Potential for migration of urban diffuse pollution to groundwater: A case study of the Brighton block Chalk aquifer, South East England

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Abstract

Diffuse urban pollution of surface and ground waters is a growing concern in many cities and towns. Traffic-derived pollutants such as salts, heavy metals and polycyclic aromatic hydrocarbons (PAHs) may wash off road surfaces in soluble or particulate forms which later drain through soils and drainage systems into surface waters and groundwater. In Brighton, about 98% of drinking water supply comes from groundwater (derived from the Brighton Chalk block). In common with many groundwater sources, the Chalk aquifer has been relatively extensively monitored and assessed for diffuse rural contaminants such as nitrate, but knowledge on the extent of contamination from road run-off is currently lacking.

This project examines the transfer of traffic-derived contaminants from the road surface to the Chalk aquifer, via urban drainage systems. Dissolved phase and sediment bound samples have been collected from road drainage systems (gully pots) and analysed for heavy metals and organic contaminants. A transect of five Chalk boreholes have also been sampled on a monthly basis for a period of 18 months, and groundwater samples analysed to examine the concentrations of key, mainly road run-off derived, hydrocarbon and heavy metal contaminants in groundwater across the Brighton area.

Results show the presence of heavy metals (Zn, Cu & Pb) in gully pot sediments with concentrations observed above guideline values. Their spatial distribution shows a complex trend. However, hot spots emerge around busy roads and junctions. The sediment bound Pb within the gully pots shows Pb-isotope ratios ($^{206}Pb/^{207}Pb$ 1.098 – 1.114) closer to the historical isotope ratios of Pb from gasoline sources ($^{206}Pb/Pb^{207}$ 1.079), rather than from other anthropogenic or background sources. Leachability studies reveal that only Zn and Cu have the potential for remobilisation into the environment with the other elements trapped within immobile phases. Polycyclic aromatic hydrocarbons (PAH) in the dissolved

phase gully pot samples collected appear mobile. The PAHs within both phases share a hotspot along a major road junction. Furthermore, traces of organics have been recorded in the urban borehole monitoring site at Preston Park. Electrical conductivity changes in groundwater have also been used to assess local changes in ionic strength which may be associated with road-derived contaminants. There is a clear seasonal variation in the tracers identified in groundwater, with higher concentrations observed during summer (low rainfall) than winter (high rainfall). Results obtained indicate transfer of urban diffuse pollutants to groundwater. However this depends on a number of factors such as; redox conditions for heavy metals to mobilise, levels of heavy metals and PAHs released in the environment, and amount of rainfall available to transport the contaminants which depends upon season. A conceptual model has been developed to explain the processes involved.

Dedication

This thesis is dedicated to the memory of my mother (Zainab Abba Jato) who supported me and was everything to me. May the Almighty grant her Jannah. Ameen

Acknowledgments

Statement of own work

I declare that the research contained in this thesis, unless otherwise indicated formally, is an original work of the author. This thesis has not been previously submitted to this or any other University for a degree, and does not incorporate any material already submitted for a degree.

Signed:

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List of abbreviations

AOD	Above ordinance datum
BCR	British certified reference
BHCC	Brighton and hove county council
BGL	Below ground level
CF	Casterbridge farm
CHS	Chlorinated hydrocarbon solvents
CZFP	Convergent zero flux plane
CDT	Conductivity depth temperature
CFC	Chloroflourocarbons
CRM	Certified reference material
DO	Dissolved oxygen
DZFP	Divergent zero flux plane
DEFRA	Department for environment, food and rural affairs
EMNA	Enhanced monitored natural attenuation
EPM	Equivalent porous medium
EU	European Union
GP	Gully pot
GWL	Groundwater level
IARC	International agency for research on cancer
IRSM	Institute of rock and soil mechanics
IPU	Isoproturon
LNAPL	Light non aqueous phase liquid
MBTE	Methyl tert-butyl ether
MNA	Monitored natural attenuation
NPS	Non-point source
NOC	National oceanographic centre
NHB	North heath barn

NB	North bottom
PP	Preston park
PGE	Platinum group elements
PEL	Predicted effects level
PAH	Polycyclic aromatic hydrocarbons
SEM	Scanning electron microscope
SMC	Soil moisture curve
SULPH	Sulphanilamide
SF6	Sulphur hexafluoride
TPH	Total petroleum hydrocarbons
TEL	Threshold effects level
THM	Trihalogenated methanes
TCM	Trichloromethane
UZT	Unsaturated zone thickness
UKCP	United Kingdom climate prediction
UZF	Unsaturated zone flow
US-EPA	United states environmental protection agency
WHO	World health organisation
WT%	Weight percentage
ZFP	Zero flux plane

Chapter 1 Introduction

1.1 Background

The use of groundwater in agriculture, industries, drinking and for domestic use makes it a critically important natural resource (Stuart and Smedley, 2009). In the UK, in South East England, 70% of water consumed comes from groundwater (Downing, 1998). Chalk is the main aquifer for water resources in the UK, Northern France, Northern Germany, Belgium and Israel (Downing et al., 1993, Kloppmann et al., 1998, Dahan et al., 1999, Brouyère et al., 2004 and Pinault et al., 2005, Ireson et al., 2009). In Brighton (Figure 1), UK, about 98% of water for domestic use comes from groundwater of the Chalk aquifer (Environment Agency report, 2008; Mortimore, 2011). Chalk (small c) is a rock type, being a micritic limestone, dominantly composed of the calcitic remains of marine organisms, particularly coccoliths (Hancock, 1980). The Chalk (capital C) is a stratigraphic interval in northern Europe, dominantly composed of chalk (Young *et al*., 1997). Water from the Chalk aquifer is supplied from source to consumer typically with little or no treatment at all. The recharge sources for groundwater have mainly been identified as precipitation, rivers and other surface waters, and inter-aquifer flows (Barret et al. 1999). This is similar in both urban and rural areas (Lerner et al. 1990). However, groundwater faces an increasing threat from urbanisation and pollution through recharge (Schirmer et al., 2013).

Unlike recharge in many rural areas, urban areas have additional major sources of recharge such as storm water, run-off water, waste water and sewage. The multiplicity of recharge sources means that the recharge has a complex pathway (Barret et al., 1999). There is some suggestion that even roads are not completely impermeable (Hollis and Ovenden, 1988) and may allow water to infiltrate into soil and bedrock. Water can also infiltrate along the edges of roads, paths, soakaways (Thomson and Foster, 1986), infiltration basins or

recharge boreholes for storm water (Appleyard, 1993). These complexities in the dynamics of recharge from non-point urban sources in the environment make it difficult to control the contribution of infiltrating waters to pollutant concentrations in groundwater, thereby, making the groundwater more vulnerable.

A study by Maltby et al. (1995), investigated the effect of urban source pollution on the quality of stream waters, and identified heavy metals (Pb, Cu, Cr, Zn and Co) and hydrocarbons (in form of PAHs), originating from motorways, as major contributors to deteriorating stream water quality. The effect of urban diffuse pollution may also be a potential threat to the overall quality of urban groundwater. Gobel et al. (2007) suggested that the quality of surface water, aquifer recharge and groundwater is highly influenced by the concentrations of hydrocarbons and heavy metals that accumulate in surface waters mainly around roads, which show higher concentrations. Mitchell et al. (2001), and most notably Rothwell et al. (2015) have identified and described road run-off in urban areas as a pollution hazard to the environment.

The Chalk aquifer is characterised by having a dual porosity and permeability within the fracture and matrix (Ireson, 2013). The Chalk has a very fine matrix grain size, and hence very small pores (20-45% (Oakes, 1977)) with a low permeability (0.5µm (Price et al., 1976)) and a very high fracture permeability (K>10-2m/day) with low porosity (Price et al., 1993). The Chalk Unsaturated Zone (CUZ) is the pathway for aquifer recharge (Rageb at al., 1997 and Lee et al., 2006) and is also responsible for contaminant transport to the aquifer (Haria et al., 2003, Mathias et al., 2007 and Ireson et al., 2008). Outside of the Chalk in the UK, France, Belgium and Denmark, chalk has also been identified as a significant hydrological pathway for contaminants in Israel (Nativ and Nissim, 1992, Nativ et al., 1995, Dahan et al., 1998 and Dahan et al., 1999).

The Brighton area shown in Figure 1.1 forms an exceptional case study for the pressures of urbanisation on a major chalk aquifer. Not only is the aquifer the main source of public water supply for the area, but there are increasing pressures on aquifer recharge from an intensely urbanised coastal strip and the associated major road system. The groundwater level in Brighton shows a rapid response to rainfall (with observed rises in level of several metres within a few days) as a result of rapid preferential flow along fractures and solution features (karst) during the winter months (Butler, 2013), and even in the summer months when there is a significant moisture deficit within the unsaturated aquifer, intense rainfall can trigger fracture flow, and drainage of the unsaturated zone matrix remains continuous (Rutter et al., 2012) A general map of the study area with a geological map of the study area are presented in Figure 1.1 and 1.2. It is therefore important to investigate the movement of urban diffuse pollutants from the surface to the groundwater through the Chalk unsaturated zone, and their resulting potential to contaminate the groundwater.

This study will investigate this process, starting with characterisation of sources of urban diffuse pollution using accumulated sediments and drainage waters, the detection of identified contaminants in groundwater samples, and experimental investigation of contaminant transport in saturated and unsaturated chalk.
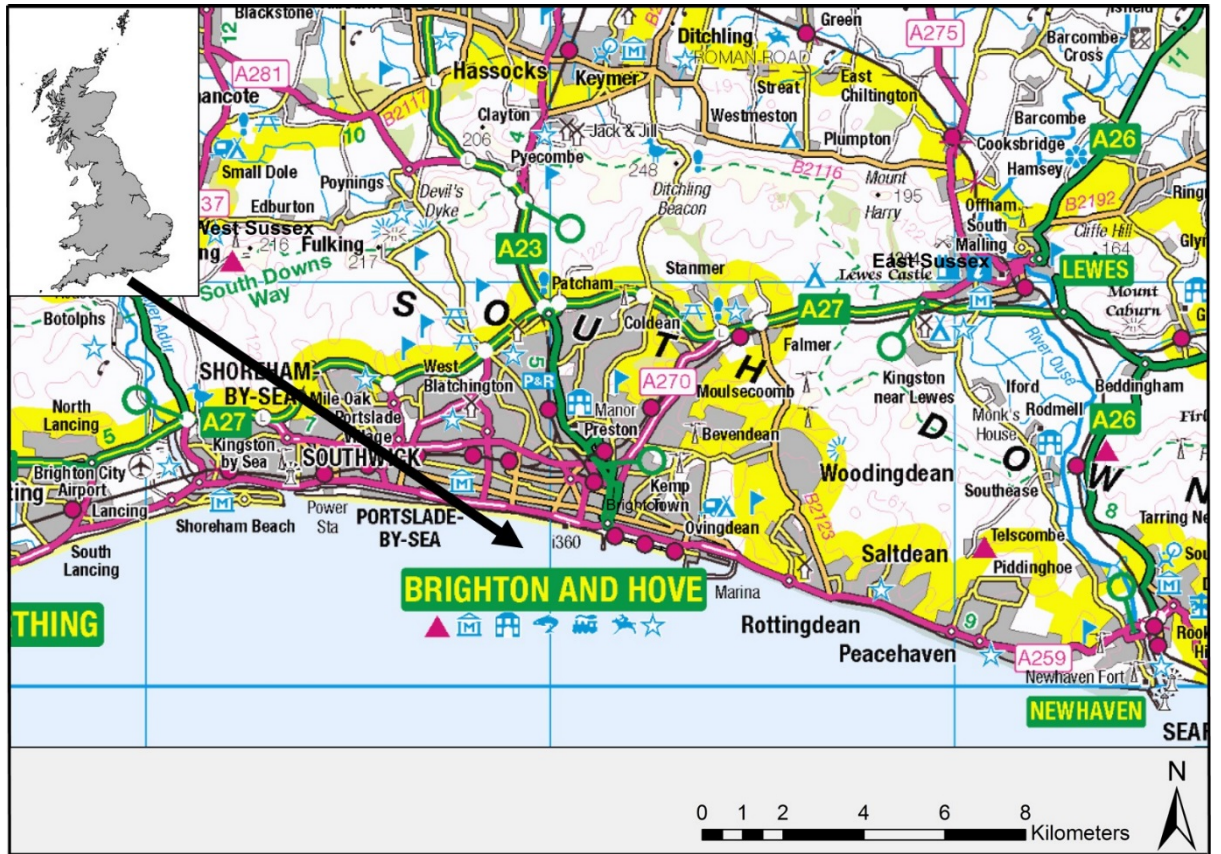
Figure 1. 1. Generalised map of England, showing the South East and the study area, Brighton from Digi map (Map by author).
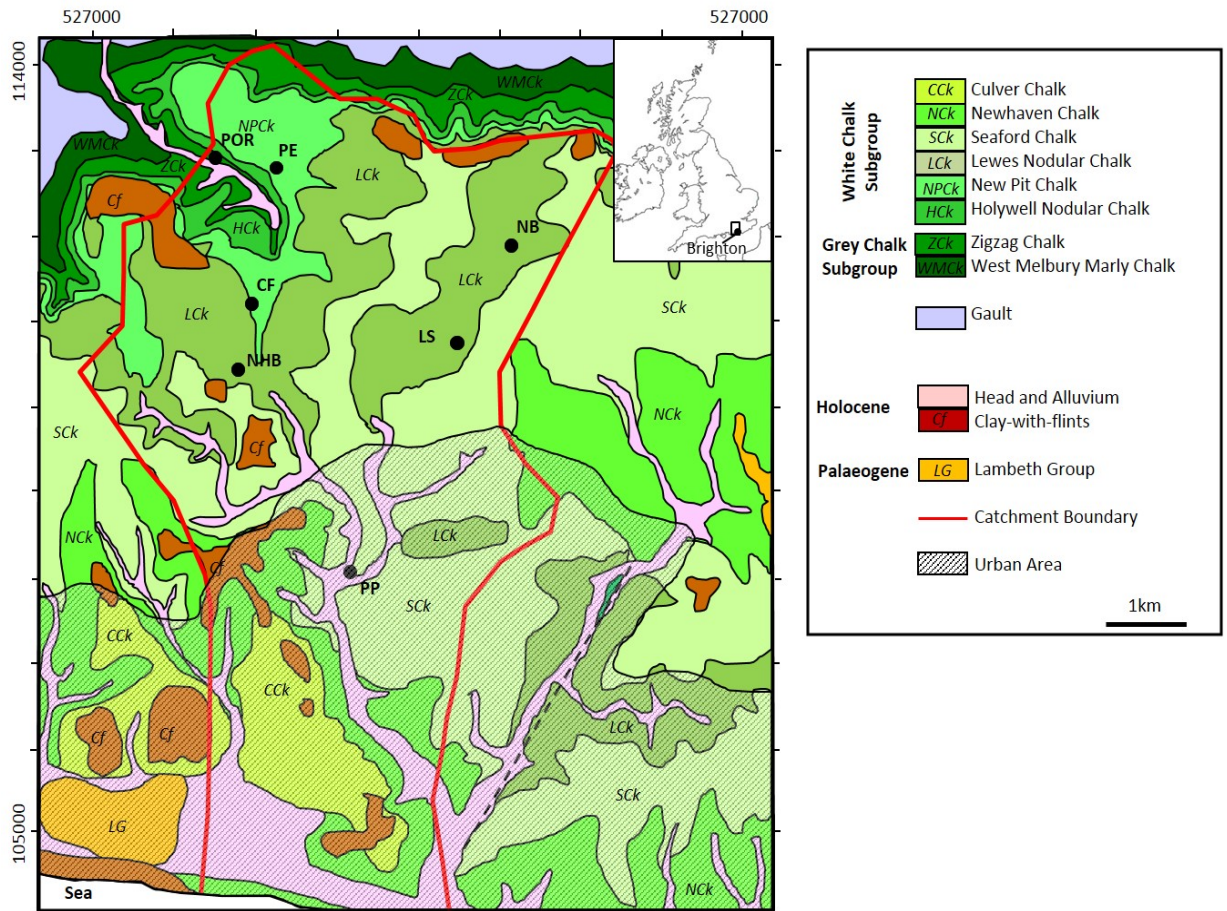
Figure 1. 2 Geological map of the study area, Brighton from British Geological Survey (BGS) modified after Rutter et al., (2012).

1.2 Research aims

To characterise the contaminant chemistry of urban drainage in order to define the source term for a source-pathway receptor model of urban roadway contamination. To determine the concentration and characteristics of urban drainage contaminants in the chalk aquifer and the mechanisms involved in retardation of contaminants in transport from the urban drainage system to the aquifer.

1.3 Research objectives

- To analyse urban drainage water and accumulated sediment for heavy metal and organic contaminants.

- To identify key compounds and element ratios that may act as tracers for urban drainage contaminants in the environment.

- To carry out experimental modelling of contaminant transport through the chalk aquifer and local soils.

- To identify urban drainage components in groundwater

- To identify the long term and seasonal concentration trends from groundwater time series data.

- To design a model that synthesises source-pathway-receptor for understanding the fate of urban contaminants in the Chalk aquifer.

1.4 Rationale

Data from the Environment Agency, Brighton and Hove City Council and the Highways England in Figure 1.3 shows the area covered by soakaways and settling ponds and the location of the monitoring boreholes. Figure 1.4 shows the distribution of gully pots within the city of Brighton and Hove, and the proportion which soakaway directly to the aquifer rather than the sewage system. The distribution of soakaways in both the major road and city road drainage network means any significant contaminant loading has the potential to infiltrate to the groundwater without the interception and diversion to sewers and ultimately water treatment plants. The flow process and chemical reactions that may result in an attenuation process will be the aquifers main defence from contamination.
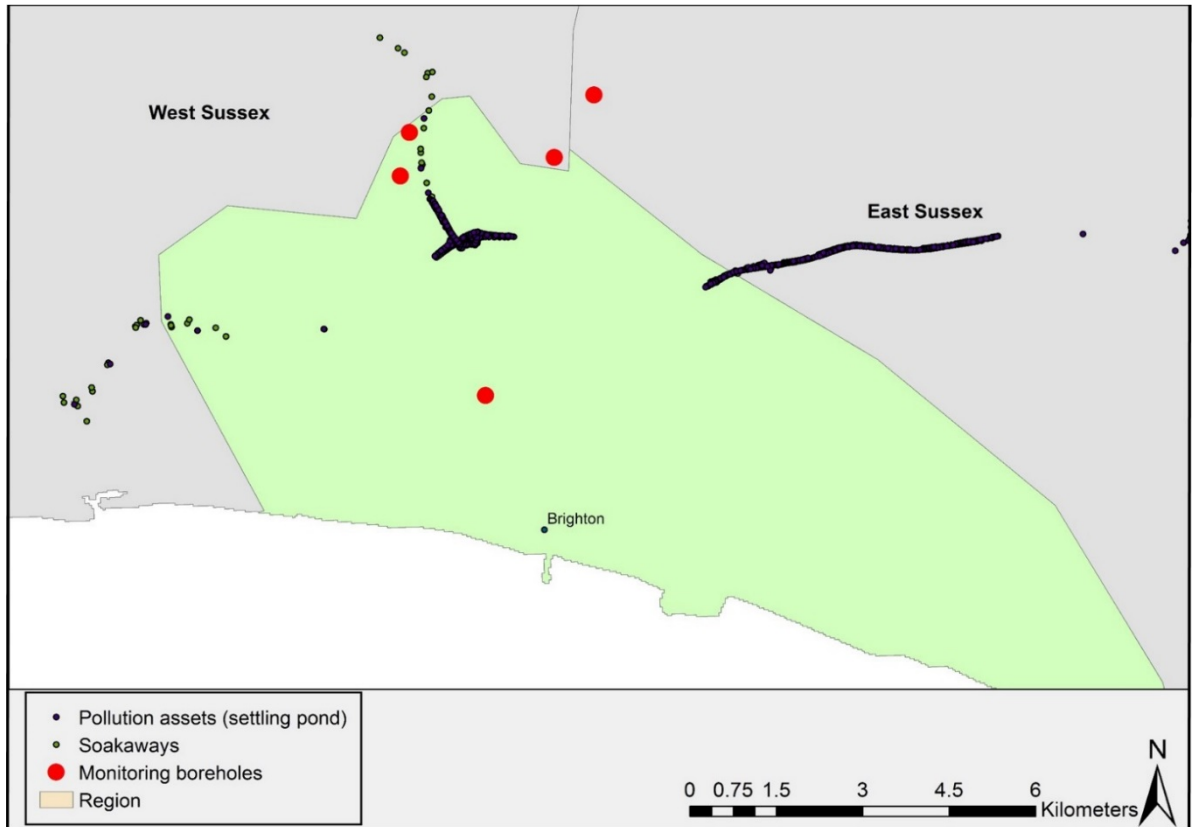
Figure 1. 3. Location of the monitoring boreholes, settling ponds and soakaways within the study area (Settling pond and soakaway data were obtained from the Environment agency. Green area represents Patcham catchment).
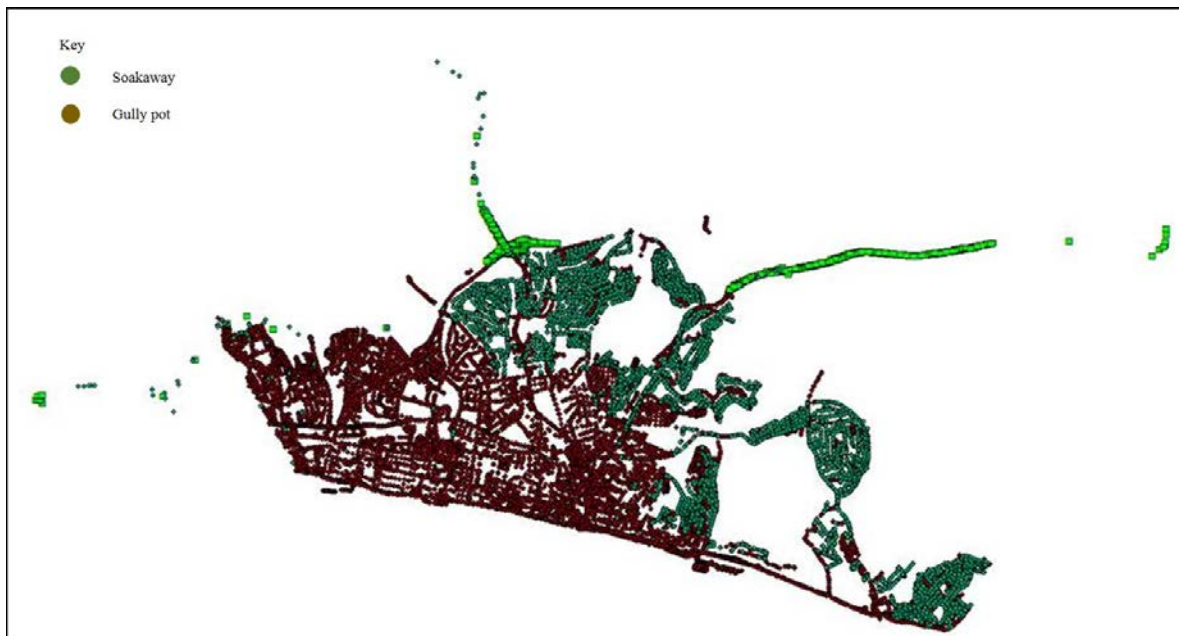
Figure 1. 4. Gully pots and Soakaway locations within the study area of Brighton. From Environment Agency.

1.5 Overall contribution to knowledge

The determination of the presence and concentration of road derived pollutants in gully pots within dissolved and sediment bound phases provides the original contribution to knowledge. Furthermore, this is backed by the presence of the contaminants in groundwater, effect of rainfall and the seasonal variation observed and impact of flow process in the Chalk aquifer.

1.6 Thesis structure

This thesis is structured into seven separate chapters.

Chapter 1 This chapter introduces the research background and states the overall aim and research objectives. Identifies the contribution to knowledge and outlines the structure of the thesis.

Chapter 2 Presents a review of the literature, including; road run-off pollutants, potential markers in groundwater, Lithology of the chalk aquifer and its vulnerability and heavy metals in groundwater.

Chapter 3 Gives an overview of methods employed during field work, groundwater sampling proses employed and in-situ measurements. Laboratory methods for identification of contaminants in surface water and sediments and groundwater. Methods for understanding flow in chalk.

Chapter 4 Presents results and discussion of organic and non-organic contaminants including platinum group element (PGE) in gully pot sediments and dissolved phase gully pot samples, showing spatial variation in the concentration of heavy metals and organics and Pb-isotope study to determine source of organics.

Chapter 5 Presents results and discussion on leachability study on gully pot sediments collected within study area using a modified BCR 701 sequential extraction method and a results of the core flooding experiment carried out.

Chapter 6 Presents results and discussion on evidence of pollution in groundwater, by presenting geochemistry of the groundwater. Samples collected from 5 locations within the same city over an 18 month period. With focus on 2 boreholes, Urban and rural (as a control site).

Chapter 7 Provides a summary of the discussions, conclusions and recommendation for further work.

Chapter 2 Literature Review

2.1. Introduction

The importance of water cannot be over-emphasised. Without water, life on earth would be impossible. There are significant pressures from human development and potential contamination on the quantity and quality of groundwater supplies, and an equally important need to protect and manage this valuable resource. To understand the process of water movement, flow or storage or in a broader term the water cycle, water is studied in three main disciplines: on the earth's surface (hydrology), atmospheric water (meteorology) and study of water in the ground (hydrogeology) (Ireson, 2012). The three disciplines combine in the study of the unsaturated zone. Understanding the unsaturated zone is important in determining process of water movement in a catchment. The meteorologist is concerned with evaporation from the land surface, the hydrologist with infiltration to the ground, while the hydrogeologist is concerned with recharge to the aquifers. The study of groundwater quality is called 'Contaminant Hydrogeology', it involves investigating and solving problems related to contamination of groundwater resources, and is the main study area of this research.

In more detail, the current study examines the transfer of urban diffuse pollution, in particular road run-off, to groundwater. This will give a deeper understanding of recharge mechanisms through the Chalk, and the vulnerability of the Chalk aquifer to road-derived contaminants. The first part of the current study involves reviewing existing literature and identifying key pollutants to be used as markers. Secondly, it involves sampling and laboratory analysis of surface water (gully pots, settling ponds and soakaways) and groundwater from the available monitoring boreholes. Later phases of the research will involve analysis of accumulated sediments (which may provide time-integrated evidence of contaminant inputs), and laboratory flow experiments, which will be used to develop

conceptual and model for the distribution and transport of road derived contaminants in the Chalk aquifer.

2.1.2 Groundwater Recharge in the Urban Environment

The development of cities has decreased the value of urban groundwater in the UK, due to the potential risk of contamination it faces from urban sources (Lerner & Barrett, 1996). More recharge tends to take place in rural areas because of the unaltered environment with minimal urbanisation taking place. Although, a considerable amount of recharge to the aquifer may take place within the urban environment (Lerner et al., 1982). The complex and ever changing nature of the urban environment gives it a wide range of recharge sources including direct recharge from surface, sewer leakage, soakaways, and septic tanks, (Greswell et al., 1994) summarised in Figure 2.1. The usual approach to studying the origin of solutes in groundwater is by using the chemical approach and considering many species together to deduce the most likely origins of the waters. Using a hydro chemical approach is cumbersome however, as the full range of potential urban contaminants is vast, a more parsimonious approach is to identify marker compounds that are consistently associated with urban contamination, and use these as tracers of the source and pathways of contaminants in the environment. Lerner (1986), Butler and Verhagen (1997) and Rivers et al. (1996) in their individual studies have found specific chemical species which are useful in identifying some particular sources. But, there is no single marker that is ideal for all sources. This study will identify markers that may be potential contaminants using data from previous work.

The main source of recharge in urban areas is directly from precipitation (Barrett et al., 1999). The evolution of cities has changed the pathway for infiltrating precipitation, thereby causing interception that affects water by changing its quality before infiltration. However, it has been observed after a careful study that most of the water infiltrates

through the road, particularly gaps between kerbstones and gutters (gully pots) (Hollis and Ovenden, 1988). This is regardless of the existence of sewers.
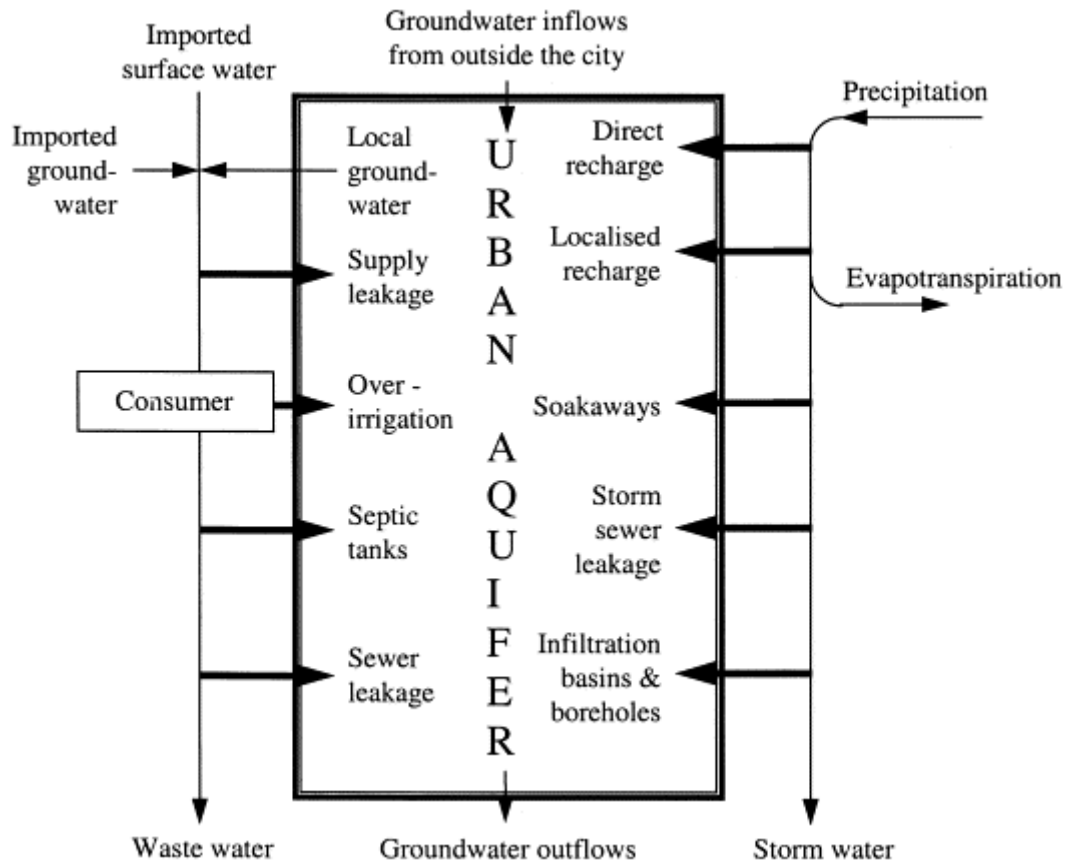
Figure 2. 1. Typical recharge sources in an urban aquifer (Barrett et al., 1999).

2.2 Road run-off pollutants

Pollutant sources from the road and traffic include road surface abrasion, tyre abrasion, brake pad abrasion, drip loss (fuel, gear oil, grease, brake fluid, antifreeze, etc.) and corrosion products (Klein, 1982; Harrison and Wilson, 1985; Ball et al., 1994; Ball et al., 1996 and Sansalone and Buchberger, 1996). Road surface abrasion depends on the condition and texture of the road surface. Tyre abrasion releases pollutants such as rubber, soot and heavy metal oxides with Zn, Pb, Cr, Cu and Ni, while brake pad abrasion releases, in particular, Ni, Cr, Cu and Pb (Muschack, 1989). Road run-off also contains Sodium

chloride (NaCl). This is used for de-icing salts on roads during winter, and typically also contains up to 10% other salts including calcium chloride ($CaCl_2$), calcium sulphate ($CaSO_4 \cdot 2H_2O$), magnesium chloride ($MgCl_2 \cdot 6H_2O$) and magnesium sulphate ($MgSO_4$) (Krauth and Klein, 1982). In addition, traffic-derived inorganic compounds and ions in runoff may include: potassium (K), calcium (Ca), magnesium (Mg), Al, silicon (Si), Fe, manganese (Mn), Cl, hydrogen carbonate (HCO_3^-), P and N compounds (Hvitved-Jacobsen and Yousef, 1996), with trace occurrences of arsenic (As), Pb, boron (B), Cd, Cr, Cu, Ni, titanium (Ti), vanadium (V), Zn and, more recently, platinum (Pt), palladium (Pd) and rhodium (Rh) from catalytic converters (Baun and Arnbjerg-Nielsen, 2001 and Gobel et al., 2007). It should be noted that pollutant availability, concentration on roads and their further distribution is a function of traffic density, wind drift, duration and intensity of storm water events.

2.2.1 Urban Water Run-off Concentrations and Sources

Urban run-off affects the quality of receiving waters due to presence of pollutants (Ngabe et al., 2000 and Gobel et al., 2007). Heavy metals (e.g. lead (Pb), zinc (Zn), copper (Cu), cadmium (Cd)) polycyclic aromatic hydrocarbons (PAH), mineral oil hydrocarbons (MOH) and readily soluble salts are commonly observed in run-off and are hazardous to receiving waters (surface, seepage and groundwater) (Pitt et al., 1994). These may derive from a range of different non-point sources adsorbing onto sediments, (Moore et al, 2010). The US-EPA defined Non-point source pollution as: *"Non-point source pollution generally results from land runoff, precipitation, atmospheric deposition, drainage, seepage or hydrologic modification. Nonpoint source (will henceforth be referred to as NPS) pollution, unlike pollution from industrial and sewage treatment plants, comes from many diffuse sources. NPS pollution is caused by rainfall or snowmelt moving over and*

through the ground. As the runoff moves, it picks up and carries away natural and human-made pollutants, finally depositing them into lakes, rivers, wetlands, coastal waters and ground waters." NPS pollutants are of different types and may well come from different sources as presented in Table 2.1.

Table 2. 1. The table below briefly classifies types and sources of non-point source pollutants in the environment on a general basis for a clear understanding of the topic. Modified from Novotny & Olem, (1994).

Types	Sources
Agriculture	Nitrate, pesticides
Urban run-off	Hydrocarbons, heavy metals, salts, sediments, nutrients, persistent organics, Pathogens etc.
Abandoned Mine	Arsenic, lead and other possible contaminants
Sewage	Untreated effluent
Others	Sediments, nutrients, pathogens

Non-point source (NPS) pollution is divided into major and minor contributors of particular types of contaminants in receiving waters, surface or groundwater. This is presented in Table 2.2. Furthermore, the effects that non-point source contaminants pose to groundwater is summarised and shown in Table 2.3.

Table 2. 2. Classification of non-point sources that contributes hydrocarbon and heavy metals in the environment. **M**=Major source, m=minor (from Luker & Montague, 1994).

	Sediment	N	P	Pathogens	Cu	Zn	Pb	As	Cd	Trace metals \ inorganics	Pesticides and biocides	Hydrocarbons / PAH's	Persistent organics
Atmospheric deposition	M	M		m									
Fossil fuel emissions	m	M						M				M	
Vehicle emissions		M	m				M					M	
Vehicle wear	m				M	M			m	M		M	
Road abrasion												M	
Road maintenance, inc. de-icing†	m						m			m	m		
Soil erosion	M	m	M	m		M							
Construction sites	M		m										
Industrial wastes			m		M	m	m		M	M	m	M	M
Roofs & other surface abrasion	m					m							
Gardens, parks and trees	m	M	M		m	m		m			M		m
Animal wastes		M	M	M									
Other wastes and spills				m							m	m	m

Forster, (1999) realised that the type, concentration and distribution of pollutants are a consequence of surface and atmospheric deposition (dry atmospheric deposition or wet atmospheric deposition). Dry atmospheric deposition defines periods where the deposited pollutants accumulate due to a lack of rainfall, fog or snow that enhances mobility (Georgij et al., 1983). Kern et al., (1992) investigated the wash off behaviour of heavy metals from asphalt and concrete roads. During dry atmospheric deposition, there is a direct transfer of

atmospheric dust, gas and aerosol to the ground. This is then washed into receiving waters at the onset of precipitation events, and is termed the first flush. Fog, rainfall, snow, and frost wash out materials from the atmosphere during wet atmospheric deposition (Gobel et al., 2007). This process is influenced not only by the dry or wet atmospheric conditions, but also regional dust amounts, storm water intensities, duration of storm water events, duration of dry weather periods and the formation of the drained surface (Xanthopoulos and Hahn, 1989).

Table 2. 3. The table below gives common environmental pollutants and their various potential effects to receiving waters (source: Author).

Pollutant	Effects on receiving waters
Sediment	✓ Sediments play a vital role in transporting contaminants, when contaminants for example, nutrients from fertilizers are washed off to surface streams, they may cause toxicity and eutrophication (Gobel, 2007). ✓ Sediment can be detrimental to receiving water quality because it causes turbidity, eliminates prey organisms, reduces light penetration, reduces photosynthesis of the aquatic plants, etc. (Luker and Montague, 1994).
Salts & Nutrients	✓ Salts usually occur from road de-icers and they give high salt loading in highway run-off, leading to elevated chloride levels in groundwater. ✓ Nutrients commonly occur from organic matter decomposition, fertiliser, acidic rainfall and other sources. The enrichment of nutrients in water bodies can result in Algal growth (and eventually excessive oxygen demand), light penetration reduction & toxins release which may lead to death of blue-green algae (Luker and Montague, 1994; Novotny and Olem 1994)
Oxygen demanding organics BOD, DOC, TOC	Biodegradable organic materials can enter waters from; plant or animal organic matter, litter, food waste, animal excreta. The process of decomposition may lead to low levels of dissolved oxygen (DO) which may affect aquatic life (Masoud et al., 2012; Novotny and Olem, 1994).
Pathogens	These consist of infectious agents & disease producing organisms which are associated with waste from animal & humans.
Heavy metals	✓ Heavy metals occur in various forms; in sediments, in immiscible liquids, as particles, soluble salts or insoluble compounds. ✓ They can occur chemically as organic or inorganic compounds, and their ionic speciation depends on redox and pH conditions. They are typically more mobile with low run-off ph. ✓ Different metals vary in toxicity; cadmium & lead are of high toxicity, although their use is now in decline. Iron changes water colour but is not a major pollutant, zinc & copper are toxic to fish etc. (Barrett et al., 1999; Gobel 2007).
Hydrocarbons	✓ Insoluble & less dense than water in most cases but heavy fuel oils are denser. They may attach to sediments. Petroleum additive MBTE (Methyl tert-butyl ether) is highly soluble in water whereas, PAHs have higher affinity for suspended particles in water. Some PAHs have known carcinogenic effects. ✓ They give problems of colour, taste & odour making waters unfit for potable abstraction. ✓ Oxidation & microbes degrade hydrocarbons in water, reducing toxicity although the process usually requires oxygen, depending on hydrocarbon type (Maltby et al., 1995; Rothwell et al., 2015; Stuart et al., 2012; Zheng et al. 2014).

2.2.2 Major ions

Major ions are usually present in all recharge waters, although their cation ratios are subjected to change due to ion exchange processes (Barrett et al., 1999). Conservative chemical species (i.e. those retained in water, and not modified by interaction with the aquifer) occur such as sulphate (SO_4), chloride (Cl), ammonium (NH_4), Nitrate (NO_3) and phosphate (PO_4) in rainwater. From major ion chemistry, distinctions between urban and rural environments can be made, heavy metals such as Pb, Zn, Cu, Cd, nickel (Ni), Cr may be present as dissolved substances from non-ferrous metal industry, steel industry, cement industry and vehicle traffic (US-EPA, 1976). Studies have linked vehicular traffic as a main source of environmental pollution and is believed to contain common elements which are possibly toxic (Charlesworth et al., 2003 and Zhu et al., 2008). Acidity (pH) and the electric conductivity (EC), which represents total amount of dissolved ions, show a high value at first flush then decrease (Gobel et al., 2007).

2.2.3 Organic Substances

The main source of organic substances in water run-off is in drip losses from vehicles (such as oils, gasoline, brake fluid, de-icing substances), abrasion of tyres and combustion engine emissions (Maltby et al., 1995). Oils and fuels consist mainly of aromatic and aliphatic hydrocarbons, together with sulfur, oxygen and N compounds (Kirchner, 1986). PAHs are created by inefficient engine combustion and are then transported in gaseous form by the atmosphere. When bound to small particles, they are washed out by rainfall and become pollutants in storm water runoff. PAHs consist of a varying number of benzene rings, and compounds with more than 3 rings are often carcinogenic or mutagenic. (Joneck and Prinz, 1996). PAHs are higher with higher storm water intensity, they occur in rainwater in the form of Naphthalene, flourene, phenanthrene, flouranthene and

benzopyrene. These results were reported in a study by Shu & Hirner, (1997) comparing between rainfall from run-off and roofs in Essen, Germany.

2.2.4 Platinum group elements (PGE) as a potential contaminant in the urban environment.

Platinum group elements were introduced as catalytic converters in the early 1990's to control exhaust emissions of gaseous pollutants such as carbon monoxide and nitrogen oxide from vehicles (Jackson et al., 2007). This has led to the rapid increase in the use of catalytic converters which emit Pt, Rh and Pd (Jackson et al., 2007). There has been an increasing concentration of PGE in the environment ever since their introduction (Zereini et al., (1997); Tuit et al., 2000; Jarvis et al., 2001; Rauch et al., (2005); Sutherland et al., (2008)). There are three main sources of PGE's in the urban environment: Industrial catalysts; pharmaceutical waste; and automobile catalysts. Automobile catalysts recently have become the most common source, using approximately 50% of annual mined PGE's particularly Pt and Pd (Johnson Matthey Plc., (2006) and Jackson et al., (2007)). Various researchers around the world have reported different concentrations of PGE's in the environment (e.g. Farago et al., (1998); Hutchinson et al., (1999); Higney et al., (2002); Ward and Dudding, (2004); Jackson et al., (2007) and Schuster, (2006).

2.3 Potential markers to identify road run-off

2.3.1 Metals

Metals in urban run-off in groundwater come from the source of recharge (Barrett et al., 1999). Several studies have reported the presence of metals (As, Pb, Zn and Fe) in receiving waters (Hvitved-Jacobson and Yousef, 1991 and Perdikaki and Mason, 1998). A study by Rothwell et al., (2015) of gully pot sediments and water around the Manchester city centre, found that some of the metals sampled from gully pots of road run-off have

exceeded the threshold effects level (TEL) when compared to standards. The TEL is the level beyond which the contaminants are believed to be toxic both within the sediment and water. Most commonly, Lead (Pb), Zinc (Zn) and Copper (Cu) have appeared to be present in most studies as persistent heavy metal pollutants in urban runoff. In the current study, a number of potential tracers have been identified from previous studies as presented in Table 2.4. The more regularly present metals have been identified and will be focused on in the current study as tracers.

Table 2. 4. A summarised list of sediment bound and dissolved phase metals showing concentrations beyond effect levels within the urban environments in different studies and their references.

Parameter: Metals (mg/kg) Organics (µg/l)	Mean concentrations average range	TEL-PEL	Reference (Source)
Arsenic	35.4	5.9- 17	Rothwell et al., 2015; Kayhanian et al., 2012
Cadmium	1.59	0.5-3.5	Rothwell et al., 2015; Gobel et al., 2006; Kayhanian et al., 2012
Chromium	103	37- 90	Rothwell et al., 2015; Kayhanian et al., 2012
Zinc	992	123- 315	Rothwell et al., 2015; Gobel et al., 2006; Kayhanian et al., 2012; Brown and Peake, 2006
Copper	231	36-197	Rothwell et al., 2015; Gobel et al., 2006; Kayhanian et al., 2012; Brown and Peake, 2006
Nickel	42	18-35	Rothwell et al., 2015; Kayhanian et al., 2012
Lead	425	35-91	Rothwell et al., 2015; Gobel et al., 2006; Kayhanian et al., 2012; Brown and Peake, 2006

2.3.2 Chlorinated by-products and other Organics

Organic compounds in the form of trihalogenated methanes (THMs) bromodichloromethane, bromoform, chloroform and PAHs (anthracene, naphthalene, benzo (a) pyrene) and trichloromethane (TCM) have been found to be markers of hydrocarbon contamination in several studies. TCM is mostly observed in industrial areas (Barrett et al., 1999). Lerner et al., (1986) investigated the Urban Triassic sandstone aquifer at a shallow level in Birmingham in the UK. Their study found high levels of TCM which was used as a marker to understand where there was infiltration from industrial waste to groundwater. Ford and Tellam, (1994) found similar results to Lerner et al., (1986) and concluded that there was 20-25% leakage from the sewer mains to the aquifer. Nazari et al., (1993) in a study of the Coventry Chalk aquifer (UK) identified widespread pollution by detecting concentrations of chlorinated hydrocarbon solvents (CHSs) in around 28 wells. Concentrations were around 1µg/l to the highest being around 547µg/l. In a more recent study carried out in Manchester, Rothwell et al., (2015) identified the concentrations of PAHs from road run-off in gully pots to be above 90% of quality guidelines in the environment, exceeding the TEL and PEL. The Table 2.5 below presents different studies which have analysed PAHs to be above guideline limits. While Figure 2.5 shows the concentrations of different types of PAHs in Manchester gully pot samples, with dissolved constituents dominated by naphthalene, fluoranthene and pyrene, and sediments dominated by mid- and higher-weight PAHs such as phenanthrene, fluoranthene, pyrene and benzo fluoranthene.

Table 2. 5. Common organic element observed in multiple studies reaching concentrations above threshold levels.

Parameter: Organics (µg/l)	Mean concentrations average range	TEL- PEL	Reference (Source)
PAHs (at least one type)	3800-11300	31-2355	Rothwell et al., 2015; Gobel et al., 2006; Brown and Peake, 2006; Ngabe et al., 2000
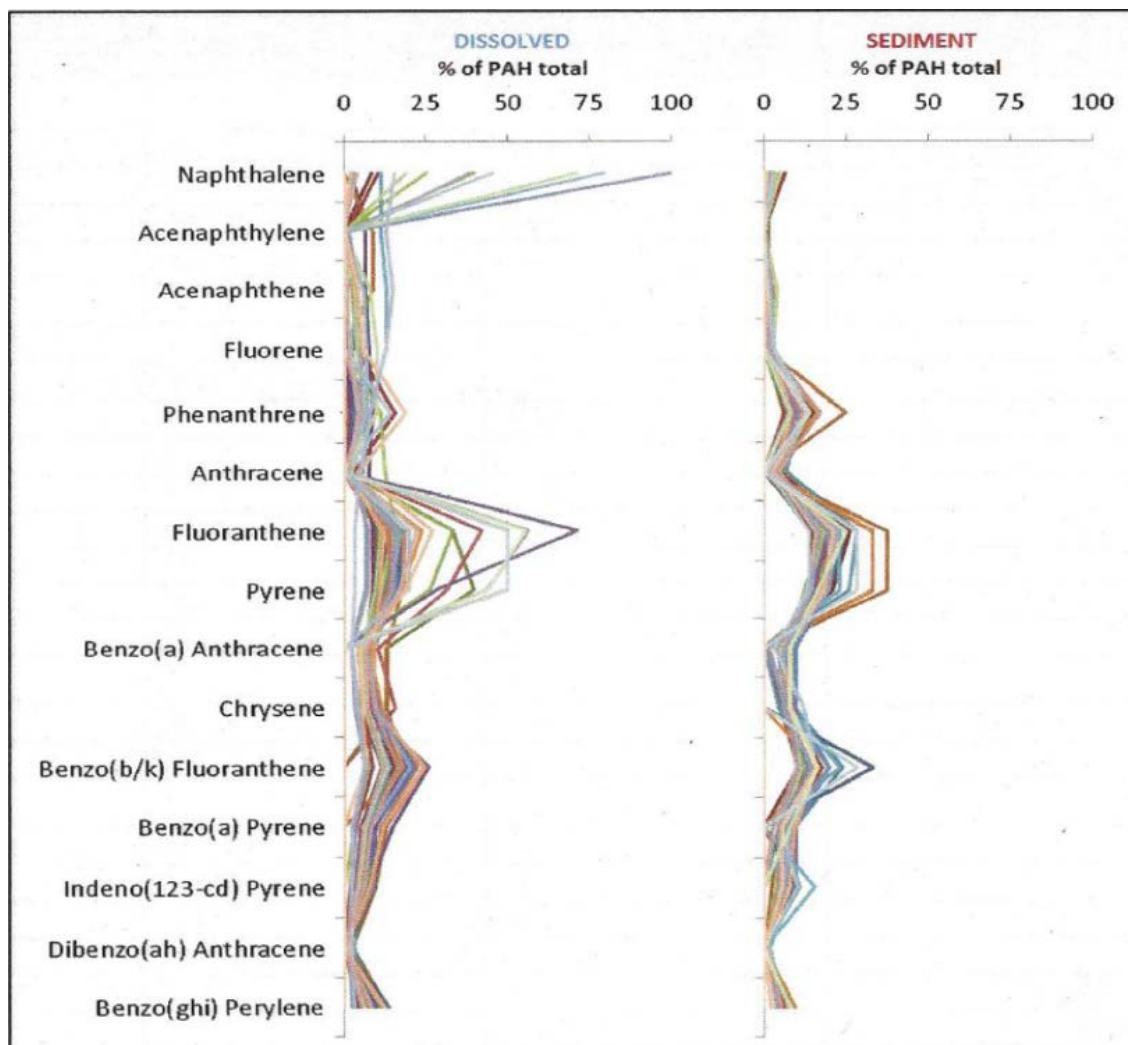
Figure 2. 2. Different forms of PAHs and their concentrations in the Manchester gully pots from Rothwell et al., (2015).

It can be inferred that metals such as As, Pb, Zn, Fe and general organics, particularly, PAHs of different forms are common pollutants from road run-off, while salts like chlorine, bromine etc. can be derived from road run-off of road-salts. Therefore, these will be used as tracers in groundwater to correlate and establish a relationship between the surface and groundwater quality within the area of the current study.

2.4 Vulnerability of the aquifer

It is a key part of this study to understand how vulnerable the Chalk aquifer is to potential pollution from contaminated urban recharge. The unsaturated zone holds the key to understanding the aquifer vulnerability, especially of the Chalk which this study deals with. Two key factors are the travel time of water and contaminants from the surface through the unsaturated zone, and groundwater response time (BGS, 1997) (the concept of the unsaturated and saturated zone flow will be discussed in detail in 2.6.5). An investigation of the water table's response to rainfall was carried out at six sites in the Upper, Middle and Lower Chalk of southern England by Lee et al., (2006). The method used was a cross-correlation of daily time series of rainfall and borehole water level. This was then used to investigate seasonal variations in groundwater-level response times, on a 3-month duration. The time lags (in days) yielding significant correlations were compared with the average unsaturated zone thickness during each 3-month period. The results showed rapid response was observed when the rainfall intensity exceeded 5 mm/day. At some sites, a very rapid response within 24 h of rainfall was observed with unsaturated zone thickness as high as 64 m thick. (BGS, 1997).

A study by Stuart et al., (2005) investigated the fate of agricultural herbicides in the Chalk aquifer groundwater of southern England, using both field and laboratory analysis. The field sampling involved using boreholes to sample regularly for testing isoproturon, chlortoluron and atrazine, which were used as markers. Results showed concentrations

above the EU drinking water standard of $0.1\mu g \, l^{-1}$. They concluded that this was associated with localized 'point' usage or disposal, often combined with more rapid preferential flow pathways to the water table (saturated zone). This backs up the earlier study by Lee et al., (2006) and gives further evidence of the vulnerability of the Chalk aquifer groundwater.

2.5 The Chalk: lithology, composition and aquifer properties

2.5.1 Description, lithology and composition

The Chalk was deposited during the exceptionally high sea levels of the late Cretaceous period. At the time there was limited continental erosion, which aided in the deposition of purely chalk (calcite) (Downing, 1993). Chalk is pure white in colour and has a soft texture. It comprises chiefly of white limestone formed of shell fragments, fine grained coccoliths and foraminifera of sizes less than $3\mu m$, and small fragments of clay minerals and biogenic materials (Mortimore and Fielding, 1990). (Allen et al., 1997) described the Chalk as a very fine grained, bioclastic (algal skeletal) pelagic deposit., The Chalk changes composition and colour going up through the stratigraphic column, from Grey to pure white Chalk, due to a decrease in clay content. A chalk depositional history interrupted by formation of marls, which are clay-rich layers of chalks, with the clays being of volcanic and detrital origin, also characterise the Chalk (Wray and Gale, 1993; Mortimore et al., 2001). Another very common feature in the Chalk is the layering by a hard siliceous material called flint. These are aligned parallel to the Chalk's bedding (Jones et al., 1999).

2.5.2 Chalk post-depositional history

During the late Palaeogene, when drainage systems developed towards the North Sea, large areas of the Chalk aquifer were eroded (Ellison et al., 2004). The Anglian and Devensian glacial periods later saw alterations of the Chalk fabric at near surface, mainly around <20

m. The glacial periods had marked effects on the Chalk with ice-wedges and patterned ground being the evidence. The freeze-thaw cycles produce a weathered mantle consisting of highly fractured Chalk. This was a near surface process, usually within the top 5-6 m (Morton, 1982).

Sea levels fell during the glacial periods to around 120- 150 m below present levels which lead to development of offshore drainage systems on the continental shelf (Belamy, 1995). During the interglacial periods, the sea levels rose above present levels, which is evidenced by the presence of raised beach deposits along the Sussex coast (Bates et al., 1998). The water level changes in the aquifer led to flow paths which in turn may have been responsible for dissolution within the chalk both above and below present water levels (Mortimore, 2000).

2.5.3 Stratigraphy of the Chalk aquifer

The classification of the Chalk has been attempted by several authors (Price et al., 1977, Jukes-Browne and Hill, 1900, Jarvis and Woodroof, 1984, Robinson, 1986, Mortimore and Pomerol, 1987, Bristow et al., and Rawson et al., 2001). The Chalk group has been divided into three subgroups (Upper, Middle and Lower Chalk) (Bristow et al., 1997) and has been inferred to have been deposited in two separate lithological provinces (Northern and Southern Provinces) (Brenchley et al., 2006). The current study employs the revised Chalk stratigraphy of Bristow et al., 1997. A description of the chalk subgroups will give a more detailed idea of the Chalk, starting from the Lower Chalk. The Lower Chalk is divided into two members, namely the West Melbury and Marly Chalk. They are rich in clay and marl layers hence also called the Grey Chalk subgroup. The Lower Chalk also contains the Plenus Marls, the top of which acts as a stratigraphic marker bed, separating the Grey Chalk subgroup from the White Chalk subgroup. Generally, the Lower Chalk is rich in terrigenous sediments and has a very low content of flints. The middle Chalk is divided

into Holywell Nodular Chalk and New Pit Chalk, it is not characterised by the presence of any flints. Both the middle and upper Chalk subgroups are also known as the White Chalk subgroup. The Upper Chalk is characterised by the presence of flints and divided into 7 members. Hydrogeological works have mostly used the traditional classification. However, the most recent and more widely accepted is the Bristow et al., (1997) classification due its simplification and further sub-division according to composition. 2.3 summarises both traditional and recent classifications of the Chalk stratigraphy.
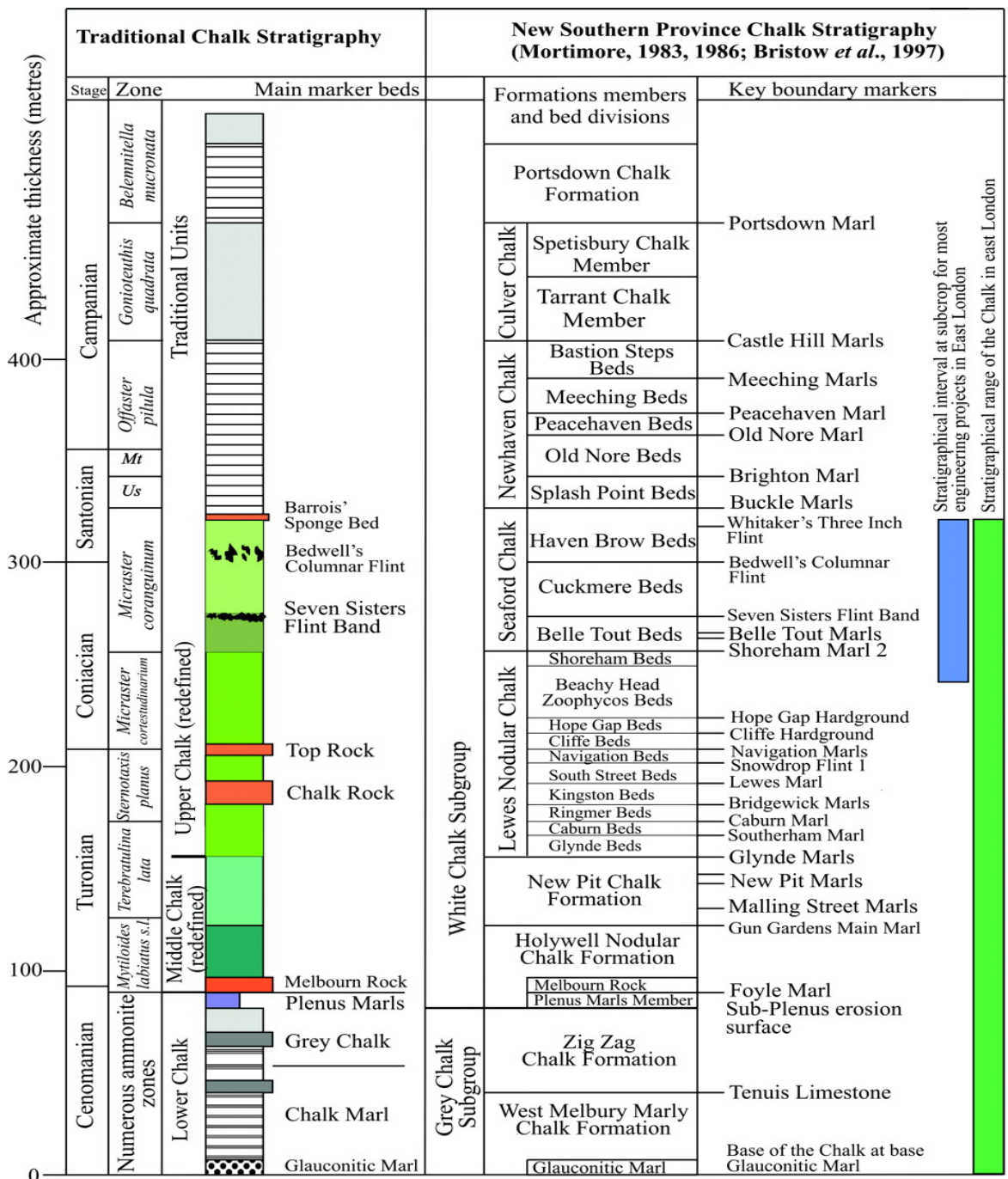
Figure 2. 3. Chalk stratigraphy showing modifications from Mortimore 1983, 1986a, b and Bristow et al., 1997. (Modified by Rawson et al., 2001).

2.5.4 The Chalk's aquifer properties (porosity and permeability).

The Chalk serves as an important source of groundwater in North Western Europe, and particularly, Britain (Downing, 1993, Brouyere et al., 2004 and Ireson et al., 2009). In the UK, the Chalk covers a wide area of about 21,500 km^2 (Downing, 1993). About 70% of

total water consumption in the South East of England comes from the Chalk aquifer groundwater resource. This area is characterised by a high population density and relatively low rainfall (Price et al., 1993 and Ireson et al., 2009). More specific to this study, in Brighton, about 98% of the total water supply in the city comes from the Chalk (Mortimore, 2011). As described in the introduction, the Chalk is a dual porosity system, with porosity occurring within matrix blocks, and as solution widened fractures. The Chalk is characterised by high primary matrix porosity of 20-45% and low permeability of about 0.5µm throat diameter (Oakes, 1977; Price et al., 1976; Price et al., 1993). Secondary porosity in the fractures is enhanced by dissolution and has a high permeability with low porosity (Lewis et al., 1993). A diagrammatic illustration of fracture and matrix porosity is given in Figure 2.4.
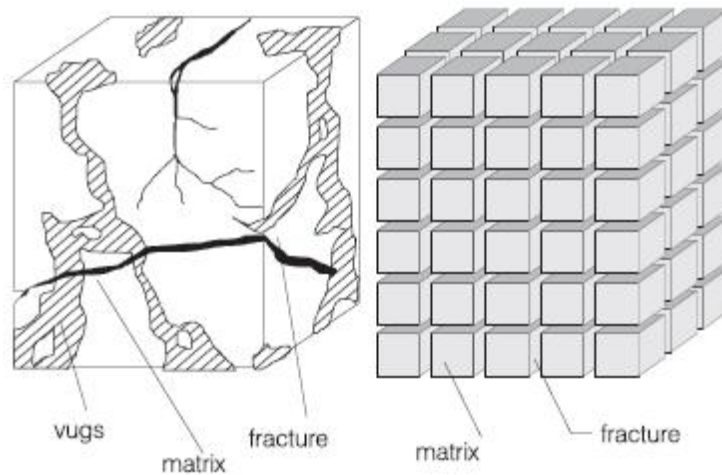
Figure 2. 4. Diagrammatic representation of a typical dual porosity and permeability in Chalk. Matrix porosity and fracture porosity (modified from Warren & Root, 1963).

Variations in the hydraulic properties of the Chalk are dependent upon its structure, weathering and depositional history. For example, weathering during the Palaeogene to Quaternary periods on the Chalk resulted in fracturing of the Chalk and therefore increased hydraulic flow rate. In the last post-glacial recession, the Chalk region had higher precipitation and recharge than present. Areas of enhanced permeability have developed

above the present day ground water level. With these, the Chalk is likely to display heterogeneous characteristics (Hancock, 1975; Ireson, 2008). The development of significant permeability is mainly restricted to the upper part of the aquifer, particularly along bedding planes (Molyneux 2012). Therefore, regardless that the Chalk sequence is around 300 m thick, it has only 30-60 m effective aquifer thickness.

In the saturated zone, the understanding is that fractures give high transmissivity to the Chalk. As a result, the saturated Chalk works as a classic dual porosity system (2.4). The fractures give it an interconnected porosity system while the matrix provides storage. In the unsaturated zone, however, it is less likely that the fractures will hold and transmit water against pore water suction in the adjacent matrix (Ireson, 2008). In essence, it displays a dual permeability system where gravity driven flow is developed in the matrix and fractures.

2.5.5 General theory and principle of flow processes in the unsaturated zone

This section reviews current knowledge on the natural processes that take place within the unsaturated zone plus theoretical assumptions used to conceptualise the processes from previous literature. The unsaturated zone is defined by pore water pressure. The water table marks the top of the fully saturated zone. However, the zone above this may still have pores completely filled with water under capillary forces (i.e. at less than atmospheric pressure). Hence the water table is defined as the surface at which water pressure equals atmospheric pressure.

The pressure head ψ, at the water table is zero. Below the water table, pressure head ψ becomes greater than zero because hydrostatic pressure is now positive. Above the water table, the pressure head is defined to be less than zero as a result of the fact that water is held in pore structures under tension by the surface tension force (Andrew, 2006). Flow (in

the saturated and unsaturated zone) occurs due to difference in hydraulic head (head) defined as the potential energy per unit weight.

Total hydraulic head is considered to be equal to summation of three components, elevation head, velocity head and pressure head. Velocity of water in the unsaturated zone is usually very slow, and as such, the velocity head is neglected and the total head, H is considered to be equal to the sum of the elevation head, h_z and pressure head, ψ.

$$H = h_z + \psi \qquad\qquad (2.1)$$

Pressure head is most commonly referred to as matric potential in relation to the unsaturated zone (Mullins, 2001; Ireson, 2006; Molyneux, 2012). This study will also use the term matric potential with symbol ψ and units will be quoted in m H_2O or m (1 m H_2O = 9.81 kPa).

If evapotranspiration and infiltration do not take place in the unsaturated zone profile for a period of time, the water within the profile will redistribute including an exchange between the saturated and unsaturated zone (Smith et al., 1970). This is due to dissipation of hydraulic gradient. If the period persists long enough, the profile will eventually reach static equilibrium (hydrostatic condition). By considering a hydrostatic profile of an idealised homogenous granular aquifer, predictions of distribution of head and storage components within the profile can be made. To define this we say, the elevation head increases with elevation with a gradient of +1 therefore the pressure head must decrease with a gradient of -1. (Price et al, 1993). This explanation is illustrated in 2.5.
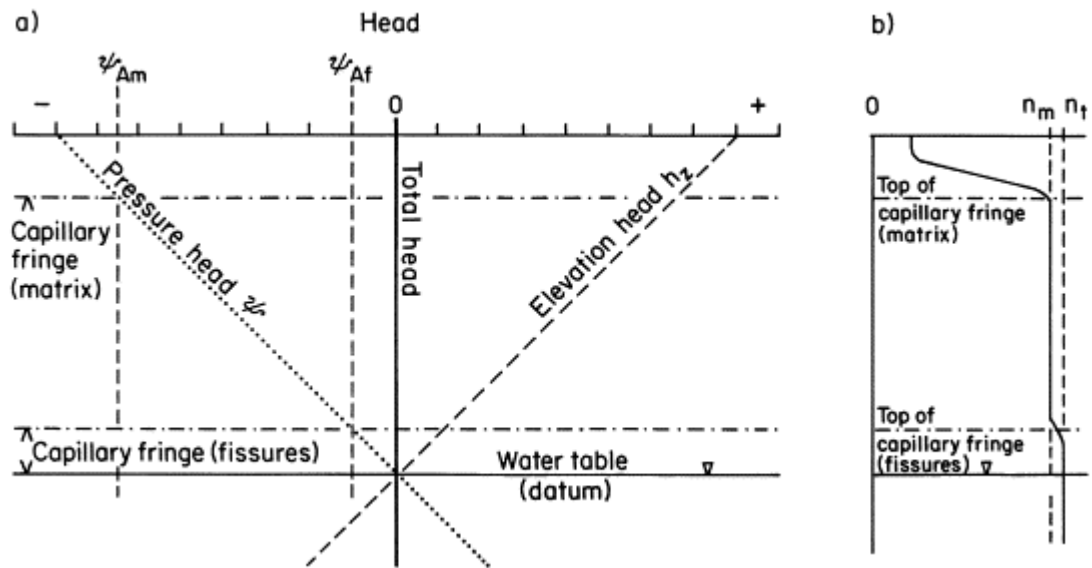
Figure 2. 5. Theoretical relationship between head, depth and water content in the unsaturated zone, after drainage to equilibrium (hydrostatic condition) (Price et al., 1993).

Hydrostatic conditions are rarely achieved in reality, due to the constant addition and removal of water from the profile by evapotranspiration and infiltration. Infiltration is mostly by rainfall which often leads to a change in the head profile and the water content profile. Figure 2.6 represents a hydrostatic scenario. 2.7 illustrates the theoretical sequence of the effects of infiltration or evapotranspiration in a homogeneous granular aquifer. The concept here is for a zero flux plane (ZFP) which has two conditions, the convergent (CZFP) and divergent (DZFP). In the state of a DZFP, water above the plane moves upward and below the plane moves downward. Hence no water moves towards the ZFP. Contrariwise, in the case of a CZFP, water below the plane moves upward but does not go across the ZFP. Likewise water above plane moves downward but not across the ZFP too (Price et al, 1993).
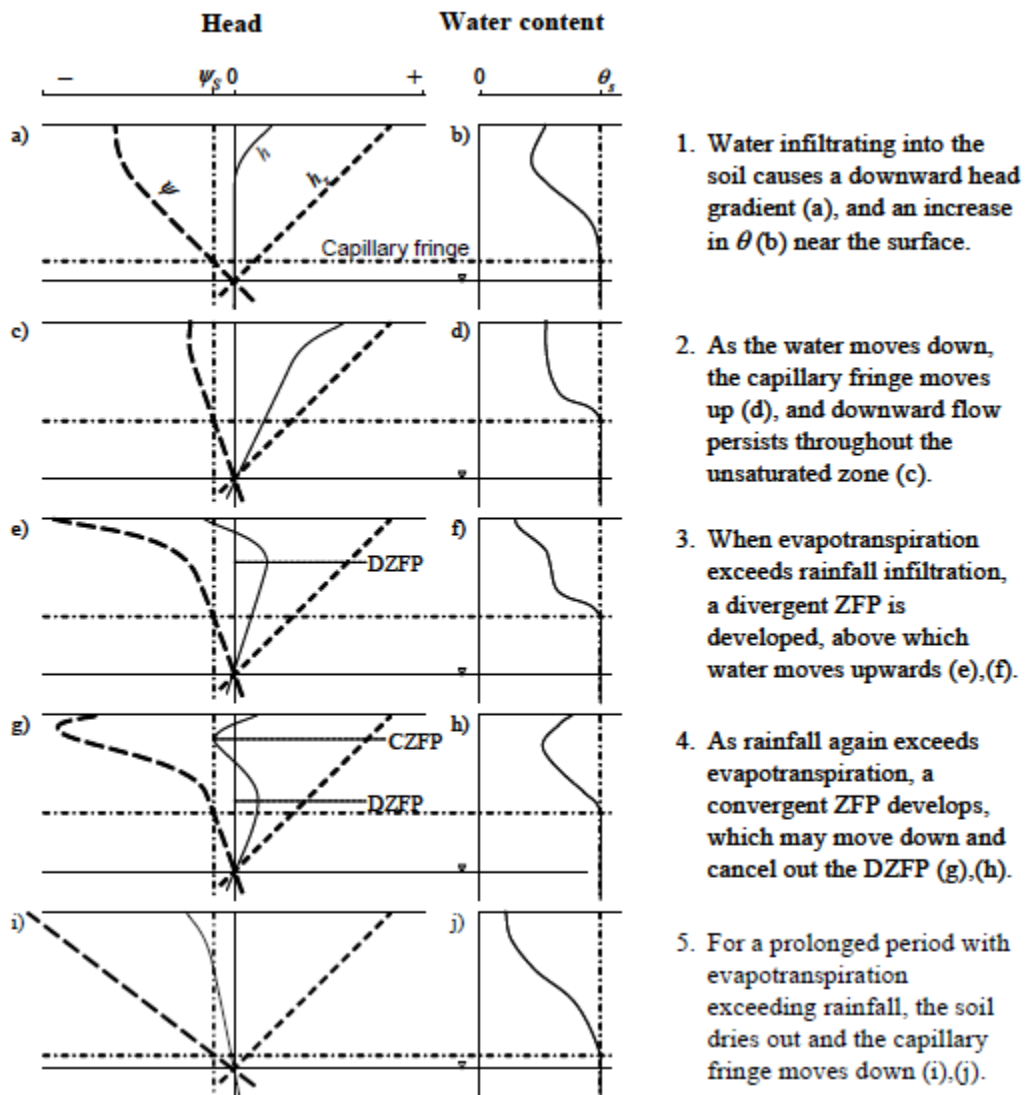
Figure 2. 6. Theoretical relationship between head, water content against depth in the unsaturated zone above fixed water table during infiltration and evapotranspiration (Price et al., 1993).
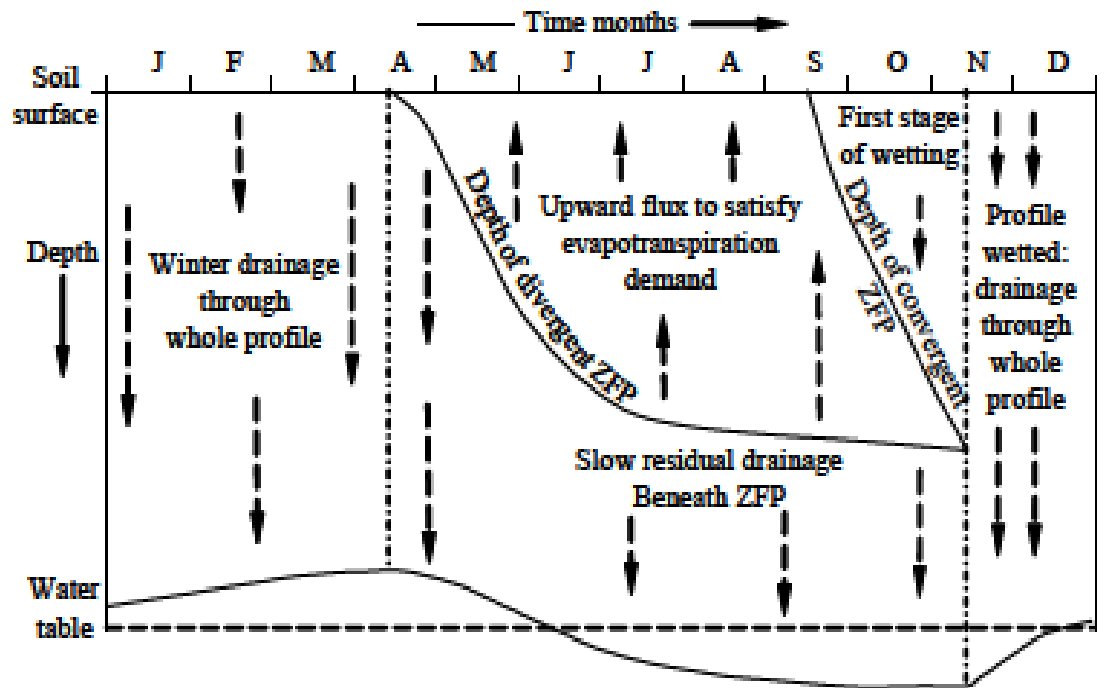
Figure 2. 7. Seasonal partition of water flux planes models within the unsaturated zone of the Chalk (Wellings and Bell, 1980).

2.5.6 Flow in the unsaturated zone

Above the water table (saturation zone) lies the capillary fringe. The pore spaces within the capillary fringe are fully saturated but have a negative matric potential. The capillary fringe exists because the pore space does not drain until pore pressure rises above a limiting value. The pore pressure in this case is known as air-entry pressure (bubbling pressure) and has a corresponding matric potential ψ_s (Hillel, 2004). Figure 2.8 is a diagram that illustrates the idea of capillary rise, which is caused by surface tension of the air-water interface and the molecular attraction of liquid and solid phases, it is often mathematically represented as:

$$\psi_s = \frac{2\gamma\cos r}{\rho\omega g R} \tag{2.2}$$

Where:

ψ_s is the air-entry matric potential (air- entry pressure from Price et al., 1993), which is equal to the negative height of capillary rise (m).

γ Is the surface tension of the fluid (kg s^{-1})

r is contact angle of the meniscus with the capillary tube (degrees).

$\rho\omega$ Is the density of fluid (kg m^{-3})

g Acceleration due to gravity (m s^{-2})

R is the radius of capillary tube (m).

For water at 18°C, γ is 0.073 kg s^{-1}. The smaller the radius of the capillary tube, the greater the height of the capillary rise, and matric potential is more negative. This theory is applicable to soils with the assumption that the pore spaces will act as a capillary tubes. Hence, the soils with the finer pore spaces will develop larger capillary rise, and therefore have a thicker capillary fringe.
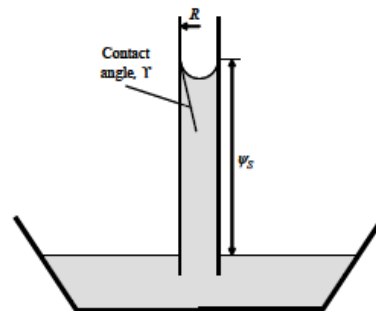
Figure 2. 8. A diagram showing how water rises in a capillary tube (Fetter 1994).

As elevation increases above the capillary fringe, the pressure head decreases. Thus, the fraction of the pore space that can hold water under capillary forces also decreases. Slow decrease in pressure (i.e. increase in tension) results in emptying of progressively smaller pores, until at high suction, where only the very narrow pores retain water. 2.9. illustrates a conceptual diagram with the one in the middle showing partial saturation in soil where the

larger pore spaces are drained, while the smaller pore spaces retain water between the soil granules.
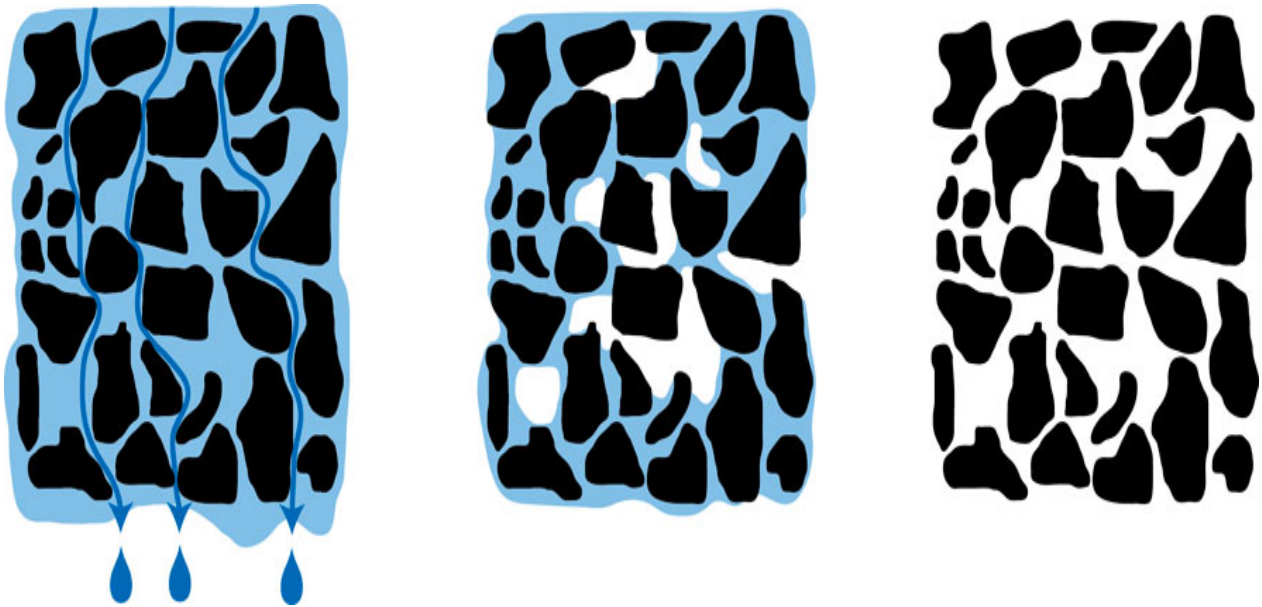
Figure 2. 9. Example of full saturation, partial and a completely dry sample.

This forms the basic idea behind the Soil Moisture Characteristic (SMC - sometimes referred to as water retention function) that is the relationship between the water content θ, matric potential ψ and unsaturated hydraulic conductivity. Figure 2.10 shows SMC curves for two different soils. It can be seen clearly that due to the fine pores of the clay soil, the decrease in wetness is gradual. In the sandy soils which have larger pores, the water empties at a relatively low suction. When the soil is compacted, the porosity is reduced, large pores decreased, and volume of medium size pores increase (Hillel, 1998).
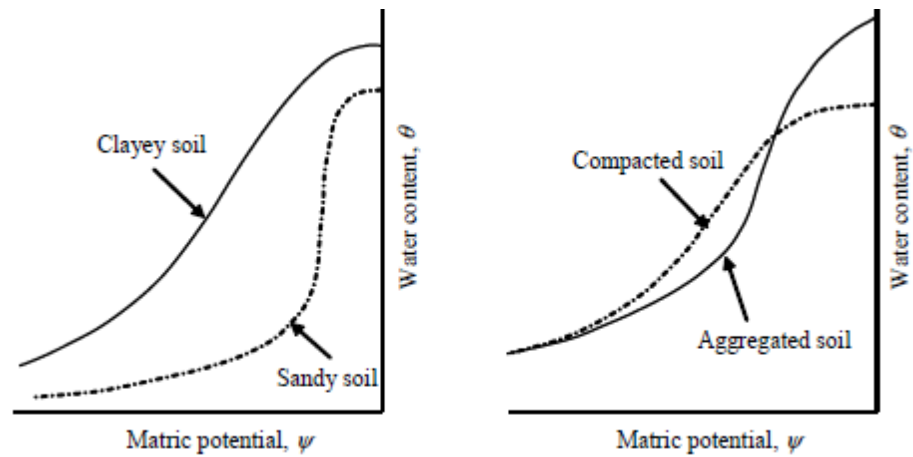
Figure 2. 10. Soil moisture characteristics curves for different soil textures and structures (modified after Hillel, 1998).

Haines, (1930) & Richard, (1941) reported that the SMC is hysteretic. This means that the relationship between the matric potential ψ and water content θ depends on history and the direction of the changes (Hillel, 2004).

2.5.7 Hydraulic conductivity in the unsaturated zone

The constant of proportionality between the volume of flow through a porous medium and the hydraulic gradient across it, is known as hydraulic conductivity, (K). It is characteristic of both solid and fluid phases and is specific to the movement of water. Hydraulic conductivity is the ability of water to travel through a medium under applied hydraulic gradient (Zimmerman et al., 1996). This idea was firstly introduced by Henry Darcy (1856) for the saturated zone of an aquifer. It is known as Darcy's law. The idea was later used for unsaturated hydraulic conductivity (Ireson et al., 2009). When soil pore space is saturated, the water filled pores are constant. As the soil desaturates, some of these pores become air filled such that the conductive space in the pore becomes occupied. Similarly, as suction develops, the larger pore become the first to empty and are the most conductive. In unsaturated soils, water flow occurs in different ways, either as film creep along the walls

of wide pores or as tube flow through narrow filled water-filled pores. Although both types of flow may occur simultaneously or jointly in areas within soil (Hillel, 1998).

Measuring either saturated hydraulic conductivity (K_s), or the unsaturated hydraulic conductivity K (ψ) directly under field conditions is difficult. As such, a monitoring laboratory method is often used to calculate the changes in water level θ over time or to monitor the hydraulic conductivity ψ changes in head gradient. Laboratory methods can be an ideal way of studying the hydraulic conductivity of the Chalk (Brouyère et al, 2004). A good and straightforward method in calculating unsaturated hydraulic conductivity is under steady state flow conditions. The method is not widely used because of wettability, is gravity driven and hence very slow. Wettability can be defined as "*the tendency of one fluid to spread on or adhere to solid surface in the presence of other immiscible fluids*" (Honarpour et al., 1986).

Cooper et al., (1990) used a steady state flow condition to measure the hydraulic conductivity of the unsaturated zone under imposed conditions in the Chalk. Steady state conditions can be achieved in core-flooding experiments within a short space of time.

Some methods have been successfully used to calculate K (ψ) (hydraulic conductivity as a function of matric potential) in the field, by imposing artificial hydrological conditions on field instrumentation as described by Cooper et al. (1990). Ireson et al. (2006) on the other hand used inverse techniques, which were based on monitoring a natural system and modelling it to infer parameter values. Some of these methods have been successful, but overall the understanding between laboratory data, field results in relation to modelling data is still not very clearly defined.

2.5.8 Mathematical representation of flow in the unsaturated zone

Darcy's law best describes flow in the unsaturated zone, which occurs with response to a hydraulic head gradient, as in the saturated zone. This is represented in Darcy's law:

$$qz = Kz\frac{dh}{dz} \qquad (2.3)$$

Where qz is the specific discharge, or Darcian velocity.

Kz Is hydraulic conductivity and $\frac{dh}{dz}$ is the hydraulic head gradient (all in the z direction). Consider a unit volume of porous media .the law of conservation of mass for steady-state flow requires that the mass flow into the volume is equal to the mass flow out of the volume, with assumption that flow is negligible in the horizontal. Hence:

Mass Inflow – Mass Outflow = 0

$$\rho\omega qz - \left(\rho\omega qz + \frac{\partial}{\partial z}(\rho\omega qz)\right) = 0$$

$$-\frac{\partial}{\partial z}(\rho\omega qz) = 0 \qquad (2.4)$$

For transient conditions, the continuity condition will include a term for the change in storage within the control volume. In saturated conditions, it is given by change in head over time multiplied by the density of water and specific storage, Ss which is the volume of water released for a unit drop in head. With the inclusion, the continuity equation therefore becomes:

$$-\frac{\partial}{\partial z}(\rho\omega qz) = \rho\omega Ss\,\frac{\partial h}{\partial t} \qquad (2.5)$$

If the chain rule is used, Darcy's law equation will be:

$$\frac{\partial}{\partial z}\left(Kz\frac{\partial}{\partial z}\right) = Ss\frac{\partial h}{\partial t} \qquad (2.6)$$

When the aquifer is not fully saturated, the term for the change in storage is represented by the change in water content over time and the hydraulic conductivity varies as a function of the matric potential. The continuity equation for the unsaturated zone is:

$$\frac{\partial}{\partial z}\left(K(\psi)(\frac{\partial \psi}{\partial z}-1)\right) = \frac{\partial \psi}{\partial t} \qquad (2.7)$$

Introducing specific capacity, c (ψ), which is now Richards's equation and can be written as:

$$\frac{\partial}{\partial z}\left(K(\psi)(\frac{\partial \psi}{\partial z}-1)\right) = c(\psi)\frac{\partial \psi}{\partial t}$$

$$(2.8)$$

These equations form the foundations of the flow process in the unsaturated zone in the context of the present study or any unsaturated flow study from Ireson et al. (2009).

2.6 Presence and distribution of hydrocarbons in the Chalk aquifer

Hydrocarbons are organic compounds which are known to be toxic and have caused global concerns over water pollution (Manoli and Samara, 1999). Receiving waters such as lakes, rivers, ponds, streams and groundwater may be effected by hydrocarbon pollution derived from sewage effluents, industrial effluents and urban and rural run-off. This study is concerned particularly with urban run-off derived hydrocarbons, (see section 2.2 above for more detail). Hydrocarbons occur in different forms in the environment, and are often grouped based on source or chemical characteristics for analytical or descriptive purposes, e.g. as Total petroleum hydrocarbons (TPH), as polycyclic aromatic hydrocarbons (PAH).

Polycyclic aromatic hydrocarbons (PAH) have a very frequent occurrence in the environment as pollutants (Maltby et al., 1994; Gobel et al., 2006 and Stuart et al., 2012).

PAHs have been reported to be carcinogenic, as a result, a number of PAHs are included in the US EPA and EU priority pollutant list, Table 2.6. (Pufulete et al., 2004). PAHs are fused compounds built on benzene rings. When a pair of carbon atoms is shared, then the two sharing aromatic rings are considered fused. The resulting structure is a molecule where all carbon and hydrogen atoms lie in one plane (Moore and Ramamoorthy, 1986 and Manoli and Samara, 1999). The environmentally significant PAHs range between naphthalene ($C_{10}H_8$) and coronene ($C_{24}H_{12}$). In this range, there are a large number of PAHs differing in the number and position of aromatic rings, with varying number, position and eventual chemistry of substituents on the basic ring system. Physical and chemical properties of PAHs vary with molecular weight (Moore and Ramamoorthy, 1986 and Manoli and Samara, 1999).

Table 2. 6. US EPA table, showing types of PAHs and possible carcinogens to humans amongst them. (From Manoli and Samara, 1999). Note: 2A/B2 Probably carcinogenic to humans/Probable human carcinogen; 2B: Possibly carcinogenic to humans; 3: Not classifiable as to human carcinogenicity; Blank: Not tested for human carcinogenicity. *IARC: International Agency for Research on Cancer; US EPA: US Environmental Protection Agency.

PAHs	Structure	Vapor Pressure (Torr)	Solubility in Water (mg L^{-1})	K_{ow}	Carcinogenic potency IARC/US EPA* classification
Acenaphthene, Ace		10^{-3}-10^{-2} at 20°C	3.4 at 25°C	21000	
Acenaphthylene, Acy		10^{-3}-10^{-2} at 20°C	3.93	12000	
Fluorene, F		10^{-3}-10^{-2} at 20°C	1.9	15000	
Naphthalene, Np		0.0492	32	2300	
Anthracene, An		2×10^{-4} at 20°C	0.05-0.07 at 25°C	28000	3
Fluoranthene, Fl		10^{-6} to 10^{-4} at 20°C	0.26 at 25°C	340000	3
Phenanthrene, Ph		6.8×10^{-4} at 20°C	1.0-1.3 at 25°C	29000	3
Benzo[α]anthracene, B[α]An		5×10^{-9} at 20°C	0.01 at 25°C	4×10^5	2A/B2
Benzo[b]fluoranthene, B[b]Fl		10^{-11} to 10^{-6} at 20°C	-	4×10^6	2B/B2
Benzo[k]fluoranthene, B[k]Fl		9.6×10^{-7} at 20°C	-	7×10^6	2B
Chrysene, Chry		10^{-11} to 10^{-6} at 20°C	0.002 at 25°C	4×10^5	3/B2
Pyrene, Py		6.9×10^{-9} at 20°C	0.14 at 25°C	2×10^5	3
Benzo[ghi]perylene, B[ghi]Pe		~10^{-10}	0.00026 at 25°C	10^7	3
Benzo[α]pyrene, B[α]Py		5×10^{-9}	0.0038 at 25°C	10^6	2A/B2
Dibenzo[α,h]anthracene, dB[α,h]An		~10^{-10}	0.0005 at 25°C	10^6	2A/B2
Indeno[1,2,3-cd]pyrene, I[1,2,3-cd]Py		~10^{-10}		5×10^7	2B/B2

2.6.1 Determining hydrocarbons in water

To determine hydrocarbons in water needs the employment of a reliable analytical procedure, a detailed method of validation and careful evaluation to provide reliable results. In order to define quantitatively the accuracy and precision of the procedure for each determinant, it is important to statistically estimate random and systematic errors. In addition, sampling and sample preparation should be considered essentially with the description of an analytical procedure, an area too often neglected. Currently, the analysis of natural waters for organic pollutants has been developed to standard, but the complexity

of the samples and concentration levels continue to promote research interest, frequently

aiming to achieving more convenient and cost-effective methods. The choice of analytical

tool also depends on concentration levels. Different methods for measuring PAHs have

been suggested (2.7) by Manoli and Samara, (1999) due to their availability and toxicity.

Table 2. 7. Summary of analytical methods for determining PAHs in water, (modified from Manoli and Samara, 1999).

Recovery	Clean up	Determination
• Liquid-liquid extraction (LLE) • Solid Phase extraction (SPE) • Solid Phase Microextraction • Immunosolvents	• Solid phase extraction • Classical column adsorption • High pressure liquid chromatography • Immunosorbents	• Gas Chromatography (GC) with Flame Ionisation Detector (FID) or Mass Spectrometry Detector (MSD) • High Pressure Liquid Chromatography (HPLC) with Ultraviolet Detector (UVD), Flourometric Detector (FMD), Mass Spectrometry Detector (MSD), Photodiode-Array Detector (PDA) • Supercritical Fluid Chromatography with Ultraviolet Detector (UVD), Mass Spectrometry Detector (MSD). (US-EPA-1988)

2.6.2 The fate of hydrocarbons in the aquifer

The presence of hydrocarbons within an aquifer is detrimental to the quality of the water

within the aquifer. Many different remediation techniques have since been used to

eliminate unwanted contaminants from underground water sources. Natural attenuation

processes became an area of interest in the early 1990s in the United States, before

eventually becoming widely accepted in Europe and other parts as a means of remediation.

The United States Environment Protection Agency (US EPA, 1988) gave definition for

natural attenuation as: *"Natural attenuation process refer to a variety of physical,*

chemical, or biological mechanisms such as biodegradation, dispersion, dilution, sorption, volatilisation and biochemical stabilisation that act favourably without human intervention, in order to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil and groundwater"

The use of a natural attenuation process as a valid option to remediate contaminants in a contaminated site is termed Monitored natural attenuation (MNA to be used from this point onwards). In the United Kingdom (UK) MNA is accepted as a remediation technique within the prevailing legal framework. Legislation regarding remediation of contaminated land and groundwater is regulated by the Environment Act from 1990 and revised in 1995 Amendment of the Environment Act (Declercq, et al. 2012). Where additional interventions are applied to stimulate contaminant breakdown or control contaminant transport (e.g. through enhancing biological activity, hydraulic control or using reactive underground barriers) then this remedial option is termed enhanced monitored natural attenuation (EMNA).

MNA and two methods of biostimulation were compared in a laboratory incubation to degrade TPH in a diesel-contaminated Tarpley clay soil with a low carbon content. The final results showed that the bio-stimulation methods degraded about 96% of the total TPH content and MNA degraded about 94% of original TPH (D. Sarkar et al. 2004). However, in other research, it was found that benzene present in a borehole limited bacteria activity (Fahy, 2003 PhD). This is significant in that bacteria are a major component in the alteration of the chemical structure of the contaminant during natural attenuation (Bleckmann et al., 2000). There is a clear evidence nonetheless that MNA is feasible in attenuating organics in the environment. Nevertheless, care should be taken as to the prevailing conditions, such as what type of soil is present, or what are the pH conditions of the water.

Karen (2013) carried out an investigative study to confirm the natural attenuation of synthetic Isoproturon (Isoproturon is a selective, systemic herbicide used in the control of annual grasses and broadleaved weeds in cereals) and sulphanilamide (SULPH)) organics in groundwater of the chalk aquifer using three processes: by analyzing the data history of a monitoring site as evidence of biodegradation to a contaminated site; using an in-situ microcosm approach determining the catabolic activity present across the site using ex-situ microcosm studies that replicate in-situ aquifer conditions and, identifying and quantifying biodegradation in the aquifer using compound specific isotope analysis.

Results for the different methods showed that for historical data, only 2% of IPU has undergone biodegradation, microcosm and historical data showed about 50% of SULPH had undergone biodegradation while the newly developed isotope analysis showed around 56% of biodegradation. Overall, there is evidence of natural attenuation taking place underground. However, this cannot be completely relied upon, as the contaminants in this case are synthetic organics and may be easily degradable as compared to natural organics. But it gives an idea that natural attenuation takes place in the chalk aquifers.

2.7 Heavy metals in groundwater

The presence of heavy metals in the environment is usually as a result of a wide range of anthropogenic sources (refer back to 2.2 and 2.2.1 for further details regarding sources of heavy metals in the environment) (Niragu, 1991). Heavy metal concentration does not determine heavy metal availability in either soils or water. Rather, the heavy metal speciation determines environmental behaviour (Bourg, 1995). For example, in a soil type environment, sorption is the dominant removal process. In which case, pollution arises when heavy metals are mobilised into a solution and transported to groundwater (Sherene, 2010). Speciation is the distribution of a metal within its different chemical forms and species.

Different processes of geochemical speciation within dissolved and solid phases. The distribution of heavy metals within the various metal species as seen in Figure 2.11 is the end result of different heterogeneous behaviours and dissolved chemical reactions that have taken place (Bourg, 1993).
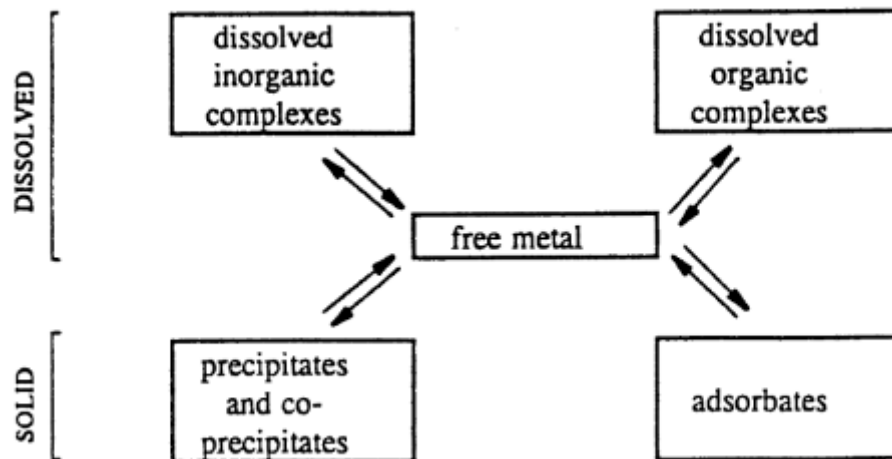
Figure 2. 11. The interchangeable phases of geochemical speciation (Bourg, 1995).

2.7.1 Solubility of heavy metal pollutants

Solubility of heavy metals can either be increased or decreased as a result of ongoing processes in the soils. Factors such as hydrolysis and dissolved complexation tend to enhance solubility, while precipitation and adsorption delay the availability of heavy metals to become mobile (Bourg, 1995). In a porous medium, precipitation of solids such as silicates, phosphates, sulphides or carbonates hinders the solubility of metals (Nriagu, 1974) Figure 2.12 explains the role of pH and Eh in solubility. Aquifer mineral surfaces often adsorb metals and reduce solubility.
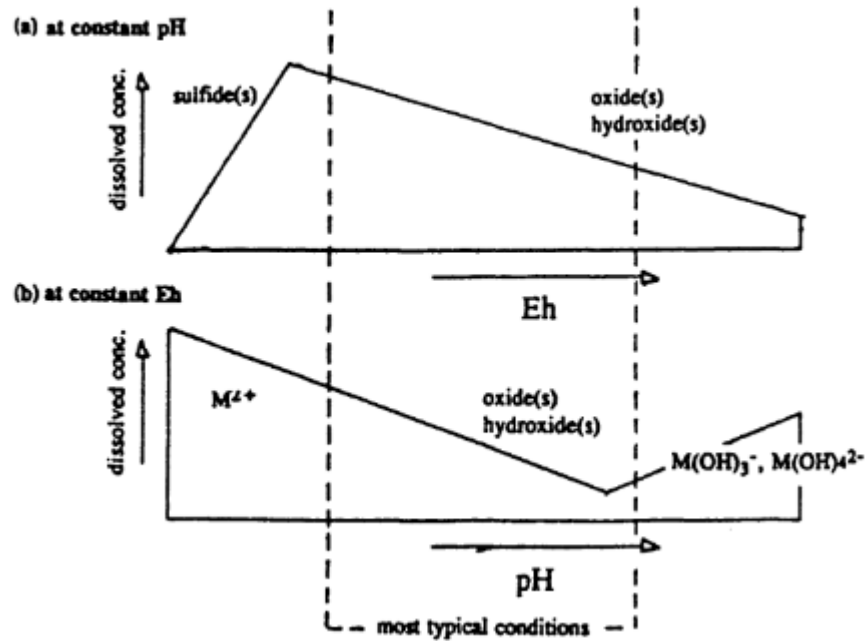
Figure 2. 12. A diagrammatic expression of the effect of pH and Eh on the solubility of metals (Bourg, 1995).

2.7.2 Mobility of heavy metal pollutants

The mobility of heavy metals depends on interactions between solid and aqueous phases, heterogeneous chemical reactions and the phenomena of particle coagulation and flocculation (Bourg, 1995). This can take place within natural conditions, in which case water flows through a heterogeneous aquifer and reacts to the chemical and biological changes encountered. However, this can also be induced. Metal mobility is highly influenced by the pH, redox conditions and presence of organics. It has generally been described that neutral or slightly high (alkaline conditions) pH values effect very little the mobility of heavy metals (Sherene, 2010). The effect of pH on metal solubility can be seen in Figure 2.12. Thus, high pH values increases sorption in heavy metals.

However, a decrease in pH showed an increase in heavy metal mobility. Sebestian, (1998) reported that lead (Pb) solubility increased drastically in a soil solution when the pH was

reduced from 6 to 3 which displayed a clear relationship between Pb mobility in soil and pH. The presence of organic matter influences the continuous retention of metals in soil, decreasing heavy metal mobility, which is heavily influenced by pH. (Carillo et al., 2000). Naidu & Harter, (1998) looking at Cd mobility in farms realised that recycling of plant residue over time was restricting Cd mobilisation by forming a metal-ligand complex with stability that is controlled by pH. Ionic strength, soil texture (a function of particle size distribution), and pore structure of the soil, which can be evaluated using bulk density, also play a significant role in the mobility of heavy metals in soils and groundwater.

2.8 Case studies on flow and transport in the Chalk

Studies have been carried out on the process of flow within the chalk unsaturated zone for a number of years. Maclean, (1969) was one of the earliest studies to be carried out on flow and transport in the Chalk. Further investigations evolved employing various methods; laboratory (Price et al, 2000) and field techniques (Smith, 1970; Wellings & Bell, 1980). More recently, researchers have combined both field and laboratory techniques in their bid to gain a deeper understanding of the Chalk flow transport and its complexities (i.e. Brouyere, 2004; Mathias, 2006; Ireson, 2008; Molyneux, 2012; Gallagher et al., 2012; Rutter et al., 2012). All the previous studies mentioned above are linked in their aim to understand the unsaturated flow in the Chalk aquifer.

2.8.1 Studies on transport of solutes within the Chalk aquifer

Flow in the Chalk was thought to be mainly through fractures. The observation of bacteria in groundwater via a monitoring borehole in a study by Maclean, (1969) and a later study by Headworth, (1972) indicated how rapidly groundwater responded to rainfall events, which suggested the dominance of fracture flow in the Chalk. However, shortly after the

study by Headworth, another study was embarked upon with the specific purpose of understanding transport in the unsaturated zone of the Chalk aquifer.

Tritium was used as a tracer, which originated from thermonuclear testing which began in 1954 (Figure 2.13). As a result it became available in the atmosphere. Smith et al., (1970) compared the tritium in rainfall content to that within pore water samples from vertical profiles in the Chalk aquifer of Berkshire to assess the flow mechanism and water velocity. This comparison can be seen in Figure 15 below. The results from this assessment showed corresponding results in peak levels of tritium and pore water within Chalk. Velocity of water was estimated to be about 0.88 m/yr. based on this observation. Smith et al. concluded that no tritium should be present below 13m from the calculated velocity results. Conversely 15% of the tritium occurred below 15m which was evidence of recharge through fractures.

Foster (1975) reinterpreted data from Smith's study and suggested that the increase in concentrations of tritium in the matrix could be as a result of a diffusive exchange between the matrix and fracture domains of the Chalk aquifer. Oakes (1977) using a conceptual model, gave a similar conclusion to Foster, suggesting that increased level of tritium in pores might be due to diffusive exchange between fracture and matrix, but that water flow was mainly through fractures. Young et al. (1976), Oakes (1977), Wellings et al. (1984) Gardner et al. (1990), and Rageb et al. (1997) have all suggested similar conclusions to Foster based on modelling.
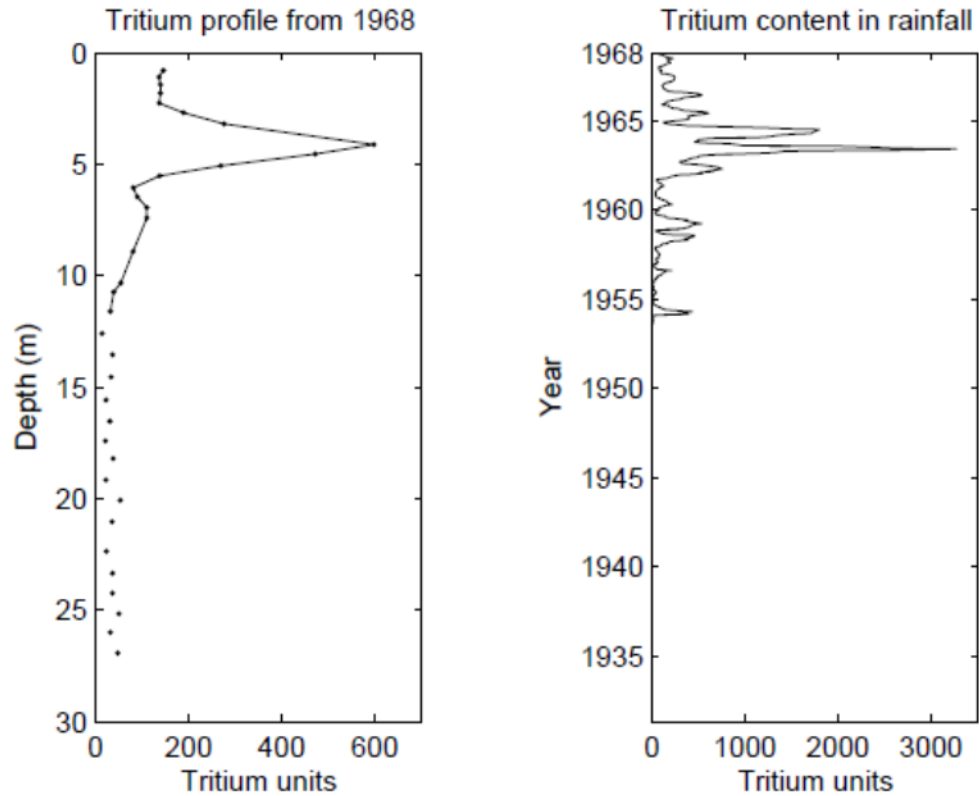
Figure 2. 13. Tritium content in Chalk profile and rainfall, smith et al., 1970 (reproduced by Mathias, 2015).

Zaidman et al., (1999) employed the use of various methods including soil physics instrumentation, laboratory testing of core, remote sensing and monitoring of field conditions to assess solute flow within the Chalk. These authors carried out a study of flow of solutes in the Chalk over a ten month period, covering two sites. Results described that solute transport is significant in fractures and that lithology plays a role in flow. Also, spatial and temporal conditions may influence the flow of solutes in the Chalk aquifer. It is obvious that Chalk's heterogeneity affects the flow of solutes. The current study employs both field and laboratory studies in monitoring the presence of particular pollutants in groundwater. Therefore the results from the study of Zaidman et al., (1999) are of specific importance.

2.8.2 Modelling studies

A few recent computer modelling studies on flow in the Chalk unsaturated zone include Mathias (2005), Brouyère (2006) and Ireson (2008). Computer models rely less on field observations and to some extent on laboratory determinations and physical properties of the Chalk. All three studies above are similar and employ the same idea of equivalent porous media (EPM). EPM allows for both fracture and matrix to be modelled at the same time based on the idea that flow occurs simultaneously. In the study carried out by Mathias et al., (2008) modelling results were able to show that flow occurs predominantly through the matrix and the activation of a fast recharge process through the fractures was highly dependent upon the rainfall intensity. Higher levels of rainfall changed the recharge patterns. The model can be seen in Figure 2.14 where all three results of soil moisture characteristics from EPM are presented.
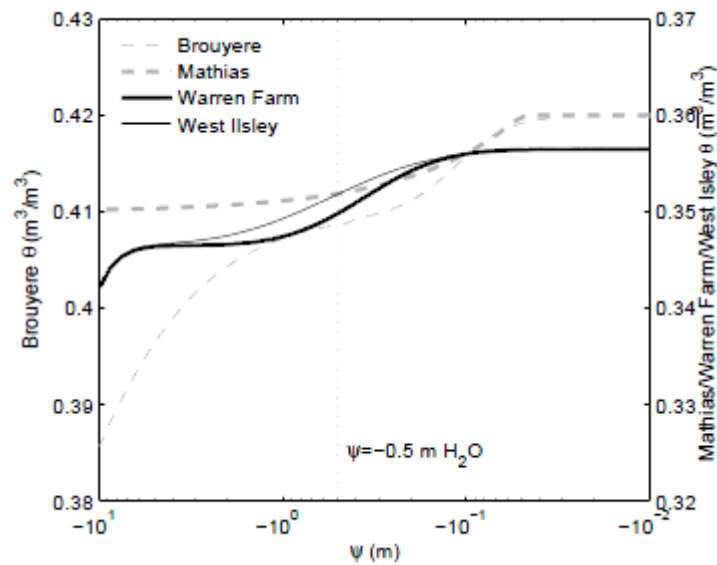
Figure 2. 14. The diagram of an equivalent porous medium (EPM) showing the soil moisture characteristics curve model. (From Ireson, 2008).

The current study will employ a conceptual model to represent the natural field conditions monitored, coupled with laboratory results obtained. Conceptual models are able to stand alone without any mathematical or numerical support or analysis (William, 1999), and are widely used in site assessment and engineering and environmental geology, and hydrogeology. A study by Gooddy et al., (2006) has demonstrated the value of using chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF6) due to the large amounts present at Boxford in the Lambourn catchment. This was used to determine groundwater movement and residence times in a lowland Chalk catchment. A conceptual model for groundwater movement was developed based on a series of theoretical mixing models. Three distinct regimes were identified as presented in Figure 2.15. This study provided a framework for modelling-based studies to strengthen catchment management decisions.
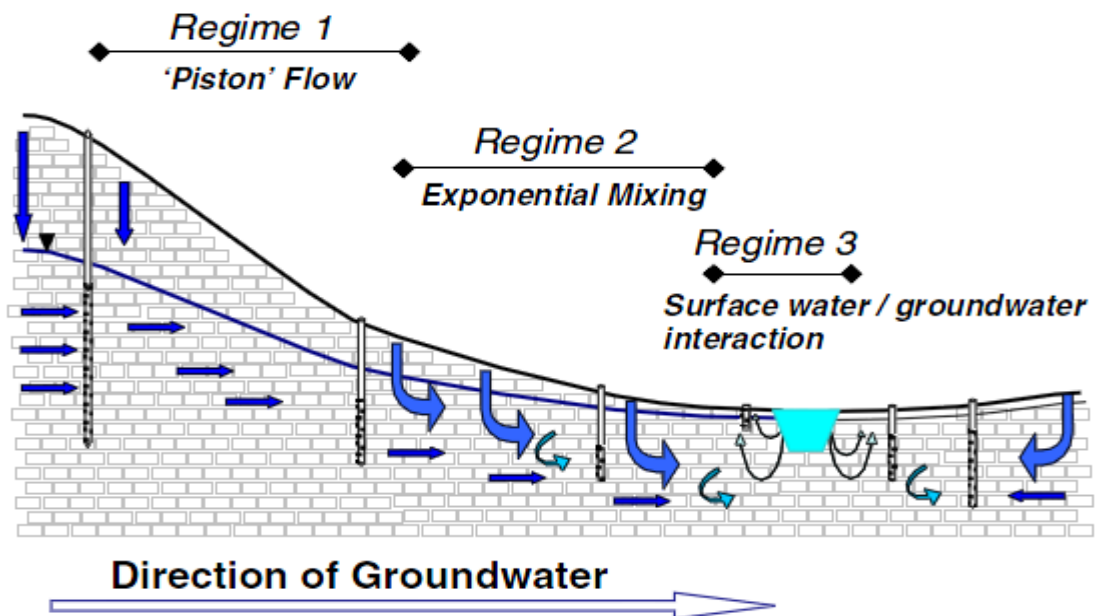
Figure 2. 15. Conceptual model showing the three groundwater flow regimes moving down gradient through the catchment. (From Gooddy et al., 2006).

2.9 Conclusion

Diffuse urban pollution can provide a source of Cu, Pb, Zn and PAHs; these and other contaminants have been detected in drainage sediment, and in aquifer waters in a number of key case studies (Pitt et al., 1999; Rothwell et al., 2015; Gobel et al., 2006; Kayhanian et al., 2012 and Brown and Peake, 2006). Continuous monitoring to understand their sources in groundwater with modelling processes that describes the flow pathway to groundwater have been ongoing, to suggest key environmental processes that control their distribution in groundwater.

The Chalk of the UK is particularly important as a study medium as it is a major aquifer in the UK and especially the South East of England. The Chalk's hydrogeological behaviour is complicated because of its dual porosity/dual permeability nature; flow process in the saturated and unsaturated zone; field monitoring, chemical tracer studies, experimental studies and computer modelling approaches have shown that flow occurs through both matrix and fracture and the Chalk is vulnerable to pollution as a result.

Investigations of chemical tracers, and potential contaminants in the UK chalk have shown that compounds such as Pb, Zn, Cu and PAHs are potential hazards. Urban runoff forms a major source for these contaminants, case studies of these have revealed that their distribution is particularly effected by source distribution, flow processes and chemical retardation.

All the studies mentioned have highlighted knowledge gaps in the areas of contaminant concentrations in the Brighton aquifer, flow pathways and potential management strategies:

- Composition of road run off
- Flow paths to water table

- Impact on aquifer

Studies so far lead us to propose the hypothesis that contaminants (hydrocarbons and heavy metals) derived from road runoff, including from vehicles, applied compounds and the components of the road surface may enter the Chalk aquifer, and accumulate over time, thereby degrading the overall quality of groundwater and that the unsaturated zone flow may retard and dilute urban diffuse pollution. These knowledge gaps have been used to define the aims and objectives of the present study.

Chapter 3 Methodology

This chapter provides the outline and foundation of the chosen research methods to address the aims of the study, set out in Chapter 1. A structure of the overall thesis is given in Figure 3.1 and goes on to introduce the field study sites.
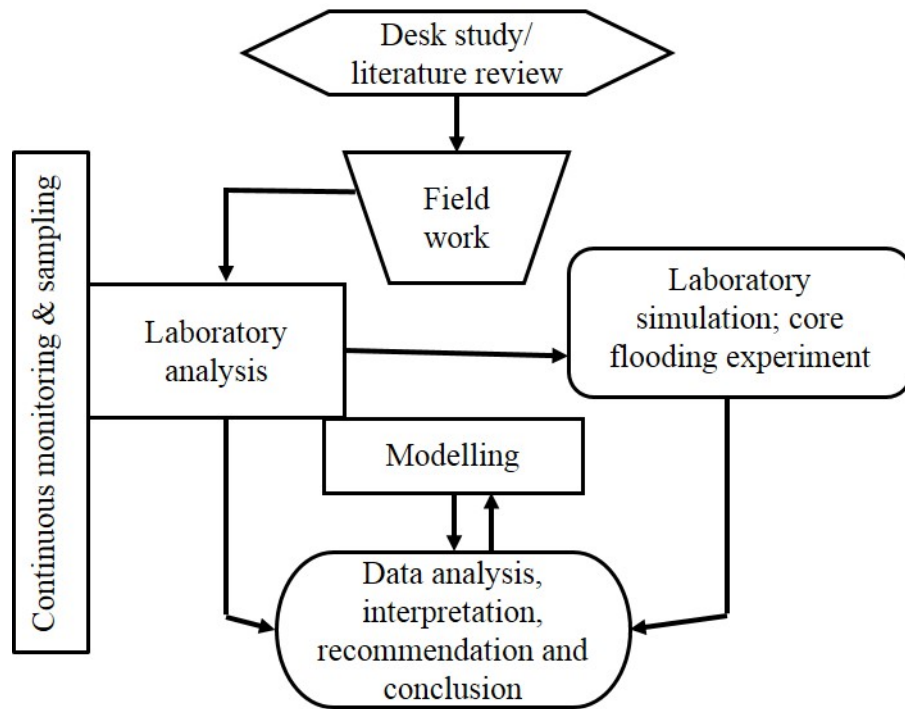
Figure 3. 1. Overall thesis structure showing processes from start to finish

3.1. Introduction

The previous chapter explained the source of road derived hydrocarbons and their presence in the environment, the behaviour and vulnerabilities of the Chalk aquifer and processes of distribution and dispersion in the Chalk. In order to address the aims of the current study, a combination of field and laboratory-based methods, with subsequent data integration, evaluation and modelling, are used. Initially, monitoring boreholes available around the study area have been instrumented with conductivity, depth and temperature monitors (CDT, to assess seasonal water fluctuations and recharge processes), and water samples

collected to examine spatial distribution of dissolved constituents (study objectives 3 and 4). In addition, a range of gully pot samples have been collected to identify key contaminants/tracers and emerging spatial patterns (objective 1 and 2). This chapter will give a detailed explanation of the field work employed and laboratory methods used for analysis.

This chapter is divided into three sections; sampling, experimental work and analysis. Sampling is further divided into road run-off sampling, which includes; gully pots, settling ponds, soakaways, and groundwater sampling. The experimental work section will cover core flooding testing procedures, which will be carried out in a later stage of this research. Meanwhile, the last part of the chapter will be a description of the analysis methods employed in detecting hydrocarbons and heavy metals in all the samples collected. The chapter will conclude with a summary of methods carried out and will lead onto the next chapter.

3.2. Sampling

3.2.1 Road run-off sampling

Road run-off consists of a variety of substances that are washed by rainfall into surrounding gully pots and eventually soakaways. This may consist of greasy materials from cars, car leaking oils, metals from motor breaks or tire wear, road de-icing salts etc. The role of the gully pots on the road side is mainly to collect the suspended solids in water. However, gully pots hold water from the road for a period before serving as a contaminant pathway to soakaways.

Water and sediments were collected from road side gully pots using a hand held shovel or scoop by lifting up the protective steel gully cover. Samples were collected from 20 gully pots along major and minor roads, and a major rail line, within urban areas of Brighton

(Figure 3.2). The gully pots sampled are located around the monitoring boreholes which will be described in this chapter. A grid location of the gully pot location is attached (Table3.1).

Table 3. 1. A list of the grid location of the gully pot locations where water and sediment samples were collected.

Sample No.	Location	Type
1	N50° 50.635' W0° 08.080'	Gully pot
2	N50° 50.652' W0° 08.090'	Gully pot
3	N50° 50.936' W0° 08.115'	Gully pot
4	N50° 51.206' W0° 08.183'	Gully pot
5	N50° 51.202' W0° 08.591'	Gully pot
6	N50° 51.120' W0° 08.679'	Gully pot
7	N50° 51.179' W0° 09.012'	Gully pot
8	N50° 51.095' W0° 09.191'	Gully pot
9	N50° 51.112' W0° 09.222'	Gully pot
10	N50° 51.306' W0° 09.280'	Gully pot
11	N50° 51.384' W0° 09.152'	Gully pot
12	N50° 51.552' W0° 08.775'	Gully pot
13	N50° 51.573' W0° 08.574'	Gully pot
14	N50° 51.215' W0° 08.660'	Gully pot
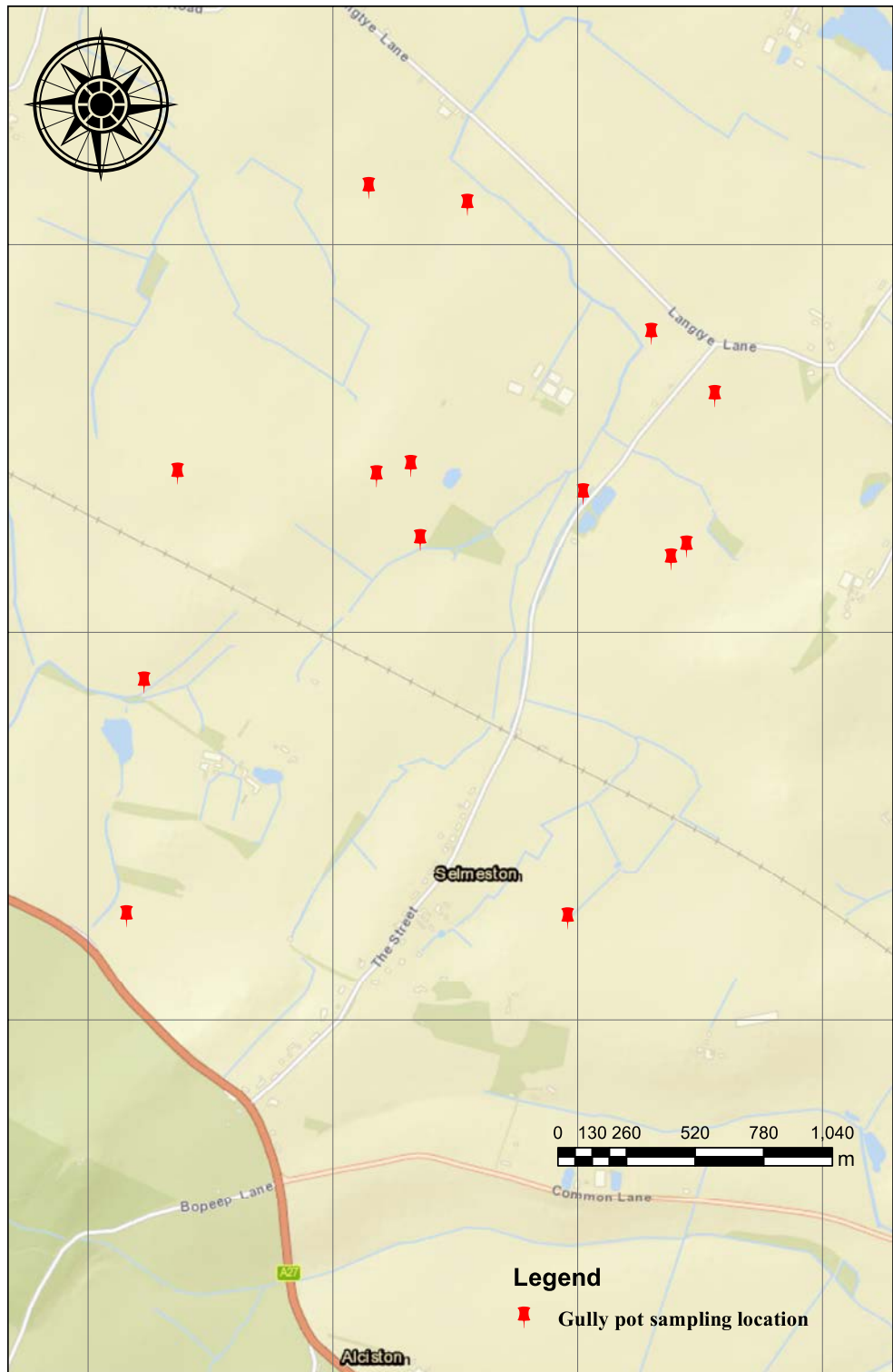
Figure 3. 2. A map of the grid locations of the sample points presented in Table 3.1 from (source: google maps).

3.2.2 Settling ponds

Settling ponds form collection areas for run-off water and sediments from storm water. Access to settling ponds at the A23 road and the Keep was granted by the Highways agency (See map in Figure 3.3).
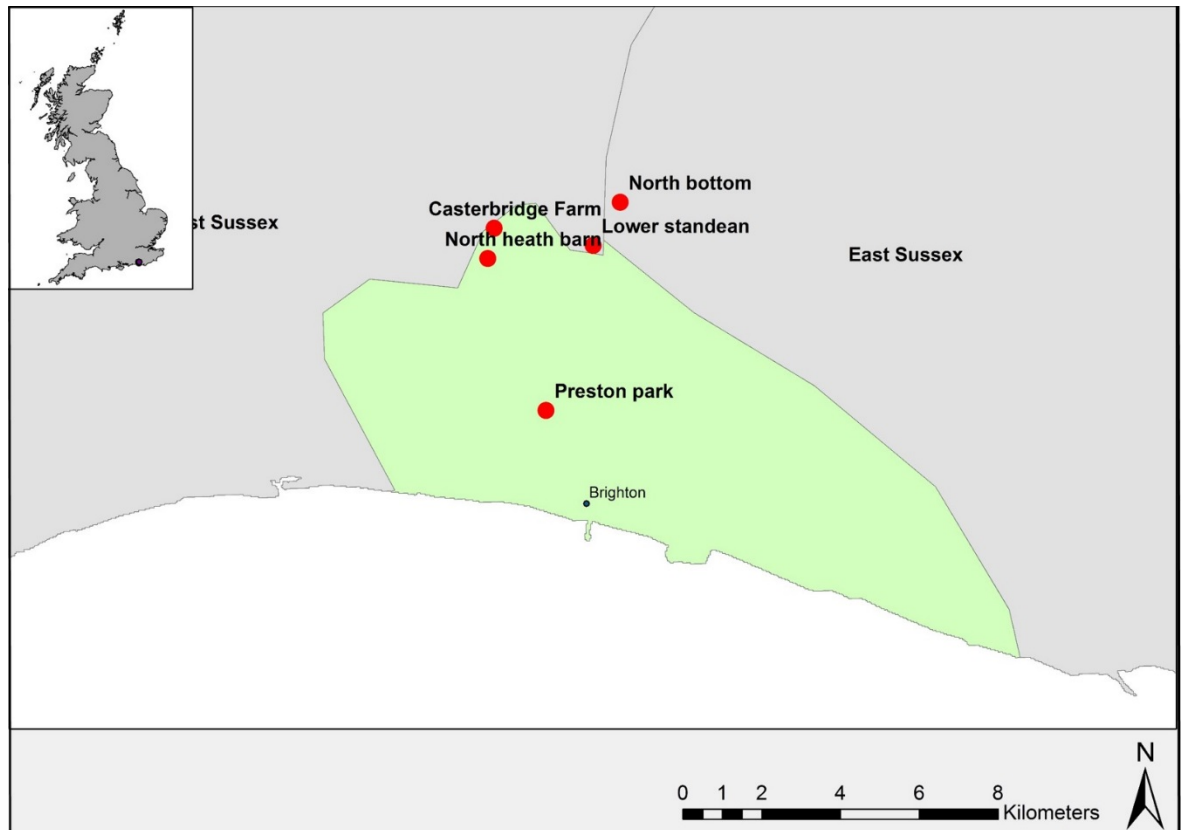
Figure 3. 3. Map showing the monitoring borehole locations of the study area, the coordinates are given in Table 3.2. (Source: Author)

3.3 Groundwater sampling

A detailed sampling plan (Table 3.4) has been designed for carrying out sampling of the five (5) monitoring boreholes used in this project. The table includes a detail plan, with steps and the procedures followed to carry out a successful fieldwork using best practices at the same time minimising errors as much as possible. Coordinates for the 5 monitoring boreholes are given in Table 3.2, Figure 3.3 give a guide to groundwater sampling plan while, a map of the locations is presented in Figure 3.3.

Table 3. 2. List of coordinates for the 5 monitoring boreholes used for continuous monitoring and sampling in the present study.

LOCATION	TOP LEVEL	EASTING	NORTHING	Z	max GWL (AOD) in winter (mAOD)	min GWL (AOD) in Summer	GWL BGL
North Heath Barn	91.5	528804	110429	91.5	63.8	20.8	27.7
Preston park	29.41	530283	106570	29.41	28.5	5.8	0.91
Lower Standean	90.19	531478	110758	90.19	74.9	40.4	15.29
Castlebridge Farm	82.5	528964	111195	82.5	58.6	36.9	23.9
North Bottom	120.15	532167	111856	120.15	97	64.3	23.15

Sample frequency has been put on a monthly basis to leave adequate time for wash off or any possible flush that may enhance recharge into groundwater. It must be noted that, the standard full purge sampling technique was not used. Sampling Bailers were used in accordance with the British standard ISO5667-11: 2009–6068.6.11:2009 on 'guidance on groundwater' sampling has been listed amongst suitable sampling methods for groundwater parameters, see Table 3.3. While sampling depth was justified by reason, using previous data to determine minimum and maximum water levels and geology from borehole logs (Molyneux, 2012) to determine the maximum and minimum water levels.

Table 3. 3. Guide to suitable groundwater sampling methods- British standard ISO5667-11: 2009–6068.6.11:2009.

Sampling — device	Groundwater parameters [✓ = suitable, (✓) = limited suitability, — = not generally suitable]												
	EC	pH	Alkalinity	Redox (Eh)	Major ions	Trace metals	Nitrates	Dissolved gases	Non-volatile organic compounds	VOCs	TOC (total organic carbon)	TOX (total organic halogen)	Microbiological agents
Depth sampler — bailer (open)	✓	—	✓	—	✓	✓	✓	—	✓	—	✓	—	✓
Discrete depth sampler — bailer (closed) or shut-in-sampler	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Inertial pump	✓	✓	✓	✓	✓	✓	✓	—	✓	✓	✓	—	✓
Bladder pump	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Gas-drive pump	✓	—	—	—	✓	✓	✓	—	✓	—	—	—	—
Gas-lift pump	✓	—	—	—	✓	✓	✓	—	—	—	—	—	—
Submersible impeller pump [a]	✓	✓	(✓)	(✓)	✓	✓	✓	(✓)	✓	(✓)	(✓)	(✓)	(✓)
Suction (surface) pump	✓	—	✓	—	✓	✓	✓	—	✓	—	—	—	✓

NOTE   This table is provided as a general guide only. The selection of an appropriate device depends on the objectives of the study, the performance and properties of the device, and the environmental conditions. Under certain conditions, a combination of sampling devices should be considered and some devices might not be appropriate for all parameters.

[a]   Where a flow-regulated submersible impeller pump is used and operated at flow rates of less than two thirds of maximum pressure head (flow rate), then this sampling device may be suitable for all parameters.

In addition to the British standard on monitoring groundwater, constant monitoring of conductance, DO, Eh, pH and temperature during low flow pumping of Lower Standean borehole at 45m below surface with a bladder pump was carried out in order to validate the bailer sampling approach. Variables stabilise after ~5-10minutes of pumping (~10-20 flow cell volumes – 150-300ml) Figure 3.4. This indicates that fresh aquifer water is being sampled after this period. Bailer samples are taken after sending 3 bailer volumes (3 litres of water) to waste, far exceeding this volume. The karstic nature of the aquifer accounts for the rapid flow rate into the borehole, and essentially means that borehole water is not stagnant. Full borehole purge sampling is therefore not necessary to obtain representative samples of aquifer water. Equally, the focussing of flow onto a few high permeability horizons means that the well is essentially filled with water from just a few specified horizons, and will not be representative of water at any given depth. Bailer sampling, with disposal of 3 bailer full prior to sampling, at depths identified as inflow points from

geophysical well logs (Moyneux, 2012) was therefore taken as the most representative and efficient method in this study.
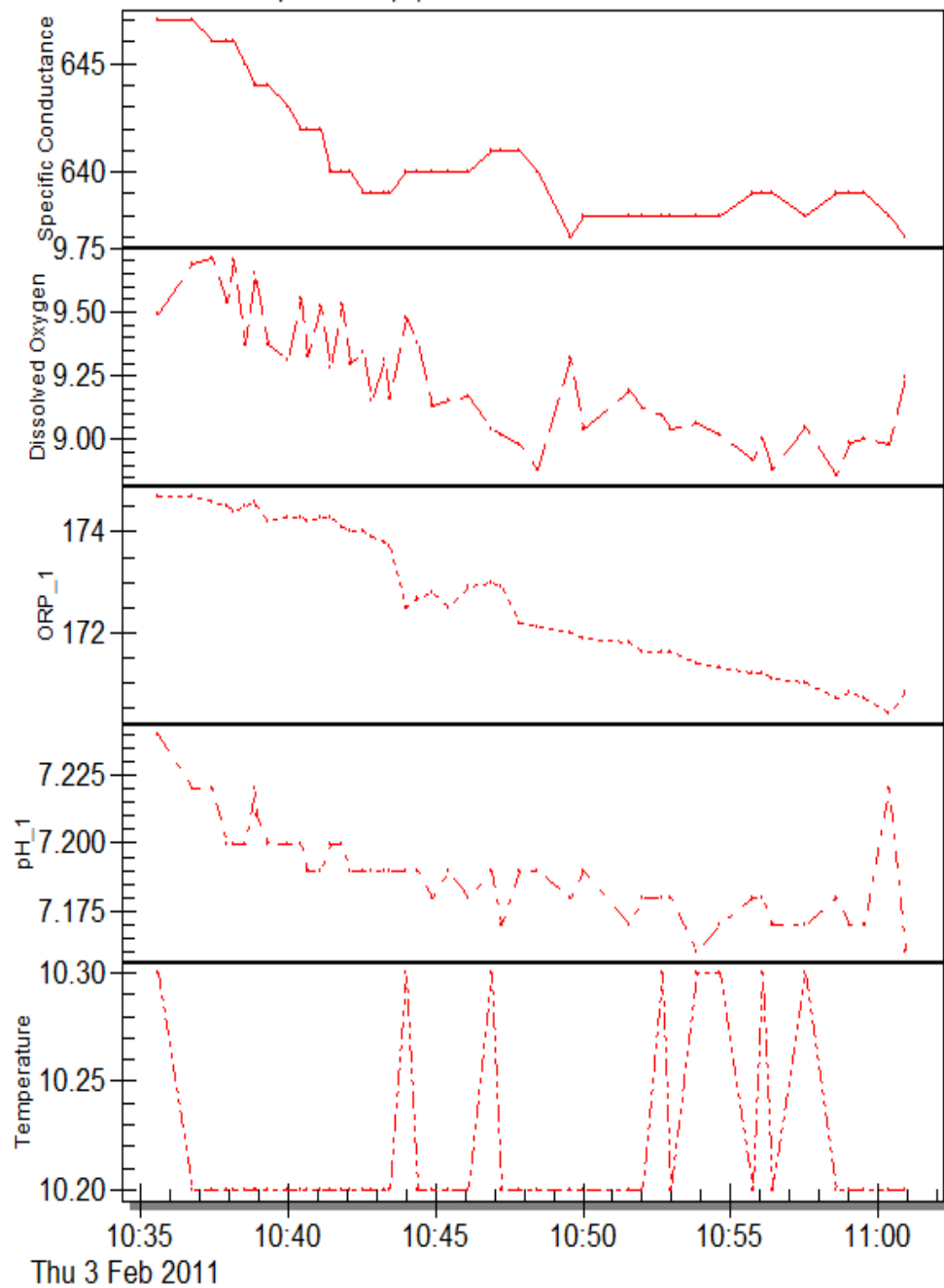
Figure 3. 4. Constant monitoring of conductance, DO, Eh, pH and temperature during low flow pumping of Lower Standean borehole at 45m below surface with a bladder pump.

To further strengthen the rationale for not carrying out a borehole purge, an additional pumping test was carried out at Preston Park because the earlier test was outside the time

period of this project, and took place at Lower Standean (a rural borehole in the Lewes Nodular Chalk). The additional test was therefore carried out at Preston Park, the main urban site for this project in the Seaford Chalk. Results from the more recent pumping test appeared similar with most of the variables stabilising after about 5-10 minutes of continuous pumping (Figure 3.5).
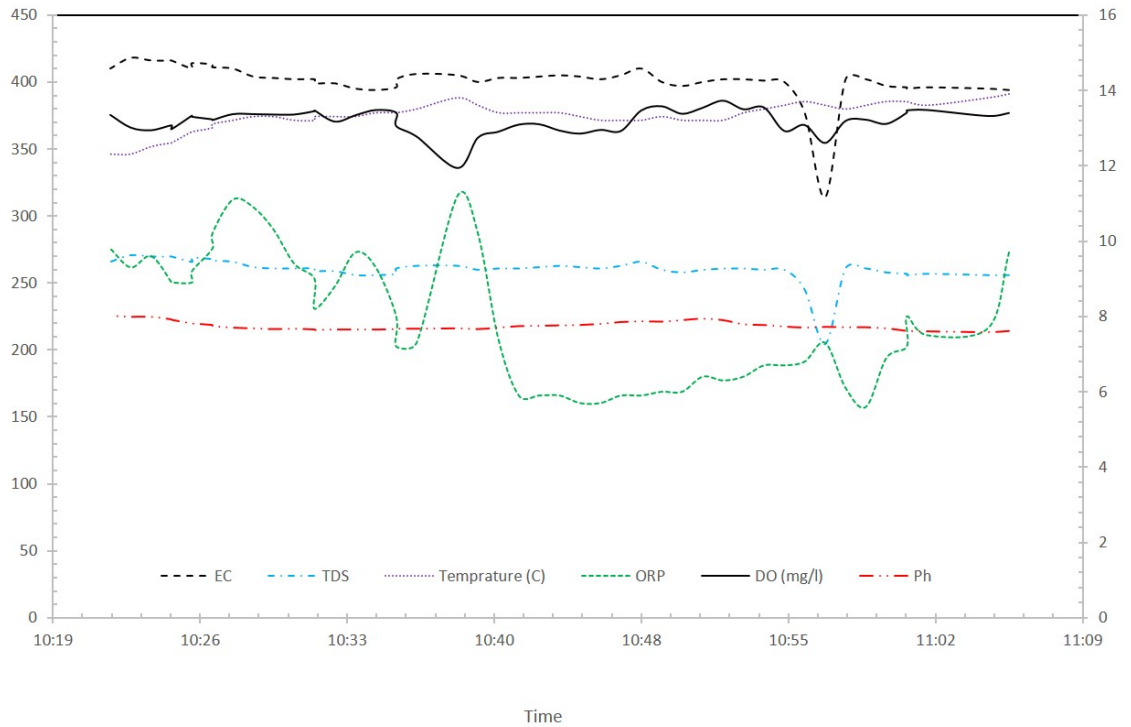
Figure 3. 5. Constant monitoring of conductance, TDS, DO, Eh, pH and temperature during low flow pumping of Preston Park borehole at 45m below surface with a bladder pump.

The University of Brighton manages monitoring of 5 boreholes; Preston Park, Lower Standean, North bottom, North Heath Barn & Caster Bridge farm, for Brighton and Hove City Council (BHCC). The boreholes have previously been used for other projects including the Flood1 project (http://nora.nerc.ac.uk/4284/1/OR08055.pdf).

Two of the boreholes, Preston Park (located downstream of the A23Junction) and Caster Bridge Farm (located adjacent to the railway line and the A23) are located close to major roads. The borehole at the former site is open access, located by the side of the main

Preston Park road. Figure 3.6 is a picture showing the Author and his supervisor sampling from a borehole. The boreholes are usually covered in a chamber with a manhole cover, accessible by opening with an Allen key. A diver is suspended from the chamber cover.

Figure 3. 6. A picture of the author and his supervisor sampling at Lower Standean, one of the borehole sites. (Photo credit: Aimee Felus)

Table 3.4 gives a detailed sampling plan used with sets of procedures followed during sampling. These procedures were mostly taken from previous studies and British Standard procedures. Other procedures were modified based on specification to current study.

Table 3. 4. Groundwater sampling plans and procedures.

Steps	Procedure	Essential Elements	Notes
Site investigation and continuous monitoring strategy	Collection of available data, meeting on location with Environment Agency/Reconnaissance visit to site with supervisors.	Environment Agency is primary source for this data	To know the accessibility of site. Survey is for quality monitoring, long time monitoring required (at least a year) to understand behavior at different periods of the year
Borehole low flow purging/pumping and measurement	Removal of stagnant water while measuring parameters like; EC, pH, temperature, & redox potential using YSI probe.	Pump machine Access to representative samples/ used bailers as a cheaper means than pumping.	Purging is to enable take sample representative to borehole & also measure parameters in situ without or before any significant change.
Sample collection, storage and transport	Sufficient samples were collected using bailers and sample plastics (air tight) & transported to the laboratory. Water level measured using a dip level meter.	Bailers, Plastic containers for sampling	Bailers are most preferable for LNAPL as they can be on water table.
Facility Installation	Installed CTD-Divers for continues monitoring of changes in Temperature & electrical Conductivity especially	CTD-Divers & cables as available from university	CTD-Divers once installed can record data for long periods of time
Inspection	Inspection & sampling is on a monthly basis, one day of field work every month and loggers downloaded once every four months because they have the capacity of storing large data over a period of time.	Water level measurement & hydraulic properties testing of boreholes	Sampling has been carried out on a monthly basis. And samples analysed immediately on return to laboratory, especially for hydrocarbons to avoid any major change & quality as hydrocarbons are vulnerable to degradation by bacteria.

3.4 Experimental work: core flood experiments

3.4.1 Sampling

Sampling for Chalk samples that will be used in the experimental work was carried out at a disused cement factory in Shoreham, a few kilometres from Brighton. The location has a good exposure of Chalk samples from the Seaford Chalk formation and Lewes Nodular Chalk, which are representative samples of the Chalk unsaturated zone that underlie Brighton. Samples were collected from both exposures as can be seen in Figure 3.7 and Table 3.5 presents the locations coordinates of the samples collected with dates, formation name and sample code.

Table 3. 5. Coordinates of chalk sampling locations for laboratory experiment.

Sample Number	Code	Position	Date	Formation
1	SCW1	N50°52.109' W0° 17.007'	17/07/2015	Seaford Chalk
2	SCW2	N50°52.099' W0° 17.246'	17/07/2015	Lewes Nodular chalk
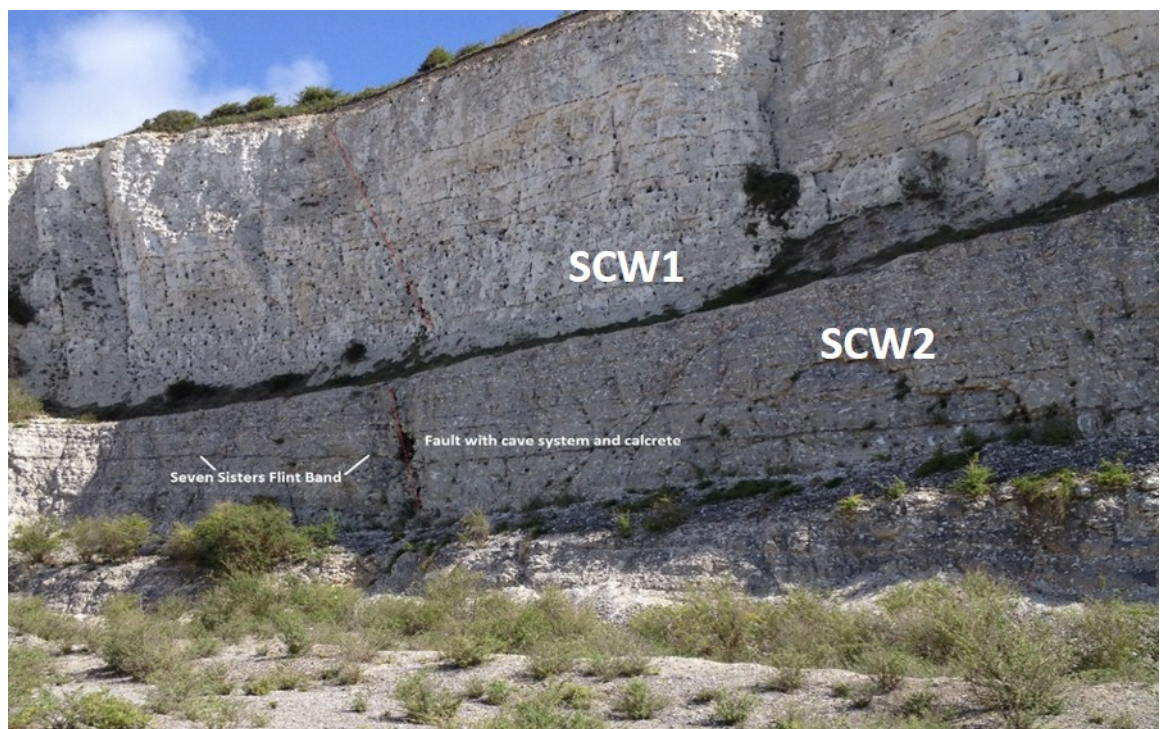
Figure 3. 7. A Chalk exposure at Shoreham cement works. (Authors own photograph)

3.4.2. Core flood experiments

Core flood experiments are a simple laboratory technique used to examine flow in a body of rock. They are carried out under a steady-state system. Core flooding experimental research involving multiphase flow characteristics has been described as the most effective method to determine the $scCO_2$-brine-rock interaction mechanisms during/after CO_2 injection and to determine the rate of CO_2 injection, and the spread of injected CO_2 in subsurface storage formations (Bacci et al., 2011 and Sun et al., 2015). Core flooding uses pressured pumps to transmit fluids. Various experimental systems of core flooding has been established to understand formation-fluid migration behaviour (Sun et al., 2016). Baraka et al., (2015) used core flood experiments to determine the effect of pH in enhancing dissolution in carbonate rocks.

Core flooding experiments are usually performed under simulated in-situ P-T (pressure-temperature) conditions, which range between 3 MPa and 40 MPa, and a working temperature of between 10–70 °C. In this study, core flooding experiments will be used to analyze injection potential and storage capacity of field-scale subsurface geological formations (the Chalk in this case), understand and model the migration behaviour of laboratory-scale solutes, changes under multiphase flow, and monitor the behaviour of hydrocarbon-water transfer and transfer rate. Core flooding experiments have been commonly used to understand multiphase flow in rock matrices (sandstone and carbonate rocks in most cases) (Sun, 2016). Most laboratory studies on deep saline aquifers have been limited to core flooding experiments (Suekane et al., 2009). Unsaturated zone flow is dominated by the matrix, hence core flood experiments will provide a reasonable simulation of flow and reaction processes.

A detailed investigation is required to understand the effect of Chalk heterogeneity (Pentland et al., 2011b) on flow and contaminant transport, and as a result, the Chalk samples for this study were collected from different geological formations to understand the effects of geological heterogeneity. In order to acquire meaningful results from core flooding tests, a series of experiments involving a variety of conditions will be undertaken.

Apparatus

The core flood equipment has three main components: the upstream, the core block, and the downstream. The Chalk sample is a key component, along with the fluid-water/hydrocarbon or water/mixture, and a pump for pumping the liquid. There is however different ways to set up the apparatus based on the set objective. A few examples of apparatus set up are given below for different objectives.

The Institute of Rock and Soil Mechanics (IRSM) set up a core flood apparatus for understanding the displacement of brine in a brine-saturated sedimentary-core-sample by Co_2 (Sun, 2015).

In a bid to develop a macroscale understanding of the behaviour of CO_2 in the rock (geosequestration) under dual-porosity conditions, a more state of the art facility was built in Monash University, Australia. The apparatus can achieve high-resolution measurements and is mainly used for 3D reconstructions of porous structure and fluid distributions in natural and artificial porous media (de Silva and Ranjith, 2013).

3.5. Analysis

The laboratory work was carried out to answer some of the key research questions, which includes analysing for hydrocarbons and heavy metals in surface (from gully pots) and groundwater (from boreholes) around the study area. Methods were chosen based on

quality and reliability. This chapter gives idea of the operation of the different methods employed, process of interpretation and reliability of process. Methods include: Inductively coupled plasma-mass spectrometer (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), Total petroleum Hydrocarbons (TPH) rapid analysis kit on Hach spectrophotometer, Chloroform extraction method for phenols, Gas chromatography mass spectrometry (GC-MS), portable X-ray fluorescence (PXRF), and X-ray diffraction (XRD).

3.5.1. Total petroleum hydrocarbons TPH (HACH)

A set of reagents produced by an American company HACH is used to analyse for the TPH parameter in water. The complete set of reagents and consumables includes; diluent solution, TPH enzyme conjugate, methanol, colour developing solution, stop solution, cuvettes, and four calibrator solutions that can be used for up to 18 tests. The method is technically known as Semiquantitive Colorimeter Immunoassay, and is a standard industry test used to assess groundwater and land contamination. The immunoassay test method uses antibody reactions to determine specific organic compounds in water and soil, but the water procedure is applied here. The walls of plastic cuvettes are layered with antibodies that are specific for TPH. The antibodies selectively remove TPH from complex sample matrices. A prepared sample and a reagent with enzyme-conjugate molecules (analyte molecules attached to molecules of an enzyme) are added to the Antibody Cuvettes. During incubation, enzyme-conjugate molecules and TPH compete for binding sites on the antibodies. Samples with higher levels of analyte have more antibody sites occupied by the analyte and fewer antibody sites occupied by the enzyme-conjugate molecules. After incubation, the sample and unbound enzyme conjugate are rinsed from the cuvette and a colour-development reagent is added. The enzyme in the conjugate catalyzes the development of colour. As a result, there is an inverse relationship between colour

intensity and the amount of TPH in the sample. The resulting colour is then compared with a calibrator to determine if the analyte concentration in the sample is larger or smaller than the threshold levels. The TPH concentration is inversely proportional to the colour development—the lighter the colour, the higher the TPH concentration. The test results are measured at 450 nm on the HACH spectrophotometer model-DR3900.

3.5.2. Chloroform extraction method

Phenol has been identified as a key urban groundwater contaminant, and is examined here via spectrophotometry (Stuart et al., 2012). The chloroform extraction method is used in cases where the phenol concentration in water is at trace levels. It extracts the phenols from water using chloroform at an increased pH of around 10. A Spectrophotometer is then used to analyse the concentration of phenols within the extracted chloroform. The spectrophotometer used in this study is from Hach Company, model 3900. The sample process involves adding Buffer solution, aminoantipyrine, potassium- ferricyanide and chloroform.

Preparation of chemical solutions

The chemical solutions were prepared as following:

- A stock solution of phenol was prepared by adding 0.1g of crystal phenol in a 250ml conical flask and diluted to 100ml with distilled water. 1ml was taken out of the 100ml and diluted with 99ml of distilled water. 1ml=1µg/l concentration of phenol.

- Ammonium buffer solution to adjust pH was prepared by dissolving 16.9g of ammonium chloride with 143mL of ammonium hydroxide diluted to 250mL with distilled water.

- Aminoantipyrine solution was prepared by dissolving 2g of 4-minoantipyrine in distilled water and diluted to 100ml. Fresh solutions were prepared daily for every measurement.

- Potassium ferricyanide solution was prepared by dissolving 8g of in distilled water and diluted to 100 ml.

Standard Curve for phenols

A standard curve for phenol was plotted (Figure 3.8). Adding 1mL of phenol stock solution to a 250mL conical flask, and diluting the phenol solution to 100ml with sodium hydrogen carbonate buffer solution. to give a concentration of 50mg/L phenol. Serial dilutions were prepared with phenol concentrations of 0.5, 1, 2, 3, 4mg/L (Table 3.6).

Table 3. 6. Absorbance of phenol stock solution measured at 460nm.

Phenol concentration (mg/l)	Abs0rbance 1	Absorbance 2	Mean	Error
0.5	0.390	0.388	0.399	-0.002
1	0.400	0.402	0.401	0.001
2	0.424	0.427	0.425	0.003
3	0.439	0.436	0.438	-0.003
4	0.445	0.452	0.449	0.007

There is around 5% human error in the calibration curve. This is displayed in the figure below.
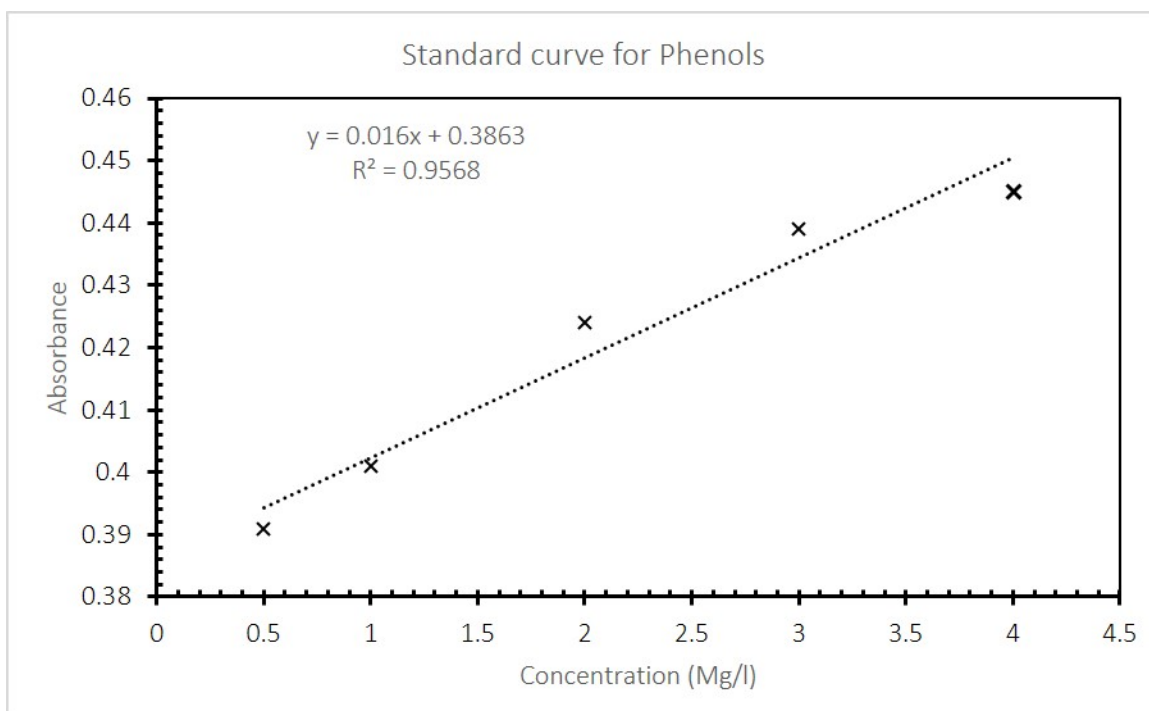
Figure 3. 8. Standard curve for phenol standards.

3.5.3. Portable X-ray fluorescence spectrometer (P-XRF)

The PXRF is an analytical instrument used to determine the concentration of metals and metalloids in soil (CL: AIRE 2008). The PXRF analyser measures the characteristic energy levels of X-rays emitted from elements when irradiated with a high-energy photon source (X-ray tube or radioactive source) (Kilbride et al., 2006). The energy of each X-ray detected identifies a particular element present in the sample, and the rate at which X-rays of a given energy are counted provides a determination of the quantity of that element present in the sample (US-EPA, 2003). Because of the radiation it emits, there is a slight risk of exposure from the instrument to the user (Kilbride et al., 2006). Health and safety rules must be obeyed at all times while using the PXRF. The instrument used for this study was an Olympus Innov-X delta PXRF. This is employed as an initial screening tool to give a generic understanding of the heavy metals and metalloids present in the gully pot soil samples and their relative concentrations before employing a more detailed technique (ICP-MS). The PXRF was used because measurements using PXRF require little or no

sample preparation. Digestion process may involve sample loss, samples available for use is in small quantity and so sample loss was minimised. Analysis was carried in three repetitions and the average was considered.

3.5.4. ICP-MS/ ICP-OES.

Inductively coupled plasma-mass spectrometry (ICP-MS) is a robust multipurpose analytical technique, with very low detection limits, parts per billion range (ppb) and high spectral resolution (10 000) for multi element isotope detection. (Ammann, 2007). The ICP-MS instrument used in this study is made by Agilent technologies, model 7900. The ICP-OES is from PerkinElmer, model 2100 DV. This has been employed to analyse for the trace metals in groundwater.

Inductively coupled plasma/optical emission spectrometry (ICP/OES), like the ICP-MS is a powerful tool for the determination of metals in various different sample matrices. However, the ICP-MS has a lower detection limit (ppb) as stated above (compared to ppm for ICP-OES), and the two ICP methods have different sample introduction techniques. With the ICP-OES, liquid samples are injected into a radiofrequency (RF)-induced argon plasma using one of a variety of nebulizers or sample introduction techniques. The sample mist reaching the plasma is quickly dried, vaporized, and energized through collisional excitation at high temperature. The atomic emission coming from the plasma is viewed in either a radial or axial configuration, collected with a lens or mirror, and imaged onto the entrance slit of a wavelength selection device (Olesik, 1991).

3.5.5. X-Ray diffraction (XRD)

X-ray diffraction (XRD) is a rapid analytical technique, used to analyse crystalline material and can give information on unit cell dimension. The samples are crushed to ensure homogeneity before being subjected to analysis. XRD analysis is based on constructive

interference of monochromatic X-rays and a crystalline sample (Antolini and Cardellini, 2001). In this study, XRD has been employed to ascertain the origin of the solids sampled from gully pots through analyzing the crystalline structure of the samples.

Table 3. 7. Showing analytical conditions under which XRD was carried out.

Instrument	Goniometer=PW3050/60 (Theta/Theta); Minimum step size 2Theta:0.001; Minimum step size Omega: 0.001 Sample stage=Spinner PW3064 Diffractometer system=XPERT-PRO Generator Settings 40 mA, 40 kV
Operating range	Start Position [°2Th.] 5.0052 End Position [°2Th.] 69.9892
Temperature	Measurement Temperature [°C] 25.00
Humidity	Ambient (humidity chamber available)
Sample amount	App. 10 mg

3.5.6 Gas Chromatography

This involves separating a mixture of analytes according to their partitioning, between a stationary phase and a mobile phase. Gas chromatography analysis was used to determine the concentrations of different PAHs in the gully pot and other samples. This was carried out in an external private laboratory, ELABs.

3.5.6 Ion Chromatography (IC)

Ion chromatography is used to analyse water chemistry. It is used to analyse for the major anions concentration in water. In this study, major anions were analysed which include; may include fluoride, chloride, bromide, nitrate, nitrite etc. The IC measures within the parts-per-billion range (ppb). The IC measures concentrations of ionic species by splitting them based on interaction with a resin column. Ionic species have different size and shapes and hence interact with the resin differently. The sample solution moves through a separate controlled chromatographic column, where column constituents adsorb ions. The ion extraction liquid (eluent) is then passed which initiates the separation of adsorbed ions.

Analysis time depends on concentration of the particular sample (Yuri and Mcnair, 1996). The current study uses a Dionex ICS-1100 ion chromatograph to analyse for major anions in groundwater.

3.5.7 Aqua Probe

The aqua probe was used to analyse for TDS, pH, Turbidity and EC of the water during sampling. It is handheld portable equipment that comprises of an electromagnetic sensitive head mounted at the end of a support rod.

3.5.8 Sequential extraction

A modified BCR 701 sequential extraction procedure was used to carry out leachability studies on the gully pot sediments. The steps, procedures and processes followed are summarised in Table 3.8. Previous researchers (Nirel and Morel, 1990; Whalley and Grant, 1994 and Kerstan, 2002) raised concerns of possible non-specificity of the reagents, along with analyte reabsorption after release during the procedure. However, this operationally defined speciation, though not able to conclusively determine the specific mineralogical phases to which possibly toxic elements are bound, is still a useful tool in the determination of the ease with which toxic elements may be mobilized from environmental matrices (Ure and Davidson, 2002). The progressively increasing chemical aggressiveness of the procedures provides a means for evaluating the mobility of metals and other elements in geologic materials.

Table 3. 8. Summary of the BCR 701 Sequential extraction steps and procedures employed in the current study.

1	Exchangeable, water and acid soluble	0.11 mol/L Acetic Acid, 40 mL, shake 16 hr
2	Reducible	0.5 mol/L Hydroxylammonium Chloride (pH 1.5 adj. 25 ml of 2 mol/L HNO_3 per L), 40 mL, 16 hr shake
3	Oxidisable	8.8 M Hydrogen Peroxide, 10 mL at 22°C 1 hr, 10 mL at 85°C 2 hr. 1 mol/L Ammonium Acetate (pH 2 adj. HNO_3), 50 mL 16 hr shake
4	Residual	0.1g Sample Fused Bead, 50 m: 10 % HNO_3 digest

3.6 Conclusion

This chapter has given an insight into the analytical processes that have been followed with techniques and methods employed to achieve the set objective of the study. By answering the research questions proposed, create a conceptual model of the research site findings. Figure 3.9 is a conceptual model with the highlights the research questions this study seeks to answer. The subsequent Chapter will attempt to answer the questions raised in the order of arrangement. It will be concluded by a more detailed model that will attempt to present study in diagram.
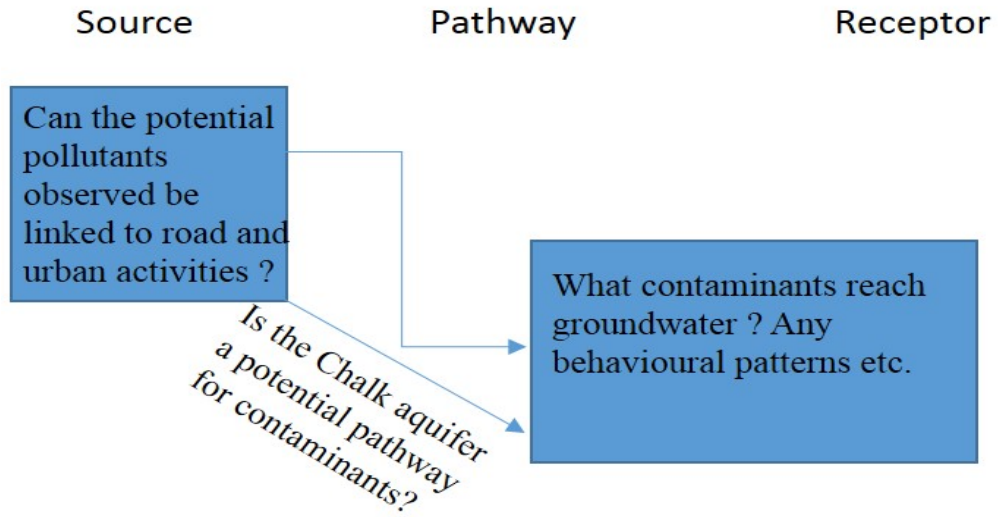
Figure 3. 9. Conceptual model stating the research question of the recent study.

Chapter 4 Geochemical characteristics and contaminant loading of gully pot water and sediments.

4.1 Introduction

This chapter presents data on the chemical characteristics, and their spatial and temporal variability, of road-derived sediments and waters collected from gully pots around the study area. The chapter also presents results from analysis of Platinum group elements (PGE) in gully pot materials, and data on their Pb isotopic composition. PGE's have become increasingly widespread in the environment since being used as a component of catalytic converters (Chapter 2), while Pb isotopic ratios have been used in a number of previous studies to discriminate sources of Pb in urban and other waters and sediments. The results are based on observations made following analysis of water and sediments from 13 gully pot locations sampled over autumn and spring weather periods, and analysed using methods stated in section 3.5. This chapter addresses part of the overall aim of the project and answers objective 1 and (to some extent) objectives 3 and 4. The results from the chapter are used to define key potential contaminants for analysis in groundwater, and to define element ratios that may allow the identification of material sourced from the road drainage system within groundwater. This chapter is divided and presented in two sections: Dissolved phase, which presents data on element concentrations observed in the water samples, and Sediment-bound, which presents data on element concentrations and Pb isotopic ratios observed in sediment samples.

4.2 Dissolved-phase pollutants - Background

Dissolved phase samples were analysed to obtain heavy metals and PAH concentrations. Results were compared with previous studies and guideline values. These guideline values are empirically derived concentration levels above which there may be adverse effects on the environment. In the dissolved-phase study, two different set of guideline values were

used. Namely, fresh water quality guidelines (predicted effects level) and WHO guidelines. The concentrations have been compared to a previous study carried out on similar materials in Manchester (Rothwell et al., 2015) and environmental regulations (WHO, 1986) to determine if results are within required guideline limits. Also, results from this chapter will lay the foundations for understanding the subsequent behaviour and potential mobilisation of contaminants to groundwater.

4.3 Results

4.3.1 Chemical characteristics of dissolved phase gully pot samples

The data presented here are of metals with significant detection limits. Mean values for dissolved phase pollutants are shown in Table 4.1. Dissolved phase Zinc and Magnesium have concentrations lower than the water quality guidelines and World Health Organisation (WHO) guidelines. Iron (Fe) on the other hand has concentration higher than the water quality guidelines and higher than the WHO guidelines. However, Manganese (Mn) shows concentrations higher than only the WHO guideline (the water quality guideline for Magnesium remains undefined). More than 30% of the gully pot locations have Fe concentrations that exceed the predicted effects level and 100% of the locations exceed the WHO guidelines for Fe. All of the 13 gully pot locations have exceeded the limits for both water quality guidelines and WHO guideline limits set for Mn. Within the dissolved phase organics analysed from the gully pots (in particular PAHs (Phenanthrene, Flouranthene, Pyrene and Benzo (a) pyrene), Flouranthene has < 10% of the locations with concentrations exceeding water quality guidelines (Table 4.3). All the locations exceed concentration limits for Benzo (a) pyrene.

Table 4. 1. Different concentrations of dissolved-phase pollutants in gully pots, compared with water quality guidelines effects levels and WHO guideline. Where: PEL=predicted effects level from the freshwater quality guidelines. GP= gully pot, ND= not defined metal elements are presented in mg/l while PAH is presented in µg/l). Freshwater guideline values (DEFRA, 2009), and WHO guideline values (WHO guidelines for water quality volume 3 & 4).

Dissolved phase Parameter	Concentration in Gully pot (mg/l)			Freshwater quality guideline (mg/l)			WHO Guideline (mg/l)	
Metals (mg/l)	Minimum	Maximum	Mean	GP exceeding PEL	GP % at PEL	PEL	Highest desirable limit	Maximum permissible limit
Zinc	0.11	0.48	0.23	0	0	7.4	5	15
Magnesium	1.02	6.95	2.4	ND	ND	ND	5	15
Iron	0.25	8.17	1.1	3	23.8	0.3 - 0.5	0.1	1
Manganese	0.12	0.26	0.17	13	100	0.5	0.05	0.5
PAHs (µg/l)								
Phenanthrene	0.17	22.03	0.19	ND	ND	ND	ND	ND
Flouranthene	0.12	27.1	13.3	1	7.6	20	ND	ND
Pyrene	0.11	12.9	3.67	0	0	20	ND	ND
Benzo (a) pyrene	0.32	2.4	0.89	13	100	0.00012	ND	ND

4.3.2 Spatial distribution of dissolved phase gully pot metals and PAH.

The element concentrations of gully pots (water and sediment) were plotted on a map using ArcGIS Inverse Weighting Interpolation to understand spatial patterns. The maps are divided into two, sediment-bound and dissolved phase samples. Dissolved phase spatial maps are shown in Figure 4.1. Benzo (a) pyrene in this case is used as a marker for PAHs. The dissolved phase elements spatial patterns presented in figure 4.1. Higher concentrations of Mg, Mn, Fe, and Benzo (a) pyrene are observed in the same location, a junction along a busy road (N50° 50.936' W0° 08.115'). While Zn shows reasonably elevated concentration in the same location, the highest concentration for Zn appears downslope close to a busy main road. This may be an indication that in the dissolved phase, contaminants are more present along busy roads and along junctions of busy roads. However, this is not a conclusion on the source of these contaminants. Further methods of investigation have been employed to ascertain source information, and the concentrations and their distribution are further discussed in the discussion section of the study.

There are lower concentrations of the elements observed appearing in other locations. For example, Zn shows a wide spread of concentration observed across about 8 gully pots. Most of the locations are along busy roads. Mg appears to display a relatively large spread with concentrations observed across 7 gully pots. Interestingly, PAH (Benzo (a) pyrene) appears to display a very limited spread, it is observed at a significant concentration in only one location, which appears to be a junction where cars are held at a traffic for some time. This is backed up by several previous studies that have confirmed motor vehicles as contributors to PAHs and other contaminants to the environment (Novotny & Olem, 1994; Ellis et al., 2000; Napier et al., 2008 and Rothwell et al., 2015).
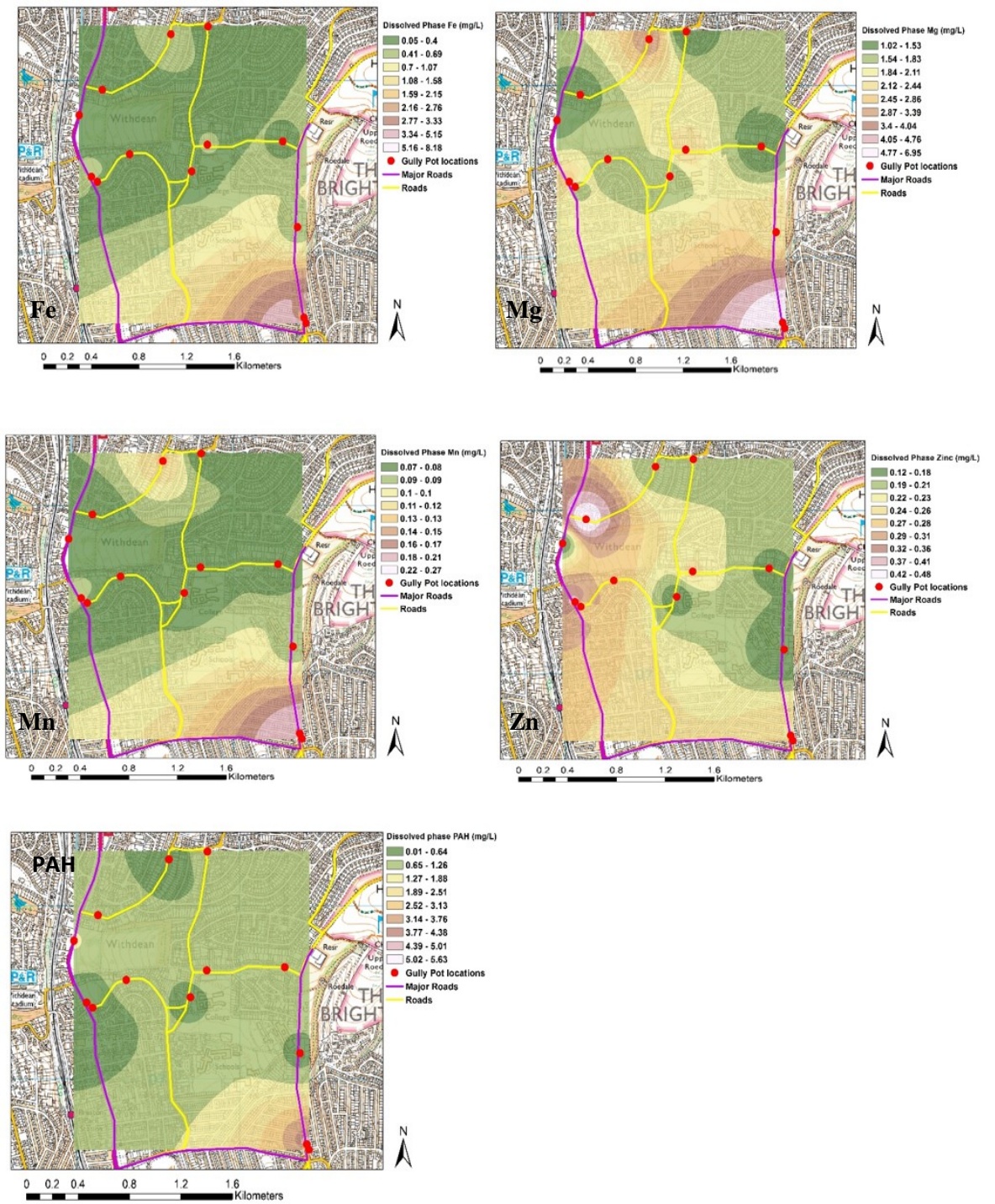
Figure 4. 1. Dissolved phase pollutants spatial patterns in elements with concentration that exceed environmental standards. Benzo (a) pyrene is used as marker for PAH.

4.3.3 Seasonal variation of dissolved phase elements

It is key in this research to establish a relationship and understand the seasonal variation between dissolved phase samples collected in the autumn and spring, to examine possible changes regarding the effect of weather on the elements present in the water samples analysed. This will give a further insight on source of contaminants in the environment. Samples collected for the purpose of this study at both periods of the year were plotted against each other (Figure 4.2) to show any broad differences between spring and autumn samples. In addition, a U-test was also carried out to determine if there is a significant difference between the autumn and spring samples. Results presented in Table 4.2 are only of elements with significant P-values, which is at $p < 0.05$. Fe, Mn and Pb show significant differences while other elements display insignificant results.

Table 4. 2. U-test scores for gully pot water elements with significant U-values when compared between autumn and spring samples.

Element	U- value	Z-score	P- value
Fe	45	2	< 0.05
Mn	36	2.461	0.0139
Pb	45	4.3	< 0.0001
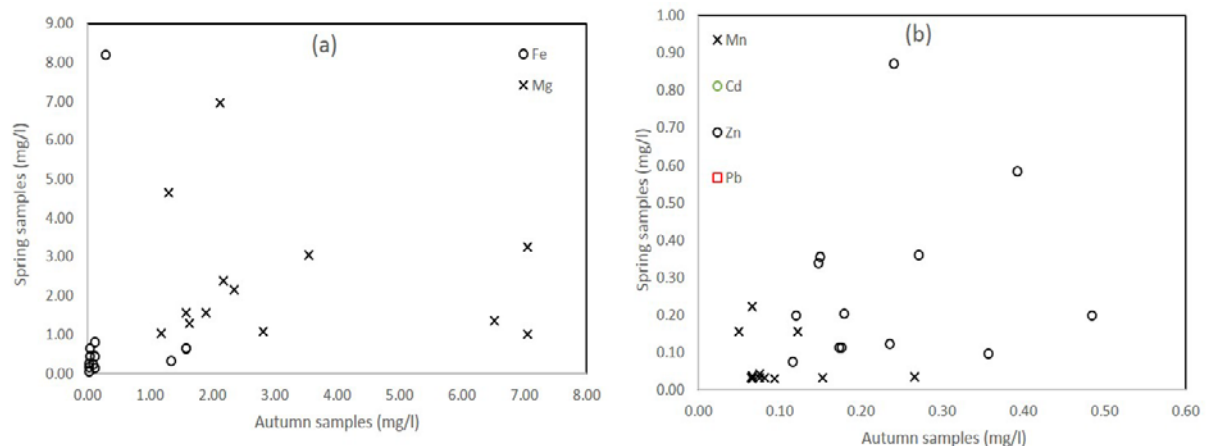
Figure 4. 2. Gully pot water samples collected in autumn 2016 and spring 2017 plotted against each other for comparison.

4.3.4 Correlation between elements within dissolved phase samples.

The distribution of heavy metals within the gully pot waters varies greatly. This is either due to the location of the gully pot (busy highway or local quiet road) or the background abundance or solubility of the type of metal. V, Cr, Pb and Cd have a concentration of less than 0.1 mg/l, meaning they are present at significantly lower concentration than Fe, Mg, Zn and Mn (which show concentrations greater than 0.1 mg/l). Gully pots (GP) 1 and 2 for example are along a busy roads (as presented in map 3.3 refer back to Chapter 3) and GP 9 and GP 12 are along a busy highway and hence are characterised by slightly higher concentrations of heavy metals (see Table 4.1 for full concentrations). The lower concentrations of metals generally appear consistent with the sampling location, either a busy road or a less busy road. Busy roads like junctions or highways show a greater metal concentration as opposed to the lower levels of concentration that has been observed on less busy roads in the gully pot water samples analysed in this study. For example, GP4, GP8 and GP10 are situated on a far less busy road and show low element concentrations. While, GP1 and 2 are on a busy road and show high element concentrations.

Furthermore, correlation of the dissolved phase gully pot sample was carried out and significant values are highlighted in red in Table 4.3.

Table 4. 3. Correlation coefficient values in colour for dissolved phase elements concentration around Brighton urban gully pot samples.

	Cr	Zn	Cd	Pb	Fe	K	V	Mg	Mn	Ca
Cr	1	-	-	-	-		-	-	-	-
Zn		1	-	-	0.1	0.4	-	0.2	0.2	-
Cd			1	-	-	-	-	-	-	-
Pb				1	-	-	-	-	-	-
Fe					1	0.8	-	0.1	0.8	0.3
K						1	-	-	0.8	0.3
V							1	-	-	-
Mg								1	0.9	0.6
Mn									1	0.5
Ca										1

4.3.5 Chemical characteristics of dissolved phase samples from settling pond and soakaways

Dissolved phase sample results from the Keep show high concentrations of only Mn. The A23 settling pond east however displays high concentration of Fe and Zn which can be linked to concentrations within sediment bound samples of the same location. Samples from the west side of the A23 show even higher concentrations of Zn and Fe with Cr, Ni and Mn in decreasing order of magnitude (Figure 4.3 and Table 4.4). Although, when concentrations are compared to environmental standards in Figure 4.1, all elements appear below the effects level.
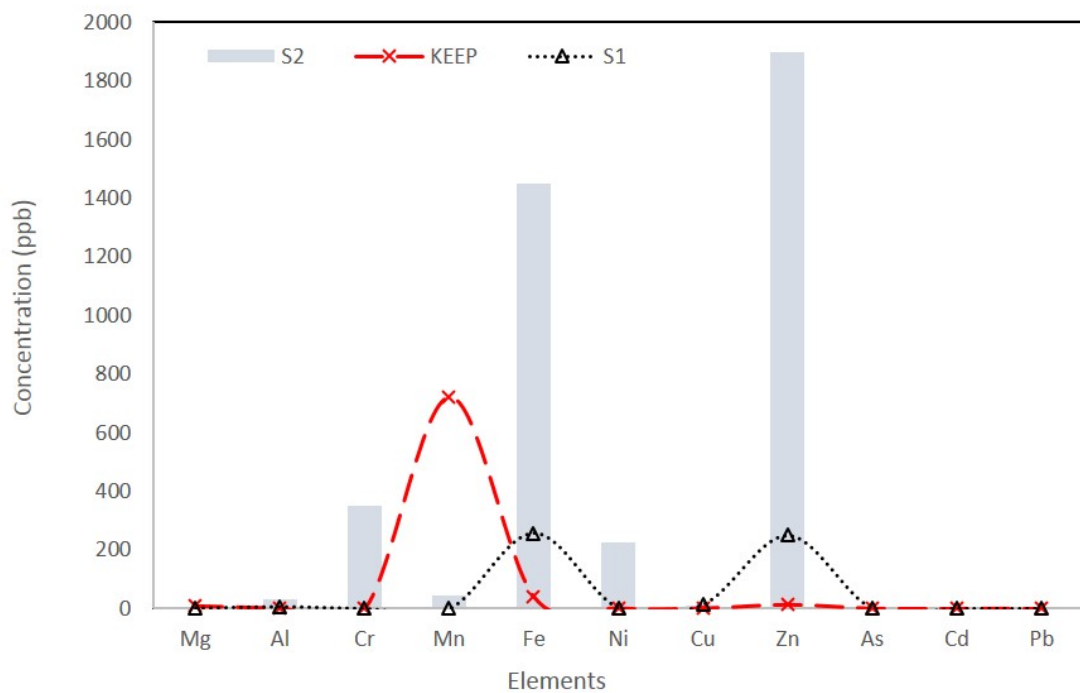
Figure 4. 3. Dissolved phase concentration of heavy metals within the settling pond water (A23 & the Keep).

Table 4. 4. Concentration of dissolved phase samples (water samples) from the Keep and A23 settling ponds around Brighton all elements are presented in the ppb range.

Elements	Keep	S2 (A23 south)	S1 (A23 west)
Mg	9.18	3.29	1.80
Al	1.59	31.40	7.25
Cr	0.31	350.59	0.43
Mn	723.34	43.91	0.25
Fe	39.22	1451.59	257.97
Ni	1.76	227.09	1.79
Cu	1.30	9.84	15.04
Zn	13.70	1897.96	249.44
As	0.74	0.46	0.52
Cd	0.27	0.26	0.35
Pb	0.05	3.73	0.64

Table 4. 5. Concentration of some selected dissolved phase elements and sediment bound elements including coordinates of the locations sampled and Benzo(a)pyrene concentration for both dissolved and sediment bound phases.

| | | | Dissolved Phase | | | | | Sediment bound phase | | | | | | |
| | Coordinates | | Heavy metals and Ions (µg/l) | | | | PAH (µg/l) | PAH (µg/kg) | Heavy metals and ions (mg/kg) | | | | | |
Number	X	Y	Zn	Mg	Mn	Fe	Benzo(a)pyrene	Benzo(a)pyrene	As	Cu	Ni	Pb	Zn	Cr
GP1	531424	106590	0.36	6.95	0.27	8.18	0.58	2.64	14	195	30	329	619	57
GP2	531411	106621	0.18	4.64	0.15	0.8	5.67	36.91	19	158	48	89	701	45
GP3	531369	107147	0.12	2.15	0.08	0.43	0.46	1.93	21	218	26	239	764	71
GP4	531276	107645	0.17	1.08	0.07	0.32	0.66	1.62	35	260	18	374	637	65
GP5	530798	107626	0.24	2.37	0.07	0.43	0.96	0.58	14	335	21	116	666	69
GP6	530698	107471	0.15	1.55	0.07	0.17	0.45	0.51	34	378	33	1101	919	48
GP7	530305	107571	0.27	1.56	0.08	0.14	1.1	3.13	64	545	74	1525	2091	10
GP8	530099	107410	0.24	1.34	0.07	0.23	0.01	0.38	30	292	18	236	625	121
GP9	530062	107440	0.39	3.03	0.09	0.65	0.2	0.72	15	391	45	242	1232	140
GP10	529985	107798	0.15	1.28	0.07	0.05	1.33	1.54	15	391	45	242	1232	140
GP11	530131	107946	0.48	1.28	0.07	0.05	0.9	0.78	12	409	34	65	218	44
GP12	530566	108269	0.18	3.24	0.12	0.64	0.2	0.78	16	262	32	206	906	122
GP13	530801	108314	0.18	1.02	0.07	0.26	0.9	3.71	24	362	41	306	1172	101

4.4 Sediment bound pollutants – Background

Results from analysed sediments from gully pots were compared to previous studies and quality guidelines for sediment standards and the environmental quality standard for hazardous substances (Directive 2013/39/EU). This data will allow for the assessment of elements enriched beyond background/ guideline values.

4.5 Results

4.5.1 Concentration in comparison to guideline values

Gully pot sediment samples analysed using P-XRF were compared with the results obtained from previous studies (Rothwell et al., 2015), sediment quality guidelines from the Habitats directive technical advisory group on water/sediment quality (WQTAG078K) and the Environmental standard guidelines directive-2013/39/EU (Table 4.4). Polycyclic aromatic hydrocarbons (PAH) analysed (Phenanthrene, Flouranthene, Pyrene and Benzo (a) pyrene) did not have concentrations above the sediment guidelines values or the environmental standards directive values. Heavy metals on the other hand, showed that Zinc, Nickel, Chromium, Copper, Arsenic and Lead have high concentrations across the sampling locations. When compared to the Environmental standard guidelines directive-2013/39/EU, 100% of the samples in 100% of the locations exceed the guideline values.

However, when compared to the sediment quality guidelines of the Habitats Directive technical advisory group on water/sediment quality (WQTAG078K) which was used in the Rothwell et al.(2015), study, >75% of the total contaminants listed above exceed the effects threshold level in the gully pots at 50% or above (Zinc 84.6%, Copper 76.9%, Lead 76.9% and Arsenic 53.8%). The remaining 25% of the heavy metals contaminants, exceed the threshold effects level at approximately 31% (Nickel 30.77% and Chromium 30.77%).

This means that the heavy metal contaminants are more heavily partitioned towards the sediment-bound phase of the gully pots. Also, that organics (PAH) have a very minor concentration in the sediment-bound phase of the gully pots. This results contradicts findings from a study by Rothwell et al., (2015) of gully pots in Manchester, where, PAHs in sediments are higher than in waters. In the current study, only Benzo (a) pyrene in sediment is higher than in waters. In Table 4.6, correlation coefficient values for sediment bound samples are presented. Significant values are highlighted in red with Zn, Pb, As and Ni showing significance. Other elements observed and presented in the table appear much less significant. These include; Cr and Cu. The positive correlation can be an indication of a similar source of origin. However, correlation alone cannot be used to determine source. Other analytical processes employed in the later parts of this study gives a clearer indication of source origin of the elements, backed by literature.

Table 4. 6. Significant correlation coefficient values are highlighted for sediment phase metals concentration around Brighton urban gully pot samples.

	Cr	Zn	Cu	Pb	As	Ni
Cr	1	0.001	0.04	0.2	0.2	0.1
Zn		1	0.3	0.5	0.5	0.63
Cu			1	0.4	0.3	0.3
Pb				1	0.7	0.36
As					1	0.2
Ni						1

Table 4. 7. Different concentrations of sediment-phase pollutants in gully pots, compared with sediment quality guidelines effects levels and Environmental standard guidelines (Directive 2013/39/EU) PEL=predicted effects level from the freshwater sediment quality guidelines. ND=not defined

Sediment-bound Parameter	Concentration in Gully pot (mg/kg)			Sediment quality guidelines			Environmental standard guidelines (mg/kg)	
Metals	Minimum concentration	Maximum concentration	Mean concentration	Gully pots exceeding PEL	Gully pot % at PEL	PEL	Min.	Max.
Zinc	619	2091	879	11	84.6	315	123	315
Nickel	18	74	35	4	30.77	35.9	18	35
Chromium	44	140	74	4	30.77	90	37	90
Copper	158	545	317	10	76.9	197	36	197
Lead	65	1525	402	10	76.9	91.3	35	91
Arsenic	14	64	24	7	53.8	17	5.9	17
PAHs (µg/kg)								
Phenanthrene	0.17	45	4.1	0	0	515	ND	ND
Flouranthene	0.37	67.84	6.73	0	0	2355	ND	ND
Pyrene	0.39	60.50	6.1	0	0	875	ND	ND
Benzo (a) pyrene	0.38	36.91	4.25	0	0	782	ND	ND

4.5.2 Sediment mineralogical composition

In order to define the mineralogy of the gully pot sediments, bulk powder X-ray diffraction (XRD) analysis was carried out to identify minerals present. Mineral identifications were carried out using Panalytical's HighScore Plus software. The XRD from all the 13 locations of the gully pot sediments are combined and presented as a single Figure in Figure 4.4. The samples are mainly composed of quartz and carbonates (dolomite, calcite and siderite) with variable concentrations in different gully pots. Gully pot 7 displays the highest quartz concentration of 83% and the lowest carbonates at 3% in Table 4.8. Gully pot 12 shows the least quartz at 55% with 33% carbonates. The remaining percentages in the table consists of organic fragments and unidentified compositions. The significant amount of quartz can be a soil derived mineral originating from surrounding soils that may have been transported to the present locations. Samples also contain (based on SEM analysis, below) silt-sized organic fragments and complex multiphase fragments which make-up the remaining percentages.
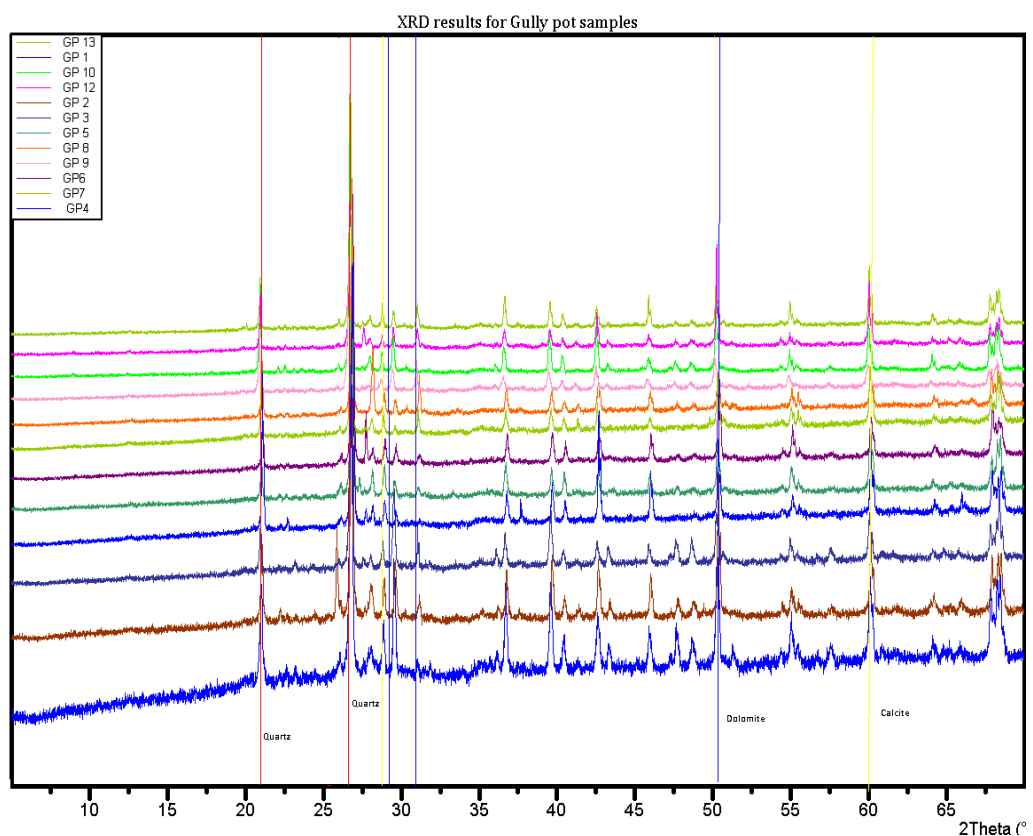
Figure 4. 4. Gully pot sediment samples XRD patterns combined for all the 13 locations sampled.

The gully pot sediment samples were further studied using SEM-EDS analysis. Samples 6a, 6b and 7b show a variety of particle concentrations and the results are presented here with images and their corresponding EDS. All images are in backscatter mode (i.e. high atomic mass samples show brightly on the images).

Table 4. 8. Quantification of minerals present (Quartz and Carbonates) in samples (Values are given in % using RIR method semi-quantitative).

Gully pot label	Quartz	Carbonates
GP1	82	15
GP2	84	13
GP3	70	25
GP4	55	34
GP5	78	3
GP6	58	32
GP7	86	3
GP8	84	4
GP9	82	17
GP10	80	19
GP11	78	20
GP12	55	33
GP13	72	24

4.5.3 BSE - SEM image and corresponding EDS graph.

The SEM-EDS results are for a selection of samples that cover the two seasons, spring and autumn. 6A represents spring samples while, B represents autumn samples. Images in each site are presented in multiples with the resulting EDS graph presented showing the

wt% of the elements (based on spot analysis). The results show high heavy metals values, all samples contain silt sized organic fragments and complex multi-phase fragments (including carbon-rich multiphase samples). The images and EDS graphs are presented from Figures 4.5 – 4.26.

The amount of particles released in the environment generated from wear through automotive friction in road traffic has increased in recent times (Garg et al., 2000). Brake wear in cars has been estimated to be about 3.2 to 8.8 mg/km (depending on the type of brake pad tested) with an average particle size of about 6µm (Sanders et al. 2003 & Peikertová et al 2013). Brake linings compose usually of complex composite materials that are potentially hazardous to the environment. Figure 4.5 - 11 show BSE- SEM images of gully pot sediments from location 6a. The corresponding EDS graphs show the element composition of each spectrum as shown in Figure 4.6 – 4.14. Barium ($BaSO_4$), lead (Pb_3O_4) and Iron (Fe_2O_3) oxide phases appear common. Other metallic fragments of sizes between 5um - < 1um are seen across the figures.
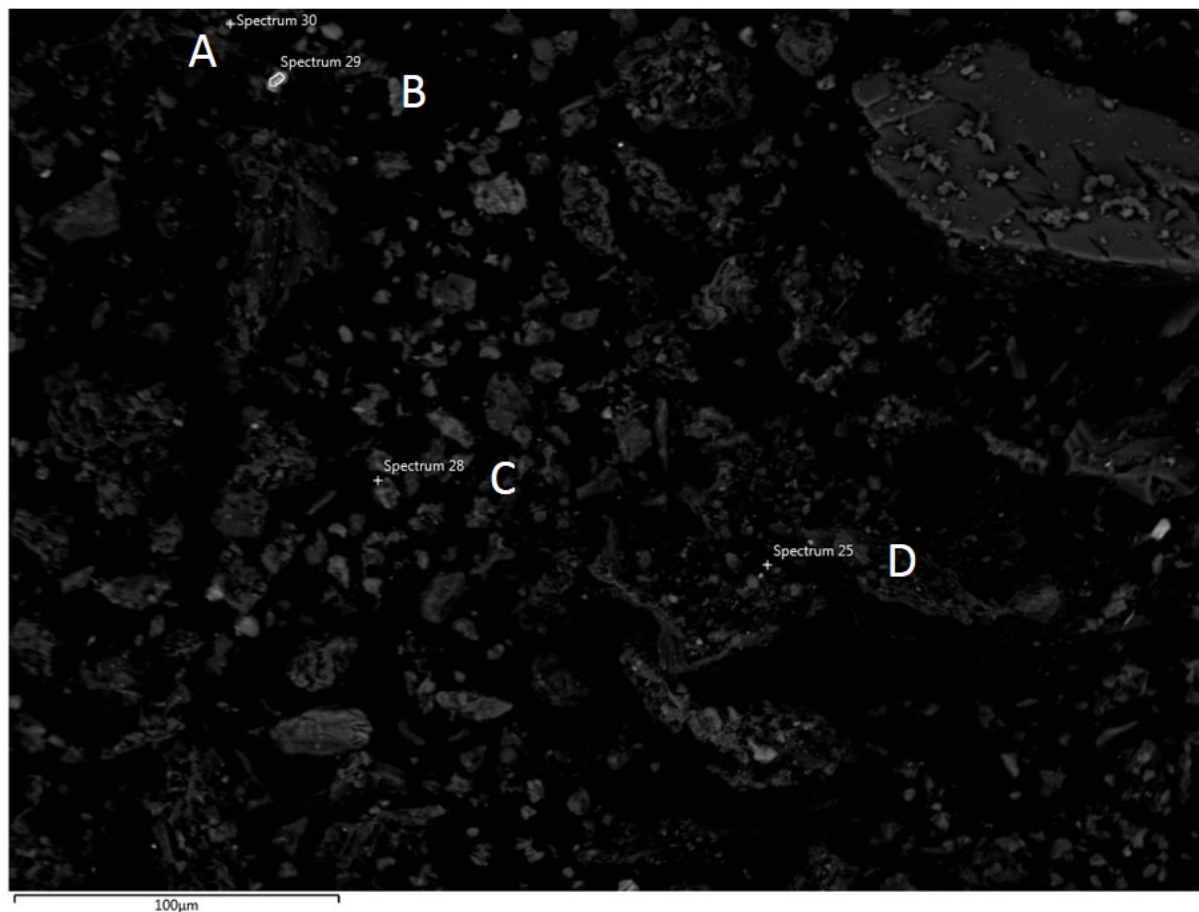
Figure 4. 5. BSE -SEM image of site 6a site 1 (A-D) of dried gully pot sediment samples.
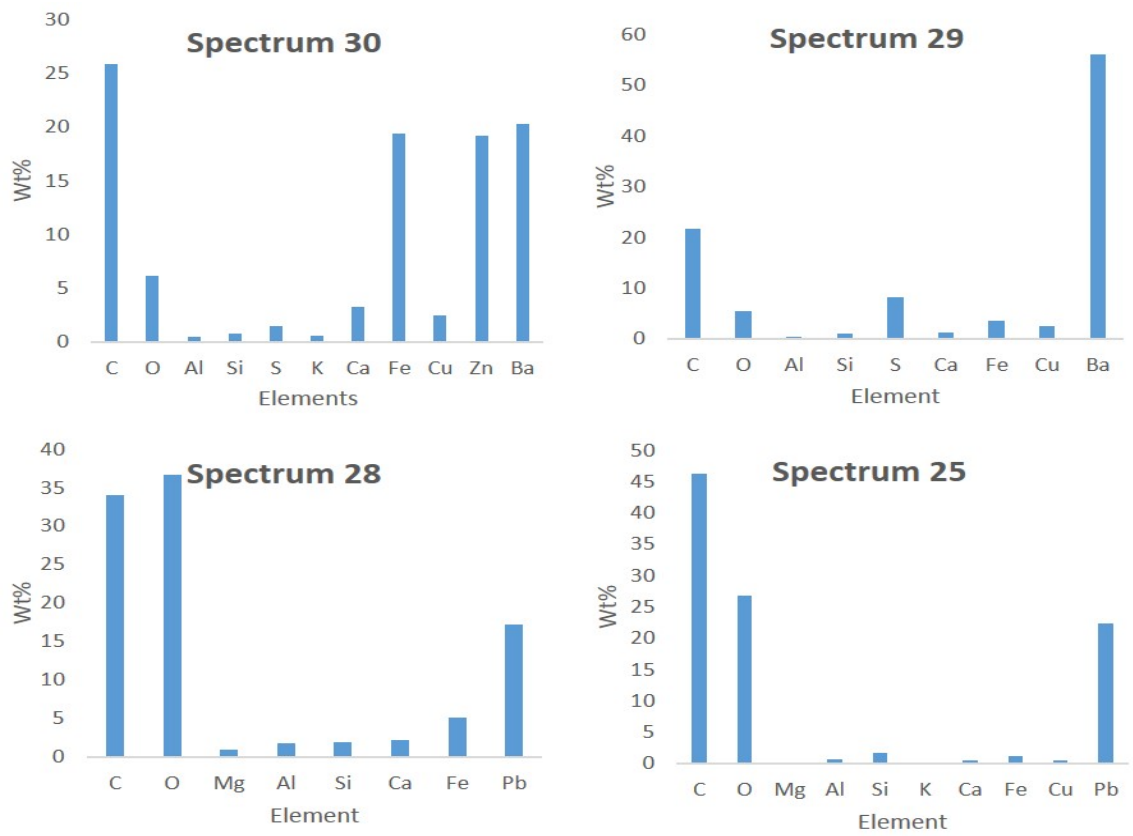
Figure 4. 6. EDS graph of sample 6a site 1 (Spectrum 25,28,29 & 30) of SEM image presented above showing elements concentration in wt% (y-axis).
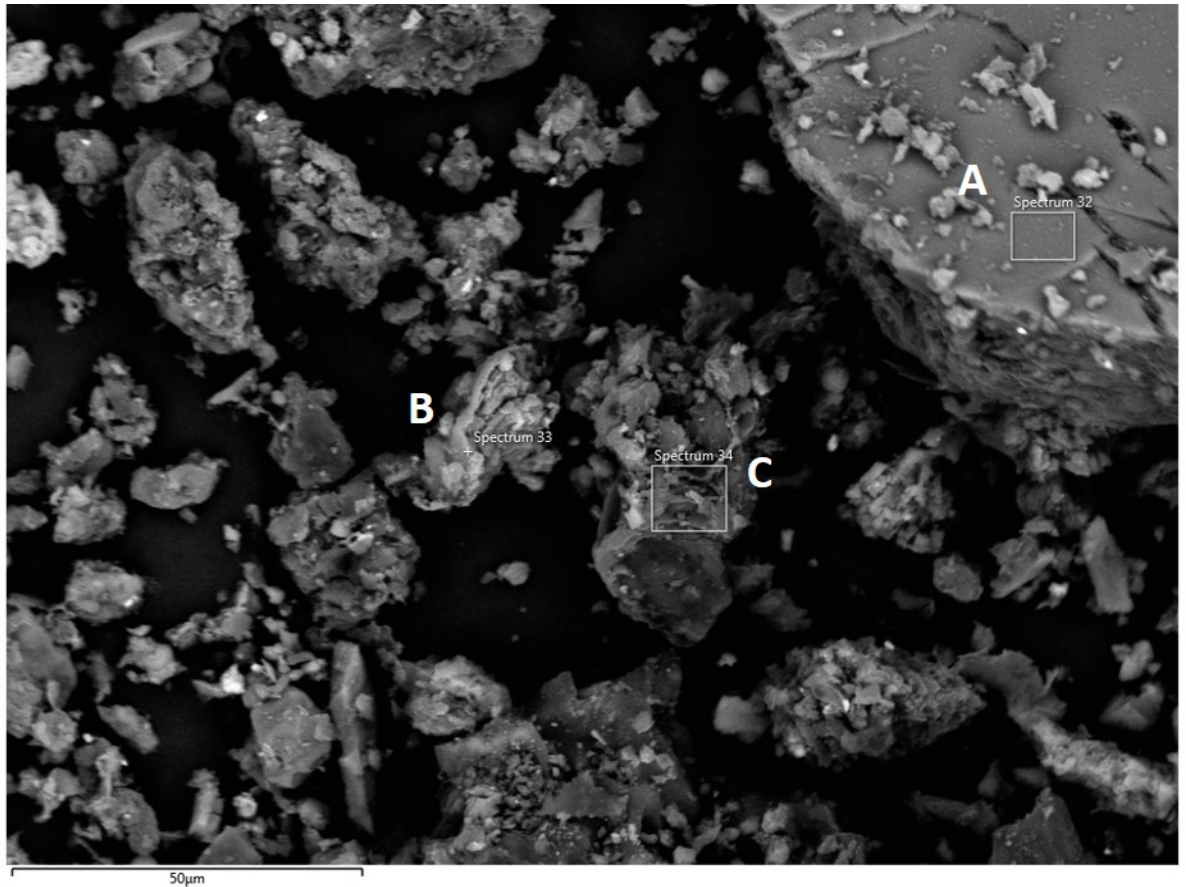
Figure 4. 7. BSE - SEM image for dry sediment sample from location 6a site 2. EDS (Spectrum 32, 33, & 34).
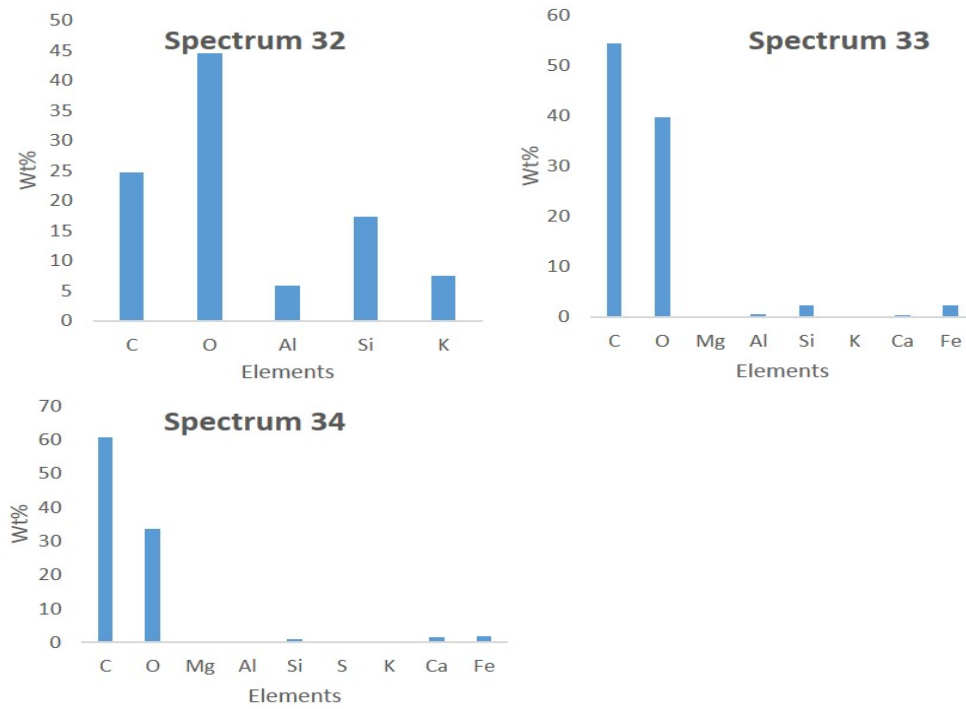
Figure 4. 8. EDS graph of sample 6a site 2 of SEM image showing wt% concentration of elements.
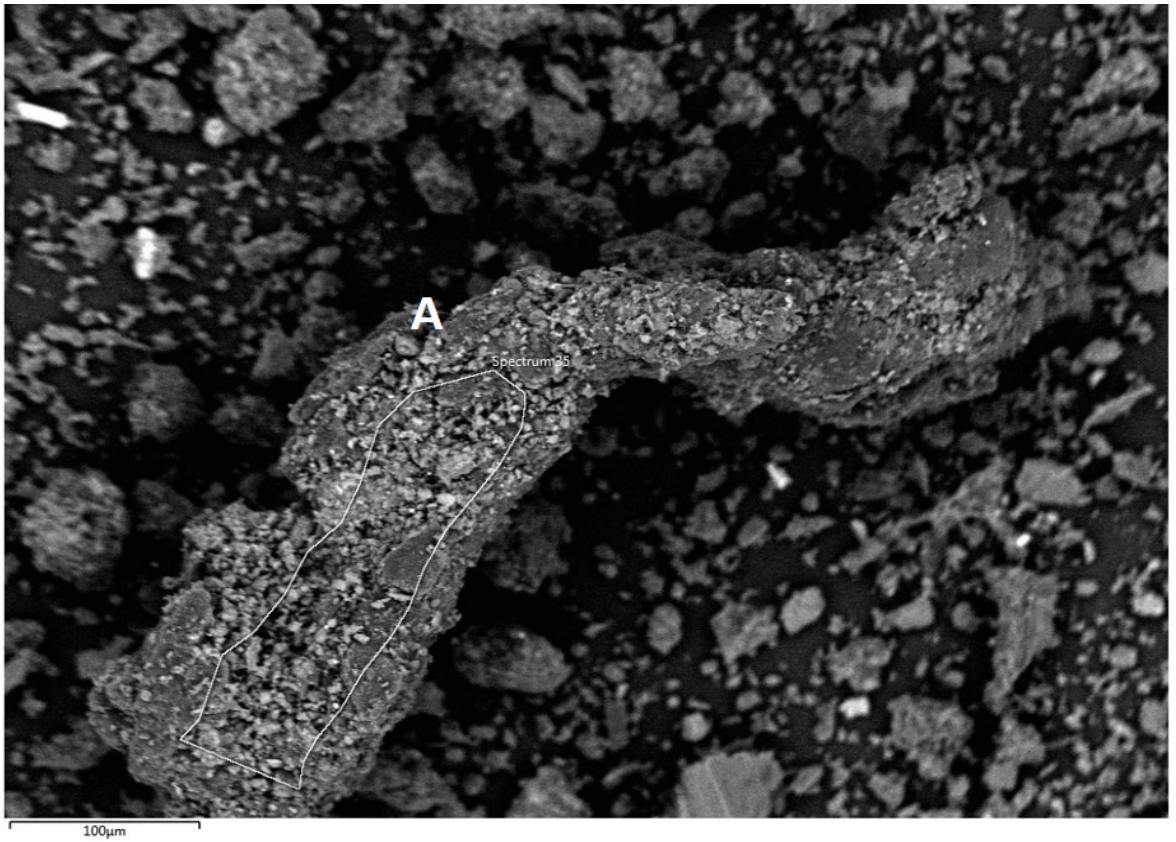
Figure 4. 9. BSE - SEM image for dry gully pot sediment sample from location 6a site 3
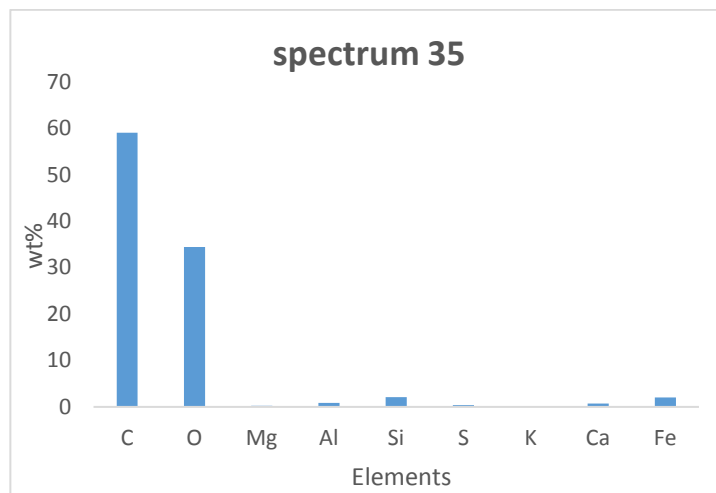
Figure 4. 10. EDS graph of elements in wt% of dry gully pot sediment samples of location 6a site 3.
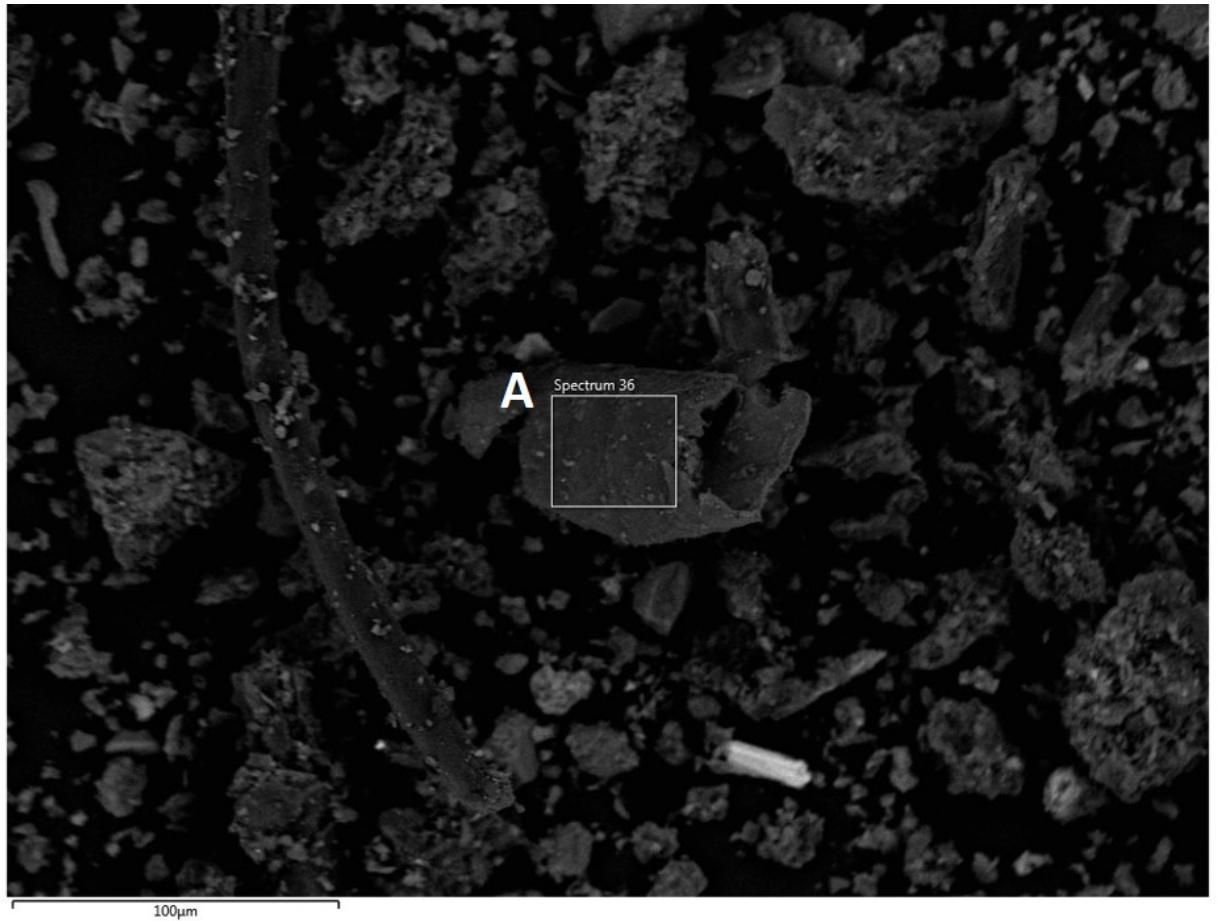
Figure 4. 11. BSE - SEM image of dry gully pot sediment sample from location 6a site 5
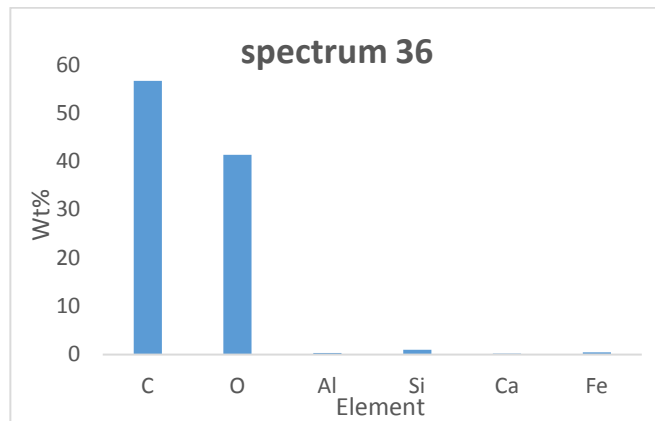
Figure 4. 12. EDS graph of dry gully pot sediment sample of location 6a site 5 (spectrum 36) with elements showing wt% concentrations.

The BSE-SEM images and their corresponding elements from sample 6b are shown in figures 4.13 – 4.19, and are characterised by metals fragments with a major composition of Pb oxide (Pb_3O_4). A metallic nickel fragment is observed in Figure 4.15 of about 16µm diameter.
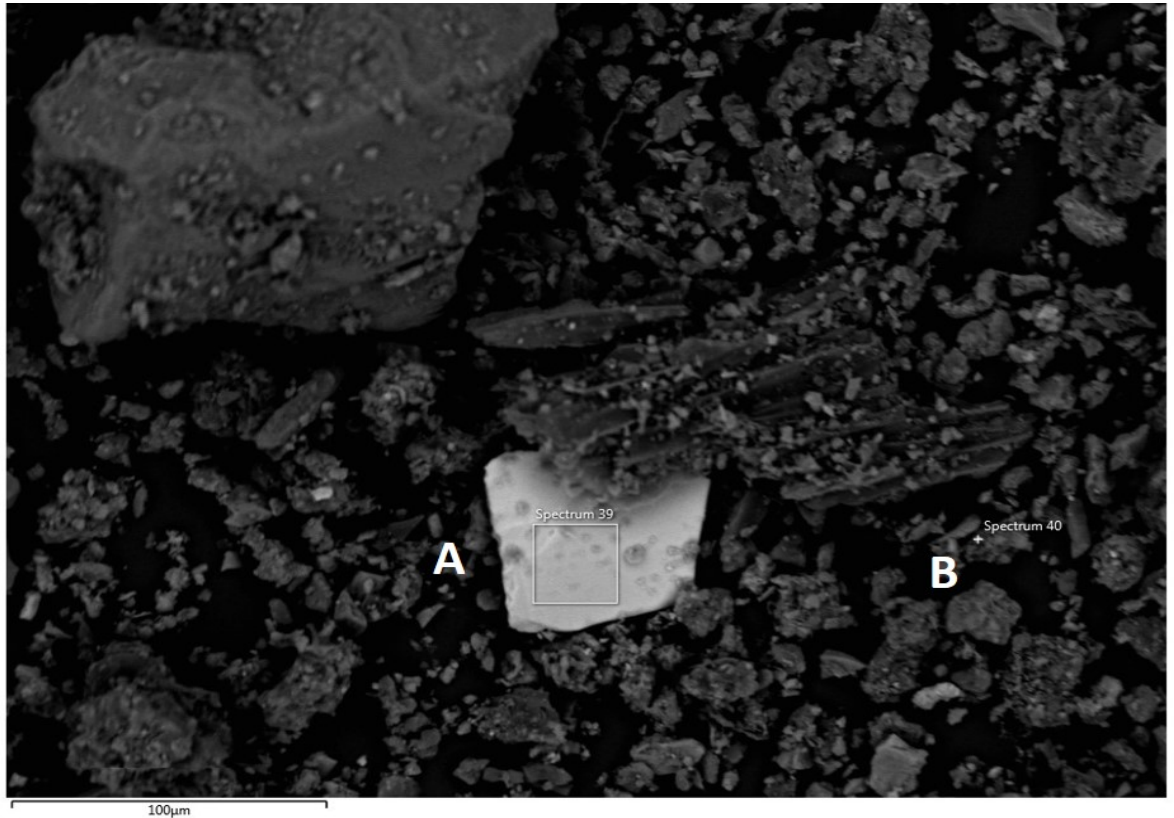
Figure 4. 13. BSE - SEM image of dry gully pot sediments from location 6b site 1 (A - B).
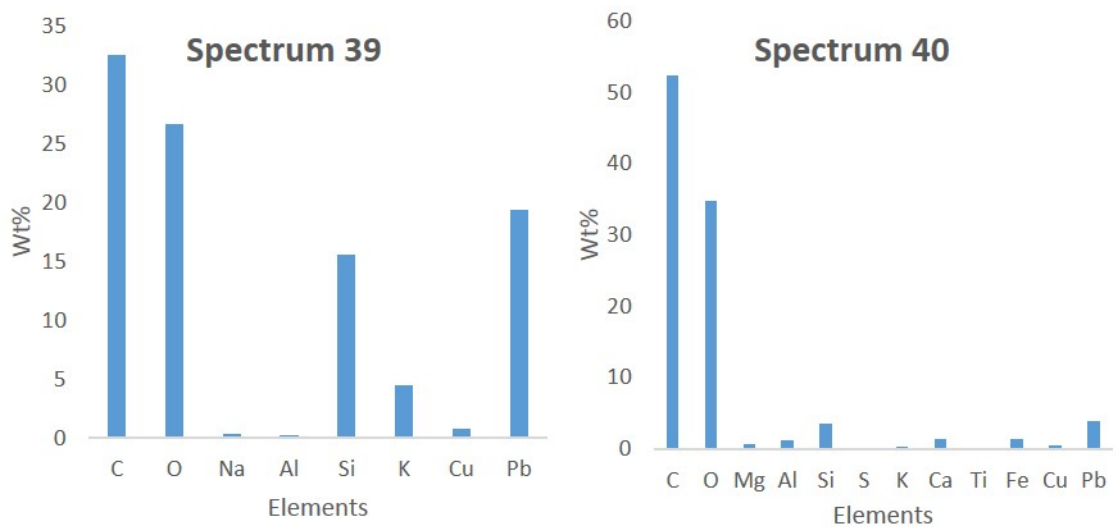
Figure 4. 14. EDS graph of 6b site 1 (Spectrums 39 & 40) element concentrations in wt%.
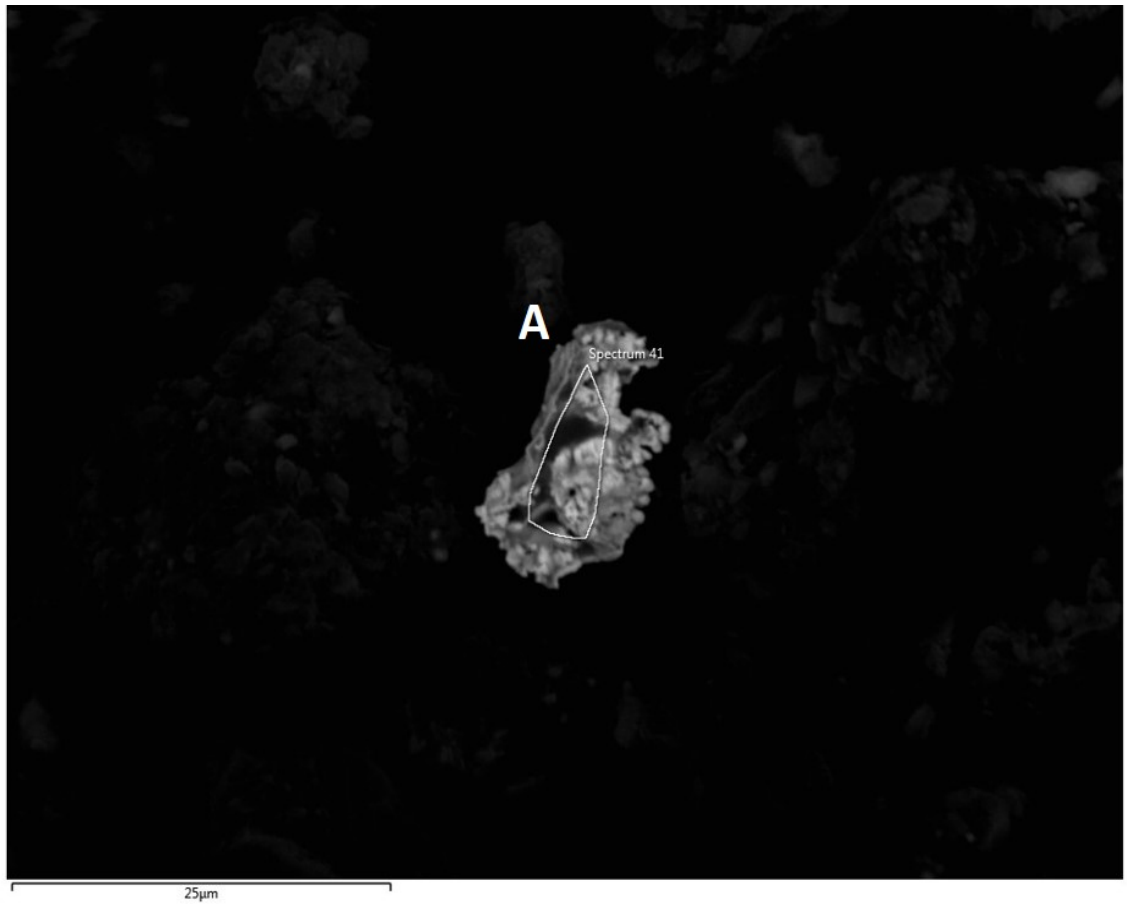
Figure 4. 15. BSE - SEM image of dry gully pot sediment sample from location 6b site 2.
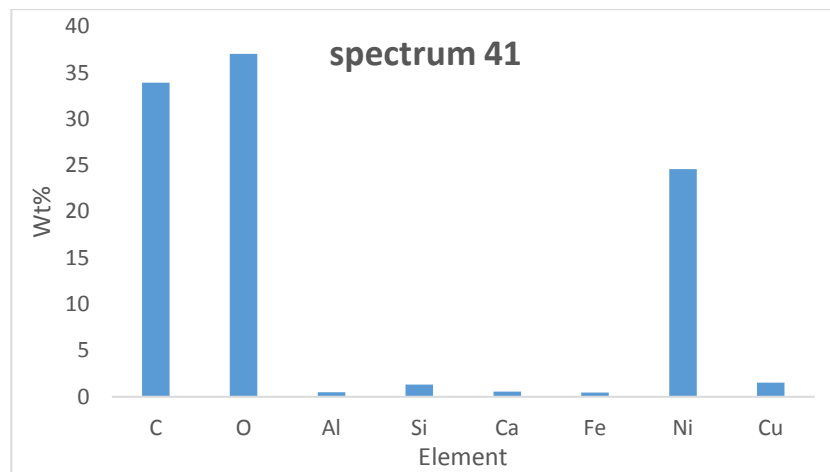
Figure 4. 16. EDS graph from SEM image of location 6b site 2.
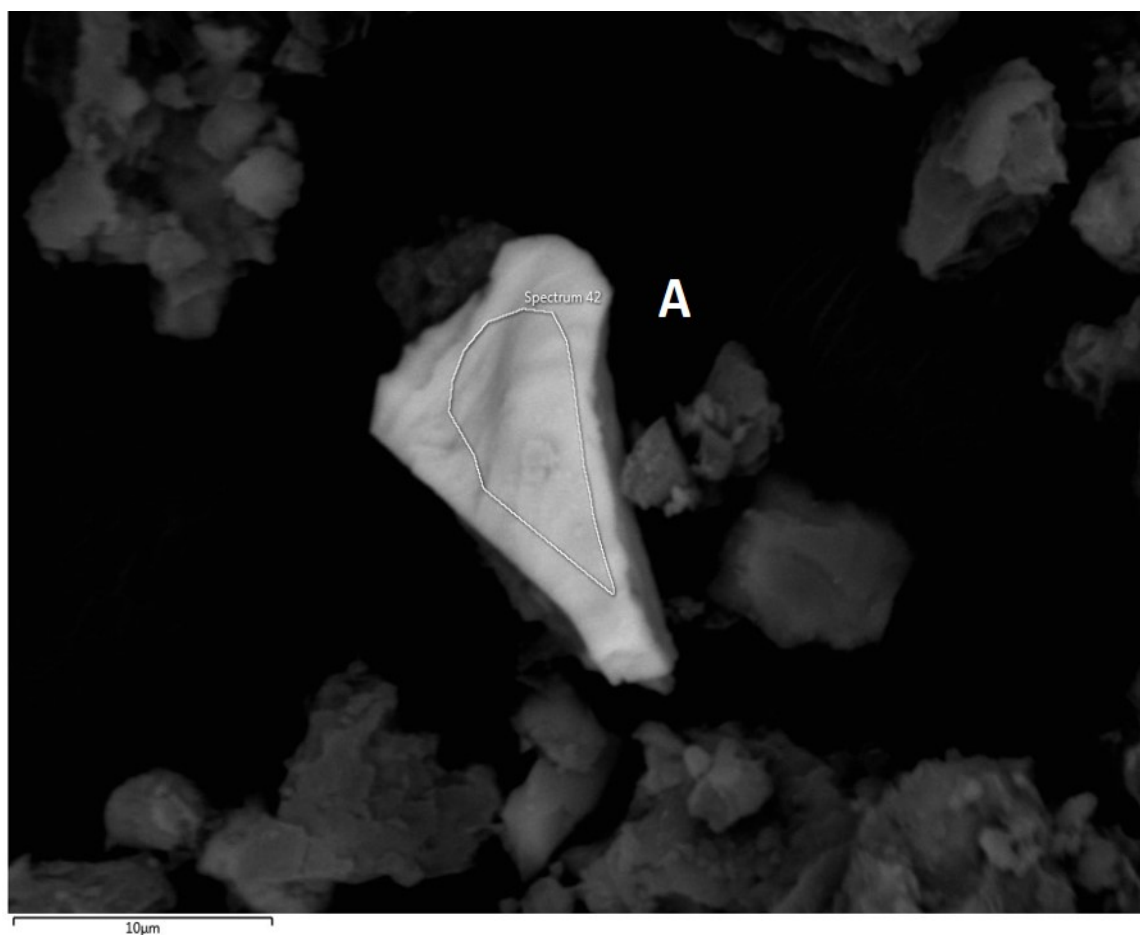
Figure 4. 17. BSE - SEM image of dry gully pot sediment sample from location 6b site 3.
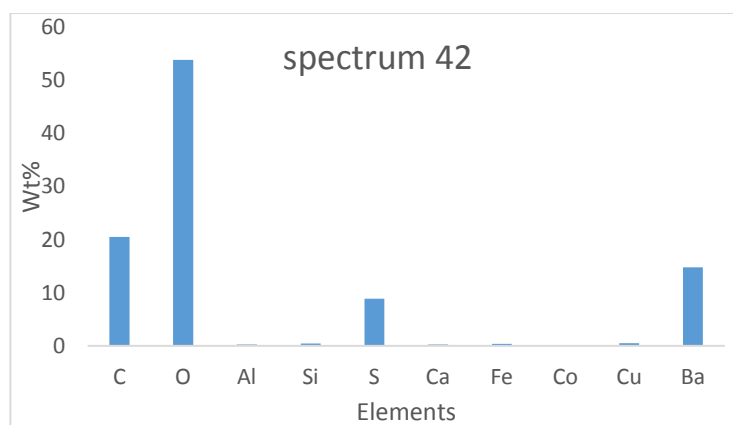
Figure 4. 18. EDS graph of SEM image presented for location 6b site 3 showing elements wt%
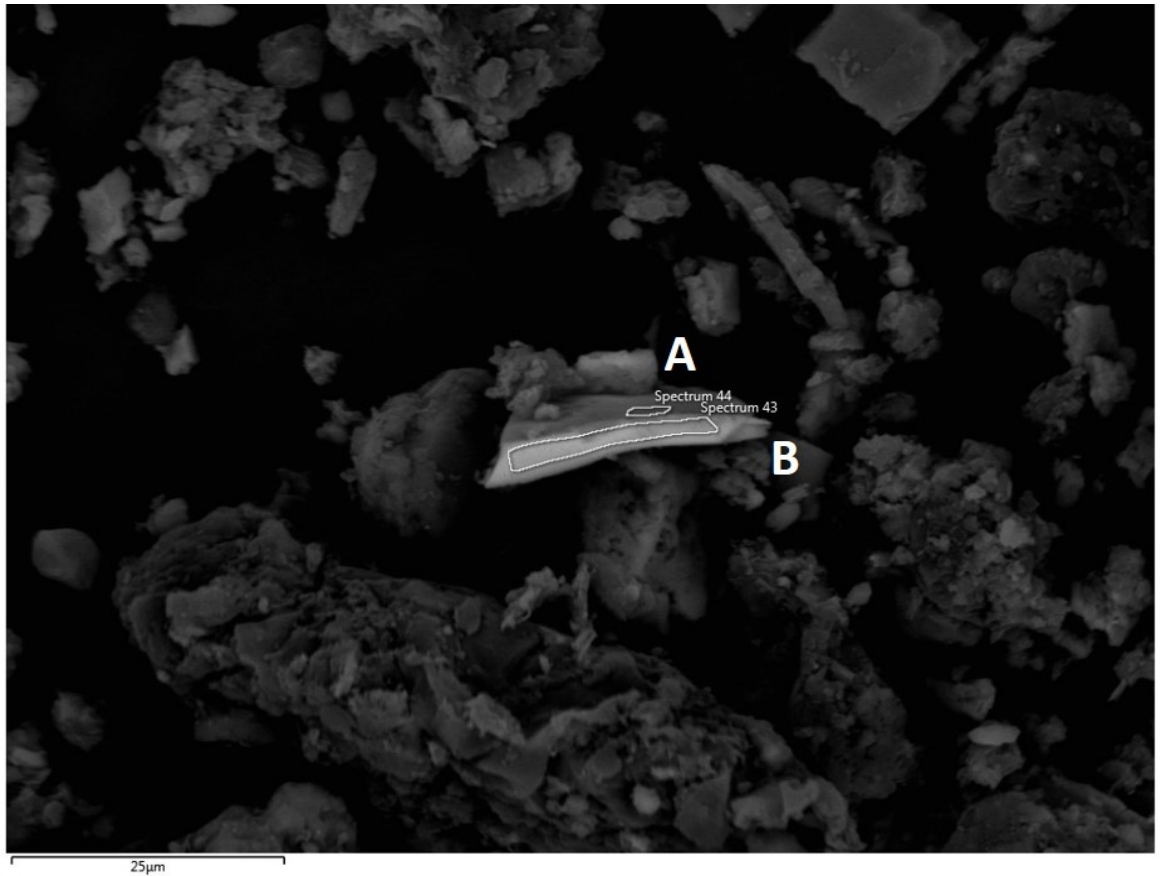
Figure 4. 19. BSE - SEM image of dry gully pot sediment sample of location 6b site 4 (Spectrum 43 & 44)
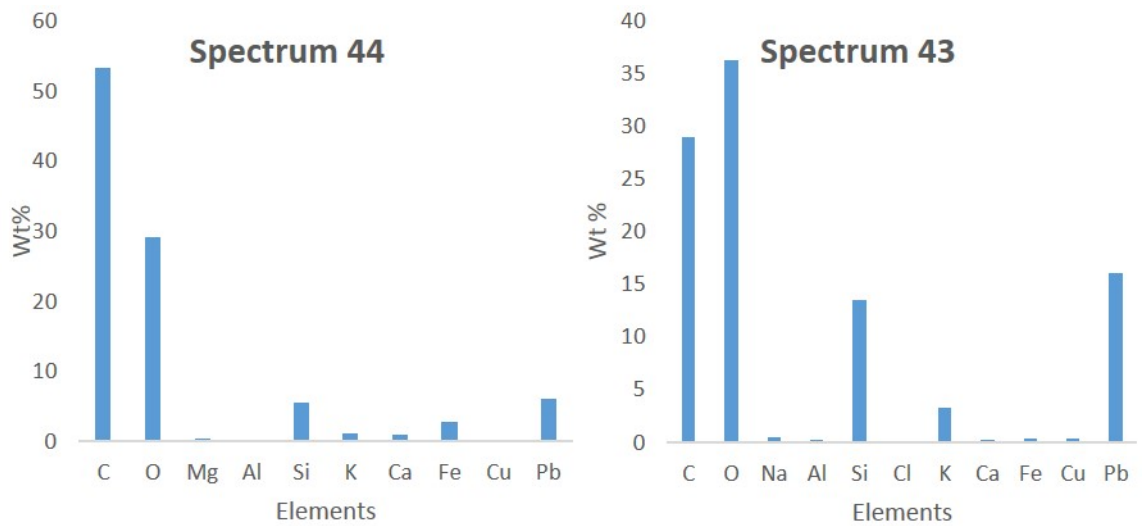
Figure 4. 20. EDS graph of SEM image from location 6b site 4 with elements displaying wt%.

The SEM images presented from Figure 4.21 – 4.26 and their corresponding EDS graphs are characterised by multi-phase fragments with some Fe- Cr metal phases of about 30µm present.
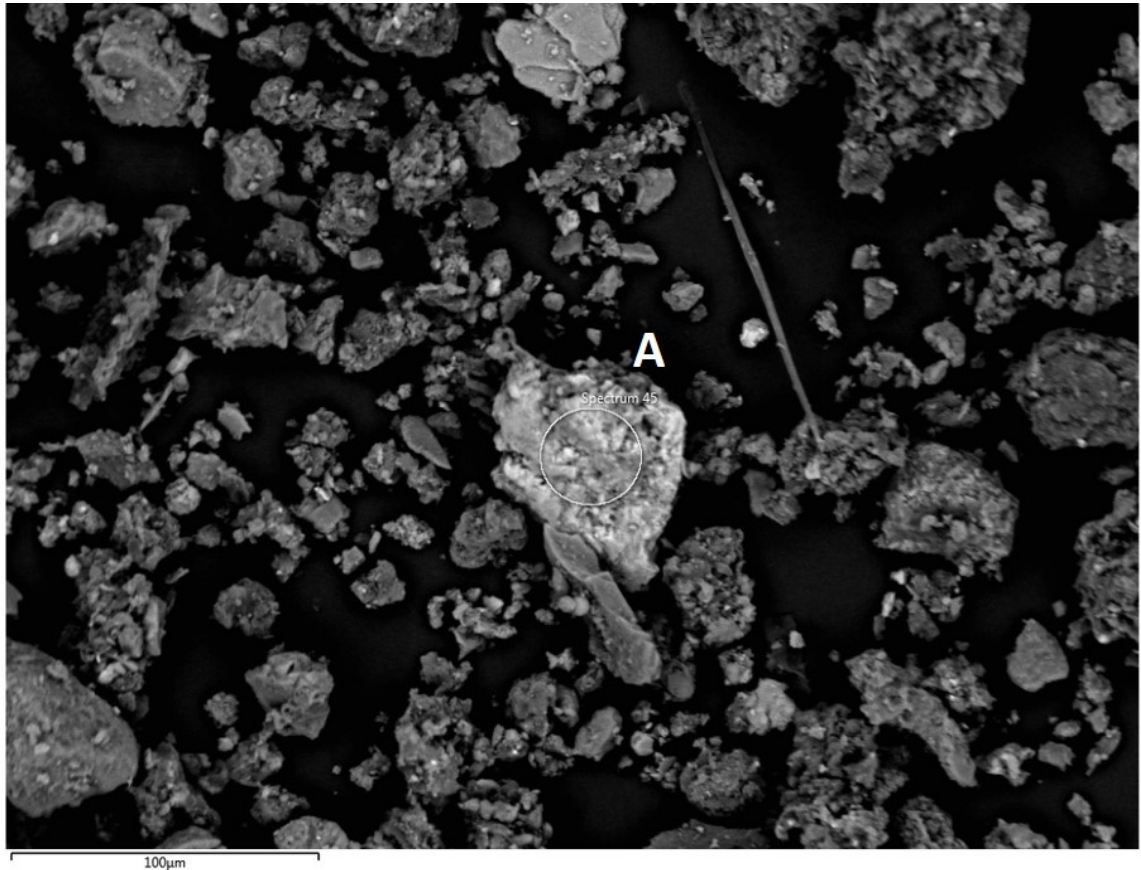
Figure 4. 21. BSE - SEM image of location 7a site1 dry gully pot sediment
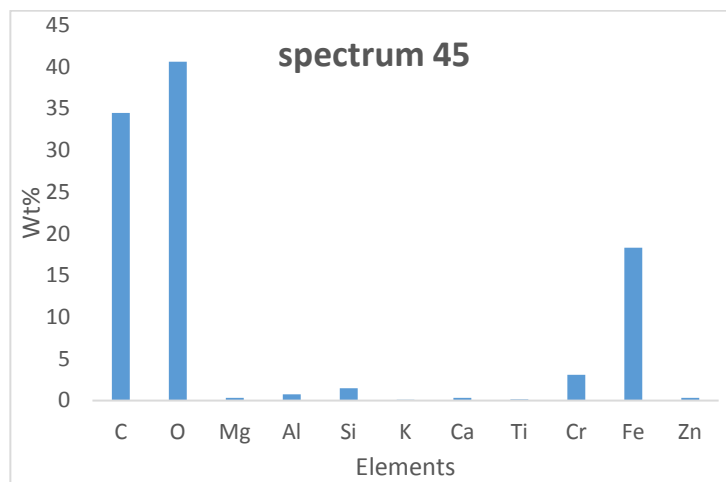
Figure 4. 22. Graph of EDS from location 7a site 1 elements showing wt% concentrations.
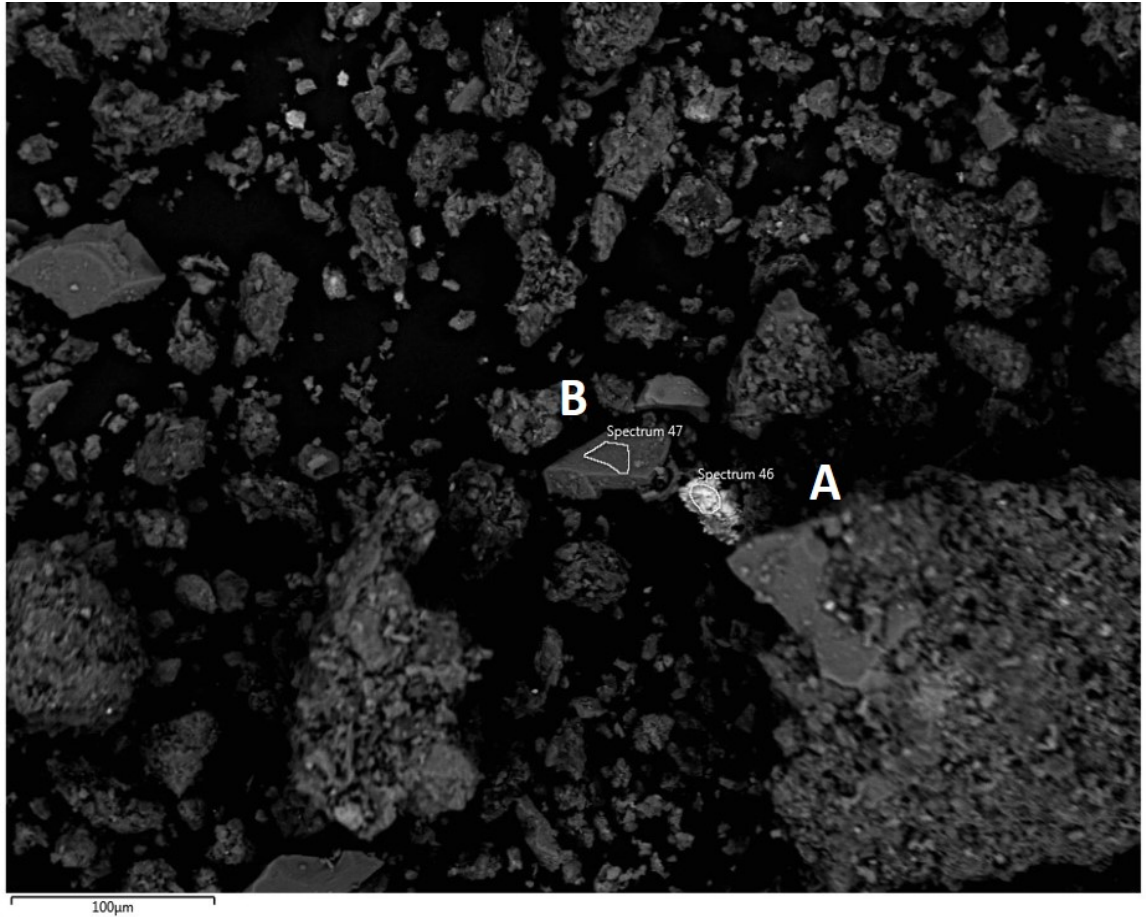
Figure 4. 23. BSE - SEM image of dry gully pot sediment samples of location 7a site 2 (Spectrum 46 & 47)
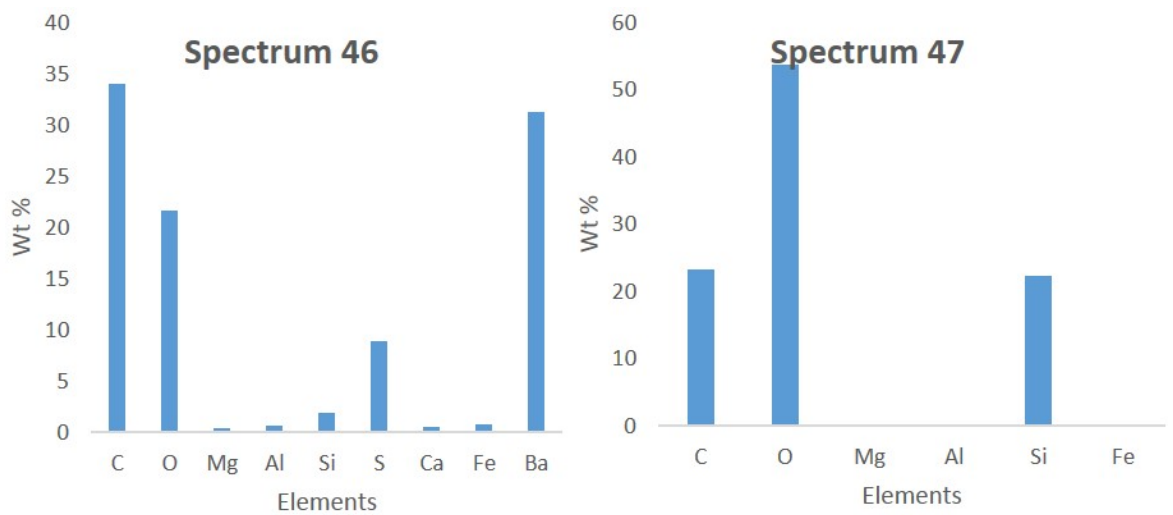
Figure 4. 24. EDS graph from SEM image of location 7a site 2 (A - B) concentrations in wt%

Figure 4. 25. BSE - SEM image of location 7a site 3
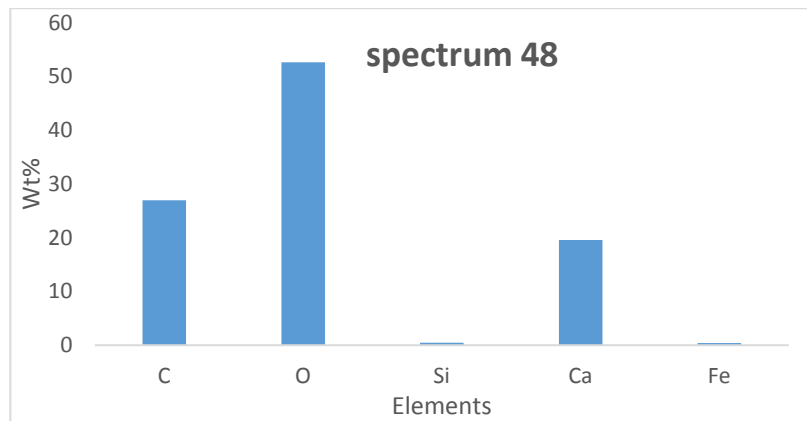
Figure 4. 26. EDS graph of location 7a site 3 wt% concentrations.

4.5.4 Spatial distribution of element concentrations within sediment bound phase

The spatial distribution of the sediment-bound phase of the gully pot contaminants show a complex pattern but a clear trend emerges in the concentration and distribution of the various contaminants (Figure 4.27). Heavy metals Arsenic (As), Copper (Cu), Lead (Pb), Nickel (Ni) and Zinc (Zn) appear to show a wide range of concentration with highest concentrations at gully pot sites 3, 9, 10 & 12 . Within heavy metals, only Nickel (Ni) is clearly elevated around a road junction. Johansson et al. (2009); Khan et al. (2011) and Rothwell et al., (2015) reported the source of Nickel on roads to be from vehicle exhaust and tyre wear and Zn mostly associated with tyre wear. Therefore, it is no surprise that Ni is the only metal observed at a significant concentration along road junctions where motor vehicles stop for some time before moving. Lead (Pb) exhibits a limited concentration with the highest concentrations observed in gully pot 7. While, Cu on the other hand displays limited concentrations with the highest concentrations observed at site 10 spread.

PAHs in the form of Benzo (a) pyrene shows higher concentration in the same location uphill at a busy junction as Ni. The same was observed in the dissolved phase elements, with PAH having its highest concentration at the same location. Meanwhile, Chromium shows higher concentration on a busy road close to rail line. From the result above a link between the pollutants and their source can be established. Polycyclic aromatic hydrocarbons (PAH) on the other hand are related to oils from vehicular movements and are observed at junctions where cars come to a hold for some time before moving on. These linkages are further backed up by SEM results (Figure 4.13), where metal fragments (apparently from vehicle wear) are observed in some of the sediment samples observed from the gully pots.
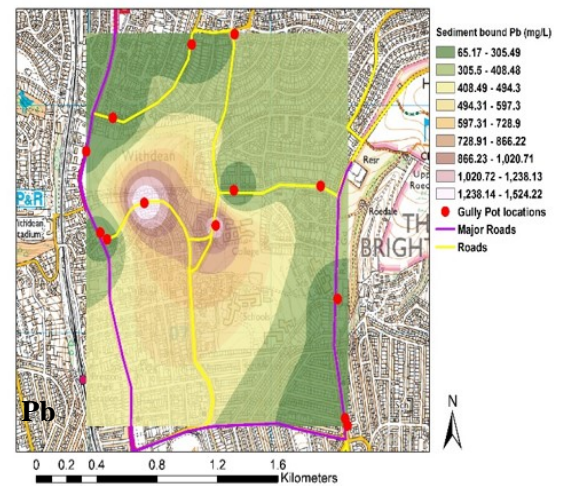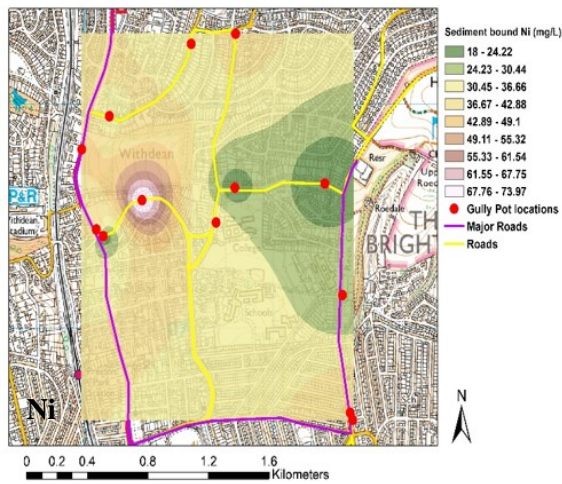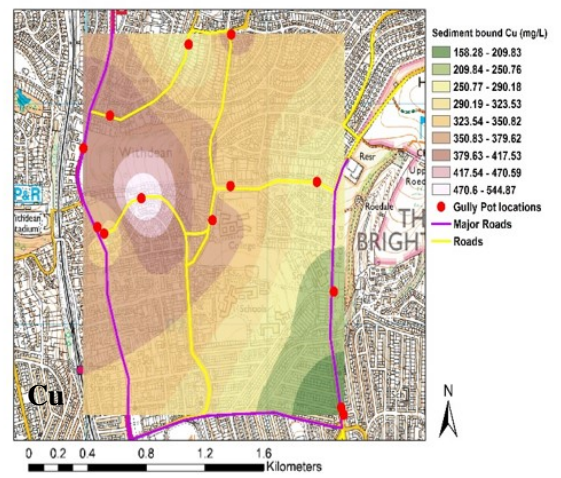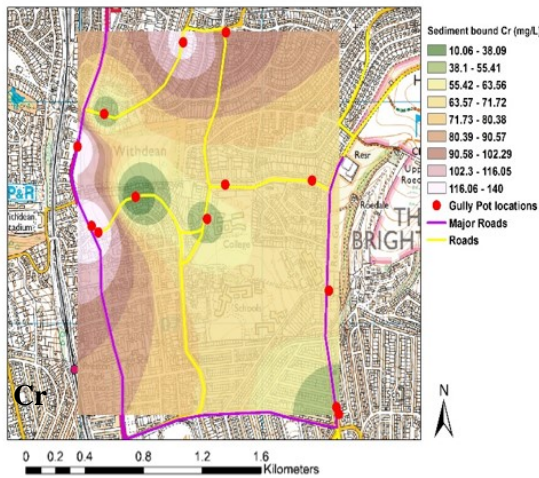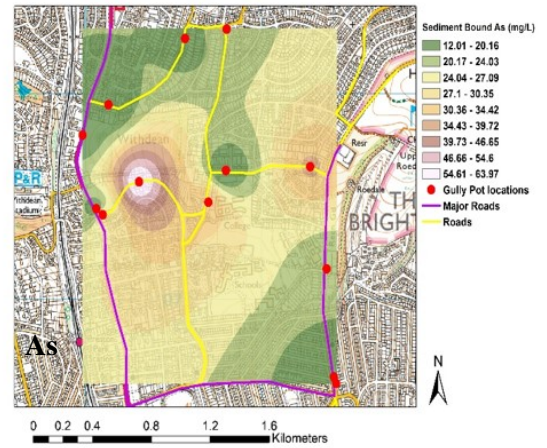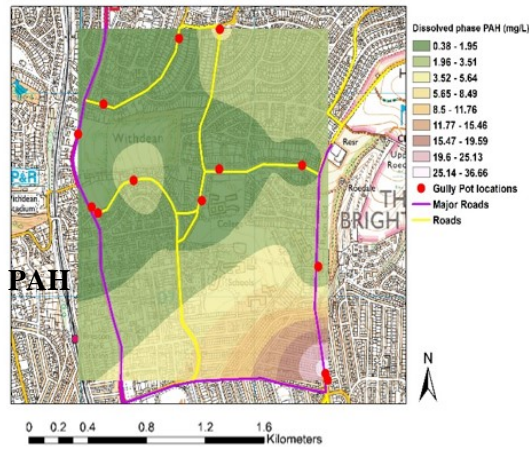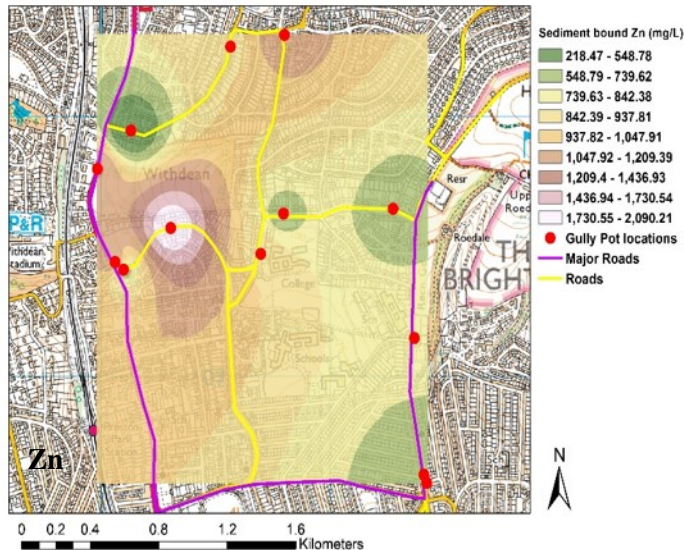
Figure 4. 27. Sediment-bound pollutants spatial pattern in elements with concentration exceeding Environmental standards. Benzo (a) pyrene is used as marker for PAHs.

4.5.5 Correlation between data

The gully pot sediment samples were analysed and the results obtained was compared against each other for correlation. Any possible emerging trends that may be provide additional information in determining the source/origin of the elements in question. Four graphs were plotted, out of which only one appeared to correlate at a statistically significant level. The graph is presented in Figure 4.28 (a) is a plot of Zn against Pb with the highest correlation value of $R^2 = 0.6$. Plots b and c show a very weak correlation and correlation value. While, plot D shows a negative correlation ($R^2 = 0.02$).
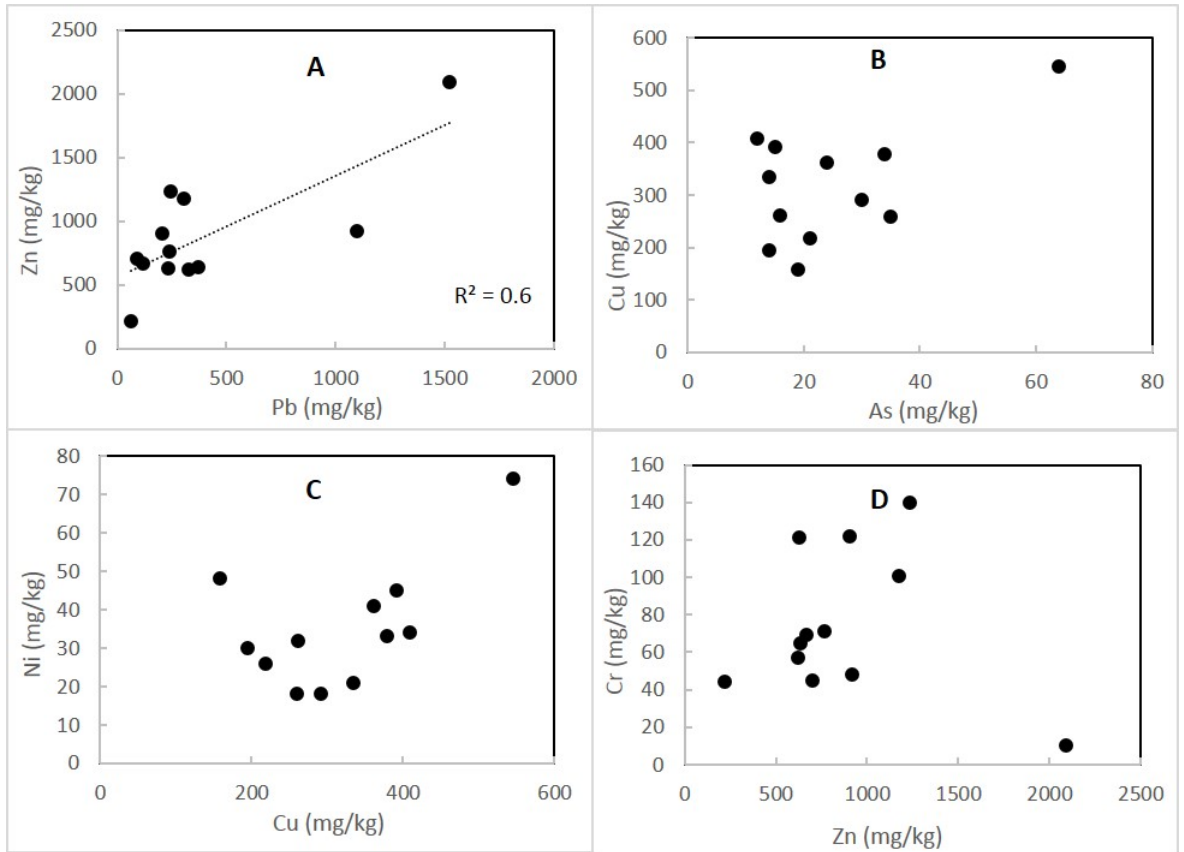
Figure 4. 28. Linear correlation of gully pot sediment samples collected in autumn 2016, (a) Zn against Pb (b) Cu against As (c) Ni against Cu and (d) Cr against Zn.

The Zn, Pb and Fe from both sediment-bound and dissolved phase gully pot samples were compared in Figure 4.29. Concentrations of heavy metals (Zn, Pb and Fe) in sediment samples appear high when compared to dissolved phase samples. This may be due to preferential retention (LaBauve et al., 1988) of contaminants in the solid phase. However, the sediment samples represent a time-integrated contaminant signature. Unlike the dissolved phase where there is potential for mixing at every rainfall event. Infiltration and evapotranspiration processes may affect original concentrations of elements in the dissolved phase and enhance enrichment of elements in sediments. The present concentration of elements within both phases is shown in Figure 4.30.
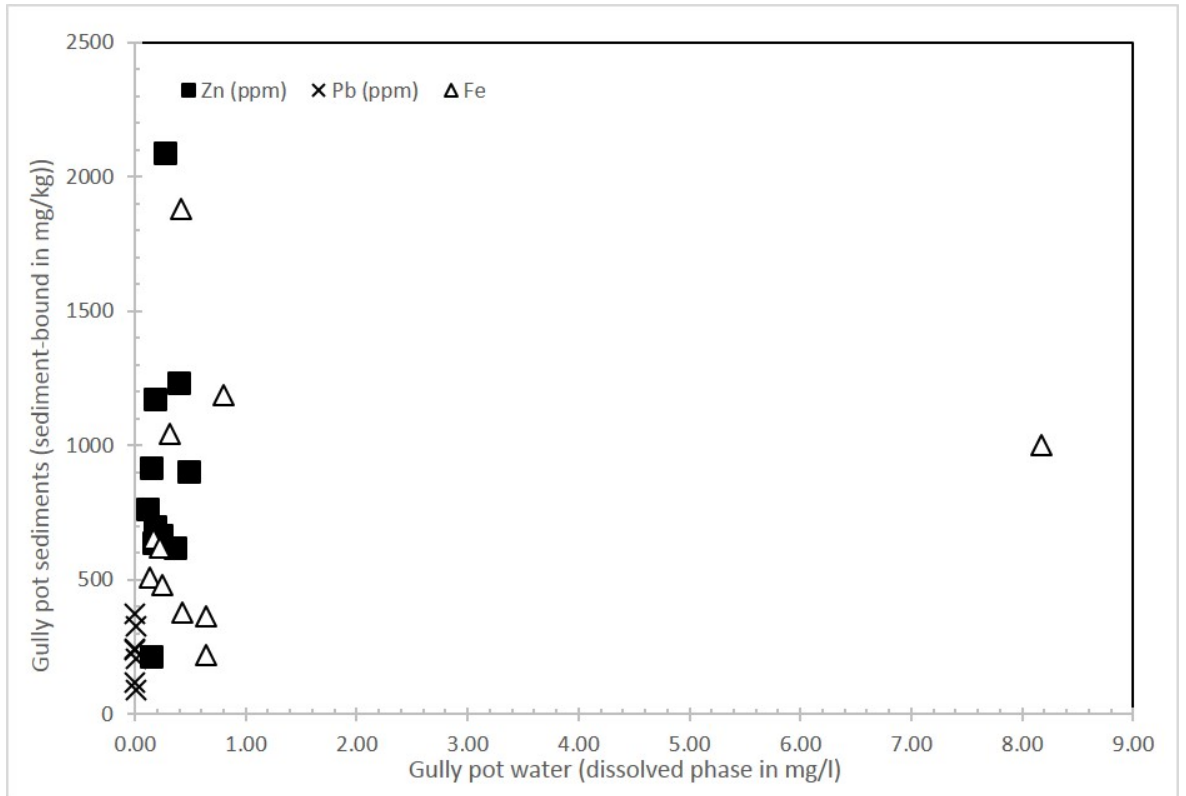
Figure 4. 29. Comparing heavy metals (Zn,Pb and Fe) in dissolved phase and sediment bound gully pot samples. All concentrations are in mg/L. presented in a log scale.
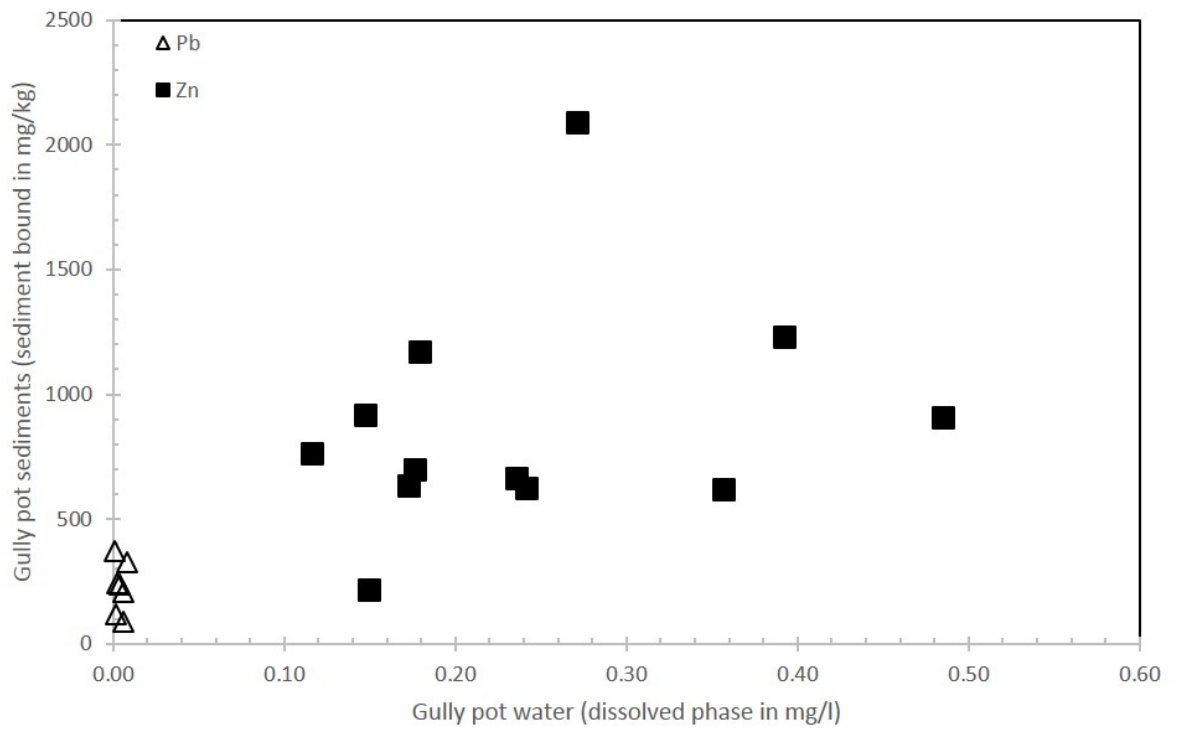
Figure 4. 30. Zinc and Lead concentrations in gully pot water and sediments.

4.5.6 Comparison of PAH in dissolved and sediment phases

Of the dissolved phase and sediment bound PAHs analysed, Benzo (a) pyrene was used as a marker out of the 15 PAH types analysed. This was done to simplify results presentation in determining the relationship between the sediment bound and dissolved phase concentrations as observed in previous studies (Rothwell et al., 2015). A graph of Benzo (a) pyrene in dissolved phase and sediment bound gully pots of the study area is presented in Figure 30. Figure 4.31 shows a linear correlation existing in in the two separate phases of the gully pot samples used in the study, with an R^2 value of 0.7. Total PAHs also show statistically significant correlation at $R^2 = 0.8$. Total PAH concentrations in the dissolved phase are greater than concentration in sediment phase except for Benzo (a) pyrene concentrations which shows an opposite trend.
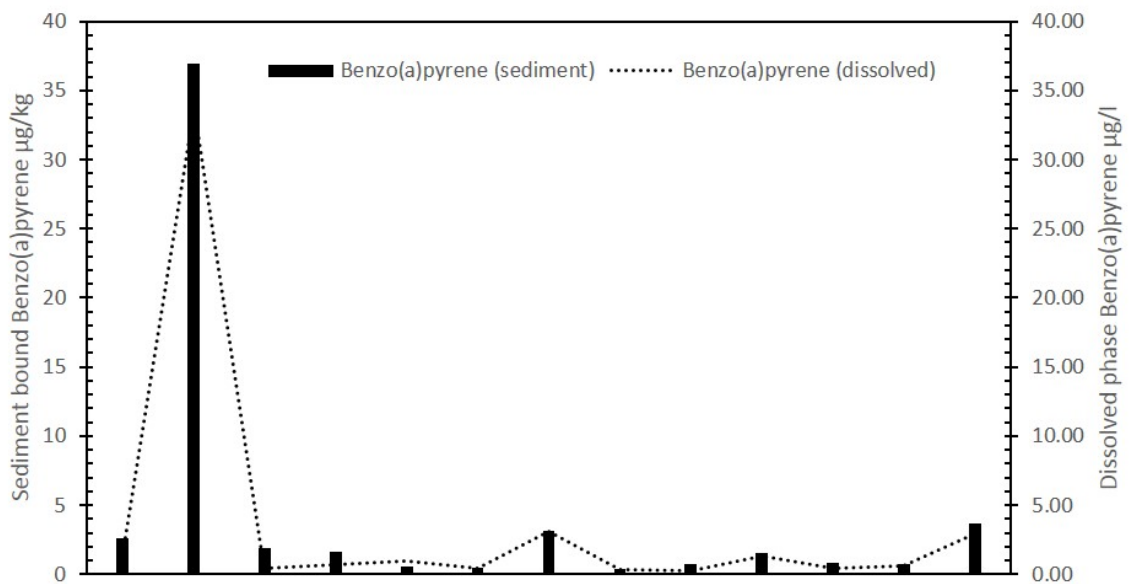
Figure 4. 31. Benzo (a) pyrene concentration in dissolved phase gully pot samples and sediment bound samples. Note: Benzo (a) pyrene was used as a marker for all PAHs analysed.
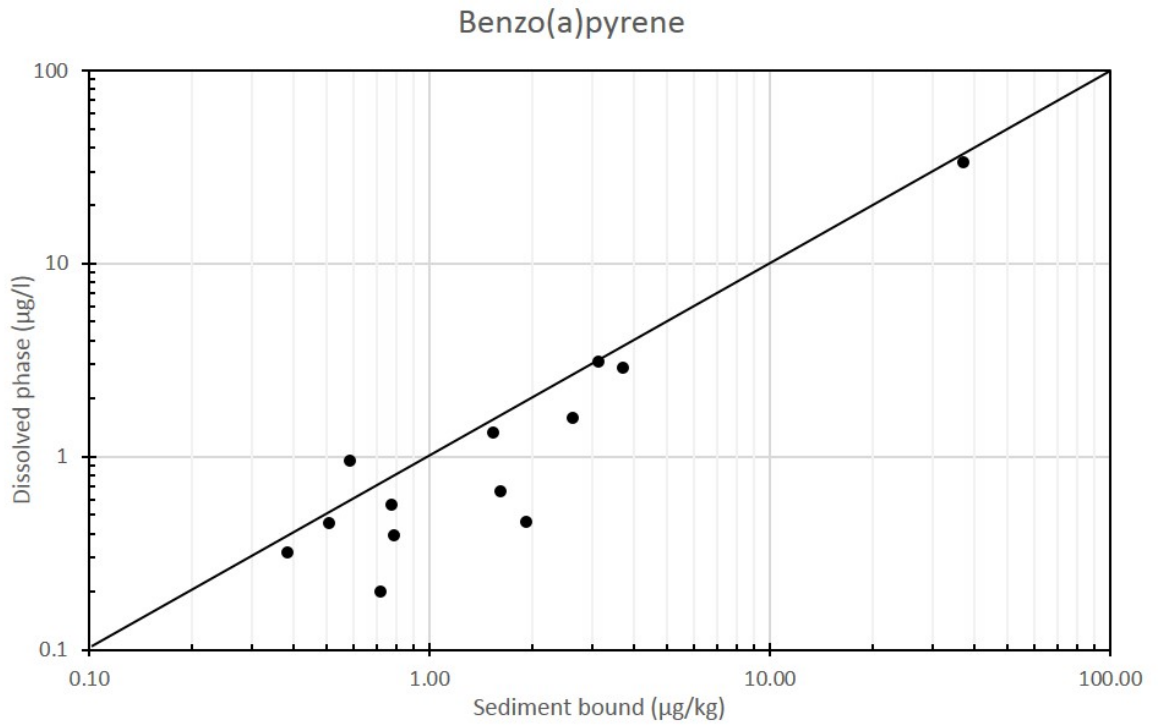
Figure 4. 32. Linear correlation between Benzo (a) pyrene in sediment bound and dissolved phase samples. Benzo (a) pyrene was used as a marker for all PAHs analysed.
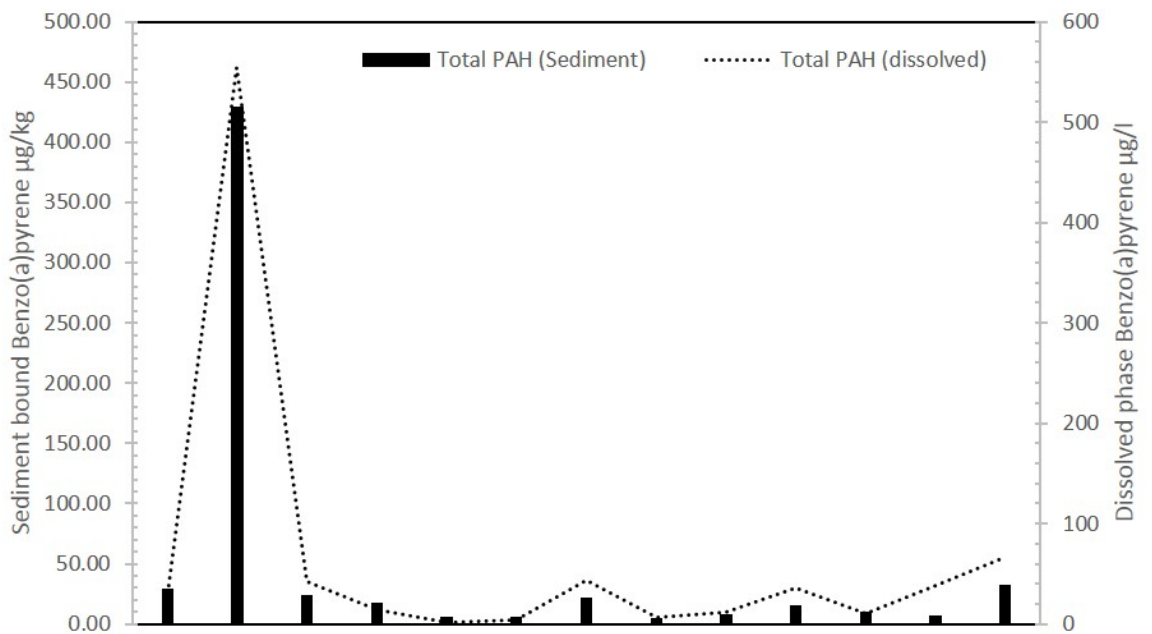
Figure 4. 33. Total PAHs concentration in dissolved phase gully pot samples and sediment bound samples.
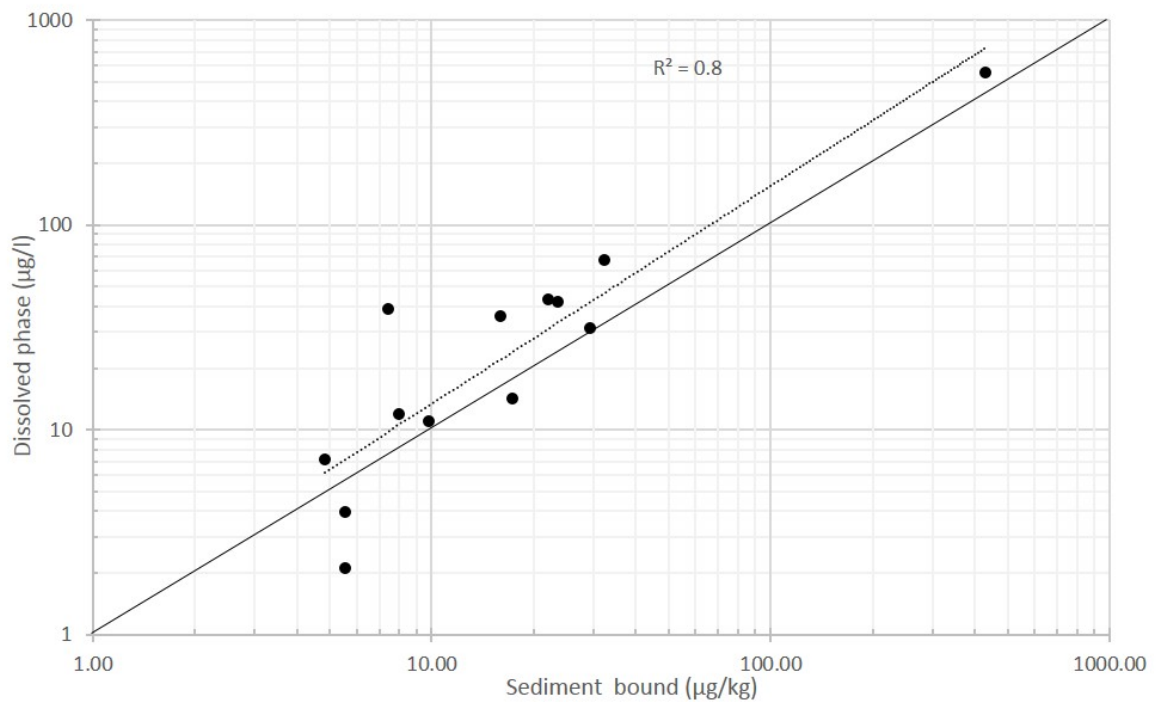
Figure 4. 34. Linear correlation between Total PAHs in sediment bound and dissolved phase samples.

4.5.7 Chemical characterisation of sediment bound settling pond and soakaway samples

The cores analysed from the soakaway show very low concentrations of all the elements analysed. Only Fe shows significantly higher concentrations than other elements, perhaps because of its natural background presence in the environment. These can be seen in the data Table in 4.9. Figure 4.35 excludes Fe to show the concentrations of the other elements analysed. The concentrations remain below detection limit when compared to standard guideline values used in Figure 4.6.

Table 4. 9. Concentration of heavy metals analysed in settling pond around the Keep with depth presented in cm (centimetres) and concentrations in ppm.

	Elements					
Depth	Fe	Ni	Cu	Zn	As	Pb
2cm	4.18	0.0036	0.0536	0.1615	0.0013	0.0195
4cm	4.4309	0.0039	0.0595	0.1679	0.0021	0.0239
6cm	4.14	0.0045	0.0553	0.1515		0.0258
8cm	4.15	0.004	0.0499	0.1271	0.0014	0.0228
10cm	4.09	0.0055	0.0497	0.1313	0.0014	0.0253
12cm	4.1091	0.0047	0.0567	0.1387	0.0025	0.0327
14cm	3.6758	0.0043	0.0609	0.1354	0.0026	0.0404
16cm	3.7969	0.0046	0.0772	0.1723	0.0029	0.044
18cm	3.39		0.0661	0.1279		0.0618
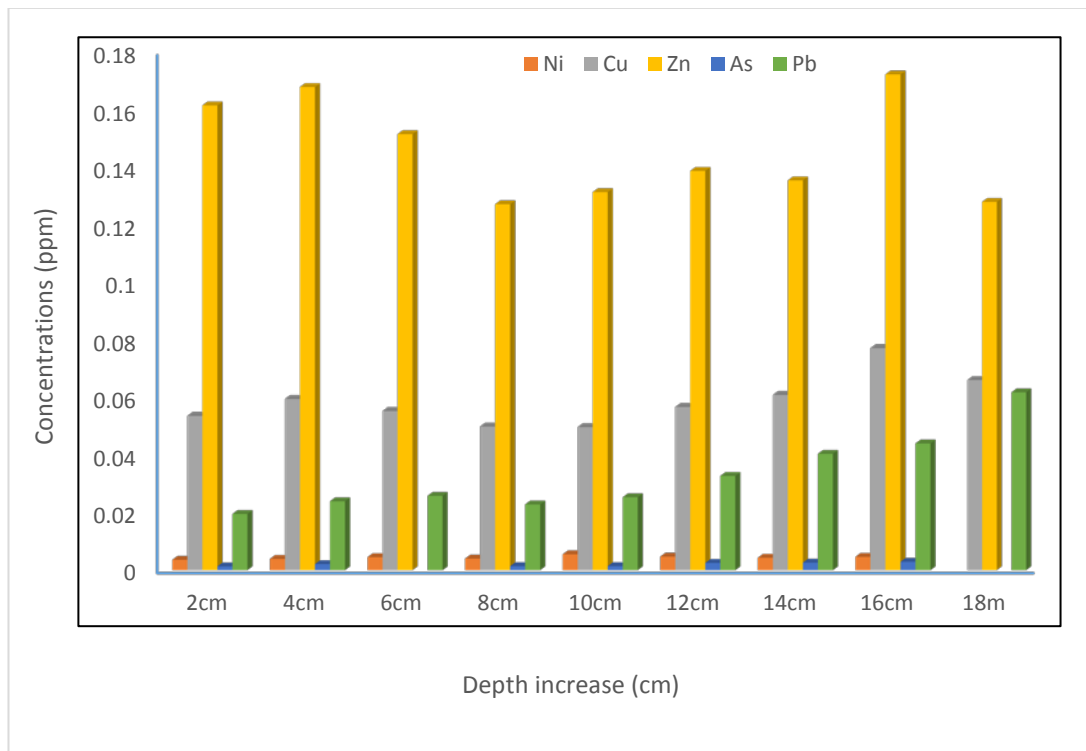
Figure 4. 35. Concentrations of the different elements analysed within the Keep settling pond.

The results from element analysis of the settling pond sediment samples along the A23 road, show similar results to the Keep soakaway water samples analysed and presented. Natural background Fe may have resulted in higher concentrations compared to other elements analysed from the samples. Concentrations of other elements (Pb, As, Zn, Ni and Cu) appear very low, below detection in some samples. Table 4.10 concentrations of the elements analysed while Figure 4.36 is a bar chart that compares between the results. Due to the high concentration of Fe, it is not included in each of the graphs above to allow other element concentration be seen. However, concentrations are presented in the Tables provided.

Table 4. 10. Concentration of heavy metals analysed in settling pond around the A23 settling pond north (concentration in ppm).

Depth	Elements					
	Fe	Ni	Cu	Zn	As	Pb
2cm	3.69	0.0038	0.0237	0.0698	0.0019	0.0204
4cm	3.83	0.0042	0.0347	0.0907	0.0015	0.0291
6cm	3.88	0.0058	0.0378	0.0822	0.0019	0.0337
8cm	3.00	0.0038	0.0284	0.0648	0.0014	0.0355
10cm	3.28	0.0038	0.0187	0.0469	0.0018	0.0226
12cm	3.01	0.0053	0.0096	0.0306	0.0011	0.0113
14cm	2.41	0.0039	0.0069	0.0262	0.0012	0.0092
16cm	2.90	0.0036	0.0044	0.0207	0.001	0.0087
18cm	2.84	0.0028	0.0032	0.019	0.001	0.0075
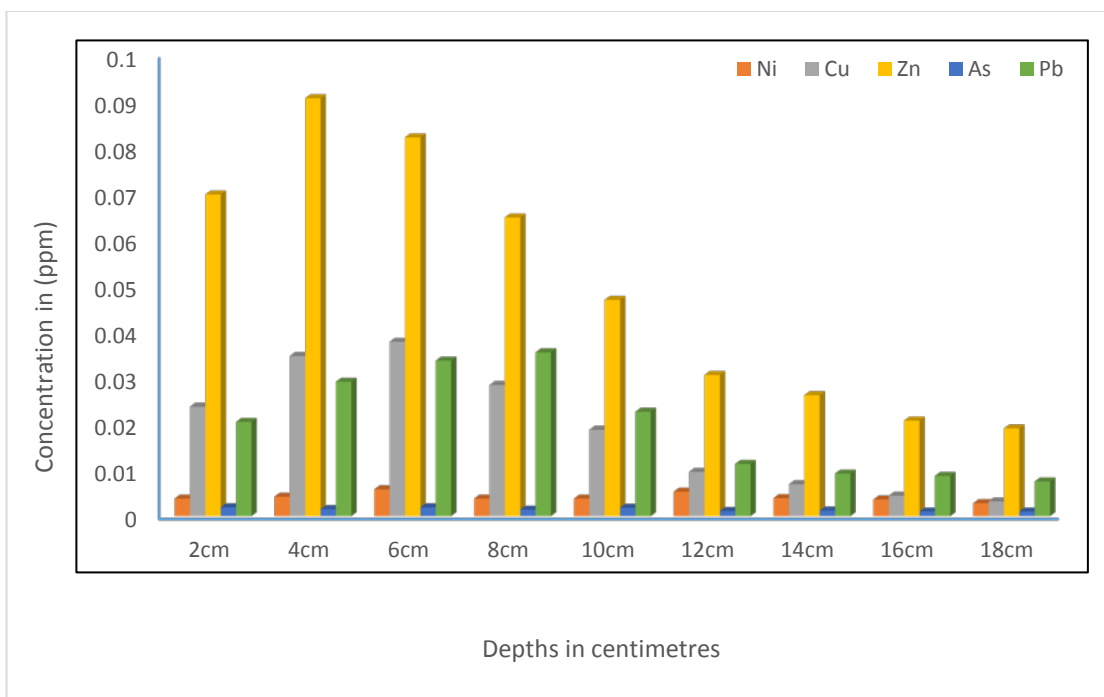
Figure 4. 36. Concentrations of the different elements analysed within the A23 settling pond.

4.6 Platinum group elements (PGE) in gully pot sediments

Platinum group elements are road derived contaminants, and their presence in the environment has increased in the past 20 years as a result of their use in catalytic converters (Jackson et al., 2007). Johnson Matthey Plc. (2006) reported that nearly 50% of annually mined PGE's are used in catalytic converters. Results from the PGE's analysed using ICP-MS (Chapter 3 for details on method) are presented in the Figure 4.37, 4.38 and 4.39 and Table 4.11 below. Five PGE's (Ru, Rh, Pd, Ir and Pt) were above detection limits in the samples. However, automotive catalytic converters use three elements – Rh, Pd and Pt. Mean concentrations of (extractable) PGE's Rh, Pd and Pt within the gully pot sediments are 0.38, 3.31 and 0.90 (ppb) respectively (Table 4.12). In descending order, the concentrations of the PGE's analysed is Pd-Pt-Ir-Rh-Ru from absolute concentrations presented in Figure 4.37 and Table 4.11. The fractions of respective PGE analysed are presented in Figure 4.38. The three metals used in catalytic converters (Pt, Pd and Rh) are correlated in Figure 4.39 with (A) Pt and Pd, (B) Pd and Rh

and (C) Pt and Rh of gully pot samples. Correlation between the three catalytic converter metals appears positive with Pd and Rh having a correlation value of $R^2= 0.3$, Pt and Rh a correlation value of $R^2= 0.5$ and the highest correlation value observed in (A) between Pt and Pd displaying an R^2 value = 0.8. Pt and Pd have been identified as the most common PGE's in the environment and have been investigated more than any other (Schuster, 2006; Whiteley and Murray, 2003; Gomez et al., 2001; Lesniewska et al., 2004a,b; Sutherland, 2003; and Kylander et al., 2003).
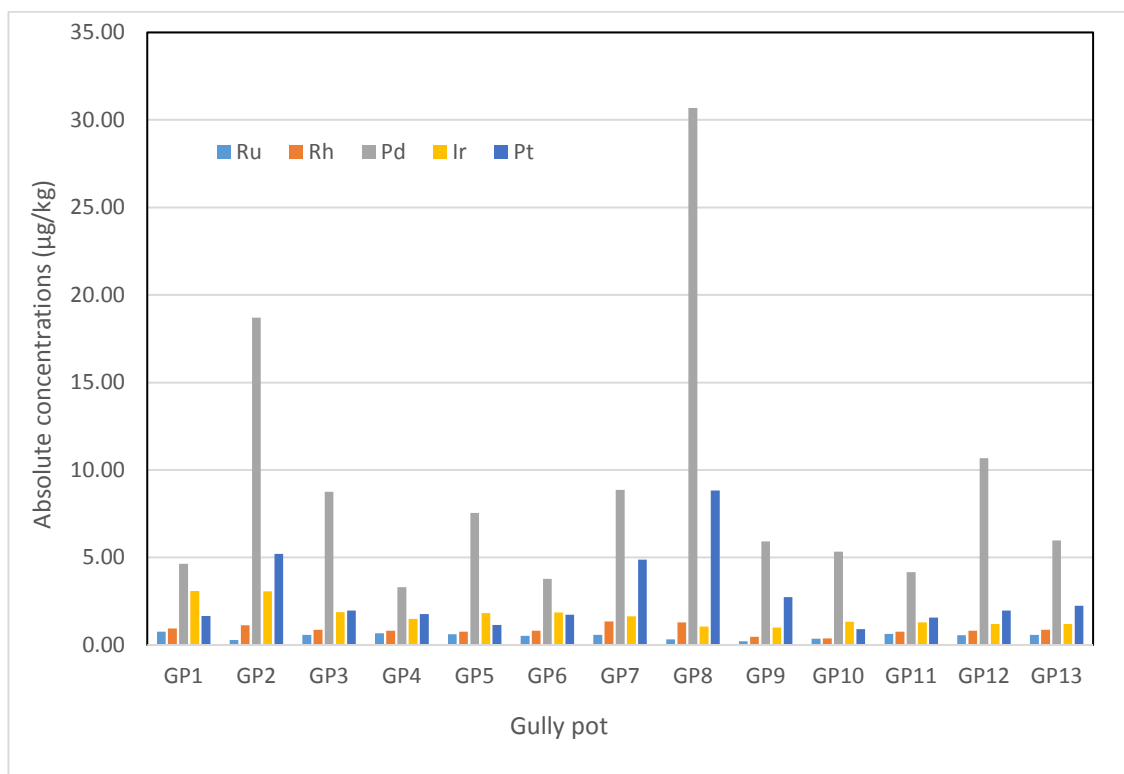
Figure 4. 37. Absolute concentrations of PGE within the gully pots sediment samples.
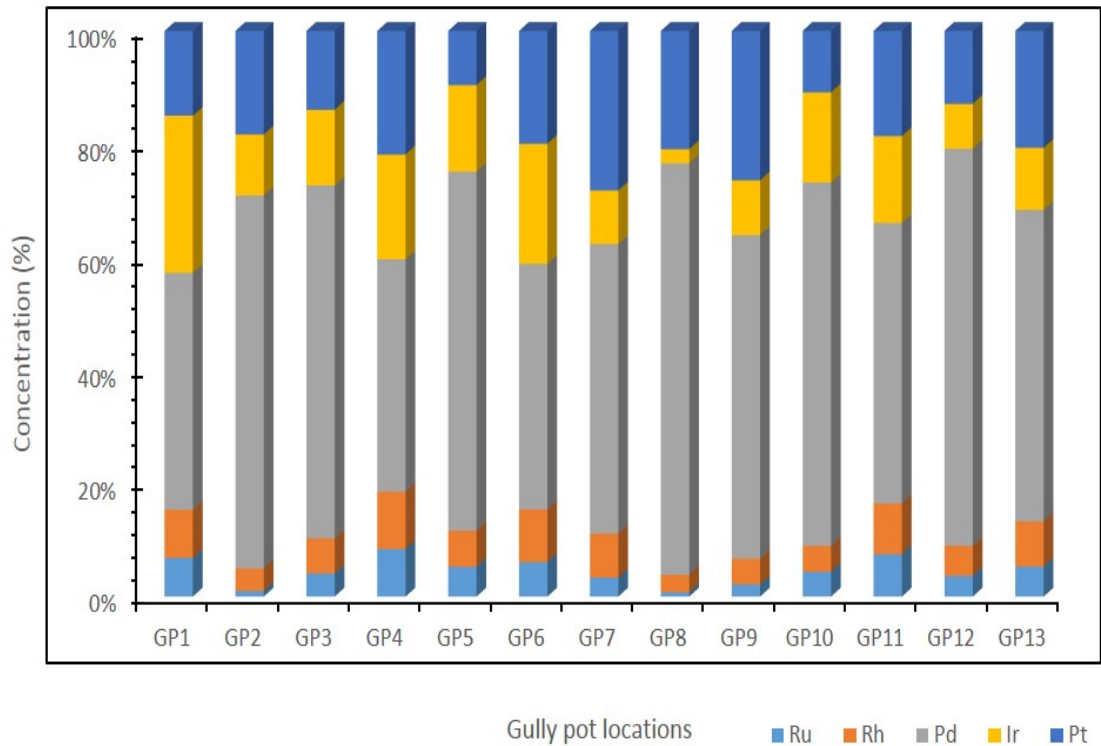
Figure 4. 38. Relative percentage of PGE in gully pot sediments from the study area.

The distribution of PGE's within the various gully pots differ (Figure 4.39). Gully pot locations on highways and junctions display higher concentrations of PGE (GP2, GP8 and GP12). While the other gully pots have lower concentrations with comparable relative PGE contents. Least concentrations are observed along a less busy road with the highest on a busy road as mentioned.

Table 4. 11. Absolute concentrations of PGEs in gully pot sediments of the study area

Location	Ru	Rh	Pd	Ir	Pt
GP1	0.75	0.94	4.64	3.08	1.66
GP2	0.28	1.13	18.70	3.07	5.20
GP3	0.57	0.87	8.76	1.87	1.96
GP4	0.68	0.82	3.31	1.49	1.76
GP5	0.62	0.76	7.54	1.82	1.14
GP6	0.53	0.81	3.78	1.85	1.74
GP7	0.58	1.35	8.87	1.64	4.89
GP8	0.33	1.29	30.69	1.05	8.83
GP9	0.22	0.47	5.92	1.00	2.73
GP10	0.36	0.38	5.34	1.33	0.90
GP11	0.63	0.75	4.16	1.29	1.56
GP12	0.55	0.81	10.67	1.20	1.96
GP13	0.57	0.87	5.98	1.19	2.24

Table 4. 12. Minimum, maximum, median and mean concentrations of PGE in gully pot sediments of the study area.

Element	Minimum	Mean	Median	Maximum
Ru	0.22	0.51	0.57	0.75
Rh	0.38	0.87	0.82	1.35
Pd	3.31	9.10	5.98	30.69
Ir	1.00	1.68	1.49	3.08
Pt	0.90	2.81	1.96	8.83
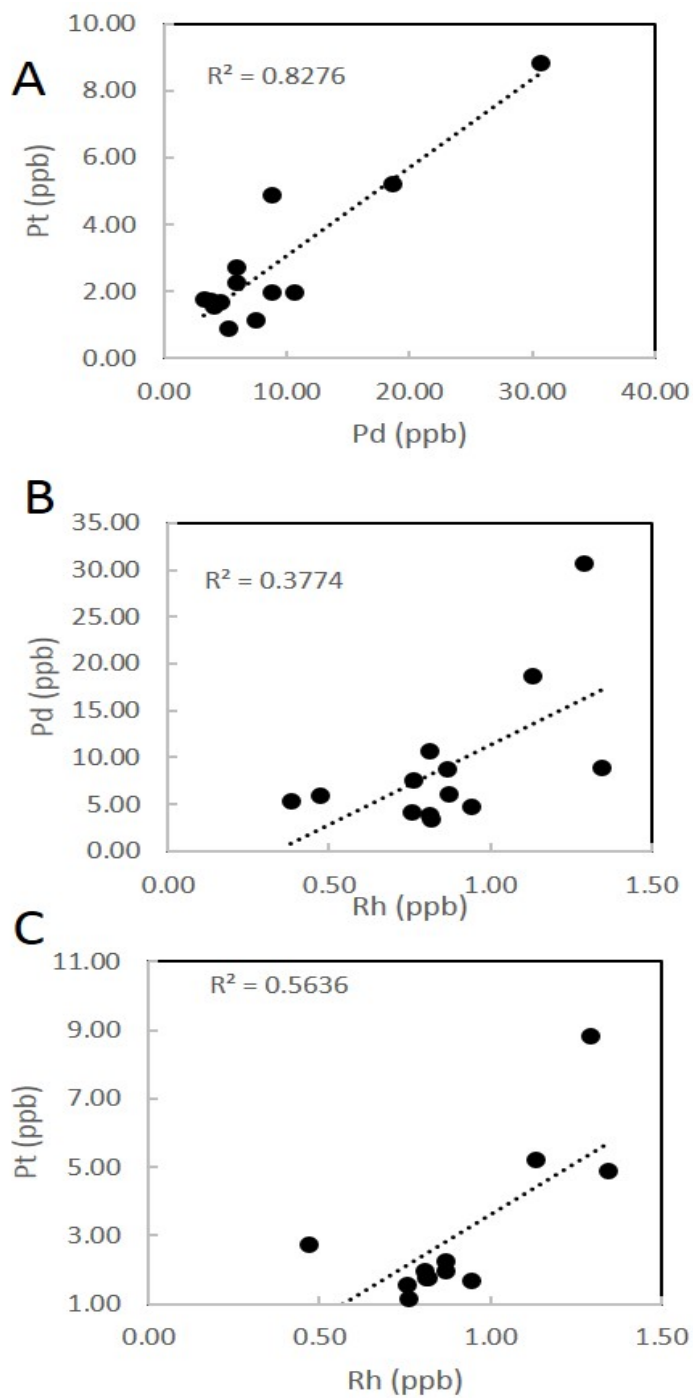
Figure 4. 39. Correlation of PGE derived from three way catalytic converters (A) Pt and Pd, (B) Pd and Rh and (C) Pt and Rh of gully pot samples.

4.7 Pb Isotope composition of gully pot sediments

A significant amount of lead (Pb) has been identified in the sediment bound phase of the gully pot samples studied (4.3 above). The gully pot sediment samples were analysed for Pb-isotope signatures to determine potential origins of Pb in the gully pots around the study area, using a Thermo scientific NEPTUNE multicollector ICP-MS, in collaboration with the National Oceanography Centre, Southampton (NOC) to understand the source origins of Pb in the gully pot sediments collected from the study area during both autumn and spring periods. Previous studies have used the techniques mentioned above to determine Pb isotope ratios, and sources of Pb, in the environment (Monna et al., 1997; Cundy and Croudace 2017). Lead isotopes study gives clarity on the potential Pb enrichment source of an environmental sample. Because the isotope signature of the material depends on the originating ore body. Pb has four stable isotopes, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb produced by the radioactive decay of ^{238}U, ^{235}U, and ^{232}Th, out of which only ^{204}Pb is non-radiogenic (Monna et al., 1997). Each possesses a unique Pb isotope signature which is dependent upon two factors; age (which starts from time of separation from ore) and conditions of genesis. Thus, a material with distinct sources of Pb isotope composition can be quantified based on the origin of the ore body the Pb was derived from (Cundy et al., 1997 & Cundy and Croudace 2017).

Determination of the exact source of Pb in the environment may be a little challenging, but sources can characterised based on Pb isotopic signatures into three groups that may be reliable (Pb derived from rocks and soils, Pb derived from industrial emissions and Pb derived from gasoline). The results show that during the period of autumn (Figure 4.37) ^{206}Pb/^{208}Pb ranges from 0.456 – 0.474 and ^{206}Pb/^{207}Pb from 1.098 – 1.114. (Figure 4.38) A graph of spring gully pot sediment samples showing Pb-isotope ratios of ^{206}Pb/^{208}Pb 0.463-0.477 and ^{206}Pb/^{207} Pb 1.099 – 1.14. Although Pb concentrations may not have displayed a

great variability, the Pb isotope ratios in sediments usually show very little variation even on a regional basis (Monna et al., 1997). A combination of both autumn and spring samples presented in Figures 4.40 and 4.41 is presented in Figure 4.42 for easier comparison of difference in range. The characterisation of Pb isotope composition of samples analysed in this study is discussed further in Chapter 4.8.
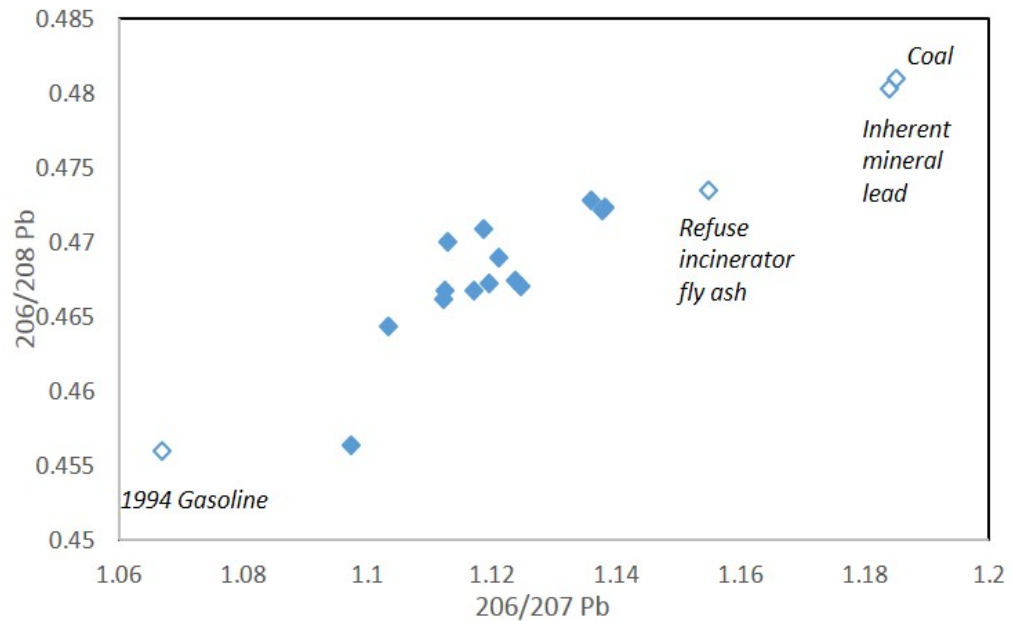
Figure 4. 40. Pb isotope ratio ^{206}Pb/^{208} Pb Vs ^{206}Pb/^{207} Pb of gully pot sediment samples collected over the period of autumn. Open diamonds (from bottom left to top right of diagram) show stable Pb isotope ratios measured for gasoline and refuse incinerator fly ash, from Monna et al., 1997, inherent mineral lead (taken as approximate to that of preindustrial clays from the south UK coast, from Croudace and Cundy 1995) and coal, after Sugden et al., 1993.
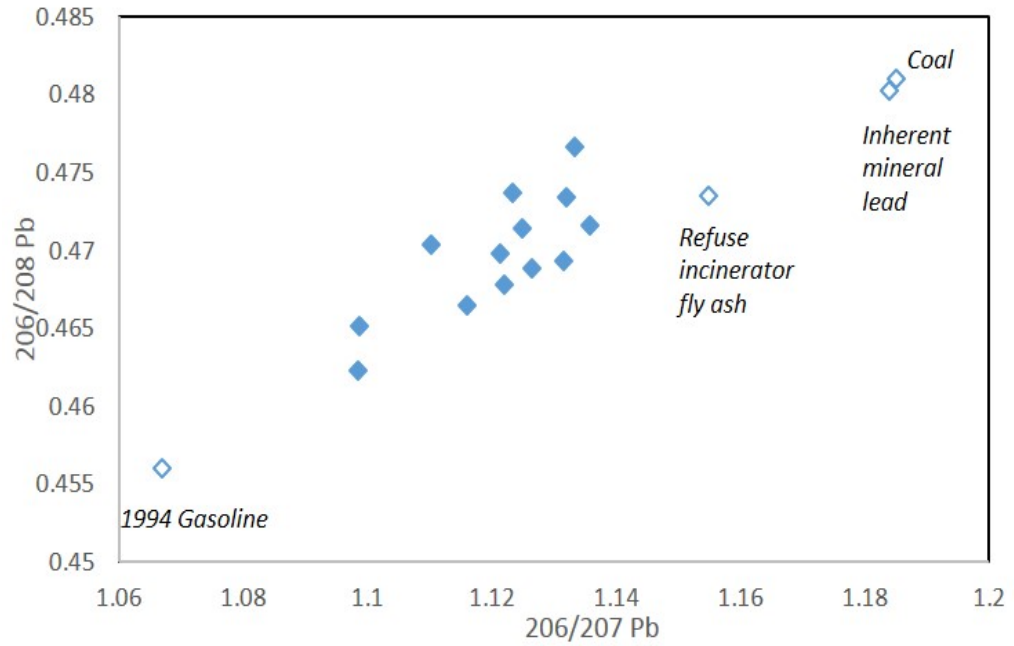
Figure 4. 41. Pb Isotope ratio $^{206}Pb/^{208}$ Pb Vs $^{206}Pb/^{207}$ Pb of gully pot sediment samples collected over the period of spring. Open diamonds (from bottom left to top right of diagram) show stable Pb isotope ratios measured for gasoline and refuse incinerator fly ash, from Monna et al., 1997, inherent mineral lead (taken as approximate to that of preindustrial clays from the south UK coast, from Croudace and Cundy 1995) and coal, after Sugden et al., 1993.
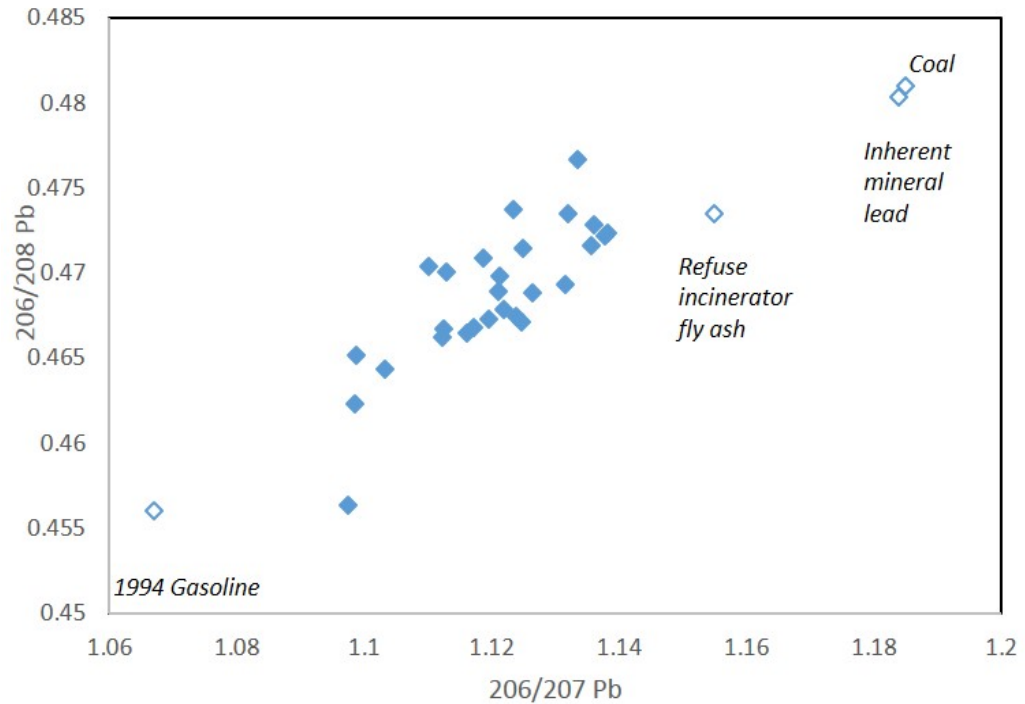
Figure 4. 42. Combined plot of Pb Isotope ratio $^{206}Pb/^{208}$ Pb Vs $^{206}Pb/^{207}$ Pb for both autumn and spring gully pot sediment samples. Open diamonds (from bottom left to top right of diagram) show stable Pb isotope ratios measured for gasoline and refuse incinerator fly ash, from Monna et al., 1997, inherent mineral lead (taken as approximate to that of preindustrial clays from the south UK coast, from Croudace and Cundy 1995) and coal, after Sugden et al., 1993.

4.8 Discussion

Heavy metals such as Zn, Pb, Cr, Cu and Ni and major ions such as Mg, Mn, Fe, K and Ca have been identified by previous works to be present as common road derived contaminants (Muschack 1989; Pitt et al., 1994; Baun and Arnbjerg-Nielsen, 2001 and Gobel et al., 2007). In the dissolved phase of the gully pot samples of the current study, results show that Mn and PAH in form of Benzo (a) pyrene appear to have concentrations above guideline values (Table 4.1). The presence of PAH exceeding guideline values is in line with previous studies (Rothwell et al., 2015).

A Pb isotope study was carried out to determine Pb source characterisation of the gully pot sediments. Data acquired presents a clear distinction in ratio between spring vs autumn

samples. The characterisation of the Pb is discussed based on source which is further determined by Pb isotopic ratios. A) Pb derived from natural rocks and soils; different Pb isotopic ratios have been recorded for different natural sources. In France, the average Pb isotope ratios have been recorded at about $^{206}Pb/^{207}$ Pb 1.193 - 1. 200, parts of North Africa recorded average $^{206}Pb/^{207}$ Pb values between 1.93 – 1.98 while in the UK, $^{206}Pb/^{207}$ Pb were recorded at 1.17 – 1.19 (Croudace and Cundy et al., 1995; Monna et al., 1997). These values appear higher than values observed in either the summer or winter samples of the gully pot sediments measured and presented in Figures 4.40 and 4.41. B) Pb from Industrial emissions; unlike Pb from natural sources, which can be defined by region or place, or Pb from gasoline which has a defined ratio in the UK (due to use of less radiogenic Pb from Australian and Canadian Precambrian ores in alkyl lead gasoline additives, see below), Pb from industrial emissions are sourced from different countries and so will display broadly contrasting concentrations. Studies indicate that incinerator fly ash can be used as an indicator for industrial emission source Pb. Ratios from Germany, France and Japan have been given as $^{206}Pb/^{207}$ Pb 1.142 – 1.159, 1.147 – 1.160 and 1.15 – 1.160 respectively (Mukai et al., 1993; Hamster et al., 1994 and Monna et al., 1995). C) Pb from gasoline sources; gasoline Pb sources have the least variation with average $^{206}Pb/^{207}$ Pb isotopic ratio of 1.079 in the UK. Gasoline Pb has been phased out over the past 30 years (Monna et al., 1997). When Pb was still in use, its concentration in gasoline depended on the ore deposit used as the source of Pb. Most of the Pb used in gasoline was sourced from the Precambrian Pb-Zn ore deposits of Australia and Canada with $^{206}Pb/^{207}$ Pb ratios ranging between 1.03 – 1.04. Another source is Moroccan Mesozoic Pb-Zn ore deposits with $^{206}Pb/^{207}Pb$ ratios from 1.16 to 1.17 (Monna et al., 1997). Comparing the Pb from gasoline to the current study indicates that, there is an appreciable input of "ancient"

(low ratio) lead, presumably from old reworked gasoline-derived Pb in the gully pot sediments of the study area.

Spatially, the dissolved phase elements and PAH display highest concentrations at the junction of a busy road (Figure 4.1). This may be a strong indication of the elements being road derived and even vehicle related. Temporally, during autumn, concentrations of PAH within the dissolved phase appear to have a no correlation between the dissolved phase samples from the different gully pot locations sampled, which may be as a result of mixing and dispersal. Whereas, the spring samples show higher correlation within the dissolved phase PAH. This may be due to the rainfall that tends to mix or disperse concentrations of the elements from their source origin. (Figure 4.2). A trend emerges in the behaviour of dissolved phase PAH as follows; during autumn, period of higher rainfall there is movement of road derived contaminants to the gully pot system results appear to show no correlation. However, during spring, a period with lower rainfall; there is reduced road run off, metals at background concentration and modified by relative solubility, sorption.

Sediment composition and mineral identification in the dried gully pot sediments using XRD and SEM (Figure 4.5) display a concentration of quartz and carbonates, with few organic fragments and a complex mixture of multi-phase particles. Sediment composition studies using SEM-EDS imaging presented in Figure 4.4 – 4.15 show that all samples contain silt sized organic fragments and complex multi-phase fragments (including carbon-rich multiphase samples). Sample 6a (Figure 4.4 – 4.11) shows the presence of $BaSO_4$ in apparently crystalline form. Previous studies have reported Ba and Ti as tracers of brake pad wear (Apeagyei et al., 2011 & Valotto et al., 2015) due to the use of $BaSO_4$ as a road paint extender and a filler in brake linings (Zannoni et al., 2016). Lead (Pb) is observed and often linked with yellow lines because of its use as $PbCrO_4$ in pigment in paint (Adachi and Tainosho, 2004). Other metallic fragments were observed from 5µm - < 1µm

across. SEM images of sample 6b (Figure 4.12) shows a nickel fragment about 16µm in diameter. While in sample 7a, in Figure 4.20 a 30 µm Fe-Cr is observed with Figures 4.22 & 4.24 showing multiphase fragments.

Generally, based on the results analysed the sediment samples exhibit a significantly higher concentrations of heavy metals than observed in the dissolved phase sample from the 13 gully pot locations (Figure 4.28, 4.29 and 4.30). The element concentration in gully pots also exceeds that of soil quality guidelines as presented in Table 4.3. Unlike in the dissolved phase, however, the solid phase is characterised by low PAH concentration levels. This may be a result of high aqueous solubility of PAHs (Abdel-Shafy & Mansour 2016). Heavy metals observed include, Zn, Cr, Pb, Cu, and Ni. Approximately 100% of the locations sampled appear to exceed sediment guideline values, with more than 75% of the samples analysed exceeding guideline values at > 50% and less than 25% of all the samples collected exceeding guideline values about at 30%. Previous studies show that Zn and Cu in the sediment bound phase, regularly exceed guideline values (Gobel et al., 2006; Brown and Peake 2006; Kayhanian et al., 2012; and Rothwell et al., 2015).

Lead (Pb) was formerly used as an anti-knock agent in petrol engines (Katherine, 2002). The subsequent use of unleaded fuel is reflected in a drop seen in dust concentrations of lead by 40% (from 941 – 569 µg/$^{-1}$ g) around Manchester, studied between 1975 and 1997 (Nageotte and Day, 1998) and a further 30% drop (to 265 µg/$^{-1}$ g) in 2000 (Robertson et al. 2003). The average value found in gully pot sediment in the present study is 402 mg/kg with a minimum of 65mg/kg and a maximum of 1525 mg/kg. From Table 4.4, Zn, Cu, Ni and Pb show significant correlation coefficients. Zinc and Cu have been suggested to derive from tyre wear in vehicles, whereas Ni is used in vehicles due its resistivity to corrosion (Charlesworth et al., 2003). High concentrations are specifically observed in this study with concentrations of Zn, Ni, Cu and Pb as 2091, 74, 545, and 1525 (mg.kg)

respectively. Polycyclic aromatic hydrocarbons show higher concentrations around the busy junction uphill at gully pots 5 (X-530798 Y-107626) and 6 (X-530698 Y-107471).

Gully pot sediment samples were also analysed for PGE in this study. Concentrations show a significant correlation (P > 0.001) between Pt and Pd, Pd and Rh and Pt and Rh. Ratios between Pd and Rh are more variable, indicating a poorer correlation than between Pt and Pd and Pd and Rh. The strongest correlation is observed between Pt and Pd. Table 4.7, displays the average concentration of PGE with minimum and maximum levels. The Mean values are, (Pd; 9.10 ppb, Pt; 2.81 ppb and Rh; 0.87 ppb). Pari and Piper (2001), studied PGE's on two major UK highways over a 12 month period, while there were varying values over the period of study, maximum values were recorded at Pt > 500 ng g-1, Rh 70 ng g-1, and Pd 70 ng g-1. Which is much higher than in the present study, even though some samples in the current study were similarly collected from some major roads. Researchers in the UK have reported studies on PGE's in the environment from the 1990's to present. A road dust study for PGE was carried out in Newcastle upon Tyne and the average values were as follows: platinum = 38.23 ng/g, palladium = 79.8 ng/g and rhodium = 17.56 ng/g (Okorie 2015). This is still considerably higher than in the current study, since road dust is transported to gully pots and becomes mixed with gully pot sediments from other sources.

4.9 Conclusion

The gully pots sampled in this study contains a high level of heavy metals (Zn, Cu, Pb, Ni and Cr) mainly contained within the sediment phase of the samples. Concentrations appear above sediment quality guideline values and Environmental standard guidelines (Directive 2013/39/EU). Polycyclic aromatic hydrocarbons (PAH) are present within both sediment and dissolved phases of the gully pot samples. These are distributed across different locations but mainly busy roads, giving evidence of roads and road activities as source.

This is further supported by the results from SEM and XRD where metallic fragments are observed with BaSO4 and Pb. BaSO4 are known tracers of break pad wear. Heavy metals within the dissolved phase are mobile, however the concentration drops drastically as a result of mixing, evapotranspiration and infiltration which leads to the residue adsorbing on to the sediments. In the sediment phase however, the heavy metal mobility highly depends on its availability, which in turn depends on the concentrations and the chemical processes responsible for making it available for re-mobilisation. This can be determined using a sequential extraction procedure, and the next chapter will look at the mobility of the heavy metals using a three step BCR 701 sequential extraction procedure.
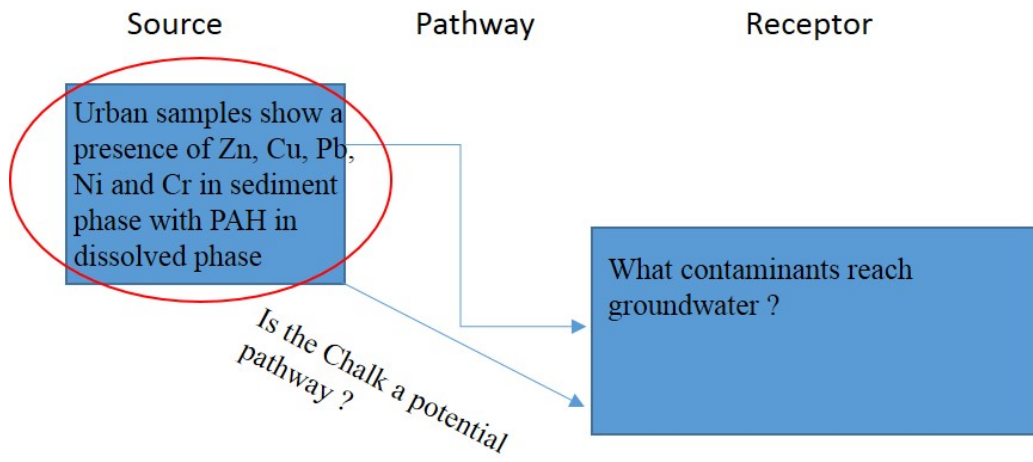
Figure 4. 43. Source-pathway-receptor model showing findings of the source aspect of the model circled in red.

Chapter 5 Leachability and chemical behaviour of heavy metal contaminants in gully pot sediments.

5.1 Introduction

The results obtained from geochemical analysis of gully pot sediments, presented in the previous Chapter (4), indicates the presence of heavy metals (Ni, Zn, Pb, Cu, and Cr) within the sediment phase of gully pot samples. In order to understand the potential for the mobilisation and subsequent transport of the metals within the sediments, it is important to establish the different forms in which these metals exist. The use of sequential extraction procedures (SEP) are some of the most successful methods that have been used in understanding the geochemical partitioning of elements within different fractions, that is, exchangeable, reducible, oxidisable, and residual fractions(Ullrich et al., (1999); Okoro and Fatoki (2012) and Nuhu Waziri (2014)) This study will employ the three step BCR 701 CRM sequential extraction procedure to understand the mobilisation and bio accessibility of the elements available within the sediment phase of the urban gully pot sediments recorded from Chapter 4.

In this chapter, results of geochemical fractionation experiments showing the percentages of potentially toxic metals and the availability of the different elements thought to be associated with the different phases (exchangeable, reducible, oxidisable, and residual fractions) are presented. Results will be compared to other studies carried out using urban sediments. A total of thirteen (13) samples were analysed in order to understand the leachability of the metals sampled from different locations within the study site. The BCR 701 sequential extraction procedure employed is given in Table 5.1.

Table 5. 1. Summary of BCR 701 steps and procedures employed in this study.

1	Exchangeable, water and acid soluble	0.11 mol/L Acetic Acid, 40 mL, shake 16 hr
2	Reducible	0.5 mol/L Hydroxylammonium Chloride (pH 1.5 adj. 25 ml of 2 mol/L HNO_3 per L), 40 mL, 16 hr shake
3	Oxidisable	8.8 M Hydrogen Peroxide, 10 mL at 22°C 1 hr, 10 mL at 85°C 2 hr. 1 mol/L Ammonium Acetate (pH 2 adj. HNO_3), 50 mL 16 hr shake
4	Residual	0.1g Sample Fused Bead, 50 m: 10 % HNO_3 digest

5.2.1 Exchangeable phase/ Acid soluble

Elements present within this phase have the highest mobility when compared to the other phases, they are also very readily available for uptake by plants (Nuhu Waziri 2014). In the present study, elements show very low concentration within the exchangeable fraction with the highest percentage of 21% displayed by Zn and lowest by Pb at 0.2% in Figure 5.1. Cd and Mn have concentrations in the exchangeable fractions at 12% and 11% respectively. The percentage of Mg associated with this phase is 6%, while that of Ni, Cr and Cu are 1% each. In a decreasing order, the percentages of the elements found within the exchangeable phase are Zn > Cd > Mn > Mg > Ni > Cu > Cr and Pb.
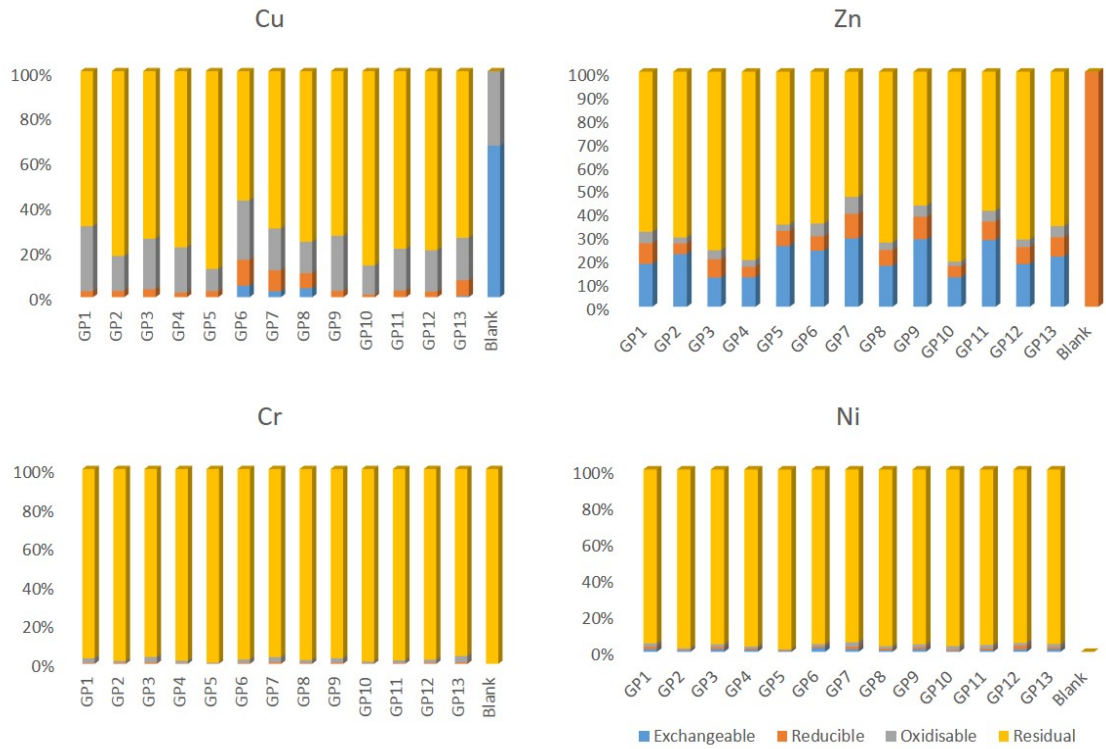
Figure 5. 1. Partitioning of heavy metals Cu, Zn, Ni and Cr from gully pot sediments within Brighton. It is presented in four phases, namely, exchangeable, reducible, oxidisable and residual. Results are given in percentages available within each phase ($\mu g/g^{-1}$).
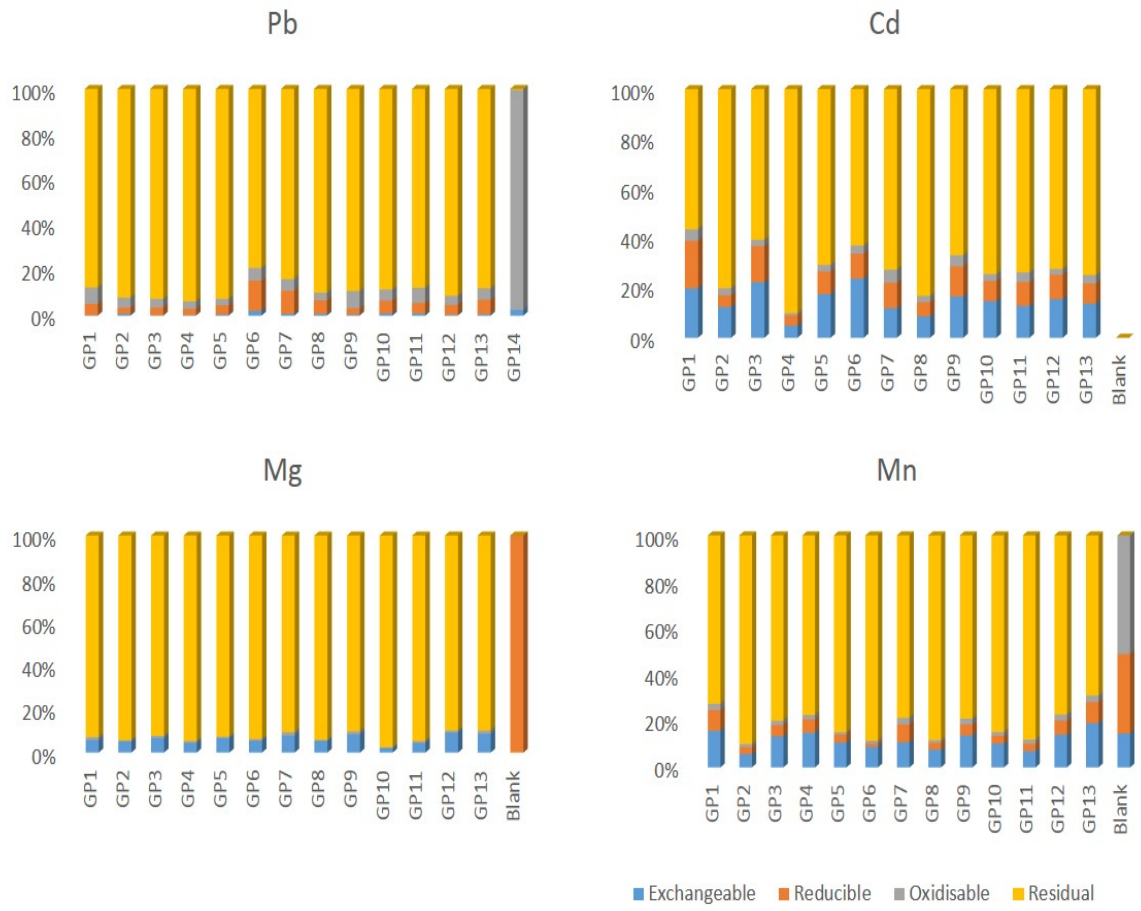
Figure 5. 2. Partitioning of heavy metals Pb, Cd, Mg and Mn from gully pot sediments within Brighton. The data are presented as four phases, namely, exchangeable, reducible, oxidisable and residual. Results are given in percentages available within each phase ($\mu g/g^{-1}$).

Table 5. 2. Gully pot sediment percentages (%) of elements analysed from the three step (BCR 701 CRM) sequential extraction and recovery calculations for the sum of the fractions.

Elements	Exchangeable phase	Reducible phase	Oxidisable phase	Recovery
Cu	1.17	4.95	19.12	66
Zn	21.14	7.61	4.38	108
Cr	0.02	0.44	1.84	98
Ni	1.18	0.99	1.47	96
Pb	0.82	6.93	4.81	86
Mg	6.07	0.02	0.86	93
Mn	11.16	4.73	1.9	78
Cd	12.93	8.78	2.85	67

5.2.2 Reducible phase

The reducible fraction is the second most easily mobilised, after the exchangeable/carbonate fraction. This fraction accounts for just about 4.31% of the total fractions. The highest concentration is seen in Cd with about 8.78% (Table 5.1). Mg has the weakest association with this fraction with 0.02%. Cu on the other hand, displays a stronger association with the reducible fraction than the exchangeable fraction with 4.95%. Zn has a less strong association with about 7.61%. Pb has a relatively strong association with this phase at 6.93%. Cr, Ni, and Mn show a weak association with concentrations of 0.44, 0.99 and 4.73 respectively. In this fraction, Cd has the strongest affinity, with the total concentrations of reducible phase bound elements found in a decreasing order to be as follows, Cd > Zn > Pb > Cu > Mn > Ni > Cr > Mg.

5.2.3 Oxidisable phase

This phase of the extraction is aimed at heavy metals that may accumulate in organic matter of any form within the sulphide phase of the sediments. This phase accounts for total of 4.66% of the overall fractions (10.6% mean), higher than the 4.31% (7.7% mean) of the reducible phase and less than both the exchangeable and residual phases at 6.81% (14.4% mean) and 84.22% (95% mean) respectively. Cu has the highest affinity for this fraction with a percentage concentration of about 19.12%. The percentage concentration of Cu appears to increase at every fraction. In an ascending order, Mg, Ni, Cr, Mn have the weakest affinity within the Oxidisable fraction at 0.86%, 1.47%, 1.86% and 1.9%. Zn like Mn and Cd shows the opposite behaviour to Cu, with percentage concentrations decreasing through the three fractions (Cd 2.85%, Zn 4.38). Based on the total values, the strength of association of the elements with the oxidisable fraction is given in a descending order as Cu > Pb > Zn > Cd > Mn > Cr > Ni > Mg.

5.2.4 Recovery and relative mobility

Recovery was calculated to validate analytical results. Recovery may be also used to infer the mobility of the metals within the more labile fractions under changing environmental conditions like Eh or pH. This is calculated or defined as follows:

$$Recovery\% = \left(\sum n \ Sequential \ extraction \frac{procedure}{total} concentration \ x \ 100 \right)$$

Where n is the number of a given element.

Most results appear to show a good recovery. However, some results display low recovery (Cd 67% and Cu 66%), while other metals as Zn show high results (Zn 108%). This could be as a result of loss of sample during extraction procedures or sample contamination which may cause likely errors leading to low or high recovery values.

5.3 Core flooding experiment - migration potential of contaminants through Chalk

This section analyses the migration potential of organics and non-organics (chloride) through chalk, in line with objective 5 of the study. To understand migration potential through the chalk using a core flood experiment. Chalk samples were collected from the field part of Seaford Nodular chalk and Wadhurst formation and cores were drilled out of them further details of sampling location were given in Chapter 3. Two different experiments were carried out using phenol as an organic and other elements such as chloride spiked in deionised water, to determine the migration potential in chalk.

5.3.1 Set up of core flood experiment.

In order to understand contaminant flow through chalk, a core flood experiment rig at the University of Brighton was used for a series of experiments. These experiments were conducted to simulate the flow of contaminants (Chloride and Phenols) through the Chalk matrix. The experimental system consisted of a stainless steel Hassler core holder, connected to an automatic pressure controller, which provided a confining pressure on the core to be tested. The test solution was driven through the core using a Jasco 980U HPLC pump, and samples were collected using a GE Healthcare fraction collector.

5.3.2 Experimental procedure

A 7cm length and 0.9cm diameter chalk core was drilled and used to fit in the core holder. The chalk core sample was fully saturated with type 1 water before crying out experiments of driving solution through. Two different input solutions were used: phenol at 44.1ppm original concentration and Chloride at 78.70ppm concentration. The fraction (Sample) collector was set at 25mins for each collection at a pump flow rate of 0.5ml/min. The

fraction collector has 95 sample tubes, and it took a total of 39.58 hours to complete an experiment.

Two sets of experiments were carried out in total. A total of 90 samples were collected in the end of an experiment, every third of the samples was analysed using Ion chromatograph for Chloride (Cl^-) and for Phenols, an external laboratory was used (ELAB) to analyse using GC-MS (Chapter 3 for more details), making a total of 30 analysed samples in each experiment.

5.4 Results

The results of the concentrations of the solute used (Chloride & Phenol) and measured before inflow and after flow through the Chalk core sample, were plotted against time (in minutes) and is presented in the Figure 5.3. The core flood experiment for chloride concentrations plotted have shown presence of breakthrough curves which emerge as a result of migration through chalk under saturated conditions. However, the concentrations appear inconsistent over time displaying high levels and low levels at different times. The behaviour appears to show a mixing process going on as the solute flows through the chalk sample. This may be as a result of a natural chloride presence within the chalk core. Under the present conditions that chloride flows through chalk matrix, there is no potential for total removal of the chloride.

In the second test carried out using saturated cores on the core flood rig, de-ionised water spiked with 50 ppm of Phenol was used. The results appeared to display contrasting behaviour to the first input solution of chloride. The breakthrough curve did not appear clearly, concentrations remain more or less same throughout experiment, with no signs of sorbing or mixing as fluid was injected into a fully saturated sample.
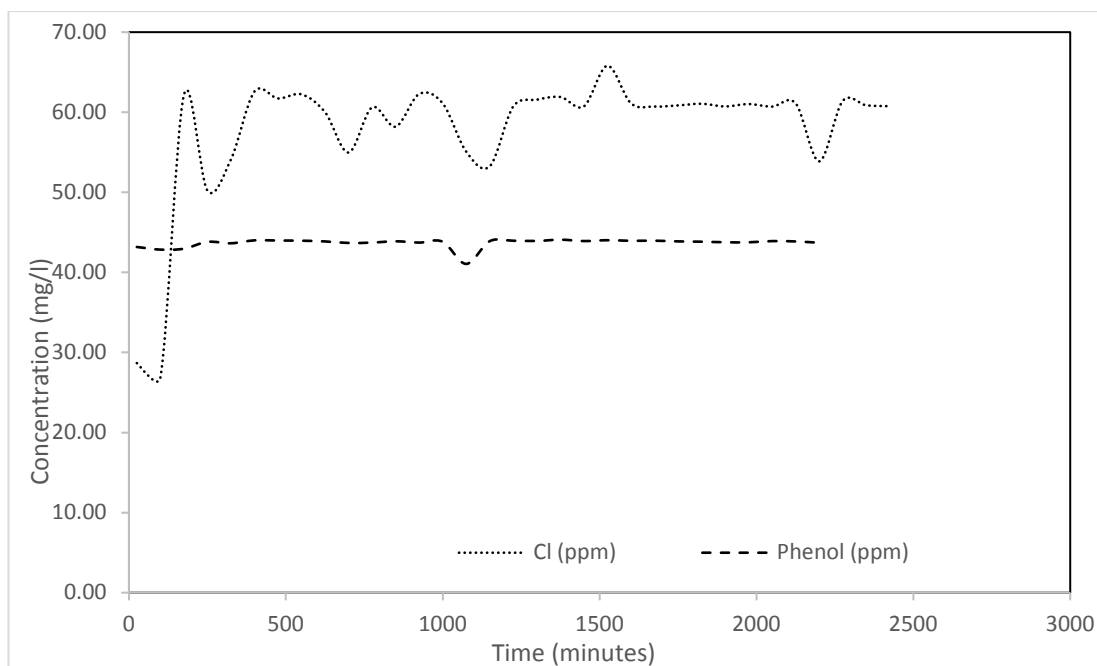
Figure 5. 3. The behaviour of Phenol and Chloride flooded through a chalk core during core flood experiment carried out

5.5 Discussion

In the sequential extraction, metals usually present in the exchangeable phase are weakly bound to sediments especially surface sediments (Gleyzes et al., 2002). Metals within the exchangeable fraction have been reported to usually have low concentrations (Charlesworth and Lees, 1999). However, in this study, some metals show greatest affinity for the exchangeable phase with Zn (21.14%), Cd (12.93%) and Mn (11.16%). Hopke et al., (1980) suggested that Zn is susceptible to leaching in urban sediments. The high results of Zn obtained in this work is similar to the one reported by Robertson et al., (2003) of Zn in urban sediment particulates of Manchester, UK. Metals present in this phase can easily be released through an ion-exchange process.

The reducible phase involves dissolution of iron and manganese oxides by controlling or regulating Eh and pH (Gleyzes et al., 2002). These ions are thought to have accumulated

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through adsorption, cation exchange and precipitation mainly. The host phases become unstable in anoxic conditions (Tessier et al., 1979). The affinity of metals to this phase is generally medium-low. Cu appears to show increasing levels through the different fractions with the highest percentage of 19.12% in comparison to the second highest Pb 4.81% in the oxidisable phase, making it the metal with most affinity for this fraction. A study carried out by Charlesworth and Lees (1999) of heavy metals distribution in street dusts of Coventry city, found that the metals observed (Zn, Ni, Cd, Cu & Pb) had the highest affinity in the organic fraction. Results more similar to the current study were found by Thuy at al., (2000) in a study of distribution of heavy metals in urban soils of Danang-Hoian Area, Vietnam and Robertson et al., (2003) in a study assessing the distribution of heavy metals in road deposited sediments in Edinburgh, Scotland. Both results showed Cu has the highest affinity to the organic fraction.

5.6 Conclusion

The results from sequential extraction using the BCR701 proceedure (Ure & Davidson, 2002) indicate that most of the elements observed appear to be predominantly immobile, with high concentrations in the residual phase. The reducible fraction has the lowest concentration of the three extractible phases. Two metals found were Cu and Zn. Cu is bound to the Oxidisable phase and Zn to the exchangeable phase. The elements of the exchangeable phase have a higher remobilisation potential, as such, Zn and Cu indicates high potential for remobilisation to the environment.

The core flooding experiment shows no chemical reaction taking place when phenol is pumped through Chalk, but, there is little reaction when Cl is pumped through the Chalk. This suggest that phenol has the tendency to flow through Chalk. When concentrations are high in the surface, there is every potential to reach groundwater. This will be seen in the

next Chapter (6) when groundwater samples are analysed for phenolic concentrations and

other urban diffuse or road related elements.
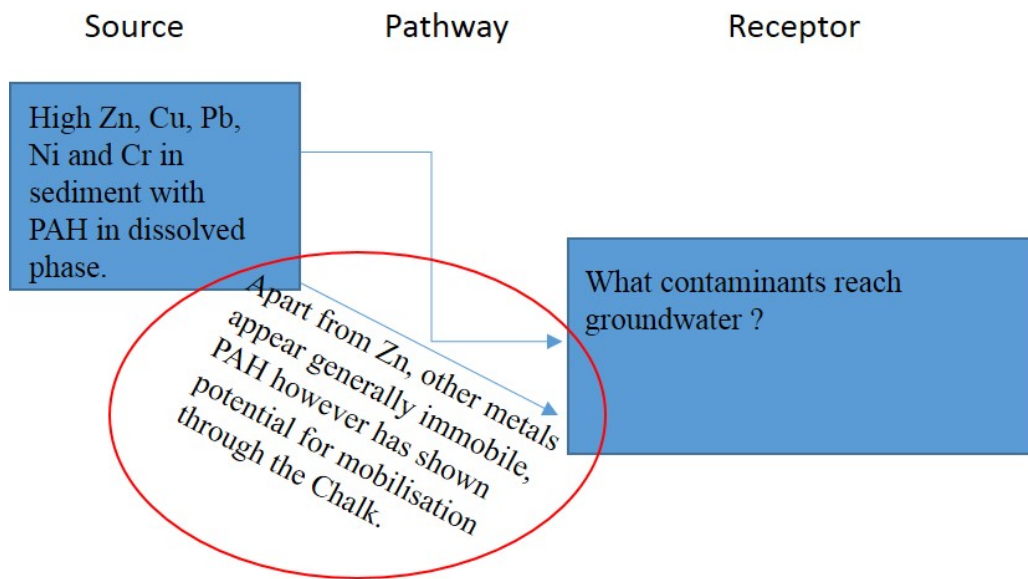
Figure 5. 4. Source-pathway-receptor model showing the question answered in this
Chapter which is in line with the pathway aspect of the model.

Chapter 6 Evidence and impact of urban diffuse pollution in groundwater

6.1 Introduction

Chapter 2 reviewed the current range of published studies on urban diffuse pollutants in the environment. Tracers were identified that would allow identification of road runoff input and potential chemical contamination in groundwater, which include Pb, Zn, Fe, Cu and organics in the form of PAH.

The presence of heavy metals in concentrations exceeding guideline values in urban run-off has been identified in chapter 4, some of which include the metals identified as tracers. This has been linked to vehicular movement on roads to be the key contributor as the hypothesis. With concentrations around traffic junctions (where cars are forced to slow down and eventually stop) showing higher concentrations and appearing to be hotspots for organic contaminants (PAH) and non-organic contaminants such as Fe and Zn with traces of PGE's bound to the sediments found in road side gully pots. While still recording organics like PAH and non-organics like Cu, Cr, Ni and As in the dissolved phase of road waters.

Furthermore, in the succeeding chapter (chapter 5), a leachability study of the elements found in the gully pot sediments was carried out using a sequential extraction procedure. This study revealed that Zn had the highest affinity for the exchangeable fraction. This demonstrates that Zn can be easily mobilised with the right conditions (a change in pH and/or redox). A generally low heavy metal concentration was observed in the reducible phase, while Cu was found to have the highest affinity to the oxidisable phase. In this regard, Zn has the greatest potential mobility to groundwater in solution.

The present chapter, as part of the objectives (3 and 4), will investigate if the mobile metallic and organic tracers identified from study of gully pot waters can be detected above background in groundwater by analysing the groundwater geochemistry of the study area. Similarly, this chapter identifies seasonal changes in tracers present within the groundwater of the study area. The behaviour of tracers in all the borehole locations will be presented, however, focus will remain on two boreholes (Preston Park and North bottom). Preston park borehole is chosen because it is the only urban site, while North bottom is chosen in place of North heath barn (NHB) even though NHB is a more rural site as a consequence of the lack of continuous data from NHB borehole site. This arises from the large seasonal variation of water level at this site (from 80m b.g.l., which is the base of the hole – to ~40m b.g.l.) which is one the influve area of the Patcham dry valley.

6.2 Tracers in groundwater

Groundwater analysis has revealed the presence of Zn, TPH and phenols at trace levels. This may be due to a number of factors such as flow process (fracture or matrix) or the presence of significant contaminant loading. These factors all have significant roles to play in the presence of urban diffuse pollution in groundwater and will be discussed in detail in the discussion section.

6.2.1 Total petroleum hydrocarbon (TPH) in groundwater

There appears to be a different pattern between boreholes located in the urban sites and the rural or semi-rural sites. Preston Park, the only urban site used in this study, shows a different behaviour in the concentration of organics. Concentrations of TPH in all the boreholes during the winter or periods with continuous rainfall remain low at < 0.5 µg/l. However, in the summer months, or periods with less rainfall a gradual increase occurs, passing limits of 0.5 µg/l as stated by guideline limits and reaching about 1.0 µg/l. This is most frequently observed in the Preston park borehole. The Casterbridge Farm borehole

displayed an unusually high concentration during the period, February – March 2017 at > 2.5 µg/l. Although, it is not classified as an urban site, a railway line is located close to the borehole which may have been responsible for the source of TPH infiltrated to the groundwater. North Heath Barn shows very low concentrations of TPH, but due to a lack of continuous data, it cannot be used or compared to the other boreholes.
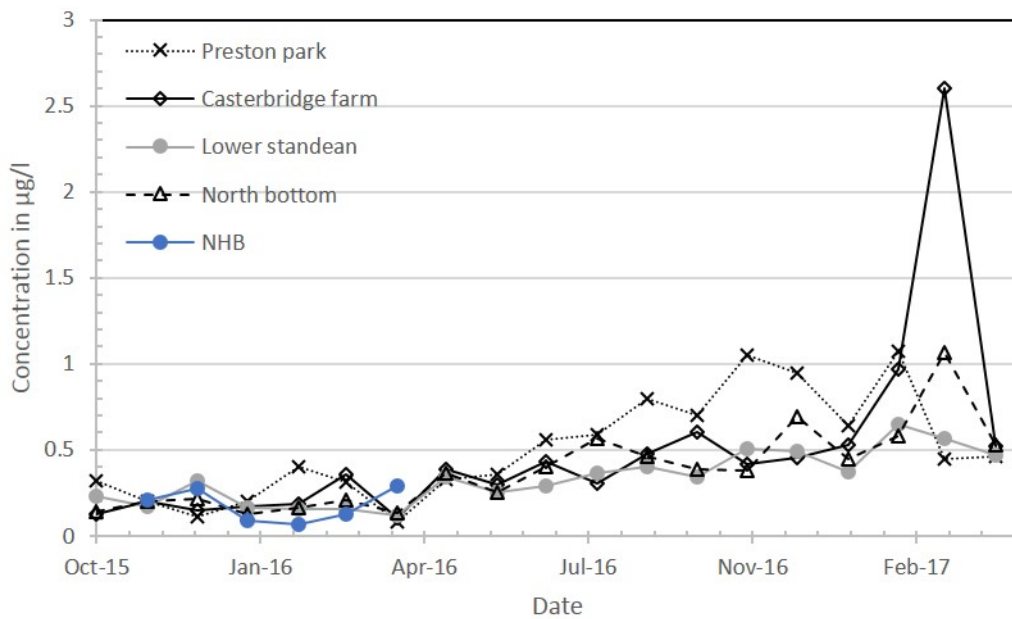
Figure 6. 1. Total petroleum hydrocarbons (TPH) concentration at the borehole monitoring sites between October 2015 and April 2017.

6.2.2 Phenol in groundwater

Although concentrations may not have reached levels for concern due to loading or flow processes which will be discussed later. There is clearly an infiltration process taking place and the concentrations are represented in the groundwater. The urban borehole (Preston Park) shows higher concentrations about 0.7 µg/l during the summer (period of less rainfall), and concentrations as low as 0.1 µg/l during period of high rainfall events. Whereas the North Bottom borehole shows opposite behaviour with a drop in concentrations during periods of low rainfall events with concentration of 0.1 µg/l and reaching as high as 0.35 µg/l during high rainfall periods. The behaviour of phenol in the

two boreholes appear almost opposite. In summary, urban or infrastructure proximal boreholes (PP, CF) are high in summer, low in winter; rural boreholes (LS, NB) are low in summer high in winter.
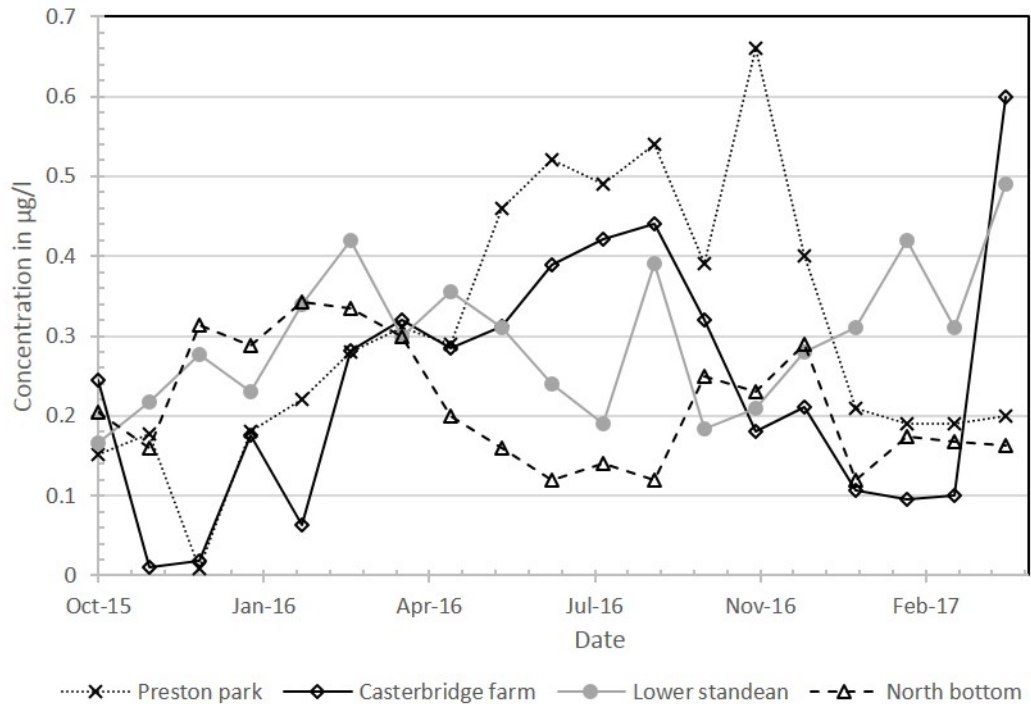
Figure 6. 2. Phenol concentrations at the borehole monitoring sites between October 2015 and April 2017.

6.2.3 Zinc (Zn) in groundwater

The behaviour and seasonal patterns observed in Zinc in Preston Park (urban site) Figure 6.3 appears similar to that of Phenol and TPH from the same location. During periods of low rainfall, an increase in concentration is noticed and the opposite happens during periods of high rainfall. In North bottom, overall levels of Zn appear low, decreasing even further during periods of low rainfall. Zn appears to have low concentrations in groundwater, with the highest recorded concetration at about 5.0 mg/l. This is lower than the baseline for chalk groundwater (Edmunds et al., 1987).
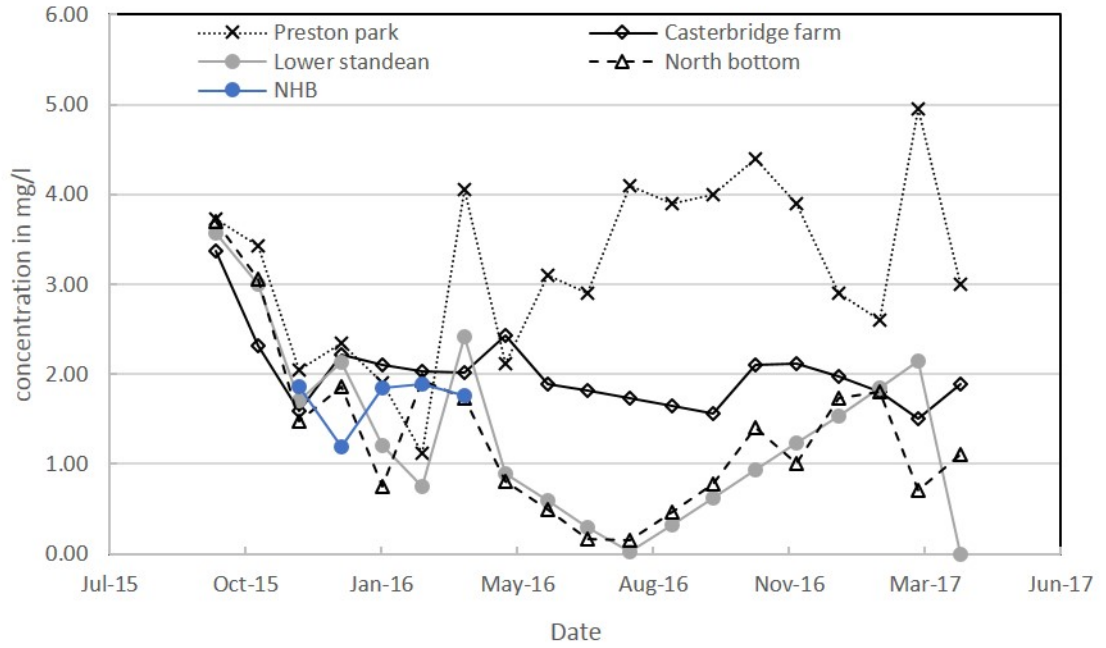
Figure 6. 3. Zinc (Zn) concentration at the borehole monitoring sites between October 2015 and April 2017.

Table 6. 1. Average values of the tracers in the monitoring boreholes as observed from October 2015 – April 2017.

Number	Site name	TPH (µg/l)	Cl (mg/l)	Phenol (µg/l)	Zn (mg/l)
1	Preston park	0.504	25.24	0.308	3.18
2	Casterbridge farm	0.48	21.82	0.24	2.01
3	Lower standean	0.33	22.59	0.29	1.33
4	North bottom	0.38	18.93	0.21	1.45
5	NHB	0.176	19.74	0.0023	1.71

6.3 Results

6.3.1 Groundwater Chemistry

Chloride and Bromide are very important anions that can be useful in understanding groundwater processes. Chloride is a major component in groundwater, but when present at high levels can affect groundwater quality. Bromide on the other hand is a minor component present in the groundwater at usually low levels. They have been used as anion tracers in groundwater, as both Bromide and Chloride do not take part in aquifer reactions unless evaporation is very high, or salts are present in the aquifer matrix. Thus the chloride/bromide ratio should be characteristic of the halogen source. Typical inputs to groundwater in the catchment would be from sea spray (which should have the same Cl/Br ratio as seawater) or road salt dissolved in run off (which would be enriched in Cl relative to seawater because of the dissolution of low Br halite (NaCl)).

In this study, the Cl/Br ratio is presented in Figure 6.5. Chloride concentrations in North Bottom, Casterbridge Farm and Lower Standean remain well within expected limits of < 30 mg/l. A few periods of higher concentration are observed in Preston Park, reaching above the normal range of > 30 mg/l. Cl and Br concentrations remain normal (Cl < 30mg/l and Br < 0.1) until the summer periods of 2016 where concentrations reach > 30mg/l of Cl and reaching as high as 0.3-0.6mg/l of Br. This may be as a result of seawater intrusion as the Preston park borehole is the more southern of the boreholes and infiltration of seawater may occur during periods of low water table, which usually occurs in the summer months as a result of low rainfall. Interestingly, the high levels remains consistent through to winter 2017. The graph in Figure 6.4 shows that average monthly rainfall dropped significantly in 2017 as opposed to average monthly rainfall levels in 2016. Where, average monthly rainfall levels reached as high as 218.8 mm and the highest recorded in 2017 at 122 mm (Table 6.2).
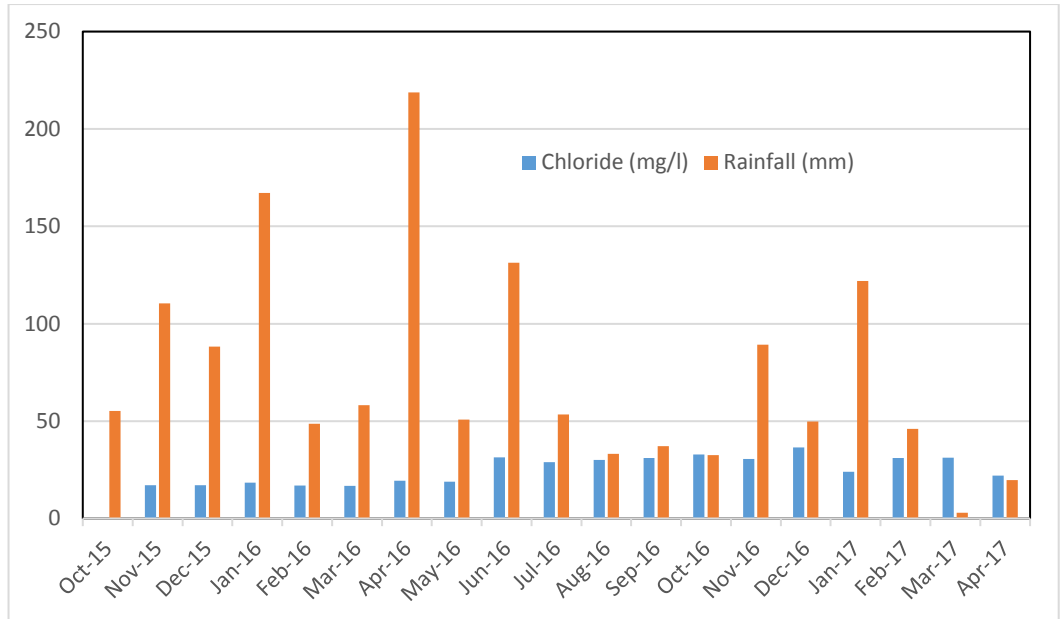
Figure 6. 4. Chloride (mg/l) concentration in groundwater compared with monthly average rainfall (mm) of the Preston Park borehole within the study area, Brighton.

Table 6. 2. Data for sampling months and concentrations of chloride in each month with average monthly rainfall of the corresponding month.

Date	Chloride (mg/l)	Rainfall (mm)
Oct-15	0	55.2
Nov-15	17.15	110.4
Dec-15	17.15	88.2
Jan-16	18.39	167.2
Feb-16	17	48.6
Mar-16	16.75	58.2
Apr-16	19.32	218.8
May-16	18.94	50.8
Jun-16	31.334	131.4
Jul-16	29	53.4
Aug-16	30	33.2
Sep-16	31	37.2
Oct-16	32.9	32.6
Nov-16	30.6	89.2
Dec-16	36.5	49.8
Jan-17	24	122
Feb-17	31	46
Mar-17	31.3	3
Apr-17	22	19.8
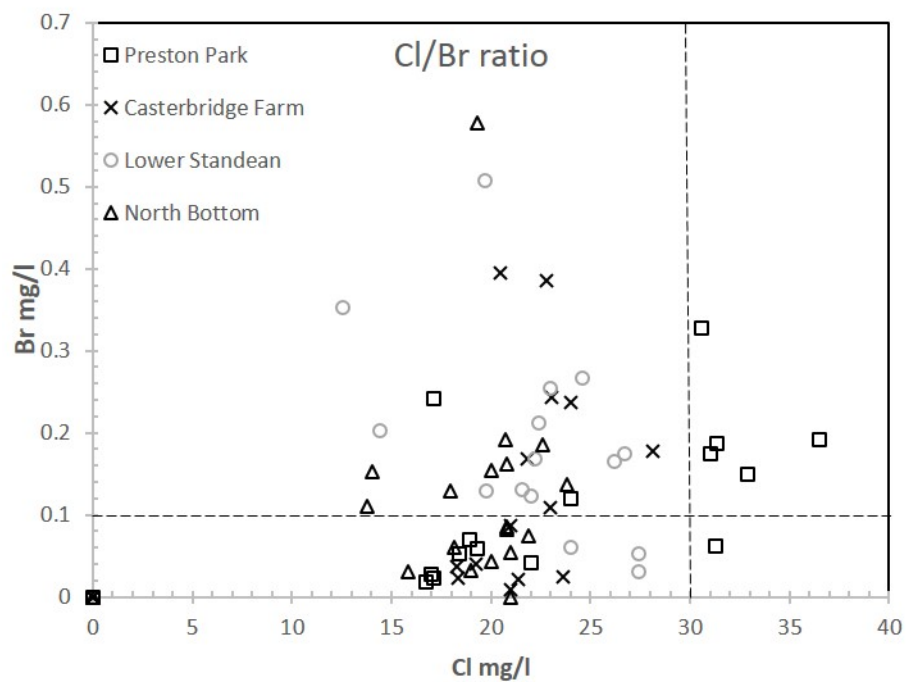
Figure 6. 5. Cl/Br ratio diagram showing relationship between Chloride and Bromide in the groundwater from the 5 borehole monitoring sites Patcham Catchment.

Groundwater chemistry concentrations have been plotted on a piper plot from the USGS (GW_Chart (Version 1.29.0.0) showing the distribution of major ions (Ca, Mg, Na, K, HCO_3, SO_4 and Cl) plotted as relative proportions. Earlier unconfined Chalk aquifer groundwater baseline studies reported waters to be of Ca-HCO_3 type (Edmunds et al., 2002; and Smedley et al., 2003). The concentrations of groundwater given in this study can generally be classified as the Ca-HCO_3 type. Preston Park (Figure 6.6) is characterised by changes in proportion of Ca and Mg. unlike in North bottom (Figure 6.7), where the concentrations of Ca and Mg are more consistent and the presence of Ca-HCO_3 appears more dominant.
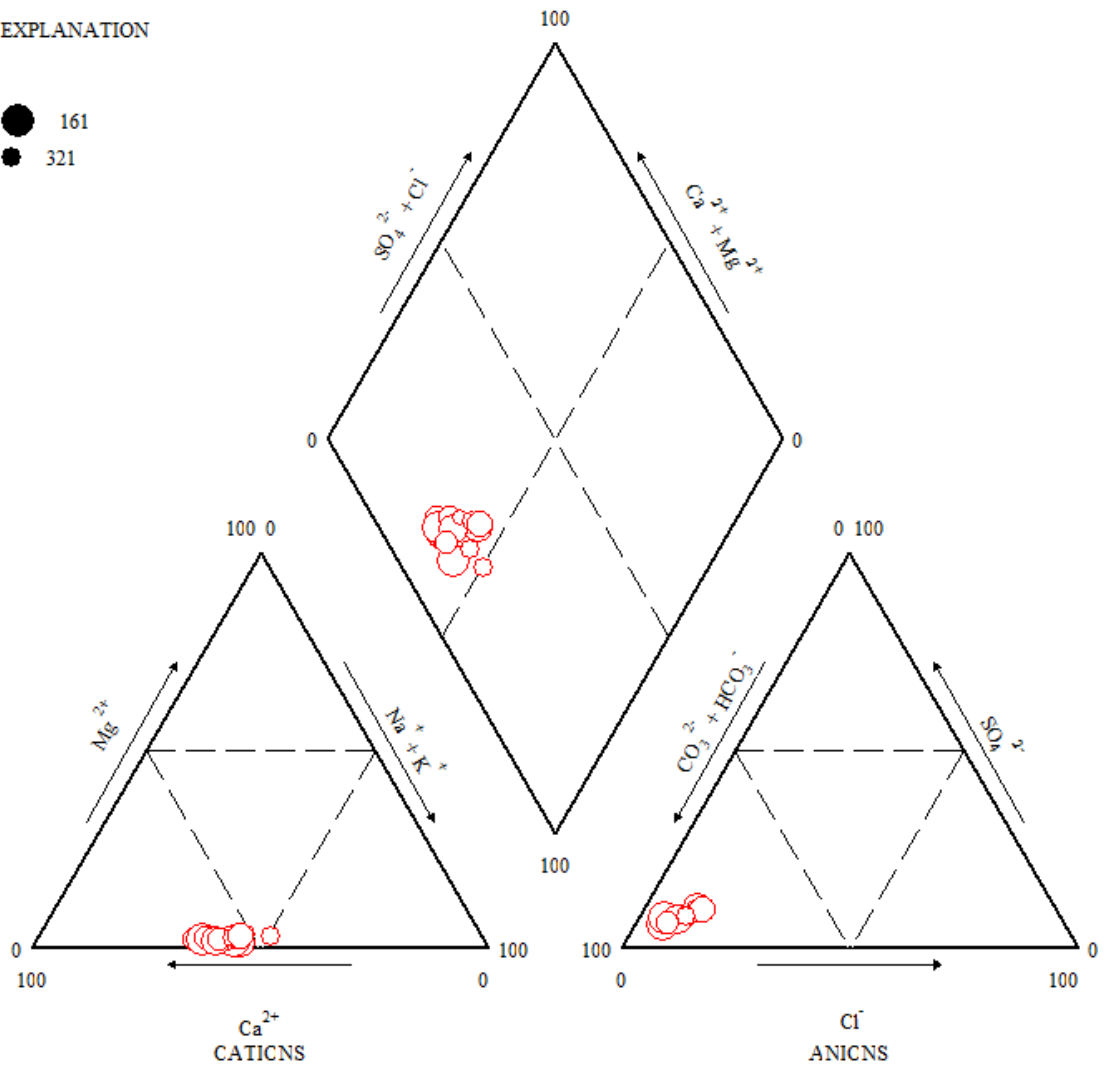
Figure 6. 6. Relative major ion composition of groundwater in the Preston Park shown as percentage of cations and anions in meq/l.
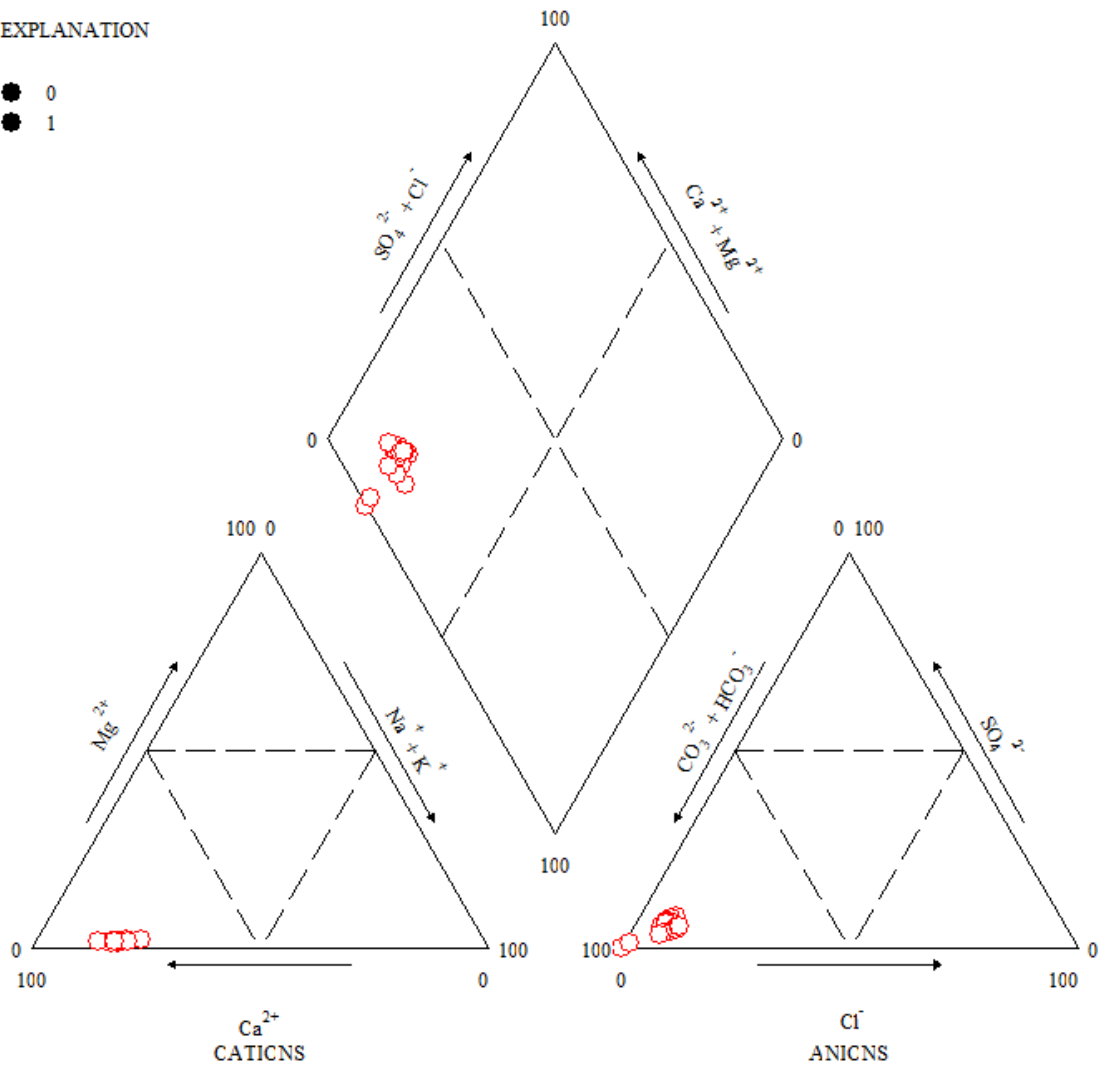
Figure 6. 7. Relative major ion composition of groundwater in the North Bottom shown as percentage of cations and anions in meq/l.

Table 6. 3. Minimum, maximum and average concentration of major ions in groundwater of Preston Park and North bottom.

Element	Preston Park			North bottom		
	Min	Maximum	Mean	Min	Maximum	Mean
Chloride	16.75	36.5	23.91	123	23.84	19.43
Bromide	0.0186	0.327	0.109	0.313	0.578	0.142
S04	0.12	30.2	20.7	0.17	21.83	13.95
Na	18	3473	843	9.49	235	182
K	10.75	125	104	0.39	85	64
Ca	82	783	609	45.4	1395	1128
Mg	1.27	30	19	1.47	24	23
TDS	161	391	278.83	175	345	253.94
HCO3	113	293	236	177	291	224
Ph	6.97	9.22	7.58	7.32	11.35	8.21

Concentrations for Cl, Br, S04 are given in mg/l while Na, K, Ca, and Mg in ppm. n=19 for each sample of every borehole.

6.3.2 Variation in Specific tracers

It is of key importance to understand the variation of tracers in groundwater over a period of time, this will gave a better understanding of tracers and their behaviour in groundwater. Furthermore, variation in the behaviour of the tracers in groundwater will help in the understanding of the potential for contamination. Divers have been installed in the boreholes to record electrical conductivity over time and the results compared with rainfall. Preston Park and North bottom out of the five monitoring boreholes are used for easy comparison between urban and rural site borehole characteristics. This is because the two sites are believed to have opposing characteristic that may have influence on the presence and potential migration of urban diffuse pollution into the groundwater around the study area. For example, Preston Park is an urban site while North bottom is a rural site. The

Unsaturated zone thickness (UZT), a key component that connects the water table to ground surface, also varies. With Preston park having an average UZT of 3 – 20 m while North bottom has an average UZT of 35 – 50 m. Flow through the Chalk unsaturated zone occurs through the matrix, fracture or both. In the matrix, the flow happens through a displacement process where water above takes place of the one below in the Chalk pore and pushes down, known as piston flow. This pattern of flow is believed to be extremely slow (Price et al. 1976). However, this can vary based on water content, high water content may result in faster piston flow. Fracture flow is thought to be faster (Lee et al., 2006) ranging from 0.1 to 100 m/day, but it is strictly dependent upon factors such as, unsaturated condition, rainfall intensity and duration (Ireson, 2009). Figure 6.8 compares conductivity with TPH, it can be seen in the plot that they have opposing behaviours which appears more obvious during the summer months (periods of low rainfall). A similar pattern is observed in Figures 6.9 and 6.10 for the plot of conductivity against Zn and phenols.
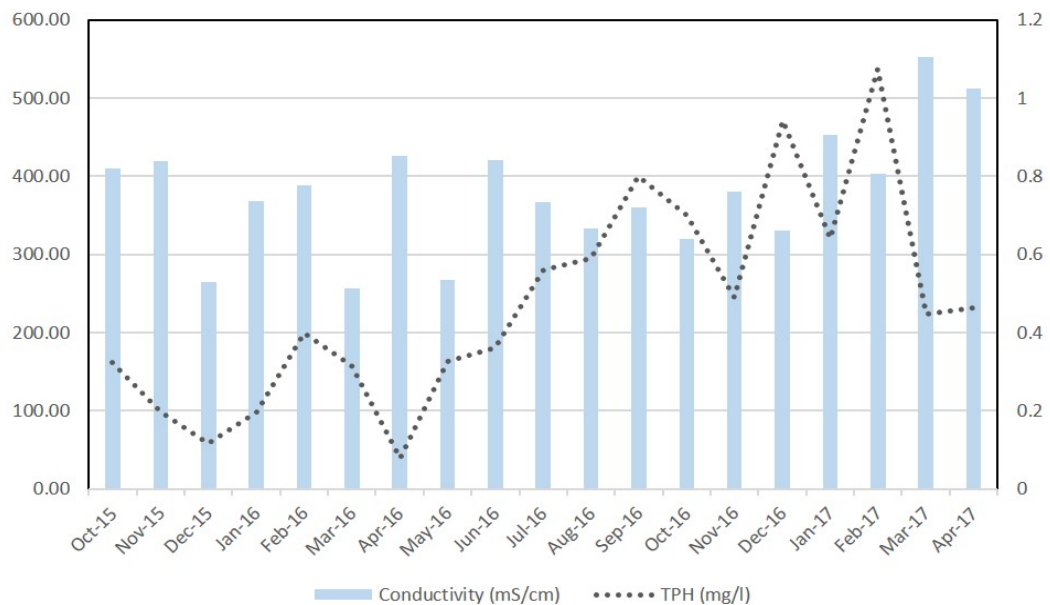
Figure 6. 8. Groundwater conductivity plot against total petroleum hydrocarbon (TPH) concentration in groundwater over a period of 18 months in Preston park borehole within the study area.
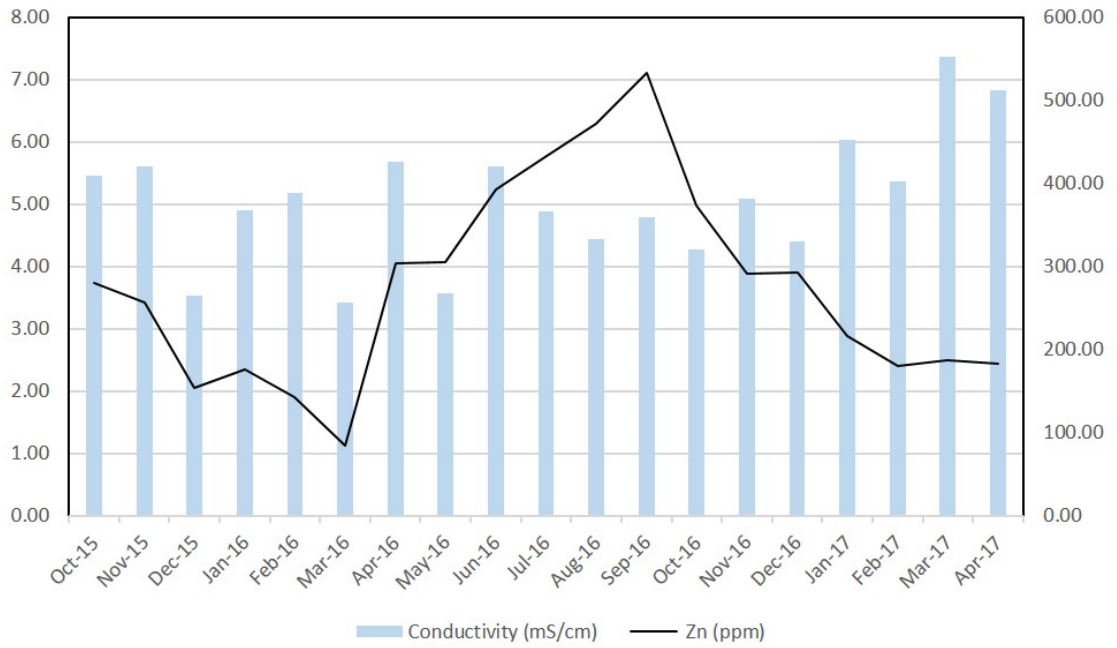
Figure 6. 9. Groundwater conductivity plot against Zn concentration in groundwater over a period of 18 months in Preston park borehole within the study area.
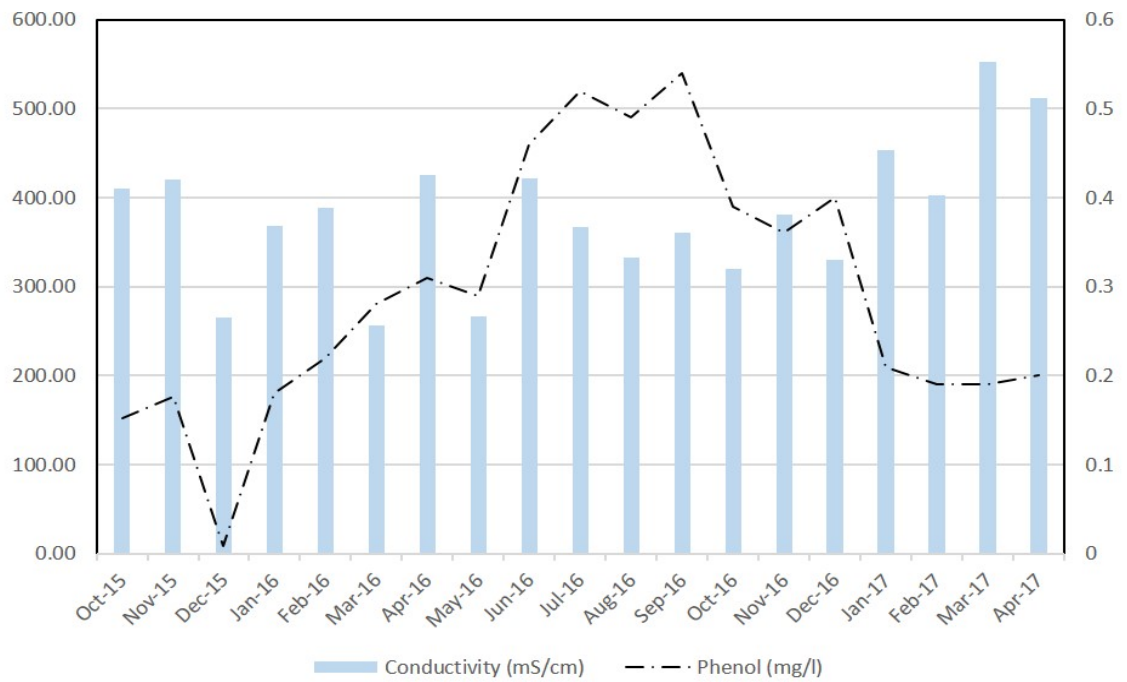
Figure 6. 10. Groundwater conductivity plot against phenol concentration in groundwater over a period of 18 months in Preston park borehole within the study area.

6.3.3 Preston Park

The Preston park borehole time series data was plotted for rainfall against groundwater level Figure 6.11, Electrical conductivity against groundwater level Figure 6.12 and TPH to represent tracers in groundwater against rainfall. Using daily and monthly records for rainfall to determine trends and seasonal variations. This will give a deeper understanding on the impact of rainfall on contaminant inflow. Groundwater level at Preston Park shows relationship to rainfall, from October 2015 to April 2016, average rainfall was high raising the groundwater level to 3 m BGL.
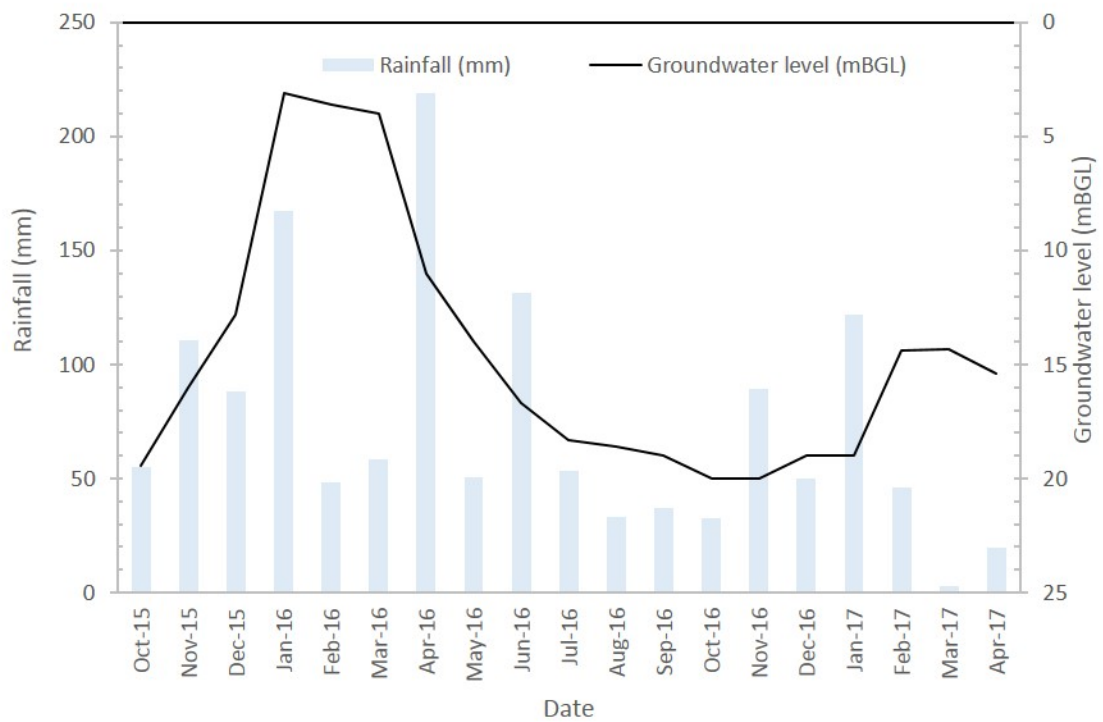
Figure 6. 11. Daily rainfall (mm) against monthly groundwater level (m) in Preston park monitoring borehole.

Electrical conductivity (EC) data is compared to monthly average rainfall during periods of high rainfall from October 2015 to April 2016 Figure 6.13. Results show a very interesting pattern, EC appears to be decreasing with increasing rainfall and increases with decreasing rainfall. EC varies in accordance with the presence of anions or cations, and temperature.

EC displays similar pattern to TPH in groundwater, thus, TPH data is presented in Figure 6.10. A seasonal pattern emerges from the comparison of TPH data against rainfall. During high rainfall levels in the winter, concentrations of TPH remain very low, while in summer (periods of low rainfall) TPH concentrations become very high. Indicating a dilution process taking place in the borehole.
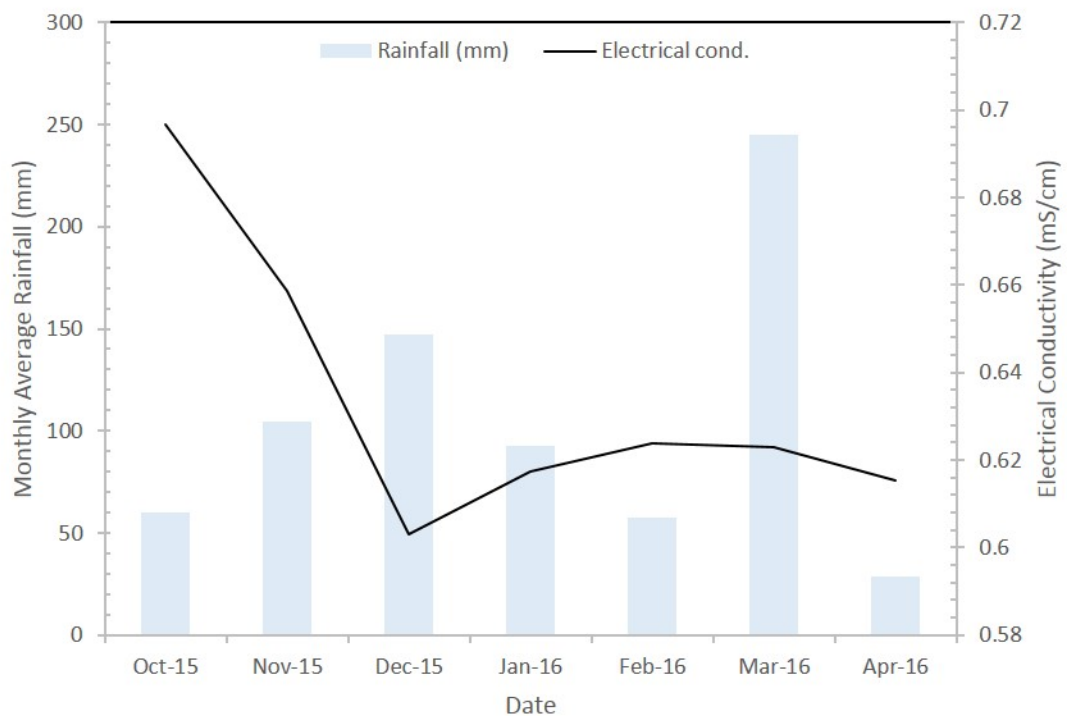
Figure 6. 12. Monthly average rainfall (mm) against groundwater electrical conductivity in Preston park monitoring borehole (October 2015 – April 2016) winter period.

A closer look at the variation between TPH and rainfall in Figure 6.14 and 615 reveals the influence of flow process in the Chalk aquifer and seasonal period on the behaviour of migration of urban diffuse pollutants. In Figure 6.14, sampling was carried out after a 10 day period of low rainfall followed by rainfall of > 16 mm on the 11th day and sampling on the 12th day during autumn (November 2016). Sample concentration was high at TPH > 0.5 mg/l. indicating little or no dilution at all.
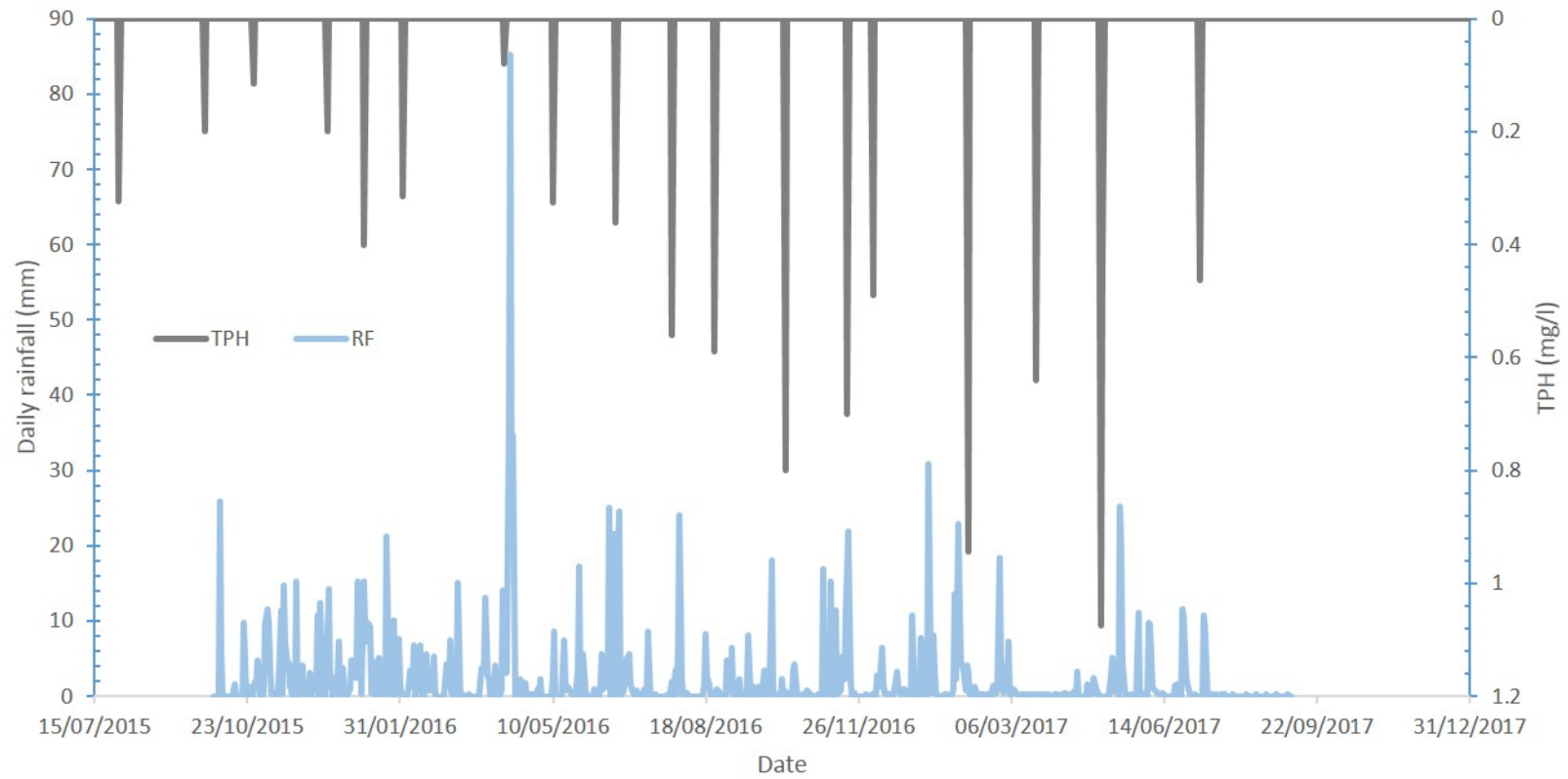
Figure 6. 13. Daily rainfall (mm) compared to monthly TPH (mg/l) input in groundwater from the Preston Park borehole.
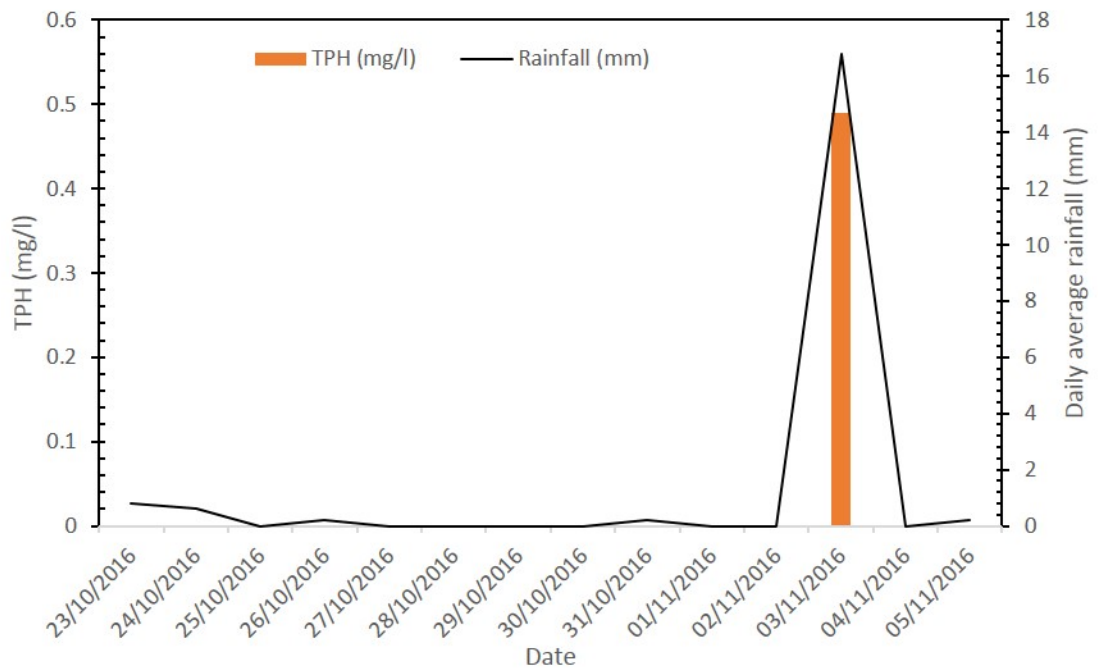
Figure 6. 14. Days of little rainfall prior to sampling during the early days of wet period to show rainfall and TPH relationship to flow process from Preston park borehole.
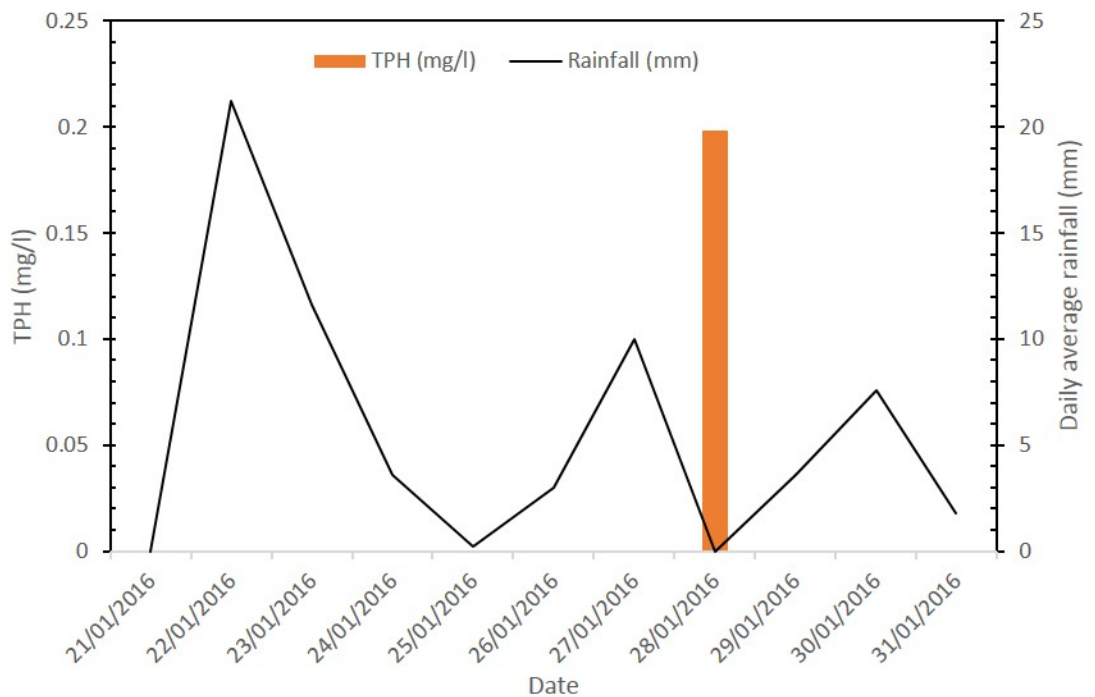
Figure 6. 15. Days of continuous rainfall prior to sampling from borehole to show rainfall and TPH relationship to flow process from Preston park borehole.

6.3.4 North Bottom

North Bottom borehole data was compared to groundwater in Figure 6.16. Water levels during the summer/periods of low rainfall become as low as 65 m BGL and in the winter/periods of high rainfall as high as 30 m BGL. This indicates that the borehole has a thicker unsaturated zone compared to Preston Park. Electrical conductivity data was consistent with rainfall throughout the monitoring period from October 2015 to April 2017 (Figure 6.17). Opposing patterns and seasonal variations did not emerge that may indicate an irregular input from rainfall. The borehole at North Bottom presents a perfect opposite to the conditions monitored in the urban borehole and therefore serves as control for the Preston park borehole.
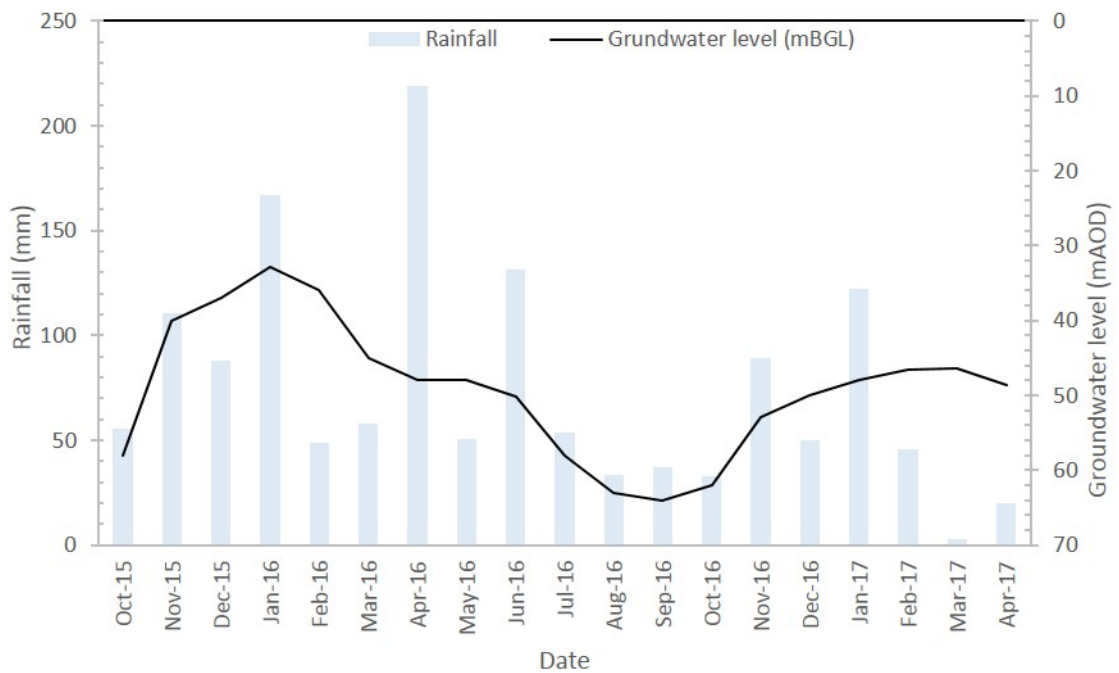
Figure 6. 16. Monthly average rainfall with groundwater level.
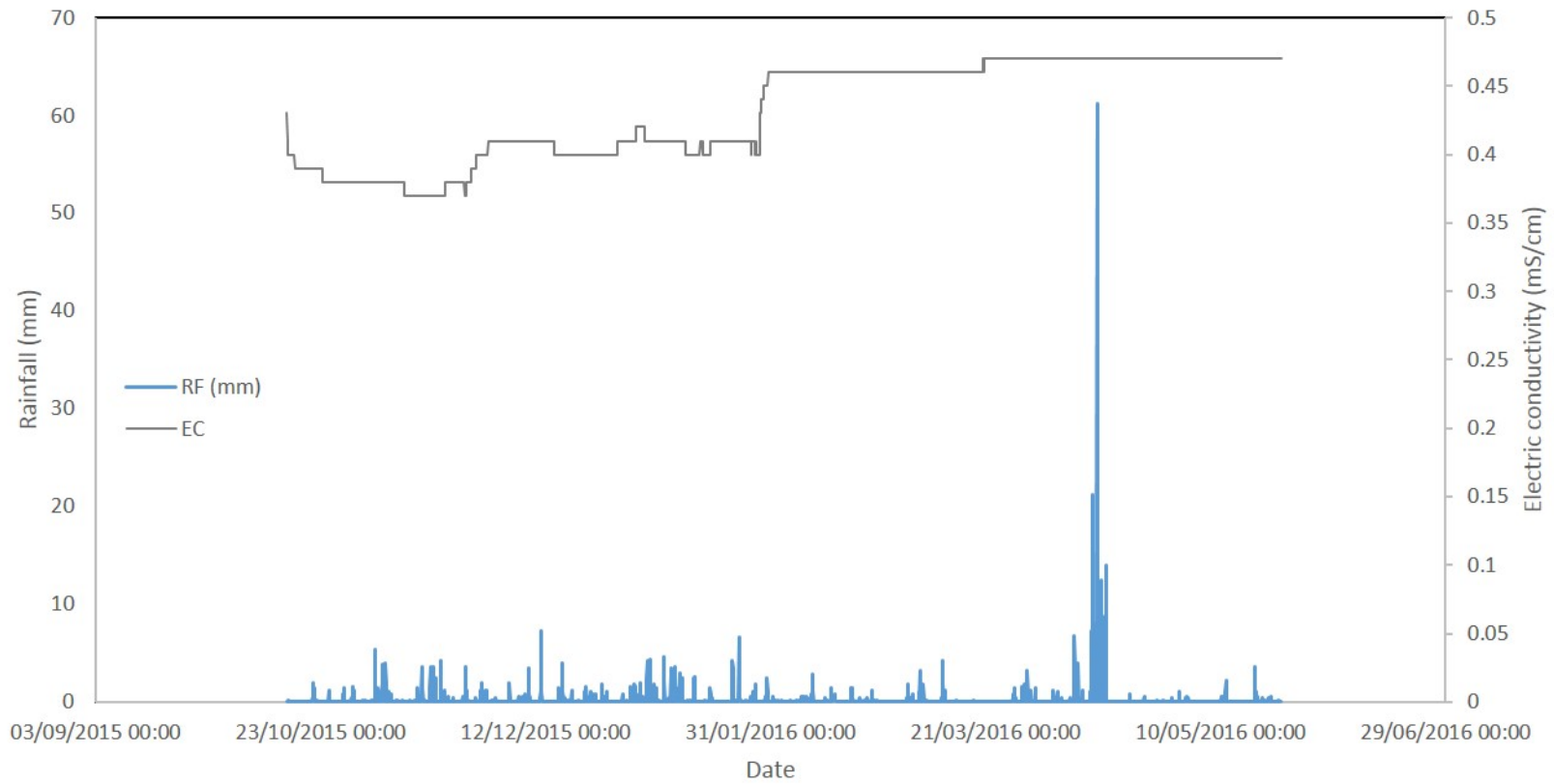
Figure 6. 17. Daily average rainfall (mm) compared to daily average electrical conductivity (mS).

6.4 Discussion

The results from this chapter describes the presence and concertation of Tracers in groundwater and gully pots. Figures 6.1, 6.2 and 6.3 show the concentrations of TPH, phenol and Zinc in groundwater respectively. Concentrations are observed with a pattern that shows a specific time period where levels exceed average concentrations in other periods. Previous studies have found organics to be of regular occurrence in the Chalk aquifer groundwater (Gobel et al., 2006; and Stuart et al., 2012) as discussed in literature (Chapter 2.6). In this study it is observed that organics in the form of TPH and phenols are present in the groundwater although at low concentrations with phenols displaying more presence than TPH. Due to its non-sorbing property, this appears in line with the core flood results obtained when type 1 water spiked with phenols was run through a chalk core, results showed no mixing occurred in the process with output fluid having nearly the same concentrations as input fluid. The Core flood experiment was carried out as part of this study, to understand flow in the Chalk aquifer using Chloride and phenol as solutions. Despite the concentrations of phenols in groundwater have not reached levels for concern, they are still significant at < 0.1 to > 0.7 µg/l in some places, considering concentrations measured at surface of about 0.32 to > 22.3 µg/l. with greater contaminant loading, levels of concentration might increase.

Heavy metals on the other hand show the presence of Zn but at very low concentrations. Zn Levels become even less significant when compared to limits recorded in surface sediments of 619 to 2091 mg/kg (Chapter 4). However, heavy metal availability depends on its mobility which in turn depends on the condition of the surrounding environment (Sherene 2010; Chapter 2.7.2). Results from the leachability studies carried out in this study (Chapter 5), revealed that Zn, Cd and Mn are available in decreasing order as listed with a percentage concentration of 21%, 12% and 11% respectively. Suggesting that Zn is

more available for mobilisation and run-off in the urban environment. However, this will require the appropriate conditions of redox and/or pH. Even so, the percentage concentration of Zn at 21% appears a smaller amount to give sufficient concentration in the aquifer that may reach pollution levels. With potential for biological processes to take place in the USZ and or natural attenuation process to occur, all these may be hindrances for a significant presence of Zn to be observed in the Chalk aquifer groundwater.

The data from electrical conductivity from the borehole and monthly rainfall and groundwater level were plotted and analysed to understand variations and patterns for potential seasonal variations in the groundwater. Results show that there is a clear pattern of seasonal changes occurring by comparing groundwater level, electrical conductivity and rainfall. The Preston Park (Figure 6.8) borehole shows a period of continuous high groundwater levels from October 2015 to April/May 2016 about 180 – 210 days, before starting to decline to low levels lasting from June 2016 to December/January 2017. This pattern is equally observed in North bottom (Figure 6.13), however the North bottom pattern appears to have even longer periods of low groundwater levels lasting up to about 8 months, from April 2016 to November 2016.

The difference in the duration of periods of low water levels between the two sites, can be attributed to factors such as, unsaturated zone thickness, water level response to rainfall, and season and flow process with sometimes evapotranspiration being a factor. The difference in topography can affect response time for example, north bottom has a thicker unsaturated zone of between 20 – 50 m thick. While, Preston Park has an unsaturated zone thickness of about 3 – 20m thick, this may lead to a quicker response observed at Preston Park than in North bottom. But the quickest response times are observed in periods of autumn and winter, generally periods of high rainfall (Lee et al., 2006). A sample taken from the groundwater, a day after rainfall prior to ten days of no rainfall showed no

dilution, with a high organic concentration levels (Figure 6.11) during early spring. Another sample taken during periods of high rainfall levels showed heavy dilutions due to low levels of organic in sample (Figure 6.12) during autumn of the same year.

Lee et al., (2006) in a study of water response to rainfall considering six sites in the Chalk aquifer of South East England. The study found out that water table response to rainfall varies from less than 1 day to 4 weeks. With the slower responses observed to occur during the end of the dry periods (late October to early November as seen in Figure 6.11.) because at this time, storage in the unsaturated zone and matric hydraulic conductivity are at a minimum. In the same study, Lee observed that the more rapid responses occurred when these conditions are reversed, during or after wet periods (winter). Which is the case in Figure 6.12 showing a low concentration of TPH at < 0.2 µg/l after a 7 day period of continuous rainfall as high as > 20 mm before sampling on the 8th day. This specifies clearly that dilution has taken place from the continuous rainfall thereby reducing concentrations of TPH in the borehole. During the winter period of January 2016.

6.5 Conclusion

This chapter examined evidence for road run-off input to Chalk groundwater and the possible impacts of seasonality. Results from CDT divers and analysed contaminant (organics and heavy metals) concentrations in groundwater over a period of 18months from five different monitoring boreholes were used, with emphasis given on two boreholes, Preston Park (urban) and North bottom (rural).

Zn and Organics in form of phenol have been observed in groundwater at low concentrations. Phenol in groundwater from the boreholes observed has a concentration between 0.2 – 0.7 µg/l in Preston Park and 0.1 – 0.35 µg/l in north bottom. Zn on the other hand has concentrations of 1 mg/kg – 4 mg/kg at Preston Park and 0.2 mg/kg – 4 mg/kg at

North bottom. This indicates a higher presence of urban diffuse pollution in Preston Park. Although, concentrations may not have reached guideline limits, it is suggested that with increasing periods of low rainfall or low groundwater level (summer) concentration of urban diffuse pollution in groundwater is likely to increase. Data used may not be sufficient however, to make such conclusions as this study only used data for a period of 18 months only.

The high and low of the concentrations reveal a seasonal variation at both locations, Preston Park and North Bottom. At Preston Park, low concentrations of contaminants in groundwater are observed during periods of high rainfall (spring and winter seasons) as a result of mixing. While higher concentrations were observed during low rainfall (summer). In North bottom however, concentrations appear to be consistent with rainfall infiltration transporting material from surface to groundwater.
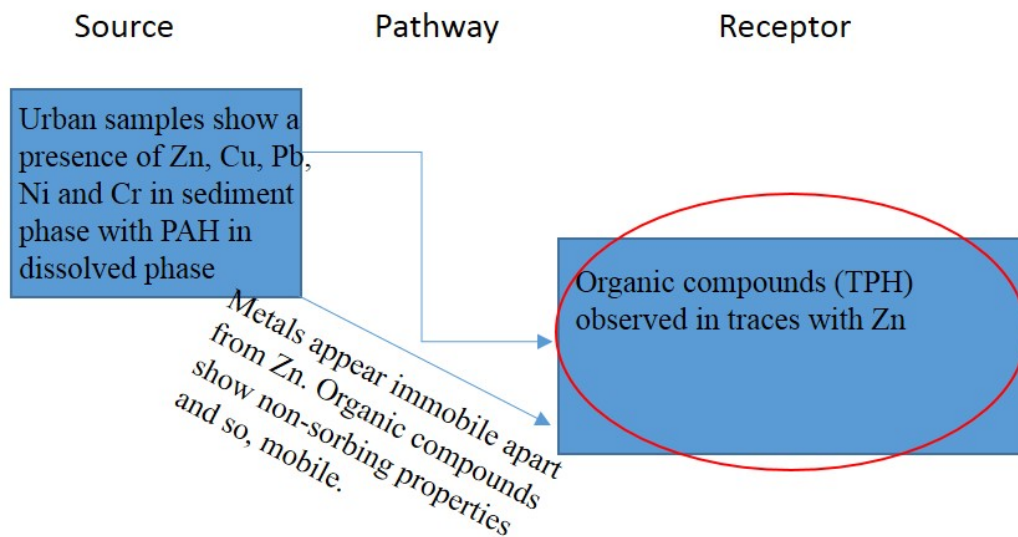
Figure 6. 18. Conceptual model stating the observed pollutants at the receptor.

Chapter 7 Discussion and conclusion

7.1 Introduction

The Brighton area forms an exceptional case study for the pressures of urbanisation on a major chalk aquifer. It serves as the main source of public water supply for the area, but there are increasing pressures on aquifer recharge from an intensely urbanised coastal strip and the associated major road system (Lerner & Barrett, 1996). The groundwater level in Brighton shows a rapid response to rainfall (with observed rises in level of several metres within a few days) as a result of rapid preferential flow along fractures and solution features (karst) during the winter months. This thesis aimed to characterise the contaminant chemistry of urban drainage in order to define the source term for a source-pathway-receptor model of urban roadway contamination. By;

- Determining the concentration and characteristics of urban drainage contaminants in the chalk aquifer

- And the mechanisms involved in retardation of contaminants in transport from the urban drainage system to the aquifer in a novel study.

Ground water monitoring has been carried out for a period 18 months from 2015 – 2017 over 5 borehole locations of the Patcham catchment within Brighton. Along with gully pot samples (sediment and water) to determine the contribution of road derived contaminants in the environment and subsequent mobilisation to groundwater in a novel study. Laboratory studies were employed to determine concentration of urban diffuse contaminants in gully pots and potential presence in groundwater. This Chapter presents a summary of the findings from this stud, discuss their significance, and gives a number of recommendations for further necessary work to be carried out.

7.2 Discussion of results

7.2.1 Dissolved phase and sediment bound gully pot samples

Previous studies (Robertson et al., 2003; Charlesworth et al., 2003 and Brown and Peake 2006) have identified road sediments and drainage waters as hotbeds for contaminants (metals and organic compounds, in particular PAHs). Sediment and water samples from gully pots were collected around the study area (Brighton) and were subjected to laboratory analysis. Results reveal the presence of some metals earlier identified as potential tracers to be used in the current study. These potential contaminants can be present within the sediment phase or dissolved phase and include; Cu, Pb, Zn and PAH (organics). Findings from the urban drainage samples reveals that the gully pots contains heavy metals, mainly in particulate and sediment-bound form above soil guideline values (Environmental standard guideline values for soil and sediments (Directive 2013/39/EU). PAHs occur above environmental standard guideline values in both the sediment and dissolved phases (Environmental standard guideline values for soil and sediments (Directive 2013/39/EU) and WHO standard guideline values for water). These are distributed across different locations. However, busy roads form a hotspot for the contaminants and road junctions appear to be hotspots for PAH. This further strengthens assertions from previous studies (Shu and Hirner, 1997; and Rothwell et al., 2015) that provide evidence of roads and road activities as a major source for heavy metals and organic compounds in the environment. From the potential tracers stated in literature, Zn, Pb, Cu with Organic compounds in the form of PAH have been identified in the gully pot sediments. Soakaway and settling pond samples show very low concentrations within the sediment and water phases, when compared to the environmental standards used in the study leachability study was carried out to understand the metals potential mobility since the overall aim is to determine is the metals could cause contamination in groundwater. A

core flooding experiment was carried out to understand the potential for organic contaminants to migrate through the Chalk.

The presence of heavy metals in the urban environment as observed from the gully pot samples studied was further investigated using evidence from SEM images. Results show the presence of Ni, Fe, Pb and $BaSO_4$ that may have been derived from vehicle and vehicle related activities. This compares to a study by Tucker et al., (2017) which analysed 75 brake pads from different cars. Results show that Ba particles appear frequently followed in frequency by Pb particles. Another study carried out in Italy on road dust sediments by Zannoni et al., (2013) recorded similar elements (Pb, Fe and Ni) as the current study, and also suggested the potential source of Ba was from brake wear and road paints. The considerable levels of Pb in the urban sediments allowed opportunity to determine metal source directly. A Pb-isotope study was conducted to determine the source characterisation of the Pb present within the study site. Lead isotope composition in the environment can be characterised into three different sources (Pb from industrial emissions, natural sources and gasoline related) based on their Pb-isotope ratios. Results presented from previous studies (Monna et al., 1997; Cundy and Croudace, 2017) appear similar to the current study, the three characterisation sources. The Pb-isotope ratios from natural sources appeared much higher than Pb-isotope ratios observed in the present study. Pb-isotope ratios from industrial emissions displayed much higher concentrations when compared to that of the present study. However, Pb- isotope ratios from gasoline related activities and from the current study ratios show very close concentrations. There appears to be mixing with Pb-isotope ratios from present study showing a spread between concentrations from gasoline related activities, industrial and Pb-isotope signatures from natural sources. The mixing may have been derived from anthropogenic sources.

7.2.2 Leachability study of heavy metals within gully pot sediments

The results obtained from the chemical characteristics of the gully pot sediments in Chapter 4 reveals the presence of heavy metals including Cu, Pb and Zn. Leachability studies were carried out on the sediment samples with the results presented in Chapter 5. Results show that the reducible fraction has the least concentration of the three extractible phases; Exchangeable (carbonates & exchangeable metals), reducible (Iron/manganese oxyhydroxides) and oxidisable (organic matter & sulphides). Two metals (Cu & Zn) showed higher concentrations with affinity to different phases. Copper (Cu), showed greater affinity to the oxidisable phase, as has shown in previous studies (Charlesworth and Lees 1999). Metals bound to the oxidisable/sulphide phases have restrictive mobility. (Bourg et al., 1995). Hence why Cu in the present study has not been observed beyond the oxidisable phase. Zinc (Zn) on the other hand has shown greater higher affinity to the exchangeable fraction. Although, it also displays presence through the other more mobile fractions. As a result, Zinc (Zn) indicates high potential for remobilisation to the environment with suitable conditions (pH and redox) for remobilisation due to its solubility (Bourg et al., 1995 & Charlesworth and Lees 1999). Chuan et al., (1996) studied the effects of redox potential and pH on the solubility of heavy metals in soils. The study found that both pH and redox potential had a great influence in heavy metal mobility in soil, looking specifically at the mobilisation of Pb, Cu and Zn. Chuan further stated that acidic and reducing conditions were more favourable for mobilisation of metals in soil. Therefore, the effect of pH is more significant than that of redox potential in the mobilisation process of heavy metals in soil. The study concluded that, the mechanism controlling the release of heavy metals for mobilisation was the pH-dependent metal adsorption reaction and dissolution of Fe-Mn hydroxides under reducing conditions. Since, metals had greater affinity to the phase.

Higher adsorption potential of Pb and Cu could also weaken the Zn retention, especially when Zn concentrations are very high in relation to other metals as reported by Kabata-Pendias, A., Pendias, H., (2001). Furthermore, the results observed for Zn in the gully pot sediments compares with a similar study on the potential mobility of heavy metals (Cu, Zn, and Pb) through soil and soakaway sediment using coupled application of sequential extraction and isotopic exchange in Nerima ward, Tokyo (Kumar et al., 2013). The study concluded that the order of retention of the three elements observed is Pb > Cu > Zn, with Zn being the least retained in the sediments and further stated that there is more concern for Zn pollution than the other elements.

The core flooding experiment was carried out to understand the possibility for organic and other dissolved contaminants to migrate through the Chalk. In this study, Phenols and Chloride spiked de-ionised water were used to flood a Chalk core. The core flood experiment results show that organic contaminants used (Phenol) does not show any potential for mixing with water within the chalk and is not involved in any inorganic chemical reaction.

7.2.3 Impact of urban diffuse pollution in groundwater

Groundwater monitoring carried out by sampling and lowering a conductivity, depth and temperature monitor (CDT diver) within 5 boreholes (located around urban and sub-urban sites) for a period of 18 months. Data collected were analysed (Chapter 3 for analytical methods used) for potential contaminants. The results have been presented in Chapter 6. Furthermore, this Chapter analysed the seasonal variation in groundwater, highlighting any likely relationships between contaminants input in groundwater and seasonal variation and even rainfall intensity in some cases and the Chalk aquifer groundwater. Results from CDT divers and analysed contaminant (organics and heavy metals) concentrations in groundwater over a period of 18months from five different monitoring boreholes were

used, with emphasis given on two boreholes, Preston Park (urban) and North Bottom (sub-urban).

Generally, Zn and Organic compounds in form of phenol have been observed in groundwater at trace levels. The concentrations seen appear well below environmental standard values (Environmental standard guideline values for water (WFDirective 2013/39/EU). Total Petroleum Hydrocarbons (TPH) in the four semi-rural boreholes show concentrations between $0.1 – 0.35$ µg/l and $0.2 – 0.7$ µg/l in the urban borehole at Preston Park. Zn on the other hand has concentrations of 1 mg/kg – 4 mg/kg at Preston Park and 0.2 mg/kg – 4 mg/kg at North bottom. This indicates a higher presence of urban diffuse pollution in the urban site (Preston Park), indicating a difference between the two sampling sites. The presence of higher elemental concentration at the urban site may be an indication of urbanisation.

Seasonal variation within the Preston park borehole was observed (Figure 6.8 to Figure 6.13). Concentrations appear to vary seasonally, the highest concentrations of both Zn and TPH have been observed during the summer periods and the lowest concentrations observed during winter. Although, concentrations still remain very well below guideline limits, it is suggested that with increasing periods of low rainfall periods or low groundwater level (summer) concentrations of urban diffuse pollution in groundwater is likely to increase and vice-versa. In the winter periods (or periods of high rainfall) there is more transport of elements to groundwater but the effects are mitigated due to the extent of dilution. In the summer period, period of low rainfall, bypass flow is lower however, there is far less dilution of road run-off in groundwater.

The story does not remain the same when observing the sub-urban borehole site, North bottom. In the North bottom borehole, the comparison between season and elemental

concentration does not appear to show contrast. Concentrations of elements in groundwater of the North bottom area seem largely to correlate with rainfall.

A conceptual model is presented in Figure 7.1 that explains the findings of this novel study. It illustrates the contribution of the gully pots to groundwater, showing the existence of natural inputs from precipitation of elements such as; Ca, K and Na. Ca may also be present as a result of calcite dissolution in Chalk aquifer. The conceptual diagram goes on to show that leaching process takes place where metals as Zn and potentially Cu end up getting to the water table through the gully pots that derive from vehicle related activities. Around the study area, not all of the gully pots are connected to a general sewer hence the chance for potential contaminants to be leached to the aquifer. Remobilisation of contaminants to the aquifer occurs in different ways; either as a solution (via leaching), or in the form of colloids and very fine particulates (largely via fracture flow) (Goody et al., 2006 & Mathias et al., 2006).

Settling pond samples showed very little concentration in the study and as seen in the diagram, the ponds appear restricted from the subsurface by barriers unlike the gully pots. The low levels of concentrations observed in the settling ponds is as a result of their source. Unlike the gully pots, settling ponds collect sediments and water from pavements and lack any reasonable input from road derived contaminants. Gully pots on the other hand collect road derived sediments and water which includes release from vehicles and other activities related to the road, leading to a higher concentration of elements in gully pots than settling ponds.
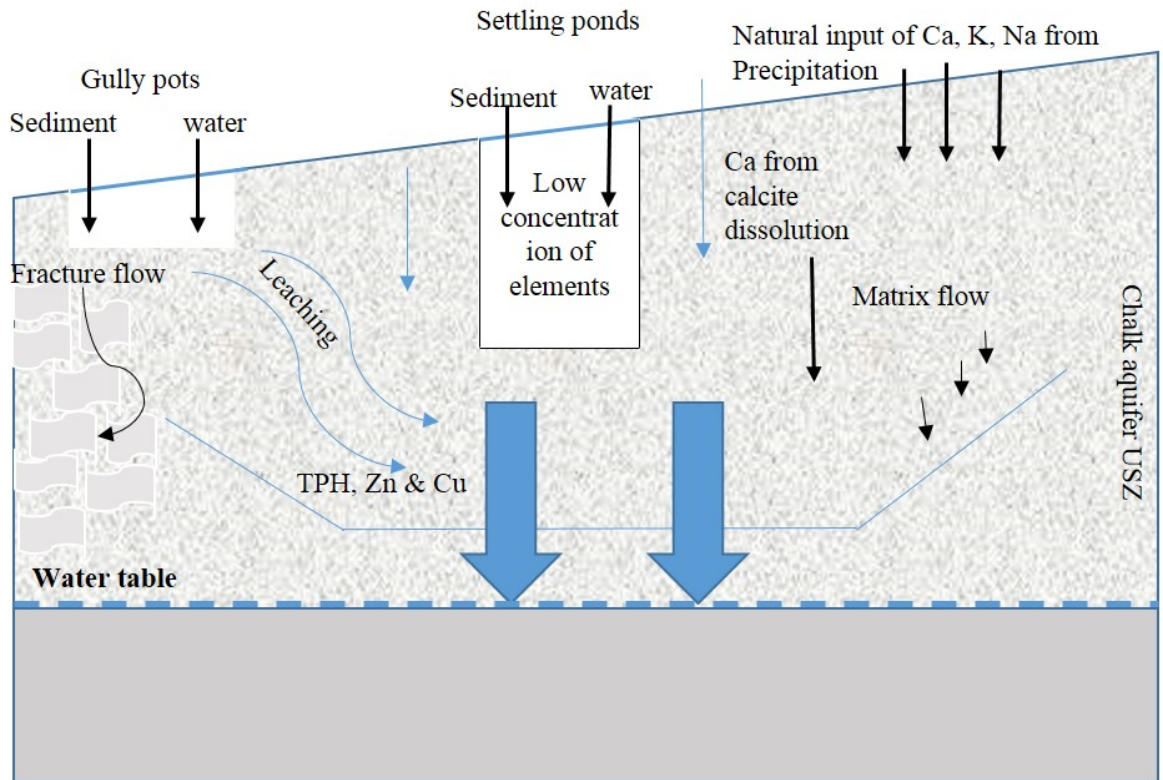
Figure 7. 1. Conceptual model summarising findings from current study in a diagrammatical illustration.

7.3 Conclusions

- Vehicle and road related activities contribute a significant amount of heavy metals and organics to the environment. These include Zn, Pb, Cu, Ni and PAH.

- The gully pot sediments sampled in the study area contain concentrations of Zn, Pb, Cu, Ni and PAH at levels beyond the environmental standard guideline values.

- The distribution of the heavy metals observed within the gully pot waters and sediments vary within gully pots and between the different locations. A complex spatial pattern emerges. However, major roads appear to serve as hotspots for heavy metals while road traffic junctions serve as hotspots for PAHs and Ni which are found in vehicle exhaust emissions.

- The significant Pb levels in the gully pot sediments show signatures of $^{206}Pb/^{207}$ Pb from 1.099 – 1.14 in spring samples and ratios of between $^{206}Pb/^{207}Pb$ 1.098 – 1.114 in the autumn. These samples appear closer to gasoline sourced Pb-isotope signatures of $^{206}Pb/^{207}$ Pb isotopic ratio of 1.079 than Pb from industrial emissions with signatures of $^{206}Pb/^{207}$ Pb 1.142 – 1.159 which are hardly obtainable in the UK due to a non-existence of many Pb processing industries. Since there are no Pb processing industries in the UK. Pb found in the environment in the current study may not have emerged from soils and rocks. This prompts the conclusion that the Pb may have derived from mixing of legacy fuel derived Pb in the environment with anthropogenic Pb from road construction (Pb in bitumen, and components of aggregate including fly ash and clinker from power stations).

- The concentrations of PGEs observed in the study area is the lowest compared to other studies presented herein, with concentrations of about Pd; 9.10 ppb, Pt; 2.81 ppb and Rh; 0.87 ppb. Pt > 500 ng g^{-1}, Rh 70 ng g^{-1}, and Pd 70 ng g^{-1} (Pari and Piper 2001) and Pt = 38.23 ng/g, Pd = 79.8 ng/g and Rh = 17.56 ng/g (Okorie 2015). The PGE thus observed from 13 locations in the present study shows that the introduction of catalytic converters has given further evidence to the presence of vehicle related road derived contaminants. While, levels observed in the current study remains low in comparison to other studies presented. The effect of PGE to the environment is beyond the scope of the current project.

- A sequential extraction procedure carried out using the BCR 701 CRM reveals that Cu is observed in the oxidisable phase with high affinity. Zinc (Zn) however, indicates a better potential for mobilisation through the different phases depending on the suitability of conditions redox and pH.

- Some evidence from urban run-off emerges in groundwater with traces of Zn and organics observed.

- A trend of seasonal variation emerges. Elements observed in the groundwater appear to show an increase in concentration during the period of summer when rainfall level drops. During the winter, when there is high levels of rainfall, concentration of elements and organics in the groundwater drops. This may be as a result of mixing and dilution by rainwater as a result of higher precipitation levels that reduces concentration. The complex nature of flow through the Chalk aquifer may not allow for an accurate prediction of the exact scenario. This remains an area of ongoing debate and further research.

7.4 Recommendation

The following recommendations are made to ensure such a vulnerable aquifer with high importance of providing about 70% water supply for domestic use to the local area is kept safe.

- A more regular clean-up of gully pots will be helpful especially along busy roads and junctions as they serve as hotspots for vehicle derived pollutants. Especially the ones not linked to the soakaway and settling pond network. This will reduce the potential for mobilisation of contaminants form sediment to aqueous phase.

- A continuous monitoring regime should be designed and put in place by the environment agency either independently or in collaboration with the University to assess the solute loading to the aquifer with changing rainfall patterns.

- With expansion in sustainable urban drainage projects and increase use of aquifer, sustainable management options for urban road drainage should be investigated.

A structural amendment might be necessary if further monitoring reveals and increase in concentration rates in subsequent years. It might essential to link gully pots to settling ponds to reduce direct infiltration.

7.4 Further work

From the study carried out, it is clear that urban diffuse pollution contributes a high amount of heavy metals and organics, with other road related contaminants to the gully pots. These may potentially mobilise to the groundwater, especially in cases where there is direct infiltration to a vulnerable aquifer.

- Further monitoring of rainfall activities and groundwater to be carried out as predictions for future rainfall patterns in the UK is that; rainfall will be potentially shorter and more intense during winter (UKCP09 - http://ukclimateprojections.metoffice.gov.uk/23189). This will be key in understanding how it affects pollution transfer to groundwater.

- A more detailed core-flooding experiment should be carried out to fully understand the processes of flow; matrix/fracture through the Chalk aquifer. This will make give a better understanding of contaminant behaviour in Chalk aquifer.

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Appendices

The data appendices to this thesis are held in a disc (disc 1) appended to this thesis.

Appendix I

Settling pond PXRF data

Appendix II

Monthly rainfall data for Brighton

Appendix III

Preston park groundwater data

Appendix IV

Pumping test carried out at Preston Park

Appendix V

Results for Phenol analysis of groundwater data

Appendix VI

Platinum group elements analysis data

Appendix VII

Sequential extraction procedure analysis data

Acetic acid

HCL

Aqua regia

Appendix 1 Settling pond PXRF data

Al	K	Ca	Mn	Fe	Ni	Cu	Zn	As	Pb
0.65	0.4914	11.91	0.2424	3.6944	0.0038	0.0237	0.0698	0.0019	0.0204
0.85	0.4737	11.97	0.1482	3.8374	0.0042	0.0347	0.0907	0.0015	0.0291
0.81	0.4626	12.14	0.0711	3.8844	0.0058	0.0378	0.0822	0.0019	0.0337
0.92	0.5091	12.94	0.0582	3.0092	0.0038	0.0284	0.0648	0.0014	0.0355
0.97	0.5807	10.78	0.0711	3.2831	0.0038	0.0187	0.0469	0.0018	0.0226
0.97	0.5767	10.19	0.0485	3.0172	0.0053	0.0096	0.0306	0.0011	0.0113
			0.0347	2.41	ND	0.0072	0.0234	ND	0.0103
1.07	0.5827	8.3313	0.0503	2.8774	0.0039	0.0069	0.0262	0.0012	0.0092
1.14	0.5833	8.4777	0.0533	2.9042	0.0036	0.0044	0.0207	0.001	0.0087
0.78	0.5831	8.15	0.0516	2.8417	0.0028	0.0032	0.019	0.001	0.0075

Appendix II - Monthly rainfall data for Brighton

Date	RF
01/10/2015	55.2
02/11/2015	110.4
04/12/2015	88.2
05/01/2016	167.2
06/02/2016	48.6
09/03/2016	58.2
10/04/2016	218.8
12/05/2016	50.8
13/06/2016	131.4
15/07/2016	53.4
16/08/2016	33.2
17/09/2016	37.2
19/10/2016	32.6
20/11/2016	89.2
22/12/2016	49.8
23/01/2017	122
24/02/2017	46
28/03/2017	3
29/04/2017	19.8
31/05/2017	95
02/07/2017	51.4
03/08/2017	1.8

Appendix III - Preston park groundwater data

Date	Nitrate	Chloride	Sulfate	Na	Mg	Al	K	Ca	Mn	Fe	Cu	Zn (ppm)	Water level (m)	Ph	ORP (mV)	Conductivity (mS/cm)	T	DO	Phenol (mg/l)	TPH (mg/l)	RF	TDS
Oct-15				322	13	0.85	116	524	0.05	0.70	0.09	3.73	19.43	7.02	67.40	410.00	15.20	60.20	0.152	0.323	55.2	196
Nov-15		17.15	15.44	284	17	0.70	88	605	0.04	0.69	0.10	3.43	16	7.01	75.60	420	12.20	67.10	0.177	0.198	110.4	228
Dec-15		17.15	13.78	356	20	0.92	118	738	0.10	0.65	0.07	2.04	12.8	7.00	89.00	265.00	12.10	85.90	0.009	0.115	88.2	321
Jan-16		18.39	18.77	337	22	0.90	116	728	4.37	0.73	0.69	2.35	3	6.97	41.20	368.00	12.30	39.8	0.18	0.198	167.2	235
Feb-16		17	17.34	323	22	0.90	121	632	2.10	0.81	0.68	1.90	3.6	7.20	41.00	388.00	12.70	41.20	0.22	0.40	48.6	320.00
Mar-16		16.75	16.073	338	20	0.81	131	594	1.22	0.98	0.10	1.12	4	7.75	131.00	256.00	13.00	43.80	0.28	0.314	58.2	161
Apr-16		19.32	22.86	3473	30	1.75	111	839	1.01	2.11	0.31	4.06	11	7.91	25.80	426.00	13.60	38.00	0.31	0.079	218.8	277.00
May-16		18.94	23.63	654	28	2.10	118	623	1.41	1.9	0.51	4.06	14	7.49	33.00	267.00	14.20	8.40	0.29	0.326	50.8	173.00
Jun-16		31.334	24.88	522	31	2.60	124	711	1.98	2.40	0.55	5.23	16.7	7.67	0.01	421.00	13.90	41.00	0.46	0.36	131.4	391.00
Jul-16		29	26	522	33	2.5	143	601	2.1	2.78	0.7	5.77	16	7.75	63.00	367.00	12.10	44.00	0.52	0.56	53.4	293
Aug-16		30	24	479	35	1.9	152	598	2.46	3.1	0.68	6.3	15	7.09	46.00	333.00	12.00	63.00	0.49	0.59	33.2	301
Sep-16		31	23	417	34	1.80	163	542	2.65	2.56	0.40	7.10	16	7.60	45.00	360.00	12.00	58.00	0.54	0.80	37.2	308
Oct-16	28.6	32.9	27.6	389	37	1.45	152	504	2.7	2.39	0.29	4.98	18	7.45	51.00	320.00	12.70	58.00	0.39	0.70	32.6	316
Nov-16	24.5	30.6	25.4	362	37	2.00	159	555	3.10	1.60	0.30	3.88	20	7.27	63.3	381	12.2	8.11	0.36	0.49	89.2	183
Dec-16	33.2	36.5	30.2	262	28	2.10	159	489	2.90	1.78	0.23	3.90	18	7.6	54	330	11.7	46	0.40	0.943	49.8	367
Jan-17	9.8	24	20.5	305	29	0.90	138	459	2.78	1.20	0.19	2.89	19	7.76	48	453	11.4	52	0.21	0.64	122	293
Feb-17	23	31	24	328	31	1.32	117	605	1.67	0.67	0.05	2.40	14.4	8.7	33.7	403	11	44.9	0.19	1.074	46	340
Mar-17	22.9	31.3	23	301	26	0.86	92	478	1.67	0.90	0.09	2.50	14.3	9.22	144	553	11.1	80	0.19	0.447	3	261
Apr-17	29	22	17	234	22	0.65	85	598	1.80	0.80	0.20	2.44	15.4	7.71	59	512	13.6	68	0.20	0.462	19.8	334

Appendix IV - Pumping test carried out in Preston park

Time	Temprature (C)	ORP	EC	DO (mg/l)	TDS	Ph	N
11:06	13.9	9.7	394	13.4	256	7.62	67
11:05	13.8	7.7	395	13.32	256	7.59	66
11:02	13.6	7.5	396	13.48	257	7.61	65
11:01	13.7	8	395	13.47	256	7.62	64
11:01	13.7	7.2	396	13.41	257	7.62	63
11:00	13.7	6.9	397	13.11	258	7.69	62
10:59	13.6	5.6	402	13.22	261	7.72	61
10:58	13.5	6.1	402	13.19	261	7.72	60
10:57	13.6	7.3	314	12.6	204	7.73	59
10:56	13.7	6.8	377	13.08	245	7.71	58
10:55	13.6	6.7	400	12.92	260	7.74	57
10:54	13.5	6.7	401	13.55	260	7.78	56
10:53	13.4	6.4	402	13.5	261	7.8	55
10:52	13.2	6.3	402	13.73	261	7.91	54
10:51	13.2	6.4	400	13.54	260	7.95	53
10:50	13.2	6	397	13.38	258	7.91	52
10:49	13.3	6	400	13.58	260	7.87	51
10:48	13.2	5.9	410	13.47	266	7.88	50
10:47	13.2	5.9	405	12.92	263	7.86	49
10:46	13.2	5.7	402	12.95	261	7.81	48
10:45	13.3	5.7	404	12.85	262	7.78	47
10:44	13.4	5.9	405	12.93	263	7.77	46
10:43	13.4	5.9	404	13.1	262	7.76	45
10:42	13.4	5.9	403	13.09	261	7.75	44
10:41	13.4	7.4	403	12.9	261	7.71	43
10:40	13.6	10.2	400	12.74	260	7.67	42

10:39	13.8	11.2	405	11.93	263	7.69	41
10:37	13.5	7.3	406	12.77	263	7.68	40
10:36	13.4	7.2	402	13.05	261	7.68	39
10:36	13.4	8	396	13.41	257	7.67	38
10:35	13.4	9.3	394	13.48	256	7.66	37
10:34	13.3	9.7	395	13.34	256	7.66	36
10:33	13.3	8.8	399	13.17	259	7.66	35
10:32	13.3	8.2	399	13.47	259	7.65	34
10:32	13.2	9	402	13.45	261	7.66	33
10:31	13.2	9.4	402	13.36	261	7.68	32
10:30	13.3	10.3	403	13.36	261	7.67	31
10:29	13.3	10.9	404	13.37	262	7.69	30
10:28	13.2	11.1	410	13.37	266	7.71	29
10:27	13.1	10.2	411	13.21	267	7.75	28
10:27	13	9.8	413	13.23	268	7.78	27
10:26	12.9	9.2	414	13.3	269	7.82	26
10:26	12.9	8.9	410	13.33	266	7.82	25
10:25	12.6	8.9	416	12.97	270	7.92	24
10:25	12.6	8.9	416	13.07	270	7.93	23
10:24	12.5	9.6	416	12.94	270	8	22
10:23	12.3	9.3	418	13.01	271	8	21
10:22	12.3	9.8	410	13.35	266	8.03	20

Appendix V - Result for phenol analysis of groundwater data

Date	PP	CF	NB	LS	NHB	Conc.
Oct-15	0.323	0.13	0.144	0.233		0.001
Nov-15	0.198	0.203	0.202	0.168	0.212	0.3
Dec-15	0.115	0.152	0.218	0.319	0.272	0.5
Jan-16	0.198	0.168	0.124	0.167	0.089	
Mar-16	0.314	0.356	0.21	0.156		
Apr-16	0.079	0.105	0.131	0.116	0.127	
May-16	0.326	0.384	0.366	0.344	0.288	
Jun-16	0.36	0.298	0.25	0.25		

Appendix VI - Platinum Group Elements analysis data

Name	Ru	Rh	Pd	Ir	Pt
Blank	2.77	53.70	45.41	141.72	45.81
GP1	0.75	0.94	4.64	3.08	1.66
GP2	0.28	1.13	18.70	3.07	5.20
GP3	0.57	0.87	8.76	1.87	1.96
GP4	0.68	0.82	3.31	1.49	1.76
GP5	0.62	0.76	7.54	1.82	1.14
GP6	0.53	0.81	3.78	1.85	1.74
GP7	0.58	1.35	8.87	1.64	4.89
GP8	0.33	1.29	30.69	1.05	8.83
GP9	0.22	0.47	5.92	1.00	2.73
GP10	0.36	0.38	5.34	1.33	0.90
GP11	0.63	0.75	4.16	1.29	1.56
GP12	0.55	0.81	10.67	1.20	1.96
GP13	0.57	0.87	5.98	1.19	2.24
BLANK	0.73	0.73	0.64	1.81	1.01
Mean	0.51	0.87	9.10	1.68	2.81
Median	0.57	0.82	5.98	1.49	1.96

Appendix VII - Sequential extraction procedure analysis data – acetic acid

	Cu	Zn	Cr	Ni	Pb	Fe	Mg	Mn	Cd
GP1	<0.000	5059	<0.000	68	43.4	563	24621	4412	5.16
GP2	<0.000	6089	1.40	38	73.1	557	55724	2679	1.62
GP3	<0.000	4495	<0.000	65	38.3	242	31894	3804	5.54
GP4	<0.000	3481	<0.000	52	93.7	1575	21802	4730	4.16
GP5	<0.000	4037	<0.000	40	46.5	396	36283	4047	2.37
GP6	597.22	7198	0.22	125	957.1	4179	29975	2848	4.26
GP7	432.09	18832	3.58	112	598.2	176	51963	4238	4.38
GP8	548.18	7151	7.80	57	257.9	1230	51891	5060	3.32
GP9	<0.000	9963	0.21	69	65.8	397	51846	4659	3.17
GP10	<0.000	1894	<0.000	24	72.1	180	18100	3850	2.59
GP11	<0.000	6071	<0.000	45	62.9	389	32742	2805	1.95
GP12	<0.000	6128	0.00	78	62.4	140	78729	5699	5.10
GP13	68.94	9441	5.94	90	138.9	78	45519	6596	5.59
GP14	1.83	<0.000	<0.000	<0.000	1.3	<0.000	<0.000	0	<0.000
% Total	**0.24%**	**12.99%**	**0.00%**	**0.12%**	**0.36%**	**1.46%**	**76.80%**	**8.01%**	**0.01%**
sum	1648.25	89837.95	19.15	861.65	2511.42	10103.70	531087.21	55426.86	49.22
count(n)	5.00	13.00	7.00	13.00	14.00	13.00	13.00	14.00	13.00
mean	329.65	6910.61	2.74	66.28	179.39	777.21	40852.86	3959.06	3.79
Stdeva	224.39	4461.47	2.55	33.17	269.77	1088.68	19656.23	1580.75	1.67

Sequential extraction procedure data –

	Cu	Zn	Cr	Ni	Pb	Fe	Mg	Mn	Cd
GP1	<0.000	5059	<0.000	68	43.4	563	24621	4412	5.16
GP2	<0.000	6089	1.40	38	73.1	557	55724	2679	1.62
GP3	<0.000	4495	<0.000	65	38.3	242	31894	3804	5.54
GP4	<0.000	3481	<0.000	52	93.7	1575	21802	4730	4.16
GP5	<0.000	4037	<0.000	40	46.5	396	36283	4047	2.37
GP6	597.22	7198	0.22	125	957.1	4179	29975	2848	4.26
GP7	432.09	18832	3.58	112	598.2	176	51963	4238	4.38
GP8	548.18	7151	7.80	57	257.9	1230	51891	5060	3.32
GP9	<0.000	9963	0.21	69	65.8	397	51846	4659	3.17
GP10	<0.000	1894	<0.000	24	72.1	180	18100	3850	2.59
GP11	<0.000	6071	<0.000	45	62.9	389	32742	2805	1.95
GP12	<0.000	6128	0.00	78	62.4	140	78729	5699	5.10
GP13	68.94	9441	5.94	90	138.9	78	45519	6596	5.59
GP14	1.83	<0.000	<0.000	<0.000	1.3	<0.000	<0.000	0	<0.000
% Total	**0.24%**	**12.99%**	**0.00%**	**0.12%**	**0.36%**	**1.46%**	**76.80%**	**8.01%**	**0.01%**
sum	1648.25	89837.95	19.15	861.65	2511.42	10103.70	531087.21	55426.86	49.22
count(n)	5.00	13.00	7.00	13.00	14.00	13.00	13.00	14.00	13.00
mean	329.65	6910.61	2.74	66.28	179.39	777.21	40852.86	3959.06	3.79
Stdeva	224.39	4461.47	2.55	33.17	269.77	1088.68	19656.23	1580.75	1.67

Sequential extraction procedure data – HAC extraction

	Cu	Zn	Cr	Ni	Pb	Fe	Mg	Mn	Cd
GP1	217	2423	22	59	1017	44653	108	2477	5
GP2	270	1216	27	26	279	15862	115	1363	1
GP3	291	2822	34	55	854	45686	119	1379	4
GP4	193	1234	13	35	1047	52532	119	1807	3
GP5	280	1006	17	36	356	33822	119	1274	1
GP6	1334	1864	29	46	5926	65882	115	435	2
GP7	1504	6741	82	100	6595	52130	111	3008	4
GP8	910	2774	63	60	2071	38029	119	1917	2
GP9	367	3340	42	55	360	37811	126	1603	2
GP10	63	725	17	36	414	11535	117	1285	1
GP11	263	1680	28	46	319	20465	125	1272	1
GP12	274	2436	32	110	622	25874	116	2481	3
GP13	1006	3633	66	62	1373	37131	122	3176	3
GP14	<0.000	33	<0.000	<0.000	<0.000	13	168	0	<0.000
mean	**536**	**2281**	**36**	**56**	**1633**	**34387**	**121**	**1677**	**3**
% Total	**1.23%**	**5.62%**	**0.08%**	**0.13%**	**3.74%**	**84.76%**	**0.30%**	**4.13%**	**0.01%**
sum	6974	31927	472	725	21232	481424	1698	23478	33
count	13	14	13	13	13	14	14	14	13
Stdeva	481	1648	22	28	2084	18007	14	895	1

Sequential extraction procedure data – Aqua regia

	Cu	Zn	Cr	Ni	Pb	Fe	Mg	Mn	Cd
GP1	5593	18861	5212	4222	17816	3414335	393508	20267	15
GP2	7907	19133	6601	5979	9246	4823291	1014241	42008	10
GP3	6194	27494	5433	4286	22503	3461081	436588	22667	15
GP4	7486	22277	7029	4274	34081	5720327	451716	24509	76
GP5	8973	10159	10809	7911	7920	6559386	505595	31964	10
GP6	6679	19515	7199	5189	35071	5065742	510441	28391	11
GP7	11334	34428	12201	6871	54752	5269334	595275	30771	27
GP8	10411	29823	13643	6058	30509	7695737	908273	58609	32
GP9	9641	19763	7208	4656	11760	4019569	550156	26749	13
GP10	4907	12221	6765	5287	6397	3623887	854173	31874	13
GP11	7022	12643	6825	4380	5956	4200337	687821	35210	11
GP12	8689	24094	6768	5397	12881	4072954	759866	31345	24
GP13	10600	29034	9007	5919	18835	3809878	469451	23955	31
GP14	<0.000	<0.000	2	<0.000	0	228	<0.000	<0.000	<0.000
mean	**8111**	**21496**	**7479**	**5418**	**19124**	**4409721**	**625931**	**31409**	**22**
	0.15%	**0.39%**	**0.15%**	**0.10%**	**0.38%**	**86.82%**	**11.44%**	**0.57%**	**0.00%**
sum	105437	279445	104702	70429	267730	61736087	8137104	408319	287
count (n)	13	13	14	13	14	14	13	13	13
stdeva	2913	9107	3299	1804	14955	1778031	255309	12765	18