± 0.00	0.27 ± 0.01	14.32 ± 0.14
	Sediment	7.36 ± 0.02	258.50 ± 0.71	0.83 ± 0.02	54.87 ± 0.10	321.11 ± 0.42	35.69 ± 0.14	941.11 ± 2.12
K	Water	0.11 ± 0.00	3.38 ± 0.02	0.23 ± 0.02	18.39 ± 0.07	1.92 ± 0.00	0.31 ± 0.00	18.05 ± 0.10
	Sediment	5.56 ± 0.00	120.09 ± 0.16	1.57 ± 0.01	38.87 ± 0.35	195.98 ± 0.38	17.76 ± 0.21	650.21 ± 5.94

APPENDIX A5. Metal concentrations in water (µg/l) and sediment (µg/g) samples collected on 20th May 2015.

Sampling Site	Matrix	Cd	Cu	Hg	Ni	Pb	Sn	Zn
		Mean and standard deviation						
A	Water	0.02 ± 0.00	2.85 ± 0.02	1.00 ± 0.06	6.34 ± 0.12	0.29 ± 0.10	0.21 ± 0.05	6.70 ± 0.10
	Sediment	0.71 ± 0.01	49.93 ± 0.95	0.05 ± 0.00	18.73 ± 0.24	69.17 ± 0.55	7.98 ± 0.49	198.85 ± 1.75
B	Water	0.19 ± 0.04	3.76 ± 0.42	0.24 ± 0.01	19.97 ± 0.12	3.73 ± 0.78	0.28 ± 0.00	20.41 ± 1.41
	Sediment	0.44 ± 0.00	54.38 ± 0.14	0.05 ± 0.00	17.71 ± 0.06	94.56 ± 0.06	8.10 ± 0.07	240.89 ± 0.28
C	Water	0.07 ± 0.01	5.29 ± 0.61	0.23 ± 0.01	25.07 ± 1.07	2.44 ± 0.00	0.65 ± 0.12	23.42 ± 0.17
	Sediment	3.09 ± 0.03	550.38 ± 3.11	0.58 ± 0.03	29.91 ± 0.21	235.92 ± 0.42	57.74 ± 0.11	821.99 ± 3.54
D	Water	0.01 ± 0.01	2.30 ± 0.06	0.06 ± 0.03	19.31 ± 0.96	0.15 ± 0.03	0.35 ± 0.03	19.28 ± 0.18
	Sediment	1.73 ± 0.01	143.49 ± 0.66	0.73 ± 0.03	24.55 ± 0.04	220.32 ± 0.71	35.78 ± 0.17	565.29 ± 2.55
E	Water	0.08 ± 0.01	11.58 ± 0.05	0.08 ± 0.01	50.81 ± 0.81	13.25 ± 0.10	1.86 ± 0.00	53.90 ± 1.45
	Sediment	0.48 ± 0.00	40.31 ± 0.07	1.68 ± 0.07	0.01 ± 0.00	168.71 ± 0.07	25.31 ± 0.04	266.59 ± 0.14
F	Water	0.04 ± 0.01	5.05 ± 0.17	0.04 ± 0.00	20.53 ± 0.80	1.21 ± 0.02	0.27 ± 0.03	21.30 ± 1.26
	Sediment	0.37 ± 0.01	47.41 ± 0.30	0.05 ± 0.00	3.08 ± 0.11	123.64 ± 0.88	10.72 ± 0.09	253.49 ± 1.98
G	Water	0.03 ± 0.01	3.74 ± 0.01	0.04 ± 0.00	16.51 ± 0.62	1.69 ± 0.08	0.39 ± 0.01	16.68 ± 0.43
	Sediment	2.22 ± 0.04	247.98 ± 2.26	0.69 ± 0.01	26.08 ± 0.37	349.12 ± 3.25	51.48 ± 0.31	985.59 ± 10.89
H	Water	0.07 ± 0.00	4.65 ± 0.17	0.04 ± 0.00	44.60 ± 1.37	2.47 ± 0.08	1.91 ± 0.04	43.54 ± 1.47
	Sediment	2.14 ± 0.00	215.48 ± 0.99	0.56 ± 0.00	26.20 ± 0.23	280.92 ± 0.71	42.82 ± 0.14	841.99 ± 3.82
I	Water	0.02 ± 0.00	2.82 ± 0.06	0.04 ± 0.00	13.88 ± 0.14	1.73 ± 0.01	0.33 ± 0.01	14.14 ± 0.51
	Sediment	0.81 ± 0.02	62.30 ± 0.37	0.05 ± 0.00	9.25 ± 0.05	102.18 ± 0.34	11.15 ± 0.01	269.29 ± 0.57
J	Water	0.63 ± 0.05	1.75 ± 0.06	0.04 ± 0.00	10.52 ± 0.47	0.02 ± 0.00	0.19 ± 0.11	9.59 ± 0.18
	Sediment	22.53 ± 0.04	233.78 ± 1.13	0.52 ± 0.00	121.74 ± 0.51	329.02 ± 0.57	40.81 ± 0.01	1017.49 ± 2.83
K	Water	0.13 ± 0.02	4.93 ± 0.40	0.04 ± 0.00	23.98 ± 2.46	3.07 ± 0.23	0.40 ± 0.06	23.00 ± 2.49
	Sediment	5.53 ± 0.17	119.36 ± 0.62	1.33 ± 0.04	37.21 ± 0.10	197.27 ± 0.47	23.12 ± 0.06	641.79 ± 2.40

APPENDIX A6. Metal concentrations in water (µg/l) and sediment (µg/g) samples collected on 1st July 2015.

Sampling Site	Matrix	Cd	Cu	Hg	Ni	Pb	Sn	Zn
		Mean and standard deviation						
A	Water	0.07 ± 0.00	2.79 ± 0.10	0.05 ± 0.02	7.31 ± 0.06	1.06 ± 0.01	0.10 ± 0.02	6.58 ± 0.07
	Sediment	0.47 ± 0.00	32.59 ± 0.37	0.01 ± 0.00	6.35 ± 0.07	50.81 ± 0.11	2.48 ± 0.18	109.05 ± 0.14
B	Water	0.05 ± 0.01	9.39 ± 0.02	0.04 ± 0.01	2.64 ± 0.26	0.05 ± 0.13	0.08 ± 0.00	2.06 ± 0.12
	Sediment	0.55 ± 0.01	63.88 ± 0.33	0.01 ± 0.00	18.69 ± 0.14	92.01 ± 0.20	5.01 ± 0.04	245.15 ± 0.71
C	Water	0.08 ± 0.02	4.71 ± 0.06	0.04 ± 0.00	5.99 ± 0.01	2.60 ± 0.06	0.11 ± 0.00	5.47 ± 0.18
	Sediment	2.82 ± 0.01	642.11 ± 3.11	0.57 ± 0.02	28.47 ± 0.38	206.45 ± 0.00	33.14 ± 0.01	825.75 ± 1.56
D	Water	0.07 ± 0.03	1.91 ± 0.01	0.04 ± 0.00	9.84 ± 0.14	0.99 ± 0.19	0.11 ± 0.00	9.34 ± 0.26
	Sediment	1.82 ± 0.00	164.83 ± 0.59	0.66 ± 0.01	23.53 ± 0.24	228.15 ± 0.14	30.07 ± 0.08	574.15 ± 1.56
E	Water	0.05 ± 0.01	3.58 ± 0.09	0.04 ± 0.00	11.56 ± 0.56	1.92 ± 0.08	0.20 ± 0.00	11.61 ± 0.60
	Sediment	0.85 ± 0.00	62.76 ± 0.04	0.01 ± 0.00	0.01 ± 0.00	125.07 ± 0.37	15.75 ± 0.08	334.25 ± 0.28
F	Water	0.03 ± 0.01	1.73 ± 0.08	0.04 ± 0.00	6.02 ± 0.39	0.97 ± 0.13	0.12 ± 0.00	6.18 ± 0.23
	Sediment	0.41 ± 0.01	293.81 ± 0.14	1.32 ± 0.02	11.72 ± 0.22	91.31 ± 0.23	22.31 ± 0.00	201.15 ± 0.42
G	Water	0.05 ± 0.01	2.03 ± 0.17	0.04 ± 0.00	9.59 ± 0.14	1.63 ± 0.24	0.18 ± 0.01	9.55 ± 0.21
	Sediment	3.39 ± 0.02	284.21 ± 0.71	1.01 ± 0.01	26.71 ± 0.04	350.95 ± 0.42	41.21 ± 0.06	999.15 ± 0.42
H	Water	0.05 ± 0.03	1.65 ± 0.01	0.04 ± 0.00	7.64 ± 0.32	1.40 ± 0.48	0.09 ± 0.00	7.51 ± 0.47
	Sediment	2.61 ± 0.02	258.51 ± 1.13	0.69 ± 0.01	28.31 ± 0.04	298.05 ± 0.28	34.61 ± 0.00	881.95 ± 2.97
I	Water	0.03 ± 0.01	1.09 ± 0.03	0.04 ± 0.00	6.55 ± 0.05	0.21 ± 0.03	0.07 ± 0.01	6.39 ± 0.09
	Sediment	1.15 ± 0.01	86.52 ± 0.27	0.13 ± 0.01	10.51 ± 0.04	118.59 ± 0.25	13.36 ± 0.05	347.75 ± 0.71
J	Water	0.06 ± 0.03	1.54 ± 0.04	0.04 ± 0.00	6.57 ± 0.07	0.32 ± 0.01	0.01 ± 0.01	6.18 ± 0.10
	Sediment	5.81 ± 0.01	243.01 ± 0.14	0.56 ± 0.02	37.31 ± 0.10	259.15 ± 0.14	25.93 ± 0.03	847.15± 1.84
K	Water	0.15 ± 0.02	3.69 ± 0.09	0.04 ± 0.00	7.80 ± 0.46	4.71 ± 0.48	0.20 ± 0.01	7.93 ± 0.56
	Sediment	4.86 ± 0.01	130.18 ± 0.38	1.06 ± 0.01	40.17 ± 0.35	205.25 ± 0.28	17.02 ± 0.06	581.05 ± 0.28

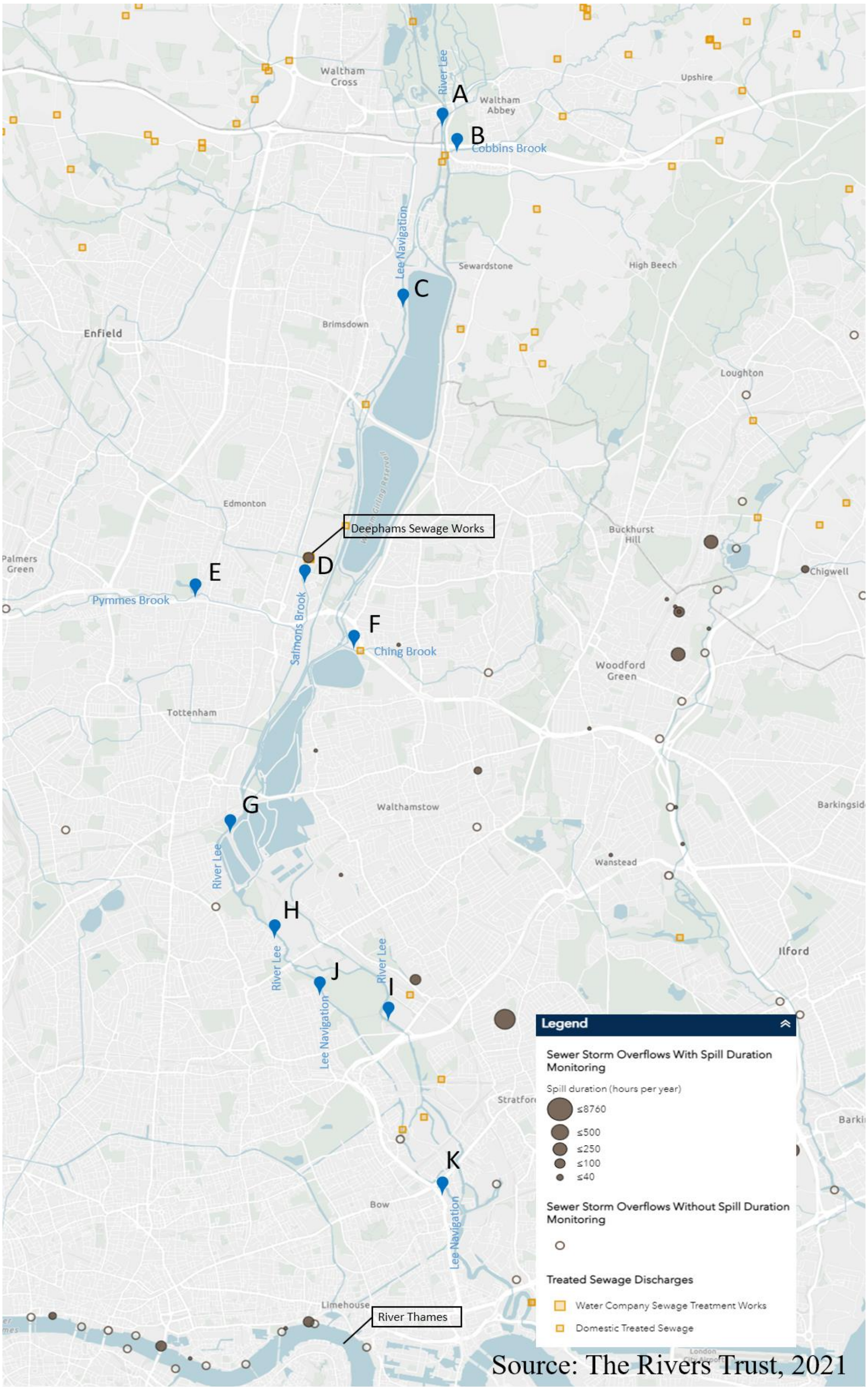
APPENDIX A7. Metal concentrations in water (µg/l) and sediment (µg/g) samples collected on 14th August 2015.

Sampling Site	Matrix	Cd	Cu	Hg	Ni	Pb	Sn	Zn
		Mean and standard deviation						
A	Water	0.14 ± 0.03	21.15 ± 0.18	0.46 ± 0.02	25.94 ± 1.11	3.93 ± 0.42	1.67 ± 0.10	33.26 ± 0.38
	Sediment	0.52 ± 0.01	37.97 ± 0.30	1.02 ± 0.00	1.34 ± 0.03	68.71 ± 0.08	4.43 ± 0.16	157.88 ± 0.65
B	Water	0.25 ± 0.01	31.38 ± 1.35	0.04 ± 0.01	33.70 ± 1.77	4.92 ± 0.75	1.83 ± 0.15	40.63 ± 0.59
	Sediment	0.49 ± 0.00	53.96 ± 0.06	1.02 ± 0.00	5.64 ± 0.06	85.96 ± 0.04	5.04 ± 0.01	278.38 ± 0.00
C	Water	0.03 ± 0.01	22.01 ± 0.48	0.03 ± 0.00	36.43 ± 1.34	2.19 ± 0.01	0.95 ± 0.02	45.24 ± 0.67
	Sediment	4.07 ± 0.00	538.28 ± 0.42	1.02 ± 0.00	18.01 ± 0.18	245.29 ± 0.42	30.82 ± 0.00	917.68 ± 0.14
D	Water	0.83 ± 0.04	14.34 ± 0.06	0.04 ± 0.01	29.81 ± 0.72	2.44 ± 0.29	1.04 ± 0.02	38.01 ± 0.89
	Sediment	1.36 ± 0.01	114.65 ± 0.55	1.02 ± 0.00	13.05 ± 0.11	185.04 ± 0.13	24.19 ± 0.01	517.38 ± 0.00
E	Water	0.12 ± 0.01	25.54 ± 0.58	0.03 ± 0.00	55.05 ± 0.31	5.15 ± 0.04	0.85 ± 0.04	62.68 ± 0.37
	Sediment	3.15 ± 0.03	48.33 ± 0.13	1.02 ± 0.00	0.14 ± 0.00	105.51 ± 0.85	12.68 ± 0.10	591.98 ± 3.39
F	Water	0.03 ± 0.01	21.33 ± 0.47	0.03 ± 0.00	28.94 ± 1.11	2.69 ± 0.23	1.02 ± 0.03	42.40 ± 0.42
	Sediment	0.34 ± 0.00	46.95 ± 0.07	1.02 ± 0.00	0.14 ± 0.00	52.77 ± 0.03	8.18 ± 0.02	158.65 ± 0.07
G	Water	0.03 ± 0.00	18.61 ± 0.00	0.03 ± 0.00	29.67 ± 0.37	2.27 ± 0.38	3.73 ± 0.02	43.32 ± 0.92
	Sediment	1.97 ± 0.01	219.58 ± 0.57	1.02 ± 0.00	15.02 ± 0.09	299.79 ± 0.00	32.23 ± 0.04	921.58 ± 1.41
H	Water	0.03 ± 0.01	19.77 ± 0.01	0.03 ± 0.00	31.77 ± 0.46	3.40 ± 0.60	1.35 ± 0.01	44.89 ± 0.14
	Sediment	2.24 ± 0.00	227.08 ± 0.14	1.02 ± 0.00	18.54 ± 0.04	262.79 ± 0.28	31.95 ± 0.07	910.88 ± 0.71
I	Water	0.14 ± 0.00	38.00 ± 0.58	0.10 ± 0.01	31.01 ± 0.85	1.59 ± 0.09	1.40 ± 0.01	45.43 ± 0.33
	Sediment	1.20 ± 0.01	99.45 ± 0.13	1.02 ± 0.00	3.61 ± 0.00	137.62 ± 0.07	13.36 ± 0.01	416.08 ± 0.14
J	Water	0.01 ± 0.01	39.46 ± 1.15	3.56 ± 0.18	23.89 ± 1.41	2.09 ± 0.42	1.38 ± 0.03	38.85 ± 1.43
	Sediment	4.23 ± 0.00	149.85 ± 0.30	1.02 ± 0.00	25.67 ± 0.17	240.69 ± 0.71	19.21 ± 0.12	616.98 ± 2.26
K	Water	0.25 ± 0.00	22.30 ± 0.71	0.40 ± 0.02	24.15 ± 0.73	3.25 ± 0.37	13.90 ± 0.13	38.28 ± 0.85
	Sediment	5.64 ± 0.00	121.53 ± 0.33	1.06 ± 0.00	29.00 ± 0.13	199.78 ± 0.27	17.11 ± 0.02	664.78 ± 0.85

APPENDIX A8. Metal concentrations in water (μg/l) and sediment (μg/g) samples collected on 23rd March 2016.

Sampling Site	Matrix	Cd	Cu	Hg	Ni	Pb	Sn	Zn
		Mean and standard deviation						
A	Water	0.09 ± 0.00	27.15 ± 0.34	0.45 ± 0.17	9.27 ± 0.17	0.74 ± 0.23	2.38 ± 0.34	11.21 ± 0.33
	Sediment	0.88 ± 0.03	73.74 ± 0.13	0.14 ± 0.01	19.56 ± 0.06	72.36 ± 0.18	7.75 ± 0.47	219.64 ± 0.00
B	Water	2.78 ± 0.01	117.71 ± 0.65	0.46 ± 0.05	50.82 ± 1.01	10.20 ± 0.11	3.20 ± 0.38	52.16 ± 0.88
	Sediment	0.45 ± 0.03	59.85 ± 0.57	0.09 ± 0.00	16.73 ± 0.04	94.97 ± 0.31	6.98 ± 0.64	228.74 ± 0.42
C	Water	0.11 ± 0.00	64.79 ± 0.14	0.80 ± 0.02	21.67 ± 0.18	5.22 ± 0.04	1.47 ± 0.16	23.56 ± 0.03
	Sediment	2.13 ± 0.01	256.87 ± 1.41	0.71 ± 0.05	32.78 ± 0.18	195.27 ± 0.79	29.15 ± 0.25	641.94 ± 0.99
D	Water	0.40 ± 0.11	31.82 ± 0.21	0.28 ± 0.05	22.50 ± 0.73	0.42 ± 0.05	1.00 ± 0.11	20.87 ± 0.18
	Sediment	1.73 ± 0.04	182.35 ± 0.31	0.84 ± 0.14	36.73 ± 0.11	238.63 ± 0.14	14.46 ± 0.16	549.24 ± 0.28
E	Water	0.44 ± 0.03	28.20 ± 0.20	0.12 ± 0.03	23.78 ± 0.63	1.60 ± 0.47	0.91 ± 0.04	23.94 ± 0.29
	Sediment	0.77 ± 0.01	83.86 ± 0.04	0.09 ± 0.00	16.18 ± 0.08	132.40 ± 0.24	6.36 ± 0.04	277.74 ± 0.42
F	Water	0.35 ± 0.00	32.46 ± 0.27	0.06 ± 0.03	20.96 ± 0.16	2.24 ± 0.08	0.46 ± 0.07	19.93 ± 0.34
	Sediment	0.18 ± 0.03	64.42 ± 0.21	0.09 ± 0.00	12.80 ± 0.01	53.86 ± 0.16	23.65 ± 0.23	126.77 ± 0.21
G	Water	0.66 ± 0.04	31.19 ± 0.39	0.29 ± 0.05	17.83 ± 0.24	3.32 ± 0.03	0.43 ± 0.01	17.69 ± 0.30
	Sediment	1.74 ± 0.04	222.17 ± 0.14	0.65 ± 0.06	36.34 ± 0.13	274.13 ± 0.85	41.63 ± 0.17	720.64 ± 0.00
H	Water	0.33 ± 0.02	46.73 ± 0.29	0.29 ± 0.02	16.62 ± 0.20	1.99 ± 0.07	0.45 ± 0.01	16.88 ± 0.17
	Sediment	2.18 ± 0.05	166.39 ± 0.48	0.43 ± 0.03	32.36 ± 0.04	214.63 ± 0.14	27.78 ± 0.10	549.24 ± 0.57
I	Water	0.65 ± 0.01	61.81 ± 0.09	0.40 ± 0.09	30.98 ± 0.34	9.31 ± 0.02	2.05 ± 0.02	32.84 ± 0.17
	Sediment	1.22 ± 0.02	112.03 ± 0.96	0.12 ± 0.16	24.69 ± 0.03	142.82 ± 0.04	15.04 ± 0.35	402.34 ± 1.56
J	Water	0.45 ± 0.02	25.55 ± 0.41	0.24 ± 0.11	17.08 ± 0.22	1.97 ± 0.25	0.24 ± 0.01	18.51 ± 0.09
	Sediment	7.54 ± 0.02	190.56 ± 0.21	0.40 ± 0.03	68.48 ± 0.01	201.23 ± 0.14	48.34 ± 0.16	640.24 ± 0.28
K	Water	0.39 ± 0.01	26.95 ± 0.24	0.29 ± 0.06	11.81 ± 0.27	2.19 ± 0.00	1.92 ± 0.05	13.47 ± 0.20
	Sediment	5.16 ± 0.03	137.41 ± 0.08	1.23 ± 0.14	51.13 ± 0.08	201.13 ± 0.00	18.39 ± 0.08	563.84 ± 0.85

APPENDIX A9. The Rivers Trust map showing the location of treated sewage discharges and sewage overflows. The map is part of the Together for Rivers Campaign.



Source: The Rivers Trust, 2021

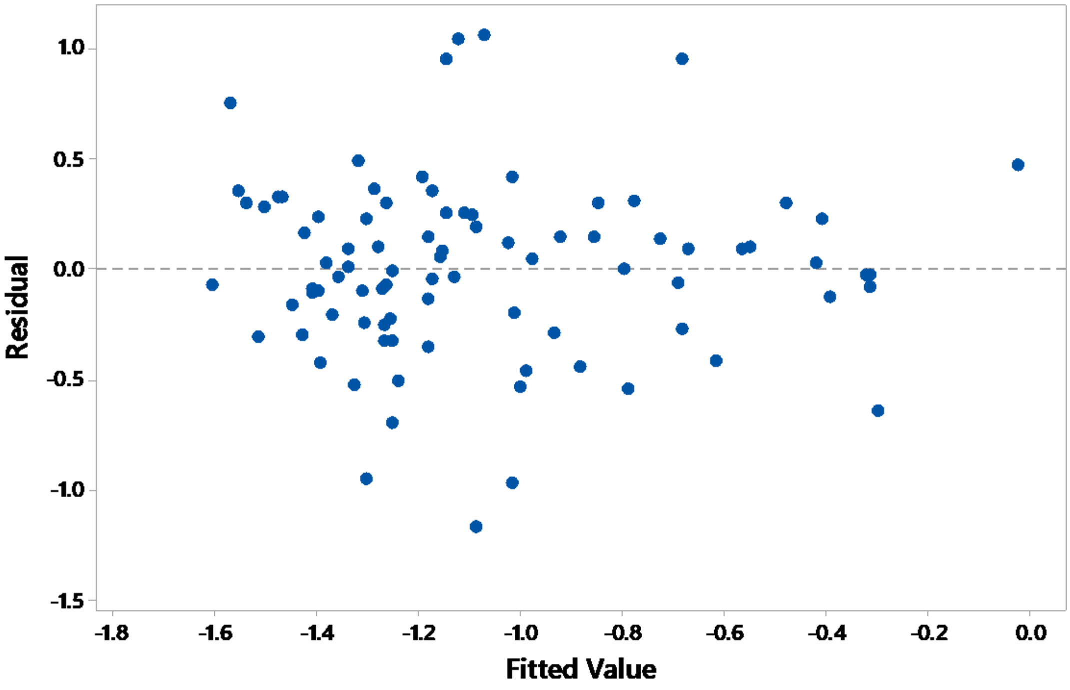
APPENDIX B1. Overview of maximum, minimum and mean (± SD) of Cu, Ni, Pb and Zn concentrations determined in surface waters at each sampling site.

	Site	Cu		Ni		Pb		Zn	
		Range in concentration (µg/l)	Mean ± SD	Range in concentration (µg/l)	Mean ± SD	Range in concentration (µg/l)	Mean ± SD	Range in concentration (µg/l)	Mean ± SD
River Lee	A	1.04 – 27.15	7.73 ± 10.28	0.66 – 25.94	9.73 ± 7.85	0.21 – 3.93	1.54 ± 1.39	1.25 – 33.26	11.02 ± 9.98
	G	1.74 – 31.19	8.62 ± 10.64	5.86 – 29.97	14.84 ± 7.23	0.76 – 6.98	2.71 ± 1.92	5.94 – 43.32	16.54 ± 11.51
	H	1.21 – 46.73	10.14 ± 10.01	5.25 – 44.60	16.22 ± 14.38	0.51 – 3.40	1.68 ± 0.98	5.45 – 44.89	17.61 ± 16.74
	I	1.09 – 61.81	14.23 ± 22.93	5.84 – 31.01	17.52 ± 10.12	0.21 – 9.31	3.25 ± 3.46	6.07 – 45.43	19.65 ± 13.84
Lee Navigation	C	2.23 – 64.79	13.58 ± 21.69	0.11 – 36.43	16.07 ± 12.68	0.14 – 7.31	2.78 ± 2.37	0.55 – 45.24	17.38 ± 14.80
	J	1.06 – 39.46	9.78 ± 14.51	6.51 – 23.89	12.76 ± 6.26	0.02 – 8.44	1.88 ± 2.75	6.18 – 38.85	14.66 ± 10.86
	K	1.92 – 26.95	8.73 ± 9.92	4.81 – 24.15	12.95 ± 8.10	0.33 – 4.71	2.19 ± 1.44	5.12 – 38.28	14.88 ± 11.39
Tributaries	B	1.72 – 117.71	21.82 ± 39.97	2.49 – 50.82	16.21 ± 17.86	0.05 – 10.20	3.59 ± 3.26	2.06 – 52.16	17.37 ± 19.24
	D	1.52 – 31.82	7.65 ± 10.65	9.26 – 29.81	16.94 ± 7.08	0.15 – 2.44	1.11 ± 0.73	9.15 – 38.01	17.50 ± 9.44
	E	1.06 – 28.20	10.41 ± 10.67	11.56 – 55.05	23.41 ± 18.84	0.92 – 13.25	3.75 ± 4.13	11.61 – 62.68	24.94 ± 21.22
	F	1.73 – 32.46	9.68 ± 11.13	5.89 – 28.94	15.35 ± 8.22	0.72 – 4.87	1.87 ± 1.39	6.18 – 42.40	17.16 ± 19.24

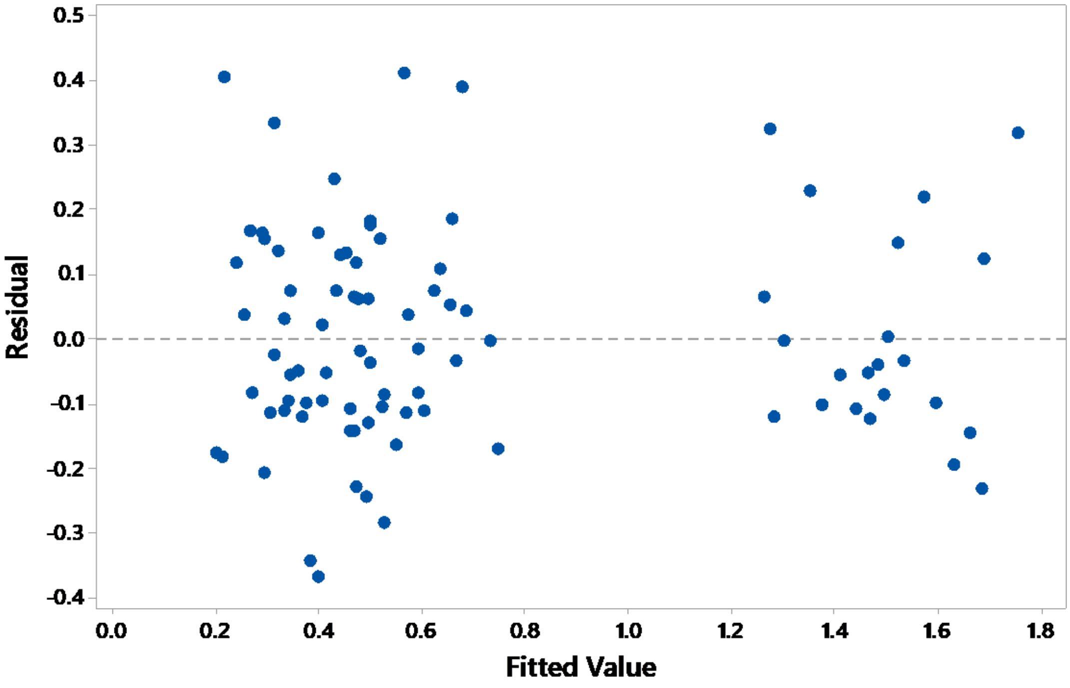
APPENDIX B2. Overview of maximum, minimum and mean (± SD) of Cd, Hg and Sn concentrations in surface waters determined at each sampling site.

	Site	Cd		Hg		Sn	
		Range in concentration (µg/l)	Mean ± SD	Range in concentration (µg/l)	Mean ± SD	Range in concentration (µg/l)	Mean ± SD
River Lee	A	0.02 – 0.15	0.07 ± 0.06	0.02 - 1.00	0.36 ± 0.35	0.10 – 2.38	0.65 ± 0.87
	G	0.02 – 0.66	0.15 ± 0.22	0.01 – 0.29	0.08 ± 0.10	0.15 – 3.73	0.87 ± 1.20
	H	0.01 – 0.33	0.08 ± 0.10	0.01 – 0.29	0.08 ± 0.10	0.09 – 1.91	0.58 ± 0.68
	I	0.02 – 0.65	0.17 ± 0.22	0.01 – 0.40	0.11 ± 0.14	0.07 – 2.05	0.60 ± 0.73
Lee Navigation	C	0.03 – 0.97	0.21 ± 0.32	0.01 –0.80	0.18 ± 0.26	0.06 – 1.47	0.46 ± 0.51
	J	0.01 – 1.82	0.39 ± 0.62	0.01 – 3.56	0.52 ± 1.23	0.01 – 1.38	0.55 ± 0.45
	K	0.01 – 0.39	0.15 ± 0.12	0.01 – 0.40	0.13 ± 0.15	0.06 – 13.90	2.16 ± 4.78
Tributaries	B	0.05 – 2.78	0.49 ± 0.93	0.01 – 0.46	0.16 ± 0.16	0.07 – 3.20	0.78 ± 1.13
	D	0.01 – 0.83	0.20 ± 0.28	0.01 – 0.28	0.09 ± 0.10	0.10 – 1.04	0.49 ± 0.38
	E	0.04 – 0.44	0.14 ± 0.13	0.03 – 0.41	0.10 ± 0.13	0.07 – 1.86	0.58 ± 0.61
	F	0.01 – 0.35	0.09 ± 0.11	0.01 – 0.20	0.05 ± 0.06	0.09 – 1.02	0.34 ± 0.31

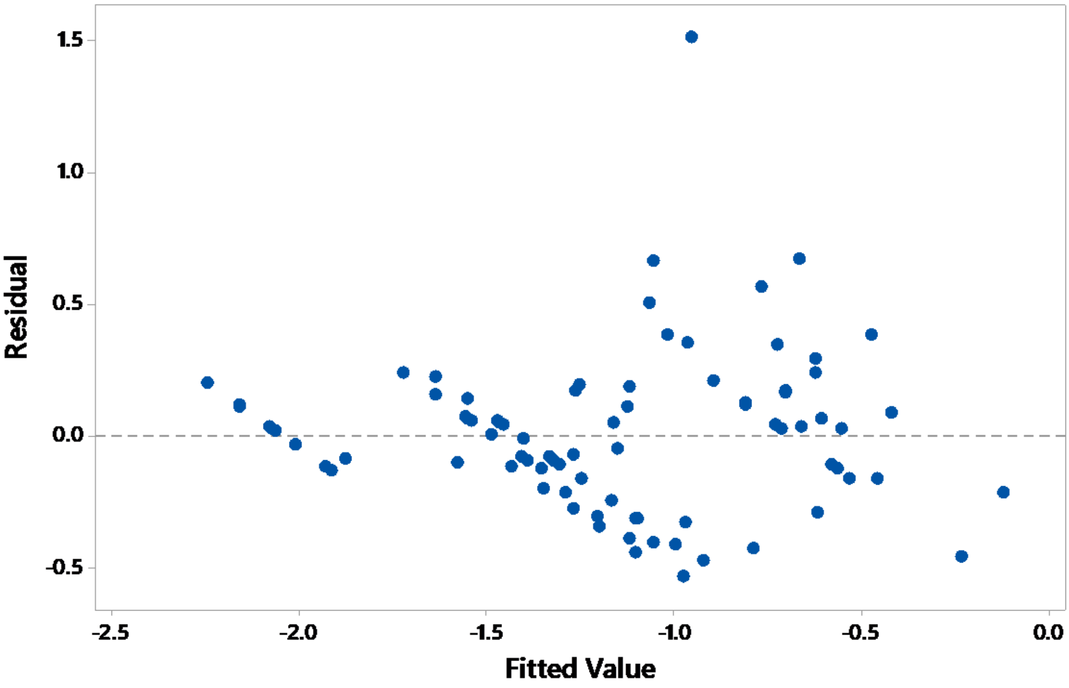
APPENDIX C1. Residuals vs Fits plot for Cd in surface waters.



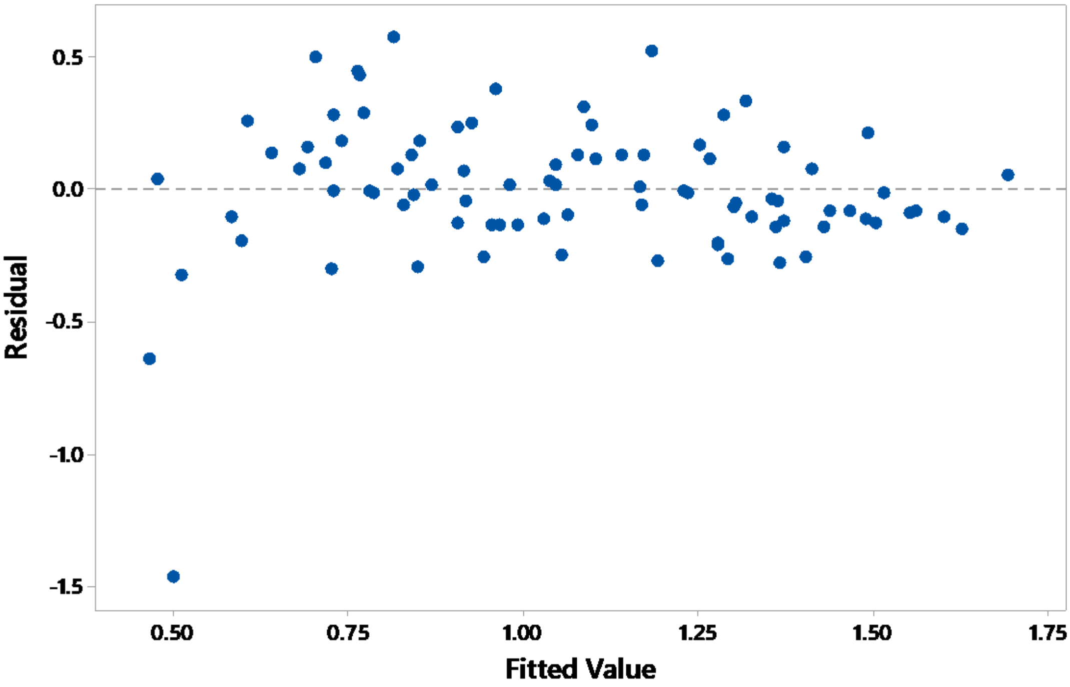
APPENDIX C1. Residuals vs Fits plot for Cu in surface waters.



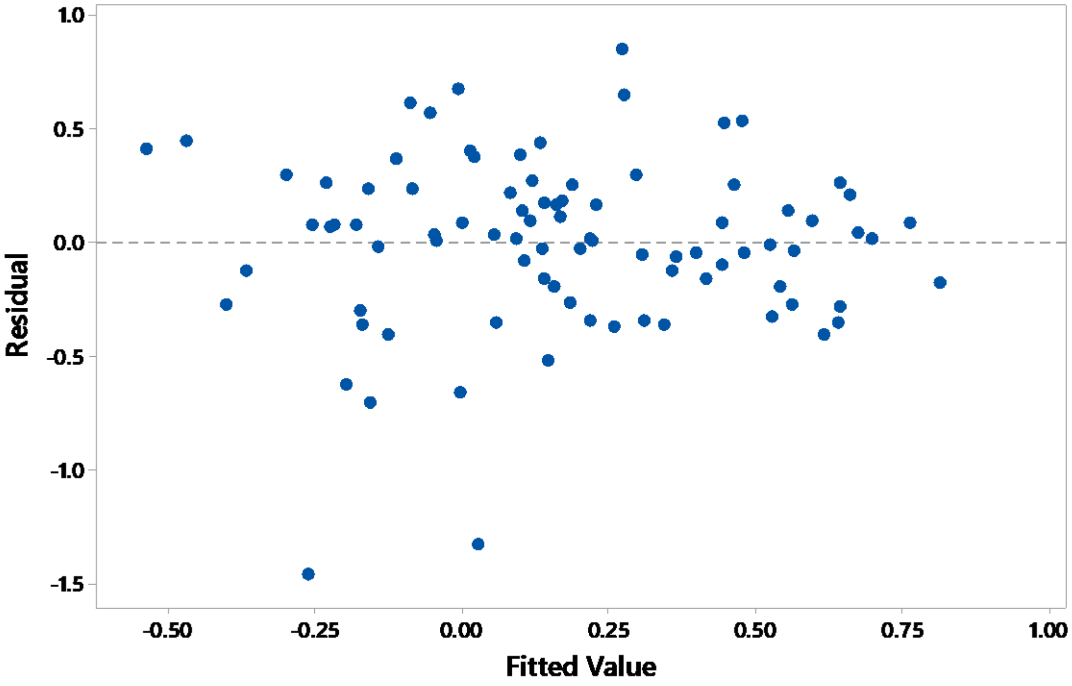
APPENDIX C3. Residuals vs Fits plot for Hg in surface waters.



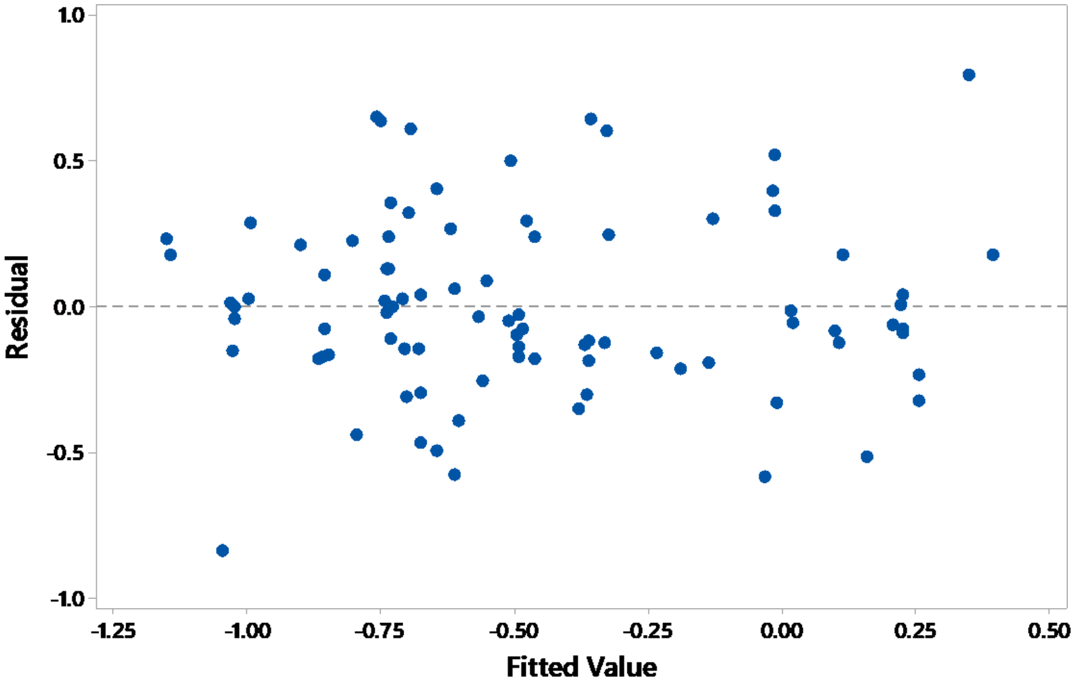
APPENDIX C4. Residuals vs Fits plot for Ni in surface waters.



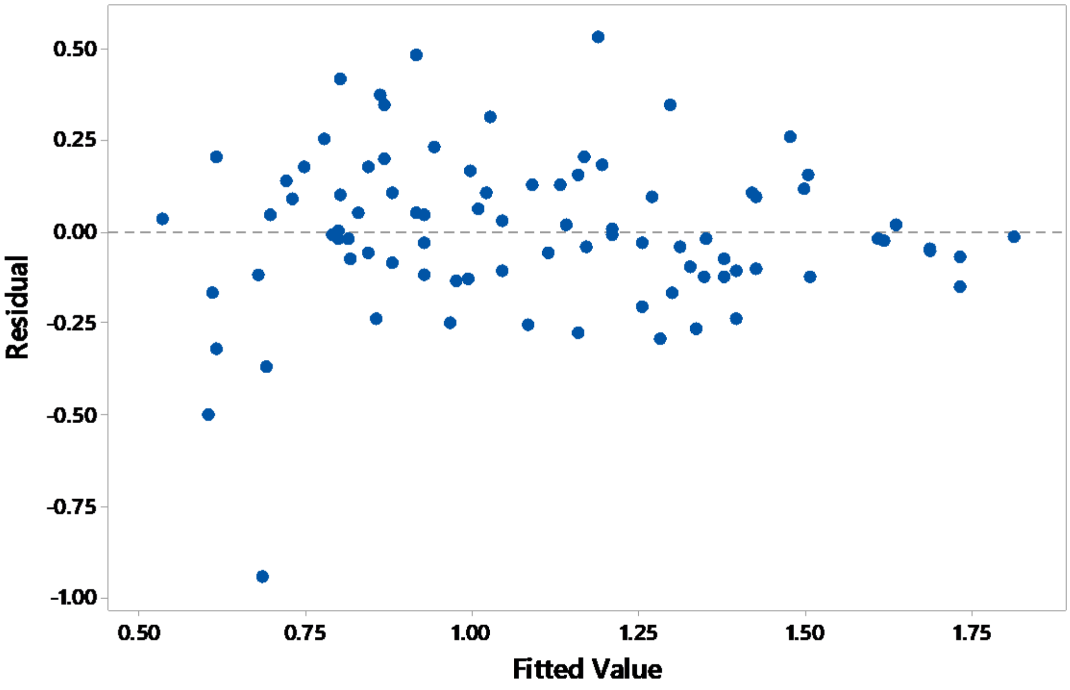
APPENDIX C5. Residuals vs Fits plot for Pb in surface waters.



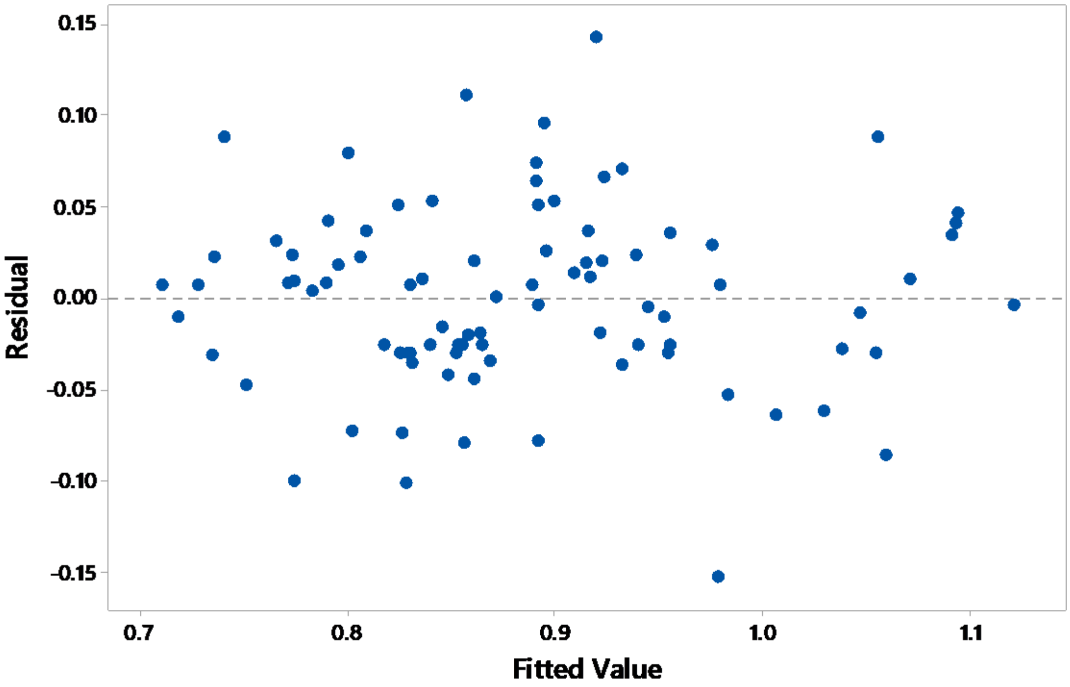
APPENDIX C6. Residuals vs Fits plot for Sn in surface waters.



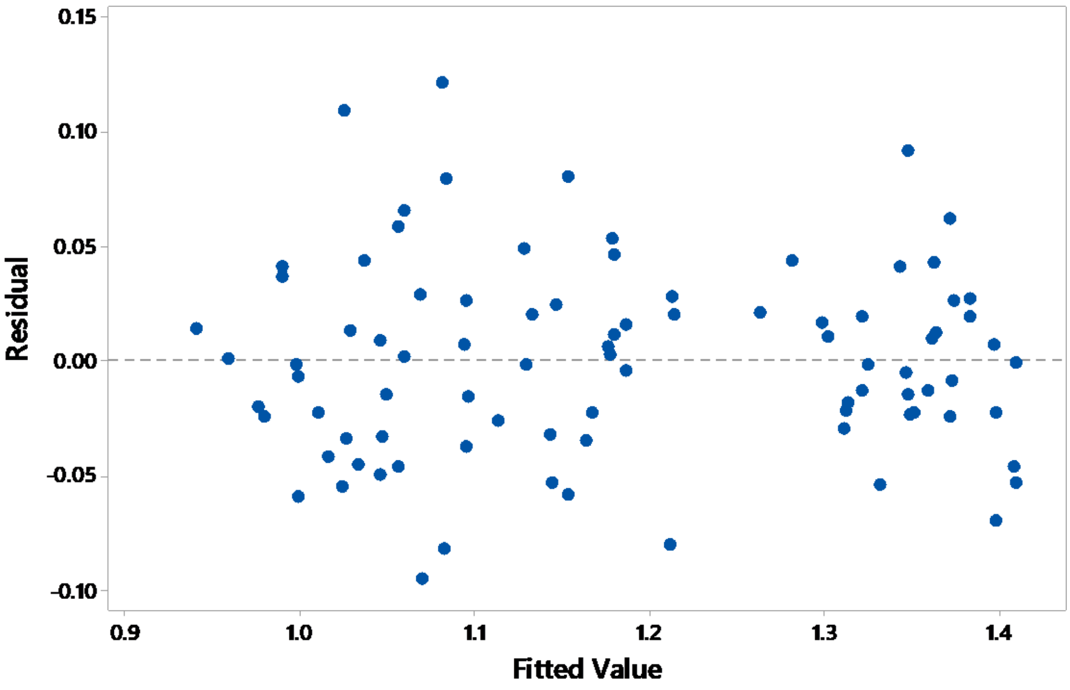
APPENDIX C7. Residuals vs Fits plot for Zn in surface waters.



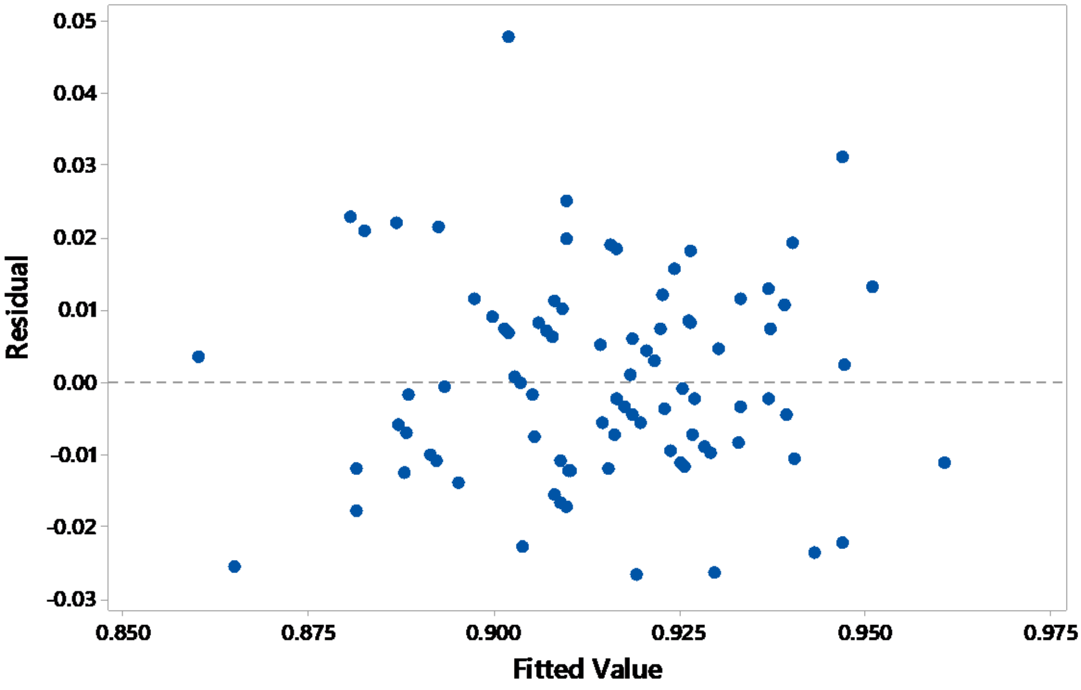
APPENDIX C8. Residuals vs Fits plot for DO in surface waters.



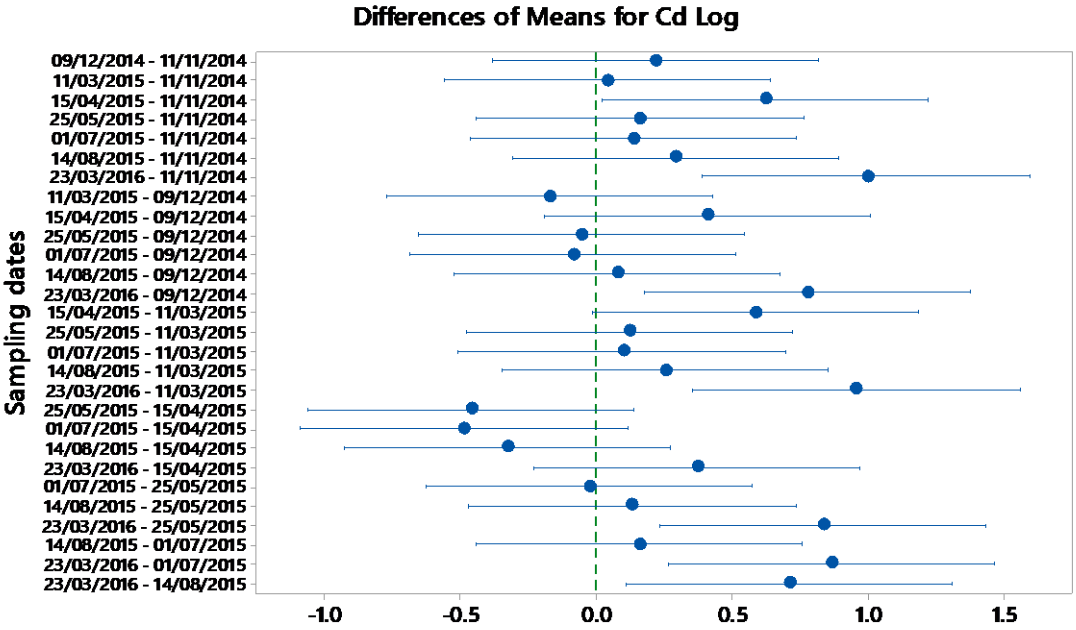
APPENDIX C9. Residuals vs Fits plot for temperature in surface waters.



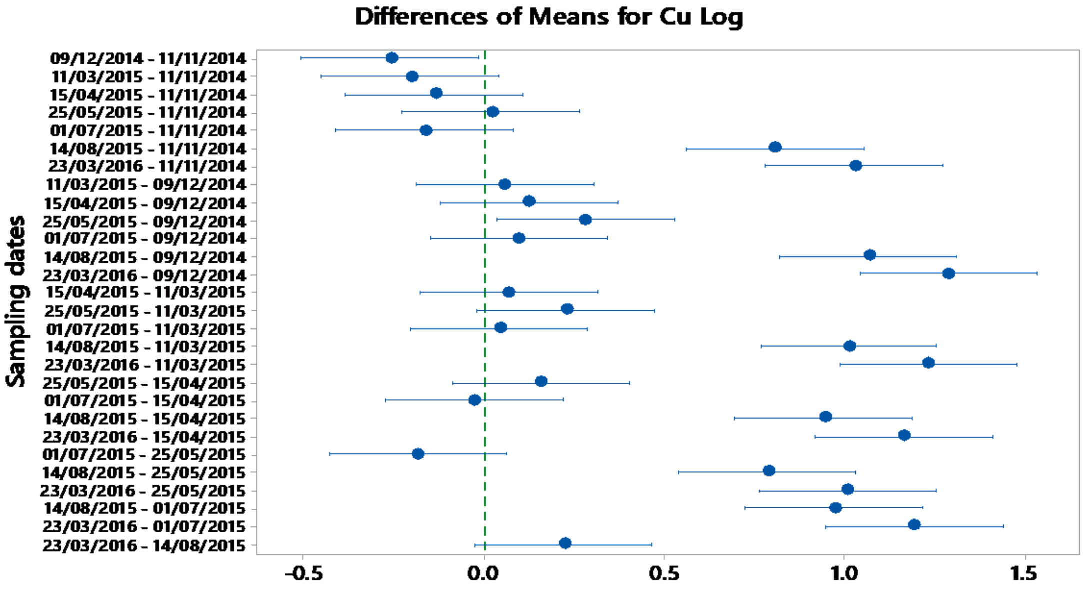
APPENDIX C10. Residuals vs Fits plot for pH in surface waters.



APPENDIX D1.[4] Tukey’s post-hoc test for difference of means of Cd between sampling dates in surface waters.



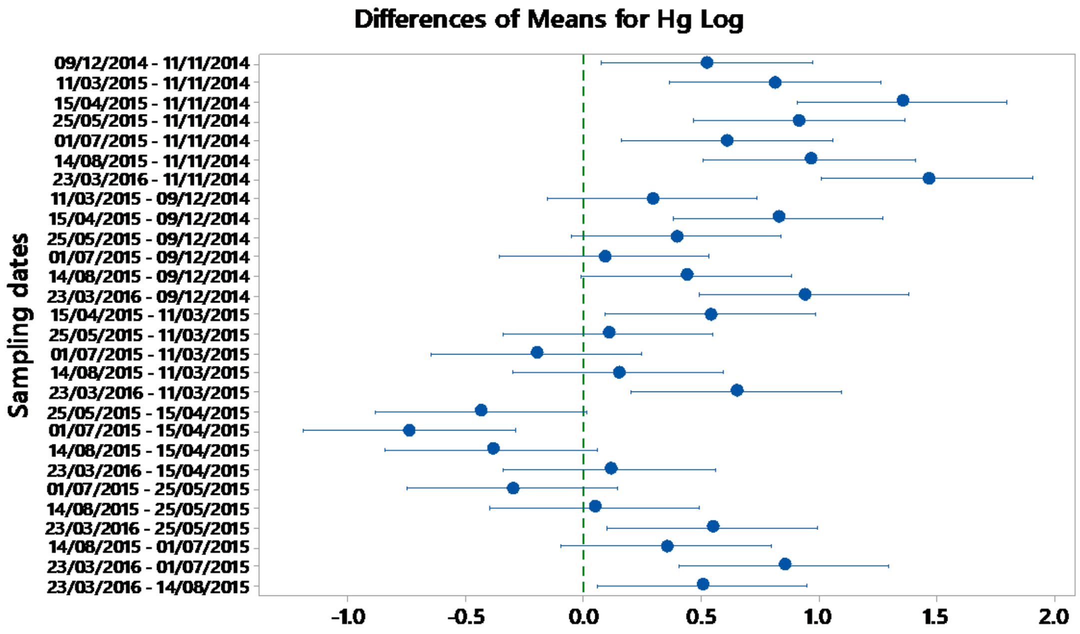
APPENDIX D2. Tukey’s post-hoc test for difference of means of Cu between sampling dates in surface waters.



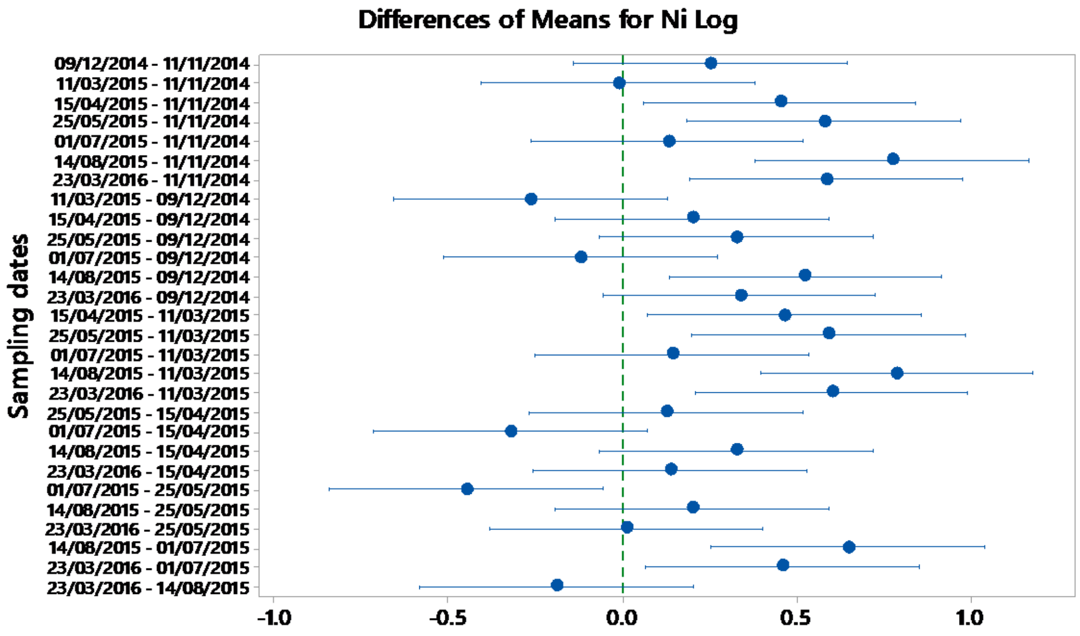
---

[4] For graphs in Appendices C1-C7: If an interval does not contain zero, the corresponding means are significantly different.

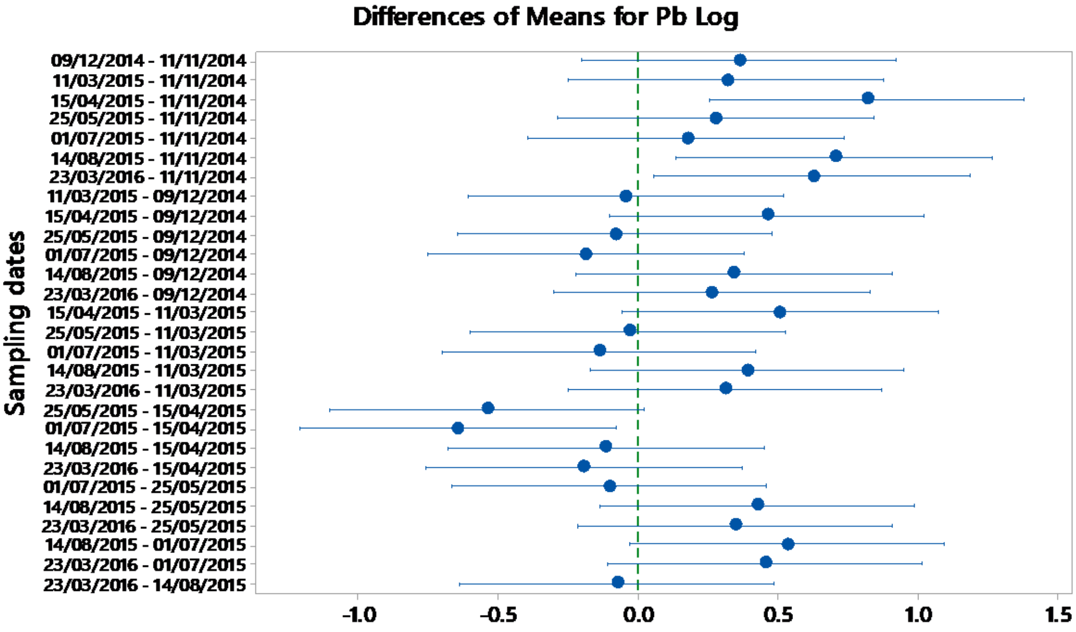
APPENDIX D3. Tukey's post-hoc test for difference of means of Hg between sampling dates in surface waters.



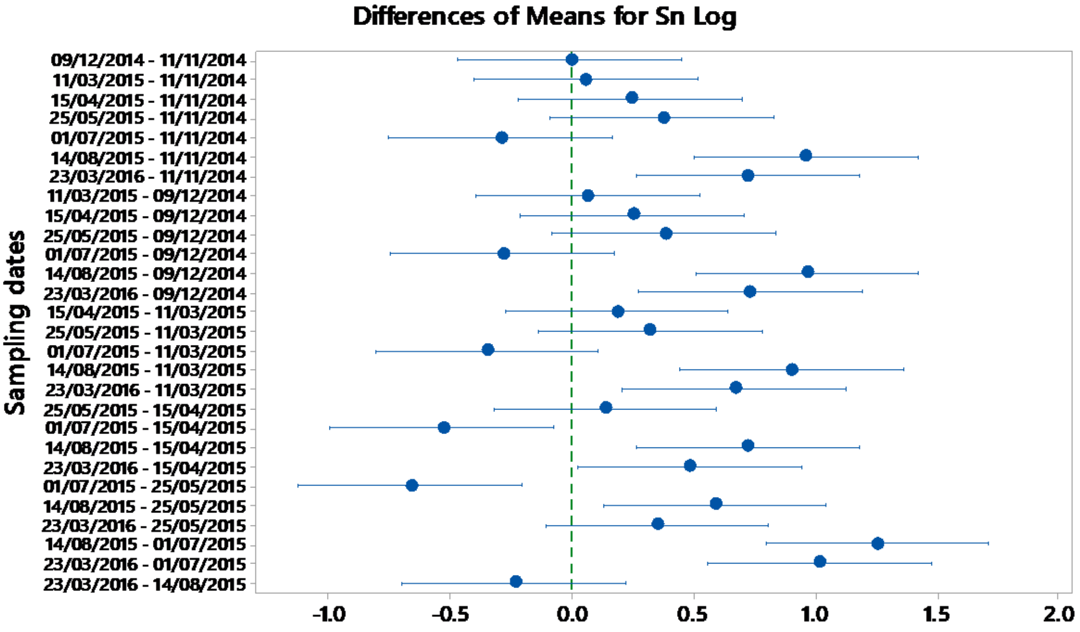
APPENDIX D4. Tukey's post-hoc test for difference of means of Ni between sampling dates in surface waters.



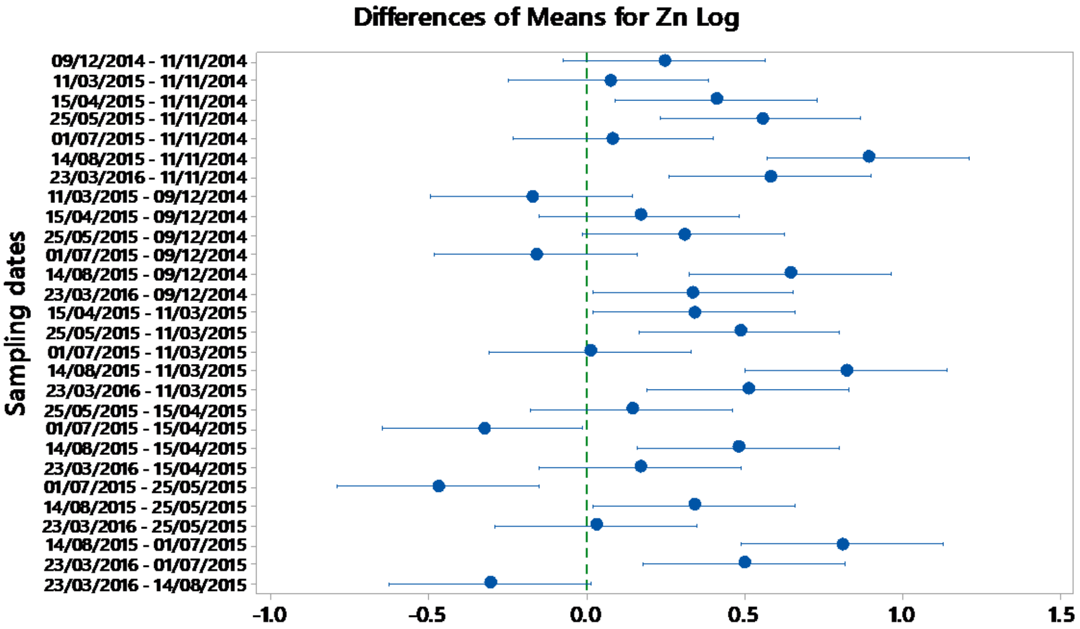
APPENDIX D5. Tukey’s post-hoc test for difference of means of Pb between sampling dates in surface waters.



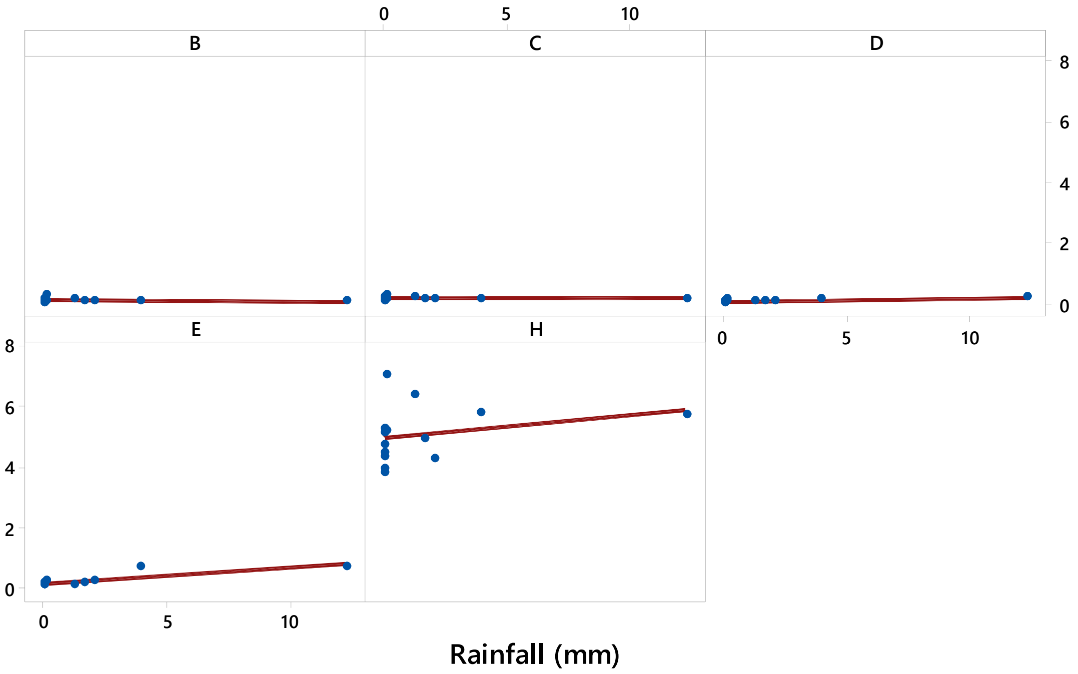
APPENDIX D6. Tukey’s post-hoc test for difference of means of Sn between sampling dates in surface waters.



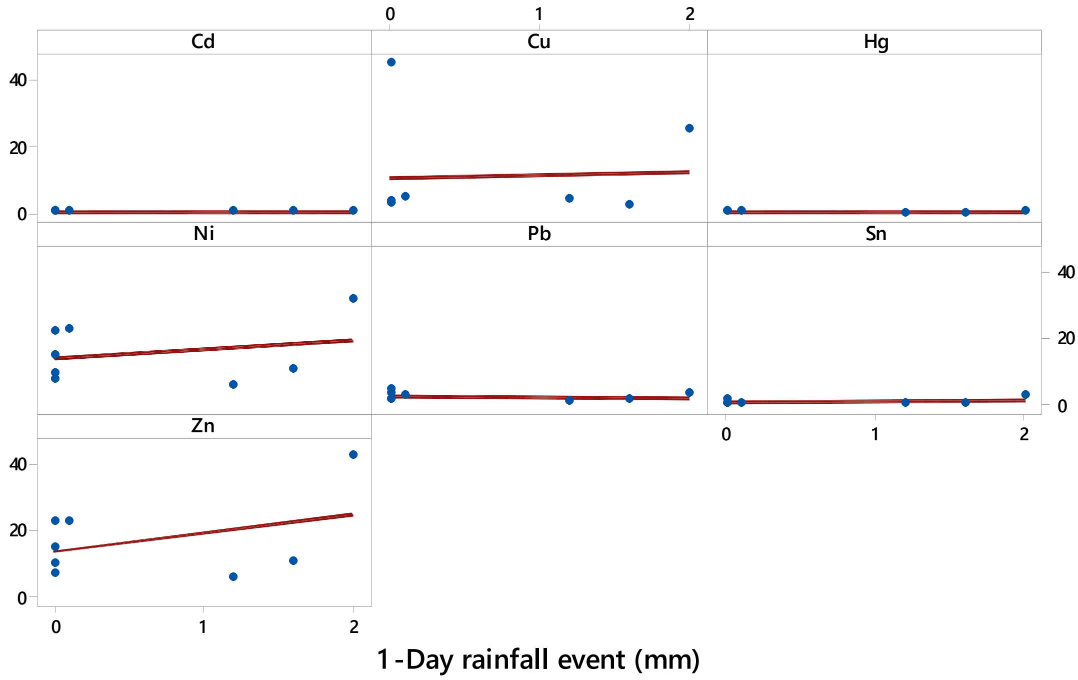
APPENDIX D7. Tukey's post-hoc test for difference of means of Zn between sampling dates in surface waters.



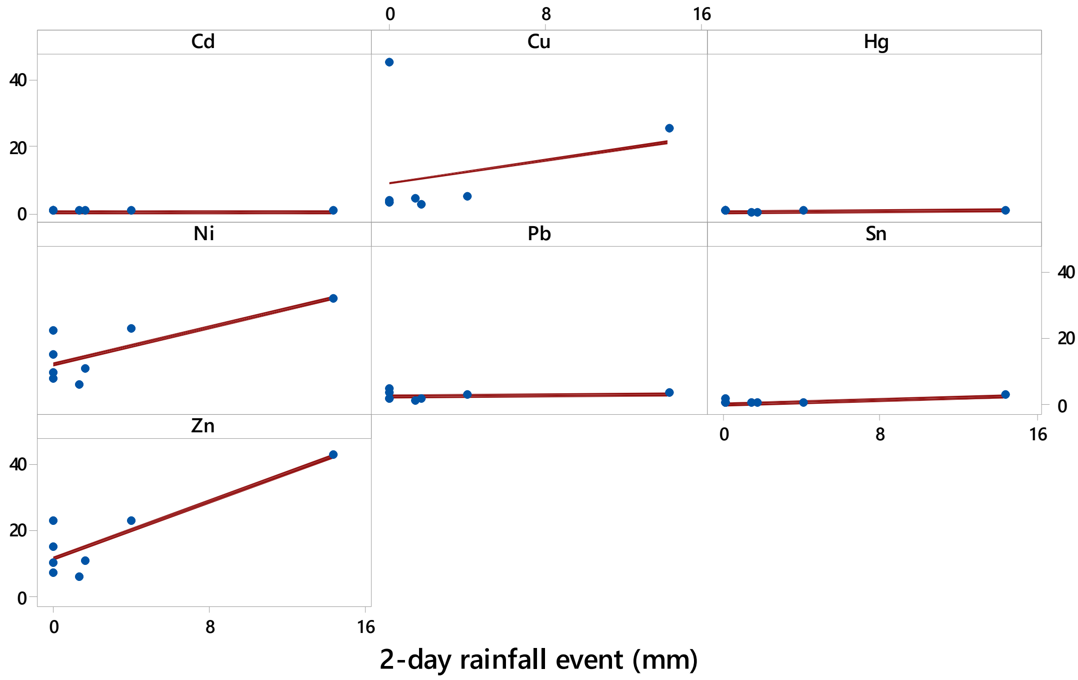
APPENDIX E1. Scatterplot for rainfall vs river flow data.



APPENDIX E2. Scatterplot for target metals vs 1-day rainfall event.



APPENDIX E3. Scatterplot for target metals vs 2-day rainfall event.



APPENDIX F1. Overview of maximum, minimum and mean (± SD) of Cu, Ni, Pb and Zn concentrations in river sediment determined at each sampling site.

	Site	**Cu**		**Ni**		**Pb**		**Zn**	
		Range in concentration (µg/g)	**Mean ± SD**	**Range in concentration (µg/g)**	**Mean ± SD**	**Range in concentration (µg/g)**	**Mean ± SD**	**Range in concentration (µg/g)**	**Mean ± SD**
River Lee	A	32.59 – 72.74	45.97 ± 12.97	1.34 – 19.56	13.70 ± 6.60	50.81 – 88.84	68.19 ± 11.35	109.05 – 219.64	164.39 ± 41.57
	G	45.04 – 284.21	206.84 ± 74.50	15.02 – 36.34	24.02 ± 6.44	59.27 – 350.95	270.84 ± 97.78	187.59 – 999.15	775.22 ± 276.95
	H	128.39 – 258.51	207.93 ± 43.38	18.54 – 32.36	26.60 ± 4.31	186.35 – 322.01	265.34 ± 45.55	549.24 – 945.81	777.17 ± 152.01
	I	46.99 – 112.03	82.42 ± 22.80	3.61 – 24.69	12.85 ± 6.26	78.43 – 142.82	117.80 ± 21.74	230.01 – 428.66	338.69 ± 74.18
Lee Navigation	C	35.00 – 642.11	320.75 ± 223.89	18.01 – 32.78	25.37 ± 4.89	146.44 – 245.29	199.44 ± 31.65	573.17 – 917.68	711.81 ± 124.89
	J	65.09 – 258.50	190.09 ± 62.31	25.67 – 121.74	56.63 ± 29.67	201.23 – 329.02	253.76 ± 48.49	469.96 – 1017.49	758.23 ± 184.80
	K	107.92 – 161.50	127.33 ± 16.25	29.00 – 51.13	38.20 ± 6.20	169.46 – 213.92	196.95 ± 12.85	534.56 – 664.78	604.58 ± 48.85
Tributaries	B	41.29 – 63.88	54.86 ± 6.72	5.64 – 21.43	16.07 ± 4.69	68.41 – 94.97	87.02 ± 9.92	193.06 – 278.38	237.69 ± 25.88
	D	99.72 – 182.35	144.49 ± 27.77	7.23 – 36.73	21.70 ± 9.41	175.08 – 238.63	205.82 ± 21.92	447.11 – 574.15	527.61 ± 42.53
	E	40.31 – 149.53	79.59 ± 41.97	0.01 – 16.18	5.91 ± 5.75	105.51 – 241.51	171.39 ± 50.64	169.85 – 606.21	372.78 ± 169.21
	F	32.90 – 293.81	91.45 ± 91.36	0.14 – 18.94	8.88 ± 5.93	49.98 – 253.02	96.16 ± 68.35	94.12 – 616.56	230.98 ± 163.55

APPENDIX F2. Overview of maximum, minimum and mean (± SD) of Cd, Hg and Sn concentrations in river sediment determined at each sampling site.

	Site	Cd		Hg		Sn	
		Range in concentration (μg/g))	Mean ± SD	Range in concentration (μg/g)	Mean ± SD	Range in concentration (μg/g)	Mean ± SD
River Lee	A	0.47 – 0.88	0.68 ± 0.15	0.01 - 1.02	0.19 ± 0.34	0.67 – 7.98	4.66 ± 3.00
	G	0.60 – 3.39	2.00 ± 0.78	0.01 – 1.02	0.66 ± 0.39	1.47 – 51.48	32.23 ± 18.80
	H	1.90 – 2.61	2.28 ± 0.28	0.05 – 1.02	0.58 ± 0.34	3.71 – 42.82	28.42 ± 14.60
	I	0.81 – 1.37	1.15 ± 0.18	0.01 – 1.02	0.23 ± 0.33	2.69 – 19.75	10.53 ± 6.07
Lee Navigation	C	2.13 – 4.07	2.93 ± 0.55	0.14 – 1.02	0.61 ± 0.29	0.83 – 57.74	26.01 ± 18.32
	J	3.63 – 22.53	7.74 ± 6.16	0.05 – 1.02	0.53 ± 0.30	2.70 – 48.34	26.77 ± 15.80
	K	3.72 – 5.64	5.01 ± 0.63	0.49 – 1.57	1.07 ± 0.38	3.30 – 23.12	15.94 ± 6.50
Tributaries	B	0.44 – 0.71	0.55 ± 0.10	0.01 – 1.02	0.18 ± 0.34	0.53 – 8.10	4.45 ± 2.79
	D	1.36 – 1.95	1.63 ± 0.23	0.40 – 1.08	0.80 ± 0.21	6.54 – 45.74	23.32 ± 13.77
	E	0.48 – 3.15	1.20 ± 0.90	0.01 – 1.68	0.53 ± 0.64	1.36 – 73.95	21.40 ± 24.12
	F	0.18 – 1.21	0.45 ± 0.32	0.01 – 1.32	0.40 ± 0.51	0.55 – 27.60	13.91 ± 10.30

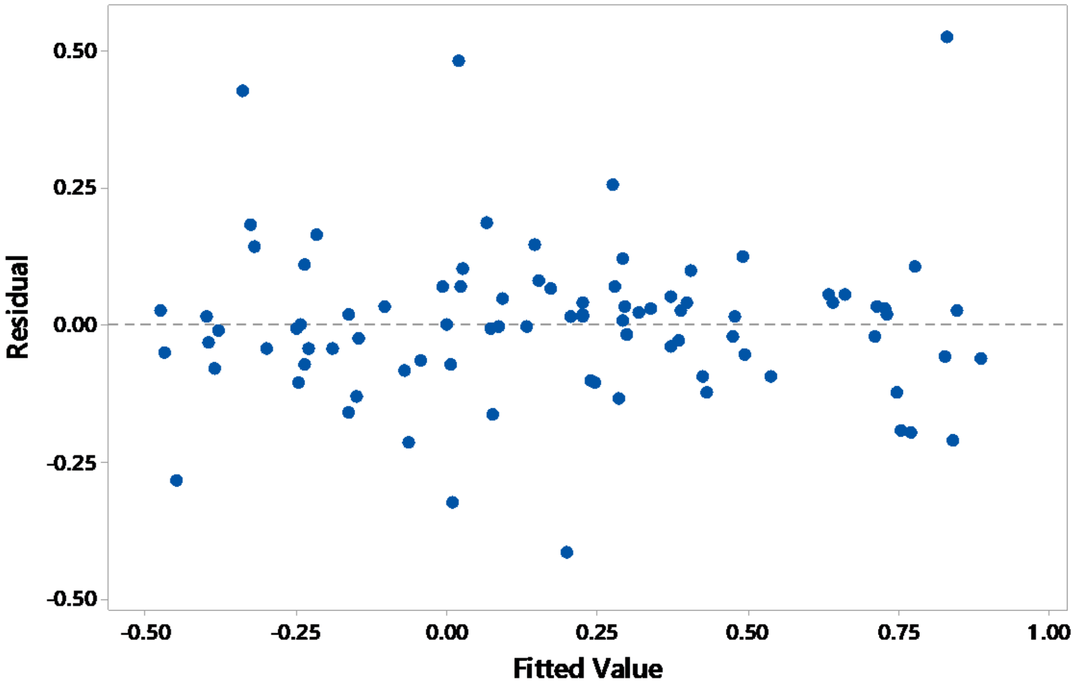
APPENDIX F3. Summary of domain normal background concentrations (NBCs) in English soils as per the British Geological Survey - BGS UKRI.

Metal	Domain NBC (μg/g)
Cd	1.0
Cu	62.0
Hg	0.5
Ni	42.0
Pb	180.0

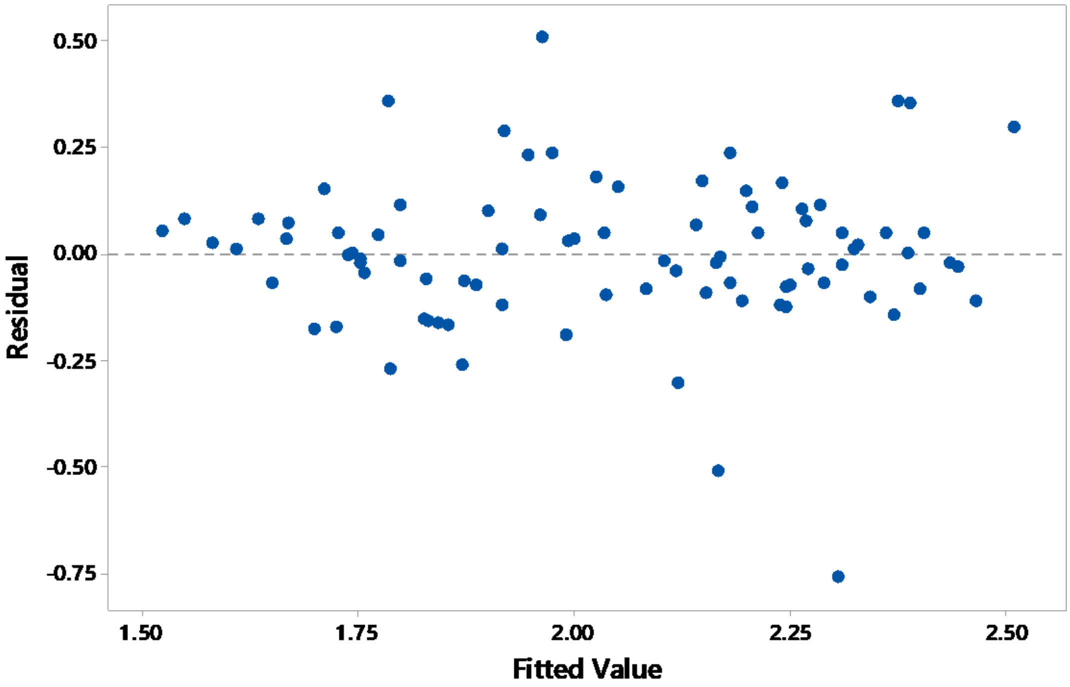
APPENDIX F4. Summary of soil metals toxic response factors developed by Hakanson (1980) and adapted by Zhang and Liu (2014).

Metal	Domain NBC (μg/g)
Cd	30.0
Cu	5.0
Hg	40.0
Ni	6.0
Pb	5.0

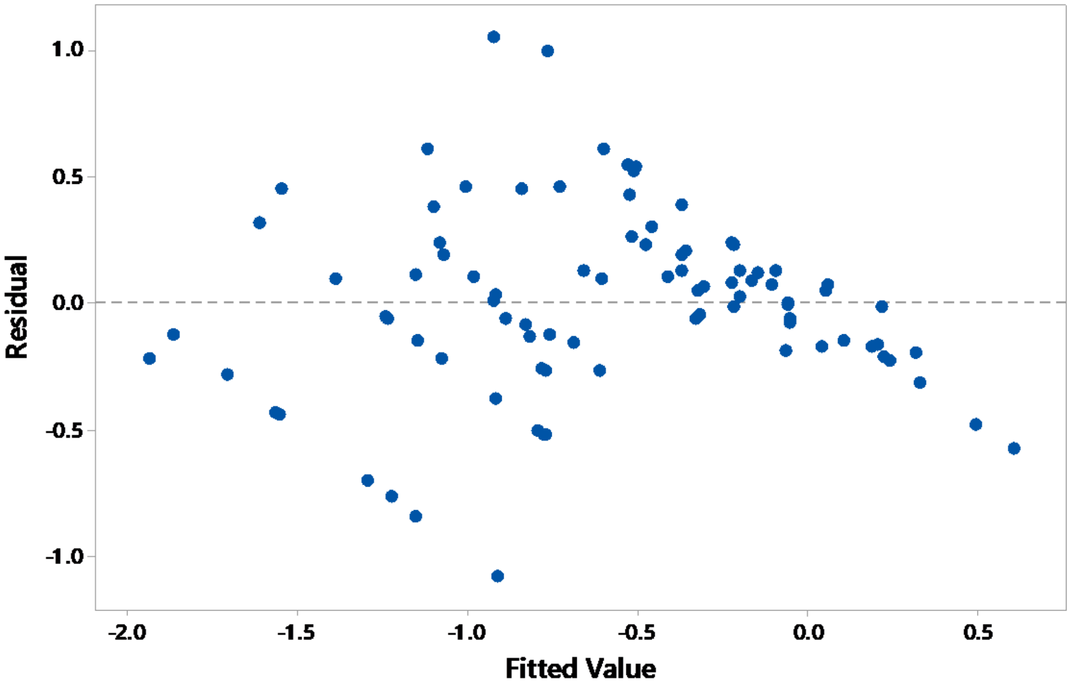
APPENDIX G1. Residuals vs Fits plot for Cd in river sediment.



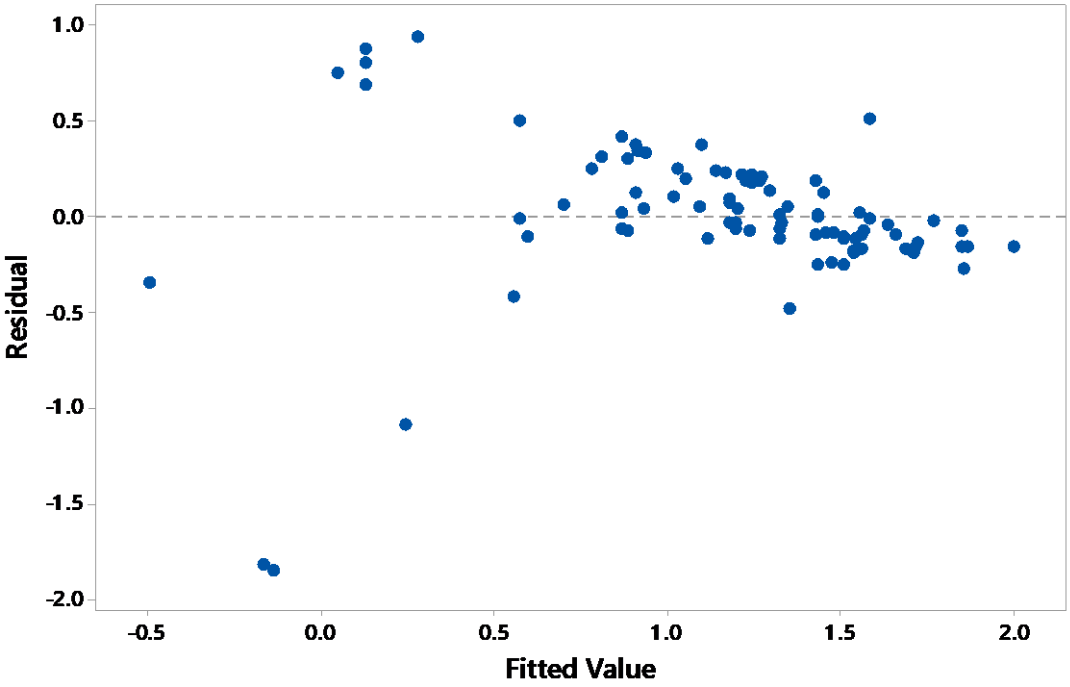
APPENDIX G2. Residuals vs Fits plot for Cu in river sediment.



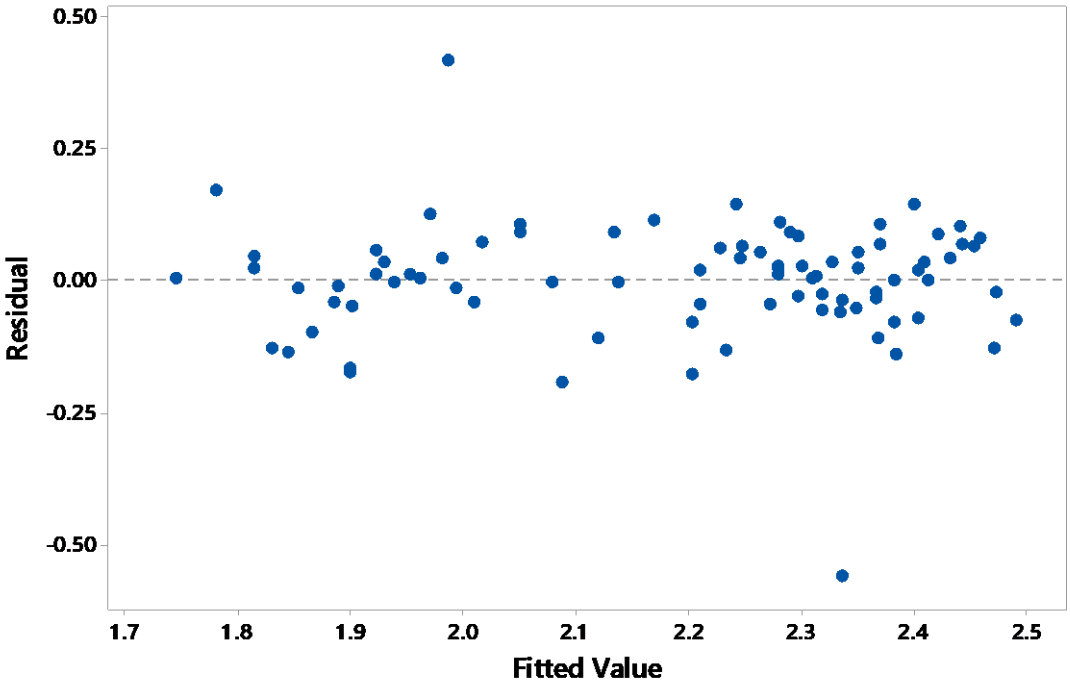
APPENDIX G3. Residuals vs Fits plot for Hg in river sediment.



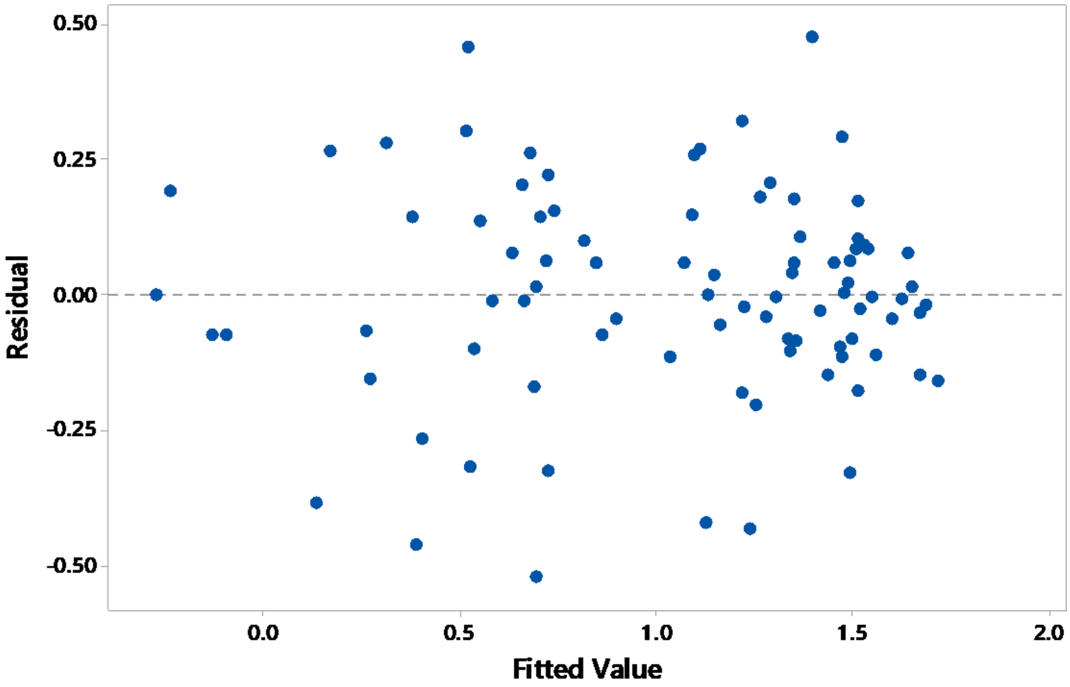
APPENDIX G4. Residuals vs Fits plot for Ni in river sediment.



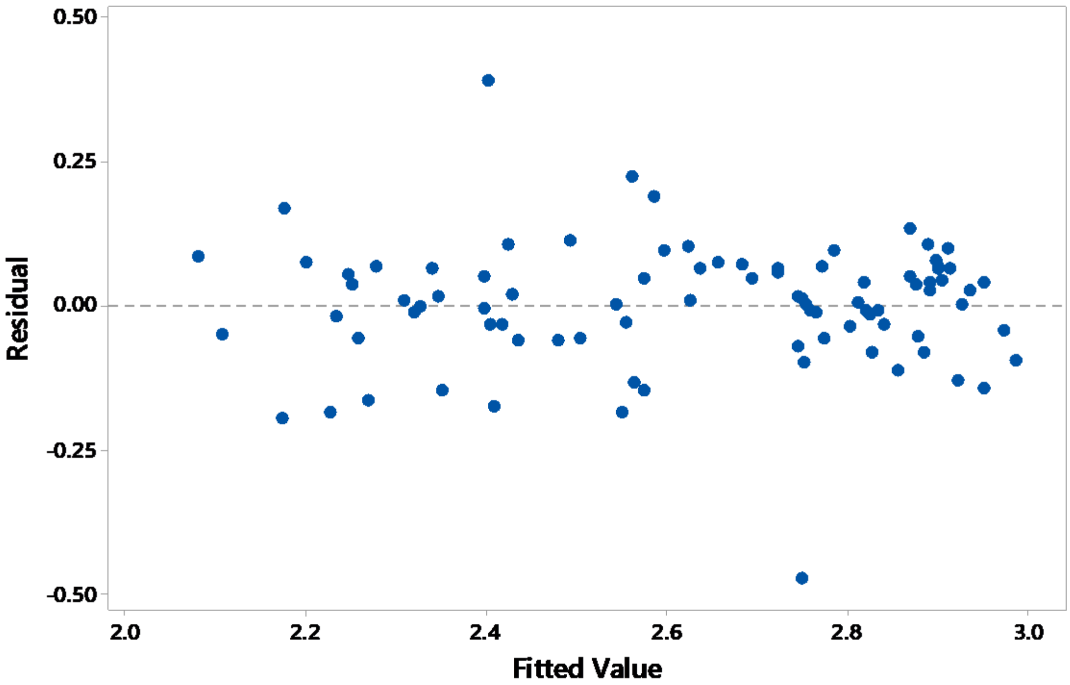
APPENDIX G5. Residuals vs Fits plot for Pb river sediment.



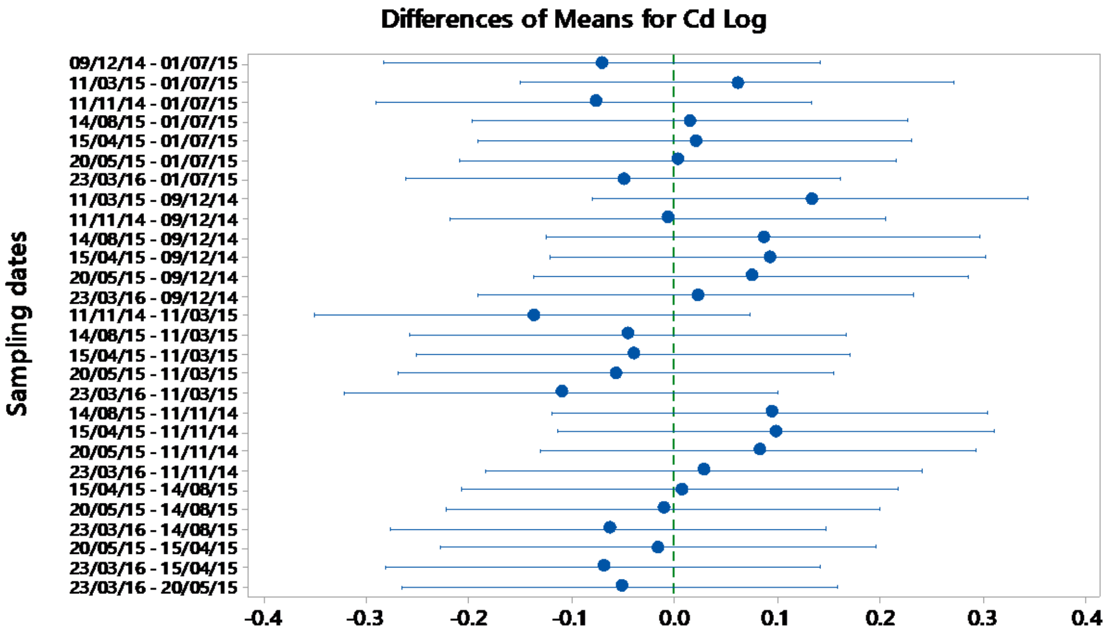
APPENDIX G6. Residuals vs Fits plot for Sn in river sediment.



APPENDIX G7. Residuals vs Fits plot for Zn in river sediment.



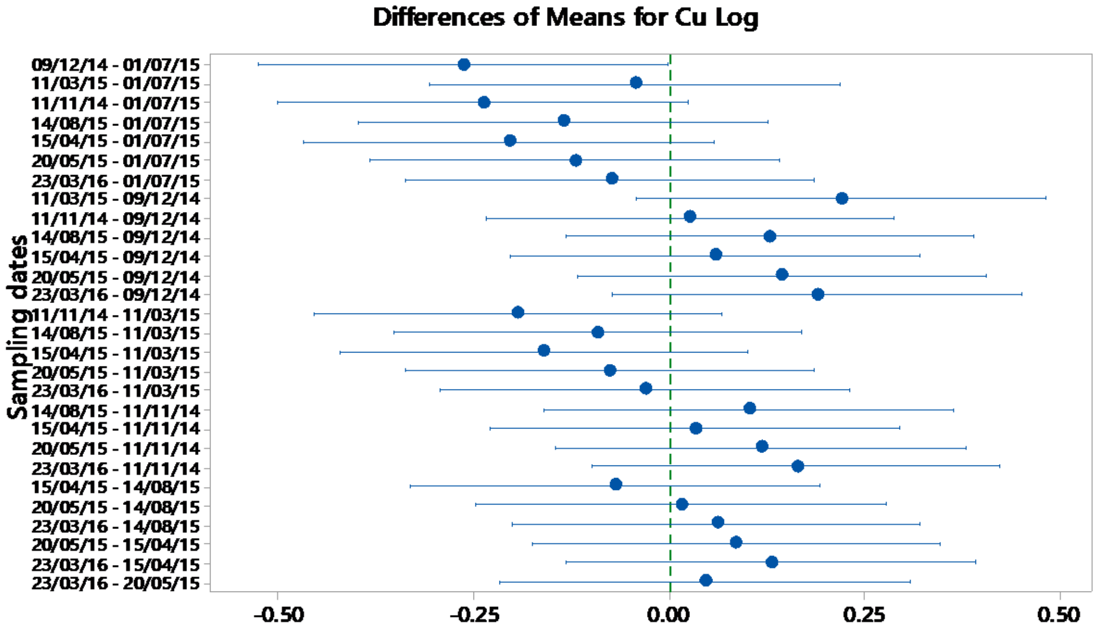
APPENDIX H1.[5] Tukey's post-hoc test for difference of means of Cd between sampling dates in river sediment.



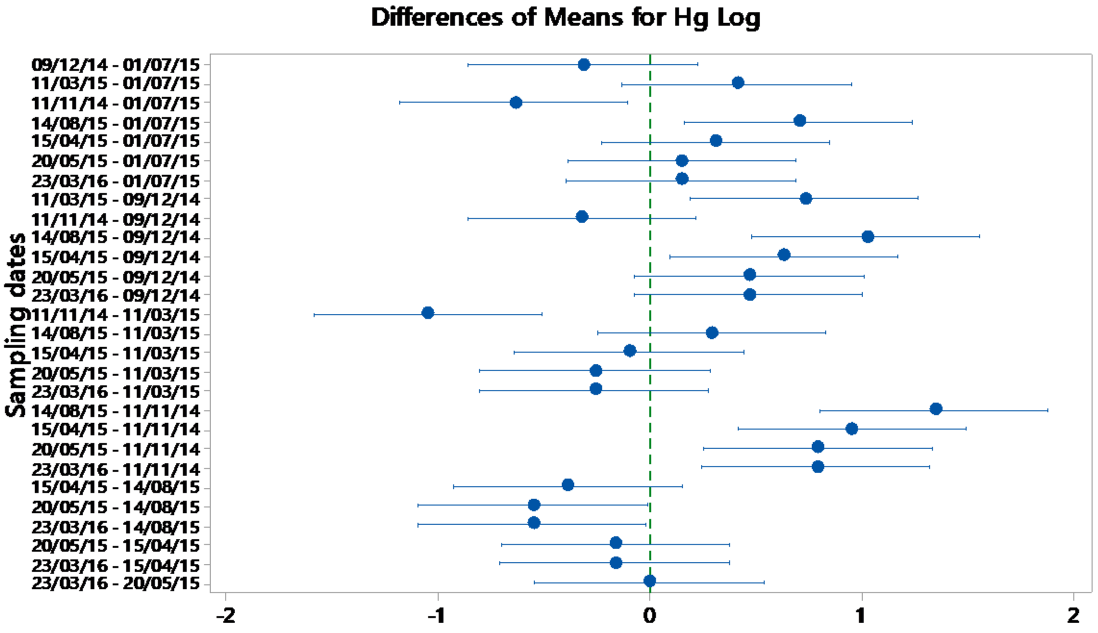
---

[5] For graphs in Appendices H1-H7: If an interval does not contain zero, the corresponding means are significantly different.

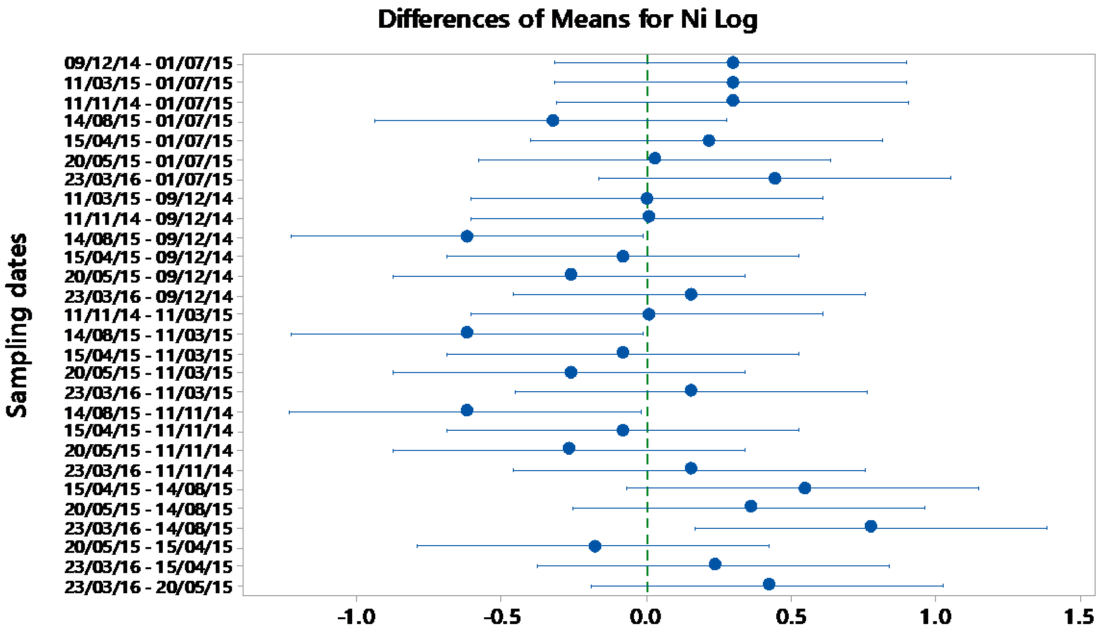
APPENDIX H2. Tukey’s post-hoc test for difference of means of Cu between sampling dates in river sediment.



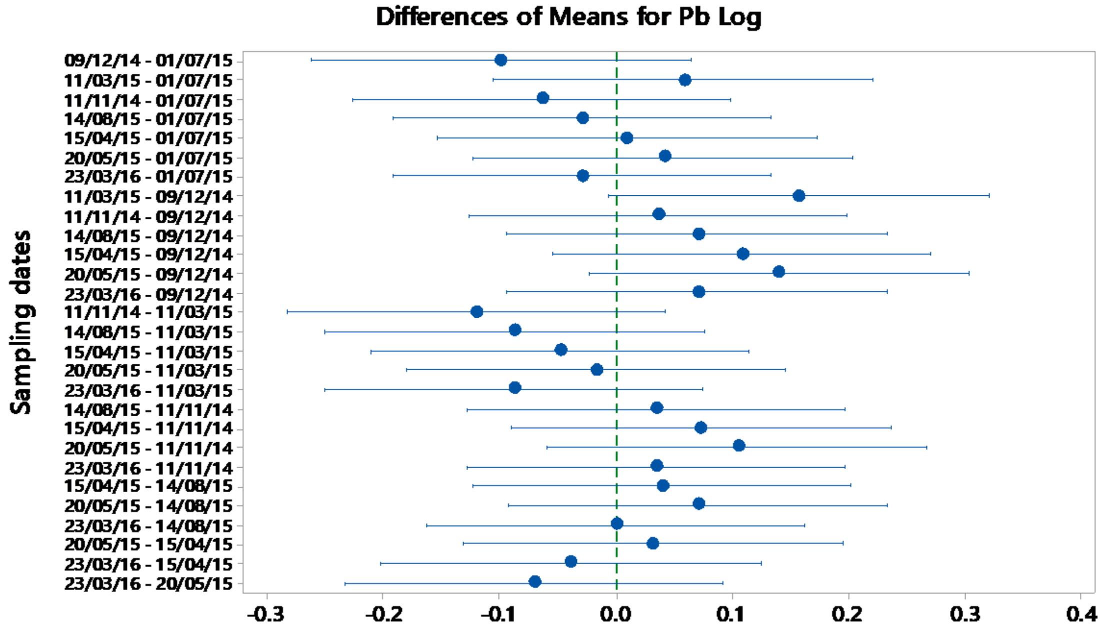
APPENDIX H3. Tukey’s post-hoc test for difference of means of Hg between sampling dates in river sediment.



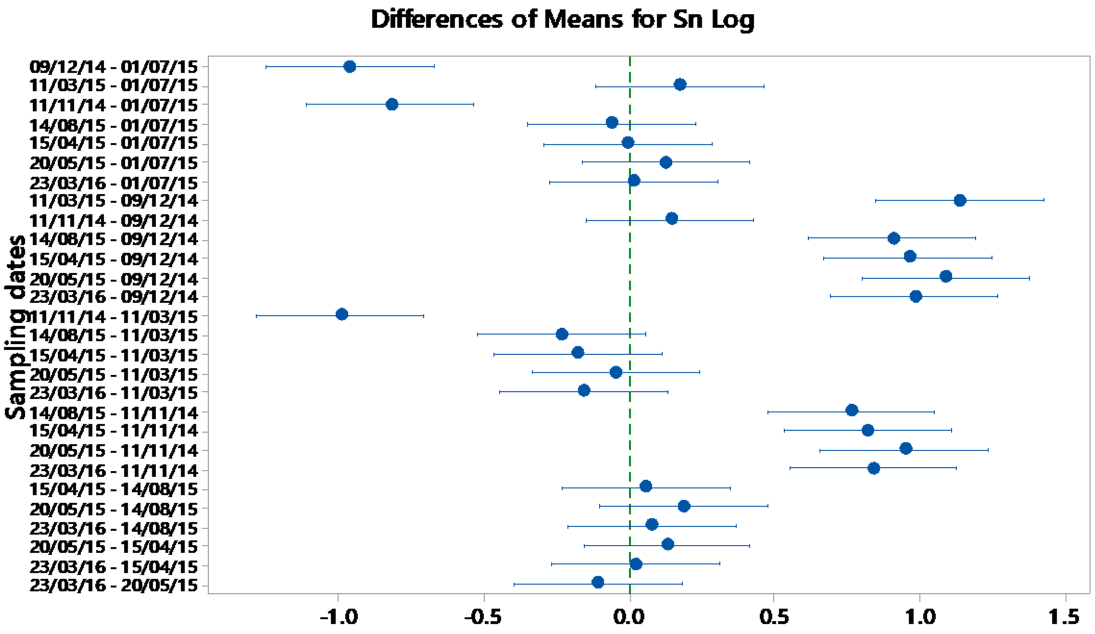
APPENDIX H4. Tukey's post-hoc test for difference of means of Ni between sampling dates in river sediment.



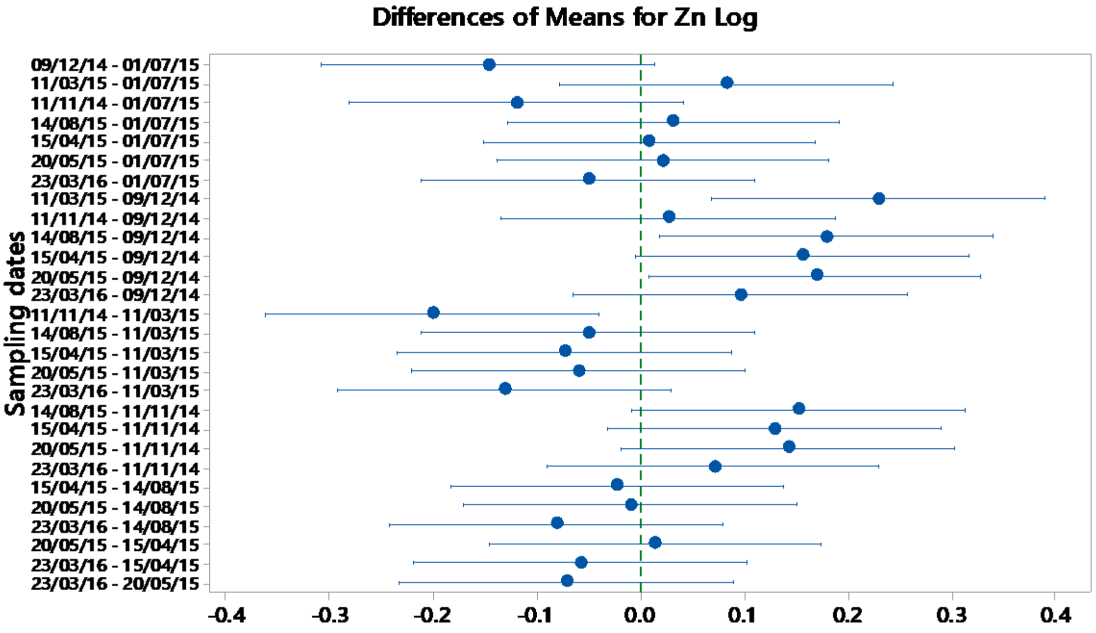
APPENDIX H5. Tukey's post-hoc test for difference of means of Pb between sampling dates in river sediment.



APPENDIX H6. Tukey's post-hoc test for difference of means of Sn between sampling dates in river sediment.



APPENDIX H7. Tukey's post-hoc test for difference of means of Zn between sampling dates in river sediment.



APPENDIX I1. Correlation analysis of target metals between water and sediment matrices on 11th November 2014.

			Metals in water						
			Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Sn**	**Zn**
Metals in sediment	**Cd**	**r***	0.15	-0.32	-0.32	0.22	-0.32	0.19	0.20
		P-value	0.67	0.34	0.34	0.52	0.34	0.58	0.56
	Cu	**r***	0.03	-0.31	-0.35	0.32	-0.28	0.20	0.29
		P-value	0.94	0.35	0.29	0.34	0.41	0.55	0.39
	Hg	**r***	0.19	-0.30	-0.30	0.38	0.28	-0.07	0.35
		P-value	0.58	0.37	0.37	0.25	0.40	0.84	0.29
	Ni	**r***	0.13	-0.41	-0.29	0.20	-0.20	0.22	0.17
		P-value	0.71	0.21	0.39	0.54	0.55	0.52	0.63
	Pb	**r***	-0.03	-0.16	-0.34	0.46	-0.31	0.24	0.45
		P-value	0.94	0.64	0.31	0.16	0.36	0.49	0.17
	Sn	**r***	-0.15	-0.43	-0.36	**0.65**	-0.19	0.11	**0.63**
		P-value	-0.65	0.19	0.28	**0.03**	0.58	0.75	**0.03**
	Zn	**r***	0.13	-0.30	-0.46	0.37	-0.30	0.12	0.34
		P-value	0.69	0.37	0.16	0.26	0.37	0.73	0.30

*Pearson correlation

APPENDIX I2. Correlation analysis of target metals between water and sediment matrices on 9th December 2014.

			Metals in water						
			Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Sn**	**Zn**
Metals in sediment	**Cd**	**r***	0.26	-0.01	-0.225	-0.19	-0.40	0.28	-0.19
		P-value	0.44	0.99	0.46	0.58	0.22	0.40	0.57
	Cu	**r***	0.28	**0.68**	-0.36	0.26	0.03	-0.13	0.24
		P-value	0.40	**0.02**	0.28	0.43	0.92	0.70	0.48
	Hg	**r***	-0.01	0.48	-0.13	0.25	0.01	-0.22	0.21
		P-value	0.97	0.13	0.71	0.46	0.97	0.52	0.54
	Ni	**r***	-0.01	0.01	-0.12	-0.30	-0.42	**0.69**	-0.33
		P-value	0.99	0.99	0.72	0.37	0.19	**0.01**	0.32
	Pb	**r***	0.80	0.37	-0.46	0.16	-0.02	0.44	0.13
		P-value	0.82	0.27	0.15	0.62	0.95	0.18	0.69
	Sn	**r***	-0.25	**0.70**	-0.28	0.29	0.20	0.20	0.23
		P-value	0.47	**0.01**	0.40	0.39	0.56	0.56	0.50
	Zn	**r***	0.38	0.53	-0.38	0.15	-0.07	0.23	0.13
		P-value	0.25	0.09	0.24	0.66	0.85	0.49	0.70

*Pearson correlation

APPENDIX I3. Correlation analysis of target metals between water and sediment matrices on 11th March 2015.

			Metals in water						
			Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Sn**	**Zn**
Metals in sediment	**Cd**	**r***	-0.21	0.13	-0.40	0.16	-0.52	0.53	0.16
		P-value	0.53	0.70	0.22	0.64	0.10	0.10	0.65
	Cu	**r***	**-0.81**	-0.06	**-0.62**	0.07	**-0.84**	0.42	0.06
		P-value	**0.01**	0.86	**0.04**	0.85	**0.01**	0.20	0.87
	Hg	**r***	-0.44	0.22	**-0.59**	0.01	-0.70	0.28	-0.01
		P-value	0.18	0.53	**0.05**	0.99	**0.01**	0.40	0.97
	Ni	**r***	-0.02	0.02	-0.25	0.05	-0.35	0.56	0.04
		P-value	0.96	0.95	0.46	0.89	0.30	0.08	0.91
	Pb	**r***	**-0.67**	0.21	**-0.71**	0.28	**-0.83**	0.53	0.27
		P-value	**0.02**	0.53	**0.01**	0.41	**0.01**	0.09	0.43
	Sn	**r***	**-0.67**	0.18	-0.51	0.29	**-0.69**	0.23	0.28
		P-value	**0.02**	0.59	0.11	0.39	**0.02**	0.50	0.39
	Zn	**r***	**-0.71**	-0.01	**-0.72**	0.22	**-0.86**	**0.68**	0.20
		P-value	**0.01**	0.99	**0.01**	0.52	**0.01**	**0.02**	0.55

*Pearson correlation

APPENDIX I4. Correlation analysis of target metals between water and sediment matrices on 15th April 2015.

			Metals in water						
			Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Sn**	**Zn**
Metals in sediment	**Cd**	**r***	**0.72**	-0.21	-0.08	0.17	0.24	-0.12	0.16
		P-value	**0.01**	0.53	0.82	0.61	0.49	0.73	0.63
	Cu	**r***	0.48	-0.33	0.07	-0.38	0.07	0.21	-0.41
		P-value	0.14	0.32	0.83	0.25	0.83	0.54	0.21
	Hg	**r***	0.08	-0.22	-0.11	0.36	-0.22	0.22	0.33
		P-value	0.81	0.52	0.75	0.28	0.51	0.52	0.33
	Ni	**r***	**0.74**	-0.07	-0.25	0.16	0.27	-0.14	0.16
		P-value	**0.01**	0.83	0.45	0.64	0.42	0.69	0.65
	Pb	**r***	0.41	-0.43	0.19	-0.17	0.06	0.19	-0.20
		P-value	0.21	0.19	0.57	0.63	0.86	0.59	0.56
	Sn	**r***	0.29	-0.27	0.27	-0.14	0.07	0.30	-0.17
		P-value	0.43	0.43	0.43	0.69	0.85	0.38	0.63
	Zn	**r***	0.42	-0.36	0.10	-0.06	0.15	0.13	-0.09
		P-value	0.20	0.27	0.77	0.86	0.66	0.69	0.80

*Pearson correlation

APPENDIX I5. Correlation analysis of target metals between water and sediment matrices on 20th May 2015.

			Metals in water						
			Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Sn**	**Zn**
Metals in sediment	**Cd**	**r***	**0.94**	-0.34	-0.20	-0.28	-0.27	-0.23	-0.31
		P-value	**0.01**	0.30	0.55	0.40	0.42	0.50	0.36
	Cu	**r***	0.12	-0.10	-0.13	0.03	0.22	0.04	-0.04
		P-value	0.72	0.76	0.70	0.94	0.52	0.89	0.92
	Hg	**r***	0.02	**0.68**	-0.36	**0.64**	**0.68**	0.54	**0.64**
		P-value	0.96	**0.02**	0.28	**0.03**	**0.02**	0.09	**0.03**
	Ni	**r***	**0.91**	-0.46	-0.13	-0.34	-0.38	-0.27	-0.38
		P-value	**0.01**	0.16	0.70	0.30	0.24	0.42	0.25
	Pb	**r***	0.39	-0.11	-0.50	0.14	-0.14	0.19	0.10
		P-value	0.24	0.75	0.12	0.67	0.68	0.58	0.77
	Sn	**r***	0.15	0.01	-0.35	0.23	-0.07	0.26	0.17
		P-value	0.66	0.99	0.29	0.51	0.83	0.43	0.61
	Zn	**r***	0.42	-0.26	-0.40	0.01	-0.30	0.07	-0.05
		P-value	0.20	0.44	0.23	0.98	0.37	0.85	0.89

*Pearson correlation

APPENDIX I6. Correlation analysis of target metals between water and sediment matrices on 1st July 2015.

			Metals in water						
			Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Sn**	**Zn**
Metals in sediment	**Cd**	**r***	0.55	-0.24	-0.45	0.11	0.42	-0.05	0.12
		P-value	0.08	0.48	0.16	0.75	0.20	0.89	0.72
	Cu	**r***	0.05	-0.07	-0.44	-0.13	0.24	-0.08	-0.12
		P-value	0.89	0.83	0.17	0.71	0.48	0.83	0.73
	Hg	**r***	0.26	-0.39	**-0.55**	0.11	0.42	0.28	0.17
		P-value	0.44	0.24	**0.05**	0.75	0.20	0.40	0.62
	Ni	**r***	**0.59**	-0.03	-0.38	-0.16	0.41	-0.10	-0.15
		P-value	**0.05**	0.94	0.25	0.63	0.22	0.77	0.66
	Pb	**r***	0.16	-0.34	**-0.59**	0.35	0.23	0.10	0.36
		P-value	0.64	0.31	**0.05**	0.29	0.50	0.78	0.28
	Sn	**r***	-0.04	-0.43	**-0.71**	0.37	0.18	0.11	0.38
		P-value	0.91	0.19	**0.01**	0.27	0.59	0.75	0.25
	Zn	**r***	0.18	-0.27	**-0.58**	0.24	0.25	0.01	0.24
		P-value	0.59	0.42	**0.05**	0.48	0.45	0.99	0.48

*Pearson correlation

APPENDIX I7. Correlation analysis of target metals between water and sediment matrices 14th August 2015.

			Metals in water						
			Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Sn**	**Zn**
Metals in sediment	**Cd**	**r***	-0.17	0.11	0.39	0.02	-0.13	**0.59**	0.16
		P-value	0.63	0.75	0.24	0.95	0.70	**0.05**	0.64
	Cu	**r***	-0.25	-0.18	-0.04	0.03	-0.43	-0.06	0.06
		P-value	0.45	0.60	0.90	0.93	0.19	0.85	0.87
	Hg	**r***	0.11	-0.11	-0.01	-0.30	0.05	**0.98**	-0.21
		P-value	0.74	0.75	0.98	0.38	0.89	**0.01**	0.54
	Ni	**r***	-0.01	-0.01	0.46	-0.45	-0.37	0.57	-0.31
		P-value	0.99	0.99	0.15	0.16	0.26	0.07	0.35
	Pb	**r***	-0.13	-0.14	0.23	-0.20	-0.49	0.19	-0.03
		P-value	0.71	0.69	0.49	0.56	0.12	0.57	0.92
	Sn	**r***	-0.04	-0.36	-0.36	-0.03	-0.48	0.02	0.10
		P-value	0.91	0.27	0.27	0.94	0.13	0.94	0.77
	Zn	**r***	-0.20	-0.21	0.02	0.14	-0.28	0.17	0.29
		P-value	0.55	0.53	0.96	0.67	0.41	0.61	0.39

*Pearson correlation

APPENDIX I8. Correlation analysis of target metals between water and sediment matrices 23rd March 2016.

			Metals in water						
			Cd	**Cu**	**Hg**	**Ni**	**Pb**	**Sn**	**Zn**
Metals in sediment	**Cd**	**r***	-0.23	-0.35	-0.05	-0.39	-0.26	-0.30	-0.35
		P-value	0.50	0.29	0.89	0.23	0.44	0.36	0.28
	Cu	**r***	-0.38	-0.19	0.41	-0.32	-0.17	-0.46	-0.32
		P-value	0.26	0.59	0.21	0.33	0.63	0.15	0.34
	Hg	**r***	-0.29	-0.30	0.17	-0.42	-0.32	-0.14	-0.42
		P-value	0.38	0.38	0.60	0.20	0.34	0.68	0.20
	Ni	**r***	-0.24	-0.36	0.01	-0.40	-0.27	-0.36	-0.38
		P-value	0.47	0.28	0.98	0.22	0.42	0.28	0.26
	Pb	**r***	-0.23	-0.26	0.10	-0.28	-0.22	-0.46	-0.30
		P-value	0.49	0.45	0.77	0.40	0.52	0.15	0.37
	Sn	**r***	-0.28	-0.30	-0.04	-0.35	-0.19	**-0.69**	-0.36
		P-value	0.40	0.36	0.91	0.29	0.58	**0.02**	0.28
	Zn	**r***	-0.29	-0.22	0.27	-0.33	-0.15	-0.41	-0.32
		P-value	0.39	0.51	0.42	0.32	0.66	0.21	0.33

*Pearson correlation

APPENDIX J1. PAHs concentrations in sediment (µg/g) samples collected on 11th November 2014.

Sampling Site		Ph	A	Fl	Py	Bz(a)A	C	Bz(b)Fl	Bz(k)Fl	Bz(a)Py	DBz(a,h) A	Bz(g,h,i) Pe
A	Mean	0.57	0.26	1.75	1.57	0.93	0.89	1.74	0.52	1.13	0.25	1.03
	StDev	± 0.01	± 0.01	± 0.03	± 0.14	± 0.15	± 0.07	± 0.04	± 0.00	± 0.05	± 0.04	± 0.11
B	Mean	0.91	0.40	4.03	3.39	1.95	2.16	3.65	1.10	2.05	0.49	2.01
	StDev	± 0.06	± 0.04	± 0.07	± 0.02	± 0.04	± 0.08	± 0.04	± 0.06	± 0.02	± 0.01	± 0.02
C	Mean	1.39	0.52	3.78	3.82	2.15	2.10	3.71	1.14	2.10	0.50	2.42
	StDev	± 0.02	± 0.04	± 0.13	± 0.16	± 0.12	± 0.12	± 0.09	± 0.06	± 0.05	± 0.03	± 0.03
D	Mean	3.95	1.04	7.18	5.87	3.43	3.01	4.33	1.35	2.99	0.66	2.17
	StDev	± 0.01	± 0.05	± 0.07	± 0.01	± 0.03	± 0.02	± 0.01	± 0.07	± 0.06	± 0.04	± 0.04
E	Mean	2.03	0.69	5.81	4.96	3.20	3.07	4.05	1.62	3.30	1.92	2.27
	StDev	± 0.05	± 0.03	± 0.06	± 0.04	± 0.00	± 0.03	± 0.05	± 0.04	± 0.00	± 0.03	± 0.03
F	Mean	1.21	0.32	2.34	2.00	1.10	1.13	1.56	0.51	1.11	0.75	0.93
	StDev	± 0.01	± 0.00	± 0.00	± 0.03	± 0.03	± 0.03	± 0.03	± 0.02	± 0.01	± 0.01	± 0.04
G	Mean	1.84	0.58	3.70	3.43	1.77	1.99	3.17	1.12	2.03	1.54	1.99
	StDev	± 0.08	± 0.00	± 0.09	± 0.07	± 0.08	± 0.09	± 0.08	± 0.03	± 0.08	± 0.19	± 0.16
H	Mean	3.93	1.40	9.89	9.39	4.51	5.01	7.65	7.55	5.11	3.47	0.04
	StDev	± 0.02	± 0.03	± 0.10	± 0.16	± 0.08	± 0.09	± 0.21	± 0.20	± 0.06	± 0.00	± 0.01
I	Mean	2.26	0.84	5.91	5.48	2.79	2.88	4.37	1.59	3.07	2.24	2.72
	StDev	± 0.03	± 0.04	± 0.08	± 0.02	± 0.01	± 0.01	± 0.00	± 0.01	± 0.04	± 0.01	± 0.02
J	Mean	1.54	1.01	5.71	6.70	2.87	3.78	6.91	6.81	3.97	3.11	0.01
	StDev	± 0.04	± 0.04	± 0.02	± 0.12	± 0.02	± 0.03	± 0.06	± 0.06	± 0.04	± 0.02	± 0.00
K	Mean	2.14	1.29	5.30	5.28	2.80	3.12	5.75	1.82	3.27	2.84	3.31
	StDev	± 0.04	± 0.02	± 0.02	± 0.04	± 0.03	± 0.05	± 0.02	± 0.05	± 0.04	± 0.03	± 0.05

APPENDIX J2. PAHs concentrations in sediment (µg/g) samples collected on 9th December 2014.

Sampling Site		Ph	A	Fl	Py	Bz(a)A	C	Bz(b)Fl	Bz(k)Fl	Bz(a)Py	DBz(a,h) A	Bz(g,h,i) Pe
A	Mean	1.22	0.48	2.56	2.35	1.28	1.30	1.94	0.71	1.37	0.93	1.05
	StDev	± 0.02	± 0.02	± 0.07	± 0.01	± 0.04	± 0.05	± 0.06	± 0.03	± 0.06	± 0.04	± 0.03
B	Mean	0.74	0.39	3.21	3.14	1.62	1.90	2.96	0.86	1.69	1.38	1.69
	StDev	± 0.02	± 0.04	± 0.04	± 0.02	± 0.01	± 0.00	± 0.02	± 0.03	± 0.02	± 0.05	± 0.02
C	Mean	1.07	0.47	3.06	3.12	1.72	2.16	3.64	1.05	2.17	1.62	2.11
	StDev	± 0.03	± 0.02	± 0.01	± 0.02	± 0.03	± 0.00	± 0.04	± 0.01	± 0.02	± 0.04	± 0.01
D	Mean	0.93	0.31	1.81	1.73	0.92	1.00	1.34	0.47	0.95	0.64	0.69
	StDev	± 0.00	± 0.03	± 0.05	± 0.01	± 0.01	± 0.01	± 0.04	± 0.02	± 0.02	± 0.00	± 0.01
E	Mean	1.35	0.58	4.15	3.63	2.31	2.45	3.56	1.10	2.47	1.45	1.88
	StDev	± 0.00	± 0.02	± 0.00	± 0.03	± 0.02	± 0.00	± 0.22	± 0.06	± 0.01	± 0.00	± 0.02
F	Mean	1.04	0.31	2.50	2.20	1.22	1.28	1.72	0.56	1.21	0.78	0.91
	StDev	± 0.02	± 0.02	± 0.04	± 0.02	± 0.01	± 0.00	± 0.01	± 0.02	± 0.00	± 0.02	± 0.02
G	Mean	2.46	0.93	7.09	6.50	3.34	4.12	6.53	6.33	3.82	2.81	0.12
	StDev	± 0.04	± 0.02	± 0.04	± 0.02	± 0.01	± 0.02	± 0.02	± 0.00	± 0.02	± 0.04	± 0.00
H	Mean	2.51	0.89	7.05	6.53	3.45	4.45	6.30	2.03	3.89	3.09	3.24
	StDev	± 0.03	± 0.02	± 0.02	± 0.02	± 0.02	± 0.08	± 0.00	± 0.01	± 0.02	± 0.02	± 0.05
I	Mean	1.46	0.64	4.32	4.20	2.27	2.75	5.55	5.42	2.77	2.22	1.91
	StDev	± 0.02	± 0.00	± 0.04	± 0.03	± 0.00	± 0.03	± 0.07	± 0.05	± 0.03	± 0.07	± 0.02
J	Mean	17.07	3.28	27.80	24.61	14.90	17.66	25.83	7.44	15.79	9.98	11.86
	StDev	± 0.01	± 0.01	± 0.09	± 0.02	± 0.06	± 0.01	± 0.05	± 0.02	± 0.03	± 0.05	± 0.02
K	Mean	1.71	0.88	3.96	4.27	2.03	2.81	7.78	6.88	2.89	2.57	2.69
	StDev	± 0.01	± 0.04	± 0.05	± 0.04	± 0.06	± 0.02	± 0.02	± 0.03	± 0.01	± 0.02	± 0.03

APPENDIX J3. PAHs concentrations in sediment (μg/g) samples collected on 11th March 2015.

Sampling Site		Ph	A	Fl	Py	Bz(a)A	C	Bz(b)Fl	Bz(k)Fl	Bz(a)Py	DBz(a,h) A	Bz(g,h,i) Pe
A	Mean	0.77	0.36	2.19	2.09	1.07	1.24	2.88	2.52	1.26	0.93	1.19
	StDev	± 0.04	± 0.04	± 0.09	± 0.02	± 0.01	± 0.02	± 0.01	± 0.06	± 0.03	± 0.01	± 0.02
B	Mean	1.02	0.43	3.69	3.43	1.91	2.23	3.88	1.19	2.09	1.77	2.05
	StDev	± 0.02	± 0.02	± 0.04	± 0.03	± 0.03	± 0.04	± 0.04	± 0.01	± 0.05	± 0.00	± 0.05
C	Mean	2.11	0.85	5.44	5.27	2.64	3.27	5.54	1.59	3.21	2.57	3.19
	StDev	± 0.04	± 0.06	± 0.03	± 0.03	± 0.01	± 0.01	± 0.07	± 0.01	± 0.02	± 0.04	± 0.06
D	Mean	5.99	1.29	9.13	7.44	3.49	3.87	4.86	1.73	3.45	2.35	2.40
	StDev	± 0.04	± 0.04	± 0.05	± 0.03	± 0.00	± 0.02	± 0.04	± 0.02	± 0.04	± 0.02	± 0.00
E	Mean	8.03	2.22	16.63	14.06	7.46	7.85	12.11	3.44	7.98	5.38	5.44
	StDev	± 0.04	± 0.01	± 0.04	± 0.06	± 0.01	± 0.11	± 0.05	± 0.02	± 0.03	± 0.02	± 0.04
F	Mean	7.45	2.13	17.17	14.51	7.25	8.01	12.85	4.24	8.34	5.46	6.18
	StDev	± 0.01	± 0.04	± 0.01	± 0.04	± 0.02	± 0.01	± 0.04	± 0.04	± 0.06	± 0.05	± 0.06
G	Mean	3.11	1.14	7.38	6.43	3.15	4.00	6.03	1.85	3.38	3.05	2.96
	StDev	± 0.01	± 0.00	± 0.04	± 0.03	± 0.07	± 0.02	± 0.04	± 0.01	± 0.06	± 0.03	± 0.02
H	Mean	1.08	0.54	3.35	3.05	1.46	1.81	2.17	1.96	1.07	0.25	0.18
	StDev	± 0.08	± 0.02	± 0.04	± 0.03	± 0.03	± 0.01	± 0.00	± 0.03	± 0.02	± 0.01	± 0.02
I	Mean	2.81	0.89	6.61	5.88	2.95	3.29	5.05	1.64	3.09	2.37	2.57
	StDev	± 0.01	± 0.04	± 0.04	± 0.03	± 0.00	± 0.01	± 0.04	± 0.09	± 0.03	± 0.07	± 0.07
J	Mean	5.79	2.05	14.35	13.58	6.17	7.77	12.71	3.75	7.50	4.78	5.17
	StDev	± 0.02	± 0.06	± 0.02	± 0.04	± 0.04	± 0.04	± 0.02	± 0.05	± 0.04	± 0.06	± 0.03
K	Mean	1.90	1.01	4.83	4.66	2.05	2.83	5.25	1.54	2.52	2.17	2.55
	StDev	± 0.02	± 0.00	± 0.04	± 0.03	± 0.06	± 0.04	± 0.06	± 0.06	± 0.06	± 0.03	± 0.03

APPENDIX J4. PAHs concentrations in sediment (μg/g) samples collected on 15th April 2015.

Sampling Site		Ph	A	Fl	Py	Bz(a)A	C	Bz(b)Fl	Bz(k)Fl	Bz(a)Py	DBz(a,h) A	Bz(g,h,i) Pe
A	Mean	0.84	0.35	2.40	2.20	1.11	1.26	2.21	0.68	1.39	1.06	1.11
	StDev	± 0.02	± 0.02	± 0.05	± 0.00	± 0.01	± 0.03	± 0.02	± 0.02	± 0.02	± 0.02	± 0.06
B	Mean	1.17	0.57	4.07	3.71	1.83	2.19	3.67	1.13	1.89	1.43	1.38
	StDev	± 0.03	± 0.02	± 0.04	± 0.04	± 0.00	± 0.04	± 0.04	± 0.01	± 0.03	± 0.06	± 0.02
C	Mean	2.03	0.81	5.35	5.24	2.53	3.22	5.41	1.55	3.12	2.29	3.06
	StDev	± 0.03	± 0.01	± 0.04	± 0.04	± 0.02	± 0.03	± 0.01	± 0.03	± 0.01	± 0.00	± 0.02
D	Mean	4.66	1.30	9.48	7.73	4.18	4.48	6.41	2.03	4.04	3.10	3.15
	StDev	± 0.02	± 0.04	± 0.04	± 0.01	± 0.04	± 0.01	± 0.04	± 0.02	± 0.01	± 0.03	± 0.06
E	Mean	7.67	2.53	16.80	14.34	7.52	8.14	11.25	4.02	7.69	5.18	5.67
	StDev	± 0.02	± 0.00	± 0.01	± 0.02	± 0.03	± 0.04	± 0.01	± 0.04	± 0.04	± 0.05	± 0.04
F	Mean	2.63	0.71	5.84	4.78	2.41	2.49	5.05	4.41	2.46	1.78	1.89
	StDev	± 0.01	± 0.01	± 0.02	± 0.04	± 0.03	± 0.04	± 0.02	± 0.02	± 0.03	± 0.01	± 0.05
G	Mean	2.86	1.08	6.65	6.01	2.84	3.46	4.29	1.62	2.72	0.03	2.06
	StDev	± 0.01	± 0.05	± 0.04	± 0.02	± 0.05	± 0.03	± 0.04	± 0.01	± 0.05	± 0.00	± 0.04
H	Mean	0.91	0.49	2.83	2.62	1.21	1.64	2.10	1.88	1.02	0.20	0.01
	StDev	± 0.00	± 0.00	± 0.02	± 0.01	± 0.05	± 0.00	± 0.02	± 0.00	± 0.01	± 0.03	± 0.00
I	Mean	1.29	0.53	3.31	2.88	1.50	1.65	2.57	0.94	1.57	1.21	1.26
	StDev	± 0.01	± 0.01	± 0.04	± 0.02	± 0.02	± 0.08	± 0.00	± 0.02	± 0.01	± 0.01	± 0.01
J	Mean	2.32	1.62	8.47	8.65	4.46	5.47	12.97	11.50	5.15	3.18	0.02
	StDev	± 0.03	± 0.04	± 0.01	± 0.03	± 0.02	± 0.01	± 0.03	± 0.02	± 0.01	± 0.02	± 0.01
K	Mean	1.49	0.74	3.06	3.06	1.47	1.92	4.01	1.24	1.84	1.59	1.46
	StDev	± 0.02	± 0.01	± 0.02	± 0.02	± 0.00	± 0.02	± 0.01	± 0.02	± 0.05	± 0.01	± 0.01

APPENDIX J5. PAHs concentrations in sediment (µg/g) samples collected on 20th May 2015.

Sampling Site		Ph	A	Fl	Py	Bz(a)A	C	Bz(b)Fl	Bz(k)Fl	Bz(a)Py	DBz(a,h) A	Bz(g,h,i) Pe
A	Mean	0.67	0.27	1.87	1.70	0.84	0.99	1.64	0.53	0.94	0.64	0.76
	StDev	± 0.01	± 0.01	± 0.02	± 0.02	± 0.01	± 0.00	± 0.01	± 0.00	± 0.02	± 0.00	± 0.02
B	Mean	1.16	0.44	3.48	3.21	1.62	1.90	3.23	0.98	1.65	1.31	1.42
	StDev	± 0.00	± 0.00	± 0.00	± 0.02	± 0.01	± 0.02	± 0.02	± 0.02	± 0.06	± 0.02	± 0.01
C	Mean	4.24	1.48	7.39	6.60	3.31	3.80	5.23	1.88	3.26	2.03	2.52
	StDev	± 0.01	± 0.02	± 0.02	± 0.02	± 0.02	± 0.01	± 0.03	± 0.01	± 0.03	± 0.03	± 0.05
D	Mean	2.00	0.71	4.59	3.80	2.19	2.51	4.00	1.27	2.45	1.81	1.90
	StDev	± 0.00	± 0.01	± 0.03	± 0.00	± 0.01	± 0.00	± 0.01	± 0.01	± 0.02	± 0.02	± 0.02
E	Mean	2.09	0.62	4.99	4.47	2.43	2.59	3.58	1.18	2.49	1.65	1.54
	StDev	± 0.02	± 0.01	± 0.02	± 0.00	± 0.03	± 0.01	± 0.02	± 0.00	± 0.01	± 0.00	± 0.02
F	Mean	2.20	0.58	4.66	3.89	2.02	2.12	2.94	1.02	1.91	1.23	1.48
	StDev	± 0.00	± 0.02	± 0.02	± 0.01	± 0.04	± 0.02	± 0.01	± 0.00	± 0.04	± 0.02	± 0.00
G	Mean	3.43	1.11	8.58	7.72	3.60	4.42	5.75	5.11	3.69	0.14	0.24
	StDev	± 0.01	± 0.04	± 0.02	± 0.02	± 0.00	± 0.02	± 0.02	± 0.02	± 0.03	± 0.02	± 0.02
H	Mean	3.19	1.05	8.51	7.62	3.73	4.62	6.02	5.37	3.89	0.11	0.03
	StDev	± 0.01	± 0.02	± 0.00	± 0.01	± 0.02	± 0.01	± 0.03	± 0.01	± 0.00	± 0.01	± 0.00
I	Mean	2.05	0.75	5.08	4.32	2.32	2.53	3.39	1.07	2.23	1.54	1.41
	StDev	± 0.01	± 0.00	± 0.02	± 0.02	± 0.04	± 0.02	± 0.00	± 0.02	± 0.00	± 0.02	± 0.02
J	Mean	2.63	1.91	13.41	13.70	6.07	7.39	11.21	9.98	6.41	4.22	0.02
	StDev	± 0.00	± 0.00	± 0.01	± 0.02	± 0.04	± 0.01	± 0.05	± 0.02	± 0.01	± 0.02	± 0.00
K	Mean	1.07	0.61	2.49	2.70	1.16	1.67	3.26	1.11	1.44	1.32	1.52
	StDev	± 0.02	± 0.01	± 0.02	± 0.02	± 0.03	± 0.04	± 0.02	± 0.02	± 0.02	± 0.01	± 0.01

APPENDIX J6. PAHs concentrations in sediment (µg/g) samples collected on 1st July 2015.

Sampling Site		Ph	A	Fl	Py	Bz(a)A	C	Bz(b)Fl	Bz(k)Fl	Bz(a)Py	DBz(a,h) A	Bz(g,h,i) Pe
A	Mean	0.38	0.19	1.24	1.06	0.61	0.66	1.35	1.17	0.60	0.39	0.46
	StDev	± 0.00	± 0.01	± 0.02	± 0.00	± 0.02	± 0.00	± 0.01	± 0.03	± 0.04	± 0.00	± 0.01
B	Mean	0.84	0.43	3.31	3.30	1.51	1.65	2.39	0.86	1.39	0.82	1.02
	StDev	± 0.00	± 0.01	± 0.00	± 0.01	± 0.00	± 0.00	± 0.01	± 0.02	± 0.02	± 0.01	± 0.02
C	Mean	1.97	1.16	6.53	6.17	3.09	3.64	6.25	5.60	2.81	1.74	2.03
	StDev	± 0.01	± 0.00	± 0.01	± 0.01	± 0.03	± 0.02	± 0.04	± 0.02	± 0.02	± 0.01	± 0.01
D	Mean	2.07	0.66	5.10	4.53	2.31	2.82	3.74	1.39	2.30	1.47	1.69
	StDev	± 0.06	± 0.01	± 0.01	± 0.00	± 0.01	± 0.02	± 0.02	± 0.01	± 0.01	± 0.02	± 0.01
E	Mean	3.92	1.30	8.54	7.31	3.72	3.81	5.24	1.85	3.35	2.03	2.25
	StDev	± 0.02	± 0.02	± 0.02	± 0.01	± 0.02	± 0.00	± 0.02	± 0.02	± 0.00	± 0.01	± 0.02
F	Mean	0.94	0.31	2.57	2.09	1.11	1.29	1.50	0.59	0.99	0.65	0.73
	StDev	± 0.00	± 0.02	± 0.04	± 0.02	± 0.03	± 0.01	± 0.02	± 0.03	± 0.04	± 0.02	± 0.00
G	Mean	0.87	0.41	2.87	2.51	1.22	1.63	0.01	1.80	1.11	0.89	0.01
	StDev	± 0.02	± 0.00	± 0.02	± 0.01	± 0.01	± 0.04	± 0.00	± 0.01	± 0.02	± 0.02	± 0.00
H	Mean	2.09	0.82	6.10	5.29	2.53	3.21	0.03	3.52	1.95	0.10	0.03
	StDev	± 0.01	± 0.03	± 0.02	± 0.03	± 0.02	± 0.00	± 0.00	± 0.00	± 0.01	± 0.01	± 0.00
I	Mean	1.28	0.50	3.30	2.99	1.50	1.75	2.38	2.15	1.39	0.03	0.02
	StDev	± 0.02	± 0.01	± 0.02	± 0.00	± 0.02	± 0.01	± 0.02	± 0.02	± 0.01	± 0.00	± 0.00
J	Mean	0.95	0.71	3.82	4.54	2.27	2.89	0.06	5.63	2.15	0.05	0.09
	StDev	± 0.02	± 0.01	± 0.01	± 0.02	± 0.00	± 0.02	± 0.00	± 0.02	± 0.01	± 0.00	± 0.01
K	Mean	1.07	0.59	2.38	2.38	1.09	1.44	0.01	3.03	1.23	0.93	0.03
	StDev	± 0.02	± 0.02	± 0.02	± 0.00	± 0.01	± 0.00	± 0.00	± 0.00	± 0.03	± 0.00	± 0.00

APPENDIX J7. PAHs concentrations in sediment (μg/g) samples collected on 14th August 2015 2014.

Sampling Site		Ph	A	Fl	Py	Bz(a)A	C	Bz(b)Fl	Bz(k)Fl	Bz(a)Py	DBz(a,h) A	Bz(g,h,i) Pe
A	Mean	0.43	0.22	1.27	1.07	0.61	0.64	0.85	0.28	0.49	0.43	0.03
	StDev	± 0.00	± 0.01	± 0.02	± 0.02	± 0.00	± 0.00	± 0.00	± 0.00	± 0.01	± 0.01	± 0.00
B	Mean	0.44	0.21	1.47	1.52	0.76	0.91	1.34	0.50	0.77	0.62	0.65
	StDev	± 0.00	± 0.00	± 0.01	± 0.00	± 0.00	± 0.00	± 0.01	± 0.01	± 0.00	± 0.00	± 0.01
C	Mean	2.47	0.89	4.96	4.60	2.34	2.58	4.67	4.15	2.11	0.03	1.53
	StDev	± 0.02	± 0.01	± 0.02	± 0.02	± 0.00	± 0.02	± 0.02	± 0.01	± 0.00	± 0.00	± 0.01
D	Mean	1.12	0.49	3.21	2.78	1.51	1.74	2.61	0.84	1.69	1.16	1.35
	StDev	± 0.02	± 0.01	± 0.00	± 0.02	± 0.02	± 0.02	± 0.04	± 0.01	± 0.02	± 0.00	± 0.03
E	Mean	1.33	0.53	4.19	3.55	2.01	2.19	2.43	0.83	1.67	1.05	1.10
	StDev	± 0.00	± 0.02	± 0.02	± 0.00	± 0.01	± 0.02	± 0.01	± 0.01	± 0.01	± 0.01	± 0.02
F	Mean	0.53	0.19	1.42	1.22	0.65	0.76	1.21	1.09	0.59	0.37	0.42
	StDev	± 0.00	± 0.01	± 0.02	± 0.00	± 0.01	± 0.02	± 0.01	± 0.01	± 0.01	± 0.01	± 0.01
G	Mean	1.93	0.81	5.73	5.19	2.54	2.95	0.01	3.12	2.39	0.02	0.15
	StDev	± 0.02	± 0.02	± 0.01	± 0.01	± 0.02	± 0.02	± 0.00	± 0.01	± 0.01	± 0.00	± 0.01
H	Mean	1.18	0.61	3.63	3.37	1.53	2.03	3.62	3.21	1.49	0.06	1.21
	StDev	± 0.00	± 0.01	± 0.01	± 0.01	± 0.01	± 0.00	± 0.01	± 0.00	± 0.01	± 0.00	± 0.01
I	Mean	0.57	0.25	1.64	1.49	0.78	0.95	1.87	1.66	0.79	0.03	0.71
	StDev	± 0.01	± 0.02	± 0.01	± 0.01	± 0.02	± 0.00	± 0.02	± 0.01	± 0.01	± 0.00	± 0.02
J	Mean	0.35	0.30	1.46	1.63	0.78	1.01	0.02	1.95	0.95	0.02	0.02
	StDev	± 0.00	± 0.01	± 0.00	± 0.03	± 0.00	± 0.00	± 0.00	± 0.02	± 0.01	± 0.00	± 0.00
K	Mean	0.34	0.21	0.90	0.91	0.44	0.64	1.57	1.42	0.69	0.01	0.02
	StDev	± 0.00	± 0.02	± 0.01	± 0.00	± 0.02	± 0.00	± 0.02	± 0.01	± 0.01	± 0.00	± 0.00

APPENDIX J8. PAHs concentrations in sediment (μg/g) samples collected on 23rd March 2016.

Sampling Site		Ph	A	Fl	Py	Bz(a)A	C	Bz(b)Fl	Bz(k)Fl	Bz(a)Py	DBz(a,h) A	Bz(g,h,i) Pe
A	Mean	0.11	0.09	0.41	0.31	0.20	0.21	0.55	0.43	0.32	0.21	0.21
	StDev	± 0.01	± 0.01	± 0.01	± 0.02	± 0.02	± 0.00	± 0.03	± 0.03	± 0.00	± 0.02	± 0.01
B	Mean	0.20	0.17	0.88	0.71	0.48	0.37	1.17	1.00	0.57	0.37	0.38
	StDev	± 0.0	± 0.00	± 0.02	± 0.02	± 0.01	± 0.01	± 0.02	± 0.02	± 0.00	± 0.02	± 0.01
C	Mean	0.27	0.15	0.78	0.81	0.57	0.38	1.11	0.99	0.59	0.41	0.43
	StDev	± 0.01	± 0.02	± 0.02	± 0.01	± 0.00	± 0.01	± 0.02	± 0.02	± 0.02	± 0.00	± 0.00
D	Mean	1.57	0.41	3.97	3.37	1.79	1.67	2.68	0.87	1.83	1.30	1.28
	StDev	± 0.04	± 0.02	± 0.01	± 0.00	± 0.09	± 0.01	± 0.00	± 0.01	± 0.01	± 0.01	± 0.00
E	Mean	1.17	0.43	3.05	2.38	1.40	0.04	1.94	0.75	1.44	0.90	1.15
	StDev	± 0.00	± 0.02	± 0.00	± 0.00	± 0.02	± 0.00	± 0.00	± 0.02	± 0.02	± 0.02	± 0.02
F	Mean	1.24	0.35	2.65	2.25	1.42	0.96	1.69	0.44	1.23	0.70	0.83
	StDev	± 0.00	± 0.00	± 0.02	± 0.00	± 0.01	± 0.00	± 0.01	± 0.02	± 0.02	± 0.02	± 0.00
G	Mean	0.49	0.12	1.12	1.01	0.64	0.55	0.95	0.36	0.81	0.45	0.62
	StDev	± 0.01	± 0.00	± 0.02	± 0.02	± 0.00	± 0.01	± 0.02	± 0.00	± 0.01	± 0.01	± 0.00
H	Mean	0.81	0.25	2.10	1.77	1.15	0.89	1.58	0.66	1.25	0.89	1.05
	StDev	± 0.00	± 0.02	± 0.02	± 0.01	± 0.02	± 0.02	± 0.01	± 0.01	± 0.01	± 0.02	± 0.01
I	Mean	1.04	0.90	1.86	1.51	0.97	0.80	1.49	0.62	1.15	0.72	0.85
	StDev	± 0.02	± 0.01	± 0.01	± 0.02	± 0.00	± 0.00	± 0.01	± 0.00	± 0.00	± 0.01	± 0.01
J	Mean	4.46	1.45	14.19	0.24	6.43	5.68	12.39	2.95	6.97	4.95	5.18
	StDev	± 0.01	± 0.03	± 0.03	± 0.01	± 0.04	± 0.02	± 0.04	± 0.03	± 0.00	± 0.00	± 0.02
K	Mean	2.57	0.35	2.79	0.14	1.41	3.15	3.79	3.27	1.67	1.27	1.50
	StDev	± 0.01	± 0.00	± 0.02	± 0.01	± 0.02	± 0.02	± 0.01	± 0.01	± 0.01	± 0.01	± 0.00

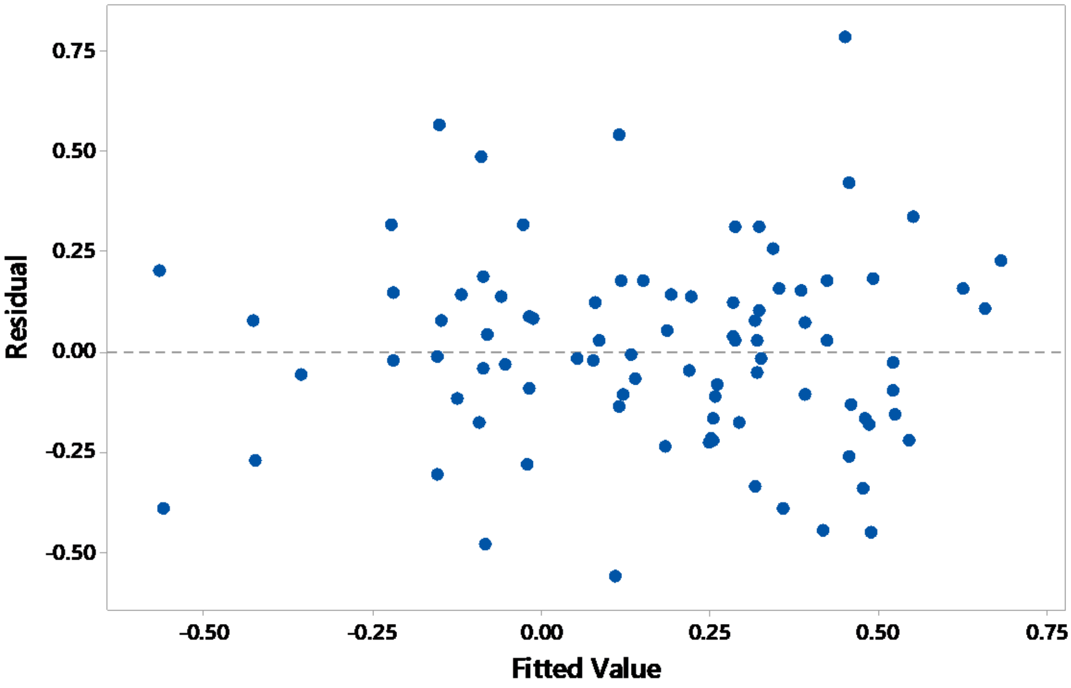
APPENDIX K1. Overview of maximum, minimum and mean (± SD) of Ph, A, Fl, Py, Bz(a)A and C concentrations in river sediment determined at each sampling site.

	Site	**Ph**		**A**		**Fl**		**Py**		**Bz(a)A**		**C**	
		Range in concentration (μg/g)	**Mean ± SD**	**Range in concentration (μg/g)**	**Mean ± SD**	**Range in concentration (μg/g)**	**Mean ± SD**	**Range in concentration (μg/g)**	**Mean ± SD**	**Range in concentration (μg/g)**	**Mean ± SD**	**Range in concentration (μg/g)**	**Mean ± SD**
River Lee	A	0.11 – 1.22	0.62 ± 0.34	0.09 – 0.48	0.28 ± 0.12	0.41 – 2.56	1.71 ± 0.71	0.31 – 2.35	1.54 ± 0.70	0.20 – 1.28	0.83 ± 0.35	0.21 – 1.30	0.90 ± 0.38
	G	0.49 – 3.43	2.12 ± 1.05	0.12 – 1.14	0.77 ± 0.37	1.12 – 8.58	5.39 ± 2.57	1.01 – 7.72	4.85 ± 2.30	0.64 – 3.60	2.31 ± 1.14	0.55 – 4.42	2.89 ± 1.38
	H	0.81 – 3.93	1.96 ± 1.17	0.25 – 1.40	0.76 ± 0.36	2.10 – 9.98	5.44 ± 2.90	1.77 – 9.39	4.96 ± 2.70	1.15 – 4.51	2.45 ± 1.31	0.89 – 5.01	2.96 ± 1.58
	I	0.57 – 2.81	1.60 ± 0.73	0.25 – 0.90	0.66 ± 0.23	1.64 – 6.61	4.00 ± 1.81	1.49 – 5.88	3.59 ± 1.66	0.78 – 2.95	1.89 ± 0.81	0.80 – 3.29	2.08 ± 0.92
Lee Navigation	C	0.27 – 4.24	1.94 ± 1.16	0.15 – 1.48	0.79 ± 0.42	0.78 – 7.39	4.66 ± 2.09	0.81 – 6.60	4.45 ± 124.89	0.57 – 3.31	320.75 ± 223.89	0.38 – 3.80	320.75 ± 223.89
	J	0.35 – 17.07	4.39 ± 5.43	0.30 – 3.28	1.54 ± 0.92	1.46 – 27.80	11.15 ± 8.33	0.24 – 24.61	9.21 ± 7.95	0.78 – 14.90	5.49 ± 4.32	1.01 – 17.66	6.46 ± 5.06
	K	0.34 – 2.57	1.54 ± 0.70	0.21 – 1.29	0.71 ± 0.35	0.90 – 5.30	3.21 ± 1.43	0.14 – 5.28	2.93 ± 1.79	0.44 – 2.80	1.56 ± 0.72	0.64 – 3.15	2.20 ± 0.92
Tributaries	B	0.20 – 1.17	0.81 ± 0.34	0.17 – 0.57	0.38 ± 0.13	0.88 – 4.07	3.02 ± 1.19	0.71 – 3.71	2.77 ± 1.06	0.48 – 1.95	1.46 ± 0.55	0.37 – 2.23	1.66 ± 0.68
	D	0.93 – 5.99	2.79 ± 1.85	0.31 – 1.30	0.78 ± 0.39	1.81 – 9.48	5.56 ± 2.78	1.73 – 7.73	4.66 ± 2.18	0.92 – 4.18	2.48 ± 1.12	1.00 – 4.48	2.64 ± 1.17
	E	1.17 – 8.03	3.45 ± 2.85	0.43 – 2.53	1.11 ± 0.83	3.05 – 16.80	8.02 ± 5.60	2.38 – 14.34	6.84 ± 4.76	1.40 – 7.52	3.76 ± 2.41	0.04 – 8.14	3.77 ± 2.82
	F	0.53 – 7.45	2.16 ± 2.25	0.19 – 2.13	0.61 ± 0.64	1.42 – 17.17	4.89 ± 5.16	1.22 – 14.51	4.12 ± 4.35	0.65 – 7.25	2.15 ± 2.14	0.76 – 8.01	2.26 ± 2.40

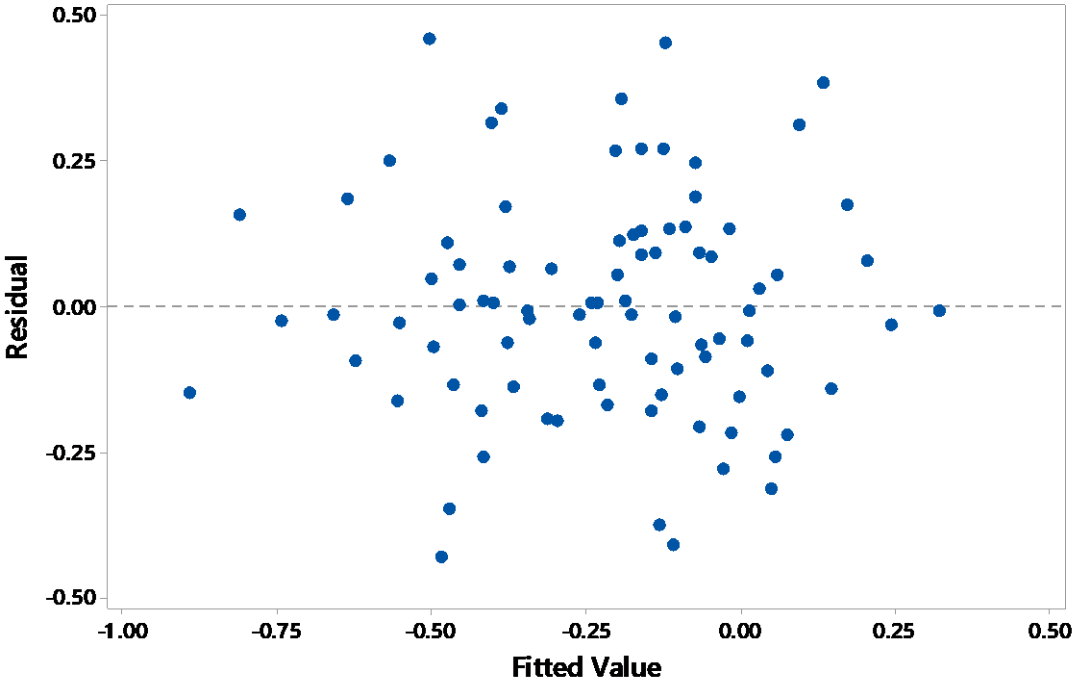
APPENDIX K2. Overview of maximum, minimum and mean (± SD) of Bz(b)Fl , Bz(k)Fl , Bz(a)Py, DBz(a,h)A and Bz(g,h,i)Pe concentrations in river sediment determined at each sampling site.

	Site	**Bz(b)Fl**		**Bz(k)Fl**		**Bz(a)Py**		**DBz(a,h)A**		**Bz(g,h,i)Pe**	
		Range in concentration (µg/g)	**Mean ± SD**	**Range in concentration (µg/g)**	**Mean ± SD**	**Range in concentration (µg/g)**	**Mean ± SD**	**Range in concentration (µg/g)**	**Mean ± SD**	**Range in concentration (µg/g)**	**Mean ± SD**
River Lee	A	0.55 – 2.88	1.65 ± 0.74	0.28 – 2.52	0.86 ± 0.72	0.32 – 1.39	0.94 ± 0.42	0.21 – 1.06	0.61 ± 0.33	0.03 – 1.19	0.73 ± 0.44
	G	0.01 – 6.53	3.34 ± 2.73	0.36 – 6.33	2.66 ± 2.06	0.81 – 3.82	2.49 ± 1.13	0.02 – 3.05	1.12 ± 1.23	0.01 – 2.96	1.02 ± 1.14
	H	0.03 – 7.65	3.68 ± 2.69	0.66 – 7.55	3.27 ± 2.23	1.02 – 5.11	2.46 ± 1.59	0.06 – 3.70	1.05 ± 1.48	0.01 – 3.24	0.72 ± 1.13
	I	1.49 – 5.55	3.33 ± 1.51	0.62 – 5.42	1.89 ± 1.51	0.79 – 3.09	2.01 ± 0.90	0.03 – 2.37	1.30 ± 0.96	0.02 – 2.72	1.43 ± 0.93
Lee Navigation	C	1.11 – 6.25	4.45 ± 1.62	0.99 – 5.60	2.24 ± 1.70	0.59 – 3.26	2.42 ± 0.89	0.03 – 2.57	1.40 ± 0.96	0.43 – 3.19	2.16 ± 0.88
	J	0.02 – 25.83	10.26 ± 8.29	1.95 – 11.50	6.25 ± 3.36	0.95 – 15.79	6.11 ± 4.54	0.02 – 9.98	3.79 ± 3.16	0.01 – 11.86	2.80 ± 4.34
	K	0.01 – 7.78	3.93 ± 2.43	1.11 – 6.88	2.54 ± 1.93	0.69 – 3.27	1.94 ± 0.88	0.01 – 2.84	1.59 ± 0.92	0.02 – 3.31	1.64 ± 1.20
Tributaries	B	1.17 – 3.88	2.79 ± 1.06	0.50 – 1.19	0.95 ± 0.22	0.57 – 2.09	1.51 ± 0.57	0.37 – 1.77	1.02 ± 0.51	0.38 – 2.05	1.33 ± 0.61
	D	1.34 – 6.41	3.75 ± 1.56	0.47 – 2.03	1.24 ± 0.51	0.95 – 4.04	2.46 ± 1.00	0.64 – 3.10	1.56 ± 0.84	0.69 – 3.15	1.83 ± 0.76
	E	1.94 – 12.11	5.52 ± 3.94	0.75 – 4.02	1.85 ± 1.23	1.44 – 7.98	3.80 ± 2.58	0.90 – 5.38	2.45 ± 1.79	1.10 – 5.67	2.66 ± 1.84
	F	1.21 – 12.85	3.57 ± 3.96	0.44 – 4.41	1.61 ± 1.69	0.59 – 8.34	2.23 ± 2.54	0.37 – 1.67	1.47 ± 1.67	0.42 – 6.18	1.67 ± 1.88

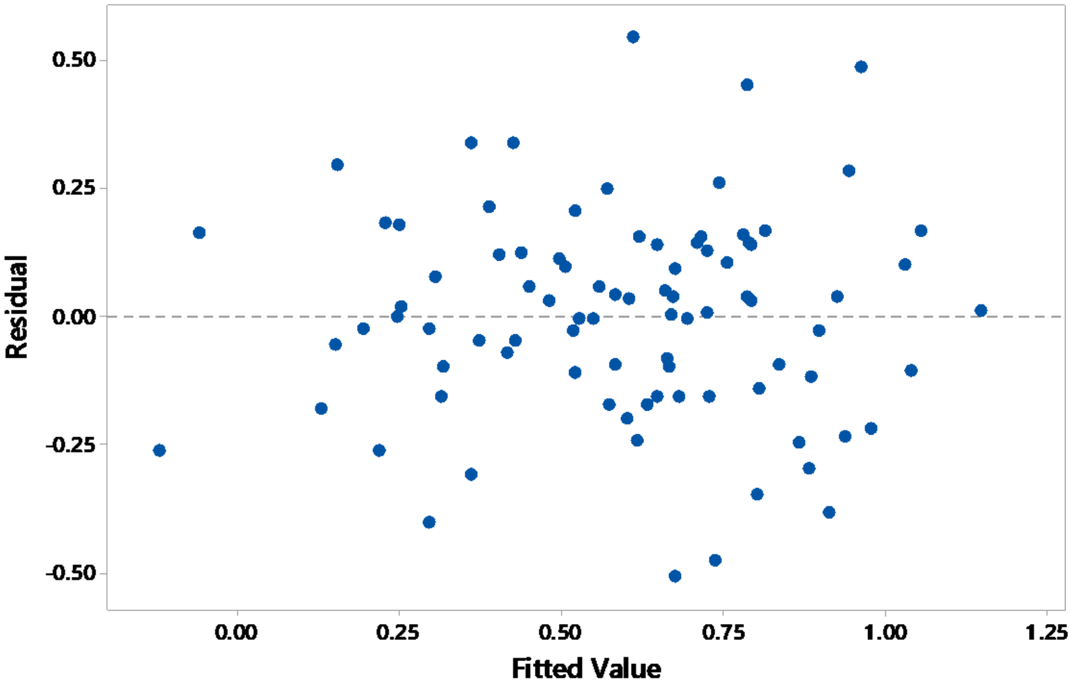
APPENDIX L1. Residuals vs Fits plot for Ph in river sediment.



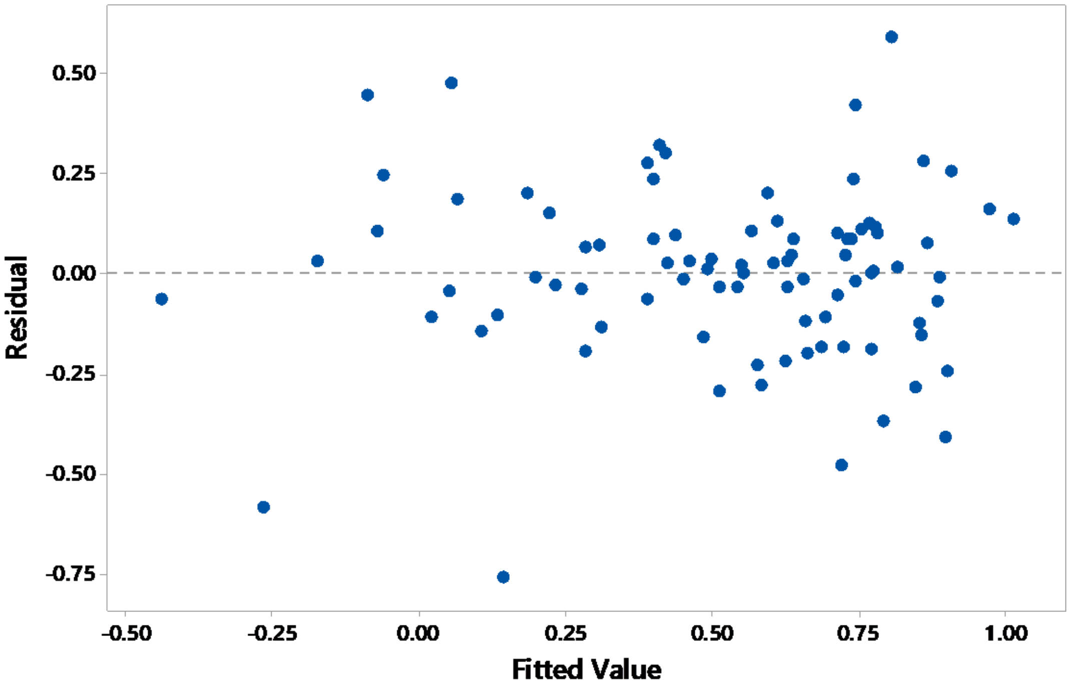
APPENDIX L2. Residuals vs Fits plot for A in river sediment.



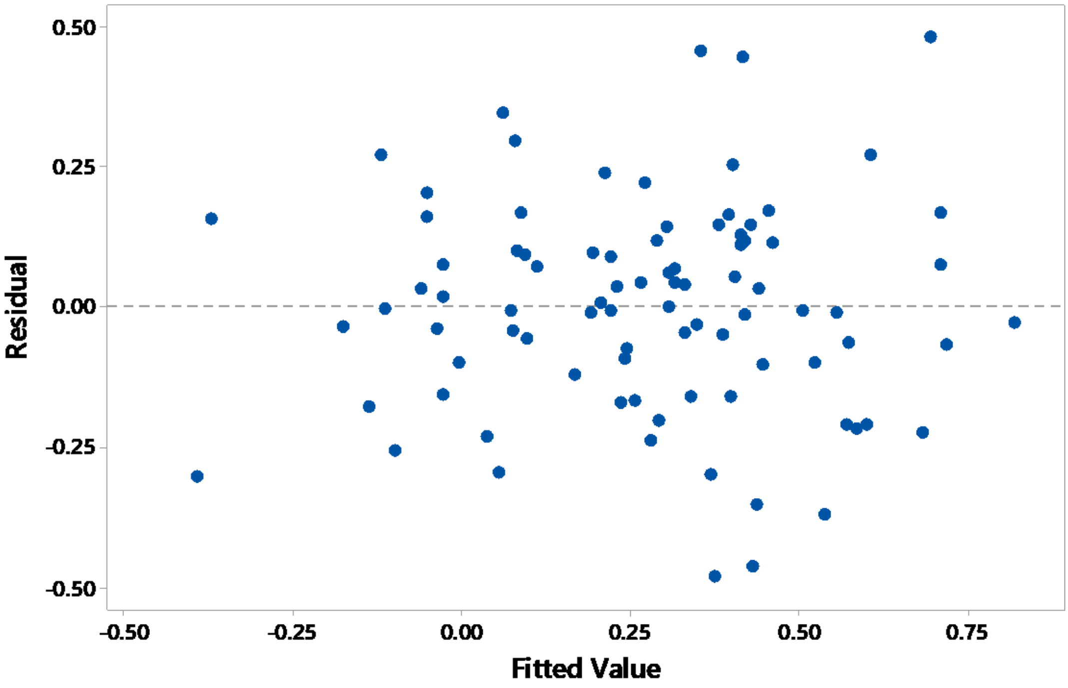
APPENDIX L3. Residuals vs Fits plot for Fl in river sediment.



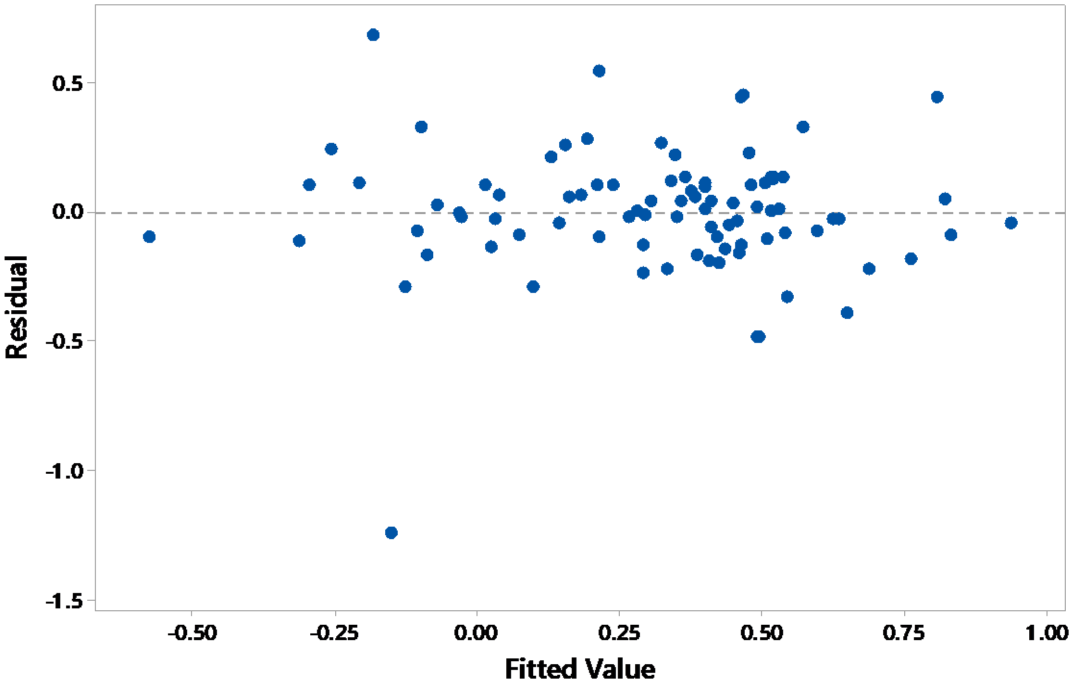
APPENDIX L4. Residuals vs Fits plot for Py in river sediment.



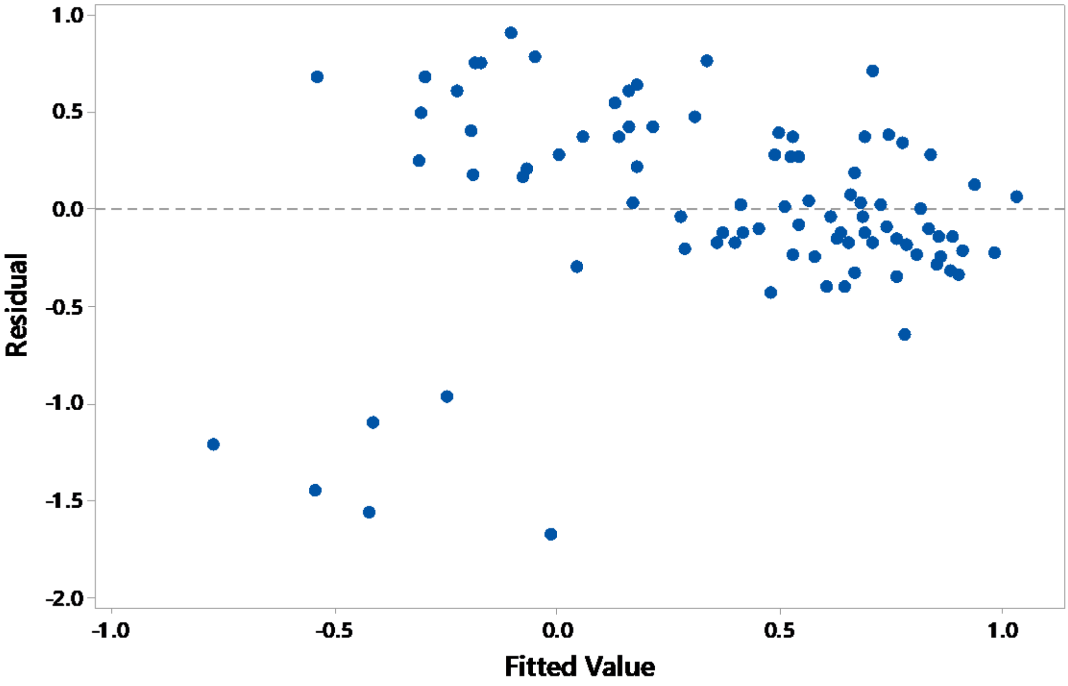
APPENDIX L5. Residuals vs Fits plot for Bz(a)A in river sediment.



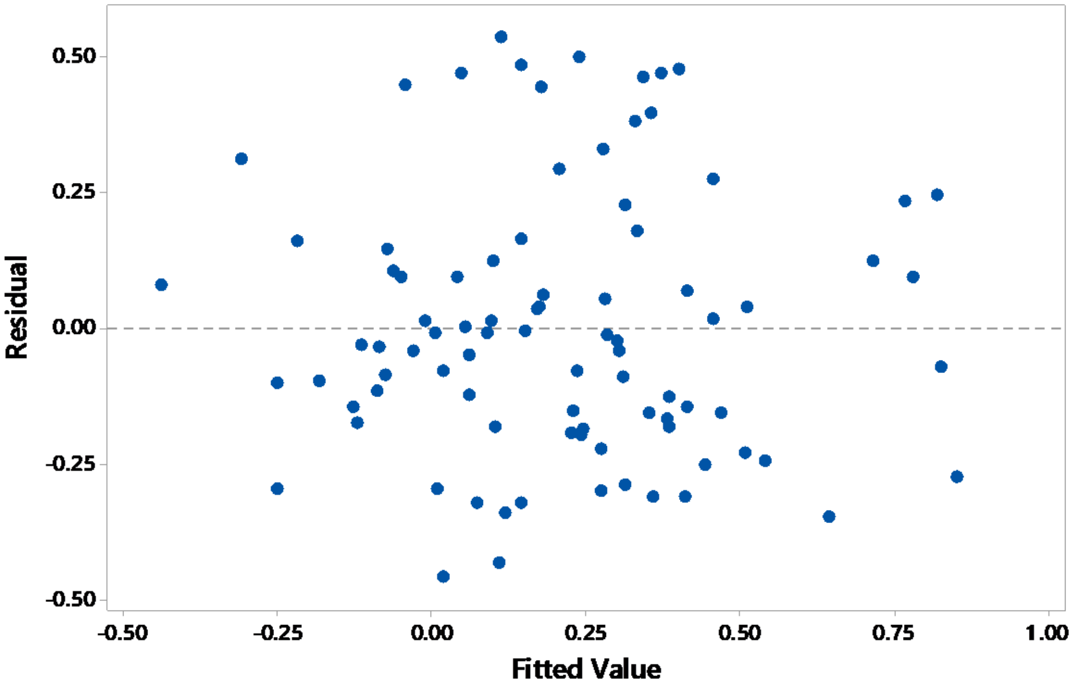
APPENDIX L6. Residuals vs Fits plot for C in river sediment.



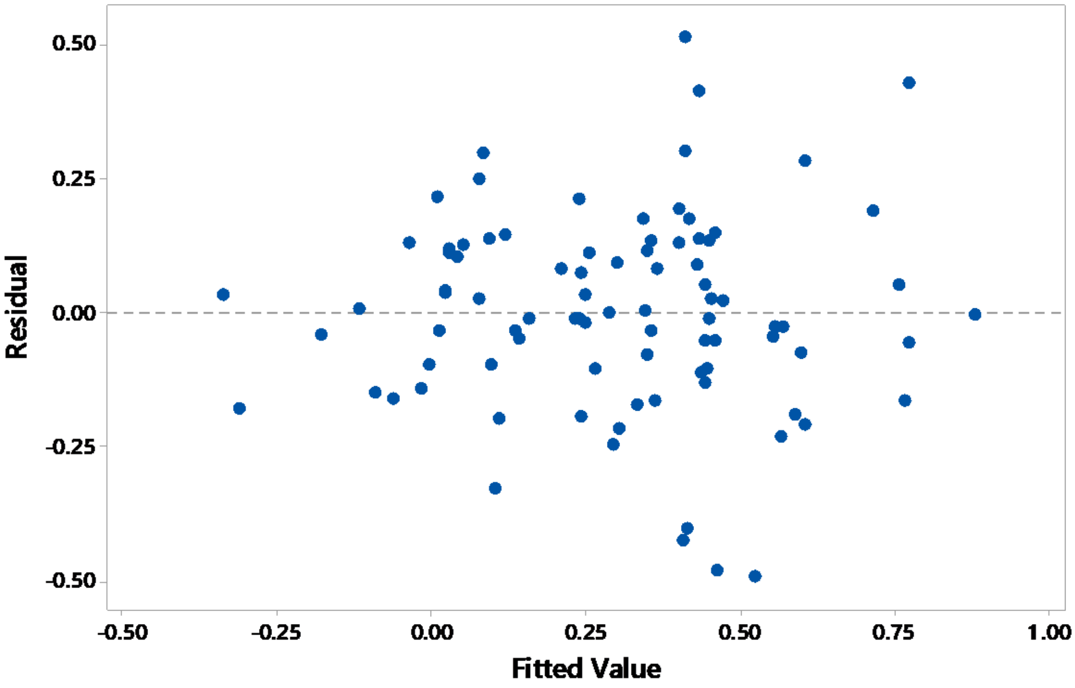
APPENDIX L7. Residuals vs Fits plot for Bz(b)Fl in river sediment.



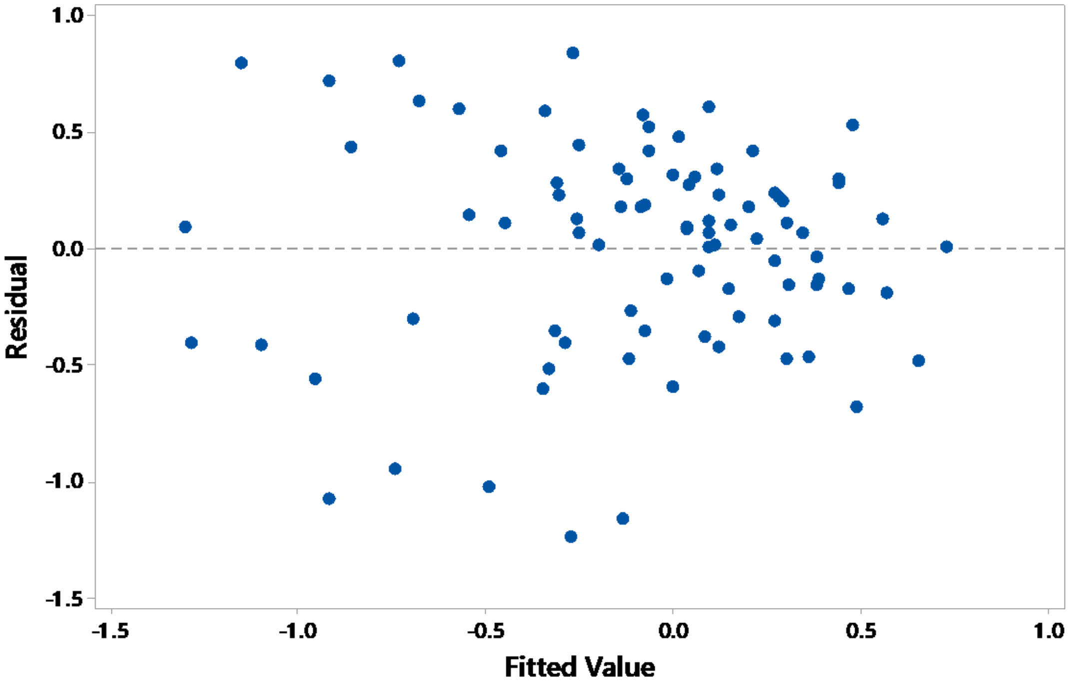
APPENDIX L8. Residuals vs Fits plot for Bz(k)Fl in river sediment.



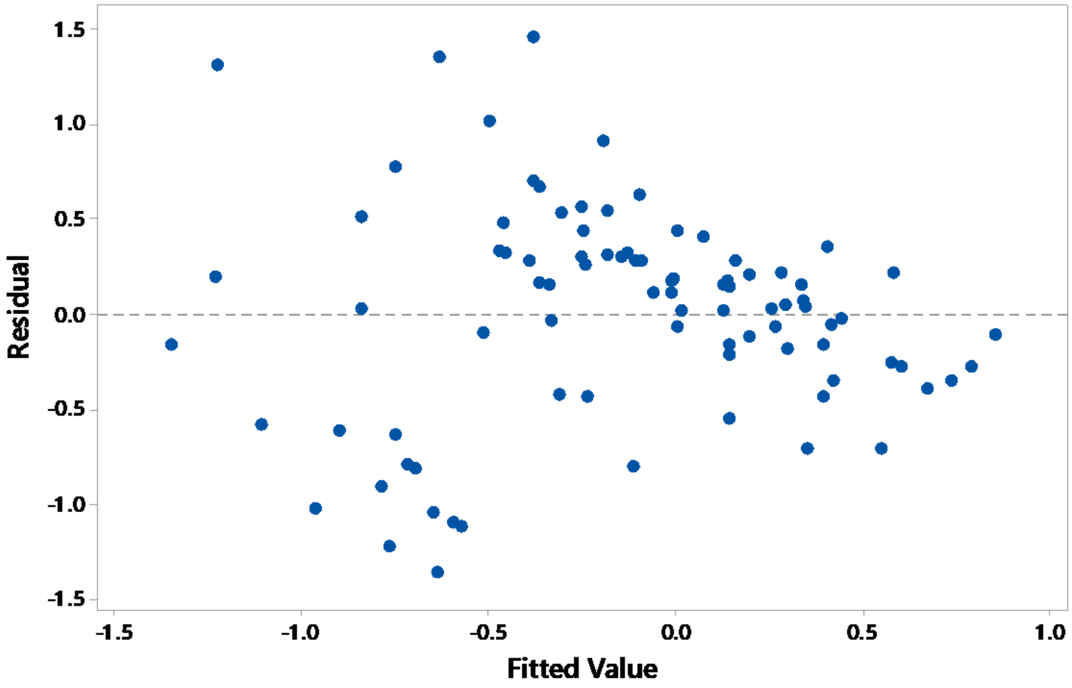
APPENDIX L9. Residuals vs Fits plot for Bz(a)Py in river sediment.



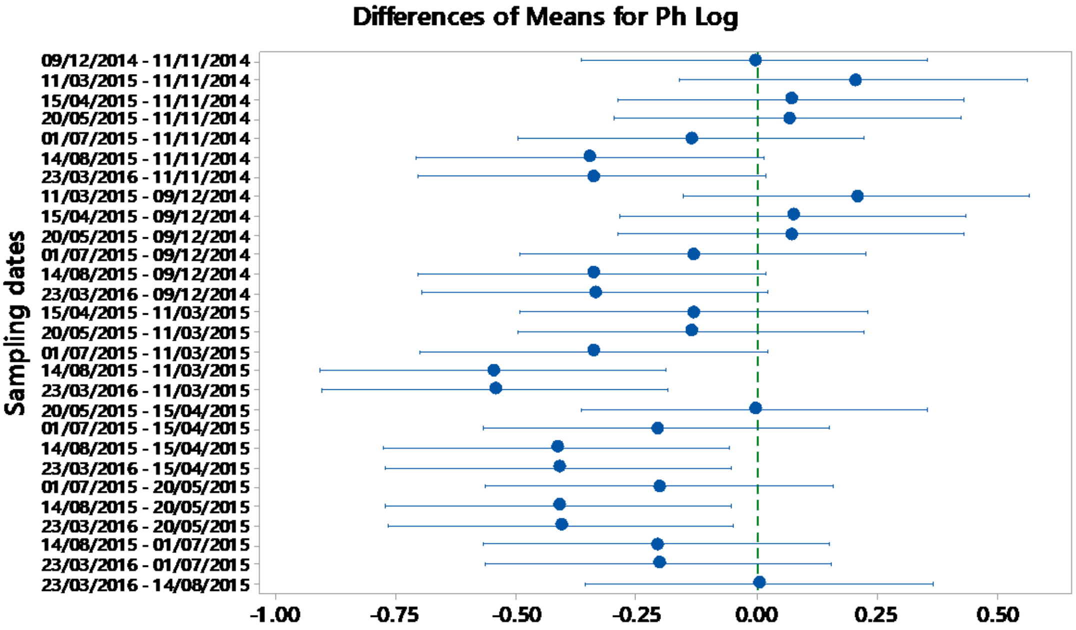
APPENDIX L10. Residuals vs Fits plot for DBz(a,h)A in river sediment.



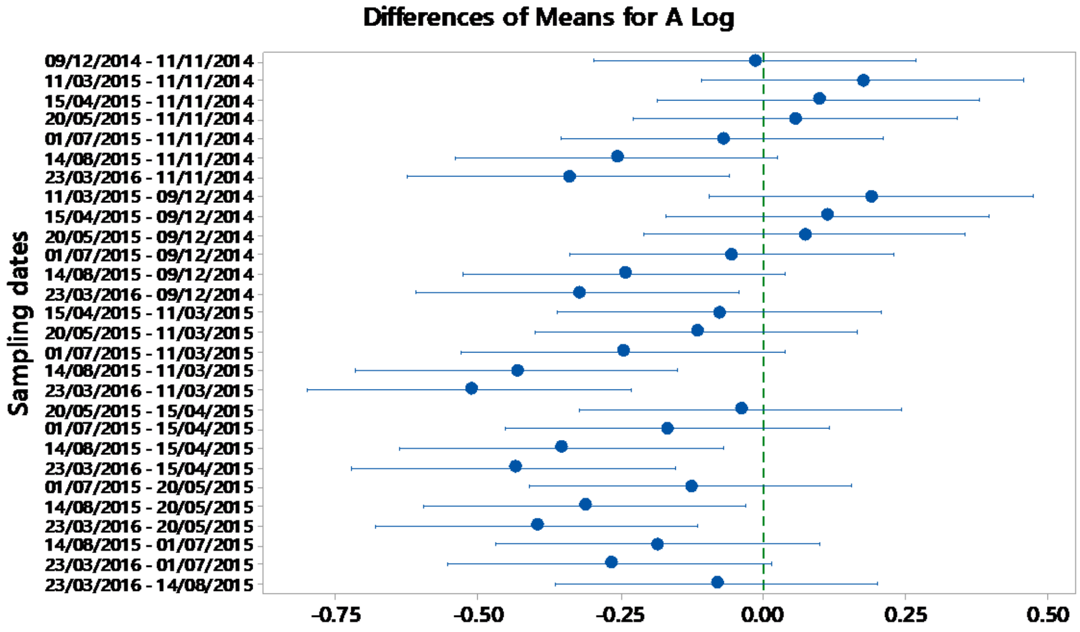
APPENDIX L11. Residuals vs Fits plot for Bz(g,h,i)Pe in river sediment.



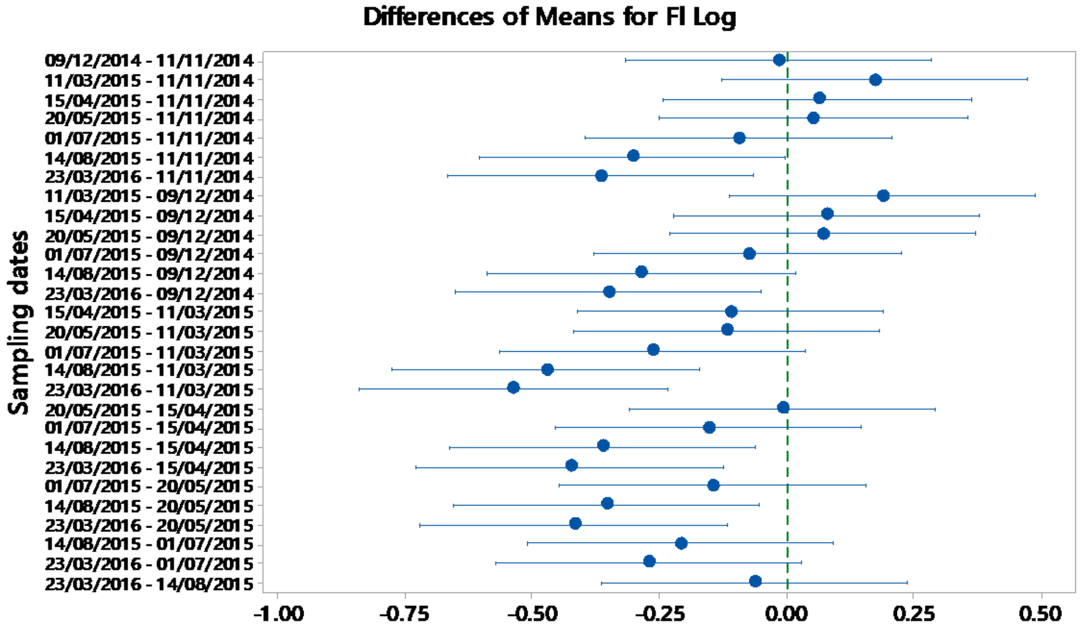
APPENDIX M1. Tukey's post-hoc test for difference of means of Ph between sampling dates in river sediment.



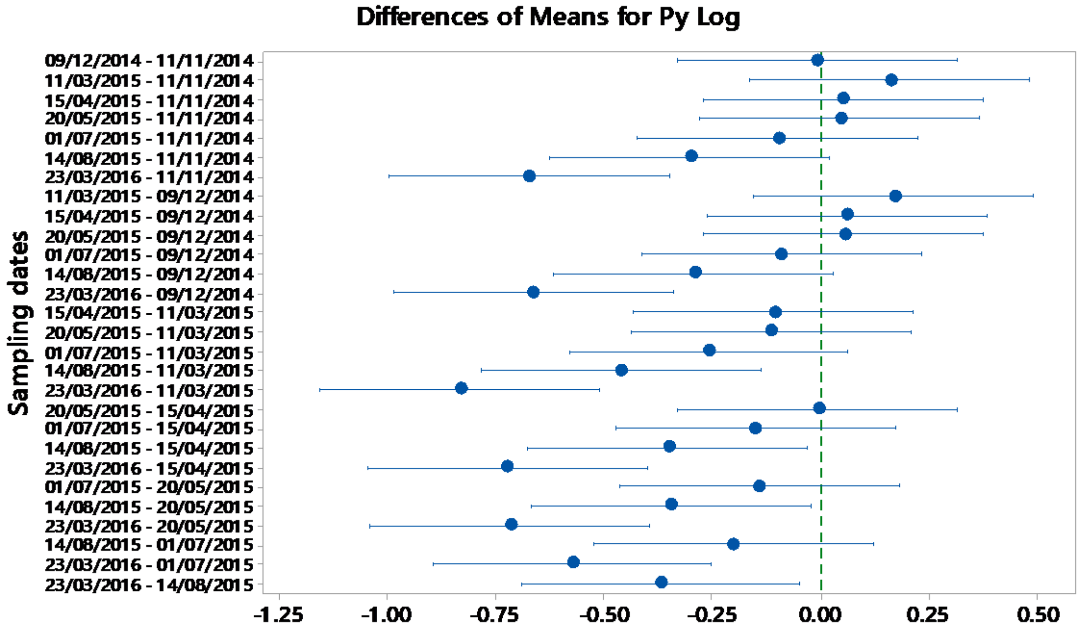
APPENDIX M2. Tukey’s post-hoc test for difference of means of A between sampling dates in river sediment.



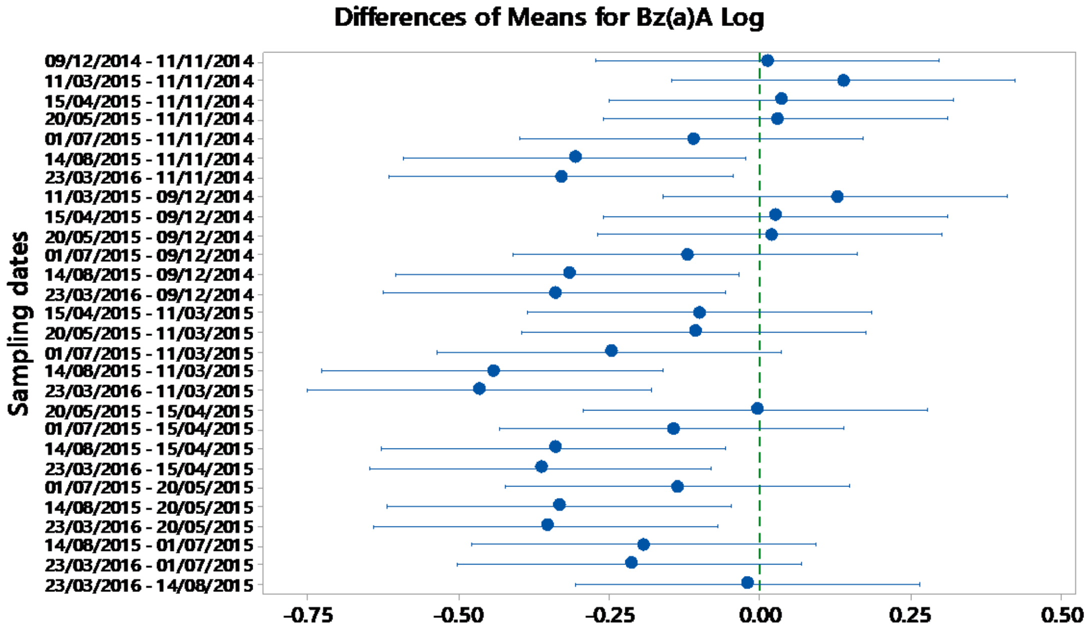
APPENDIX M3. Tukey’s post-hoc test for difference of means of Fl between sampling dates in river sediment.



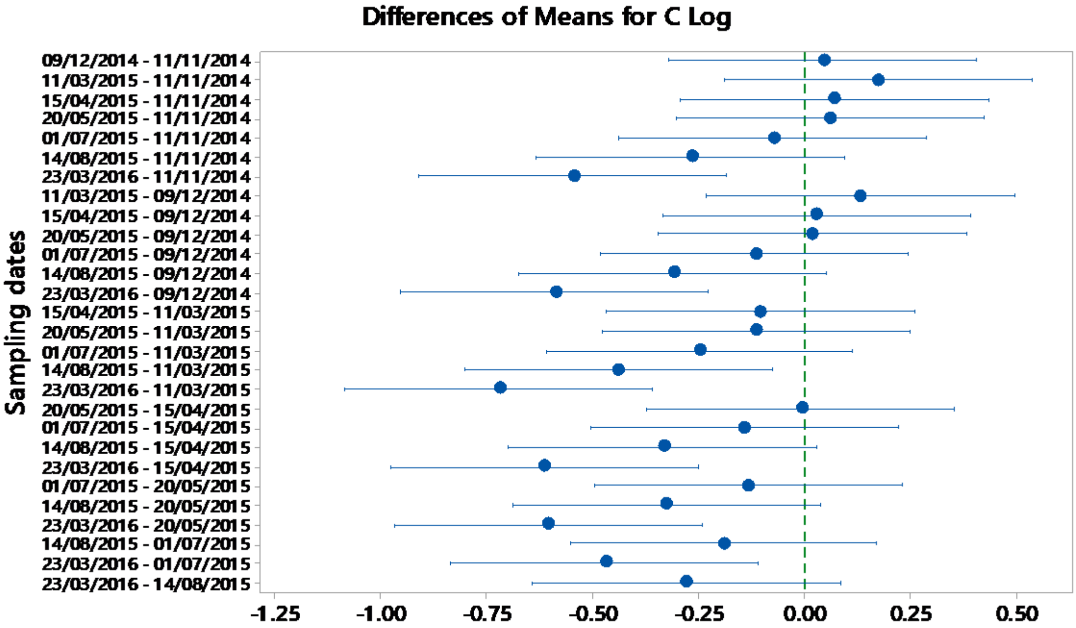
APPENDIX M4. Tukey's post-hoc test for difference of means of Py between sampling dates in river sediment.



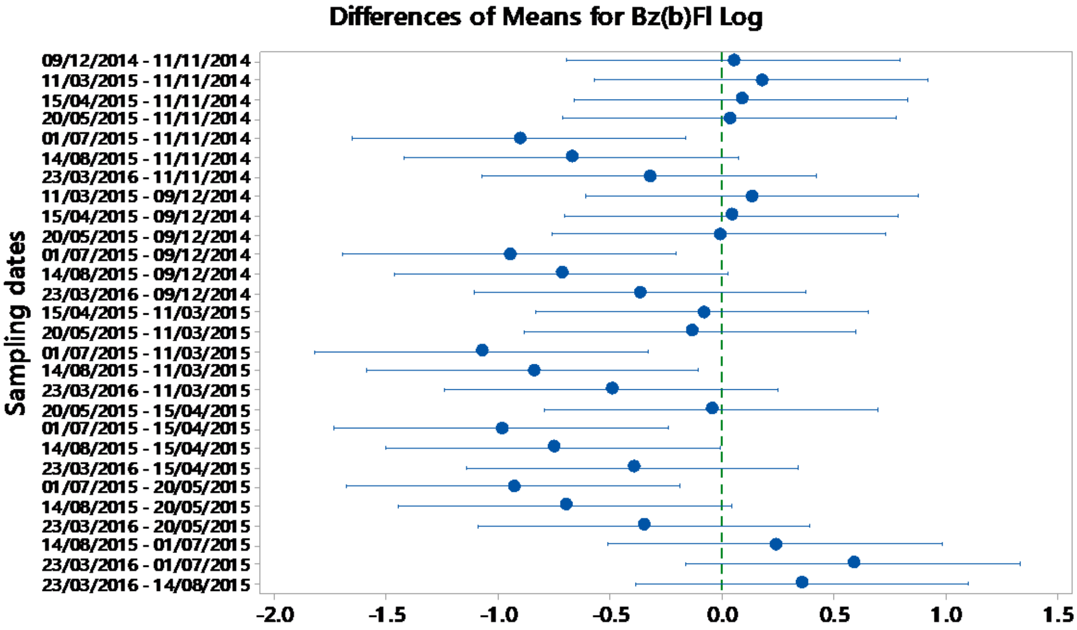
APPENDIX M5. Tukey's post-hoc test for difference of means of Bz(a)Abetween sampling dates in river sediment.



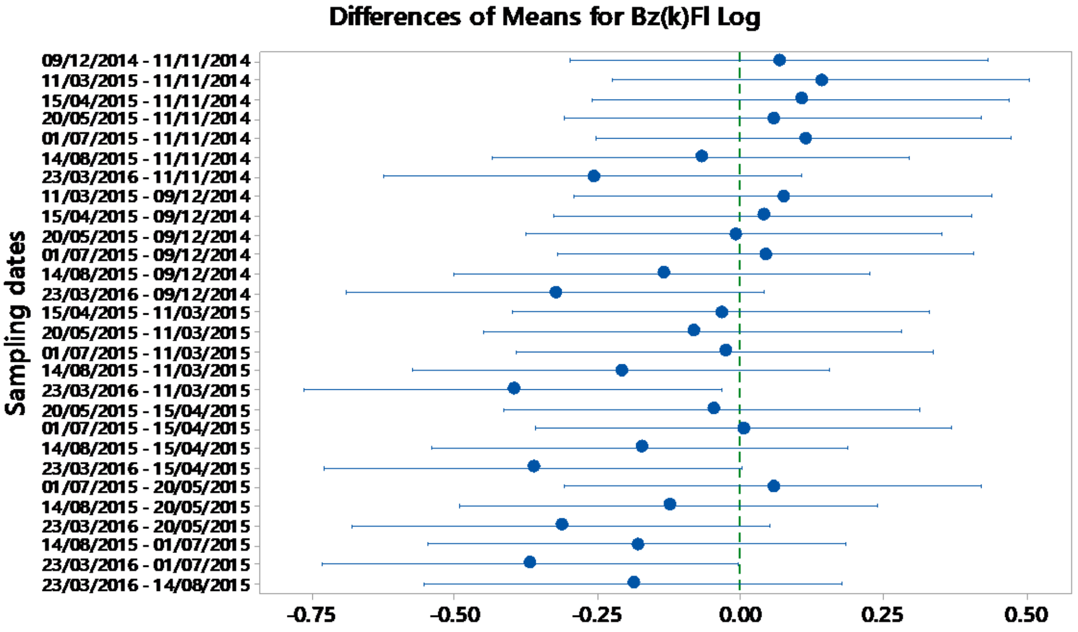
APPENDIX M6. Tukey's post-hoc test for difference of means of C between sampling dates in river sediment.



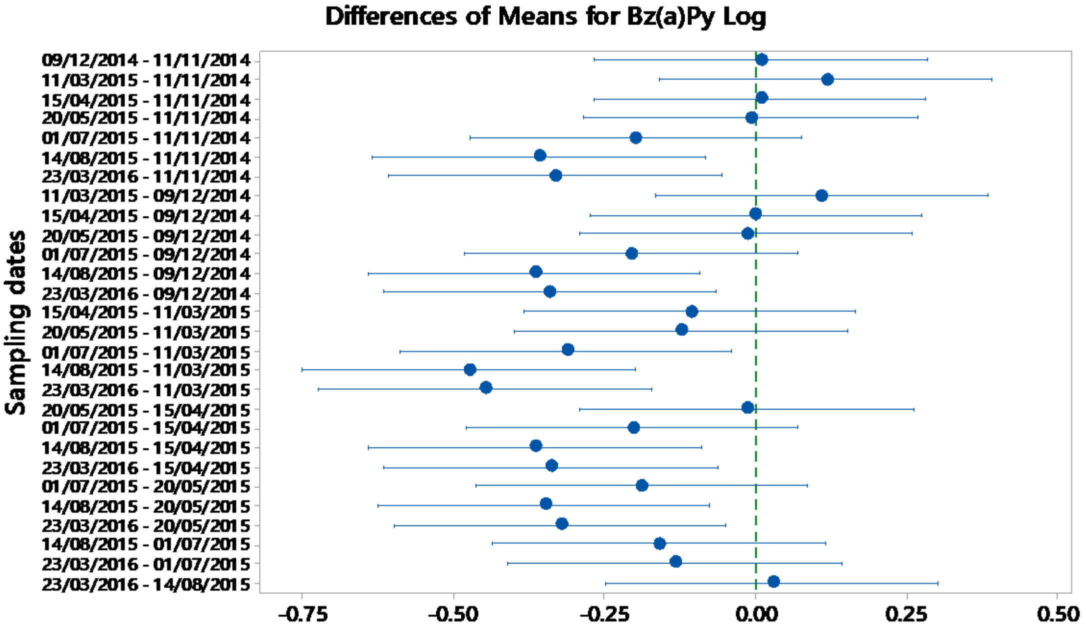
APPENDIX M7. Tukey's post-hoc test for difference of means of Bz(b)Fl between sampling dates in river sediment.



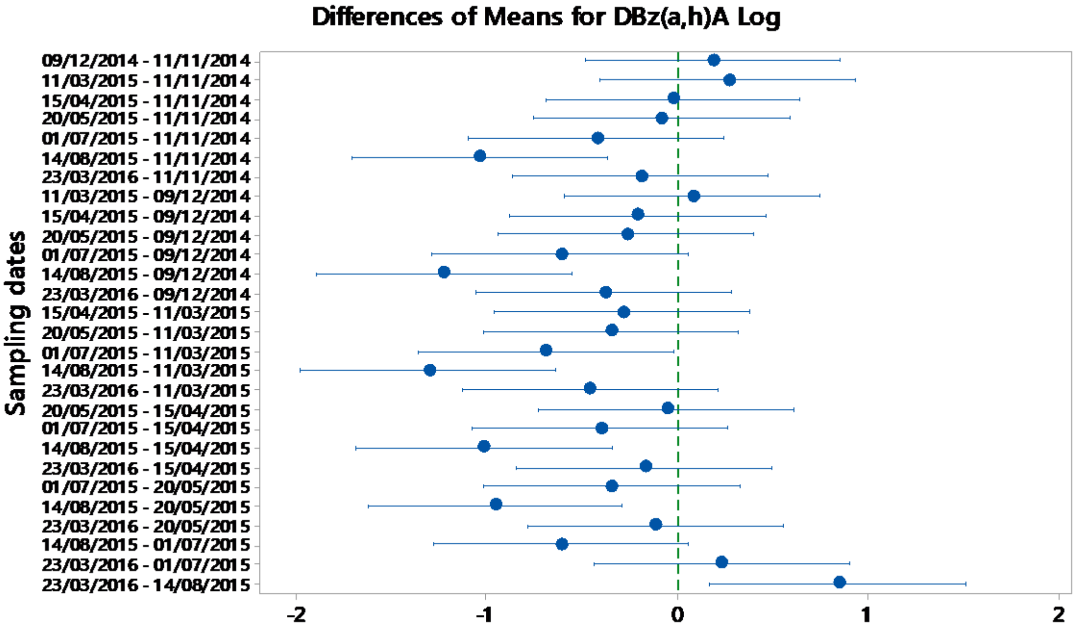
APPENDIX M8. Tukey's post-hoc test for difference of means of Bz(k)Fl between sampling dates in river sediment.



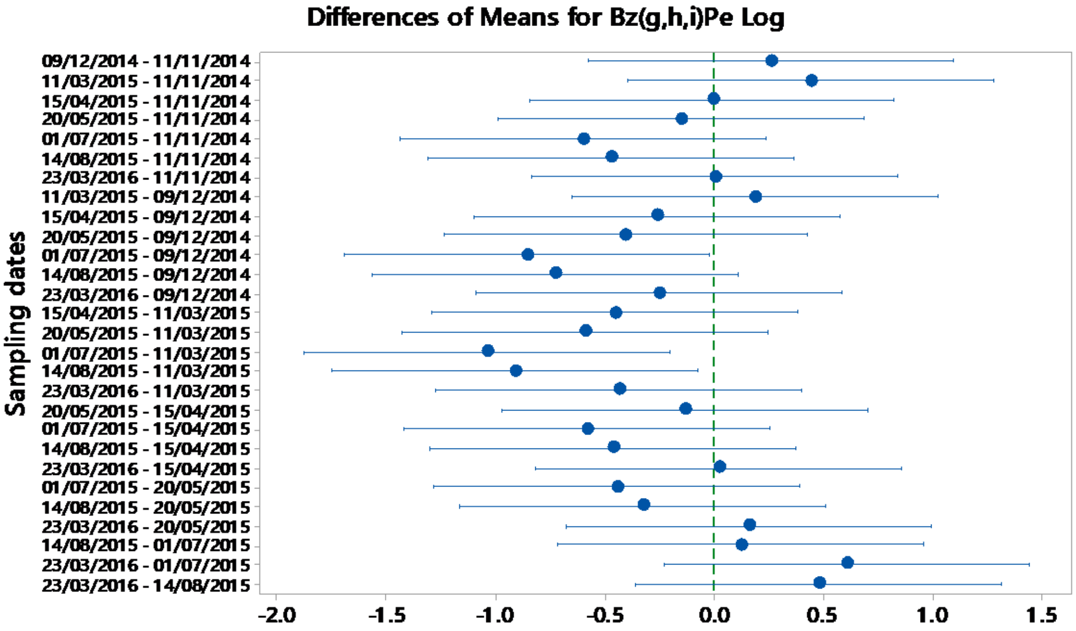
APPENDIX M9. Tukey's post-hoc test for difference of means of Bz(a)Py between sampling dates in river sediment.



APPENDIX M10. Tukey’s post-hoc test for difference of means of DBz(a,h)A between sampling dates in river sediment.



APPENDIX M11. Tukey’s post-hoc test for difference of means of Bz(g,h,i)Pe between sampling dates in river sediment.



APPENDIX N1. Overview of dissolved oxygen, pH and temperature in surface water by sampling site on day of sampling – prior to the laboratory batch test experiment.

Site	Dissolved Oxygen (mg/l)	Temperature (˚C)	pH
A	13.34	10.2	8.3
E	10.93	15.9	8.3
F	10.21	9.7	8.9
H	9.28	13.0	8.6
K	13.08	9.4	8.9
Range	9.28 - 13.34	9.40 - 15.90	8.30 - 8.90
Mean ± SD	11.37 ± 1.78	11.64 ± 2.78	8.60 ± 0.30

APPENDIX N2. Overview of dissolved oxygen, pH and temperature in surface water by sampling site at the start of the laboratory batch test experiment.

Site	Dissolved Oxygen (mg/l)	Temperature (˚C)	pH
A	4.79	17.6	8.3
E	3.90	18.2	8.1
F	3.70	19.3	8.8
H	4.35	17.7	8.4
K	4.75	19.5	8.7
Range	3.70 - 4.79	17.60 - 19.50	8.13 - 8.78
Mean ± SD	4.30 ± 0.49	18.46 ± 0.89	8.46 ± 0.28

APPENDIX N3. Overview of dissolved oxygen, pH and temperature in surface water by sampling site on the completion of laboratory batch test experiment.

Site	Dissolved Oxygen (mg/l)	Temperature (˚C)	pH
A	2.67	19.5	8.2
E	2.17	19.9	8.1
F	2.22	20.5	8.6
H	2.30	19.8	8.1
K	2.66	20.4	8.4
Range	2.17 - 2.67	19.45 - 20.45	8.07 - 8.59
Mean ± SD	2.40 ± 0.24	19.98 ± 0.43	8.27 ± 0.22

APPENDIX N4. Overview of TOC and DOC in surface water by sampling site prior and on the completion of laboratory batch test experiment.

Site	TOC before batch test (mg/l)	TOC during batch test (mg/l)	DOC before batch test (mg/l)	DOC during batch test (mg/l)
A	13.01 ± 0.08	18.37 ± 0.03	10.94 ± 0.05	15.07 ± 0.08
E	14.77 ± 0.12	21.78 ± 0.09	11.88 ± 0.12	18.59 ± 0.14
F	13.05 ± 0.06	18.11 ± 0.15	12.93 ± 0.07	14.95 ± 0.11
H	14.15 ± 0.12	19.01 ± 0.01	12.30 ± 0.06	16.03 ± 0.02
K	15.74 ± 0.10	24.01 ± 0.11	11.36 ± 0.11	20.24 ± 0.07
Range	13.01 – 15.74	18.11 – 24.01	10.94 – 12.93	14.95 – 20.24
Mean ±SD	14.14 ±1.17	20.25 ± 2.56	11.88 ± 0.78	16.98 ± 2.34

APPENDIX O1. Overview of road runoff calculations methodology for metals and PAHs predicted loads.

Particles emitted from road transport activities making significant contributions to ambient atmospheric particulate matter (PM), especially from exhaust emission and from different non-exhaust processes, such as brake wear, tyre wear and road surface wear, which given the current level of understanding, these sources of PM_{10} emissions are not easily quantified (Grigoratos and Martini, 2014; Ketzel *et al*., 2007). To estimate the overall pollutant loadings to the road surface discharging into the surface waters at the Lower Lee catchment, the emissions of selected pollutants originated from different processes were calculated as loads estimate (kg/year) as part of the substance flow analysis modelling for the study area. The method utilised was based on the approach developed by Middlesex University in collaboration with Thames21 (Thames21, 2019; Revitt *et al*., 2020).

The mathematical model was applied, integrating data on AADT, length of roads (identified from Digdat maps, 2018), and emission factors for engine, brake, tyre and road surface wear. The AADT data from TfL was obtained for the year of 2013 and used as multiplier to calculate the amount of pollutant deposited on road surface per vehicle type for each of the following emission categories: tyre wear, engine emissions, brake wear and road surface wear. This mass deposited data was combined with catchment rainfall data and a runoff coefficient to produce an annual average concentration which was used to calculate an annual average loading estimate (µg/year) and then converted into kg/year.

Appropriate unit conversion took place, when necessary, for example, as part of the methodology, available parameters had to be converted to a pollutant mass per vehicle-kilometre travelled. A summary of values used and calculations for emission applied for each parameter are presented below:

Calculation for exhaust emission:

Table O1.1 Pollutant emission factors (EF) for combustion of road transport fuels (after Pulles *et al*., 2012; Wenborn *et al*., 1999).

Substance	Fuel	EF (mg/kg/veh)
Cd	Petrol	0.00029
	Diesel	0.00005
Cu	Petrol	0.0040
	Diesel	0.0073
Hg	Petrol	0.0084
	Diesel	0.0023
Ni	Petrol	0.00094
	Diesel	0.00010
Pb	Petrol	0.0015
	Diesel	0.0003
Zn	Petrol	0.036
	Diesel	0.019
A	Petrol	0.00020
	Diesel	0.01435
Fl	Petrol	0.00340
	Diesel	0.02275
Bz(b)Fl	Petrol	0.00160
	Diesel	0.01195
Bz(a)Py	Petrol	0.00110
	Diesel	0.01335
Bz(ghi)Pe	Petrol	0.002600
	Diesel	0.044925

Table O1.2 Average fuel consumption data for different vehicle types under urban driving conditions (after the Department for Transport's Fuel Consumption ENV01 for the year 2013).

Vehicle type	Fuel consumption (l/km)
Passenger cars (petrol)	0.056
Passenger cars (diesel)	0.049
Light commercial vehicles (LDVs) (petrol)	0.128
Light commercial vehicles (LDVs) (diesel)	0.102
Heavy goods vehicles (HGVs) (rigid axle)	0.317
Heavy goods vehicles (HGVs) (articulated)	0.362
Motorcycles	0.0355
Taxis	0.049
Buses/Coaches	0.475

The calculation of estimated pollutant emissions per vehicle-kilometre travelled due to exhaust emissions was carried out using the following equation:

Daily engine emissions of pollutant per kilometre

= EF (mg/kg/veh) x FD (kg/l) x FC (l/km)

= Result in mg/vkm

Where EF is Emission Factor, FD is Fuel Density (0.77 kg/l for petrol and 0.834 kg/l for diesel) and FC is Fuel Consumption.

Calculation for brake wear emissions:

Table O1.3 Brake wear emission factors (total particulates) for different vehicle types (after Klein *et al*., 2017).

Vehicle type	(mg/vkm)
Passenger cars	14
LDVs	26
HGVs	55
Motorcycles	8
Taxis	14
Buses/Coaches	63.5

Table O1.4 Selected pollutant concentrations in brake linings and brake lining dusts (after Gadd and Kennedy, 2000; Rogge *et al*. 1993).

Substance	**Emission factor (µg/mg)**
Cd	0.0026
Cu	10
Hg	0.0003
Ni	0.73
Pb	1.29
Zn	7.5
A	0.0021
Fl	0.00069
Bz(b)Fl	0.00042
Bz(a)Py	0.00074
Bz(ghi)Pe	0.00034

The calculation of estimated pollutant emissions per vehicle-kilometre travelled due to brake wear was carried out using the following equation:

Pollutant emissions per kilometre (µg/vkm):

= EF (mg/vkm) x PC (µg/mg)

= Result in µg/vkm, so ÷ 1000 to convert to mg/vkm

Where EF is Emission Factor and PC is Pollutant Concentration in brake wear material

Calculation for tyre wear emissions:

Table O1.5 Tyre wear emission factors (total particulates) for different vehicle types (after Klein *et al*., 2017).

Vehicle type	**Emission factor (mg/vkm)**
Passenger cars	100
LDVs	159
HGVs	850
Motorcycles	60
Taxis	100
Buses/Coaches	332.50

Table O1.6 Selected pollutant concentrations in tyre and tyre wear debris (after Thorpe and Harrison, 2008; Boulter, 2006).

Substance	Pollutant concentration (μg/mg)
Cd	Motorbikes: 0.00065 Cars: 0.0013 LDVs: 0.0006 HGVs: 0.00042 Buses and coaches: 0.00042
Cu	Motorbikes: 0.0014 Cars: 0.0028 LDVs: 0.0020 HGVs: 0.0018 Buses and coaches: 0.0018
Hg	Motorbikes: 0.00001 Cars: 0.00002 LGV: 0.00001 HGV: 0.00001 Buses and coaches: 0.00001
Ni	Motorbikes: 0.001 Cars: 0.002 LGV: 0.001 HGV: 0.001 Buses and coaches: 0.001
Pb	Motorbikes: 0.001675 Cars: 0.00335 LGV: 0.00115 HGV: 0.00645 Buses and coaches: 0.00645
Zn	Motorbikes: 2.75 Cars: 5.50 LDVs: 2.40 HGVs: 11.00 Buses and coaches: 11.00
A	Motorbikes: 0.00054 Cars: 0.00107 LGV: 0.00075 HGV: 0.00085 Buses and Coaches: 0.00085
Fl	Motorbikes: 0.00768 Cars: 0.01535 LGV: 0.008 HGV: 0.01 Buses and Coaches: 0.01
Bz(b)Fl	Motorbikes: 0.003975 Cars: 0.00795 LGV: 0.0064 HGV: 0.0064

	Buses and Coaches: 0.0064
Bz(a)Py	Motorbikes: 0.00329 Cars: 0.00658 LGV: 0.0050 HGV: 0.0045 Buses and Coaches: 0.0045
Bz(ghi)Pe	Motorbikes: 0.0074 Cars: 0.0148 LGV: 0.010 HGV: 0.00865 Buses and Coaches: 0.00865

The calculation of estimated pollutant emissions per vehicle-kilometre travelled due to tyre wear was carried out using the following equation:

Pollutant emissions per kilometre

= EM (mg/vkm) x PC (µg/mg)

= Result in µg/vkm, so ÷ 1000 to convert to mg/vkm

Where EF is Emission Factor and PC is Pollutant Concentration in tyre wear material

Calculation for road surface wear emissions:

Table O1.7 Road surface wear emission factors (total particulates) for different vehicle types (after Klein *et al*., 2017).

Vehicle type	Emission factor (mg/vkm)
Passenger cars	165.00
LDVs	840.00
HGVs	840.00
Motorcycles	74.00
Taxis	165.00
Buses/Coaches	840.00

Table O1.8 Selected pollutant concentrations in asphalt road surfacing (after Lindgren, 1996).

Substance	Pollutant concentration (µg/mg)
Cd	0.00013
Cu	0.0446
Hg	0.00002
Ni	0.0616
Pb	0.010855
Zn	0.0888
A	0.00676
Fl	0.00635
Bz(b)Fl	0.01309
Bz(a)Py	0.00819
Bz(ghi)Pe	0.01402

The calculation of estimated pollutant emissions per vehicle-kilometre travelled due to road surface wear was carried out using the following equation:

Pollutant emissions per kilometre

= EM (mg/vkm) x PC (µg/mg)

= Result in µg/vkm, so ÷ 1000 to convert to mg/vkm

Where EF is Emission Factor and PC is Pollutant Concentration in road surface wear material.

Other values/data used in the calculations are as follows:

- road measurements (roads within 1 km catchment area of each sampling site and discharging directly into surface water) and AADT values (for 2013, derived from TfL statistics).
- Year (365 days)
- Annual rainfall
- % of pollutant deposited and removed in runoff (10 % and 35 % for engine, 50 % and 35 % for brake, 85 % and 35 % for tyre, 95 % and 35 % for road surface wear respectively).

- Runoff dimensionless coefficient - defining the proportion of rainfall landing on a surface that is converted into runoff. The range of runoff coefficients quoted for asphalt surfaced roads is 0.75 – 0.95 with values towards the higher end of this range for good quality surfaces (Klein *et al.*, 2017). A value of 0.90 has been used for this research.

APPENDIX P1. Predicted loads (kg/year) of selected metals by activities at site A, Lower Lee catchment.

Activity	Cd	Cu	Hg	Ni	Pb	Zn
Waste non-hazardous	1.000000	32.200000	0.120000	12.200000	10.000000	130.000000
Waste treatment	1.000000	20.000000	0.100000	20.000000	31.100000	100.000000
Production of electricity (EfW power plants)	1.197963	86.729241	0.178000	18.367963	12.600000	150.052961
Manufacture of basic metals and metal products	1.006630	59.012510	0.128000	12.176440	12.731920	143.754000
Manufacture of non-metallic mineral products	7.180000	90.560000	0.340000	82.260000	84.344000	209.860000
Manufacture of rubber and plastics products	1.440000	38.380800	0.072000	33.712800	14.400000	144.000000
Manufacture of cement	0.527500	13.350000	0.057975	15.205500	10.484000	56.470250
Food and Drink	0.323340	3.203798	0.038681	3.321564	3.234649	13.761809
Manufacture of textiles	0.020000	3.800000	0.057400	4.200000	4.000000	20.000000
Road runoff	0.000869	0.544908	0.000190	0.106378	0.079987	7.507591

APPENDIX P2. Predicted loads (kg/year) of selected metals by activities at site B, Lower Lee catchment.

Activity	Cd	Cu	Hg	Ni	Pb	Zn
Waste non-hazardous	0.500000	16.100000	0.060000	6.100000	5.000000	65.000000
Waste treatment	1.000000	20.000000	0.100000	20.000000	31.100000	100.000000
Manufacture of rubber and plastics products	0.240000	6.396800	0.012000	5.618800	2.400000	24.000000
Food and Drink	0.323340	3.203798	0.038681	3.321564	3.234649	13.761809
Road runoff	0.000093	0.062566	0.000023	0.011788	0.008986	0.577299

APPENDIX P3. Predicted loads (kg/year) of selected metals by activities at site C, Lower Lee catchment.

Activity	Cd	Cu	Hg	Ni	Pb	Zn
Waste non-hazardous	0.250000	8.050000	0.030000	3.050000	2.500000	32.500000
Paper/wood production	0.629231	10.946154	0.107231	12.810154	7.692308	45.718538
Manufacture of rubber and plastics products	0.240000	6.396800	0.012000	5.618800	2.400000	24.000000
Manufacture of chemicals and chemical products	4.042526	54.678316	0.601811	56.302316	21.035789	271.600842
Food and Drink	0.323340	3.203798	0.038681	3.321564	3.234649	13.761809
Manufacture of textiles	0.020000	3.800000	0.057400	4.200000	4.000000	20.000000
Road runoff	0.000269	0.160808	0.000060	0.031258	0.023371	1.826743

APPENDIX P4. Predicted loads (kg/year) of selected metals by activities at site D, Lower Lee catchment.

Activity	Cd	Cu	Hg	Ni	Pb	Zn
Wastewater	12.400000	1460.000000	2.820000	573.000000	117.000000	4550.000000
Waste non-hazardous	2.000000	64.400000	0.240000	24.400000	20.000000	260.000000
Waste treatment	0.500000	10.000000	0.050000	10.000000	15.550000	50.000000
Paper/wood production	0.629231	10.946154	0.107231	12.810154	7.692308	45.718538
Production of electricity (EfW power plants)	3.593889	260.187722	0.534000	55.103889	37.800000	450.158883
Manufacture of basic metals and metal products	1.006630	59.012510	0.128000	12.176440	12.731920	143.754000
Manufacture of rubber and plastic products	0.960000	25.587200	0.048000	22.475200	9.600000	96.000000
Manufacture of chemicals and chemical products	1.010632	13.669579	0.150453	14.075579	5.258947	67.900211
Food and Drink	0.970021	9.611394	0.116043	9.964691	9.703947	41.285426
Manufacture of textiles	0.040000	7.600000	0.114800	8.400000	8.000000	40.000000
Road runoff	0.001289	0.792414	0.000282	0.153123	0.115526	9.770000

APPENDIX P5. Predicted loads (kg/year) of selected metals by activities at site E, Lower Lee catchment.

Activity	Cd	Cu	Hg	Ni	Pb	Zn
Waste non-hazardous	2.250000	72.450000	0.270000	27.450000	22.500000	292.500000
Paper/wood production	2.516923	43.784615	0.428923	51.240615	30.769231	182.874154
Refineries	9.600000	93.265000	0.016667	91.300000	81.050000	1281.733333
Manufacture of basic metals and metal products	1.006630	59.012510	0.128000	12.176440	12.731920	143.754000
Manufacture of rubber and plastic products	1.200000	31.984000	0.060000	28.094000	12.000000	120.000000
Food and Drink	1.940043	19.222787	0.232085	19.929383	19.407894	82.570851
Manufacture of textiles	0.080000	15.200000	0.229600	16.800000	16.000000	80.000000
Road runoff	0.001964	1.208033	0.000439	0.226635	0.173798	11.864485

APPENDIX P6. Predicted loads (kg/year) of selected metals by activities at site F, Lower Lee catchment.

Activity	Cd	Cu	Hg	Ni	Pb	Zn
Production of electricity (EfW power plants)	1.197963	86.729241	0.178000	18.367963	12.600000	150.052961
Manufacture of basic metals and metal products	2.013260	118.025020	0.256000	24.352880	25.463840	287.508000
Manufacture of rubber and plastic products	0.480000	12.793600	0.024000	11.237600	4.800000	48.000000
Food and Drink	0.323340	3.203798	0.038681	3.321564	3.234649	13.761809
Manufacture of textiles	0.080000	15.200000	0.229600	16.800000	16.000000	80.000000
Road runoff	0.002073	1.271402	0.000464	0.239125	0.182988	12.524803

APPENDIX P7. Predicted loads (kg/year) of selected metals by activities at site G, Lower Lee catchment.

Activity	Cd	Cu	Hg	Ni	Pb	Zn
Paper/wood production	0.629231	10.946154	0.107231	12.810154	7.692308	45.718538
Manufacture of basic metals and metal products	1.006630	59.012510	0.128000	12.176440	12.731920	143.754000
Food and Drink	0.323340	3.203798	0.038681	3.321564	3.234649	13.761809
Road runoff	0.004022	2.552533	0.000927	0.478244	0.366706	24.219692

APPENDIX P8. Predicted loads (kg/year) of selected metals by activities at site H, Lower Lee catchment.

Activity	Cd	Cu	Hg	Ni	Pb	Zn
Waste non-hazardous	0.750000	24.150000	0.090000	9.150000	7.500000	97.500000
Paper/wood production	1.258462	21.892308	0.214462	25.620308	15.384615	91.437077
Manufacture of rubber and plastic products	0.960000	25.587200	0.048000	22.475200	9.600000	96.000000
Food and Drink	2.586723	25.630383	0.309447	26.572511	25.877191	110.094468
Manufacture of textiles	0.060000	11.400000	0.172200	12.600000	12.000000	60.000000
Road runoff	0.002338	1.538652	0.000554	0.287552	0.220854	14.350636

APPENDIX P9. Predicted loads (kg/year) of selected metals by activities at site I, Lower Lee catchment.

Activity	Cd	Cu	Hg	Ni	Pb	Zn
Waste non-hazardous	0.500000	16.100000	0.060000	6.100000	5.000000	65.000000
Road runoff	0.002274	1.410079	0.000520	0.264126	0.202409	13.103844

APPENDIX P10. Predicted loads (kg/year) of selected metals by activities at site J, Lower Lee catchment.

Activity	Cd	Cu	Hg	Ni	Pb	Zn
Waste non-hazardous	0.750000	24.150000	0.090000	9.150000	7.500000	97.500000
Manufacture of chemicals and chemical products	1.010632	13.669579	0.150453	14.075579	5.258947	67.900211
Manufacture of textiles	0.020000	3.800000	0.057400	4.200000	4.000000	20.000000
Road runoff	0.001713	1.105375	0.000395	0.201615	0.157596	9.209402

APPENDIX P11. Predicted loads (kg/year) of selected metals by activities at site K, Lower Lee catchment.

Activity	Cd	Cu	Hg	Ni	Pb	Zn
Waste non-hazardous	1.250000	40.250000	0.150000	15.250000	12.500000	162.500000
Paper/wood production	1.258462	21.892308	0.214462	25.620308	15.384615	91.437077
Production of electricity (EfW power plants)	4.791852	346.916963	0.712000	73.471852	50.400000	600.211844
Manufacture of basic metals and metal products	2.013260	118.025020	0.256000	24.352880	25.463840	287.508000
Manufacture of rubber and plastic products	1.440000	38.380800	0.072000	33.712800	14.400000	144.000000
Manufacture of chemicals and chemical products	1.010632	13.669579	0.150453	14.075579	5.258947	67.900211
Manufacture of cement	0.527500	13.350000	0.057975	15.205500	10.484000	56.470250
Food and Drink	0.646681	6.407596	0.077362	6.643128	6.469298	27.523617
Manufacture of textiles	0.020000	3.800000	0.057400	4.200000	4.000000	20.000000
Road runoff	0.005617	3.530403	0.001286	0.650932	0.504464	30.341987

APPENDIX Q1. Predicted loads (kg/year) of selected PAHs by activities at site A, Lower Lee catchment.

Activity	A	Fl	Bz(b)Fl	Bz(a)Py	Bz(g,h,i)Pe
Waste non-hazardous	0.400000	0.400000	4.000000	4.000000	0.400000
Manufacture of basic metals and metal products	0.860000	12.030000	18.500000	10.465000	5.340000
Road runoff	0.008346	0.017456	0.020867	0.014029	0.010365

APPENDIX Q2. Predicted loads (kg/year) of selected PAHs by activities at site B, Lower Lee catchment.

Activity	A	Fl	Bz(b)Fl	Bz(a)Py	Bz(g,h,i)Pe
Waste non-hazardous	0.200000	0.200000	2.000000	2.000000	0.200000
Road runoff	0.000889	0.001737	0.002145	0.001443	0.000985

APPENDIX Q3. Predicted loads (kg/year) of selected PAHs by activities at site C, Lower Lee catchment.

Activity	A	Fl	Bz(b)Fl	Bz(a)Py	Bz(g,h,i)Pe
Waste non-hazardous	0.100000	0.100000	1.000000	1.000000	0.100000
Manufacture of chemicals and chemical products	2.520000	6.200000	72.800000	57.600000	32.880000
Road runoff	0.002404	0.004993	0.005971	0.004022	0.002897

APPENDIX Q4. Predicted loads (kg/year) of selected PAHs by activities at site D, Lower Lee catchment.

Activity	A	Fl	Bz(b)Fl	Bz(a)Py	Bz(g,h,i)Pe
Wastewater	4.110000	0.850000	2.300000	3.750000	1.330000
Waste non-hazardous	0.800000	0.800000	8.000000	8.000000	0.800000
Manufacture of basic metals and metal products	0.860000	12.030000	18.500000	10.465000	5.340000
Manufacture of chemicals and chemical products	0.630000	1.550000	18.200000	14.400000	8.220000
Road runoff	0.011832	0.024722	0.029555	0.019907	0.014581

APPENDIX Q5. Predicted loads (kg/year) of selected PAHs by activities at site E, Lower Lee catchment.

Activity	A	Fl	Bz(b)Fl	Bz(a)Py	Bz(g,h,i)Pe
Waste non-hazardous	0.900000	0.900000	9.000000	9.000000	0.900000
Refineries	0.942500	0.555000	1.000000	1.000000	0.205000
Manufacture of basic metals and metal products	0.860000	12.030000	18.500000	10.465000	5.340000
Road runoff	0.017051	0.035292	0.042342	0.028646	0.020860

APPENDIX Q6. Predicted loads (kg/year) of selected PAHs by activities at site F, Lower Lee catchment.

Activity	A	Fl	Bz(b)Fl	Bz(a)Py	Bz(g,h,i)Pe
Manufacture of basic metals and metal products	1.720000	24.060000	37.000000	20.930000	10.680000
Road runoff	0.018010	0.037259	0.044701	0.030233	0.021970

APPENDIX Q7. Predicted loads (kg/year) of selected PAHs by activities at site G, Lower Lee catchment.

Activity	A	Fl	Bz(b)Fl	Bz(a)Py	Bz(g,h,i)Pe
Manufacture of basic metals and metal products	0.860000	12.030000	18.500000	10.465000	5.340000
Road runoff	0.035938	0.072937	0.088376	0.059694	0.042580

APPENDIX Q8. Predicted loads (kg/year) of selected PAHs by activities at site H, Lower Lee catchment.

Activity	A	Fl	Bz(b)Fl	Bz(a)Py	Bz(g,h,i)Pe
Waste non-hazardous	0.300000	0.300000	3.000000	3.000000	0.300000
Road runoff	0.021594	0.043032	0.052659	0.035510	0.024876

APPENDIX Q9. Predicted loads (kg/year) of selected PAHs by activities at site I, Lower Lee catchment.

Activity	A	Fl	Bz(b)Fl	Bz(a)Py	Bz(g,h,i)Pe
Waste non-hazardous	0.200000	0.200000	2.000000	2.000000	0.200000
Road runoff	0.019793	0.040535	0.048865	0.033046	0.023728

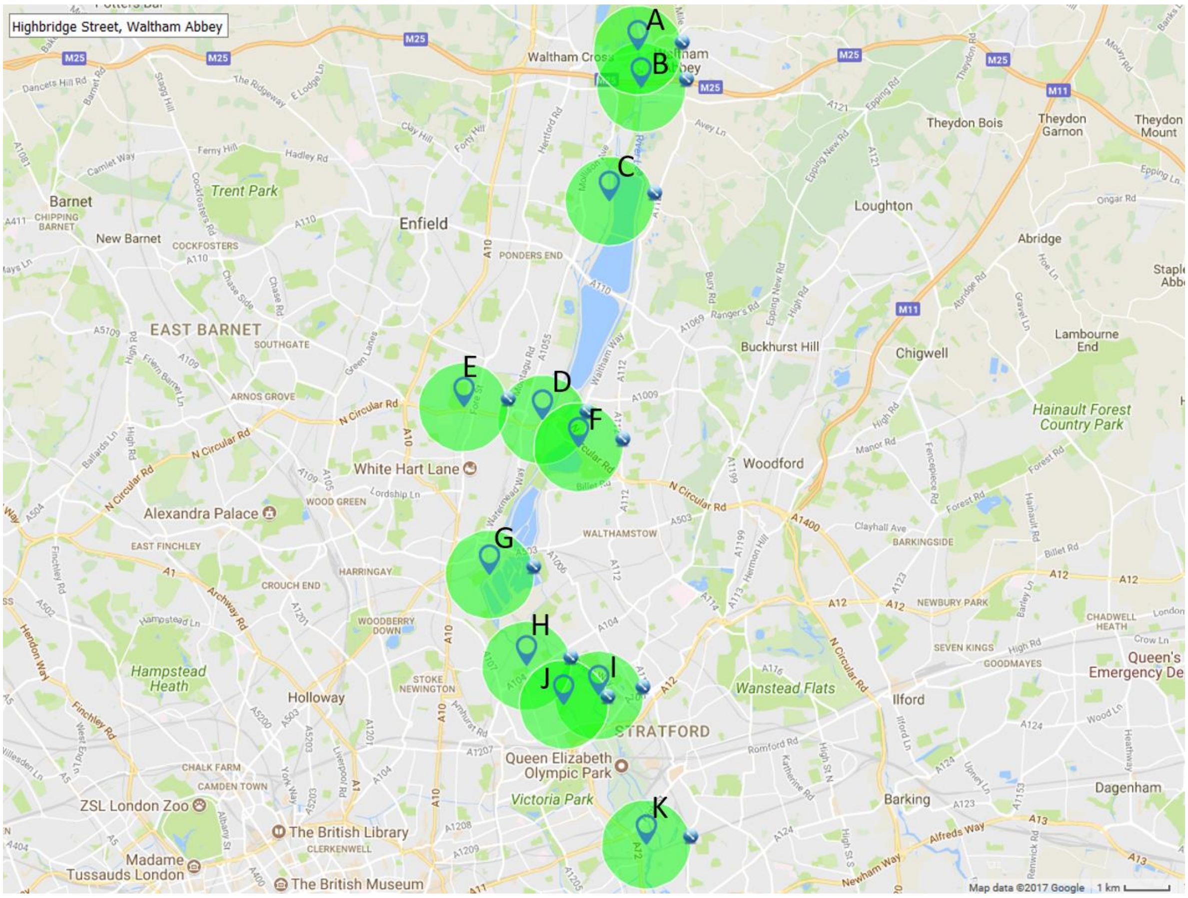
APPENDIX Q10. Predicted loads (kg/year) of selected PAHs by activities at site J, Lower Lee catchment.

Activity	A	Fl	Bz(b)Fl	Bz(a)Py	Bz(g,h,i)Pe
Waste non-hazardous	0.300000	0.300000	3.000000	3.000000	0.300000
Manufacture of chemicals and chemical products	0.630000	1.550000	18.200000	14.400000	8.220000
Road runoff	0.014882	0.030157	0.036606	0.024817	0.017888

APPENDIX Q11. Predicted loads (kg/year) of selected PAHs by activities at site K, Lower Lee catchment.

Activity	A	Fl	Bz(b)Fl	Bz(a)Py	Bz(g,h,i)Pe
Waste non-hazardous	0.500000	0.500000	5.000000	5.000000	0.500000
Manufacture of basic metals and metal products	1.720000	24.060000	37.000000	20.930000	10.680000
Manufacture of chemicals and chemical products	0.630000	1.550000	18.200000	14.400000	8.220000
Road runoff	0.048281	0.098588	0.119094	0.080698	0.058190

APPENDIX R1. Map of 1 km radius sub-catchment at each sampling site at the Lower Lee catchment.



Source: Google Maps, 2020

APPENDIX S1. Image of sampling site C on 14 August 2015 – Lower lee catchment.

Source: Luciana Alves

APPENDIX T1. Ratios of mean predicted metal loads (without wastewater, refineries and production of electricity activities) /sediment field data by sampling site.

	Sampling site	Cd	Cu	Hg	Ni	Pb	Zn
River Lee	A	18.51	5.68	4.72	13.37	2.50	5.02
	G	**0.98**	0.37	0.42	**1.20**	0.09	0.29
	H	2.47	0.48	1.54	3.64	0.27	0.60
	I	0.44	0.21	0.27	0.45	0.04	0.23
Lee Navigation	C	1.88	0.27	**1.38**	3.36	0.21	0.48
	J	0.23	0.22	0.49	0.49	0.07	0.26
	K	1.63	2.04	**0.97**	3.66	0.48	1.57
Tributaries	B	3.75	**0.83**	**1.15**	2.18	0.48	**0.86**
	D	4.36	1.52	**1.19**	5.27	0.43	**1.43**
	E	7.52	3.05	2.55	26.40	**0.66**	2.45
	F	6.50	1.65	**1.36**	6.30	**0.52**	1.91

Key: Values in a range of 0.5 to 1.5 (±50 %) are marked in bold.

APPENDIX T2. Ratios of mean predicted metal loads (without wastewater activity)/sediment field data by sampling site.

	Sampling site	Cd	Cu	Hg	Ni	Pb	Zn
River Lee	A	20.28	7.57	5.64	14.71	2.68	5.93
	G	**0.98**	0.37	0.42	**1.20**	0.09	0.29
	H	2.47	0.48	**1.44**	3.64	0.27	**0.60**
	I	0.44	0.21	0.27	0.45	0.04	0.23
Lee Navigation	C	1.88	0.27	1.56	3.36	0.21	0.48
	J	0.44	0.21	0.27	0.49	0.04	0.23
	K	2.59	4.76	1.63	5.58	**0.74**	2.46
Tributaries	B	3.75	**0.83**	**1.15**	2.18	0.48	**0.86**
	D	6.56	3.20	1.86	7.81	**0.61**	2.28
	E	15.54	4.22	2.58	41.86	**1.14**	5.89
	F	9.19	2.59	1.80	8.37	**0.65**	2.56

Key: Values in a range of 0.5 to 1.5 (±50 %) are marked in bold.

APPENDIX T3. Ratios of mean predicted metal loads (without refineries activity) /sediment field data by sampling site.

	Sampling site	Cd	Cu	Hg	Ni	Pb	Zn
River Lee	A	20.28	7.57	5.64	14.71	2.68	5.93
	G	**0.98**	0.37	0.42	**1.20**	0.09	0.29
	H	2.47	0.48	**1.44**	3.64	0.27	**0.60**
	I	0.44	0.21	0.27	0.45	0.04	0.23
Lee Navigation	C	1.88	0.27	**1.38**	3.36	0.21	0.48
	J	0.44	0.21	0.27	0.49	0.04	0.23
	K	2.59	4.76	1.63	5.58	**0.74**	2.46
Tributaries	B	3.75	**0.83**	**1.15**	2.18	0.48	**0.86**
	D	14.16	13.30	5.37	34.21	**1.18**	10.91
	E	7.52	3.05	2.55	26.40	**0.66**	2.45
	F	9.19	2.59	1.80	8.37	**0.65**	2.56

Key: Values in a range of 0.5 to 1.5 (±50 %) are marked in bold.

APPENDIX T4. Ratios of mean predicted metal loads (without production of electricity activity)/sediment field data by sampling site.

	Sampling site	Cd	Cu	Hg	Ni	Pb	Zn
River Lee	A	18.51	5.68	4.72	13.37	2.50	5.02
	G	**0.98**	0.37	0.42	**1.20**	0.09	0.29
	H	2.47	0.48	**1.44**	3.64	0.27	**0.60**
	I	0.44	0.21	0.27	0.45	0.04	0.23
Lee Navigation	C	1.88	0.27	**1.38**	3.36	0.21	0.48
	J	0.44	0.21	0.27	0.49	0.04	0.23
	K	1.63	2.04	**0.97**	3.66	0.48	**1.47**
Tributaries	B	3.75	**0.83**	**1.15**	2.18	0.48	**0.86**
	D	11.96	11.50	4.70	31.67	**1.00**	10.05
	E	15.54	4.22	2.58	41.86	**1.14**	5.89
	F	6.50	1.65	**1.36**	6.30	**0.52**	1.91

Key: Values in a range of 0.5 to 1.5 (±50 %) are marked in bold.

APPENDIX T5. Ratios of median predicted metal loads/sediment field data by sampling site.

	Sampling site	Cd	Cu	Hg	Ni	Pb	Zn
River Lee	A	1.45	**0.63**	**0.91**	**0.87**	0.17	**0.72**
	G	0.23	0.03	0.10	0.32	0.02	0.04
	H	0.39	0.11	0.21	**0.64**	0.04	0.12
	I	0.21	0.10	0.24	0.27	0.02	0.11
Lee Navigation	C	0.09	0.03	0.06	0.17	0.02	0.04
	J	0.06	0.04	0.14	0.13	0.02	0.06
	K	0.23	0.15	0.10	0.41	0.06	0.13
Tributaries	B	**0.60**	0.12	**0.55**	0.33	0.04	0.10
	D	**0.57**	0.09	0.14	**0.53**	0.05	0.13
	E	1.94	**0.62**	**0.90**	3.78	0.11	0.43
	F	**1.12**	0.28	**0.98**	1.55	0.12	0.33

Key: Values in a range of 0.5 to 1.5 (±50 %) are marked in bold.

APPENDIX T6. Ratios of minimum predicted metal loads/sediment field data by sampling site.

	Sampling site	Cd	Cu	Hg	Ni	Pb	Zn
River Lee	A	0.00	0.02	0.02	0.08	0.00	0.07
	G	0.01	0.06	0.09	0.03	0.01	0.07
	H	0.00	0.01	0.01	0.02	0.00	0.03
	I	0.00	0.03	0.05	0.07	0.00	0.06
Lee Navigation	C	0.00	0.00	0.00	0.00	0.00	0.00
	J	0.00	0.02	0.01	0.01	0.00	0.02
	K	0.00	0.03	0.00	0.02	0.00	0.04
Tributaries	B	0.00	0.00	0.00	0.00	0.00	0.00
	D	0.00	0.01	0.00	0.02	0.00	0.02
	E	0.00	0.03	0.04	22.66	0.00	0.07
	F	0.01	0.04	0.05	**1.41**	0.00	0.13

Key: Values in a range of 0.5 to 1.5 (±50 %) are marked in bold.

APPENDIX T7. Ratios of maximum predicted metal loads/sediment field data by sampling site.

	Sampling site	Cd	Cu	Hg	Ni	Pb	Zn
River Lee	A	8.17	**1.24**	0.33	4.21	**0.95**	**0.96**
	G	0.30	0.21	0.13	0.35	0.04	0.14
	H	**0.99**	0.10	0.30	**0.82**	0.08	0.12
	I	0.36	0.14	0.06	0.25	0.04	0.15
Lee Navigation	C	**0.99**	0.09	**0.59**	1.72	0.09	0.30
	J	0.04	0.09	0.15	0.12	0.02	0.10
	K	**0.85**	2.15	0.45	**1.44**	0.24	**0.90**
Tributaries	B	**1.41**	0.31	0.10	**0.93**	0.33	0.36
	D	6.36	8.01	2.61	15.60	0.49	7.92
	E	3.05	**0.62**	0.26	5.64	0.34	2.11
	F	1.66	0.40	0.19	**1.29**	0.10	0.47

Key: Values in a range of 0.5 to 1.5 (±50 %) are marked in bold.

APPENDIX T8. Ratios of mean predicted PAH loads (without wastewater, manufacture of chemical and chemical products and manufacture of basic metals and metal products activities) /sediment field data by sampling site.

	Sampling site	A	Fl	Bz(b)Fl	Bz(a)Py	Bz(ghi)Pe
River Lee	A	**1.47**	0.24	2.44	4.28	0.46
	G	0.05	0.01	0.03	0.00	0.04
	H	0.43	0.06	**0.83**	**1.23**	0.45
	I	0.33	0.06	**0.61**	**1.01**	0.16
Lee Navigation	C	0.13	0.02	0.23	0.41	0.05
	J	0.20	0.03	0.30	0.49	0.11
	K	**0.77**	0.19	1.57	2.61	0.34
Tributaries	B	0.45	0.07	**0.78**	**1.44**	0.18
	D	6.34	0.30	2.76	4.78	**1.17**
	E	1.67	0.19	1.82	2.64	0.42
	F	0.03	0.01	0.01	0.01	0.01

Key: Values in a range of 0.5 to 1.5 (±50 %) are marked in bold.

APPENDIX T9. Ratios of mean predicted PAH loads (without wastewater activity)/sediment field data by sampling site.

	Sampling site	A	Fl	Bz(b)Fl	Bz(a)Py	Bz(ghi)Pe
River Lee	A	4.57	7.27	13.69	15.44	7.88
	G	**1.16**	2.25	5.56	0.44	5.28
	H	0.43	0.06	**0.83**	**1.23**	0.45
	I	0.33	0.06	**0.61**	**1.01**	0.16
Lee Navigation	C	3.31	**1.35**	16.60	24.20	15.26
	J	**0.61**	0.17	2.07	2.85	3.05
	K	4.08	8.16	15.36	20.79	11.90
Tributaries	B	0.45	0.07	**0.78**	**1.44**	0.18
	D	2.97	2.59	11.94	13.35	7.86
	E	2.44	1.69	5.17	5.39	2.43
	F	2.84	4.92	10.39	9.40	6.40

Key: Values in a range of 0.5 to 1.5 (±50 %) are marked in bold.

APPENDIX T10. Ratios of mean predicted PAH loads (without manufacture of chemical and chemical products activity) /sediment field data by sampling site.

	Sampling site	A	Fl	Bz(b)Fl	Bz(a)Py	Bz(ghi)Pe
River Lee	A	4.57	7.27	13.69	15.44	7.88
	G	**1.16**	2.25	5.56	0.44	5.28
	H	0.43	0.06	**0.83**	**1.23**	0.45
	I	0.33	0.06	**0.61**	**1.01**	0.16
Lee Navigation	C	0.13	0.02	0.23	0.41	0.05
	J	0.20	0.03	0.30	0.49	0.11
	K	3.19	7.67	10.72	13.38	6.87
Tributaries	B	0.45	0.07	**0.78**	**1.44**	0.18
	D	7.45	2.47	7.70	9.03	4.09
	E	2.44	1.69	5.17	5.39	2.43
	F	2.84	4.92	10.39	9.40	6.40

Key: Values in a range of 0.5 to 1.5 (±50 %) are marked in bold.

APPENDIX T11. Ratios of mean predicted PAH loads (without manufacture of basic metals and metal products activity)/sediment field data by sampling site.

	Sampling site	A	Fl	Bz(b)Fl	Bz(a)Py	Bz(ghi)Pe
River Lee	A	1.57	0.24	2.44	4.28	0.46
	G	0.05	0.01	0.03	0.00	0.04
	H	0.43	0.06	**0.83**	**1.23**	0.45
	I	0.33	0.06	**0.61**	**1.01**	0.16
Lee Navigation	C	3.31	**1.35**	16.60	24.20	15.26
	J	**0.61**	0.17	2.07	2.85	3.05
	K	1.66	0.47	5.94	10.02	5.37
Tributaries	B	0.45	0.07	**0.78**	**1.44**	0.18
	D	1.86	0.43	7.00	9.10	4.94
	E	1.67	0.19	1.82	2.64	0.42
	F	0.03	0.01	0.01	0.01	0.01

Key: Values in a range of 0.5 to 1.5 (±50 %) are marked in bold.

APPENDIX T12. Ratios of median predicted PAH loads/sediment field data by sampling site.

	Sampling site	A	Fl	Bz(b)Fl	Bz(a)Py	Bz(ghi)Pe
River Lee	A	1.51	0.22	2.37	3.86	0.45
	G	0.30	**0.98**	2.49	0.21	6.26
	H	0.22	0.04	0.40	**0.88**	**1.48**
	I	0.16	0.03	0.34	0.41	0.08
Lee Navigation	C	0.12	0.02	0.20	0.40	0.04
	J	0.20	0.03	0.25	0.46	5.45
	K	**0.84**	0.35	2.97	5.53	2.89
Tributaries	B	0.24	0.03	0.36	**0.66**	0.08
	D	**1.17**	0.18	2.07	3.37	**0.74**
	E	**1.34**	0.13	**1.31**	1.73	0.27
	F	2.59	4.62	10.86	8.59	5.82

Key: Values in a range of 0.5 to 1.5 (±50 %) are marked in bold.

APPENDIX T13. Ratios of minimum predicted PAH loads/sediment field data by sampling site.

	Sampling site	A	Fl	Bz(b)Fl	Bz(a)Py	Bz(ghi)Pe
River Lee	A	0.09	0.04	0.04	0.04	0.35
	G	0.30	0.07	8.84	0.00	4.26
	H	0.09	0.02	1.76	0.03	2.49
	I	0.08	0.02	0.03	0.04	**1.19**
Lee Navigation	C	0.02	0.01	0.01	0.01	0.01
	J	0.05	0.02	1.83	0.03	1.79
	K	0.23	0.11	11.91	0.12	2.91
Tributaries	B	0.01	0.00	0.00	0.00	0.00
	D	0.04	0.01	0.02	0.02	0.02
	E	0.04	0.01	0.02	0.02	0.02
	F	0.09	0.03	0.04	0.05	0.05

Key: Values in a range of 0.5 to 1.5 (±50 %) are marked in bold.

APPENDIX T14. Ratios of maximum predicted PAH loads/sediment field data by sampling site.

	Sampling site	A	Fl	Bz(b)Fl	Bz(a)Py	Bz(ghi)Pe
River Lee	A	1.79	4.70	6.42	7.53	4.49
	G	**0.75**	2.41	2.83	0.29	1.80
	H	0.21	0.03	0.39	0.43	0.09
	I	0.22	0.03	0.36	**0.65**	0.07
Lee Navigation	C	1.70	**0.84**	11.65	17.67	10.31
	J	0.19	0.06	0.70	**0.91**	**0.69**
	K	1.72	4.54	4.76	6.40	3.23
Tributaries	B	0.35	0.05	0.42	1.67	0.10
	D	3.16	**1.27**	2.89	3.56	2.61
	E	0.37	**0.72**	1.53	1.31	**0.94**
	F	**0.81**	1.60	2.88	2.51	1.73

Key: Values in a range of 0.5 to 1.5 (±50 %) are marked in bold.

APPENDIX U1. Chapters 1-4 and critical evaluation presented in 2016 as part of the transfer (MPhil to PhD) process

Chapters 1-4.pdf

Critical Evaluation.pdf

APPENDIX U2. Published paper: Metal Water-Sediment Interactions and Impacts on an Urban Ecosystem

MetalWater-Sediment Interactions and Imp