THE TRANSPORT BEHAVIOUR OF CREOSOTE AND COAL TAR IN SEVERN ESTUARY ALLUVIUM

A thesis submitted for the Degree of Master of Philosophy

By

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Dedications

To Charlotte.

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Abstract

This thesis presents the results of research undertaken into the transport behaviour of coal carbonisation by-products (coal tar and creosote) in alluvial deposits in the Severn Estuary, UK.

Coal tar, and its derivative creosote, comprise viscous multi-component hydrocarbon liquids with a low aqueous solubility. A number of former industrial sites located on the Severn Estuary have been investigated. The geology beneath these sites comprises deposits of alluvial clay in excess of 10m thickness with subordinate peat bands. These deposits are conventionally assumed to be of low permeability. However, hydrocarbon contamination has been observed within and beneath the clay strata.

Characterisation of alluvial deposits found the clay component to be dominated by silicate mineralogy. The alluvial clay typically has a low organic carbon component whilst subordinate peat horizons contains much higher levels of organic carbon.

Detailed logging of alluvial soils identified vertical to sub-vertical fossil root structures penetrating the soil matrix. This network of macro-pores provides a preferential transport pathway for Dense Non-Aqueous Phase Liquids (DNAPLs).

Organic Carbon Partition Coefficents (K_{oc}) were derived for the polynuclear aromatic hydrocarbon phenanthrene, which is a principal component in coal tar and creosote, to alluvial clay and peat. The K_{oc} values were consistent with those reported by other authors for natural soil organic carbon.

In the absence of water, creosote is wetting of alluvial clay,

The soil matrix of alluvial clay has a low permeability and the fossil pore structures present a significantly higher permeability pathway. Soil sampling and preparation can significantly disturb the root structures in the soft alluvial deposits, leading to misleading geotechnical parameters.

ABBREVIATIONS

ASE	Accelerated Solvent Extraction
BC	Black Carbon
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
CSM	Conceptual Site Model
CWG	Carburetted Water Gas
DNAPL	Dense Non-Aqueous Phase Liquid
EPT	Equilibrium Partitioning Theory
EQS	Environmental Quality Standard
F_{oc}	Fraction of Organic Carbon
GCMS	Gas Chromatography Mass Spectrometry
K_{oc}	Organic Carbon Partition Coefficient
K_{ow}	Octanol/Water Partition Coefficient
Ks	Soil/Water Sorption Coefficient
LCP	Light Cable Percussion (Drilling)
LNAPL	Light Non-Aqueous Phase Liquid
MAH	Mono-Aromatic Hydrocarbon
m. bgl.	Meters Below Ground Level
MGP	Manufactured Gas Plant
NAPL	Non-Aqueous Phase Liquid
NSO	Nitrogen, Sulphur, Oxygen
OS	Ordnance Survey
PAH	Polynuclear Aromatic Hydrocarbon
SOM	Soil Organic Matter
U100	100mm diameter undisturbed soil sample
XOM	Xenobiotic Organic Matter

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1. Introduction

1.1. Background

In 1792 William Murdoch constructed the World's first coal gas manufacturing apparatus for the purpose of lighting at his residence in Redruth, Cornwall. The UK's first coal gas company, the London and Westminster Gas Light and Coke Company, began operation in 1812. The towns and cities across the UK followed suit and industrial areas became able to operate night shifts with sufficient lighting.

Hatheway (2002) stated a number of criteria for the location of the Gas Works sites. Gas Works were located in close proximity to central business districts to allow optimal distribution at minimal costs. The principal study sites detailed within this research are all located in close proximity to historically industrialised dock areas around the Severn Estuary.

It was also desirable for the facility to lie topographically below the distribution area to allow the gas, which was lighter than air, to rise throughout the distribution network. This, coupled with a need to locate the site near a transport network, has resulted in most of the studied facilities having a dockside location.

The author has, in his professional role as a Geotechnical and Geo-Environmental Engineer, undertaken ground investigations at a number of former Manufactured Gas Plants and Coal Tar Distilleries and a contemporary Creosoting Facility located on the Severn Estuary. The process of Coal Gasification produced a number of toxic by-products including coal tar, a viscous hydrocarbon liquid. A lapse attitude towards environmental protection historically, including the common practice of placing tar in unlined pits, has resulted in these facilities being heavily contaminated at shallow depth. The behaviour of coal tar and its distillation products, including creosote, are dominated by the fact that they are Dense Non-Aqueous Phase Liquids (DNAPLS, i.e. they are of low aqueous solubility and denser than water).

The superficial geology beneath these facilities is dominated by clay and silt deposits and groundwater risk assessments performed in accordance with contemporary UK guidelines, using parameters from standard laboratory analysis, suggest that the deep ground waters beneath these alluvial soils would be protected by the thick layer of ‘low permeability’ clays. However, field observations were at odds with the results of the groundwater risk assessments with free-phase tar and dissolved phase compounds being encountered within and beneath the alluvium. The current research aims to determine the source of the discrepancies and propose more suitable parameters for performing risk assessments.

1.2. Aims

The aims of the current research are as follows;

1. To perform a literature review on the historical process of coal carbonisation to identify factors responsible for the chemistry of the carbonisation by-products coal tar, and it’s distillate creosote.

2. To determine the geology, mineralogy and structure of Severn Estuary Alluvium to identify factors which affect the transport of DNPALs through this media.

3. To determine the size, distribution and frequency of bio-pores in Severn Estuary Alluvium and identify reasons why these structures may be disrupted or destroyed during sampling and testing.

4. To assess the partitioning behaviour of creosote compound to soil organic carbon from Severn Estuary Alluvium.

5. To determine the permeability of clay containing bio-pores.

6. To derive parameters to assist in the prediction of DNAPL contaminant transport in Severn Estuary Alluvium.

1.3. Thesis Structure

Section 2 outlines the Source-Pathway-Receptor methodology of groundwater risk assessment employed in the UK and summarise the corresponding Environment Agency software. In addition, a background to coal tar and creosote impacted sites studied by Terra Firma Wales Ltd is provided along with a conceptual site model for a selected study site.

The literature review presented in Section 3 initially details the chemistry of the contaminant sources in sub-section 3.1. The chemistry of coal is discussed in Section 3.1.1.1. and the carbonisation process is detailed in Section 3.1.1.2. Coal tar, the by-product of coal carbonisation, is discussed in Section 3.1.1.3. and 3.1.1.4 and its distillation by-product, creosote, is detailed in Section 3.1.1.5. The environmental fate of contaminants is discussed in Section 3.1.1.7. Section 3.1.1.8. presents chemical test data from coal tar/creosote impacted sites studied by Terra Firma Wales Ltd.

In sub-section 3.2 the literature review considers the contaminant pathway. The geology through which the contamination flows is presented. The principle input parameters for conducting an Environmental Risk Assessment, the Organic Carbon

Partition Coefficients and environmental half lives, are reviewed. In addition, wetting and capillary phenomena of free-phase coal tar/creosote is considered.

Section 4 presents the methods employed to explore the geology and chemistry of the study sites and details the laboratory experiments use to determine the partitioning behaviour of coal tar compounds to site-specific soils. Laboratory experiments used to determine the mineralogy of the superficial geology and its geotechnical parameters, including its permeability, are also presented.

The results of these experiments are presented and discussed in Section 5.

Section 6 considers the implications of the current research on groundwater risk assessment and proposes modifications applicable for assessments performed in the Severn Estuary.

Whilst the previous generation of coal gasification works have become obsolete, the current interest in the technology of in-situ gasification within coal seams will lead to a resurge in interest in the contamination problems associated with this process. Lui *et al* (2007) identified that phenolic compounds, polynuclear aromatic compounds and heterocyclic compounds were present in groundwater after in-situ gasification.

2. Groundwater Risk Assessment

2.1 Standard UK Procedures for Groundwater Risk Assessment

Model Procedures for the Management of Land Contamination are presented in detail in the Environment Agency publication ‘Contaminated Land Report 11 (Environment Agency, 2004). Contemporary industrial facilities are regulated by Pollution Preventions and Controls (PPC), enforced by the Environment Agency, to ensure the facility does not cause deterioration of the environment.

Where land has previously been occupied by industrial facilities, it is accepted that the opportunity to maintain a clean environment by Pollution Preventions and Controls has already passed as the contamination is already present in the environment. In such cases risk assessment is necessary to determine whether the contamination poses an unacceptable risk to human health or the wider environment. Risk assessment allows determination of the amount of ‘clean up’ necessary as it may not always be financially or technically feasible to return the land to it pre-industrial condition.

The term ‘Risk’ has been defined by the Department for Environment, Food and Rural Affairs, Environment Agency and Institute for Environment and Health (DEFRA *et al*, 2000) as follows;

“Risk is the combination of the probability, or frequency, of occurrence of a defined hazard and the magnitude of the consequence of the occurrence”

Groundwater Risk Assessment within the UK is performed within the context of “pollution linkage” using a Source, Pathway, Receptor conceptual model.

For a risk to be present there needs to be a source of contamination, for example coal tar. Contamination is defined by the Environment Agency as;

“a substance that is in, on or under the land and has the potential to cause harm or to cause pollution of controlled waters”

A receptor is defined by the Environment Agency as;

“something that could be adversely affected by a contaminant, such as people, an ecological system, property, or a water body”

For example, polycyclic aromatic hydrocarbons (PAH) are a major component of coal tar and creosote and many of these are known potent human carcinogens.

All of the study sites overlie confined secondary aquifers, located beneath the alluvial clay, which could potentially be used for potable water supply via abstraction. In such a situation, the groundwater abstraction well, and thus humans, would be considered the receptor. The confined groundwater eventually reaches estuaries and the eco-systems therein may also be considered receptors.

A pathway is defined by the Environment Agency as;

“a route or means by which a receptor can be exposed to, or affected by, a contaminant”

In the case of groundwater risk assessment, the pathway will include the soil/rock between the source and the receptor which will serve to retard the flow of free-phase contamination and groundwater which will carry dissolved contaminants. Beneath the study sites alluvial clay is the pathway between the shallow contamination beneath the former facilities (source) and the confined aquifer (receptor).

The Environment Agency Remedial Target Worksheet Computer Programme v.3.1 allows engineers to calculate the flow rate of dissolved contaminants between a source and receptor. The algorithms used in the computer model are presented in detail in the publication Remedial Target Methodology (Environment Agency, 2006).

The computer programme conceptualises the soil through which the dissolved contaminant flows as a chromatographic column. The soil forms a solid stationary phase. Groundwater flows through the soil and dissolved hydrocarbon contaminants partition to the organic content of the soil at a degree determined by the Organic Carbon Partition Coefficient, K_{oc}. Published data for partition coefficients between soil organic matter and hydrocarbon compounds are available in Environment Agency literature (for example Review of the Fate and Transport of Selected Contaminants in the Soil Environment. Environment Agency, 2003b) although the nature of soil organic matter is highly site specific and generic data should be viewed cautiously (See Section 3.2). The contaminant flow is thus retarded relative to the groundwater flow by a retardation factor (R_f). The flow rate of the groundwater and the dissolved contaminants are thus calculated from the hydraulic gradient and permeability data.

During the transport from the source to the receptor, processes of natural degradation and dilution/dispersion serve to reduce the concentration of the contaminants. Natural degradation data is usually sourced from the publication Environmental Degradation Rates (Howard, 1991). However, these processes are highly site specific and data for individual compounds may not be appropriate for multi-component contaminants, such as coal tar and creosote, where biocidal components may exceed the minimum inhibitory concentration of the soil bacteria tasked with biodegradation.

Given the apparent low permeability of the alluvial clay deposits beneath the study sites (c. 1×10^{-10} ms^{-1}, see Section 5.8), low hydraulic gradients and the significant thicknesses of the clay (>10m, see Section 2.3), the Environment Agency Groundwater Risk Assessment software predicts flow rates such that it would take millennia for contaminants to penetrate through the clay and reach the confined aquifer beneath.

The effectiveness of fine grained soils as a barrier to creosote and coal tar migration is detailed in Environment Agency (2003a) where silt soil is calculated as being capable of sustaining a 5m high pool of coal tar or creosote.

However, groundwater wells have indicated dissolved and free phase contaminants present in the confined aquifers beneath the study sites (see Field Observation, Section 5.1). Given the age of the coal gasification technology, the contamination has to be less than 200 years old.

The predicted and observed site conceptual models can therefore be considered at odds. The expected and observed site conceptual models are presented in Figure 2.1.

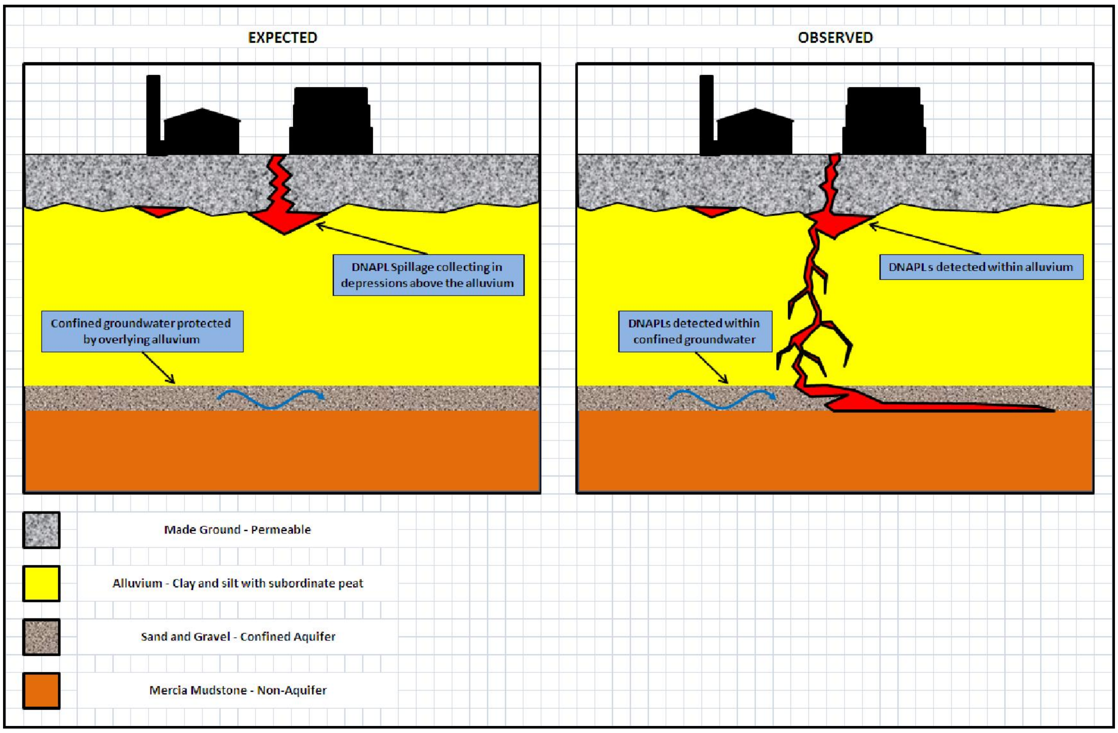


Figure 2.1. Schematic Comparison of the Expected and Observed Site Conceptual Models (Courtesy of Terra Firma Wales Ltd).

2.2 Environment Agency Groundwater Risk Assessment Software

Within England and Wales basic groundwater risk assessments for contaminated sites are often performed using the Environment Agency Remedial Target Worksheet v.3.1. The concentrations of contaminants at the study site are entered into the worksheet, along with geotechnical parameters relating to the geology of the study site, hydrogeological data and physicochemical data for the determinant being studied. The worksheet operates a series of algorithms which consider contaminant mobility and natural attenuation processes between the study site and a chosen sensitive receptor in the sites vicinity. The worksheet presents a remedial target concentration for the determinant in the soil or groundwater beneath the study site. The remedial target is the concentration in soil and/or groundwater necessary beneath the site to ensure that, when natural attenuation processes and dilution/dispersion are considered, a chosen target concentration is not exceeded at the sensitive receptor. The target concentration is usually a published environmental guideline, such as the Environmental Quality Standard (EQS).

Sorption of an organic contaminant to soil serves to retard the progress of that contaminant in a process akin to the retention of an organic contaminant to a lipophilic stationary phase in a reverse-phase chromatography column.

The retardation serves to prolong the contaminants journey between the source and the receptor thereby increasing the time during which biodegradation can occur. Retardation relative to groundwater flow is expressed as a retardation factor (R_f). In addition, diffusion serves to dilute the contaminant concentration en-route by spreading vertically and horizontally about the axis of groundwater flow.

Fundamental to the calculation of the retardation factor (R_f) for determinants in groundwater is the soil-water partition coefficent (K_s). For non-polar organic chemicals the v.3.1 worksheet calculates K_s as shown in Equation 2.1.

$$K_s = K_{oc}.F_{oc} \qquad (2.1)$$

(taken from Table 5.3 of Environment Agency, 2006)

Where K_{oc} is the organic carbon-water partition coefficient for the determinant in question. K_{oc} represents the partitioning behaviour of the contaminant between soil organic carbon and the aqueous phase and comprises the ratio of contaminant concentration in solution to that sorbed to soil organic carbon. F_{oc} is fraction of organic carbon of the aquifer soil.

Quantifying the soil-water partitioning behaviour for ionic organic chemicals required consideration of the prevailing pH, and acid dissociation constant of the contaminant, to determine the amount of ionised species present in the groundwater. The soil-water partition coefficient (K_s) for ionic organic species is calculated as shown in Equation 2.2.

$$K_s = F_{oc}.[K_{oc,n}\,(1+10^{pH-pKa})^{-1} + K_{oc,i}\,(1-(1+10^{pH-pKa})^{-1})] \qquad (2.2)$$

(taken from Table 5.3 of Environment Agency, 2006)

where $K_{oc,n}$ is the sorption coefficient for the determinant under neutral conditions, $K_{oc,i}$ is the sorption coefficient for the determinant when ionised, pH is the pH of the groundwater environment and pKa is the acid dissociation constant of the determinant.

2.3. Background to Study Sites and Conceptual Site Model

2.3.1. Study Sites

Between 2006 and 2012 Terra Firma Wales Ltd (Consulting Geotechnical and Geo-Environmental Engineers, Cardiff) undertook investigations at a number of coal tar or creosote impacted sites located upon deposits of Severn Estuary Alluvium. In addition, chemical data provided by Terra Firma Wales Ltd for Coal Carbonisation facilities not located on alluvium have been included. The author of this research assisted in these investigations in his role as Geo-Environmental Engineer and Terra Firma Wales Ltd has provided access to the site investigation reports. Due to confidentiality issues the Terra Firma Wales Ltd reports cannot be reproduced in the current research, although selected data pertaining to the study sites is referenced throughout this research and used to construct a Conceptual Site Model. The study sites are summarised in Table 2.1.

Table 2.1. Summary of Terra Firma Wales Ltd Study Sites			
Site	**Historical Source of Contamination**	**Superficial Geology**	**Data Provided by Terra Firma Wales Ltd**
Site A (Severn Estuary)	Adjacent to Gas Works	Alluvium	Soil Chemical Analysis Borehole Logs
Site B (Severn Estuary)	Gas Works	Alluvium	Soil Chemical Testing Groundwater Data Borehole Logs
Site C	Gas Works	Quaternary Sands and Gravel	Soil Chemical Analysis
Site D	Gas Works	Jurassic Sandstone and Limestone	Soil Chemical Testing
Site E (Severn Estuary)	Wood Treatment Plant	Alluvium	Soil Chemical Testing Groundwater Data Borehole Logs
Site F (Severn Estuary	Coal Tar Refinery	Alluvium	Soil Chemical Testing Groundwater Data Borehole Logs
Site G	Gas Works	Alluvium	Soil Chemical Testing

Soil chemical test data and borehole log data provided by Terra Firma Wales Ltd is considered in the Literature Review (Section 3).

The Severn Estuary study sites were underlain by between 10m and 26m of alluvium dominated by silt and clay deposits with minor peat bands.

Ground investigation data provided by Terra Firma Wales Ltd revealed that the groundwater beneath the alluvium on both sides of the Severn Estuary is confined. During drilling the boreholes remain effectively dry until the gravel beneath the clay is struck, whereupon the groundwater contained therein rises several meters within the borehole revealing that the water beneath the alluvium is confined under pressure by the overlying alluvium. The level to which the water rises is known as its piezometric level.

The piezometric surfaces recorded in the confined aquifer at the study sites are summarized in Table 2.2.

Table 2.2: Summary of Recorded Piezometric Surfaces at selected study sites during drilling

Study Site	Depth at which confined groundwater encountered (m. below ground level)	Depth to which confined water rose within monitoring station (m. below ground level)
Site E (Based on BH 101)	13.20	7.00 – 7.50
Site F (Based on BH 1)	10.20	?
Site G (Based on BH 1)	14.90	7.00

In addition to data provided by Terra Firma Wales Ltd, soil samples have been collected from the study sites by the author for detailed logging and analysis at Cardiff University as detailed in Sections 4 and 5 of this research.

2.3.2. Conceptual Site Model

The Conceptual Site Model is based on site investigation data provided by Terra Firma Wales Ltd. Between 2006 and 2012 Terra Firma Wales Ltd undertook extensive investigation works at study site E. Historical maps of the site reveal that the site has been used as a timber yard since the first Ordnance Survey (OS) edition (1884). A 'Timber Float' was identified in the west of the site during the first edition although this was shown to have been backfilled by the 1901 OS edition. The site contained a 'Saw Mill' on its eastern boundary from the first edition until its absence on the 1956 edition.

The site was traversed with railway sidings from the first OS edition and these were absent by the 1993 OS edition.

Over twenty deep boreholes have been performed at the site under the supervision of Terra Firma Wales Ltd. Ground conditions typically comprise 1.5m of made ground comprising brick, sandstone, concrete, timber, ash, sand and gravel over alluvium. The made ground was seen to extend up to 4.2m depth at the location of the former timber float.

The alluvium deposits encountered were dominated by silt/clay soils with subordinate bands of peat. The peat deposits were typically less than 1.0m thickness and were limited in lateral extent. Alluvial deposits typically extended between 13.0m and 14.8m depth below ground level (b.g.l.). Laboratory permeability testing performed on alluvial silt/clay under the direction of Terra Firma Wales Ltd recorded permeability values in the order of 10^{-10}ms^{-1} (see Section 5).

The alluvium is underlain by a sand and gravel confined aquifer. During drilling groundwater was encountered at the top of the gravel deposit and this rose to around 7.0m to 7.5m below ground level within the boreholes.

A plan of study site E and principal boreholes is presented as Figure 2.2.

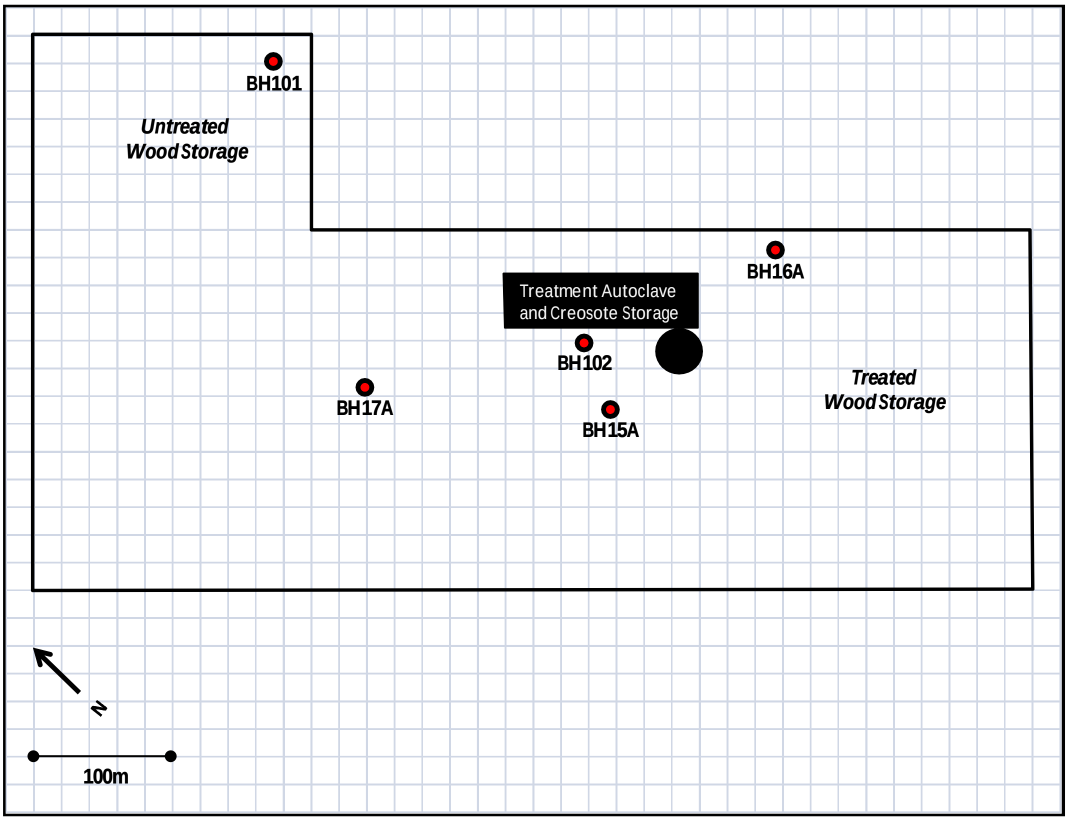


Figure 2.2. Plan of Study Site E including principal boreholes

An east-west Conceptual Site Model is presented as Figure 2.3 based on site specific ground investigation data from Terra Firma Wales Ltd.

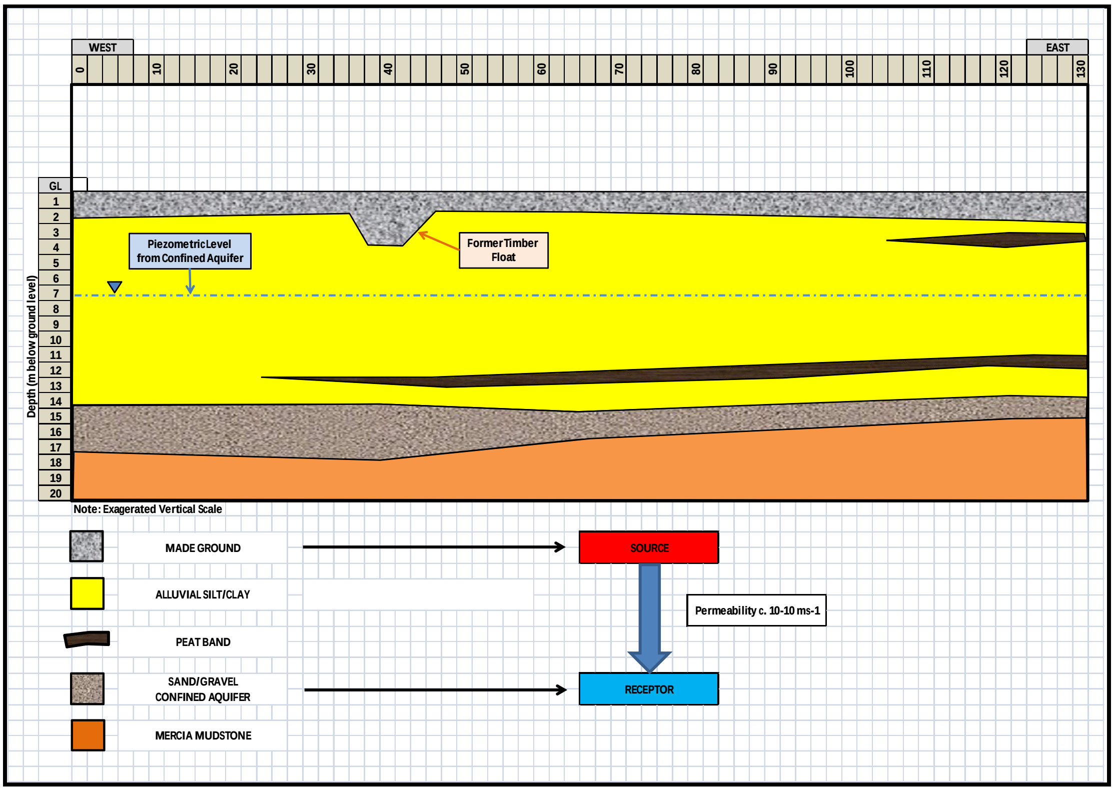


Figure 2.3. Conceptual Site Model for Study Site E

Based on the above Conceptual Site Model and the permeability data obtained by Terra Firma Wales Ltd, the permeability equation from the Environment Agency Groundwater Risk Assessment Software the following flow rate is calculated;

Terra Firma Wales Ltd recorded laboratory permeability values for the alluvium in the order of 1 x 10^{-10} ms^{-1} (8.64 x 10-6 md^{-1}).

The rate of groundwater flow through soil is calculated by the equation 2.3,

$$v = (k \times i) \qquad (2.3)$$

Where v is groundwater velocity, k is soil permeability and i is hydraulic gradient. Hydraulic gradient represents the change in hydraulic head per unit length of soil. If a 1m head of hydrostatic pressure is present over a 1m length of alluvium it would take 317 years for groundwater to flow 1.0m (i.e. 1.0m/(8.64 x 10-6 md^{-1} x 365 days)).

Partitioning of organic contaminants would serve to further reduce the rate of contaminant flow relative to groundwater.

3. Literature Review

3.1. Contaminant Sources

In 1589 a patent was taken out on the process of coal carbonisation to produce coke for metallurgical processing.

The year 2012 marks the bicentenary of the first UK coal gas works facility, the London and Westminster Gas Light and Coke Company. Towns and cities around the UK followed suit and gas companies sprung up close to central business districts. The coal tar contamination at former gas work sites is therefore less than 200 years old. Coal tar from former metallurgical coking sites can be older, although metallurgical coking sites are not considered in the current research.

3.1.1. Chemistry of Coal Tar and Creosote

The study sites considered in this research have been formerly occupied by, or lay adjacent to, industrial facilities which generated coal tar as a by-product (i.e. Manufactured Gas Plant) or stored and used refined products of coal tar (i.e. Tar Distillery and Creosote Wood Treatment Plant).

This section, through literature review, including site investigation reports provided by Terra Firma Wales Ltd, details the chemistry of coal tar and coal tar creosote from the sites located around the Severn Estuary and other sites worldwide. The section characterises the bulk properties of coal tar and coal tar creosote which affect their fate and transport in the environment. Key compounds are identified which can be used as indicators of the presence of this multi-component contamination.

3.1.1.1. Chemistry of Coal

Coalification is the process by which vegetation matures to coals of increasing rank. The biochemical stage concludes with the conversion of cellulose to humic acid, and this is followed by the geochemical stage (Jones & Godefrey, 2002). Coalification is characterised by a loss of volatiles (CH_4, H_2O, CO_2 and CO) and relative increase in the percentage carbon with increasing rank from organic matter with less than 50% carbon, through peat, lignite, sub-bituminous coal and bituminous coal to anthracite, with carbon concentrations approaching 100%. Kopp *et al* (2000) identified a decrease in the atomic oxygen/carbon ratio and hydrogen/carbon ratio with increasing rank. Coalification temperatures are thought to range from 100˚ C to 170˚ C for bituminous coals and from 170˚ C to 250˚ C for anthracites (Taylor *et al*, 1998).

Coal comprises a complex cross-linked structure. Levine *et al* (1982) describes coal structurally as dominated by organic material, typically representing 85% to 95% (wt/wt) of dry coal. Various inorganic materials, particularly alumina-silicates and pyrites (especially in high-sulphur coals) comprise 5 % – 15 % of the coal. Coal has an extensive network of pores resulting in high surface areas (>100 m^2/g for bituminous and sub-bituminous coals and lignites).

On an atomic level Levine *et al* (1982) describe a sample bituminous coal as relatively small aromatic and naphthenic rings, coupled to one another by “bridges” of aliphatic chains and hetero-atoms (i.e. nitrogen, oxygen and sulphur). In addition to the covalent bridges, there are a significant number of polar groups, such as hydroxyls (-OH), that can contribute to the integrity of the coal structure via electrostatic binding.

During the carbonisation process, the cross-linked coal structure is broken into its constituent parts and existing constituents are altered. Walker *et al* (2007) undertook extensive studies into high volatile bituminous coals from Indiana. Samples were carbonised in retorts at temperatures of between 275˚C and 425˚C and subsequently analysed. Above 375˚C an increase in aromaticity was indicated in the study coals by an increase in the vitrinite reflectance, a decrease in Infra-Red absorbance in the aliphatic region (2800 – 2000cm^{-1}), and a relative increase in the aromatic absorbance (700 – 900 cm^{-1}).

The predominance of aromatic chemistry is apparent in the tars resultant from coal carbonisation. Typical operating temperatures of a Manufactured Gas Plant retort range from 600˚ C to >900˚C depending on the retort design.

3.1.1.2. Carbonisation of Coal

Coal tar is a by-product of coal carbonisation. Carbonisation of coal entails the destructive heating of coal in the absence of air and may be undertaken for a number of objectives.

At first the emphasis was placed on the production of coke for steel making; all the other products, apart from a tar residue, were gaseous and discarded to the atmosphere. It was not until the end of the eighteenth century that work was begun to explore possible uses for both the gaseous products and the tar. By 1840 the development of gas lighting had progressed to the point where coal gas was being used routinely for illumination (Taylor and Gagan, 2002). Coal tar was historically produced as a by-product of manufactured gas operations until approximately 1950 (Environment Agency, 2003a).

The temperature of coal carbonisation is dependent on the desired product. Gentry (1927) defines low temperature carbonisation to mean the destructive distillation of coal at, or below, the cracking temperature of the hydrocarbons in to primary tar. Due to the inherent heterogeneity between coals of different ages and source, the temperature at which cracking occurs spans over a range generally accepted to lie in the region of 500˚C and 800˚C. Where town gas production is of primary importance (i.e. former Gas Works) early engineers recognised that the greatest yield was achieved at high temperatures and retorts were operated accordingly. High temperature coking is used in the metallurgical industries (Gentry, 1927). The coal tars used to generate the creosote employed at the study site E are a by-product from coke production for the metallurgical industry.

Creosote and coal tar are examples of multi-component DNAPLs (Environment Agency 2003a). The chemical components of creosote and coal tar are too numerous to warrant individual consideration and it is usual practice to consider selected key contaminants during environmental risk assessment. Determinants are selected for which there is detailed physicochemical and toxicological published literature to allow groundwater risk assessment in accordance with the Environment Agency Remedial Target Methodology (Environment Agency 2006). Such data is sourced from Environment Agency Publications such as P5-079/TR1 (2003b).

3.1.1.3. Coal Tar Generation

The term ‘coal tar’ is used to describe the thick viscous liquid by-product of coal carbonisation. Birak *et al* (2009) highlight the fact that coal tar at a contaminated site may have arisen from any one of a number of technologies employed to carbonise coal. Gas manufacture through coal carbonisation spans from the early 1800’s until it demise in 1950’s, although coal carbonisation for the metallurgical industry continues to the present day.

Initially (c.1800) coke plants were constructed using ‘bee-hive’ ovens to generate coke from bituminous coal, with no consideration given to capturing the coal gas (known as ‘off-gas’) generated in the process. Later, some coke plant facilities were modified to allow the capture of the ‘off-gas’. The gas generated by coal carbonisation contains impurities including ammoniacal liquor, tar, hydrocarbon oils and sulphur compounds. Prior to distribution the gas required cleaning.

The majority of the tar and water vapour contained in the gas at the outlet of the retort house was removed as liquor in the condensers. Most of the associated ammonia and hydrogen sulphide was dissolved in this liquor. The residual tar was removed using Livesey washers. The remaining ammonia and some hydrogen sulphide and hydrogen cyanide were removed by scrubbing the gas with water or weak ammoniacal liquor (DoE, 1995).

In 1812 the first commercial gas works was established in London to provide street lighting (Rhodes, 1945). The early engineers recognized to some extent the value of low temperature processes, but as the production of gas was of primary importance to them, they resorted to the practice which gave the greatest yield and so adopted the high temperature method exclusively (Gentry, 1928).

The development of electric lighting in the 1880's provided the incentive for the development of additional uses of coal gas, such as heating and cooking (DoE, 1995). Gas used for these domestic purposes was named 'town gas'.

For use as town gas further purification was required to reduce the hydrogen sulphide content of the gas. Gas leaving the ammonia scrubber could contain up to 20,000 ppm hydrogen sulphide, but the statutory requirements for the quality of distributed gas set a limit of 0.7 ppm. The early gas works used slaked lime (calcium hydroxide) to remove hydrogen sulphide (DoE, 1995). Between 1850 and 1900 this technology was superseded by the use of iron oxide to remove hydrogen sulphide. The iron oxide also served to remove hydrogen cyanide from the gas.

Birak *et al* (2009) recognised three primary methods by which gas was manufactured, each of which produced a different type of tar with its own chemical fingerprint. Coal gas comprises the volatiles collected when bituminous coal is heated in sealed chambers. Pre-1850, this was performed in horizontal cast iron retorts at temperatures typically of 600 – 800˚C. Post 1850, the introduction of clay retorts allowed temperatures of >900˚C to be achieved. Post 1910, vertical retorts were re-introduced, with lower operating temperatures. An outline of retort design is presented by Gentry (1928).

Carburetted Water Gas (CWG) was generated by passing steam over red-hot coke. The reaction was strongly endothermic. The resultant gas contained hydrogen and carbon monoxide known as water-gas. Oil was then sprayed into this gas to increase its calorific value, creating CWG.

In locations where coal was not readily available (i.e. Eastern USA) alternative hydrocarbon sources have been employed. In the production of oil gas, oils alone were heated and cracked to produce a mixture of mostly hydrogen and methane, along with other illuminates (Rhodes, 1966). However, given the abundance of coal in the UK all of the Manufactured Gas Plant considered in this research were operated on coal feedstock.

The plants were generally situated within urban areas where the gas was used (DoE, 1995). This minimised the length of pipe work required to distribute the gas. Due to the positioning of these former coal carbonisation sites, they often represent highly desirable plots of land which remain undeveloped on account of the contamination therein.

Throughout the current report the term ‘coal tar’ will be used to collectively describe all viscous liquid coal carbonisation by-products, as details of specific technologies employed at the study sites were not documented.

Murphy *et al* (2005) note that tars not sold to refiners were either landfilled or disposed of in open pits. Hamper (2006) states that historically, tars with a water content of greater than 3% was unsalable to refiners.

3.1.1.4. Coal Tar Analysis

Pindoria *et al* (1996) undertook elemental analysis on coal tar from a manufactured gas plant and a coke oven in Chile. The tars contained 86.2% and 80.3% carbon respectively, 4.81% and 8.41% hydrogen respectively, 0.68% and 0.57% nitrogen respectively and 8.3% and 10.7% oxygen and sulphur (undifferentiated) respectively. ^{13}C and ^{1}H n.m.r. analysis performed by Pindoria *et al* (1996) revealed that within the tar from the manufactured gas plant 94% of the carbon was in aromatic compounds and 86% of the hydrogen was in aromatic compounds.

Abraham (1922), using sulfonation testing, revealed that over 90% of the mass of tar is aromatic. Birak *et al* (2009) notes that a significant portion of coal tar lies above the range of standard analytical techniques with the pitch fraction constituting up to 70% of coal tar. Morgan *et al* (2008) quote compound comprising up to 210 aromatic rings identified during analysis.

Historically solubility in light petroleum naphtha was used to separate coal tar into the asphaltenes, the non soluble fraction, and malthenes, the soluble fraction (Abraham, 1961). Data for coal tars indicate that the asphaltene content is highest in higher temperature tars (Birak *et al*, 2009). Abraham (1961) quotes between 20% and 40% asphaltenes in coal tar from vertical retorts, 25% - 40% asphaltenes in tar from coke ovens and 60% 80% asphaltenes in horizontal retorts.

Brown *et al* (2006) analysed eleven samples of coal tar from ten former manufactured gas plant sites across the USA. Samples were analysed for mono-aromatic hydrocarbons (MAH), polycyclic aromatic hydrocarbons (PAH) and alkylated aromatics. In addition the aromatic and aliphatic fractions were quantified and their water and ash contents were studied.

Brown *et al* (2006) observed that, whilst MAH and PAH concentrations varied by up to an order of magnitude or more between coal tar samples, the relative distribution of PAH and MAH were similar for all the eleven samples. In all instances coal tar was dominated by naphthalene, 1-methyl-naphthalene, 2-methylnaphthalene and phenanthrene.

Brown *et al* (2006) also observed that the 2-ring (naphthalenes), 3-ring (phenanthrenes and anthracenes) and 4 ring (flouranthenes and pyrenes) PAHs displayed an inverse relationship between the degree of alkylation and their relative concentration in coal tar (i.e. un-substituted naphthalene>1 carbon substituted naphthalene>2 carbon substituted naphthalene>3 carbon substituted naphthalene etc.). In respect to benzene, 2 carbon-substituted benzene dominated.

A typical MAH and PAH profile, based on Brown *et al* (2006) sample M4 is presented in Figure 3.1.

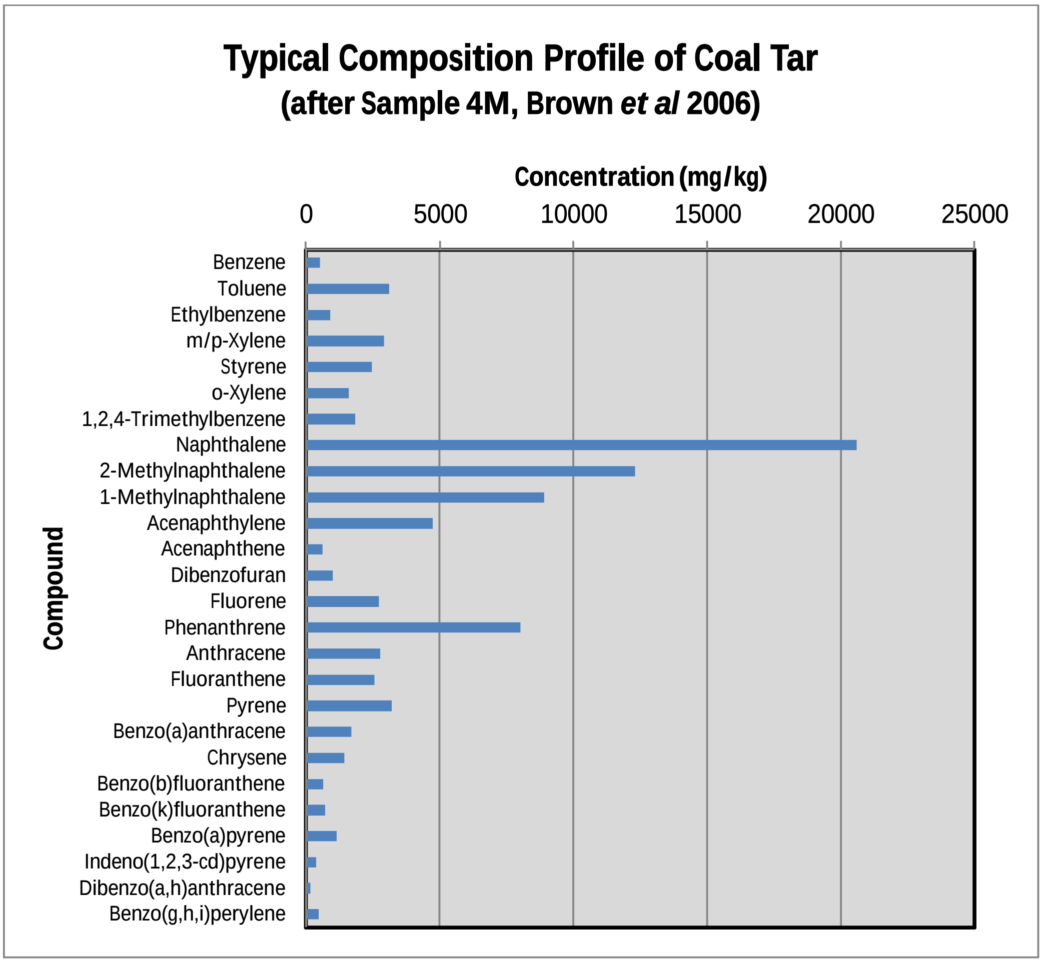


Figure 3.1: Typical MAH and PAH Profile of Coal Tar (after Brown *et al*, 2006)

Tiruta-Barna *et al* (2006) published compositional data for coal tar from an old manufactured gas plant in France. This is reproduced in Figure 3.2.

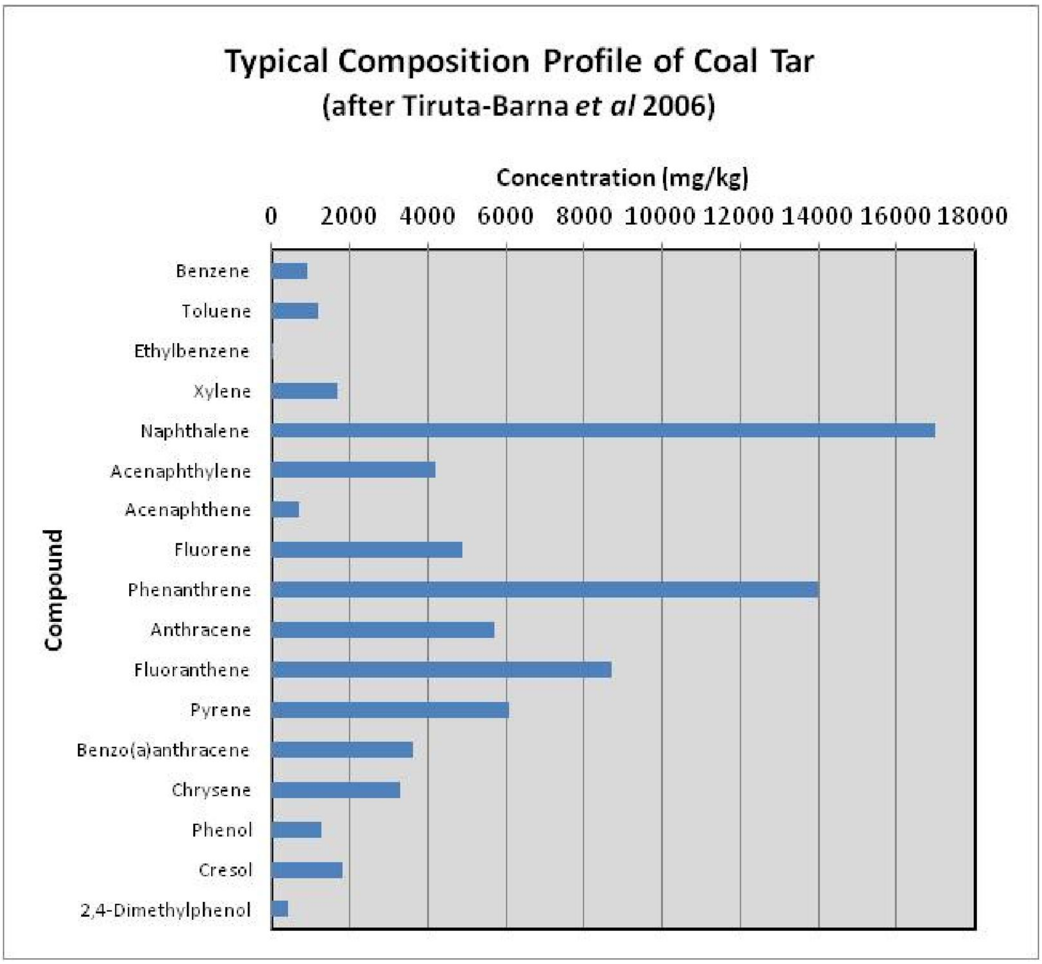


Figure 3.2: Typical MAH and PAH Profile of Coal Tar (after Tiruta-Barna *et al*, 2006)

Coulon *et al* (2009) analysed the PAH composition of coal tar from a former gas holder at an undisclosed location. The PAH profile is presented in Figure 3.3.

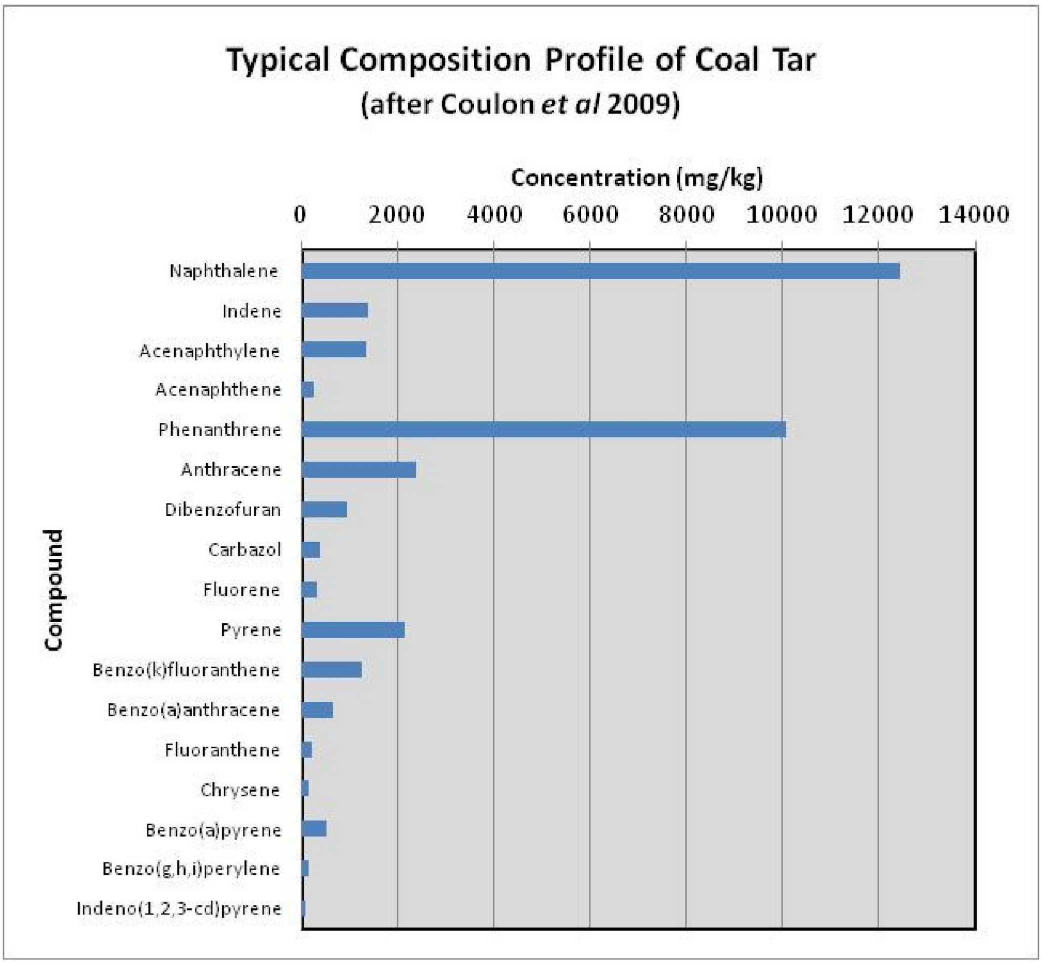


Figure 3.3: PAH Profile of Coal Tar (after Coulon *et al*, 2009)

The PAH profiles from the analyses detailed in Figures 3.1 to 3.3 reveal predominance of naphthalene and a significant contribution from phenanthrene. Likewise, naphthalene was found to be the dominant PAH and phenanthrene a major contributor in coal tar analyses by Birak *et al* (2009)

In ten of the samples considered by Brown *et al* (2006), the aromatic/aliphatic split revealed that the aromatic fractions constituted between 88-99% of the mass of the hydrocarbons. It was also concluded that ash and water content were most likely a consequence of processes subsequent to coal tar formation, such as on-site handling and environmental exposure.

In aromatic hydrocarbon molecules the carbon atoms are sp^2 hybridised resulting in three electrons in a plane oriented 120° apart, σ-bonding with the adjacent hydrogen or carbon atom. In addition, a fourth 2p electron orbits above and below this plane, π-bonding with adjacent 2p electrons. The resultant charge distribution has a significant effect on the physical properties of aromatic molecules, which are typically more soluble in water and less volatile than an aliphatic molecule with the same amount of carbon atoms. Aqueous solubility and vapour pressure data for the six carbon hydrocarbons n-hexane, and benzene, the fourteen carbon n-tetradecane and phenanthrene and the twenty carbon n-eicosane and benzo(a)pyrene are presented in Table 3.1. for comparison.

Table 3.1: Example of Physicochemical Data for Aliphatic and Aromatic Compounds

Determinant	Aqueous Solubility (mg/l)	Vapour Pressure (atm)
C6		
n-Hexane	9.5	1.99E -01
Benzene	1780	1.25 E-01
C14		
n-Tetradecane	0.0007	3.83 E-05
Phenanthrene	1.1	1.12 E-06
C20		
n-Eicosane	3.00 E-07	2.23 E-07
Benzo(a)pyrene	0.0038	2.10 E-10

(Data from Gustafson *et al* 1997)

Hetero-cyclic aromatic compounds contain a hetero-atom (nitrogen, sulphur or oxygen) in lieu of a carbon atom in the chemical structure. Birak *et al* (2009) quotes coal tar containing up to 560 mg/kg quinoline, 33 mg/kg acridine, 620 mg/kg carbazole and 3230 mg/kg dibenzothiophene.

Brown *et al* (2006) revealed that coal tar viscosities range from 12 cP (0.012 Pa.s) to 1.9×10^6 cP (1900 Pa.s) at 40°C. Tars predominated by high molecular weight compounds are more viscous than those predominated by low molecular weight compounds and weathering can deplete low molecular weight compounds by dissolution and volatilisation, leading to an increase in viscosity. Brown *et al* (2006) noted that the mean molecular weight of ten tar samples analysed covered a range from 316 g mole^{-1}– 3216 g mole^{-1}.

The Environment Agency (2003b) state that the density of creosote typically ranges between 1010 kg/m^3 and 1130 kg/m^3, depending on the amount and type of any carrier fluid, whilst the density of coal tar typically ranges from 1010 to 1100 kg/m^3. Coal tar and creosote are considered Dense Non-Aqueous Phase Liquids (DNAPL) on account of having a generally low aqueous solubility and a density greater than that of water.

3.1.1.5. Weathering of Coal Tar

Following the introduction of natural gas, town gas production declined. The majority of town gas works closed by the 1960s (DoE, 1995). Therefore, coal tar samples are almost exclusively encountered in environmental media at defunct sites and the tar has been in-situ for a number of decades. For example, the gas works at Study Site D was demolished before 1923 and the tar recovered in 2009 must, therefore, have been in the soil environment for at least 86 years. The tar is therefore subject to processes of weathering. Fresh samples of coal tar may still be obtained from contemporary metallurgic coking works. Coking is exclusively a high temperature carbonisation process and the resultant tar chemical signature should reflect the upper end of typical Manufactured Gas Plant operating temperatures.

Alshafie *et al* (2004) observed the phenomena of semi solid film formation at the interface between aged creosote and water (creosote is further detailed in Section 3.1.1.6). The films are believed to comprise asphaltenes, which contain polar functional groups, such as hydroxy, within their macromolecules. This allows them to interact with water, via hydrogen bonds, at the creosote/water interface, forming a film under quiescent conditions. The film serves to reduce the mass transfer of contaminants between the liquid creosote phase within the film and the surrounding aqueous phase. An example of such a film is shown in Figure 3.4.

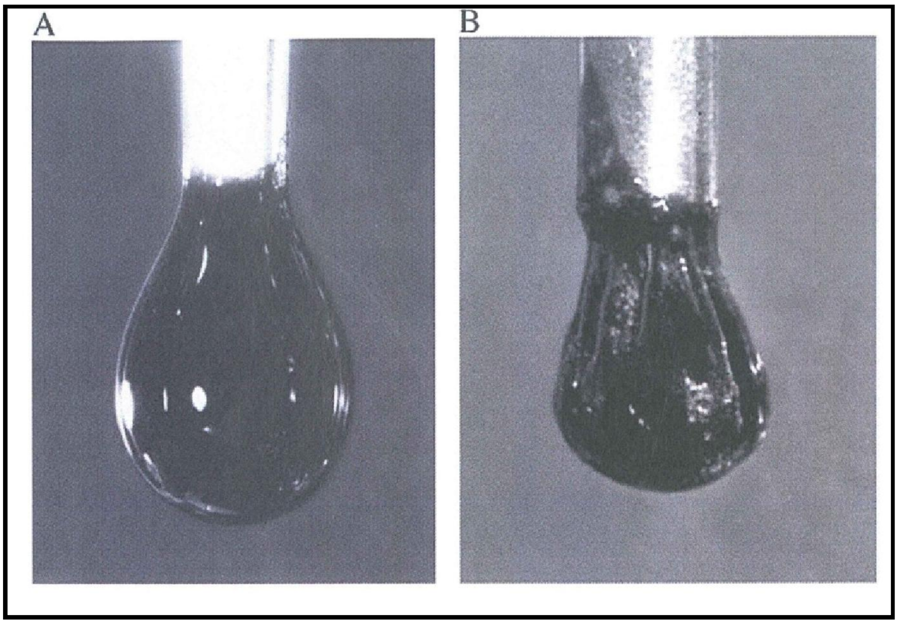


Figure 3.4: Pennant Drop Test proving presence of interfacial film. The drop is formed underwater (A) and several hours later a film is present at the interface when the creosote is withdrawn (B) (Alshafie *et al*, 2004)

Biological processes, which take place in the natural environment, can modify organic contaminant molecules at the spill location or during their transport in the subsurface. Such biological transformations, which involve enzymes as catalysts, frequently bring about extensive modification in the structure and toxicological properties of the contaminant (Suthersan, 1999).

For microorganisms to proliferate in the soil environment a source of carbon, nitrogen, phosphorus and sulphur and a variety of trace nutrients is required. Given the competition for carbon in soil environment, certain natural microbes have developed the ability to utilise synthetic molecules.

Microorganisms have developed a wide variety of respiration systems. In all cases of aerobic respiration, the electron acceptor is molecular oxygen. Anaerobic respiration uses an oxidised inorganic or organic compound other than oxygen as an electron acceptor. The substrates are oxidised to CO_2 or H_2O (Suthersan, 1999).

Biodegradation of PAHs depends on the complexity of the chemical structure and the extent of enzymatic adaption. In general, PAHs which contain two or three rings such as naphthalene, anthracene and phenanthrene are degraded at reasonable rates when O_2 is present. Compounds with four rings such as chrysene and pyrene and pentacyclic compounds, in contrast, are highly persistent and are considered recalcitrant (Suthersan, 1999). Metabolic pathways involving the addition of polar functional groups, such as –OH, can increase the aqueous solubility of aromatic substrates, leading to increased dissolution.

3.1.1.6. Manufacture and Chemistry of Creosote

Coal Tar Creosote is a distillation product of Coal Tar (ASTDR, 2002). Historically creosote represented the liquid fraction of coal tar and solvents were sometimes added to reduce the viscosity of the creosote.

Polycyclic Aromatic Hydrocarbons (PAHs) typically make up at least 75% of creosote (ASTDR 2002). Among the PAHs benzo(a)pyrene (BaP) is one of the most thoroughly investigated as it is classified as a potential human carcinogens (IARC, 1983) so it was chosen as a marker for creosote treatment and is also taken as a marker for the toxicity of creosote (Ikarashi *et al*. 2005).

In Europe, at present, there exists three types of preservatives according to European Standard EN13991 with the labels Grade A, Grade B and Grade C. However, the use of Grade A oils is currently forbidden according to guideline 2001/90/EC on account of having >50 mg/kg benzo(a)pyrene. According to EN 13991, Grade A and Grade B oils are characterised by the criteria detailed in Table 3.2.

Table 3.2: Technical Data of Wood Preservatives from Coal Tar (EN 13991)

Technical Data	**Unit**	**Method of Estimation**	**Grade A oils**	**Grade B oils**
Density at 20˚C	(g/ml)	BS 144 App. B	1.04 – 1.15	1.02 – 1.15
Water Content	(% w/w)	ISO 760	max. 1	max. 1
Crystallization Temperature	(˚C)	EN 13991 App. A	max. 23	max. 23
Water-extractable Phenols	(% w/w)	EN 1014-4	max.3	max.3
Insoluble Matter	(% w/w)	BS144 App. G	max. 0.4	max. 0.4
Boiling Range		EN 13991 App. B		
Distillate to 235˚C	(vol.-%)		max. 10	max. 20
Distillate to 300˚C	(vol.-%)		20 – 40	40 – 60
Distillate to 355˚C	(vol.-%)		55 - 75	min. 70
Benzo(a)pyrene	(ppm)	EN 1014-3	max. 500	max. 50
Flash Point Pensky Martens	(˚C)	EN ISO 2719	min. 61	min. 61

Adapted from (RUTGERS, 2003)

Grade B oils are currently used at study site E. The concentration of benzo(a)pyrene is greatly reduced in Grade B creosote as heavy distillates with a boiling temperature of >355˚C are not permitted to contribute more than 30% of the total volume of the oil.

Lesiatoi (2007) performed GCMS analysis on selected samples of creosote free-product used at study site E. A summary of the PAHs, phenols and heterocyclic compounds analysed is presented in Table 3.3.

Table 3.3: Summary of PAH and Phenol Analysis of Creosote

Determinant	Concentration (ppm)
Naphthalene	22,9246
Acenaphthylene	760
Acenaphthene	11,5692
Fluorene	50,636
Phenanthrene	153,630
Anthracene	16,746
Fluoranthene	86,951
Pyrene	40,692
Benzo(a)anthracene	235
Chrysene	114
Phenol	1,535
2-Methylphenol	1,060
2,3-Benzofuran	555
Quinoline	15,983
Indole	5,057
Dibenzofuran	96,642
Dibenzothiophene	31,062
7,8-Benzoquinoline	6,562
Acridine	6,331
Carbazole	8,224

Adapted from Lesiatoi (2007)

The analysed fresh creosote is dominated by naphthalene with a significant contribution from phenanthrene and acenaphthene. The absence of detectable quantities of higher molecular weight PAHs larger than benzo(a)anthracene is indicative of a secondary distillation step undertaken to reduce the concentration of benzo(a)pyrene below the 2001/90/EC guideline of 50 ppm.

The physicochemical properties of the numerous components of creosote and coal tar vary greatly with both relatively soluble and volatile components (such as phenol and naphthalene) and insoluble and non-volatile components (such as benzo(a)pyrene). This phenomena results in partitioning of the components within environmental media. The Environment Agency have published peer-reviewed physicochemical data for selected organic compounds including key components of creosote and coal tar. Selected physicochemical data is reproduced in Table 3.4.

Table 3.4: Summary of Physicochemical Properties of Selected Key Components of Coal Tar and Creosote

Determinant	Property	Value
Phenol	Aqueous Solubility (20˚ C)	84,000 mg l^{-1}
	Henrys Law Constant (25˚ C)	1.63 x 10^{-5} (Dimensionless)
	Log Water/Octanol Partition Coefficient (Log K_{ow})	1.47 (Dimensionless)
	Organic Carbon Partition Coefficient (K_{oc})	28.8 l kg^{-1}
Naphthalene	Aqueous Solubility (20˚ C)	31 mg l^{-1}
	Henrys Law Constant (25˚ C)	1.74 x 10-2 (Dimensionless)
	Log Water/Octanol Partition Coefficient (Log K_{ow})	3.37 (Dimensionless)
	Organic Carbon Partition Coefficient (K_{oc})	3.11 mg l^{-1}
Phenanthrene	Aqueous Solubility (20˚ C)	1.1 mg l^{-1}
	Henrys Law Constant (25˚ C)	1.31 x 10^{-3} (Dimensionless)
	Log Water/Octanol Partition Coefficient (Log K_{ow})	4.57 (Dimensionless)
	Organic Carbon Partition Coefficient (K_{oc})	4.36 mg l^{-1}
Benzo(a)pyrene	Aqueous Solubility (20˚ C)	0.0038 mg l^{-1}
	Henrys Law Constant (25˚ C)	1.86 x 10^{-5} (Dimensionless)
	Log Water/Octanol Partition Coefficient (Log K_{ow})	6.04 (Dimensionless)
	Organic Carbon Partition Coefficient (K_{oc})	6.01 mg l^{-1}

Adapted from EA 2003b.

A more extensive table of physicochemical properties for principal components of coal tar and creosote is presented in Annex A.

3.1.1.7. Environmental Fate of Coal Tar and Creosote

The coal tar and creosote spillages investigated in the current research have typically comprised two principal components, with a free-product (i.e. un-dissolved) zone at the source (i.e. shallow made ground) and within and beneath the alluvium. Down-gradient of the free-phase plume, contaminants are encountered in the aqueous phase.

3.1.1.7.1. Free-phase Transport

The relatively low solubility of many of the components of coal tar and creosote means that free-product plumes are often encountered beneath spillage sites a significant period after the spillage.

It often takes a long time for movement to cease following initial release into the subsurface because creosote is only slightly denser than water and has a relatively slow downward (gravity–driven) migration. The relatively high viscosity of creosote, with ranges between 20cP (0.020 Pa.s) and 50 cP (0.050 Pa.s), also facilitates long migration timescales. It is not uncommon to encounter sites where creosote DNAPL is still moving following its introduction to the subsurface as much as 50 or 60 years earlier (Environment Agency, 2003a). Coal tar is quoted as typically having a viscosity of between 20cP (0.020 Pa.s) to 100 cP (0.100 Pa.s) by the Environment Agency (2003a) whilst Birak *et al* (2009) quotes a dynamic viscosity range of 260 cP (0.260 Pa.s) to 18,000 cP (18 Pa.s) for coal tar samples, 9.1 cP (0.0091 Pa.s) to 21,000 cP (21 Pa.s) for water gas tars and 200 cP (0.2 Pa.s) to 660,000 cP (666 Pa.s) for oil-gas tars at 35˚ C. Traxler (1964) observed that rheological studies of coal tar at temperatures over 100˚ C revealed Newtonian behaviour although at lower temperatures and stresses it was anticipated that non-newtonian behaviour is likely to be observed.

Differing rates of NAPL migration behaviour has been identified above and below the phreatic level in soil. Jackson *et al* (undated) described the soil void space below the groundwater horizon as comprising a two-phase system of water-NAPL and above the groundwater (vadose zone) as comprising a three phase system of air-water-NAPL (i.e. air is absent from soil pore space below the groundwater table). Jackson *et al* (undated) identified that the three phase system had a lower residual NAPL saturation than the otherwise equivalent two-phase system below the groundwater table. Mercer and Cohen (1990) for example reported vadose zone NAPL saturations in the range of 10% to 20% and groundwater zone saturation in the range of 15% to 50%. Wilson *et al* (1990), using the LNAPL Soltrol-130, recorded saturations of 9.1% and 27.1% in the three-phase and two phase systems respectively.

The differing characteristics of the two and three phase systems are most notable where a water table is suppressed (such as pumped de-watering during remedial works or engineering works). Once dewatering occurs, NAPL will primarily be displacing air in which case the density difference will be far greater and the vertical migration of the NAPL will be facilitated (Jackson *et al* (undated)).

In NAPL contaminated porous media, it is important to understand the wetting behaviour of liquid phase (Birak *et al* 2009). Wetting behaviour arises from an interplay of adhesive forces between the selected liquid and the solid phase and cohesive forces within the liquid. Wettability can be expressed in terms of contact angle between the NAPL and solid media, such as a clean surface of geological material. Experimental determination of this angle may be performed in submersion to replicate the aforementioned two-phase system. Three contact angles can be measured; the advancing contact angle created during formation of the droplet in the experiment, the static contact angle which occurs once equilibrium is achieved, and the receding contact angle which occurs when the droplet is withdrawn. Bear (1972) describes water-wet materials as having contact angles below 90˚ and oil-wet materials as having a contact angle of greater than 90˚. In two phase, water-wet systems, residual NAPL exists primarily as discontinuous blobs within a single pore or several adjacent pore bodies (Jackson *et al* (undated)). In water-wet systems water thus coats soil grains and can reduce the degree of intermolecular interaction between the oil contaminant and the soil.

There is evidence to suggest that wettability can be altered by pH. Zheng and Powers (1999) identified numerous polar functional groups within asphaltenes. Both acidic and basic functional groups are present. Drawing comparison with the heterocyclic nitrogen in quinoline, Zheng and Powers (1999) describe how, at low pH, the heterocyclic nitrogen in asphaltenes could accept a proton, thus becoming positively charged. Zheng *et al* (2001) presented a conceptual model for a quartz surface (a silicate mineral) which contained a net negative charge. Under neutral pH conditions the mineral surface achieves a stable film of water due to electrostatic attraction between the polar water molecule and the silanol group. The film of water is thus too stable to be displaced by interstitial NAPLs. However, as pH is reduced, a point is achieved where the protonation of basic functional groups created a sufficient net positive charge on the asphaltenes to breach the water film and contact the mineral surface. Once the water film is breached a mechanism of aggregation of the asphaltenes was proposed, leading to oil-wetting conditions. At high pH, acidic functional groups become deprotonated, leading to a net negative charge on the asphaltenes and thus repulsion between the mineral surface and the NAPL.

Zheng and Powers (1999) assessed the ‘strength’ of the basic functional groups by potentiometric titration, using a non-aqueous phase titration so that the solvent was miscible with the NAPL. The testing found creosote to contain more organic bases than coal tar and the basic functional groups were found to be ‘weak’ bases.

Generally, the residual NAPL will reside in the largest pores where capillary forces are smallest (Jackson *et al* (undated)). This fact will have a significant impact on the behaviour of the NAPLS observed in Severn Estuary Alluvium, where clay and silt dominated strata is penetrated by subordinate peat bands, often with a dilated structure, and fossil bio-pores. The soil structure of Severn Estuary Alluvium is discussed later in Section 5.

Birak and Miller (2009) detailed interfacial tension between coal tar and water at neutral pH of between 20 – 25 dynes cm^{-1} although noting that such data was limited and that coal tar may prove to be variable. Zheng and Powers (2003) note that the interfacial tension can be near zero at high pH due to a mechanism associated with the deprotonation of acidic functional groups.

The Environment Agency Remedial Target Worksheet Computer Model cannot model free-phase (i.e. un-dissolved) hydrocarbons.

3.1.1.7.2. Vapour Phase and Aqueous Phase Transport

Following the spillage of a hydrocarbon into the soil environment losses are made from the surface of the hydrocarbon plume by volatilisation and aqueous dissolution.

The following general trends in hydrocarbon behaviour have been observed by the Total Petroleum Hydrocarbon Criteria Working Group (Gustafson *et al*, Vol.3, 1997);

1. Solubility of a particular group of hydrocarbons decreases with an increase in molecular weight.

2. Volatility of a particular group of hydrocarbons, expressed as Henrys' Law Constant (i.e. partitioning between air and water), decreases with increased molecular weight.

For hydrocarbons the volatility can be expressed in terms of vapour pressure. The vapour pressure is a pressure at which, in a sealed system, the vapour phase is in equilibrium with the liquid phase. When a soil environment is not a sealed system, the vapour is lost to the atmosphere and equilibrium is not realised leading to further volatile losses. The greater the vapour pressure, the more volatile the substance (Fetter 1993).

For pure (i.e. single component) hydrocarbon spillages the solubility of that substance is expressed as aqueous solubility. Aqueous solubility expresses the mass of substance that will dissolve completely in a given volume of water (Environment Agency, 2003b). However, since coal tar and creosote comprise complex multi-component mixtures, the aqueous phase equilibrium concentration of any component can be calculated with a modification of Raoult's law. In accordance with Raoult's law, each component of coal tar and creosote exert a partial pressure related to the molar concentration of that component and its vapour pressure. This can be adapted to calculate the aqueous solubility of that substance.

Raoult's law relates the aqueous concentration of a compound, i ,at equilibrium, Ci_{aq} (mg/l) to its molar fraction, X_i, in the coal tar

$$Ci_{aq} = X_i (Ci_{sol}/FR_i) \qquad (3.1)$$

where Ci_{sol} is the aqueous solubility of the component i (mg/l) and FR_i is the solid/liquid reference fugacity ratio of component i (Brown *et al* 2006). Fugacity is an effective value used to relate the idealized behaviour assumed in the equation to real systems. Fugacity ratios are available in literature such as Mackay *et al* (1992).

The compounds in coal tar are too numerous to analyse and consider individually and consequently Brown *et al* (2006) considered the bulk properties of coal tar in relation to the mean molecular weight of the tar. Brown *et al* (2005) express the mole fraction of a selected component of coal tar, X_i, in terms of the mean molecular weight of the coal tar as follows;

$$X_i = C^{i}_{ct} (MW_{ct}/MW_i) \qquad (3.2)$$

where C^{i}_{ct} is the concentration of component i in the coal tar (g/g) and MW_i is the molecular weight of that component and MW_{ct} is the mean molecular weight of the coal tar (g $mole^{-1}$). Brown *et al* (2006) found this method to be effective in predicting equilibrium aqueous concentrations of phenanthrene and pyrene in coal tars with a mean molecular weight up to 1000 g $mole^{-1}$.

In addition to the relatively low solubility of the creosote and coal tar, the phenomena of skin formation around coal tar blobs has been investigated by Alshafie *et al* (2004) (See Section 3.1.1.5). The skin forms at the DNAPL/water interface when long-chain contaminants with hydrophilic functional groups are drawn to the interface. The skin serves to reduce the mass transfer of components of the coal tar into the aqueous phase. As a consequence, under quiescent conditions, less of the components of coal tar and creosote may enter solution than the physicochemical data would suggest.

Volatile losses of hydrocarbons in aqueous phase are expressed by Henry’s law. Henrys law states “there is a linear relationship between the partial pressure of a gas above a liquid and the mole fraction of the gas dissolved in liquid” (Environment Agency, 2003b). Coulon *et al* (2009) recognised that the weathering process is hampered when tar is located within a sealed environment, such as gas holders, since volatile and soluble components cannot escape.

The physicochemical properties of a coal tar in the environment should not be considered constant. Over time many of these (viscous NAPLs) have become more viscous through the dissolution of their low molecular weight components (Jackson *et al*, undated). Low Molecular Weight Compounds typically have the highest vapour pressure and aqueous solubility (see Annex A).

Partitioning of the components of creosote/coal tar results in varying transport rates and mechanisms for its components. The Environment Agency Hydrological Risk Assessment worksheet considers contaminants on an individual basis and contaminant flow is calculated for a mechanism akin to reverse-phase chromatography, with contaminants being retarded relative to groundwater flow by interaction with a stationary phase comprising soil organic matter (see Section 2).

The octanol-water partition coefficient (K_{ow}) has been defined as "a measure of the degree to which an organic substance will preferentially dissolve in water or an organic solvent". It is experimentally derived from a substance by mixing it in equal amounts of water and octanol (Environment Agency 2003b). K_{ow} is usually expressed as a logarithm (i.e. log K_{ow}).

Hydrocarbons such as PAH have a characteristic high log K_{ow} value indicating a low aqueous solubility (i.e. PAH is hydrophobic).

Hydrophobic hydrocarbons in aqueous phase are attracted to soil organic carbon. The organic carbon partition coefficient (K_{oc}) expresses the tendency of a compound to be adsorbed onto the organic carbon within the soil i.e. partitioning of the solute between soil water (l) and organic carbon (kg) (Environment Agency, 2003b).

However, the behaviour of similar compounds in a mixture with water will be different to the behaviour of those compounds in a simple binary mixture of just one compound and water. For example, the effective solubility of a compound is a function of both its solubility and molar fraction within the complex mixture. As a consequence a decrease in the concentration of a highly soluble component may lead to an increase in the relative solubility of a less soluble component since these remaining substances will contribute a greater partial pressure as the more volatile low molecular weight compounds are lost.

Contaminants in the soil environment partition into several compartment (soil organic matter, air filled voids, water filled voids). It is possible to predict the relative distribution of a contaminant into each compartment under equilibrium conditions. This is referred to as Equilibrium Partitioning Theory (EPT).

The relative distribution of organic contaminant between porewater and sediment organic carbon can be predicted on the basis of organic carbon-water partition coefficients (K_{oc}) (USEPA, 2006). Likewise, the distribution between water and air is predicted by the Henry's Law Constant and partitioning between water and octanol is predicted by the octanol-water partition coefficient (K_{ow}).

The propensity of a contaminant to occupy the various compartments can be displayed graphically on a Partitioning Triangle (Figure 3.5).

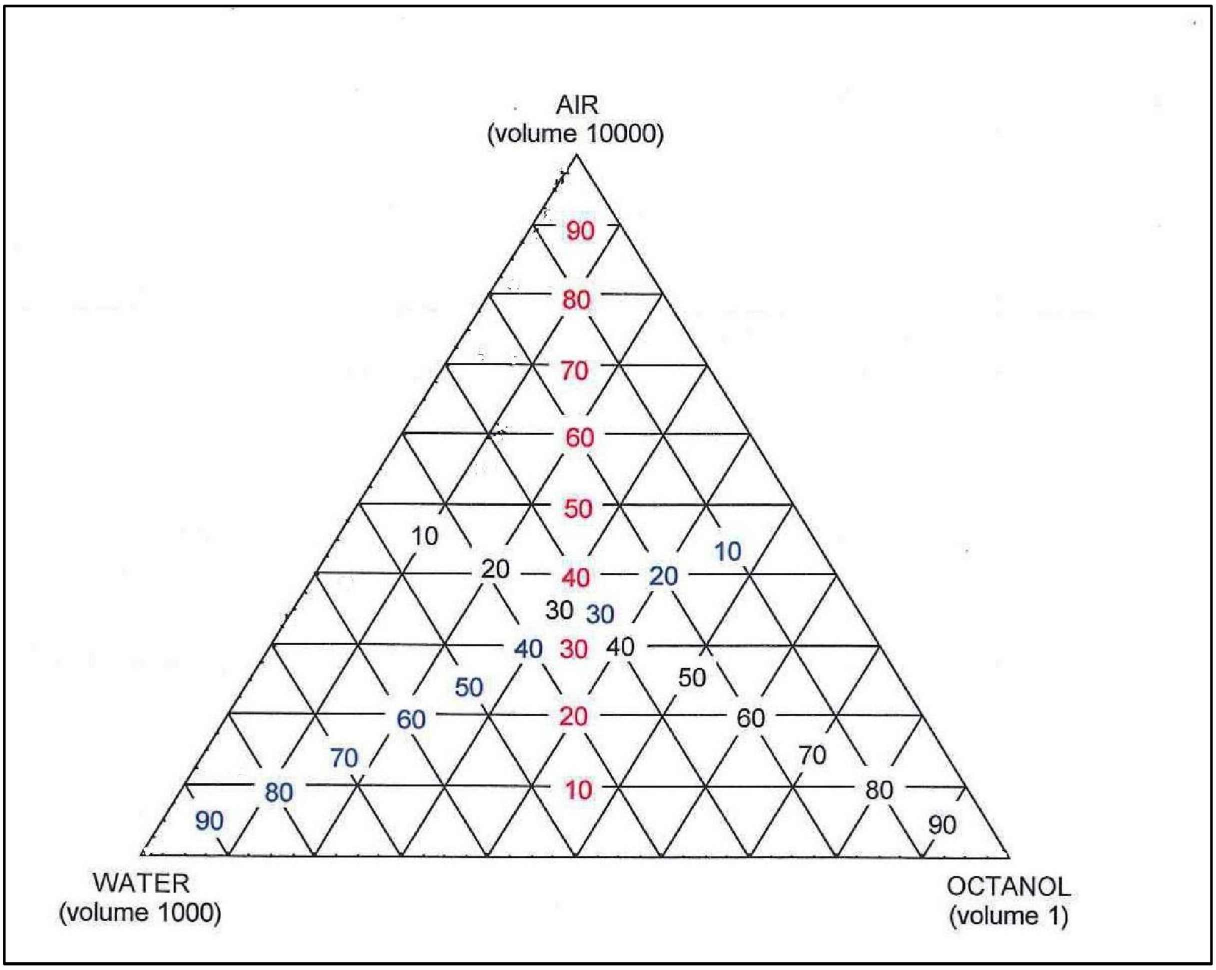


Figure 3.5. Partitioning Triangle (adapted from EA, 2003)

For example, phenol is characterised by a high Aqueous solubility and will reside near the 100% water compartment in the bottom left of the triangle. Benzene is characterised by high vapour pressure and high Henry's Law Constant and will therefore reside near the 100% air compartment at the apex of the triangle. High molecular weight PAHs are hydrophobic with a low aqueous solubility and low vapour pressure and low Henrys' Law constant and will, therefore, reside near the 100% octanol department, in the bottom right of the triangle.

If the DNAPL of interest contains a co-solvent, such as a low molecular weight alcohol, the presence of the co-solvent may invalidate the use of Raoult's law and result in an enhancement of the various components solubilities in groundwater. The co-solvent effect typically only occurs for relatively high co-solvent concentrations (for example 20% co-solvent or more by mass in DNAPL) and tends to be relatively short-lived (the co-solvent will deplete itself quickly from the DNAPL at an early time)(Environment Agency, 2003a).

Laboratory scale column experiments (e.g. Broholm *et al*, 1999) have identified differing transport rates for creosote components in soil. Broholm, using 25 creosote components, observed breakthroughs in his column experiment in the following order, benzene = pyrrole = toluene = o-xylene = p-xylene = ethylbenzene = phenol = benzothiophene = benzofuran < naphthalene < 1-methylpyrrole < 1-methylnaphthalene = indole = o-cresol = quinoline < 3,5-dimethylphenol = 2,4-dimethylphenol < acridine < carbazole < 2-methylquinoline < fluorine < dibenzofuran < phenanthrene = dibenzothiophene. Interestingly, this order could not have been predicted from physicochemical characteristic, such as K_{ow}. Broholm *et al* (1999) found that the polar NSO compound (i.e. organic compounds containing nitrogen, sulphur or oxygen atoms), BTEX and phenols were more likely to migrate through fractured clay than PAHs.

Field observations of plumes have identified variations in the recalcitrance of the components of coal tar resulting in varying degradation rates and changes in the relative composition along plumes. For example, Zamfirescu (2001) observed half-life distances within a coal tar plume (i.e. down gradient of the source) of 20m for benzene compared with 122m for anthracene and 303m for dibenzofuran. Anthracene was seen to degrade within the first 50m and stay at a constant concentration thereafter.

The environmental half-lives of individual contaminants in dissolved phase within groundwater are presented in Environmental Degradation Rates (Howard 1991). The published half lives of selected coal tar contaminants under aerobic and anaerobic conditions are summarised in Table 3.5.

Table 3.5. Published Groundwater Half Lives

Determinant	**Environmental Half life (Groundwater)**
Naphthalene	1 day – 258 days
Phenanthrene	32 days – 1.10 yrs
Benzo(a)pyrene	114 days – 2.90 yrs
Phenol	12 hrs – 7 days

Adapted from Howard (1991).

However, beneath the study sites these compounds are usually encountered as part of a multi-component mixture and initially as a free-phase hydrocarbon. Hatheway (2002) states that these (coal) tar residues are highly resistant to natural degradation or attenuation in the environment and their lives, therefore, are measured in geological time.

Modelling the flow of coal tar and creosote, therefore, presents a number of problems since the initial composition of the contaminant will vary between sites and even within a site, and the relative composition of the contaminant will also vary with transport and time. Initial modelling needs to account for the flow of a free-phase plume, which are typically tens of meters in scale, whilst down-gradient of this, dissolved phase flow needs to be considered.

3.1.1.8. Chemical Test Data from Terra Firma Wales Ltd

Terra Firma Wales Ltd provided chemical test data from analyses performed on environmental media from the study sites detailed in Section 2.

During the investigation of the study sites Terra Firma Wales Ltd typically analysed samples for PAH, phenolic compounds and, occasionally, BTEX compounds (Benzene, Toluene, Ethylbenzene and Xylene). Terra Firma Wales Ltd submitted environmental media to commercial laboratories for analysis (STL Midlands Ltd or Derwentside Environmental Testing Services Limited). At the investigated sites, coal tar was usually combined with environmental media including natural soils, made ground and groundwater either through spillage or disposal during operation or subsequent spillage or mixing during post operation demolition and/or remediation. The coal tar has, therefore, been diluted by the media although the relative concentrations of the constituents can still be considered.

Selected samples are discussed in this Section and detailed in Figure 3.6. Due to confidentiality issues with these development sites, they are identified as Site A to Site D.

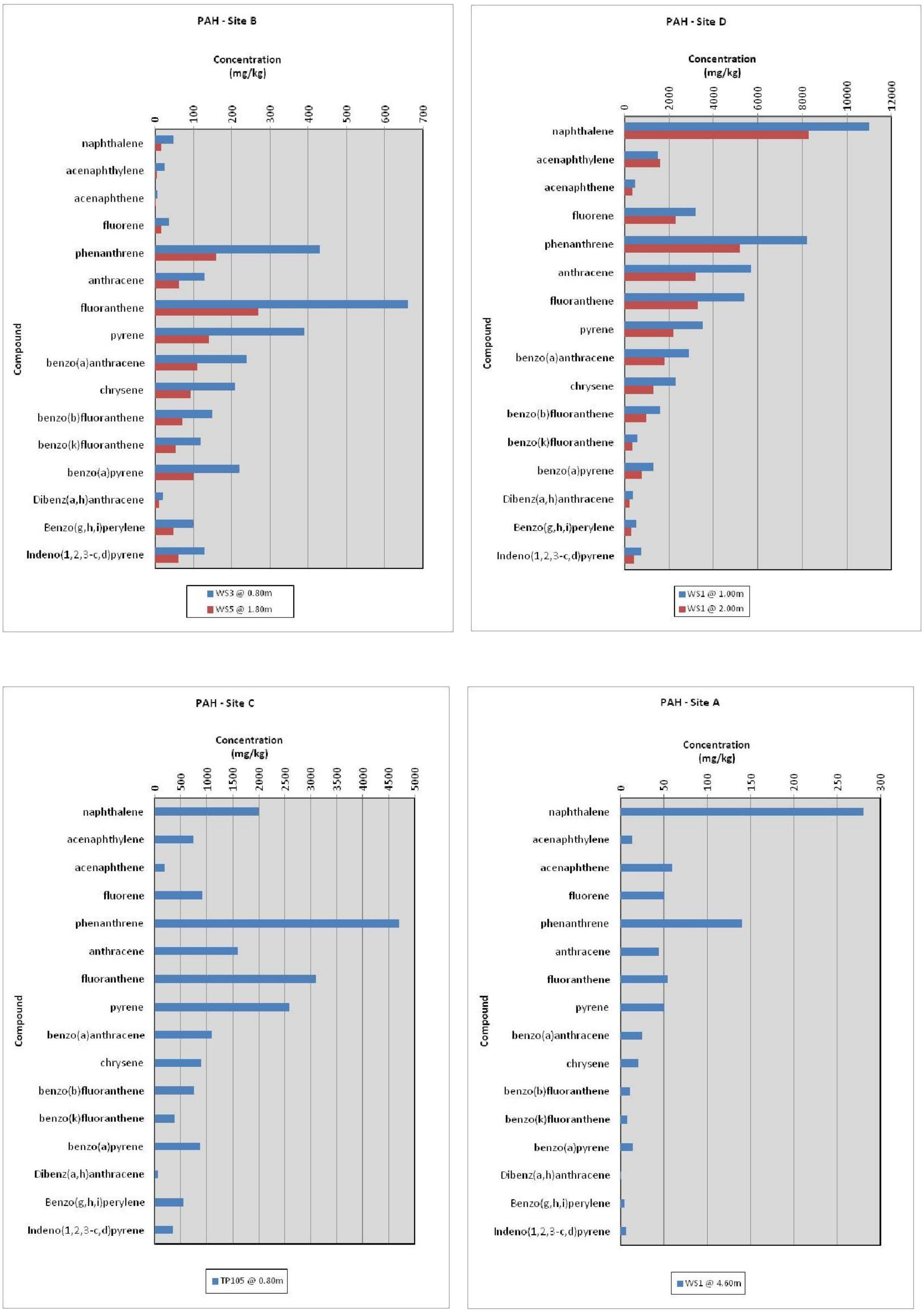
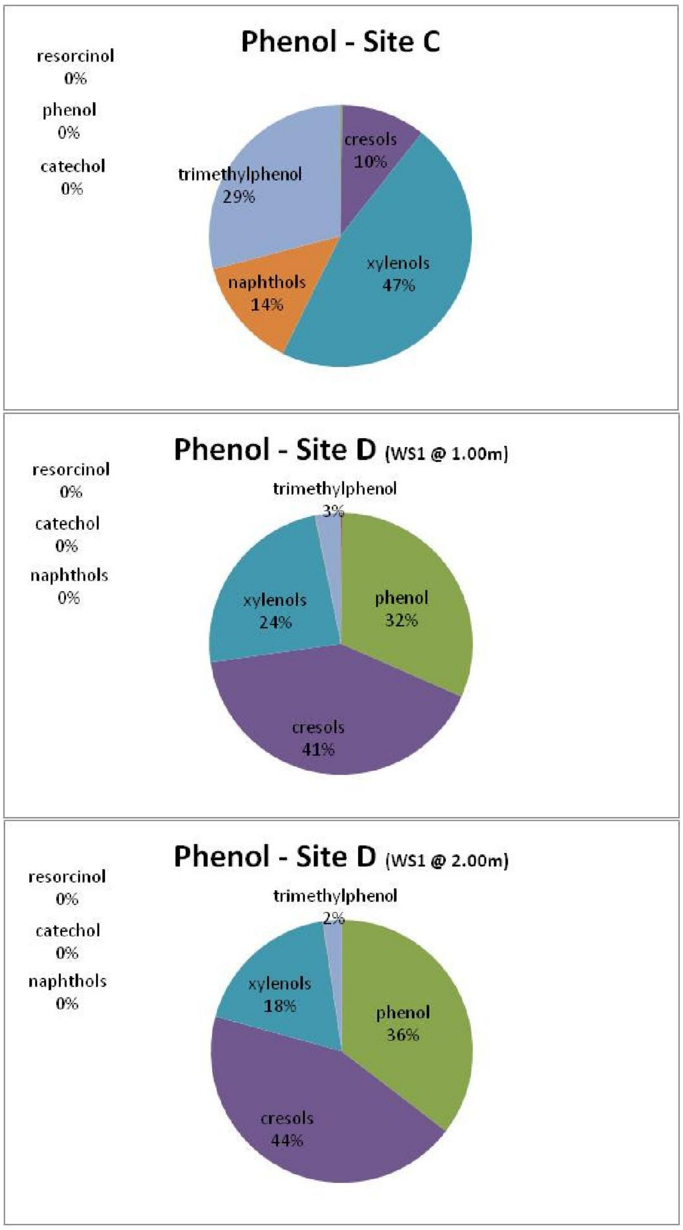


Figure 3.6: Profile of the EPA 16 Polycyclic Aromatic Hydrocarbon concentrations in heavily contaminated soils from four former Manufactured Gas Plant Sites in the UK. (Data courtesy of Terra Firma Wales Ltd).

It is apparent from Figure 3.6 that the PAH contamination profiles provided by Terra Firma Wales Ltd are consistent with those from other Manufactured Gas Plant located in the UK and Worldwide as detailed in Section 3.1.1.4. A significant contribution from phenanthrene is observed at all of the sites considered. Naphthalene is also generally significant although its lesser contribution at study site B may be attributed to weathering and volatile loss (naphthalene is the most volatile and soluble PAH and is thus less environmentally recalcitrant). Higher molecular weight polyaromatic hydrocarbons are seen to make a less significant contribution, although the analysis is limited to six-ring PAHs.

Terra Firma Wales Ltd undertook speciated Phenol analysis on three coal tar samples. The relative proportions of the phenol species are presented in Figure 3.7.



Site	SITE C	SITE D	
Sample I.D.	TP103 @ 1.00m	WS1 @ 1.00m	WS1 @ 2.00m
	Soil Concentration (mg/kg)		
catechol	0	0.21	0
resorcinol	0	2.6	1.1
phenol	0.63	680	790
cresols	29	890	980
xylenols	130	520	410
naphthols	38	1.4	1.4
trimethylphenol	81	68	51

Figure 3.7. Relative composition of ‘Total Phenol’ from three samples of coal tar from three sites in the UK. (Data courtesy of Terra Firma Wales Ltd)

The analysis undertaken by Terra Firma Wales Ltd has revealed that the 'Total Phenol' composition is dominated by substituted phenols, with mono phenol (C_6H_5-OH) providing a limited contribution (i.e. 36% to below analytical detection limit) of the total concentration. It is typical practice to perform groundwater risk assessments using the recorded concentration of 'Total Phenol' and modelling this concentration using the physiochemical parameters for mono phenol. This, however, could prove to be very misleading as the physicochemical properties of the phenol species vary significantly and each component will, therefore, have a different propensity to reside in the solid (organic carbon) and aqueous phases of the environment. For example, with reference to the International Programme on Chemical Safety (IPCS) web-based database, operated by the World Health Organisation, the phenol species are ordered as follows in relation to solubility; 3,5-xylenol (5 g/L), 2,4-xylenol (7.9 g/L), naphthols (6 – 8 g/L), p-cresol (19 g/L), m-cresool (24 g/L), o-cresol (25 g/L), mono-phenol (84 g/L), catechol (430 g/L), resorcinol (1400 g/L).

Whilst the above discussion has reviewed data on key determinants of coal tar used by Geotechnical and Geo-Environmental Consultants for Groundwater Risk Assessment, Birak *et al* (2009) point out that, based on distillation data, coal tar is composed mostly of compounds with a boiling point above 355˚ C. Brown *et al* (2006) recorded mean molecular weight for the eleven tars analysed ranging from 316 g $mole^{-1}$ to 3213 g $mole^{-1}$. The EPA 16 PAH analysis suite analyses species with a molecular weight up to 278.36 g $mole^{-1}$ (Dibenzo(ah)anthracene). It is therefore apparent that a large percentage of the components of coal tar are not routinely examined during a typical ground investigation. These higher molecular weight compounds represent the most recalcitrant portion of the tar as they are the least volatile, the least soluble and most viscous components.

The mean molecular weight of a tar affects the aqueous solubility of species contained therein. At present it is common practice to model contaminants individually, without consideration of their place within a complex mixture.

3.2. Contaminant Pathway

3.2.1. Introduction

Liquid coal tar spillages at former Manufactured Gas Plant and Creosote Plant occur at the surface (i.e. spillage, leakage of above ground plant) or at relatively shallow depth (for example leakage from buried pipes, tar holders, tanks or defunct gasometer bases). Following release into the environment a portion of the spillage will partition into the vapour phase and a portion may also solidify. The remaining tar will migrate as un-dissolved tar (free-product) driven by gravity, or partition into the aqueous phase and migrate through the sub-surface dissolved in groundwater flow.

The flow of coal tar and creosote in the sub-surface is resisted by the superficial (unconsolidated) and solid (consolidated) geology beneath the spillage site. The permeability of a soil is an indication of its resistance to groundwater flow, with a low value of permeability (reported in ms^{-1}) indicating a high resistance to groundwater flow. Low permeability media has a slow rate of groundwater transition. Groundwater flow will preferentially follow paths of least resistance. In addition the organic content of a soil will retard the progress of organic contaminants as they will preferentially partition into the soil organic phase.

Factors which oppose the flow of contaminants in the soil environment prolong the transition period between the spillage and sensitive receptors in the vicinity of the spillage. The geological sequence and physical characteristics of the geological media, along with groundwater conditions, dictate the rate of contaminant migration.

3.2.2. Superficial Geology

A mantle of made ground is encountered in industrialised areas around the Severn Estuary. The made ground is necessary to make the surface of the alluvium trafficable. Made ground material is highly variable containing remnants of natural materials and anthropogenic fragments (brick, ash, concrete, timber) and does not, therefore, lend itself to generalised description. Alluvium lies beneath the made ground.

Alluvium is defined as “the general term for detrital deposits made by rivers or streams or found on alluvial fans, flood plains etc. It does not include subaqueous sediment of lakes and seas” (Lapidus, 1990).

The superficial alluvium deposits surrounding the Severn Estuary are detailed on three published 1:50,000 scale Geological Maps, British Geological Survey (BGS) Sheets 263 (1986, Cardiff), 249 (1975, Newport) and 279 (1980, Weston Super Mare). These maps date the deposits as Pleistocene (i.e. deposited in the last 2 million years (Ma), see Jones and Keen, 1993) to recent (i.e. geologically contemporary). The extent of these deposits around the Severn Estuary is displayed in Figure 3.8.

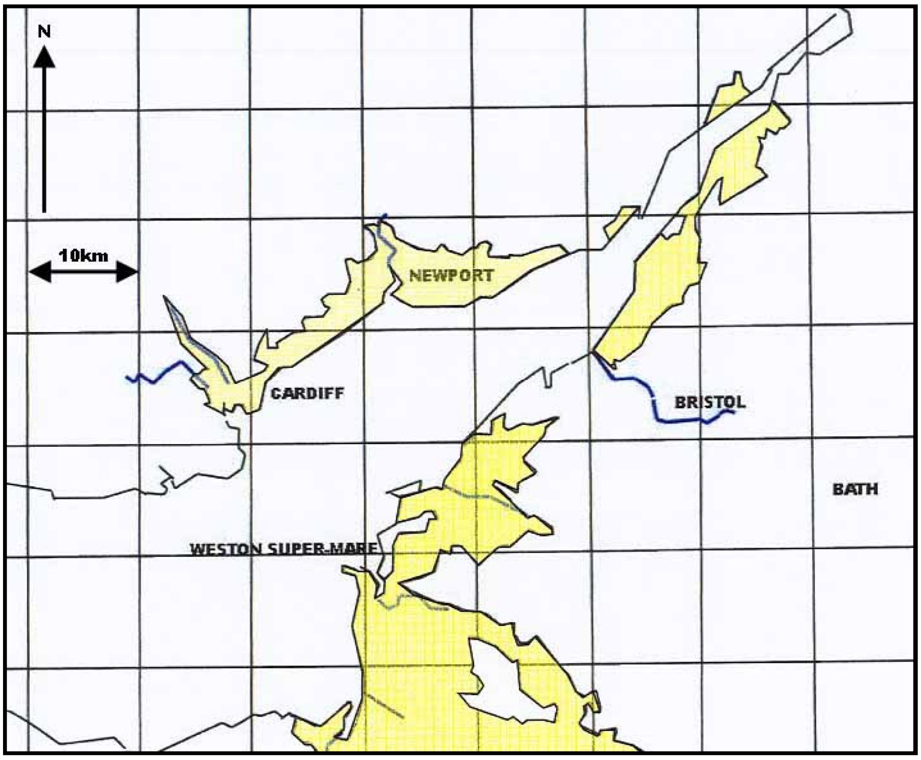


Figure 3.8: Extent of Severn Estuary Alluvium (adapted from BGS Survey Maps)

The Geological Memoir for the Newport Geological Sheet (Squirrell *et al*, 1969) indicates that the coastal flats of the Bristol Channel are covered by alluvium comprising mud (i.e. clay) and silt, deposited during post-glacial sea transgressions, with peat deposits representing halts in the transgression. The Geological Memoir for the Bristol region (Kellaway and Welch, 1993) suggests that above (i.e. eastwards of) a notional line between Newport and Western Super Mare, estuarine alluvium was deposited during the Flandrian (10,000 Before Present (BP) to present), commencing at a time of low sea level c. 9,000 years BP followed by a marine transgression.

The rate of marine transgression over the last 9000 years (radiocarbon years) in the Severn Estuary is summarised in Allen (1990), based on data from Shennan (1983) and Allen and Rae (1988). It is apparent from Shennan (1983) that the rate of sea-level rise decreased around 6000 yrs ago. Allen and Rae (1988) suggested that the relative sea level rise in the estuary since Roman Times (ca. A.D. 150) could be in the region of 1.6m to 1.7m, with a current rate of sea level rise of a few millimetres a year. Sea level rise is presented in Figure 3.9.

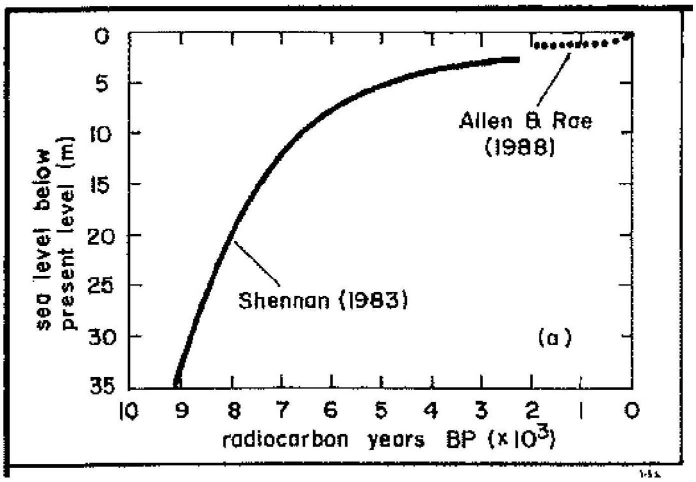


Figure 3.9. Sea level over the last 9000 yrs relative to present day sea level (from Allen, 1990)

In accordance with BS:5930 (1999) silt lies in the particle size range 0.06mm to 0.002mm diameter and clay comprises particles of <0.002mm diameter. The dominance of ‘fine’ soil particles in the deposits is indicative of a low-energy depositional environment. Clay and silt soils have a low aqueous permeability since the fine particles result in small pore spaces between the soil grains and, in addition, the electrostatic surface of clay can attract water, slowing its progress. Barnes (2010) quotes typical permeability values for silty to clay soils of 10^{-8} ms^{-1} to less than 10^{-9} ms^{-1}. Thick deposits of low permeability soil acts as an effective barriers for contaminant flow between contaminant spillages at the surface and aquifers beneath these impermeable soils as the flow of liquid contaminants and dissolved contaminants is reduced to an extremely low rate.

In their study of the Severn Levels, located between Cardiff and the River Wye, Walker *et al* (1998), describe the peat bands within the alluvium as terrestrial and semi terrestrial, resulting from changes in the relationship between land and sea during the middle Flandrian. Walker *et al* (1998) references similar observations in the alluvium around South Wales and the southern Severn Estuary. Allen and Fulford (1986) conclude that peat deposits represent episodes of marine regression followed by an episode of fen, carr and raised bog development, perhaps with minor marine fluctuations, which was, in turn, succeeded by a further phase of estuarine sedimentation.

The basal deposits of the alluvium comprise sandy gravel deposits (i.e. clasts in excess of 0.06mm diameter) indicative of a higher energy depositional environment. At Weston-super-Mare the basal gravel was very clayey.

3.2.3. Solid Geology

The solid geology underlying the alluvium around the Severn Estuary in the vicinity of the former industrialised areas, Cardiff, Newport, Portishead and Weston Super Mare are detailed in the three Geological Maps for the region (British Geological Survey (BGS) Sheets 263 (1986, Cardiff), 249 (1975, Newport) and 279 (1980, Weston Super Mare))

The 1:50,000 Scale Geological Map for Newport (BGS Sheet 249, Solid Edition, 1975), shows the site be underlain by rocks of the Keuper Marl (now known as the Mercia Mudstone Group) of Triassic Age.

The 1:50,000 Scale Geological Map for Cardiff (BGS Sheet 263, Solid Edition, 1986) shows the site to be underlain by rocks of the Mercia Mudstone Group.

The 1:50,000 Scale Geological Map for Weston-super-Mare (BGS Sheet 279, Solid and Drift Edition, 1980) shows Weston-super Mare and Portishead to be underlain by the Keuper Marl (i.e. the Mercia Mudstone Group).

The British Geological Survey Lexicon of Named Rock Units website describes the Mercia Mudstone Group as “Dominantly red, less commonly green-grey, mudstones and subordinate siltstones with thick halite-bearing units in some basinal areas. Thin beds of gypsum/anhydrite widespread; sandstones are also present”.

During drilling at the study sites the Mercia Mudstone, where encountered, comprised a red-brown mudstone which weathered to a stiff to very stiff clay near its boundary with the overlying alluvium.

It is the authors’ experience that environmental regulatory authorities generally accept the interpretation of the Severn Estuary alluvial silt/clay as an effective barrier to the migration of liquid and dissolved contaminants on account of its assumed low permeability based on its clast size.

3.2.4. Hydrogeology of Solid Geology

The superficial deposits at the study sites are underlain by rocks of the Mercia Mudstone Group. The 1:100,000 scale Groundwater Vulnerability Map for the region (Sheet 36, Environment Agency 1996) classifies this geology as a non-aquifer. The Environment Agency define a non-aquifer as being negligibly permeable, although they do state that groundwater flow through such rocks, although imperceptible, does take place and needs to be considered when assessing the risk associated with persistent pollutants.

In April 2010 the Environment Agency revised its Groundwater Vulnerability designations to align the data with other aspects of the Water Framework Directive. Under the revised designations the solid geology beneath the four Severn Estuary sites is classified as ‘Secondary B’ which is defined as “Predominantly lower permeability layers which may store and yield limited amounts of groundwater due to localised features such as fissures, thin permeable horizons and weathering” (Environment Agency 2010).

3.2.5. Geotechnical Parameters

3.2.5.1. Particle Size Distribution

A natural soil is composed of mineral clasts. The composition of a soil in terms of the size of clasts contained therein is referred to as Particle Size Distribution (PSD). PSD influences the rate at which liquids flow through a soil media as the size of pore space between clasts is dictated by the size of the clasts, with small clasts having small pore spaces, and consequently having a low permeability.

In saturated fine grained soils, the resistance to flow leads to the phenomena of effective stress, whereby applied stress initially leads to an increase in pore water pressure which subsequently decreases as water slowly dissipates, leading to the stress being slowly transferred onto the soil skeleton.

In accordance with BS: 5930 (1999) soil particles less than 2 µm are termed clay. Individual clay minerals can combine in soils to form units with a net negative charge. Cations can counter this charge. The polar water molecule can also be attracted to the charged surface of clay. The electrostatic interactions of clay minerals lead to cohesion.

3.2.5.2. Atterberg Limits

The resistance to deformation of soil containing a significant portion of clasts less than 425 µm can be influenced by the moisture content of that soil. As the moisture content increases the interactions between soil particles are reduced, and the shear strength of the soil becomes reduced.

Plasticity, in the case of clay mineral systems, is defined as the property of a material which allows it to be repeatedly deformed without rupture when acted upon by a force sufficient to cause deformation and which allows it to be retain its shape after the applied force has been removed (Andrade *et al*, 2011).

The minimum amount of water necessary to make a clay plastic is commonly called the “plastic limit”. As water content increases the clay becomes a paste, in which the yield strength steadily diminishes and can no longer maintain a moulded shape. The moisture content which corresponds to this state is called “liquid limit” (Andrade *et al*, 2001). These parameters are collectively referred to as Atterberg Limits.

3.2.5.3. Shear Strength

The shear strength of the soil is the magnitude of shear stress that can be sustained by that soil. Shear strength influences a soils resistance to deformation under an applied stress, and is therefore an indication of a soils ability to resist deformation during sampling and subsequent handling.

Direct values for soil shear strength can be derived from soil shear box or shear vane testing, whereby apparatus is used to apply a stress until failure is achieved. During borehole drilling in-situ Standard Penetration Tests (SPT) can give an indication of the soils shear strength.

SPT results are reported in terms of the number of blows from a drop weight required to drive a test cone 300mm through the soil (known as ‘N’). An indication of the relationship between the SPT ‘N’ value and the unconfined compressive strength is provided by Terzaghi and Peck (1967) as detailed in Table 3.6.

Table 3.6. Approximate Correlation between SPT ‘N’ Values and Unconfined Compressive Strength

SPT ‘N’ Value	**Unconfined Compressive Strength (kPa)**
<2	<25
2 – 4	25 – 50
4 – 8	50 – 100
8 – 15	100 – 200
15 – 30	200 – 400
>30	>400

Adapted from Terzaghi and Peck (1967)

3.2.6. Contaminant Partitioning to Soil Organic Carbon

3.2.6.1. Introduction

As detailed in Section 3.1, hydrophobic hydrocarbon contaminants such as PAH partition into organic solvents as indicated by their high log K_{ow} value. PAH dissolved in groundwater will adsorb onto soil organic matter. The amount of organic carbon contained within a soil is reported as Fraction of Organic Carbon (F_{oc}). A soil with a high F_{oc} therefore has a greater amount of sorption sites for the hydrophobic contaminant.

During the operation of the v.3.1 Worksheet the F_{oc} value is limited to 2.0% or less. Analysis of alluvial soils has been undertaken for this research and subordinate organic rich horizons (peat) were identified with organic carbon fractions in excess of 30% (see Section 5.5).

F_{oc} of a soil is determined by combustion analysis, whereby the soil is combusted at 900° C and the amount of CO_2 generated is measured.

3.2.6.2. Contaminant Sorption

The relationship between hydrophobic contaminant sorption and soil organic carbon has long been established. Karickhoff (1981) states cases of the phenomenon being detailed as far back as 1962 (i.e. Goring, 1962).

Equilibrium sorption is described graphically by a sorption isotherm, which is a plot of pollutant concentration in the sorbed phase (denoted S) versus pollutant concentration in solution at equilibrium (denoted C_e). Sorption isotherms are typically measured at constant temperature and at constant sorbent concentration (Karickhoff, 1981). Karickhoff identified that if the equilibrium aqueous phase pollutant concentration is kept below 10^{-5}M or below one half of the solute water solubility (whichever is lower), sorption isotherms to natural sediment were linear.

Karickhoff (1981) describes how batch experiments were performed on a number of sediment and soil samples from across the USA with greatly varying properties in relation to such parameters as clay mineral content and cation exchange capacity. In the test samples detailed, clay contents ranged from 6.8% to 69.1%, silt contents ranged from 13.6% to 71.4%, Cation Exchange Capacities ranged from 3.7 meq/100g to 33.0 meq/100g and organic carbon contents ranged from 0.11% to 2.38%. Despite the variance in soil properties, when sorption of phenanthrene and pyrene was considered solely in relation to organic carbon content, variations in the organic carbon partition coefficient, K_{oc}, were seen to be less than two-fold.

Similar behaviour was observed by Hasset *et al* (1980) using aromatic and heterocyclic hydrocarbons.

Lou *et al* (2008) also considered the effects of different clay minerals and organic carbon contents to evaluate the contribution of each soil fraction to the sorption of phenanthrene. The results demonstrated that Dissolved Organic Carbon in the soil impeded phenanthrene sorption through binding, while humins controlled sorption capacity (Lou *et al* 2008). It was also concluded that clay minerals could contribute significantly to phenanthrene sorption when organic carbon was low. The surface of some clay minerals have a net negative charge which has been shown to lead to wetting by water (See Section 3.2.7.).

It can safely be generalised that, for neutral organic compounds of limited solubility ($<10^{-3}$M) that are not susceptible to speciation changes or other special complex formation in the sediment/soil suspension of interest, sorption is “controlled” by organic carbon and is amenable to the K_{oc} format of quantification (Karickhoff 1981).

The term ‘fraction of organic carbon’ (f_{oc}) potentially encompasses a wide range of compounds, which are dependent on the origin and history of the soil in question. Soil organic carbon can have natural (i.e. plant debris, humic and fluvic gels, natural fats) or anthropogenic (insoluble coal tar fractions, coal, ash, pulverised fly ash etc), origins.

More recent work has revealed that in addition to the organic content the nature of the organic matter has a significant impact on sorption capacity and non-linearity. More than one type of organic matter, as well as the presence of organic particles, can be present in the soil sample (Karapanagioti *et al*, 1999).

Karapanagioti (1999) summarised that, to rationalise the results of sorption experiments, authors had adopted categories for organic matter. Grathwohl (1990), Huang and Weber (1997) considered the relationship between the Organic Carbon Partition Coefficient, K_{oc}, and O/H ratios in organic matter. Young and Weber (1995) and Xing and Pignatello (1997) divided organic matter with differing sorption properties into a) soft or rubbery and b) hard or glassy. Weber and Huang (1996) introduced the terms amorphous and condensed organic matter. Yang *et al* (2008) state that the amorphous ‘soft’ organic materials include gel-like humic and fluvic substances, as well as lignin which, in general, is regarded to be geologically young.

The Dual Reactive Domain Model (DRDM) was introduced by LeBoeuf and Weber (1997) and further validated by Huang *et al* (1997b). This model is predicted on a hypothesis that soil organic matter comprises two principal reactive domains; a highly amorphous, swollen or 'soft' domain and a condensed, tightly cross-linked or 'hard' domain. It is further hypothesized that the two different soil organic matter domains exhibit distinctly different sorption behaviours. Sorption by the highly amorphous domain appears to be linear and fast and to exhibit no solute-solute competition, whereas sorption by the condensed domain appears to be non-linear and slow and to exhibit solute-solute competition (Weber *et al,* 1998)

Weber *et al* (1998) suggest that substituted ionisable and polar organic compounds can be sequestered into soil matrices through covalent bonding or hydrogen bonding to soil organic matter and/or specific sorption on external surfaces and on the interlayer surfaces of clay minerals leading to sorption and desorption hysteresis (i.e. the recalcitrance of some fraction of sorbed solute to desorb readily to the phase from which it was removed).

The phenomenon of sorption hysteresis is also apparent in non-polar organic compounds. Several authors have attempted to justify the phenomena by consideration of intra-particle and intra-aggregate diffusion models (e.g. Ball and Roberts, 1991; Weber *et al* 1991). However, Weber *et al* (1998) write; "Given the evidence of the relatively fast rates and, low capacities, and inaccessibility associated with sorption by mineral pore surfaces, diffusion into purely inorganic porous domains is not likely to contribute significantly to a rate related overall desorption hysteresis for soils and sediment".

Weber *et al* (1998) studied sorption isotherms for 12 soil samples with soil organic matter ranging from geologically young humic soil organic matter to diagenetically altered soil organic matter (kerogen). ^{13}C-Nuclear Magnetic Resonance testing revealed that the geologically younger soil organic matter contained aliphatic carbon, carbohydrate carbon, aromatic carbon and carboxylic carbon suggesting these soils were humic in character. The diagenetically altered soil organic matter contained only aliphatic and aromatic carbon and had a lower oxygen to carbon atomic ratio suggesting the soil organic matter was kerogen. It was observed that soils containing kerogen organic matter exhibited greater sorption-desorption hysteresis than those whose organic matter comprised humic acids.

Huang and Weber (1997c), referenced in Weber and Huang (1998) observed that during phenanthrene absoprtion experiments soils containing only humic organic matter (i.e. ‘soft’ soil organic matter) achieved sorption equilibrium within two to four weeks whereas shale and kerogen organic matter (i.e. ‘hard’ soil organic matter) required in excess of three months to achieve sorption equilibrium.

Bayard *et al* (2000) considered the influence of naturally occurring soil organic matter (SOM) and xenobiotic organic matter (XOM) on the sorption of naphthalene. Experiments were operated over relatively short periods of time (24 – 60 h) to assess rapid sorption phenomena (pseudo-equilibrium). Naphthalene sorption appeared proportional to the amount of coal tar added to the sand or soil, and a much higher affinity of naphthalene for XOM than SOM was observed (Bayard *et al*, 2000). In addition, sorption experiments were undertaken with naphthalene placed with other organic pollutants from coal tar such as phenanthrene or fluoranthene in solution or crystal form. The research concluded that the other pollutants did not compete significantly with naphthalene for soil sorption sites as the other pollutants were of such low solubilities in comparison to naphthalene.

Sorption of PAHs to carbonaceous materials in river floodplain soils was researched by Yang *et al* (2008). The carbonaceous materials category includes coal, black carbon (BC), charcoal and other condensed organic particles. Other authors had previously studied sorption to carbonaceous materials using pure reference materials but Yang *et al* used carbonaceous materials which have transported from a mining region to the floodplain soils by natural mechanisms and have thus aged naturally. Soils were pulverised and soil particles were separated in to light and heavy fractions (less than, and greater than 2 g cm^{-3}, respectively).

The light fraction of the samples was analysed by coal petrography and showed abundance of coal (vitrinite, fusinite, semi-fusinite) and other coal derived particles, such as coke. Most of them are vitrinite from sub-bituminous coal rank, coke, charcoal, fly ash and a relatively high amount of carbon-rich clayey matrices containing very small (few microns in size) coal and coal particles (Yang *et al*, 2008). Sorption experiments with original soil and their sub-fractions showed very high sorption capacity and distinct non-linearity associated with carbonaceous materials in the samples (Yang *et al*, 2008).

The sorption behaviour of black carbon has been researched by Koelmans *et al* (2006) and Cornelissen *et al* (2006). Black carbon (BC) is the product of weathering of graphitic carbon in rocks and of incomplete combustion of fossil fuels and vegetation (Koelmans *et al*, 2006). Incomplete combustion of fossil fuels leads to re-condensation reactions in the gas phase that produce highly aromatic globular structures in grape-like aggregates (Goldberg, 1985). Whilst black carbon has many anthropogenic sources, petrogenic BC has been identified in pre-industrial marine sediments (Mitra *et al*, 2002; Dickens *et al*, 2004). Researchers have identified that persistent organic pollutants, especially pollutants with a planar structure, have an extremely high affinity for black carbon. It surpasses the affinity of 'normal' sediment or soil organic matter with up to three orders of magnitude and the absolute height of BC-water distribution coefficients (K_{BC}) ranges up to 10^9 l/kg for native PAHs (Jonker and Koelmans, 2002). Koelmann *et al* (2006) reports that when subject to a high load of persistent organic pollutants the BC-water distribution coefficient is lowered, leading to non-linear isotherms. It is suggested that saturation of adsorption sites and variable site geometries and energies account for the non-linearity. In the literature two modes of Persistent Organic Pollution (POP) fixation are proposed for BC particles: a) physical occlusion inside restricted pores or between aromatic macrostructures during BC formation, and b) reversible adsorption on exterior and pore surfaces after BC formation (Koelmans *et al*, 2006).

Cornelissen *et al* (2006) considered the competitive nature of sorption between phenanthrene and native PAH and between phenanthrene and natural organic matter. The aim of the research was to account for the lower sorption capacity of BC in sediment compared to 'clean' BC. It was concluded that native PAH from sediment competed with phenanthrene for sorption sites on BC. The research also concluded that phenanthrene sorption to BC was not hindered by an organic matter coating, although this conclusion is in conflict with research performed on activated carbon where fouling of the sorbent was observed (e.g. Carter and Weber, 1994; Bauda *et al*, 2004).

Plant structures are apparent within Severn Estuary alluvium peat and within some alluvial bio-pores. Alemany and Pugmire (1984), undertook ^{13}C Nuclear Magnetic Resonance (NMR) analysis on peat samples collected in the USA. The studies concluded that altered cellulose and lignin were preserved in peat without the destruction of the cellular morphology. Partitioning behaviour of PAHs to cellulose has received little attention considering cellulose is one of the most abundant organic matter compounds on earth. Jonker (2008) states just two cases other than his own study. Jonker undertook a series of sorption experiments using 13 PAHs ranging from phenanthrene (3 aromatic rings) to indeno(1,2,3-cd)pyrene (5 aromatic rings) spanning a log K_{ow} range from 4.6 – 7.

Partitioning of PAHs to cellulose is about 400 times (2.6 log units) weaker than partitioning into octanol. Sorption of PAHs to soot and charcoal (collectively referred to as black carbon (BC)) is about 3.5 – 5.5 log units stronger than sorption to cellulose (Jonker, 2008).

The research detailed above is summarised in the Table 3.7.

Table 3.7: Summary of Research into Sorption Behaviour of Organic Matter

Author	**Determinant**	**Soil and Soil Organic Matter (SOM)**	**Note**
Karickhoff (1981)	Phenanthrene and Pyrene	Variety of American Soils. SOM undifferentiated. 0.11% to 2.38% Organic Carbon.	Consideration only given to Organic Content and not type of SOM.
Karapanagiototi *et al* (1997)	Phenanthrene	Canadian River Alluvium including coal, pyroclastic particles, amorphous organic matter (AOM) and charcoal.	Samples containing coal exhibited high Koc values whilst samples containing organic coatings on quartz exhibited low Koc values and fast sorption kinetics
Weber *et al* (1998)	Phenanthrene	Young humic SOM and diagenetically altered kerogen SOM.	
Bayard *et al* (2000)	Naphthalene	Fontainbleau Sand as pure mineral matrix (no SOM), La Cote Saint Andre Soil (TOC 1.49%) and coal tar particles (TOC 38%)	Natural and Xenobiotic Organic Carbon Considered and consideration also given to competition for sorption sites.
Koelmans *et al* (2006) (Review)	Persistent Organic Pollutants (POPs) including PAHs, PCBs, Dioxins and Pesticides	Black Carbon (BC)	POPs display extremely efficient sorption to BC, up to three orders of magnitude greater than ‘normal’ SOM
Cornelissen *et al*. (2006)	Phenanthrene competing with native PAH and Natural OM	Black Carbon	Non-competitive behaviour noted between Phe and Natural OM. Competition between Phe and Native PAH.
Yang *et al* (2008)	Phenanthrene	Mosel River (Germany) flood plain soils containing coal from the Saarland Coal region .	Carbonaceous material associated with coal was found to exhibit a high sorption capacity.
Lou *et al* (2008)	Phenanthrene	Two soils. Black Soil 3.94% OC – Smectite clay mineral Red Soil 0.66% OC – Kaolinite clay mineral	Dissolved Organic Carbon competes for sorption with Phe. Mineralogy important sorbent when OC is low.
Jonker (2008)	13 PAHs from Phenanthrene to Indeno(1,2,3-cd)pyrene	Cellulose	Sorption of PAHs to cellulose is significantly weaker than sorption to BC.

3.2.6.3. Mathematics of Sorption

Equilibrium-controlled sorption isotherms are principally described by one of three isotherm models namely Linear, Freundlich and Langmuir.

Zheng *et al* (1998) describe that the linear sorption isotherm assumes that the sorbed concentration (S) is directly proportional to the dissolved concentration (C_e):

$$S = K_s C_e \qquad (3.3)$$

where K_s is the distribution coefficient described in terms of L kg^{-1}.

The Freundlich isotherm is a non-linear isotherm which can be expressed in the following form;

$$S = K_f C_e^n \qquad (3.4)$$

where K_f is the Freundlich constant, ^{n} is the Freundlich exponent, dimensionless. Both K_f and ^{n} are empirical coefficients. When the exponent ^{n} is equal to unity, the Freundlich isotherm is equivalent to the linear isotherm.

Jonker (2008) described the Freundlich equation as shown in (3.5), modified by considering the logarithm of the parameters used in the equation (3.4);

$$\text{Log } S = \text{Log } K_f + n \text{ Log } C_e \qquad (3.5)$$

The Langmuir isotherm equation is a non-linear isotherm equation. The Langmuir isotherm equation is detail in Bolster (2006) and Liu (2006). The Langmuir equation is presented as (3.6)

$$S = (S_{max}\, K_L\, C) / (1 + K_L\, C) \qquad (3.6)$$

Where S is the sorbed concentration (mg kg^{-1}), S_{max} is the maximum sorption capacity of the soil (mg kg^{-1}), K_L is the Langmuir binding strength coefficient (L mg^{-1}) and Ce is the equilibrium concentration (mg L^{-1})

The Langmuir Isotherm assumes that the adsorbent has a finite number of sorpotion sites, S_{max}. The adsorbate is assumed to form a monolayer on the adsorbent. As saturation is approached the rate of sorption decreases leading to the characteristic Langmuir curve, which tails off until sorption ceases.

Koelmans *et al* (2006) show that many authors found sorption of PAHs to BC is best expressed using the Freundlich equation (e.g. Bucheli and Gustafson, 2000; Kleineidam *et al*, 2002; Cornelissen and Gustafson, 2004; Yang *et al*., 2004).

It should be noted that isotherms performed a single low concentration are approximate and not representative of the full range of sorption behaviours over the full range of possible concentrations. All sorption models approach the linear model at low sorbate concentration (Site, 2000).

3.2.7. Literature Review on Wetting and Capillary Rise

For the purpose of Environmental Risk Assessment fine grained (i.e. clay and silt) soils are usually assumed to have a low permeability to water and, thus, dissolved and free phase contaminants.

Alluvium contains subordinate peat bands comprising plant fibres in various states of decay. Fibre plant straws typically consist of exceptionally long cells – bast fibres – that in many cases have a lumen, a hollow tube inside the fibre cell (Haudek and Viti, 1978). The fibre filled pores can, therefore, be conceptualised as containing a network of microscopic pores. Horizontal DNAPL transport through fossil plant fibres in peat, at an elevation above the groundwater table, is considered a potential preferential pathway for DNAPL contaminant flow.

Capillary phenomena arise as a result of differences in pressure across a curved liquid-solid interface (Tavisto *et al*, 2003). The theoretical maximum height, h, to which a column of liquid will rise within a capillary tube (m) is given by Equation 3.7.

$$h = 2\gamma \cos \theta / \rho \, g \, r \qquad (3.7)$$

where γ is the liquid-air surface tension (J/m^2), θ is the solid/liquid contact angle, ρ is the density of the liquid (kg/m^3), g is the acceleration due to gravity (m/s^2) and r is the radius of the capillary tube (m).

A prerequisite for capillary rise is that the liquid has a propensity to wet the solid capillary medium.

The intermolecular interaction between a contaminant and a soil surface determines its’ wetting behaviour. Charge distribution affects this interaction. Aliphatic hydrocarbons are typically non-polar on account of hydrogen and carbon having similar electro-negativities (2.2 and 2.6 respectively on the Pauling scale (see Atkins & Jones, 2002).

Aromatic hydrocarbons are more polar in charge distribution than aliphatic hydrocarbons on account of the sp^2 hybrdisation of electrons in the carbon rings resulting in a P-orbital above and below the ring structure leading to electron-density above and below the carbon ring structure. Consequently aromatic hydrocarbons have a slightly higher aqueous solubility than their aliphatic counterparts.

Heterocyclic atoms (e.g. N and O) are more electronegative than H and C (i.e. Pauling Scale 3.0 and 3.4 respectively) leading to polarity in the molecule structure. Polar functional groups such as alcohol (-OH) in phenol also lead to polarised charge distributions.

It is generally accepted that most natural porous media, and quartz and other silicate minerals in particular, which have not been invaded by complex organic liquids such as crude oil or creosote, are water-wet due to their surficial negative charge that attracts polar water molecules (Cohen *et al*, 2007).

The (water/NAPL) contact angle (Ø) indicates whether the porous medium will be preferentially wetted by NAPL or water and may vary between 0˚ and 180˚ (Mercer

& Cohen, 1990). If Ø ≤ 70˚, the system is water-wet; if Ø ≥ 110˚ it is NAPL-wet; and if Ø = 70˚ - 110˚, it is considered neutral (Anderson, 1986).

Cohen *et al* (2007) and Birak and Miller (2009) summarise experiments performed on water/NAPL/silicate mineral systems (i.e. Barranco and Dawson (1999), Zheng *et al* (2001), Hugaboom and Powers (2002), Dong *et al* (2004) and Powers *et al* (2006). At near neutral pH the contact angles suggest a water-wet system.

As detailed in Jackson *et al* (undated) 2 systems can occur in soil. Above the phreatic level soil may be sub-saturated in respect to water. Pores may, therefore, be dry. Below the phreatic level pores will be water filled (saturated).

However, in air/NAPL/silicate mineral systems research (see Cohen, 2007) suggests that creosote is wet relative to air. This phenomena is shown graphically in Figure 3.10.

In view of the preference for water wetting of the mineral surface when water is present the current research concentrated on creosote in capillaries not containing water whilst the clay was at natural moisture content. However, in water wet systems NAPLs will seek pore spaces as these will represent areas where capillary forces are smallest (see Jackson *et al* (undated)). Hydraulic forces, however, may overcome capillary resistance and can drive non-wetting DNAPL into formerly water filled pores (Cohen *et al*, 2007).

The effect of pH on wettability, which is related to asphaltenes, is discussed in Section 3.1.1.5. of this research.

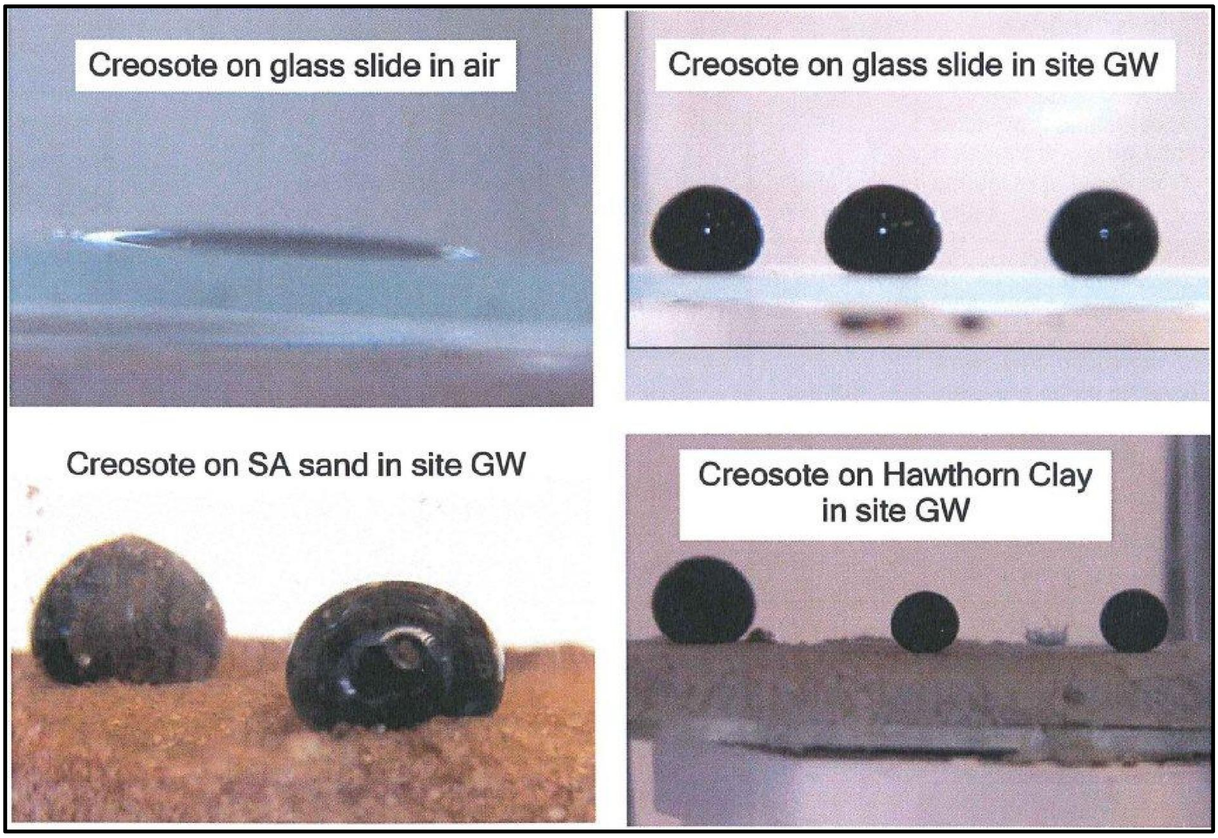


Figure 3.10: Examples of an oil wet system of creosote/glass/air (top left) and water wet systems of creosote/mineral/water (taken from Cohen *et al*, 2007).

Staples and Shaffer (2001) considered the time required for the above equilibrium state to be achieved. In addition to the parameters discussed above, viscosity was found to determine the rate of capillary rise, with viscous drag increasing with a reduction in capillary diameter.

Capillary rise has been reported as a relatively rapid phenomenon. Tavisto *et al* (2003) reported an experiment using perfectly wetting capillary tubing, of 100 μm radius, which achieved column height within an order of hours. Staples and Shaffer (2002) references the use of high speed photography for monitoring capillary flow and presents experimental data in the order of seconds to hours. Contamination at the study sites has been present in the soils for a number of years so it is reasonable to assume equilibrium has been achieved in respect to capillary flow.

3.2.8. Literature Review of Bio-pores

The role of bio-pores in groundwater transport has been indentified previously. Devitt and Smith (2002), studied loam soils in the USA. In the USA desert sites are often used for the disposal of hazardous waste since the majority of precipitation is assumed to be lost by evapotranspiration thereby limiting percolation of rainfall into the ground.

However, the deep penetration of roots and natural die-off of plants over time could provide avenues for macropore by-pass associated with old root channels (Devitt and Smith, 2002). Water, with a potassium bromide tracer, was applied to plots of soil with and without old root channels. 48 Hours after application it was proven that water applied to plots with previous root systems penetrated deeper than water applied to plots without previous root systems. It was also confirmed that a significant cross-sectional area of the soil was not contributing to flow at the same rate.

Macropores have been shown to have a significant impact on the flow of water through peat soils. Natural soil pipes have been shown to contribute 10% of discharge in areas of deep peat catchment (Holden and Burt, 2002). Flow in pores larger than 1mm diameter has been shown to contribute approximately 30% to the infiltration of water into peat (Holden *et al*, 2001). Baird (1997) found macropores to contribute between 51% and 78% of the flow at the peat surface and Blodua and Moore (2002) noted that preferential flow paths allowed traces to flow to depths within peat which would otherwise not be achievable where they not present.

Holden (2009) studied the influence of macroporosity in peat on the transport of water. Pores of less than 0.25mm diameter were found to play a minor role in infiltration. Whilst pores constitute a small percentage of the soils volume, they contribute significantly to total flow. At the surface of the peat, Holden (2009) observed that 80% of flow occurred through 0.260% of the peats volume. At 5cm depth the rate of flow was an order of magnitude lower and 85% of flow occurred through 0.010% of the soil volume.

The volume of macropores relative to the soil mass has been termed ‘effective porosity’. This is considered independently of the porosity of the soil matrix, which are tortuously interconnected and contributes much less to the soils permeability for fine grained soils. Azevedo *et al* (1998) found 86% of the flow through loamy soil occurred through an effective porosity of 190 cm^3 m^{-3} (equivalent to 0.019% of soil volume).

DNAPL flow through apertures in rock is detailed in Environment Agency (2003a). Fracture entry pressures are directly proportional to interfacial tension and inversely proportional to fracture aperture. This results in preferential DNAPL migration through the larger aperture fractures of a fracture network (Environment Agency, 2003a). An aperture of less than 0.041 mm is capable of sustaining a head of 2m of creosote, and an aperture of less than 0.087mm is shown to be able to stop the migration of a 1m head of creosote.

The impact of bio-pores on contaminant transport in soils has been extensively studied at shallow depth where the impact of fauna has been considered. Edwards *et al* (1993) provides a summary of research into the vertical burrows of earthworms (Lumbricus terrestris). The burrows have been identified as preferential contaminant pathways, described as short-circuiting the soil profile. The paper highlights the significant contribution of such bio-pores to groundwater flow and also acknowledges the technical difficulties in recording the distribution and effect of such features.

Edwards *et al* (1998) recorded earthworm burrows in excess of 4mm diameter with those in the 2 mm to 4mm being attributed to juvenile worms. In the case of worm burrows the pore diameter was inversely proportional to the number of pores although the larger pores 1.0mm to 5.0mm were responsible for a greater portion of the porosity. The bio-pores observed within Severn Estaury Alluvium were typically up to 2.5mm diameter (See Section 5).

Oades (1993) considered the pressures generated by flora and fauna modes of bio-pore formation assuming that an earthworm is unlikely to exert more than 0.2 MPa and plants being able to exert up to 9 MPa.

Douglas, J., T., (1986) advocates the use of dye-staining and simple counting to record soil fissures and pores in soil cores to assist with estimating the permeability of soils during logging. Smetten (1992) described bio-pores as routes for rapid and chaotic water flow calling flow through the mineral soil matrix as ‘pedestrian’ by comparison. Smetten (1992) proposes equations for estimating a soils permeability based on the size and frequency of earthworm bio-pores.

It is apparent that soil macropores have been identified as preferential routes for groundwater water transport, and hence dissolved contaminants, through the less permeable matrix of soils, allowing transport at a significantly higher rate than the soil matrix. Macropores constitute a small percentage of the soils total volume but account for a significant percentage of groundwater flow on account of their low resistance to flow.

4. Methods

4.1. Field Observations

All of the study sites detailed within this research have been subject to ground investigation by the author in his role as a Geotechnical and Geo-Environmental Engineer at Terra Firma Wales Ltd. The author has been in full-time supervision during the site investigations. Investigations were performed using Light Cable Percussion Boreholes and investigation strategies were performed in accordance with BS:EN 10175 (2001) and soils were logged by the author in accordance with BS:5930 (1999).

Light Cable Percussion (LCP) Drilling is a technique whereby a borehole is advanced by driving a hollow steel tube (clay cutter or shell) using a drop weight. The tubing is advanced into the soil and winched out to recover a sample of the soil. The hole created is held open by a steel casing, which is also advance with a drop weight. The technique allows a 100mm diameter sampling tube to be fitted into the shell to collect an ‘un-disturbed’ sample (U100).

When drilling through contaminated soil located over ‘clean’ soil the ‘telescopic drilling technique’ is employed whereby a hole is initially drilled with a 150mm casing. Once the 150mm casing has advanced through the contaminated soil, the 150mm casing is cleaned and the hole continued in 100mm casing.

In addition to the above site investigation protocols, necessary to satisfy the regulatory authorities (i.e. Environment Agency, Local Authority Environmental Health Officers, etc) the author has been mindful of the objectives of the research and full time presence during these investigations allowed site conditions to be constantly monitored and observed.

Due to client confidentiality Terra Firma Wales Ltd reports cannot be annexed within the current research.

4.2. Sampling and Sub-Contracted Chemical Analysis

Extensive soil samples and groundwater samples have been collected during site investigations around the Severn Estuary and submitted for chemical analysis at commercial laboratories. Some of these sites are considered in the current research.

During site investigations telescopic drilling techniques and drill casing were employed to prevent cross contamination of different strata. Selected shallow groundwater wells were installed within the made ground and deep groundwater wells were installed within the confined sand and gravel aquifer located beneath the alluvial clay. The monitoring wells allowed the collection of groundwater samples following purging of the wells in accordance with Environment Agency protocols.

During investigations at study site E the author collected an almost continuous run of 100mm diameter, 450mm length, undisturbed samples (U100s) through alluvial deposits in three boreholes (BH15A – BH17A) extending from the top of the alluvium (3.5m bgl to 5.5m bgl) to its base (13m bgl to 14m bgl). Soil samples are stored in cold storage (4˚ C) and dispatched in cool boxes to commercial laboratories within 24 hrs of recovery.

These samples were submitted to Severn Trent Laboratories for analysis for polynuclear aromatic hydrocarbons, in accordance with laboratory procedures including MCERT and UKAS Protocols. Most significantly, soil samples are not being divided into to the various domains of the soil sample (i.e. soil matrix and biopores). The results of the sub-contracted chemical analysis are presented in Appendix F.

4.3. Detailed Logging of Alluvium

Selected soil samples of alluvium collected by the author were subject careful dissection and detailed logging. A range of sample-types were considered predominantly comprising 100mm diameter undisturbed samples (U100's), 35mm split-spoon samples, clay cutter (Figure 4.1) samples and lined windowless sampler borehole cores. Samples were obtained from contaminated and uncontaminated sites. Over sixty samples were subject to detailed logging. The logging sheets are presented in Annex B.

Figure 4.1: View of the base of a clay-cutter with an internal diameter of 100mm, divided into 3 sections.

The pore structures were observed in samples from the study sites located on both sides of the Severn Estuary.

Soil samples collected within a plastic casing (U100 samples and Windowless Sampler Borehole samples) were carefully cut from their casing by splitting the casing vertically using an angle grinder. Once extruded from their casing, the samples were oriented vertically and dental scalars were used to carefully pick off the disturbed zone at the top of the sample to expose a virgin surface. The pores in the exposed surface were then logged. Once the surface was logged, samples were split along their vertical axis to expose a vertical face to confirm that pores extended vertically/sub-vertically through the length of the sample.

Detailed measurements of pore diameters were made during the logging using digital callipers. The cross-sectional area of the logged samples varied, depending on the drilling technique used. Sampling with a U100 sampler results in a circular core with a 100mm diameter (0.0079m^2 cross sectional area). A clay cutter divides a 100mm diameter sample into 3, resulting in samples with a cross-sectional area of 0.0026m^2. A standard split-spoon sampler used for Standard Penetration Tests (SPTs) creates cores with a 35mm diameter (0.00096m^2 cross-sectional area). Windowless samplers employ a large range of sample diameters, dependent on the diameter of the sampler which typically lies <80mm diameter. The logged samples were sometimes fragments of the whole cores, in which case the samples were measures to deduce their cross-sectional area.

Pore data from twenty two samples, taken from a range of depths at study sites E and A, are detailed in Section 5.3. The cross-sectional area of these samples ranged from 0.0079m^2 to 0.00096m^2. The cross-sectional area of the pores was calculated from their recorded diameter, assuming the pores were effectively circular. Since the cross-sectional area and number of the pores of each size range was known, along with the cross-sectional area of the sample, the number of pores per m^2 of soil could be estimated.

4.4. Chemical Analysis of Detail Logged Samples at Cardiff University

In order to determine the distribution of tar compounds in, and within the vicinity of, bio-pores the following procedure was adopted;

Selected contaminated soil samples from study sites E and G were used. Pores containing creosote/coal tar were stained black by the hydrocarbon, in contrast to the typically brown to grey matrix of the natural soil. Following extraction from the sample casing, as detailed in Section 4.3, samples were split along their vertical axis to expose pores longitudinally. The material contained within pores, and the stained soil immediately surrounding the pores, was isolated using dental scalars and collected within 40 ml glass vials. Matrix soil was selected which was remote from contaminated pores. Matrix soil was collected in a separate 40ml glass vials.

Following separation the samples were dried in an oven at 40˚C for 48 hrs, crushed and weighed into samples of approximately 1g mass. The dried samples were loaded into an Accelerated Solvent Extraction (ASE) cell with excess anhydrous sodium sulphate as a desiccant. The samples were subject to Accelerated Solvent Extraction in a DIONEX ASE100 at the Characterisation Laboratories for Environmental Engineering Research (CLEER), Cardiff University. Dichloromethane was used as a solvent and samples were subject to ASE Programme 3, comprising a temperature of 100˚ C, 5 minutes static time, a 60% flush volume and a 60 second purge. The solvent volume was recorded.

The solvent extract was subject to speciated PAH analysis by Gas Chromatography Mass Spectrometry (GCMS) at Cardiff University. The analysis was performed on a Perkin Elmer Clarus 500 GCMS. The analytical programme comprised a start temperature of 100˚ C held for 2 minutes followed by a ramp of 4.0˚ C min^{-1} up to

310° C, which was then held for 4 minutes. PAH identities were confirmed and quantified against a 50 ppm PAH standard from Restek. In addition the molecular fragments weights and eluting times were automatically compared to a database from the National Institute of Standards and Technology (NIST) to further confirm the identity of individual species. The GCMS software contains a database of characteristic eluting fragments associated with parent molecules and provides possible identities for the source of the observed GCMS pattern.

The CGMS analysis was run with a PAH standard from Restek and peak integration was used to quantify the concentration of PAHs present in the solvent and thus derive PAH concentrations in soil.

The results of this analysis are presented in Section 5.4.

4.5. Soil Characterisation

4.5.1. Mineralogy

The interaction of the coal tar with the soil depends on the mineralogy, and hence the charge distribution, of the soil. Hydrocarbon contamination is generally non-polar in character and competes with polar water molecules for soil interaction in the groundwater environment.

The mineralogy of selected alluvium samples was explored using the X-Ray Diffraction facilities at the CLEER Laboratory, Cardiff University. Samples obtained from various depths from four study sites were analysed. The samples comprised alluvial clay/silt with the exception of a sample of alluvial peat from study site E. The samples were collected from soils not impacted by hydrocarbon contamination, confirmed by visual and olfactory inspection by the author and chemical testing performed by the author on behalf of Terra Firma Wales Ltd. The tested samples are listed in Table 4.1.

Table 4.1: Identity of Samples subject to X-Ray Diffraction Analysis

XRD Test I.D.	Source Site	Borehole	Depth
BBH 4	Study Site E	BH 101	4.0 m
BBH 8		BH 101	8.0 m
BBH 12		BH 101	12.0 m
BBH PEAT		BH 101	6.6 m
bh1 8	Study Site F	BH 1	8.0 m
bh1 16		BH 1	16.0 m
PORTIS A	Study Site G	BH 1	8.0 m
PORTIS B		BH 1	12.0 m
PORTIS C		BH 1	14.0 m
WSM A	Study Site A	BH 1	8.0 m
WSM B		BH 1	12.0 m
WSM C		BH 1	16.0 m

The selected samples were prepared by desiccation in an oven at 40˚ C for 48 hrs and subsequently ground to a fine powder using a pestle and mortar. The samples were then pressed into a holder and inserted into a Phillips PW3830 X-Ray Diffraction Analyser.

To further refine the analysis the mineral samples were subject to elemental analysis by Inductively Coupled Plasma Optical Emissions Spectrometry (ICP-OES). Samples were prepared by microwave digestion in aqua-regia (HCl and HNO_3). Elemental analysis of selected cations was performed by Terra Firma Wales Ltd and the results of this analysis are presented in Table 5.3. The elemental data was entered into the X-Ray Diffraction interpretation software (X'Pert Industries) to limit the possible minerals considered.

The results of the X-Ray Diffraction analyses are presented in Annex C and discussed in Section 5.5.1.

4.5.2. Soil Organic Content

The soil organic content, along with the organic carbon partition coefficient, are fundamental parameters for determining the retardation of organic contaminant flow relative to groundwater flow during hydrological modelling.

Total Carbon and Total Inorganic Carbon, and thus (by difference) Total Organic Carbon, were analysed by combustion analysis in the CLEER Laboratory, Cardiff University.

Prior to analysis the samples were desiccated at 40˚C for 48 hrs and crushed using a pestle and mortar. The combustion analysis was performed at 900˚C using a

Shimadzu SSM-5000A. The Total Carbon analyser was first calibrated using D(+)Glucose Anhydrate (40% Carbon) from Fisher Chemicals.

Prior to Inorganic Carbon analysis the soil samples were fixed with 0.5ml of phosphoric acid. The Inorganic Carbon analyses were calibrated using pure calcite ($CaCO_3$) from Elemental Microanalysis Ltd (Part 501-034, 12% Inorganic Carbon).

The results of this analysis are presented and discussed in Section 5.5.2.

4.5.3. Moisture Content and Atterberg Limits

Selected soil samples from BH101 at study site E were subject to moisture content analysis and the liquid limit and plastic limit of the alluvium was determined for a representative sample of alluvium from 9.00m depth in accordance with the methods outlined in BS1377: Part 2: 1990. In addition, Terra Firma Wales Ltd provided moisture content and plasticity data for alluvial samples taken from a site located north of study site E.

The liquid limit is defined as the moisture content at which a soil is deemed to pass from a plastic to a liquid state. The test soil is passed through a 425 um sieve prior to analysis to remove coarse clasts. The soil sample is then placed beneath a standard 30˚, 80g cone penetrometer. The cone is allowed to fall freely into the sample. The moisture content of the sample is varied by wetting/drying until a moisture content is found which allows 20mm of penetration by the dropped cone. This moisture content is the liquid limit.

The plastic limit is defined as the moisture content at which a soil becomes too dry to exhibit plastic behaviour. A sample of the cohesive soil is rolled by hand on a rolling plate into a thread of 6mm diameter, which is then reduced to a thread of 3mm diameter. The rolling gradually reduces the moisture content of the soil and the process is repeated until a moisture content is reached where the thread cracks. This moisture content is the plastic limit.

Plasticity analysis was performed by Geo-Laboratory Testing Services, Bynea. The Geotechnical test data is presented in Annex D and plasticity results are discussed in Section 5.5.3.

4.5.4. Particle Size Distribution

The particle size distribution of a soil has a bearing on the permeability of that soil with the fines grades (i.e. silt and clay) typically having the lowest permeability.

In October 2008 the author commissioned Geo-Laboratory Testing Service Ltd to undertake Particle Size Distribution (PSD) analysis on twelve samples from continuous cores of alluvium, from study site E, taken from 4.0m to 14.5m depth. PSD analysis was performed in accordance with the methods of BS 1377 Part 2:1990 (Wet Sieve Analysis Clause 9.2.9.4).

During analysis a series of sieves of descending grade are stacked upon one another. Soil is placed at the top of the stack and the stack is vibrated whilst water is passed through the system. The soils trapped on each sieve are dried and weighed to reveal the relative distribution of grades.

PSD analysis was performed by Geo-Laboratory Testing Services, Bynea. The Geotechnical test data is presented in Annex D and PSD results are discussed in Section 5.5.4.

4.5.5. In-Situ Strength

The in-situ strength of a soil has a bearing upon its durability during sampling and hence its ability to preserve fine structures.

During drilling at the study sites in-situ Standard Penetration Tests (SPT's) were performed at regular intervals. SPT's were performed in accordance with the methods described Section 9 of BS1377 (1990) using a split spoon sampler. In accordance with the British Standard the results of the SPTs were recorded as an "N" value of blow-counts required to advance the sampler 300mm following a 150mm seating drive.

In-situ strength testing is discussed in Section 5.5.5 and typical borehole logs containing in-situ Standard Penetration Test (SPT) data are presented in Annex E.

4.6. Partition Coefficients

4.6.1. Introduction

Due to the high volumes of spilt coal tar/creosote beneath the study sites, and the relatively low solubility of these organic contaminants, free phase contamination was encountered beneath the sources. However, beyond the margins of the free phase plume, dissolution into groundwater occurs. The sorption of dissolved phase organic contaminants onto geological material leads to retardation of that contaminant relative to groundwater flow. Equilibrium Partitioning Theory (EPT) is fundamental to the assessment of hydrological risk assessment (see Section 3.1). A series of experiments were performed to quantify factors that affect the dissolved phase sorption of selected contaminants to Severn Estuary alluvium.

4.6.2. Materials and Methods

Phenanthrene and phenol were chosen as type contaminants for the assessment of sorption phenomena. Both form principal components of creosote and coal tar with Lesiatoi (2007) reporting a concentration of 1.54×10^5 ppm phenanthrene and 1.54×10^3 ppm phenol in raw creosote.

Phenanthrene is a polynuclear aromatic hydrocarbon (PAH). It was chosen on account of its relatively high solubility in comparison to larger PAH molecules (1.1 mg/l (EA, 2003) and relatively low volatility (Dimensionless Henrys' Law Constatnt 1.31×10^{-3} (EA, 2003)). Phenanthrene (97%+) crystals were supplied by Acros Organics.

Phenol was studied since it is often chosen as a marker contaminant by the Environment Agency on account of its high solubility and rapid transport characteristics. In contrast to PAHs, phenol represents a high mobility hydrocarbon.

Biochemical grade 99%+ phenol was supplied in crystalline form by Fisher Scientific.

Alluvium was collected from study site E from an area that had previously been chemically tested by Terra Firma Wales Ltd and was known to not be contaminated by PAHs, Phenols, BTEX or Petroleum Hydrocarbons. The alluvium comprised, independently, silt and peat. The silt used in the sorption experiment was recovered from study site E (BH101, 9.0m). Peat used in sorption experiments was recovered from study site E (BH101, 6.6m – 6.8m). Further details of these materials are presented in Section 3.2 and 5. Soils were desiccated in an oven at 60˚ C for 48 hrs, ground, and passed through a 400 μm sieve and vigorously mixed to ensure homogeneity. The resultant powder was then stored in a desiccation chamber above anhydrous copper sulphate until required.

Isotherm tests were performed using a variant of the methods of Arash Shirani (Pers.Comm.). Arash Shirani, a PhD researcher at Cardiff University School of Engineering, studied the sorption of phenanthrene to pulverised fly ash using batch experiments. The process is detailed below.

Stock solutions of phenanthrene were prepared by adding a known weight of crystal phenanthrene to 10 ml of methanol. This was then added to 1 litre of deionised water. When groundwater from the confined aquifer beneath study site E was used in lieu of deionised water, the groundwater was first filtered using 1.5 μm pore glass micro-filter paper. The mixture was placed in a shaker for 1 hr and left for 24 hrs at room-temperature in a 1 ltr amber jar with a Teflon lined lid. The solution was then filtered to remove any excess, un-dissolved phenanthrene crystals. The solution was diluted to the required concentration using deionised water or filtered groundwater. Tests were performed at concentrations less than half of the solubility of the contaminant (Solubility of phenanthrene 1.1 ppm, Environment Agency (2003)) as recommended in Karickhoff (1981).

A solution of creosote saturated in deionised water was prepared by adding excess (i.e. more than could be dissolved) creosote to 1 litre of deionised water in a separation flask. The creosote was Type B creosote from an active creosote works (study site E). The creosote was added beyond the point at which a free-phase formed. The mixture was vigorously shaken and then left under quiescent conditions for 2 hrs, over which time phase separation had occurred to leave a dominant Dense Non-Aqueous Phase Liquid (DNAPL) in the base of the separating flask, saturated distilled water in the centre and a very subordinate Light Non-Aqueous Phase Liquid (LNAPL) floating on the top of the water. The DNAPL Phase was tapped off and discarded. The aqueous phase was collected and transferred to another separating flask and the upper aqueous phase and LNAPL Phase were discarded. The aqueous phase was again left under quiescent conditions for 2 hrs to allow any remnant DNAPL and LNAPL phase to form. As previously the DNAPL and LNAPL phases were discarded, and as much of the aqueous solution as possible was retained for batch testing.

Phenol stock was prepared by the addition of phenol crystals to deionised water and subsequent agitation. When a saturated stock was required, crystals were added to a point at which dissolution ceased. The stock was subsequently passed through a 1.5 µm pore size glass micro-filter to ensure the absence of un-dissolved residual crystals. Stock was diluted as required with deionised water.

Once stock solutions of phenanthrene, phenol or dissolved creosote were prepared, the batch experiment was performed as follows;

1. Clay or peat soil was desiccated at 60˚ C for 48 hrs and filtered through a 400 µm sieve. Small masses of desiccated soil were added to pre-weighed 40ml amber glass vials and reweighed. Soil was not added to selected vials.

2. 25 ml of stock solution was measured and poured into each 40 ml amber glass vial. Vials were fitted with Teflon lids.

3. Vials were fitted into an agitator and run at 160 rpm for 24 hrs (or longer for kinetic experiment). The kinetic experiment was performed as it was necessary to establish the time in which equilibrium was established to confirm that sorption experiments exceeded this time. Kinetic experiments were performed for up to 306 hrs.

4. After agitation the content of the vial was passed through a glass micro-pore filter into a clean 40 ml glass vial. 10ml of hexane was added.

5. The filtrate/hexane mixture was agitated for 1 hr at 160 rpm and left to settle, allowing the hexane to separate from the filtrate.

6. A pipette was used to transfer a small volume of the hexane into glass vials for GCMS Analysis.

Hexane was used to extract phenanthrene following the example of Derwentside Environmental Testing Services (DETS) Limited, the commercial laboratory used by the author during professional work.

Mike Cohen (Pers. Comms) of DETS Limited confirmed that hexane is used during the extraction of Semi-Volatile Organic Compounds (SVOCs) including phenanthrene. Hexane has the advantage of floating on top of the water, leading to ease of pipetting.

Desorption experiments were performed by transferring the used filter-paper and filtered soil into a clean 40ml amber vial with 25ml of deionised water. These vials were agitated for a period of 24 hrs before filtration and hexane extraction as discussed above.

Several variables were explored during the sorption testing. The various test conditions are summarised in Table 4.2.

Table 4.2. Summary of Sorption Tests

Test No.	**Test Solution**	**Sorbent**	**Equilibrium Contact Time**	**Comment**
1 (29/10/2008)	Phenanthrene distilled water	Peat	24 hrs	Desorption also performed
2 (14/01/2009)	Phenanthrene distilled water	Peat and silt/clay	24 hrs	Desorption also performed
3 (24/02/2009)	Creosote in distilled water[1]	Peat and silt/clay	24 hrs	Unsuccessful
4 (03/03/2009)	Phenanthrene distilled water	Peat	1hr – 306 hrs	Sorption Only
5 (05/05/2009)	Phenanthrene distilled water	Peat	24 hrs	Sorption Only
6 12/04/2009)	Phenanthrene in distilled water	Peat	24 hrs	Sorption Only
7 (13/05/2009)	Phenanthrene in solution in groundwater water[2]	Peat	24 hrs	Extraction unsuccessful due to foaming
8 (23/06/2009)	Phenol solution in distilled water[2]	Peat	24 hrs	Extraction Unsuccessful
9 (15/06/2009)	Saturated phenol in solution in distilled water[2]	Silt/clay	24 hrs	Extraction Unsuccessful

1. Creosote was diluted until free-product was no longer present.
2. Initial concentration could not be determined when extraction was unsuccessful.

Following solvent extraction, the concentration of phenanthrene/phenol was determined at the CLEER Organics Laboratory, Cardiff University using GCMS. Targeted phenanthrene analysis was performed using the following programme;

Initial Oven Temperature of 50˚C for 0.00 min;

Ramp 1 – 10.0˚C/min to 100˚C – Hold for 0.00 min;

Ramp 2 – 5.0˚C/min to 200˚C – Hold for 0.00 min;

Ramp 3 – 10.0˚C/min to 250˚C – Hold for 3.00 min.

During analysis the GCMS was calibrated using phenanthrene standards produced by Restek.

Phenol analysis was initially performed using the recommended GCMS programme detailed below;

Initial oven temperature of 75˚C for 2.00 min;

Ramp 1 - 75˚C to 250˚C @ 15˚C min^{-1}, hold 250˚C for 4 min.

However, using this programme resulted in a phenol peak which could not be resolved from the eluting hexane solvent. Therefore, a lower initial oven temperature was employed which allowed separation of the solvent and the phenol. The programme is detailed below;

Initial oven temperature of 40˚C for 5.00 min;

Ramp 1 - 40˚C to 250˚C @ 15˚C min^{-1}, hold 250˚C for 4 min.

Samples of phenol standard were run with the extract samples. The phenol standard was supplied by Restek.

Experiments using creosote and phenol were abandoned due to difficulties achieving satisfactory extractions of the hydrocarbons from the filtrate (i.e the concentration recovered from solvent extraction was inconsistent between identical blank samples and significantly less than the expected concentration). The expected concentration of phenol in the blank samples (i.e the samples not containing soil) were calculated from the weight of the phenol added to the known volume of solvent.

Despite attempts to dissolve creosote it is possible that unperceivable globules of free-product remained in the stock solution.

Experiments using groundwater were abandoned due to the formation of a froth during extraction. It has been surmised that this may be due to a bio-film from groundwater biota.

4.6.3. Data Handling

The aqueous phase contaminant concentration data were used to establish sorption equilibrium by assuming that all contaminants not recovered from the aqueous phase were partitioned into the soil sorbed phase.

The initial contaminant concentration in the aqueous phase (C_o) was calculated from blank samples which contained no soil. The equilibrium aqueous phase concentration (C_e) was taken to be the concentration of contaminant recovered by solvent extraction. The mass of contaminant sorbed onto the solid phase per unit mass soil (S) was calculated by the following Equation 4.1 adapted from Yang *et al*, 2008.

$$S = (m_{cont} - Ce\ V)/m_{soil}, \qquad (4.1)$$

where;

S is the mass of contaminant sorbed to the solid phase, per unit mass of soil (mg/kg)

m_{cont} is the mass of contaminant spiked into the system (mg)

C_e is the contaminant concentration in aqueous phase (mg/l)

m_{soil} is the dry mass of soil (kg).

V is the volume of water (l).

The resultant equilibrium data were subjected to a series of linear and non-linear regression techniques to establish the relationship between S and C_e.

4.7. Capillary Experiment

A portion of the pores encountered in the alluvium contained fossil plant fragments. Capillary rise experiments were performed using fossil plant fragments to provide qualitative proof that the fossil plant fragments could serve as a means of DNAPL transport via capillary flow.

The fragments were predominantly fibrous and roughly circular in cross section with diameters typically <2.5mm, being predominantly orientated in a vertical to sub-vertical position. Larger irregular fragments were encountered in peat bands and as isolated fragments in random orientation. All fossil plant fragments were extremely delicate once removed from the surrounding soil matrix.

4.7.1. Capillary Rise Experiments with Fossil Plant Fibres

Initially fossil plant fragments were carefully isolated from 4.0m and 13m depth, BH101, study site E, by careful dissection. The soil samples were from a ‘clean’ area of the site, confirmed by Terra Firma Wales Ltd, and did not initially contain any creosote impact from their history.

Sample BH101 4.0m lay above the groundwater table and recorded a soil moisture content of 33%. Sample BH101 13.0m was obtained from below the groundwater table and recorded a soil moisture content of 57%. Due to the delicate nature of the plant fibres, samples of length greater that 32mm could not be isolated.

Five samples of plant fibres from both soil samples were isolated. Each fibre was individually suspended vertically above a dish of creosote with one end of the sample contacting the creosote (see Figure 4.2).

Figure 4.2: Sample of plant fibre isolated from 4.0m depth, BH101, study site E, suspended in Type B creosote.

To assess the flow behaviour of creosote in bio-pores containing plant fibres in the confinement of the soil matrix, an undisturbed soil sample (U100) from BH1 9.00m – 9.45m, study site F, was placed in a dish which was filled using Type B Creosote such that the base of the sample sat in 5mm depth of creosote (Figure 4.3). Type B Creosote was obtained from wood treatment plant at study site E.

Figure 4.3: Undisturbed sample BH1, 9.00m – 9.45m, study site F, following splitting after 24hrs contact with creosote at the base (bottom of photo). Note the abundant network of vertical to sub-vertical fibre-filled pores. Creosote is apparent as brown staining around some pores (highlighted in red) and a selection of pore without creosote impact are highlighted in blue

4.7.2. Capillary Rise Experiments within Open Pores

Capillary rise within open pores (i.e. without plant material) was studied using clay samples taken from 8.0m depth from BH101, study site E and 9.0m depth from BH1, study site F. The clay samples had a moisture content of 47% and 42% respectively. Moisture content testing after the experiments did not reveal significant changes in moisture content during the experiment. The clay was kneaded to homogenise the material and rolled into cylinders approximately 150mm in length. Small diameter holes were drilled through the centre of the clay cylinders using drill-bits or, below 1.0mm, thin brass rods of known diameter. The diameters were confirmed with vernier callipers. The base of the cylinders were then submerged in a shallow bath of Type B creosote (Figure 4.4). Prior to performing the main experiments samples were left in the bath for periods from 60 seconds to two hours which revealed that equilibrium was achieved within the pores in less than 60 seconds. Experiments were performed at 20˚ C temperature.

Test samples were left in the bath for a period of 1 hour after which the cylinders were removed from the bath and split. The capillary rise of the creosote was calculated by measuring the length of the creosote stain within the capillary compared to the submerged depth of the sample (Figure 4.4). Tests at each diameter were performed in triplicate.

Figure 4.4: Homogenised alluvium sample (BH101, 8.0m, Study Site E) with man-made 2mm pore, suspended (from below) within Type B Creosote. Note the creosote curving upwards on the outside of the sample indicating a concave meniscus, synonymous with capillary rise.

4.7.3. Capillary Rise in Glass Tubing

Capillary rise was studied using narrow diameter glass tubing as an analogy to the silicate minerals observed in the Severn Estuary alluvium, with Pyrex comprising 81% SiO_2 (See Iuliano *et al*, 2007). Glass capillary tubing with internal diameters of 0.90mm, 1.10mm and 2.80mm were suspended vertically within Type B Creosote. Tubing was contained within dry sterile wrapping prior to the experiment. The tubing was left with their bases in creosote for twenty fours before measurement. The rise within the tubing was recorded using digital callipers.

The results of this testing is presented and discussed in Section 5.7.

4.8. Sub-Contracted Soil Permeability Testing

In March 2006 Geo-Laboratory Testing Service Ltd was instructed by the author to undertake permeability testing on continuous cores of alluvial silt and clay from study site E using the methods of K.H. Head: Volume 3: Section 20.4.2, detailed in BS1377 (1990), (BH15A, Geo-Laboratory Report GEO/1900/06). Most significantly, in preparing the sample for testing an extruder piston is required to drive the soil sample out of the U100 sampling casing and into the test cell. During this process significant pressures are generated at the interface of the extruder and the soil sample.

In September 2008 permeability testing on a re-compacted sample of basal gravel from BH101, 14.5m depth was undertaken at Geo-Laboratory Testing Service Ltd under the instruction of the author (Geo-Laboratory Report GEO/6802/08). The test was performed in accordance with the methods of Head K.H. Vol.2 Section 10.7.

The results of Geotechnical testing are presented in Annex D and sub-contracted permeability tests are discussed in Section 5.8.

4.9. Permeability of Pores

The hydraulic conductivity of small diameter pores in clay soil, and hence the soils permeability, was assessed using constant head permeability apparatus in the Soil Mechanic Laboratories of Cardiff University. A variant of the Constant Head Test method described in Section 5 of BS:1377 (1990) was employed.

Given the soft nature of the natural alluvium it could not be transferred into the permeameter test cell and achieve a satisfactory seal without damaging the natural root structures. It was therefore necessary to homogenise and mould the clay into the test cell.

The tests were performed as follows;

1. Clay soil at natural moisture content was kneaded to homogenise the material. The material was moulded into a constant head permeability test cell with a brass rod located centrally.

2. The brass rod was carefully extracted from the soil, leaving a small diameter pore.

3. Prior to attaching the test cell to the constant head reservoir, the cell was flooded to ensure the absence of air bubbles. Once attached, any residual air bubbles were chased through the apparatus pipework.

4. Water was collected beneath the test cell in a large measuring cylinder and the time per 100 mL of flow, was recorded until 1 L had passed through the porous sample.

The tests were performed in triplicate with pores of 1.01 mm and 1.53 mm diameter to represent the pore diameters encountered during detailed logging (see Section 5.3).

The permeability test apparatus are shown in Figure 4.5.

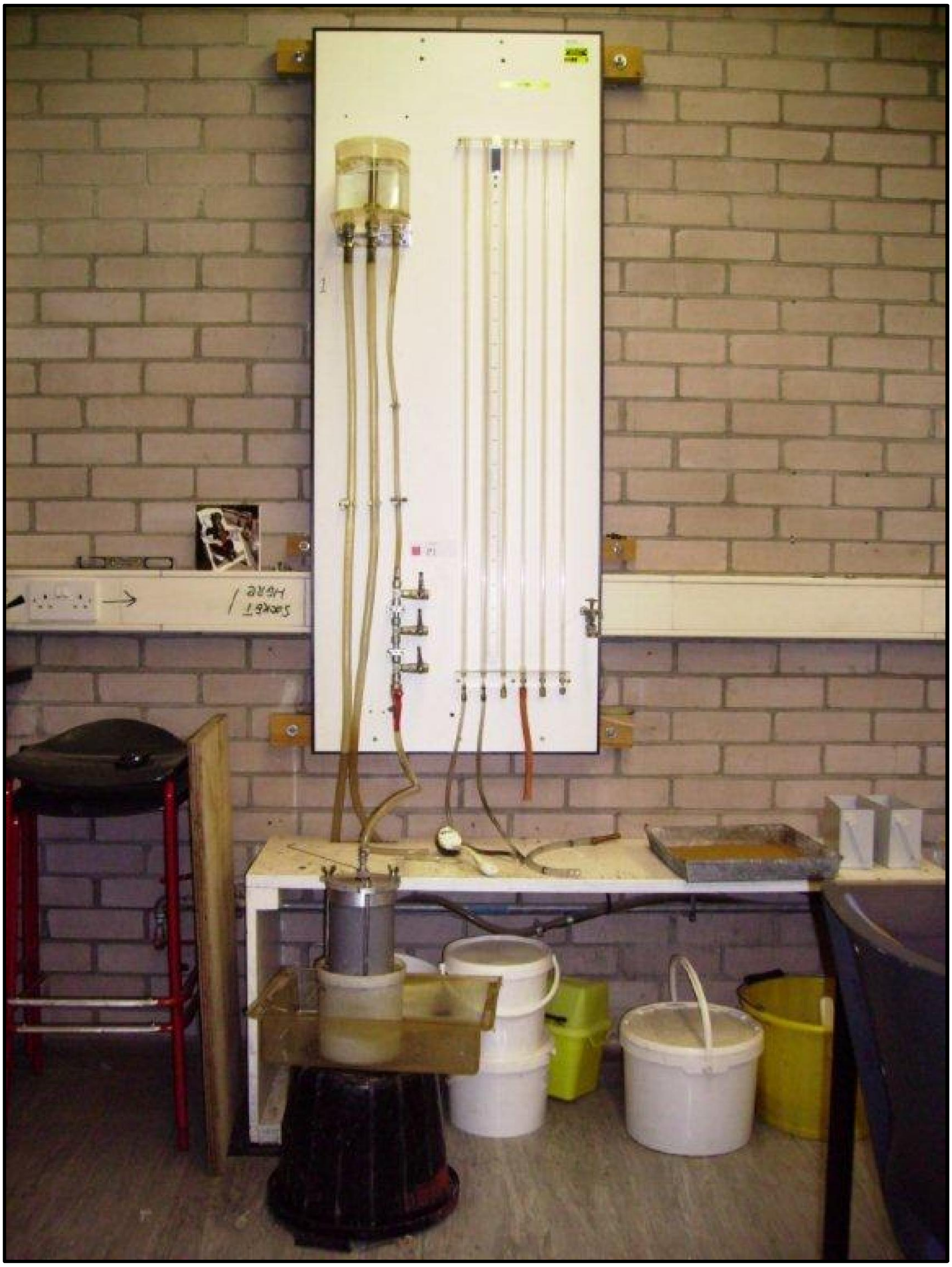


Figure 4.5. Permeability Test Apparatus (Permeameter)

Flow was directed through the pore and not the body of the soil and hence it was not possible to measure hydrostatic head within the soil sample via the manometer glands, as is standard practice with granular soils. Hydrostatic head was therefore calculated after the constant head reservoir apparatus via a siphon tube attached to the underside of the test cell. The siphon tube was allowed to fill and was then raised to a level at which flow ceased. The difference in height between the siphon tube at cessation of flow and the reservoir water level was taken to be the hydrostatic head.

The temperature of the water in the tests apparatus was recorded to allow temperature correction as detailed in Figure 4 of Section 5 of BS:1377 (1990). During testing the average water temperature in the reservoir was 8˚ C.

Tests at each pore diameter were performed in triplicate using a freshly prepared soil sample each time. When several tests were undertaken on the same soil sample soil erosion occurred and the permeability increased as pore erosion increased its' diameter.

The test as detailed in BS:1377 (1990) determines the permeability of an homogenous soil sample. The current work has assessed the effective permeability of an impermeable soil sample, with permeable pores, to allow the flow characteristics of a porous soil to be determined for use in Environmental Risk Assessment models originally designed for homogenous soils.

The soil sample in the test cell had a diameter of 85mm although the diameter of the soil sample in the cell was irrelevant as the flow occurred solely through the central pore. The matrix of the soil has been assumed to be of negligible permeability (published permeability values for unfractured clay are typically <10^{-9} ms^{-1}, see

Barnes, 2010). To allow a useful value to be derived the surface area of the test sample has been assumed to be $1m^2$ (i.e. 1 pore in $1m^2$ of soil).

The results of the permeability testing performed in the Soil Mechanic Laboratory of Cardiff University are presented and discussed in Section 5.9.

5. Results and Discussion

5.1. Field Observations on Contaminant Distribution

During full time site supervision the following general observations were made, providing qualitative evidence as to the transport behaviour of creosote and coal tar in alluvium;

1. Beneath the locations of former plant areas there was significant visual and olfactory evidence of coal tar/creosote contamination within the made ground, including pockets of free-product within interstitial spaces.

2. Beneath the location of former industrial plant areas there was visual and olfactory evidence of coal tar/creosote contamination within the alluvial clay. Discolouration (black staining) was seen to occur within vertical to sub-vertical fossil root structures.

3. Deep groundwater from beneath the alluvium was observed to contain droplets of hydrocarbon free-product beneath plant areas and down hydraulic gradient of these areas. The hydrocarbon was seen to sink within sample jars under quiescent conditions, confirming the oil was a DNAPL.

4. Alluvial clays were almost always ‘soft’ to ‘very soft’ indicating high moisture contents, approaching or exceeding the soils liquid limit. The clay structure was extremely susceptible to disruption during sampling, handling and sample preparation for testing.

The field observations reveal that in areas of former and contemporary industrial sites where coal tar/creosote has been spilt at shallow depth the coal tar/creosote can migrate into the alluvium via a network of macroscopic fossil root structures. These structures remained impacted at sites where production had ceased decades ago. The fossil root structures are easily disturbed, which could reduce the apparent permeability of soils following sampling and handling.

Further details of detailed logging are presented in the Section 5.3.

5.2. Sub-Contracted Chemical Analysis

Extensive sampling and testing has been performed at the study sites for the purpose of site investigation, prior to development. The sampling has been performed at commercial laboratories in accordance with standard practices and consequently these samples represent the average chemical content of the soil, irrespective of the various compartments of the soil discussed in Section 5.3 (i.e. soil pores and soil matrix). Three boreholes from study site E are discussed below.

Boreholes 15A to 17A are located in areas of the study site E which have been impacted by creosote historically. These boreholes were continuously sampled using 100mm diameter undisturbed samples (U100s). A sub-sample of soil was collected following each extrusion of the soil from the U100 sample casing. These sub-samples were placed in amber glass jars with Teflon lids and placed in cool-boxes for immediate transfer to Severn Trent Laboratories (STL) where the samples were subject to analysis for nineteen Polynuclear Aromatic Hydrocarbons (PAH).

The results of the testing are presented Annex F and summarized on Figures 5.1. to 5.3. Due to confidentiality issues associated with the site, the corresponding Terra Firma Wales Ltd borehole logs (BH15A to BH17A) cannot be reproduced, although the ground conditions are generalised alongside the graphs in Figures 5.1 to 5.3. Yellow represents clay/silt soils whilst black bands represent peat or organic clay horizons. Groundwater levels recorded by Terra Firma Wales Ltd are indicated by triangles.

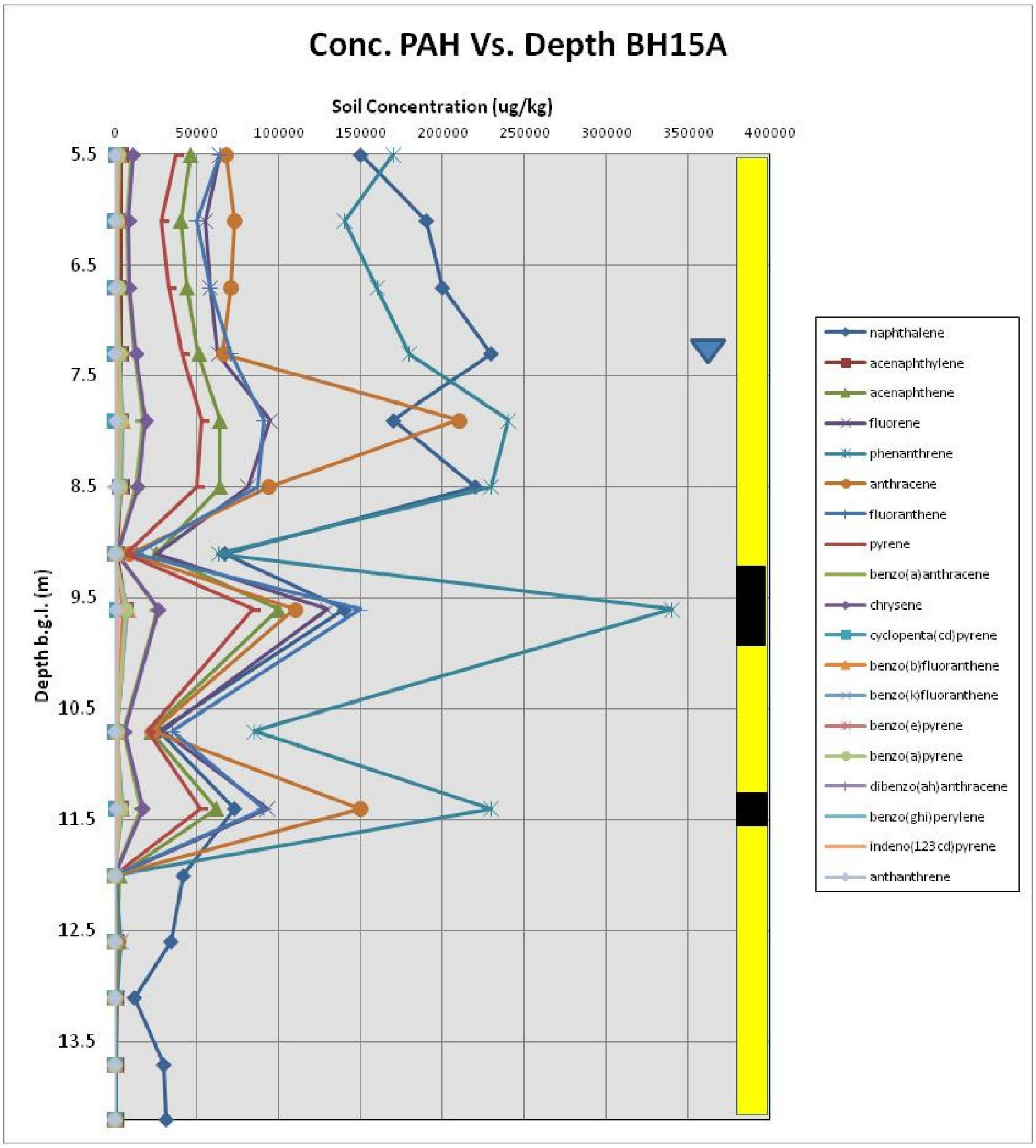


Figure 5.1: Soil PAH Concentrations Vs Depth from BH15A, study site E. (Yellow bar represents clay/silt soils, black bands represent peat/organic clay and triangle indicates piezometric level).

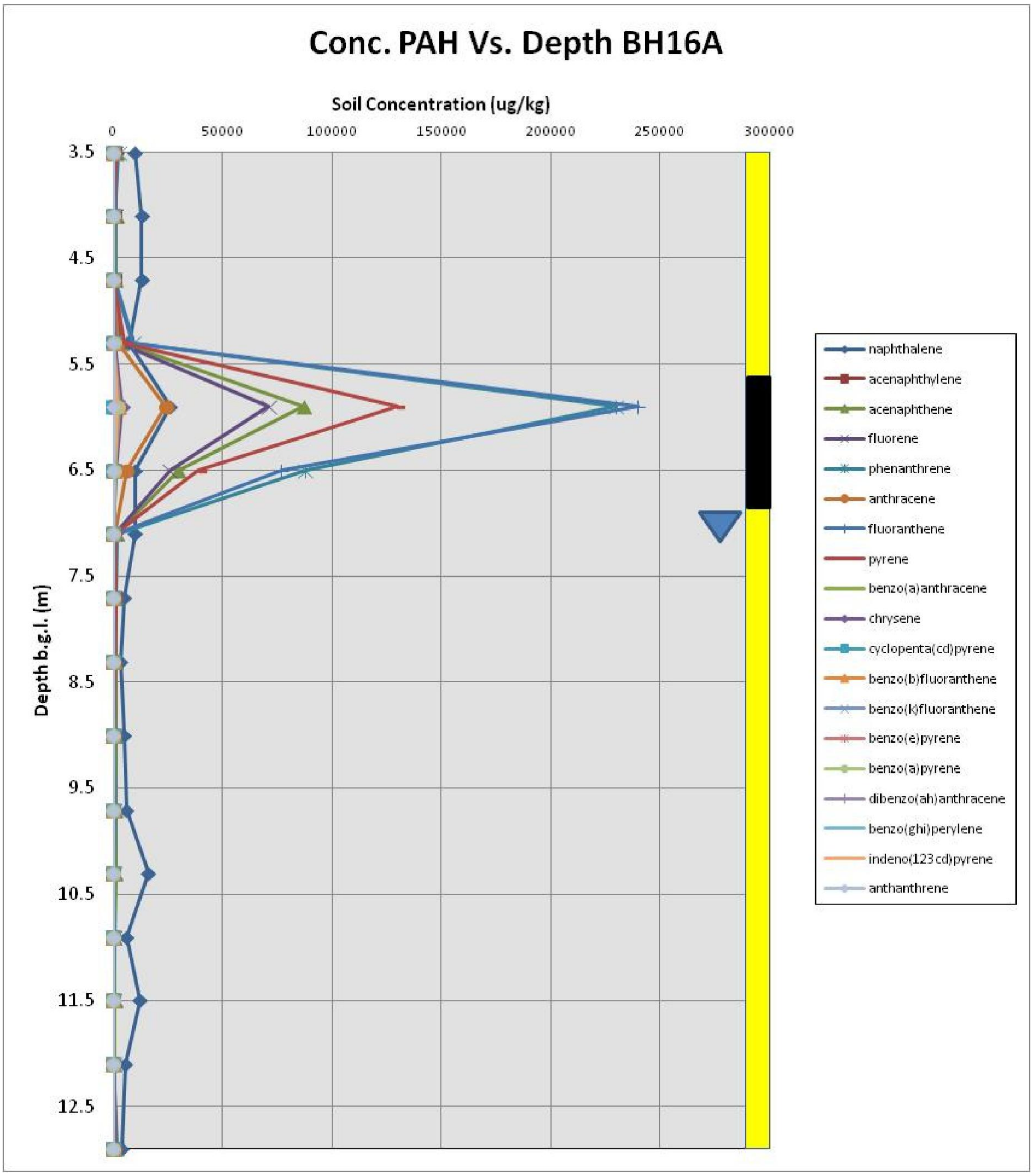


Figure 5.2: Soil PAH Concentrations Vs Depth from BH16A, study site E. (Yellow bar represents clay/silt soils, black bands represent peat/organic clay and triangle indicates piezometric level).

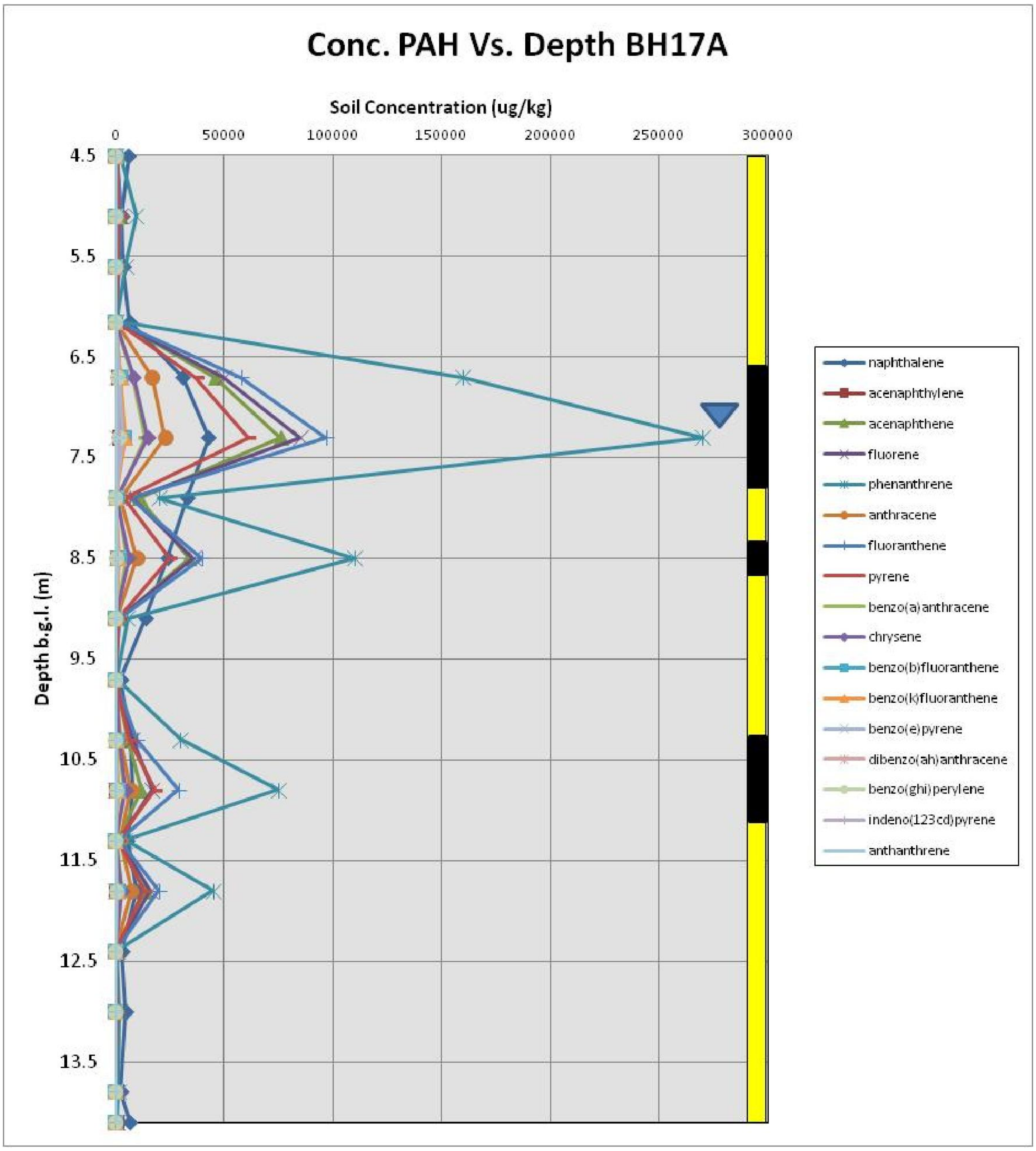


Figure 5.3: Soil PAH Concentrations Vs Depth from BH17A, study site E. (Yellow bar represents clay/silt soils, black bands represent peat/organic clay and triangle indicates piezometric level).

The analyses detailed in Figures 5.1 to 5.3 were performed on soil samples without specific separation into respective domains identified within alluvium as detailed in Section 5.3 of this document. Concentrations of Total Polycyclic Aromatic Hydrocarbons (calculated as the summation of concentration of the 19 PAHs tested) ranged from 2.8 mg/kg (BH18A, 9.8m) to 1200 mg/kg (BH15A, 9.6m). The study site has a history of creosote usage. Creosote comprises low to middle distillates of coal tar and this was apparent in the composition of the PAH signature with the predominance of the lower molecular weight PAHs.

In BH15A, BH16A and BH17A PAH levels are generally high above the standing groundwater level observed in monitoring wells (c. 7.5m b.g.l.). Above the groundwater capillary fringe soil will be sub-saturated in respect to water and the creosote does not, therefore, need to displace the water to occupy the soil pore spaces (at neutral pH water is preferentially wetting of silicate minerals in respect to creosote, thus coating the surface of minerals, see Section 3). In BH16A the highest levels of contamination are restricted to a narrower zone between 5.3m and 7.1m depth coincident with a peat horizon. Likewise, high concentrations of PAH are associated with peat/organic clay bands in the other boreholes. These deposits have a high organic content and, in accordance with Equilibrium Partitioning Theory, hydrophobic hydrocarbons are highest in soils with a high organic content.

Phenanthrene generally predominates. The relative contribution of individual species appears to vary little although the relative proportion of naphthalene appears to vary most significantly. Variations may be due to loss by volatilization during weathering which would lead to preferential loss of lower molecular weight PAH species, or partitioning to soil organic matter, which would lead to preferential enrichment of high molecular weight (i.e. more lipophilic) PAH species.

Highest levels of PAH in the alluvial soil profile were generally encountered in zones identified as peat or organic clay (i.e. clay with significant portion of peat) during logging (indicated by black bands in Figures 5.1 to 5.3). These soils have a high fraction of organic carbon (foc) and therefore present abundant hydrophobic sites for PAH sorption. Clay and silt soils (indicated by yellow bands) have a low foc and therefore offer less sites for PAH sequestration.

5.3. Detailed Logging of Alluvium

In keeping with the results of the geotechnical analysis, during logging the alluvium was seen to comprise predominantly clay/silt size minerals with subordinate bands of peat and usually a basal gravel. Alluvial peat and clay was often ‘firm’ near the surface due to desiccation, soon becoming soft to very soft with depth. A typical borehole log from an investigation site located on Severn Estuary Alluvium is presented in Appendix E.

During the detailed logging it was apparent that the Severn Estuary alluvium contained a number of structural features which may not be apparent under typical logging conditions. The clay/silt was often thinly laminated. The matrix of the clay/silt was often penetrated by bio-pores. The bio-pores were almost always vertical to sub-vertical in orientation (Figure 5.4). Pores either contained fibrous plant fragments, which partially or completely filled the pore, or were completely open. Some pores were observed to terminate within samples whilst others were seen to extend throughout the length of the longest samples (up to 450mm length in the case of U100 samples).

Figure 5.4: Vertical section of Alluvium from study site E. Note the vertical pore structure. (BH102, 6.00m – 6.45m, Study Site E).

In soil collected from contaminated area the pores were often coal tar/creosote stained (Section 5.5) and malodorous if filled with tar free-product. Contaminated pores were observed beneath the phreatic level, suggesting water can be displaced by the DNAPLs. This is consistent with what would be expected since the DNAPL is denser than water and introduced from above.

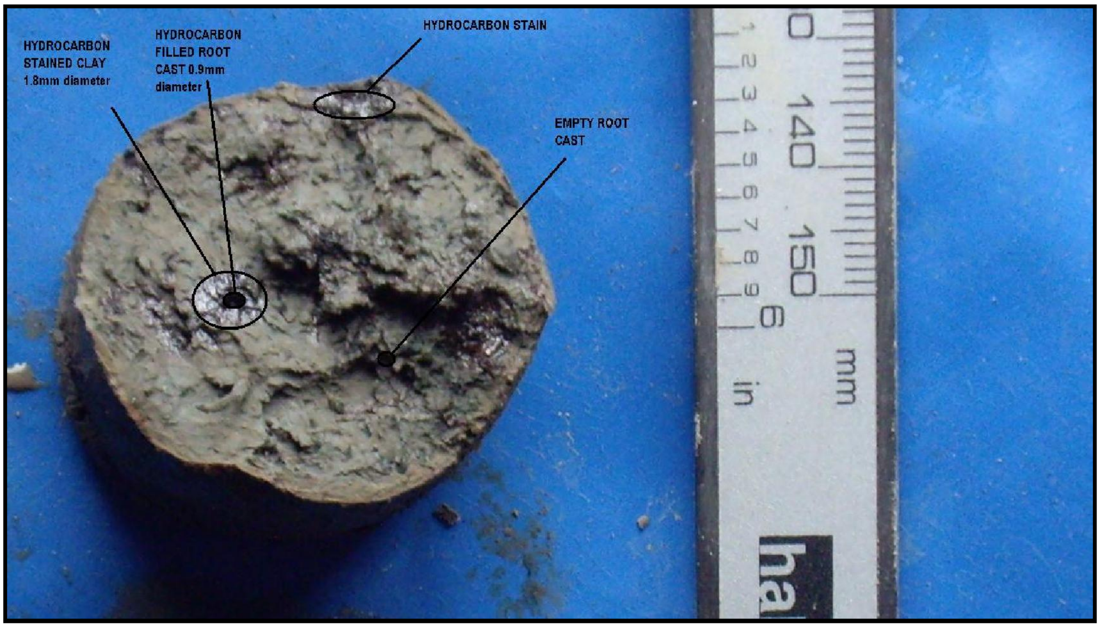


Figure 5.5: Typical example of alluvium from a contaminated site. Note the hydrocarbon stained pore (Study Site G, BH1, 3.00m – 3.45m).

Pore structures were less prevalent beneath the phreatic horizon (Figure 5.6). This may be due to the fact that these soils are softer as a consequence of a higher moisture content. The presence of organic material below the phreatic horizon would suggest that conditions were conducive to plant growth during deposition (Figure 5.7). The phreatic horizon would have risen in tandem with sea-level rise.

Figure 5.6: Example of alluvium recovered from depth. (Study Site G, BH1, 10.00m – 10.45m).

The pore structures were observed in samples from the study sites located on both sides of the Severn Estuary.

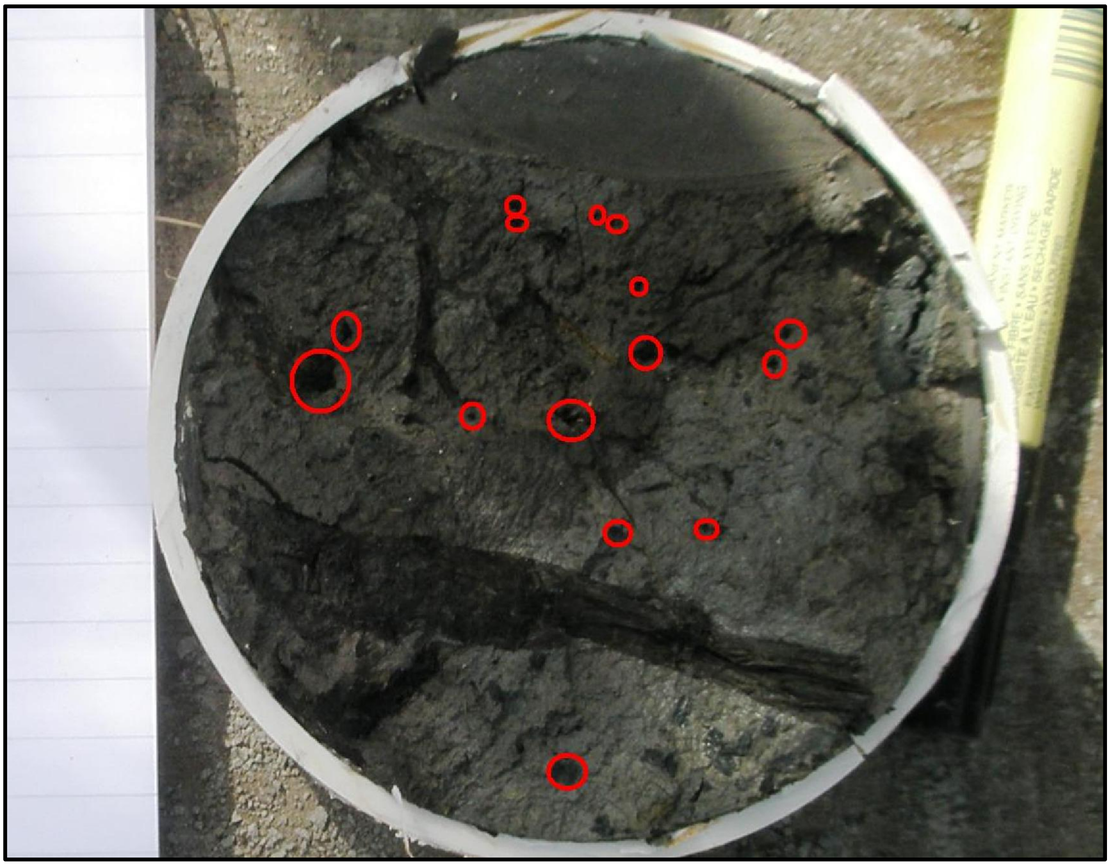


Figure 5.7: Alluvium from study site F. Note pore structures and horizontal woody fragment (Selected vertical pores highlighted in red).

Detailed measurements of pore diameters were made during the logging using digital callipers. Pores typically ranged from ‘pin-holes’, too small to measure, to pores of nearly 2.5mm diameter. The cross-sectional area of the logged samples varied, depending on the drilling and sampling technique used.

Pore data from twenty two samples taken from a range of depths at study site A and study site E are detailed in Figure 5.8. The cross-sectional area of these samples ranged from 0.0079m^2 to 0.00096m^2. The cross-sectional area of the pores was calculated from their recorded diameter, assuming the pores were effectively circular. Since the cross-sectional area and number of the pores of each size range was known, along with the cross-sectional area of the sample, the number of pores per m^2 of soil could be estimated.

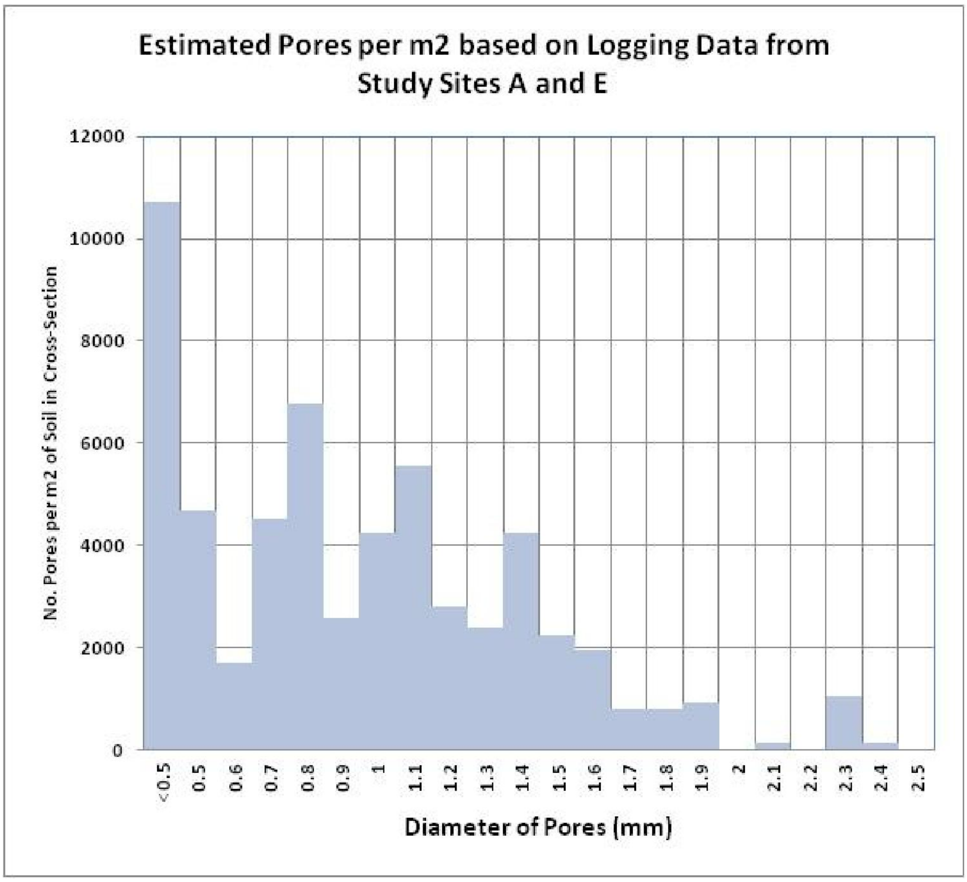


Figure 5.8: The Estimated number of pores of selected diameters per meter squared of soil surface. Based on twenty two alluvium soil samples up to 100mm in diameter from study sites A and E. Note that pores <0.5mm in diameter (too small to measure accurately) were assumed to have a diameter of 0.25mm.

From these data it was possible to calculate the area of the pores per unit area of soil. The results are displayed in Table 5.1.

Table 5.1: Total Area of Pores per m^2 of Soil in Selected Sample from Study Site E and A

Location	Borehole	Depth (m b.g.l.)	Total Area of Pores, m^2, per m^2 of Alluvium in plan
E	BH101	4.0	1.79×10^{-2}
E	BH101	5.0	5.83×10^{-4}
E	BH101	7.0	2.56×10^{-3}
E	BH101	8.0	7.90×10^{-3}
E	BH101	9.0	1.06×10^{-2}
E	BH101	10.0	5.55×10^{-3}
E	BH101	11.0	2.82×10^{-3}
E	BH101	12.0	2.03×10^{-2}
E	BH102	3.0	6.28×10^{-4}
E	BH102	4.0	4.67×10^{-4}
E	BH102	5.0	1.37×10^{-2}
E	BH102	5.5	2.30×10^{-2}
E	BH102	6.0	7.00×10^{-3}
E	BH102	6.5	2.85×10^{-3}
E	BH102	8.0	8.09×10^{-3}
E	BH102	10.0	1.96×10^{-2}
E	BH102	13.0	1.91×10^{-2}
A	BH1	1.0	7.02×10^{-3}
A	BH1	3.0	1.96×10^{-2}
A	WS1	2.0	1.94×10^{-3}
A	WS1	3.0	7.55×10^{-4}
A	WS1	4.5	2.03×10^{-3}

Plant fragments observed within some pores were seen to be extremely delicate. Plant fibres supported by the soil matrix were observed to extend up to lengths exceeding the longest soil samples (450mm).

The detailed logging of samples from the four study sites has revealed that the alluvial clay/silt exhibits consistent physical characteristics throughout the Severn Estuary. The alluvium contains abundant penetrations of open and fibre filled pores with diameters of less than 2.5mm. Visual and olfactory inspection of soil samples recovered from contaminated areas shows that the pores can contain viscous Non-Aqueous Phase Liquids such as coal tar and creosote. Therefore, contrary to the common assumption that alluvial clay is an effective, impermeable barrier to liquid contaminant migration on account of it being dominated by clay and silt size clasts, it is able to transport DNAPL contaminants via a network of macroscopic structure which act as conduits. The current study has recorded examples of pores accounting for up to 2.3% of the horizontal surface area of the alluvium. This represents a pore volume of up to 23 litres per m^3 of alluvium.

Holden (2009) described this type of macroporosity as ‘effective’ porosity. In addition, clay soils typically contain c.50 % soil porosity from interstitial voids between soil grains (Terra Firma Wales Ltd, Pers. Comms.), although their contribution to permeability is negligible as the pathway between these voids is so tortuous.

A portion of the pores encountered in the alluvium contained fossil plant fragments. The fragments were predominantly fibrous and roughly circular in cross section with diameters typically <2.5mm, being predominantly orientated in a vertical to sub-vertical position.

Larger irregular fragments were encountered in peat bands and as isolated fragments in random orientation. All fossil plant fragments were extremely delicate once removed from the surrounding soil matrix.

5.4. Chemical Analysis of Detail Logged Samples at Cardiff University

Accelerated Solvent Extraction of samples of separated matrix soils and pore soil revealed significant concentrations of naphthalene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene in some of the solvent extracts. The concentration of these determinants in soil matrix and soil pore domains are presented in Table 5.2.

Table 5.2: Summary of ASE Testing of Alluvium Domains

		Soil Concentration (mg/kg)					
Sample Source	**Sample I.D.**	**Naphthalene**	**Fluorene**	**Phenanthrene**	**Anthracene**	**Fluoranthene**	**Pyrene**
G BH1 3m	Matrix PM3	0.0	0.0	0.0	0.0	0.0	0.0
G BH1 3m	Pore PR3	0.0	38.5	283.2	45.0	3.0	92.0
G BH1 4m	Matrix PM4	0.0	0.0	0.0	0.0	0.0	0.0
G BH1 4m	Pore PR4	0.0	5.5	79.2	18.8	0.5	32.9
E BH102 6m	Matrix 6M	0.0	0.7	11.1	2.1	0.0	0.7
E BH102 6m	Pore 6R	5.5	6.8	48.0	2.0	0.1	3.6
E BH102 8m	Matrix 8M	0.0	0.0	0.0	0.0	0.0	0.0
E BH102 8m	Pore 8R	6.7	10.2	39.1	2.6	0.4	8.9

It can be seen from Table 5.2 that significantly higher soil concentrations of creosote/coal tar occur within the pores than within the surrounding soil matrix. PAH was not detected in the soil matrix samples from study site G (PM3 and PM4, BH1) and in one of the matrix samples from study site E (8M, BH102). PAH was detected in the matrix sample from 6m depth, study site E (6M, BH102). Study site E was contaminated by creosote while study site G was contaminated by coal tar.

In matrix sample 6M naphthalene and fluoranthene were absent and the recorded concentrations of fluorene, phenanthrene and pyrene ranged from approximately one tenth to one fifth of the concentration recorded in the corresponding bio-pore sample. The concentration of anthracene was slightly higher in the matrix sample. A comparison of the GC traces for typical soil pore and soil matrix samples is presented in Figure 5.9. It is apparent in the figure that the pore soil contains significantly higher PAH concentrations than the matrix sample. However, pores make up less than 3% of the soil volume.

The highest concentrations of PAH contamination were recorded from the total analysis of soil from BH15A where concentrations of naphthalene, fluorene, phenanthrene and anthracene were recorded at 230 mg/kg, 130 mg/kg, 340 mg/kg and 210 mg/kg, respectively despite these samples comprising a mixture of matrix and bio-pore soil. However, BH15A was most proximate to a former buried creosote tank which may account for the exceptionally high recorded concentrations. The highest concentration of fluoranthene and pyrene were recorded in BH16A (240 mg/kg and 130 mg/kg respectively at 5.90m depth) which also lay in close proximity to the aforementioned tank. It is likely that if the bio-pores had been isolated from soil matrix taken from BH15A even higher concentrations would have been recorded.

In general, significantly lower concentrations of naphthalene were recorded in the samples subject to ASE. Volatile loss during oven drying may account for some reduction of this volatile PAH. Alternatively, its absence in samples from study site G may be explained by the fact that the contamination at study site G may be significantly older, with the MGP facility having ceased between 1931 and 1966. Whereas study site E is still an active creosote works.

It should be noted that since the analysis of total soils included testing of undifferentiated pores and matrix the actual pore concentration is diluted by matrix soil.

The presence of bio-pores allows contaminant concentrations to exceed theoretical soil saturation levels based solely on interstitial pore space alone (i.e geotechnical theory may be used estimate the theoretical soil saturation level based on the diameter of soil clasts, not taking account of additional void structures in the soil mass)

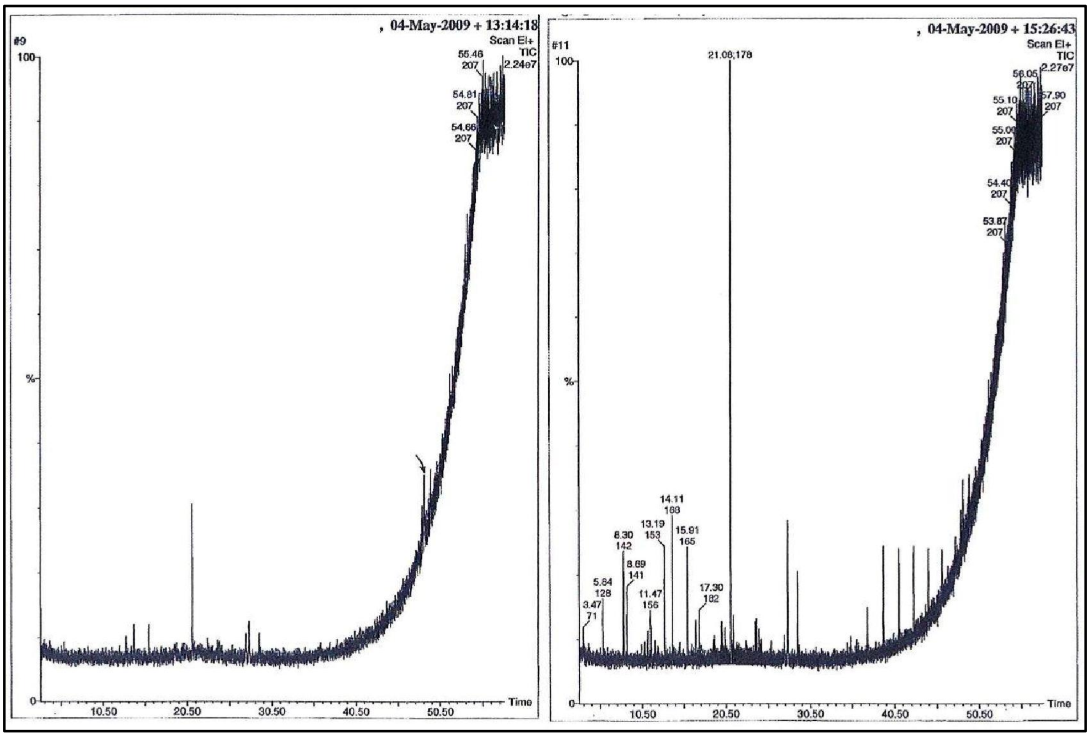


Figure 5.9: Comparison of GC Trace of soil from a Pore (Right) and Soil Matrix (Left) from 6m depth, BH102, study site E.

5.5. Soil Characterisation

5.5.1. Mineralogy

A typical X-Ray Diffraction trace for alluvial clay/silt is presented as Figure 5.10 and a typical trace for alluvial peat is presented as Figure 5.11. The full set of X-Ray Diffraction traces is presented in Appendix C.

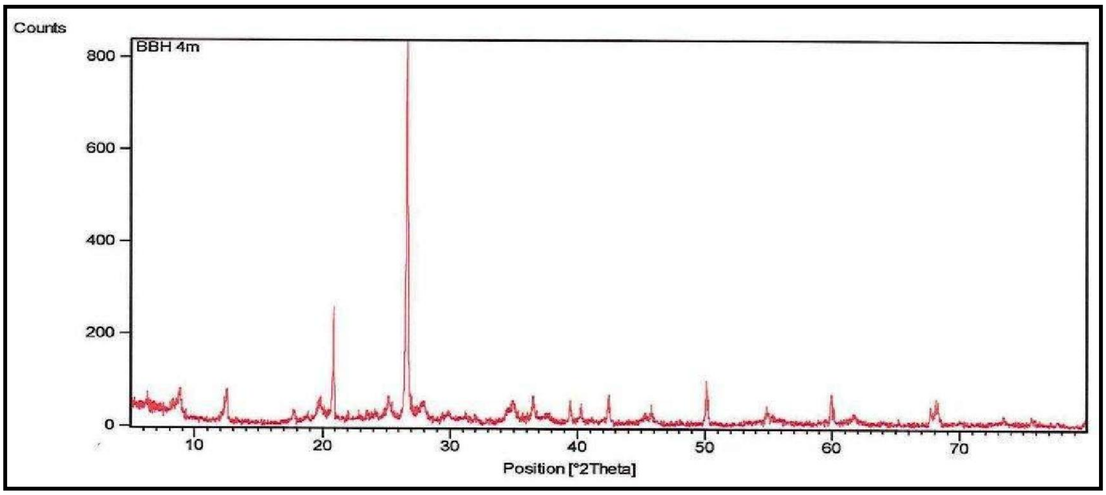


Figure 5.10: X-Ray Diffraction trace for alluvial clay/silt from BH101 4.0m, Study Site E.

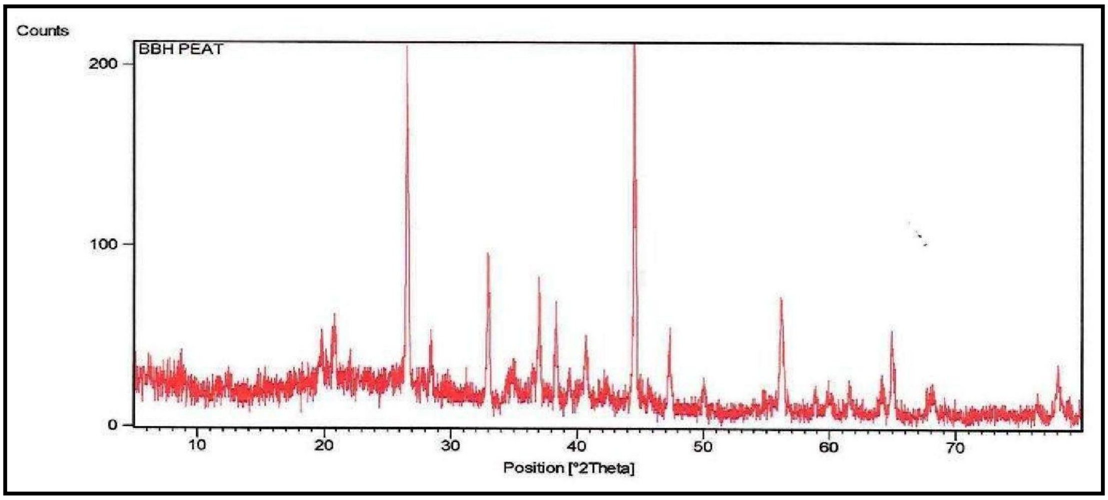


Figure 5.11: X-Ray Diffraction trace for alluvial peat from BH101 6.6m, Study Site E.

The interpretation of the diffraction patterns was executed automatically by X’Pert Industries Software. Due to the exhaustive data sets contained within this programme further data screening was undertaken by Jeff Rowlands, CLEER Laboratory Technician experienced in X-Ray Diffraction interpretation.

It is apparent from the traces presented in Appendix C that the alluvial clay/silt from the various depths and locations around the Severn Estuary is dominated by the same mineralogy. All eleven traces exhibit the most dominant peak at a diffraction angle of approximately 26.7˚. Further significant peaks were encountered at diffraction angles 8.9˚, 12.7˚, 20.9˚, 36.7˚, 39.5˚, 42.6˚, 45.9˚, 50.1˚, 55.0˚, 60.1˚ and 68.26˚. Further subordinate peaks were also recorded. The peak patterns were input into X’Pert Industries software.

To refine the search results samples PORTIS B and WSM B were subject to Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis to determine the identity of principal cations contained within the silicate. The ICP-OES analysis was performed at the CLEER Laboratories, Cardiff University. Calcium, magnesium, potassium, aluminium and iron were identified as significant contributors. Terra Firma Wales Ltd submitted a sample of alluvium from study site E to Derwentside Environmental Testing Services Limited for quantified analysis of these elements. The results of the analysis are presented in Table 5.3.

Table 5.3. Results of Analysis on Alluvium Sample	
Element	**Concentration**
Calcium	7,600
Magnesium	5,700
Potassium	7,600
Aluminium	18,000
Iron	37,000

Results courtesy of Terra Firma Wales Ltd

The identified elements were entered into the X'Pert Industries software as limiting criteria to narrow the field of potential minerals.

The X'Pert Industries database revealed that mineral illite ($K\ Al\ (Si_3\ Al)\ O_{10}\ (OH)_2$) had diffractions peaks coincident with the principal peaks at 26.7˚ and 20.9˚ and the minerals kaolinite ($Al_2\ (Si_2O_5)\ (OH)_4$) and montmorillonite ($(Na,\ Ca)_{0.3}\ (Al,Mg)_2\ Si_4O_{16}\ (OH)_2 . {}_xH_2O$) have peaks coincident with the principal peak at 26.7˚. These minerals also have peaks coincident with several of the subordinate peaks.

Figure 5.11 shows that the trace for peat, too, has a strong peak at diffraction angle 26.7˚ and also contains the peak pattern similar to the other traces. In addition, a strong peak exists at 44.6˚. X'Pert industries software found that graphite had peaks coincident with the two principal peaks of the peat sample.

The interpretation has revealed that alluvium across the Severn Estuary is dominated by silicate mineralogy and that the mineral composition of the alluvial clay/silt is consistent across the study area suggesting a consistent source of the geological material across the estuary during the entire duration of deposition, and effective mixing of this material. These minerals are seen to intrude into the peat deposits studied.

5.5.2. Soil Organic Content

The results of the analyses are summarised in Table 5.4.

Table 5.4: Summary of Organic and Inorganic Carbon Analysis

Sample	Total Organic Carbon (%)	Total Inorganic Carbon (%)
Calibration – Glucose	40.519 – 40.929	-
Calibration - $CaCO_3$	-	12.120 – 12.590
Site A – BH1 2.3m (Peat)	24.89	0.000
Site A – BH1 4.0m (Silt/Clay)	0.0063	0.000
Site A – BH1 17.7m (Peat)	14.38	0.000
Site A – BH1 25m (Clayey Peat)	10.32	0.825
Site A – BH1 27m (Clay)	0.0009	0.000
Site A – WS2 2.7m (Peat)	39.41	0.000
Site E – BH101, 6.6m – 6.8m (Peat)	28.53 - 29.10 (28.82*)	0.000
Site E – BH101, 9.0m (Silt/Clay)	0.46	0.000

* - Average Value

It can be seen from Table 5.4 that the alluvial silt/clay contains trace amounts of organic carbon and undetectable to trace amounts of inorganic carbon.

The peat from study site A was recorded as containing between 10.32% and 39.41% Total Organic Carbon and between 0% and 0.83% Inorganic Carbon. These variations are consistent with the on-site observations that the peat was, to varying degrees, combined with silt/clay representing episodes of marine inundation during deposition.

The peat band from study site E (6.6m depth) was analysed twice and recorded an organic carbon content of 28.53% and 29.10% and undetectable levels of inorganic carbon. This material was used for all subsequent sorption analyses involving peat and, during these analyses, is assumed to have an average organic carbon content of 28.82%.

5.5.3. Moisture Content & Plasticity Index

Plasticity Index test data from Geo-Laboratory Testing Services Ltd (Report GEO/6802/08) are presented in Annex D.

The results of the moisture content and plasticity testing are summarised in Table 5.5.

Table 5.5: Summary of Moisture Content and Plasticity Testing for Alluvium from BH101, Study Site E

Sample Depth (m. bgl.)	Soil Type	Moisture Content (%)	Liquid Limit (%)	Plastic Limit (%)	Plasticity Index (%)
4.00	Clayey SILT	33	-	-	-
5.00	v. slightly sandy Clayey SILT	38	-	-	-
6.00	v. slightly sandy clayey SILT	52	-	-	-
8.00	v. slightly sandy clayey SILT	47	-	-	-
9.00	v. slightly sandy clayey SILT	43	48	24	24
10.00	v. slightly sandy clayey SILT	52	-	-	-
11.00	v. slightly sandy clayey SILT	52	-	-	-
12.00	v. slightly sandy clayey SILT	46	-	-	-
13.00	v. slightly sandy clayey SILT	57	-	-	-
13.30	Sandy clayey GRAVEL	2.6	-	-	-
14.50	Clayey sandy GRAVEL	7.0	-	-	-

In addition to the above results, Terra Firma Wales Ltd provided plasticity data for alluvium from a site located north of study site E. Plastic limits for alluvium ranged from 21% to 39% and liquid limits ranged from 41% to 73%, with plasticity indices ranging from 20% to 35%. The moisture content of the samples was generally in the plastic range above groundwater and in the liquid range below ground water.

The majority of the alluvial soil has a moisture content approaching the upper limit of plastic behaviour, or exceeding the soils liquid limit. Such clay/silt soils are typically soft to very soft, making them susceptible to disruption during sampling and subsequent handling, making their fine structures susceptible to disruption.

5.5.4. Particle Size Distribution

Particle Size Distribution analysis of samples from BH101, study site E, revealed that the majority of the alluvial deposit contained between 69% and 81% silt sized particles (0.002 mm to 0.063) and between 19% and 30% clay sized particles (<0.002 mm). The content of particles greater than 0.063 mm ranged from 0% to 8%. The predominance of fine soil particles is usually indicative of low soil permeability.

A peat band was encountered at 6.7m depth which recorded 60% sand and gravel size (>0.063mm), 24% silt and 16% clay.

Soil from the confined aquifer beneath the alluvium (samples 13.3m and 14.5m) contained between 90% and 91% above silt size, between 2% and 7% silt and between 2% and 8% clay.

5.5.5. In-Situ Soil Strength

In-Situ Soil Strength was calculated from Standard Penetration Tests (SPTs) performed during drilling.

Severn Estuary alluvial silt/clay and peat are generally ‘soft’ to ‘very soft’ (see Section 5.1) although desiccated crusts are sometimes encountered at shallow depth which exhibit ‘firm’ consistency. In accordance with BS:5930 (1999) clay described as ‘very soft’ has an un-drained shear strength of less than 20 kPa whilst ‘soft’ clay has an un-drained shear strength of between 20 - 40 kPa.

The low strength makes the soils fine structures susceptible to disruption during sampling and subsequent handling. It is anticipated that the soils become modified during preparation for permeability testing by standard methods, making the results misleading.

5.6. Partition Coefficients

5.6.1. Sorption to Alluvium

Initially results entered into Excel and displayed graphically as S Vs. C_e allowed a visual assessment of the data. To allow comparison to the data from Jonker (2008), the results of sorption testing were also analysed using the Log Freundlich Isotherm (equation 3.5).

The unmodified isotherm graphs for the sorption of phenanthrene to Severn Estuary peat are presented in Figures 5.12 to 5.15.

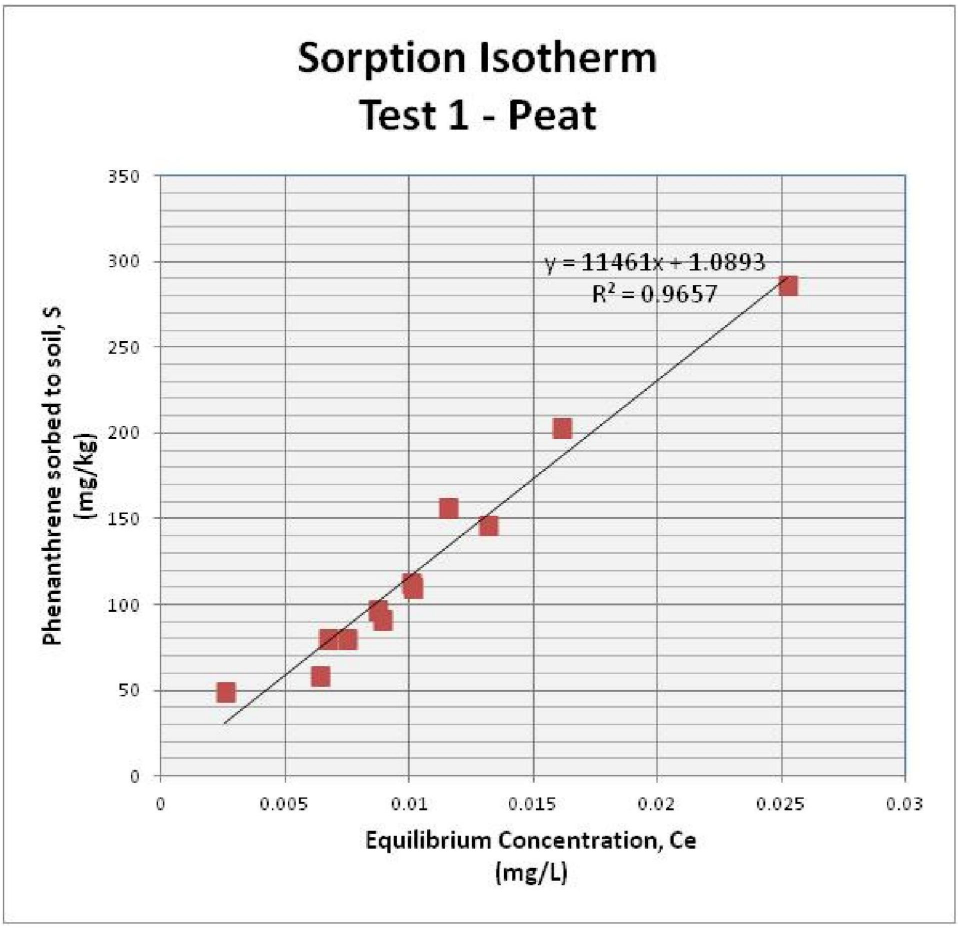


Figure 5.12: Unmodified S Vs C_e data for sorption of phenanthrene to Severn Estuary peat (Study Site E, BH101, 6.6m – 6.8m, Test 1).

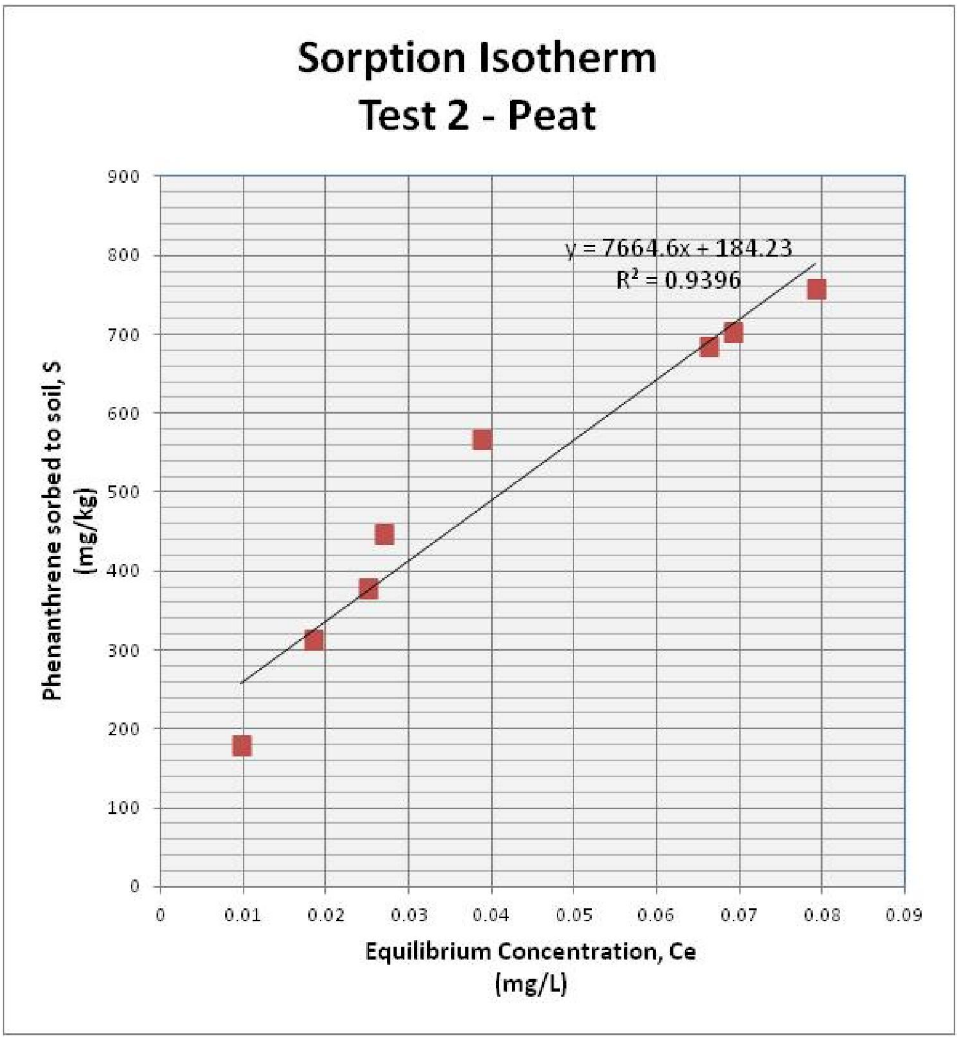


Figure 5.13: Unmodified data for S Vs C_e for sorption of phenanthrene to Severn Estuary peat (Study Site E, BH101, 6.6m – 6.8m, Test 2).

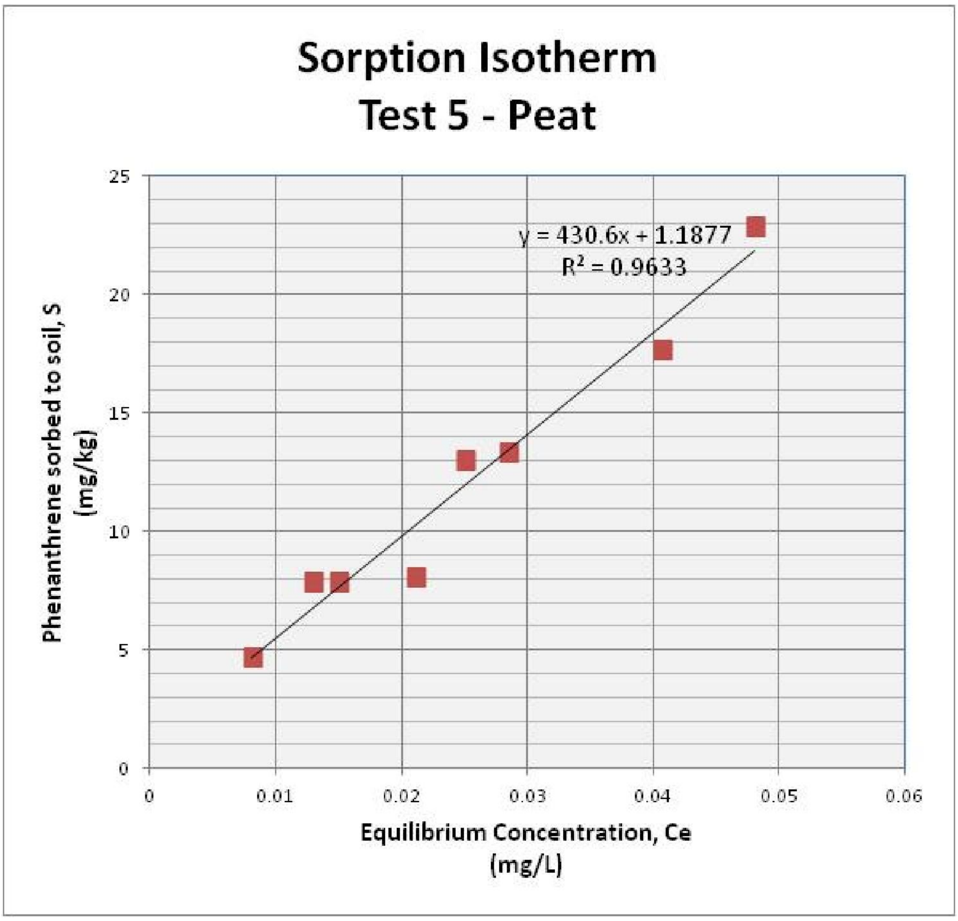


Figure 5.14: Unmodified data for S Vs C_e for sorption of phenanthrene to Severn Estuary peat (Study Site E, BH101, 6.6m – 6.8m, Test 5)

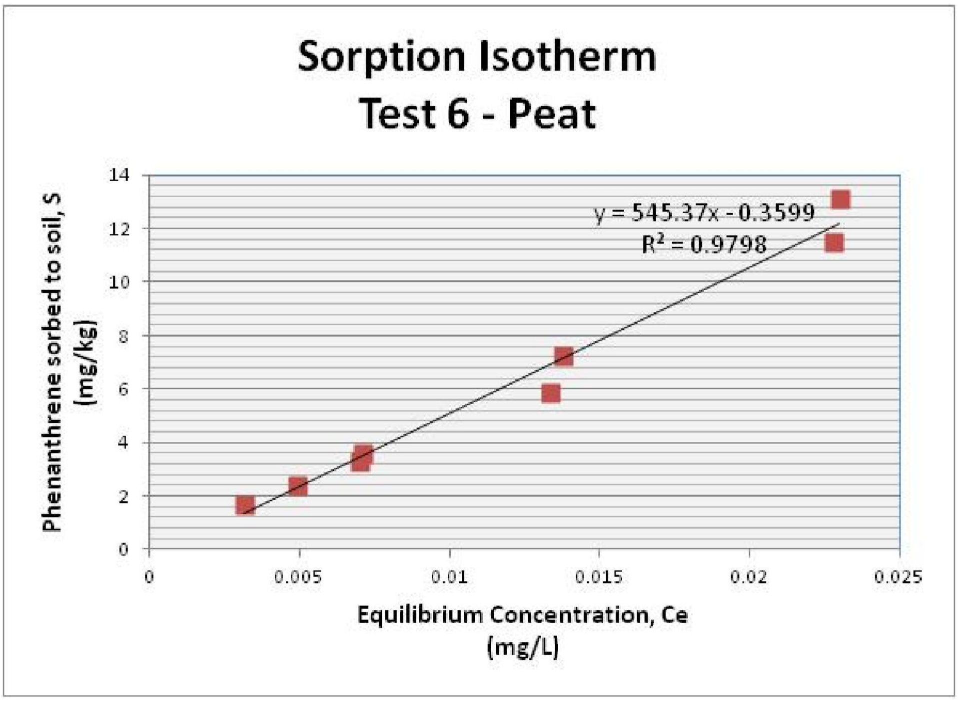


Figure 5.15: Unmodified data for S Vs C_e for sorption of phenanthrene to Severn Estuary peat (Study site E, BH101, 6.6m – 6.8m, Test 6)

The unmodified sorption isotherm for the sorption of phenanthrene to Severn Estuary clay is presented in Figure 5.16.

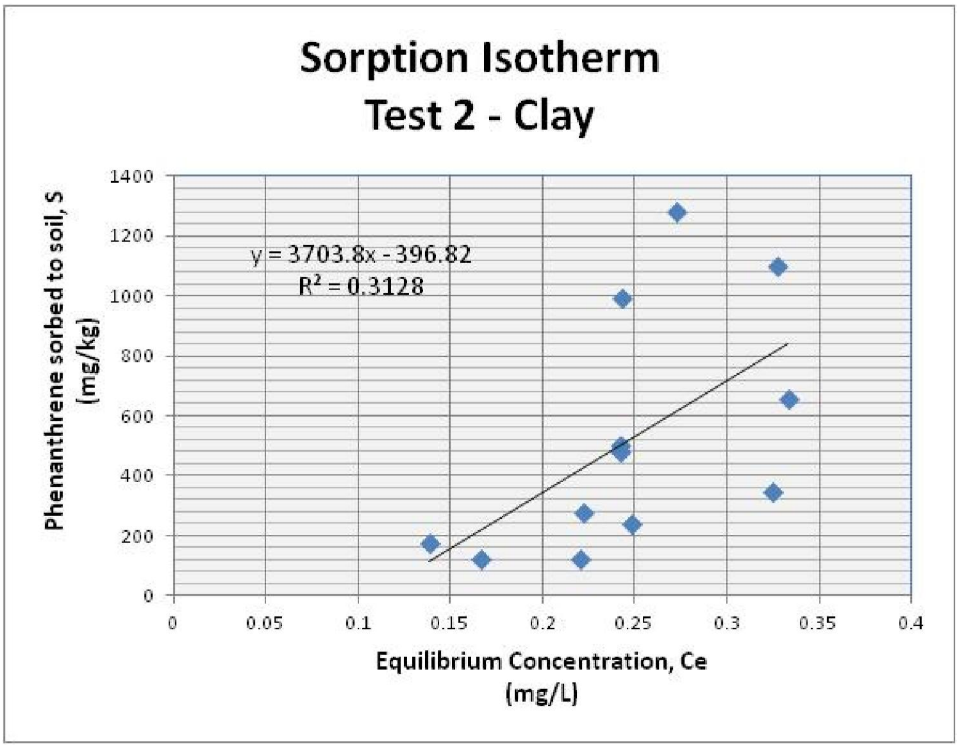


Figure 5.16: Unmodified data for S Vs C_e for sorption of phenanthrene to Severn Estuary clay. (Study Site E, BH101, 9.0m, Test 2)

The Freundlich linearised isotherms, calculated using equation (3.5), as described by Jonker (2008), for the sorption of phenanthrene to Severn Estuary peat are presented in Figures 5.17 to 5.20.

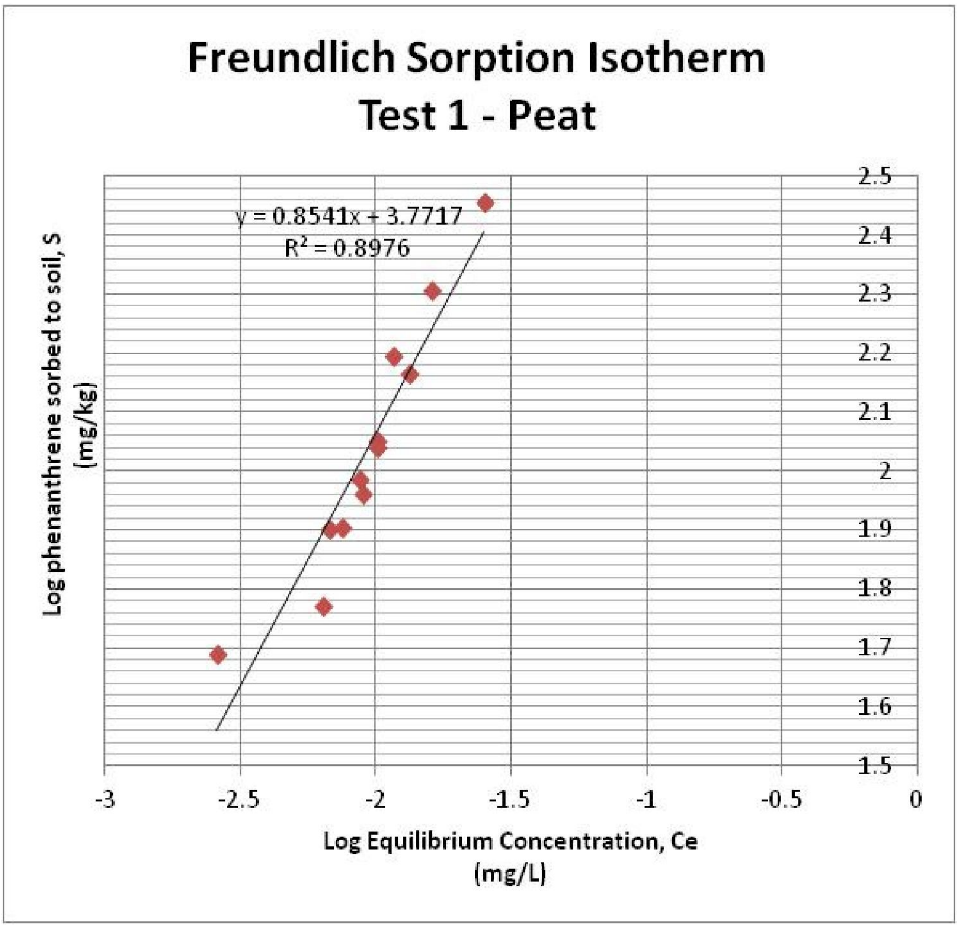


Figure 5.17: Freundlich Linearised for sorption of phenanthrene to Severn Estuary peat (Study Site E, BH101, 6.6m – 6.8m, Test 1)

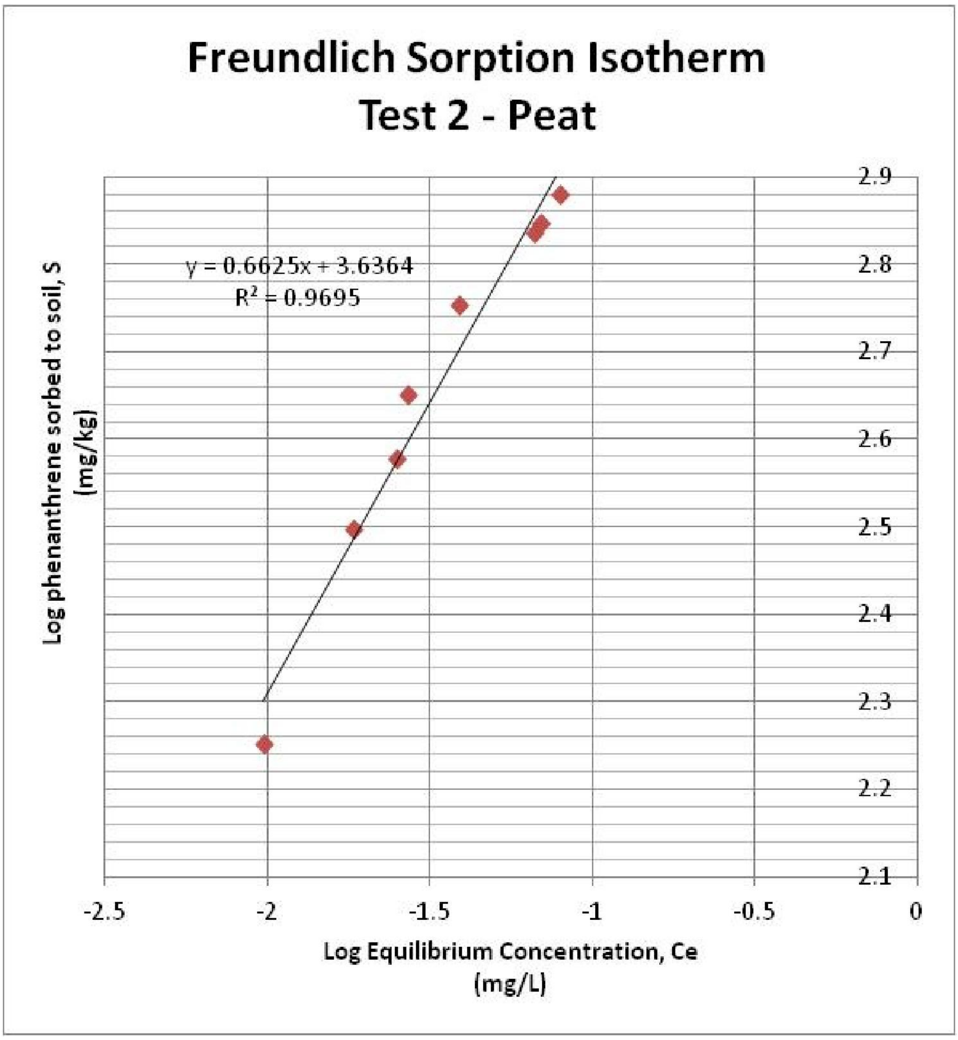


Figure 5.18: Freundlich Linearised for sorption of phenanthrene to Severn Estuary peat (Study Site E, BH101, 6.6m – 6.8m, Test 2)

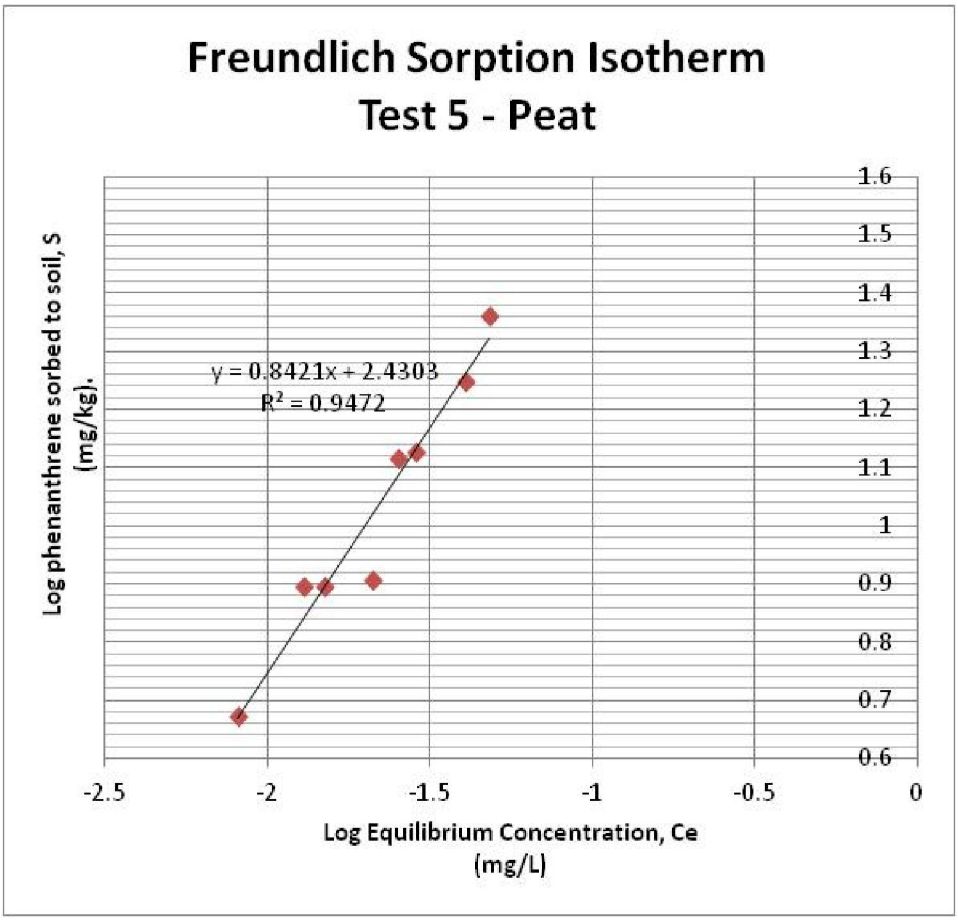


Figure 5.19: Freundlich Linearised of sorption of phenanthrene to Severn Estuary peat (Study Site E, BH101, 6.6m – 6.8m, Test 5)

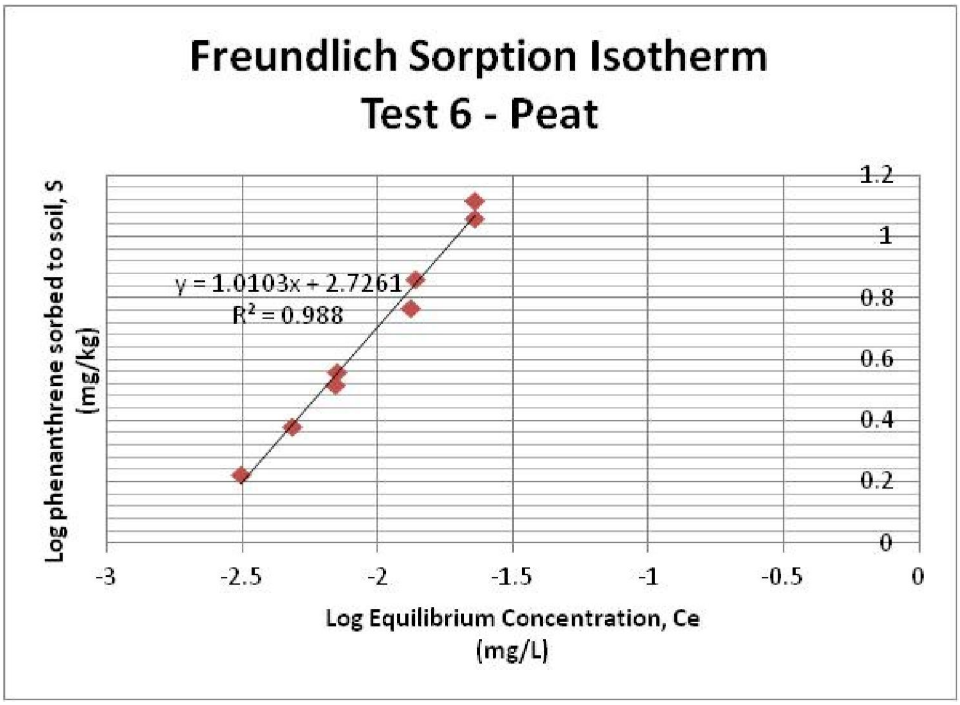


Figure 5.20: Freundlich Linearised of sorption of phenanthrene to Severn Estuary peat (Study Site E, BH101, 6.6m – 6.8m, Test 6)

The graph of the Freundlich linearised sorption data for phenanthrene to Severn Estuary clay is presented in Figure 5.21.

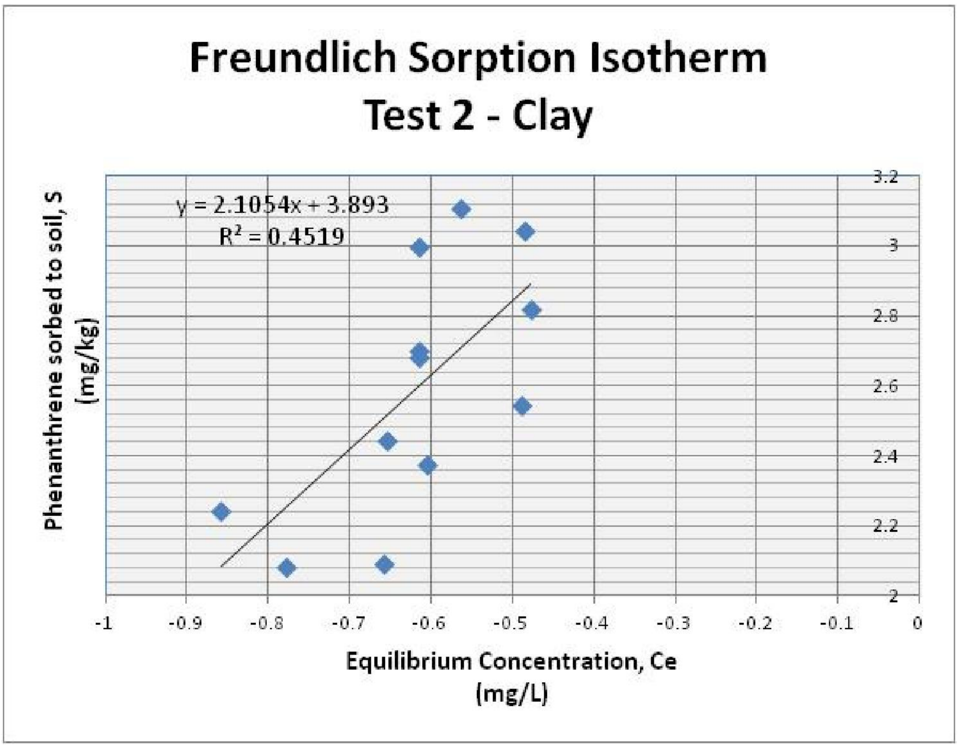


Figure 5.21: Freundlich Linearised for sorption of phenanthrene to Severn Estuary clay (Study Site E, BH101, 9.0m, Test 2)

The Log S and Log C_e data from the experiment, and n calculated from the gradient of the graph, was used to calculate Log K_f for each data point. Excel calculated a gradient for a best fit line. From the rearranged Freundlich equation (3.5), values of K_f were calculated.

In addition to the unmodified isotherm and Freundlich isotherm, the sorption data was entered into the Langmuir Isotherm using the Isotherm Spreadsheet published by Bolster (2007). These isotherms are presented in Appendix G.

Desorption experiments were performed on the samples from Test 1 and Test 2. The results of the desorption tests are presented, unmodified, in Figures 5.22 and 5.23.

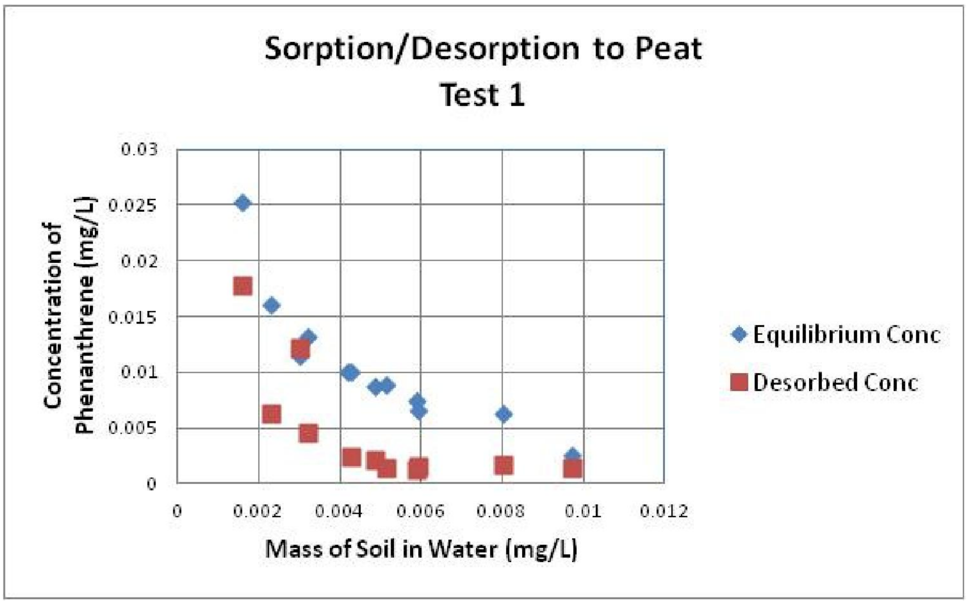


Figure 5.22: Unmodified data for sorption and desorption of phenanthrene to Severn Estuary peat (Study Site E, BH101, 6.6m – 6.8m, Test 1)

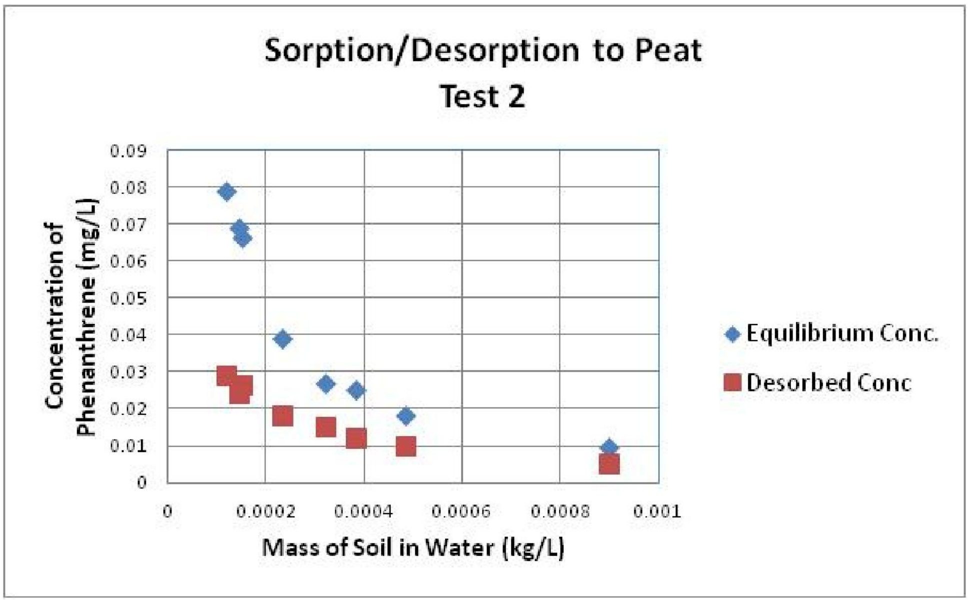


Figure 5.23: Unmodified data for sorption and desorption of phenanthrene to Severn Estuary peat (Study Site E, BH101, 6.6m – 6.8m, Test 2)

5.6.2. Kinetics of Phenanthrene Sorption to Peat

During Test 4 the phenanthrene and soil suspension were agitated for contact period of between 1 hour and 306.75 hours before extraction. The graph of the final equilibrium concentration Vs mass of phenanthrene sorbed is presented in Figure 5.24.

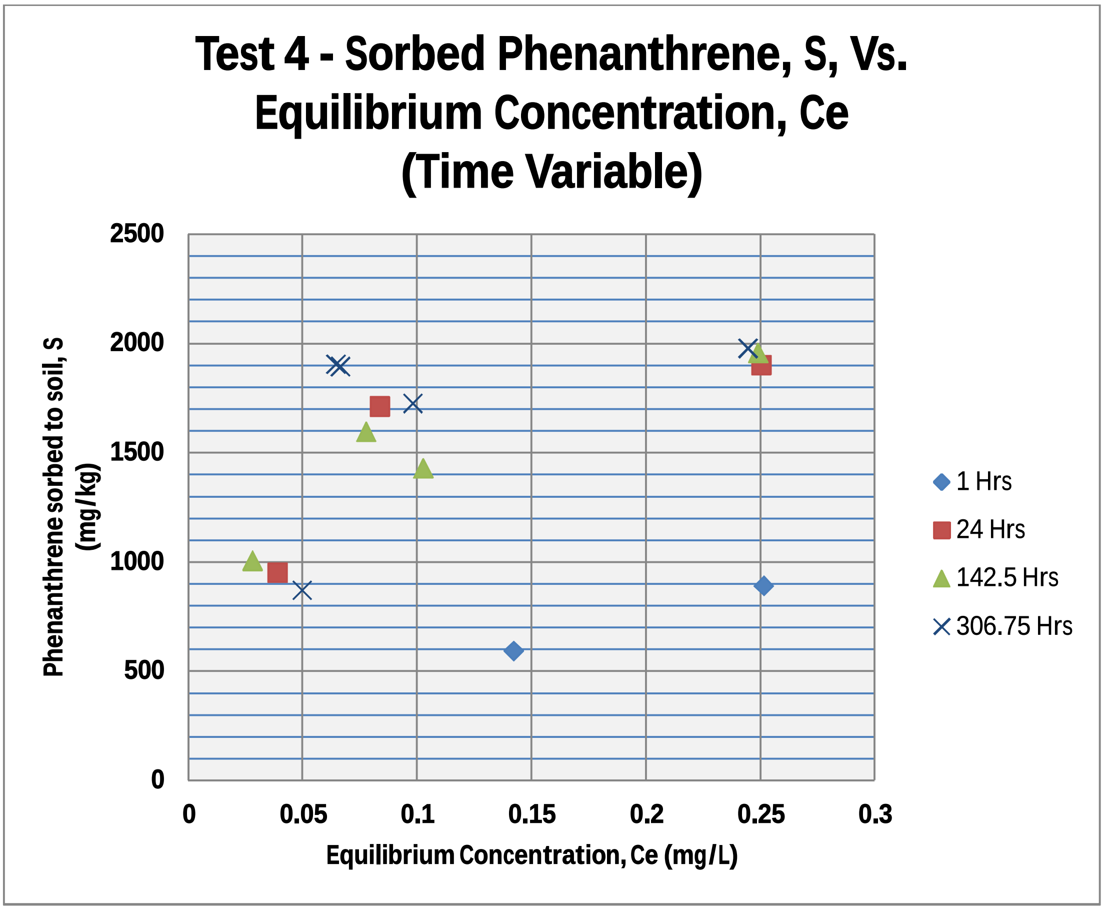


Figure 5.24: Equilibrium Concentration Vs phenanthrene sorbed to Severn Estuary peat with various run times.

5.6.3. Discussion on Sorption

Test 7, performed with groundwater, was unsuccessful due to foaming of the hexane during extraction. It was proposed by C. Emanuel (Ph.D. Microbiology Researcher at Heath University Hospital, Cardiff. Pers. Comm.) that the microbial content of the groundwater could have formed bio-films, resulting in foaming and inaccurate solvent extraction.

The slope of the line plotting the liquid phase concentration (C_e) Vs. the solid phase concentration for various of the soil mass and liquid phase concentrations is K_s (TPHCWG, Vol.3, 1997).This value has been calculated from the unmodified isotherm graphs. The R^2 value has been calculated by Excel for the data sets. In addition, the Organic Carbon Partition Coefficient has been calculated from this data using Equation 5.1.

$$K_{oc} = K_s/F_{oc} \qquad (5.1)$$

where;

K_{oc} is the Organic Carbon Partition Coefficient,

K_s is the Soil/Water Sorption Coefficient and,

F_{oc} is the fraction of organic carbon (mg organic carbon/mg soil)

From Section 5.6, the fraction of organic carbon in the peat sample used (study site E, BH101, 6.6m – 6.8m) was 0.2882 (i.e. 28.82%), and the fraction of organic carbon in the silt/clay sample (9302, BH101, 9m) was 0.0046 (i.e. 0.46%).

The results of the unmodified isotherm equations are summarised in Table 5.6 along with published values of K_{oc} for soil and Black Carbon (BC);

Table 5.6: Summary of Parameters calculated for Alluvium using Unmodified Isotherm Data and Selected Published Parameters

Source	**Soil Type**	**K_s**	**R^2**	**K_{oc}**
Test 1	Peat	11461	0.9657	3.9E +04
Test 2	Peat	7664.6	0.9396	2.66E +04
Test 5	Peat	430.6	0.9633	1.49E +03
Test 6	Peat	545.4	0.9798	1.89E +03
Test 2	Clay	3703.8	0.3128	8.05E +05
TPHCWG	-	-	-	8.14E +03
Yang *et al* (2008)	River Alluvium (coal contaminated)	-	-	1.23E +06
Luo *et al* (2008)	Loam (foc 3.94%)	-	-	2.3883E +04
Luo *et al* (2008)	Clay (foc 0.66%)	-	-	4.3485E +04
Jonker & Koelmans (2002)*	Black Carbon			1E+09

* - Type of PAH not specified

The calculated n and K_F values from the Freundlich linearizations are summarised in Table 5.7, along with published data for sorption of phenanthrene to cellulose.

Table 5.7: Summary of Results of Log Freundlich Linearisations				
Source	**Sorbent**	**Log K_F**	**N**	**R^2**
Test 1	Peat	3.7717	0.8541	0.8976
Test 2	Peat	3.6364	0.6625	0.9695
Test 5	Peat	2.4303	0.8421	0.9472
Test 6	Peat	2.7261	1.0103	0.988
Test 2	Clay	3.893	2.1054	0.4519
Jonker (2008)	Cellulose	2.23	1.01	-
Salloum *et al* (2002)	Cellulose	2.98	-	-
Wang *et al* (2007)	Cellulose	2.19	-	-

The parameters derived for phenanthrene sorption using the Langmuir Isotherm employing the spreadsheets published by Bolster (2007) are presented in Table 5.8.

Table 5.8. Summary of Results for Phenanthrene Sorption using Langmuir Isotherms employing C. H. Bolster (2007) Spreadsheets				
		Langmuir		
Source	**Sorbent**	**K_L**	**S_{max}**	**E**
Test 1	Peat	0.109	1.06×10^5	0.966
Test 2	Peat	18.902	1.26×10^3	0.990
Test 5	Peat	2.442	2.08×10^2	0.957
Test 6	Peat	0.005	1.01×10^5	0.978
Test 2	Clay	5.3×10^7	2.00×10^2	-0.716

The unmodified isotherm data (Figures 5.12 to 5.16 and Table 5.8) reveals that if it is assumed that sorption is solely controlled by the organic content of the soil, the amount of phenanthrene sorbed per unit mass of organic carbon by alluvial peat, as expressed by K_{oc} (1.49E +03 to 3.9E +04), sits in the region of the K_{oc} values quoted by Lou *et al*, (2008), for loam and clay soils (2.3883E +04 and 4.3485 E +04 respectively) and those quoted by the Total Petroleum Hydrocarbon Criteria Working Group (Gustafson *et al*, 1997) (8.14E +03). The K_{oc} values are in the region of two to three orders of magnitude lower than those quoted for coal contaminated alluvium (1.23E +06, Yang *et al*, 2008) and up to 6 orders of magnitude lower than the Koc value quoted for Black Carbon (Jonker and Koelman (2002). Black carbon has been described as a 'supersorbent' for planar hydrocarbons such as PAH, PCBs, dioxins and furans (see Koelmans *et al,* 2006) with reported K_{oc} values up to 10^9 l/kg. The discrepancy between the sorption capacity of carbon in peat and carbon in coal contaminated alluvium is consistent with observations made elsewhere where 'hard' and 'soft' domains have been identified (e.g. LeBouef and Weber (1997) and Huang *et al* (1997b)).

The Severn Estuary peat is geologically immature (less than 9000 yrs old) and has not endured the degree of diagenesis experienced by coal. Peat will act as a significant sink for organic contaminants due to its high organic content (28.82% in test samples).

The peat used in the sorption testing was desiccated and crushed into a powder before use. However, in its natural state peat has a micro-porous structure. In Section 5.7 the forces which act on coal tar and creosote in the free-phase are considered. In this situation the relatively open structure of peat, and the micro-porous structure of the fossil wood contained therein, will additionally contribute to the ability of peat to act as a sink for free-phase creosote/coal. Boreholes 15A to 17a, study site E, recorded high levels of creosote coincident with peat horizons (see Section 5.2).

It is apparent from the tests involving alluvial silt/clay, which comprises almost pure mineral, with trace organic content (0.46%), has a limited capacity to sorb phenanthrene. The sorption data shows significant scatter of the data for clay although there is a trend toward sorption being related to the mass of clay sorbent in the solution, as expected. The K_{oc} value derived for the organic content of the clay is approximately 1 order of magnitude higher than those published by the other authors mentioned above. Whilst the organic component of the test clay has an apparently higher Koc than the tested peat this may be attributed to the clays negligible organic carbon content and the assumption that the phenanthrene is solely sorbed to the clays organic carbon. (i.e. clay had a fraction of organic carbon of 0.0046) . Whilst early authors, such as Karickhoff (1981), overlooked the contribution of the soil mineral content to sorption, later research considered its contribution (e.g. Lou *et al* 2008).

In addition the significant scatter within the clay sorption data could be due to variance in mineral surface area per unit weight of sorbent as a consequence of differing clast shape and/or size.

It is also conceivable that the mineral component of soils with low organic content may serve to spread out the available organic carbon, maximising it surface and preventing clumping and loss of sorption surfaces.

The data from the Freundlich linearised experiments (Figures 5.17 to 5.21 and Table 5.9) revealed that K_f values for alluvial peat were of the same order as those published for cellulose. It should be remembered that the peat used comprised 28.82% organic material with the rest made up of minerals, as opposed to cellulose, which would comprise entirely organic material.

An indication of the applicability of a particular isotherm for a data set is indicated by the model efficiency, presented as r^2 in the authors excel spread sheets or as the model efficiency value E on the C H Bolster spreadsheet (described as ‘goodness of fit’ by Bolster and Hornberger (2007)). In either case a model efficiency of unity indicates a perfect data fit and lower numbers indicate a poorer fit.

The unmodified sorption isotherms recorded r^2 values of between 0.9396 and 0.9798 for the peat data and 0.3218 for the clay data. The Freundlich isotherm recorded r^2 values of between 0.8976 and 0.9880 for the peat data and 0.4519 for the clay data.

The C H Bolster Langmuir Isotherm recorded E values of between 0.957 and 0.990 for the peat data and -0.716 for the clay data.

The UK Environment Agency Groundwater Remedial Target Software (v 3.1) still attribute the retardation of non-polar organic contaminants as solely a function of sorption to soil organic content and the model is usually operated using published K_{oc} values taken, for example, from the TPHCWG (Gustafson *et al*, 1997) or EA publications (i.e. Environment Agency 2003b). These publications present a single K_{oc} value for a contaminant in contact with a ‘typical’ soil.

Given the range of Koc values in published data and derived during the current research it is not sufficient to consider the Organic Carbon of all soils as equal. It is therefore essential that published K_{oc} values are treated with great caution as the capacity of organic carbon to sorb organic contaminants can vary by several orders of magnitude depending on the type of organic carbon and the geological history of the soil.

Desorption experiments have shown that a portion of the sorption process is reversible. During Test 1, with an initial phenanthrene concentration of 0.477 mg/l, between 0.3% and 3.9% of the phenanthrene sorbed by the peat was returned to solution when the peat was placed in deionised water. During Test 2, with an initial phenanthrene concentration of 0.477 mg/l, between 6.5% and 32.1% of the phenanthrene sorbed by the peat was returned to solution when the peat was placed in deionised water.

There are likely to be some minor losses due to experimental procedures such as transfer from vessels. The discrepancy between sorption and desorption may be indicative of strong/irreversible sorption of the majority of the phenanthrene. A hysteresis in sorption in a common phenomenon. Koelmans *et al* (2006) undertook studies of the mechanisms of sorption and concluded that slow desorption rates can occur when the contaminant has an opportunity to occlude into voids within the organic carbon. Under such circumstances removal times for occluded fractions range from decades to millennia (see Jonker *et al*, 2005).

Test 4 (Figure 5.24) showed a significant increase in the mass of phenanthrene sorbed per unit mass of soil between the 1 hr and 24 hrs contact time. There was overlapping of data (i.e. no evidence of further sorption) from 24 hrs, 142.5 hrs and 306.75 hrs suggesting that equilibrium occurred before 24 hrs contact time.

Sorption testing has revealed that the sorption capacity of the organic matter in Severn Estuary Peat is on a par with similar natural soils and less effective than Black Carbon and Coal. The research confirms that the sorption capacity, per unit mass of organic carbon of a soil is specific to the soil and calculating sorption using generic published organic carbon partition coefficients could result in significant miscalculation. Wherever possible, contaminant sorption should be calculated using site specific data.

5.7. Capillary Rise

5.7.1. Capillary Rise in Fossil Plant Fibres

The rate of upwards creosote flow in isolated plant fibres was too rapid to record. The obtainable length of plant fibre was limited due to the extremely delicate nature of the fibres. In all ten experiments the creosote was observed to rise the entire length of the fibres which extended up to 30mm above the creosote.

The tests performed on plant fibres in confinement of soil matrix observed creosote rising up to 120mm within the fibres after 24hrs of contact with creosote.

5.7.2. Capillary Rise in Open Pores

An example of capillary rise observed in an open pore is presented in Figure 5.25.

Figure 5.25: Evidence of capillary rise within an open 2mm man-made pore in alluvium from Study Site E following splitting of the sample after 1 hour in bath.

The results of the capillary rise experiments performed on artificially formed open pores in alluvium are presented in Table 5.9.

Table 5.9: Capillary Rise in Artificial Open Pores within Alluvial Clay

Diameter of Tube (mm)	**Capillary Rise Test 1 (mm)**	**Capillary Rise Test 2 (mm)**	**Capillary Rise Test 3 (mm)**	**Average Height of Capillary Rise (mm)**
Study Site E (BH101, 8.0m)				
3	5.2	5.3	5.3	5.3
2	9.7	10.0	9.9	9.9
1	12.3	14.7	15.2	14.1
0.5	19.7	19.6	19.7	19.7
Study Site A (BH1, 9.0m)				
3	5.0	5.3	5.1	5.1
2	9.9	10.1	10.1	10.0
1	14.6	15.3	15.1	15.0
0.5	20.1	20.3	20.0	20.1

The results of the capillary rise experiments using glass tubing are presented in Table 5.10;

Table 5.10. Results of Capillary Rise Experiments using Glass Tubing

Diameter of Tube (mm)	**Capillary Rise Test 1 (mm)**	**Capillary Rise Test 2 (mm)**	**Capillary Rise Test 3 (mm)**	**Average Height of Capillary Rise (mm)**
0.9	13.4	13.4	13.4	13.4
1.1	13.1	13.2	13.2	13.2
2.8	6.6	6.6	6.9	6.7

The results of the capillary rise experiments using glass and alluvium are presented graphically in Figure 5.26.

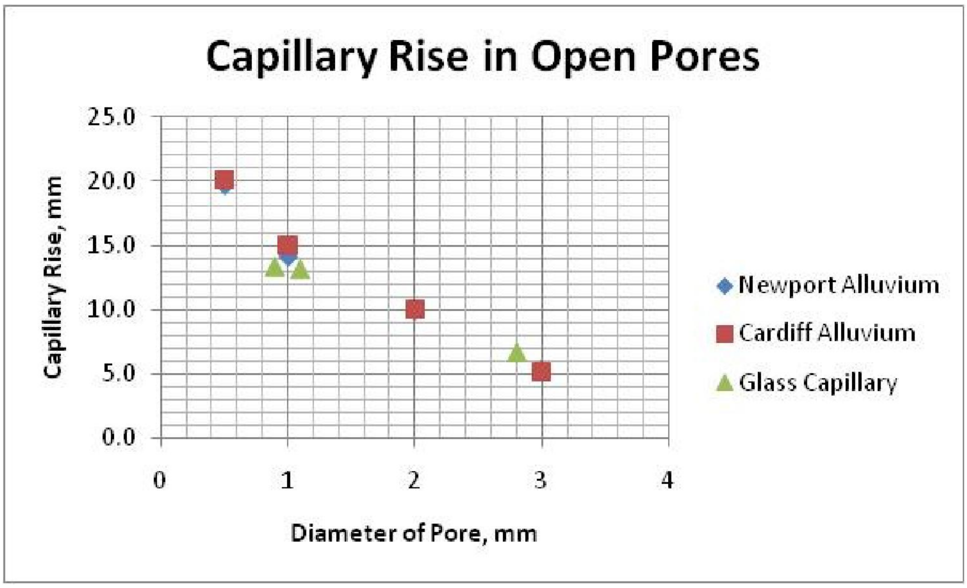


Figure 5.26. Graph of the Average Capillary Rise Vs Pore Diameter after 1 hour of contact for open pores in alluvium and within glass capillary tubing

Capillary rise experiments have revealed that, in an air/NAPL/silicate mineral system creosote is wetting. Plant fibres create a network of microscopic pores and the capillary rise is rapid and significant.

The experiments involving artificial open pores of the same dimensions as those encountered naturally allow capillary rise. The degree of capillary rise within artificial pores in alluvium compares favourably with those observed in glass capillaries.

The effective diameter created by plant fibres are not currently know. However, since these plant structures have evolved to carry liquids within living plants using capillary forces it is hardly surprising that these preserved structures are effective at NAPL transport.

Cohen (2007) reported a sessile contact angle between creosote and glass in a creosote/glass/air system of 170° (i.e. a glass/creosote contact angle of 10°). Substituting this angle into equation (5.2) along with the capillary rise data above allows the calculation of the liquid-air surface tension, γ.

$$h = 2\gamma \cos \theta / \rho\, g\, r \qquad (5.2)$$

rearranged;

$$\gamma = h\, \rho\, g\, r / 2 \cos \theta \qquad (5.3)$$

The parameters substituted into the equation are presented in Table 5.11.

Table 5.11: Parameters used to calculate liquid-air surface tension, γ

Parameter	Value	Source
Density of creosote, ρ.	1085 Kg/m^3	Mid-point of range quoted by RUTGERS (2003)
Acceleration due to gravity, g.	9.81 ms^{-2}	
Contact angle, θ.	10°	Calculated from Cohen *et al*, 2007

Using the average capillary rise data and the creosote/glass contact angle calculated from Cohen *et al* (2007) the liquid-air surface tension was calculated using the above parameters and equation (5.3) the results are summarised in the Table 5.12.

Table 5.12. Summary of calculated liquid-air surface tension values	
Diameter of Capillary (mm)	**Calculated liquid-air surface tension, γ (J/m^2)**
Study Site E (BH101, 8.0m)	
3	0.0430
2	0.0535
1	0.0381
0.5	0.0266
Study Site F (BH1, 9.0m)	
3	0.0414
2	0.0541
1	0.0406
0.5	0.0272
Glass Tubing	
0.9	0.0326
1.1	0.0393
2.8	0.0507

The experiments using silicate minerals recorded a liquid/air surface tension in the range of 0.0266 J/m^2 to 0.0541 J/m^2. The variations may be due to microscopic variations within the clay samples used. Published values for the surface tension of creosote were seen to vary. For example, Priddle and MacQuarrie (1993) quote a surface tension of 0.045 Jm^2 for their sample, TOXNET (2004) quote a surface tension of 0.015 Jm^2, Zapf-Gilje et al (2003) quote a surface tension of 0.007 Jm^2. Creosote would be expected to vary from site to site as differing production (i.e. distillation) methods will lead differing rheological properties, weathering can also alter the relative composition of creosote. In addition, various hydrocarbon solvents, such as diesel, have been added to creosote historically to alter its rheological properties.

During the above experiments samples were at their natural moisture content and capillary rise through the soil matrix (i.e. the soil matrix beyond the soil pore structures) was not observed over the duration of the experiments. However, when an undisturbed alluvium sample was desiccated by oven drying at 45˚ C for 48 hrs and placed in type B creosote, the creosote rose in the matrix to a height of between 45mm and 65mm within 24 hrs. The sample is displayed in Figure 5.27. This observation is consistent with the finding of Cohen *et al* (2007) that water is preferentially wetting of silicate over creosote although creosote is wetting of silicate in the absence of water.

Figure 5.27. Creosote rising through the soil matrix of a desiccated soil sample. Rises of between 45mm and 65mm were observed after 24 hrs of contact with creosote.

In addition to the gravity driven flow usually considered in groundwater/contaminant transport equations, it has been shown that, above the phreatic surface, capillary forces can play a significant part in the migration of creosote through alluvial clay via a network of open and fibre filled pores. The fossil plant fibres encountered in some pores appear especially effective at wicking creosote due to their internal network of microscopic pores essential to the function of the plant.

For the calculation of capillary forces above the phreatic level in silicious clay a liquid/air surface tension in the range of 0.0266 J/m^2 to 0.0541 J/m^2 is recommended although the result was calculated on the basis of limited NAPL/glass contact angle data. Derivation of a larger data set of contact angle data is through further research would be desirable.

Whilst the organic matter in peat has a propensity to sorb PAH from solution (see Section 5.6), thereby retarding its movement in aqueous phase, its' open fibrous structure is likely to contribute to the transport DNAPL free-product via capillary forces. This would explain observations made by the author (study site A), where coal tar free product had migrated several tens of meters horizontally from its source (a Gasworks) along a thin layer peat horizon.

5.8. Sub-Contracted Permeability Tests

Recorded permeability results ranged from 4 x 10^{-11} ms^{-1} to 6.2 x 10^{-10} ms^{-1}. The results of this testing are presented in Annex D and summarised in Table 5.13.

Table 5.13: Summary of Permeability Testing of Alluvial Clay and Silt

Sample Depth (m. b.g.l.)	Recorded Permeability ($m\ sec^{-1}$)	Soil Description
5.50 – 5.95	4 x 10^{-11}	Slightly gravelly silty CLAY
6.10 – 6.55	1.0 x 10^{-10}	Silty CLAY
6.70 – 7.15	1.6 x 10^{-10}	Silty CLAY
7.30 – 7.75	6.2 x 10^{-10}	Silty CLAY
7.90 – 8.35	5.6 x 10^{-10}	Silty CLAY
8.50 – 8.95	2.2 x 10^{-10}	Silty CLAY
9.10 – 9.65	1.5 x 10^{-10}	Silty CLAY
9.60 – 10.05	6.1 x 10^{-10}	Silty CLAY
10.80 – 11.25	5.3 x 10^{-10}	Silty CLAY
11.40 – 11.85	4.5 x 10^{-10}	Silty CLAY
12.00 – 12.45	1.0 x 10^{-10}	Silty CLAY
13.10 – 13.65	2.0 x 10^{-10}	Silty CLAY
13.70 – 14.15	1.0 x 10^{-10}	Silty CLAY
14.20 – 14.65	2.2 x 10^{-10}	Silty CLAY

The alluvial clay is extremely soft and the process of soil sampling and sample preparation can disrupt the soil structure. The transfer of the soil sample from the U100 sampling tube to the permeability test cell requires a hydraulic extruder to drive the sample from the U100 sample tube. High pressures can be generated at the interface of the soil sample and the extruder plate. Soil samples may also require trimming with a laboratory knife. Figure 5.28 shows the degree of damage observe during this process. In-situ soil strength tests undertaken during drilling (Standard Penetration Tests) reveal a softening of the alluvium below the water table (A sample borehole log is presented in Annex E).

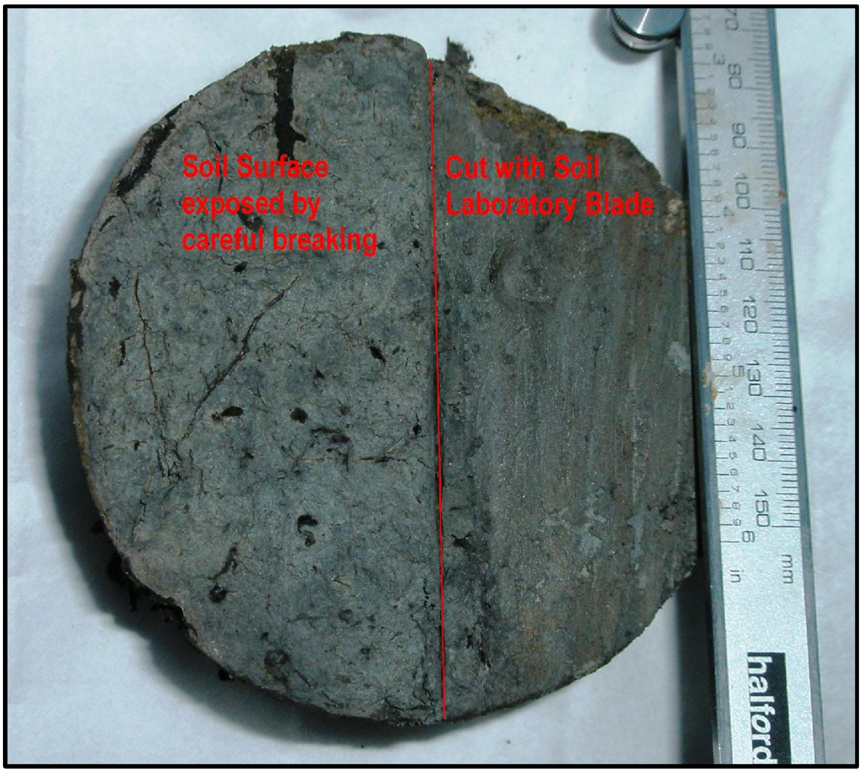


Figure 5.28. Example of the damage caused during sample trimming.

It is therefore likely that the test results from the sub-contracted permeability tests represents the permeability of the soil matrix, with the rootlet structures having been crushed and smeared during sampling, extrusion and preparation. The results are consistent with published data for a typical homogenous clay (for example Barnes, 2010). The permeability of clay matrix could be determined if natural alluvium were kneaded to remove macrostructures and compacted into permeability test apparatus.

The testing performed on a remoulded sample of basal gravel recorded a permeability of 6.8 x 10^{-4} ms^{-1} (Gravel samples cannot be recovered in an undisturbed state during drilling so it is necessary to collect the gravel and re-compact it at the laboratory to replicate its in-situ state).

5.9. Permeability of Pores

The coefficient of permeability, k, is calculated as shown in equation 5.4.

$k = (q/i)\ (Rt/A)$ (5.4)

Where;

q = average flow rate

i = hydraulic gradient, taken to be the difference in head between the top and bottom of the sample, assuming the pressure to be hydrostatic at the top of the sample and zero beneath the sample.

Rt = Temperature correction factor (derived from Figure 4 of Section 5 of BS:1377)

A = Cross-sectional area of sample in mm^2. Assumed to be 1000000 mm^2 to allow easy conversion of the results to reflect the results of detailed logging.

The average flow rate, q, is determined from the average volume of water collected,

Q, over a test period, t.

$q = Q/t$.

Water flow for the duration of the permeability test was assumed to occur solely through the artificial pore with no flow occurring through the clay matrix. Clay samples submitted for sub-contracted analysis, during which the fine structures are believed to have been disrupted, recorded permeabilities of between 6.2 x 10-10 ms^{-1} to 4 x 10-11 ms^{-1} (effectively impermeable). Published permeability values for clay without pores or fractures are typically less than 10^{-9} ms^{-1} (Barnes, 2010). Such permeabilities would provide a negligible contribution to flow over the duration of the tests performed using artificial pores.

The results of the constant head permeability tests at presented in Table 5.14 and 5.15.

Table 5.14: Results of Constant Head Permeability Test with 1.01mm Pore

Diameter	Length	Head, i	Volume	Time (1)	Time (2)	Time (3)	Average	Q/t
mm	mm	mm	Ml	S	S	s	S	mL/s
1.01	140	1275	100	87	84	85	85.33333	
			200	179	176	176	177	
			300	263	255	256	258	
			400	350	344	346	346.6667	
			500	439	430	434	434.3333	
			600	527	519	524	523.3333	
			700	616	606	610	610.6667	
			800	704	694	699	699	
			900	554	543	548	548.3333	
			1000	880	870	876	875.3333	1.142422

Table 5.15: Results of Constant Head Permeability Test with 1.53mm Pore

Diameter	Length	Head, i	Volume	Time (1)	Time (2)	Time (3)	Average	Q /t
mm	mm	mm	Ml	S	S	s	S	mL/s
1.53	140	1275	100	16	15	16	15.66667	
			200	31	31	31	31	
			300	47	47	47	47	
			400	63	62	63	62.66667	
			500	79	78	79	78.66667	
			600	94	93	94	93.66667	
			700	109	109	109	109	
			800	125	125	125	125	
			900	140	140	140	140	
			1000	156	156	156	156	6.410256

The effective permeability of a 1.01mm pore within $1m^2$ soil sample is thus calculated as follows;

The hydraulic gradient, i, is thus a fall of 1275mm of head over 140mm of sample equating to;

1275/140 = 9.1

The average flow, q, is 1000 mL/875.3 s = 1.14 mL S^{-1}

At 8 C a Temperature Correction Factor of 1.38 is derived from Figure 4 of Section 5 of BS:1377 (1990).

Therefore, the effective permeability, q, of a 1.01mm pore in 1 m^2 of soil is;

(1.14/9.1) (1.38/1000000) = 1.72 X 10^{-7} ms^{-1}.

The effective permeability of a 1.53mm pore within $1m^2$ soil sample is thus calculated as follows;

The hydraulic gradient, i, is thus a fall of 1275mm of head over 140mm of sample equating to;

1275/140 = 9.1

The average flow, q, is 1000 mL/156 s = 6.41 mL S^{-1}

At 8 C a Temperature Correction Factor of 1.38 is derived from Figure 4 of Section 5 of BS:1377.

Therefore, the effective permeability, q, of a 1.53mm pore in 1 m^2 of soil is;

(6.41/9.1) (1.38/1000000) = 9.72 X 10^{-7} ms^{-1}.

The effect of pores on permeability can be considered as additive and thus the effect of a known number of pores of a particular diameter encountered per square meter during detailed logging can be calculated by adding the appropriate effective permeability values from above.

For example, if the soil contains 500 open pores of 1mm diameter and 100 open pores of 1.5mm diameter per 1m^2 of soil the net effect would result in a permeability of;

$(500 \times 1.72 \times 10^{-7}) + (100 \times 9.72 \times 10^{-7})$

$= 8.6 \times 10^{-5} + 9.72 \times 10^{-5}$

$=1.832 \times 10^{-4}$ ms^{-1}, a permeability akin to sandy soil.

Continuing with the above calculations, the resultant permeability of a number of open pore per meter squared surface of soil are presented in Table 5.16.

Table 5.16. Effective Permeability of Porous Clay Soils

1.01mm Diameter Pores						
Number of Open Pores per m^2 of Soil Surface	10	50	100	500	1000	5000
Effective Permeability of Soil	1.72×10^{-6} ms^{-1}	8.6×10^{-6} ms^{-1}	1.72×10^{-5} ms^{-1}	8.6×10^{-4} ms^{-1}	1.72×10^{-4} ms^{-1}	8.6×10^{-4} ms^{-1}
1.53mm Diameter Pores						
Number of Open Pores per m^2 of Soil Surface	10	50	100	500	1000	5000
Effective Permeability of Soil	9.72×10^{-6} ms^{-1}	4.86×10^{-5} ms^{-1}	9.72×10^{-5} ms^{-1}	4.86×10^{-4} ms^{-1}	9.72×10^{-4} ms^{-1}	4.86×10^{-3} ms^{-1}

Detailed logging discussed in Section 5.3 encountered higher numbers of pores per meter squared (i.e. c.4000 pores of 1mm diameter and c. 2000 pores of 1.5mm diameter per meter squared, plus many other pores of different diameters).

If permeability is assumed to be additive 4000 x 1mm pores and 2000 x 1.5mm pores (and ignoring intermediate pore sizes) would result in a soil permeability of;

$$(4000 \times 9.72 \times 10^{-7}) + (2000 \times 1.72 \times 10^{-7}) = 4.23 \times 10^{-3}\ \mathrm{ms}^{-1}$$

This is a permeability akin to a typical sand deposit.

However, it is highly likely that assuming all pores are open and continuous will overestimate the permeability of the soil as a percentage of pores will be discontinuous and a percentage will contain organic fragments. In addition pores can become easily clogged by suspended soil particles.

The least porous layer within the soil sequence will be a limiting factor in groundwater flow. Root structures were generally least preserved near the base of the alluvium.

The current permeability testing used straight vertical artificial pores. The logged pores were not straight and the route for the water is thus more torturous and less permeable.

Environment Agency (2003a) detailed that 0.087mm aperture in fractured rock could stop the migration of a 1m head of creosote. The pore diameter at which DNAPL flow is halted has not been determined in the current research, although a percentage of biopores may be below this diameter.

Permeability determination using artificial pores is therefore likely to overestimate the permeability whilst standard laboratory methods underestimate the permeability of alluvium since contamination has been able to penetrate over ten meters of alluvium in less than 200 years.

6. Conclusions

In the field of Environmental Risk Assessment alluvial clay is often assumed to be an impermeable stratum and the great thicknesses of this deposit around the Severn Estuary are traditionally assumed to provide an effective barrier against the migration of Dense Non-Aqueous Phase Liquids (DNAPLs). However, field observations made by the author (Section 5.1) are contrary to this hypothesis, with coal tar and creosote having been seen to penetrate over 10m thickness of alluvium to reach the gravel aquifer beneath.

Severn Estuary alluvium is a geologically recent deposit of less than 9000 yrs age (Section 3.2). X-Ray Diffraction has determined that the deposit is dominated by silicate mineralogy and geotechnical testing has revealed the alluvium to comprise silt and clay size particles (Section 5.5). The clay has a very low organic carbon content and subordinate bands of peat have an organic carbon content up to c. 30%.

Standard sampling and testing of alluvial clay has led to very low permeabilities (c. 10^{-10} ms^{-1}) being recorded. However this is due to disruption of the soft soil during sampling and test preparation (Section 5.8). Carefully sampled and dissected samples of alluvial clay revealed a network of fine pores. Beneath contaminated sites these pores were seen to serve as conduits for contamination flow. Contamination was seen to lie predominantly within these pores with the soil matrix holding little contamination (Section 5.4). Permeability tests performed on artificial pores has recorded permeability values several orders of magnitude higher when clay is penetrated by a large number of macro-pores (Section 5.9). Detailed logging should be performed where macroscopic and microscopic features may be present within an otherwise impermeable strata.

Soil preparation for chemical analysis may lead to homogenisation of the soil. However a soil may contain various domains (Section 5.3) and these should be considered individually during contamination testing.

Publications present generic partition coefficients for common contaminants to soil organic carbon. However it has been seen that there is great variance in the types of soil organic carbon (3.2). Most significantly geologically mature organic carbon (for example coal) has a higher propensity to sorb aromatic contaminants that geologically young organic carbon. Site specific K_{oc} values have been derived for alluvium (Section 5.6).

Give the complexities of modelling the transport of a multi-component DNAPL, it is essential to undertake boreholes down-gradient of a plume to provide true data to verify the results of equilibrium portioning calculations.

7. Further Works

At the time of submission of these works the author, working in conjunction with Terra Firma Wales Ltd, Stephen Craig Limited and Celtic Technologies Limited, commenced work on a remedial scheme for the treatment of orphan creosote waste in the deep confined aquifer at study site E. The remedial scheme aims to capture creosote which has historically penetrated through over ten meters of alluvial clay.

The proposed works will comprise a wall of interceptor wells with sumps which will capture creosote from the groundwater for separation on the surface and will ultimately allow the volume of creosote reaching the confined aquifer to be quantified. Used in conjunction with data from a recently installed shallow (i.e. above the alluvium) DNAPL interceptor system at the site the data should allow the mass transfer of DNAPLs through alluvium to be accurately modelled.

Further permeability testing of a broader range of artificial pores in clay would assist with more accurate estimation of the permeability of porous clays. The development of a method of satisfactorily sampling and permeability testing natural soils in a completely undisturbed state would be extremely useful, negating the need to undertake predictive calculations. Alternatively, an in-situ method of permeability measurement would prove useful. Microscopic studies of alluvium would extend the range of recorded pores beyond the visible range.

Methods for improved preservation of macropores in soft clay would assist greatly in the accurate logging of alluvium. Professor Walter Tschinkel (2010) has been exploring novel technique for making casts of ant nests including dental plaster, paraffin wax and molten aluminium and zinc. The molten metal technique consists of pouring heated aluminium (melting temperature 659˚ C) or zinc (melting temperature 420˚ C) into soil pores, allowing the metal to set and subsequently excavating and washing the cast. Zinc has been found to be better as preserving fine structures on account of its lower melting temperature. The process may provide a means of capturing the fine 3D structures of alluvial clay for someone with sufficient resources. Other methods of dye or chemical tracing may improve the logging and assist with determining the percentage of pores which serve as conduits for groundwater transport. For example Mooney *et al* (2006) used varnish impregnation to preserve soil root macro-structures.

It would be useful through future research, to determine the percentage of total pores which serve as continuous conduits to contamination transport. This would be most effectively performed at a site where contamination acts as a distinct traces (for example black creosote in yellow-brown clay).

In addition, a percentage of pores contain fossil root fragments has not yet been quantified. A method of permeability testing of undisturbed natural samples would serve to reduce the ambiguity.

Permability testing performed during the current research has been performed with water. If dedicated permeability apparatus could be employed, it may be possible to perform the tests with creosote. This will enable the determination of the pore size capable of sustaining a particular head of creosote above the sample.

An effective method of disrupting the contaminant pathway would be of merit at locations on alluvium being developed for industrial use or landfill. An investigation into the effect on the ground permeability of permeation treatment (i.e. grouting) or geotechnical treatment such as rolling may identify efficient methods for sealing fossil pore structures.

Methods of reducing the mobility of historical DNAPL contamination within the ground, by increasing partitioning to soil, increasing viscosity, reducing solubility or accelerating biodegradation would be of great environmental and economic interest.

Given the variations in the partition coefficients between different soils it would be desirable for the purpose of Environmental Risk Assessment to construct a database of partition coefficients for the principal geological units of the UK. Likewise, the determination of Environmental Half Lives for specific sites of interest would assist greatly in accurate Environmental Risk Assessment modelling.

Capillary calculations for a NAPL/Silicate/Air system were based on a single published contact angle value and further work in relation to the contact angle would provide greater confidence in this value.

REFERENCES

Abraham, H., 1922. Determination of bituminous substances including asphalts tars and pitches. Standard Methods of Chemical Analysis. A Manual Analytical Methods and General Reference for the Analytical Chemist and for the Advanced Student, vol II. D. Van Norstrand Company, New York, pp 1289 – 1327.

Abraham, H., 1961. Asphalts and allied substances: their occurrence, modes of production, uses in the arts, and methods of testing. Vol. 2 of Industrial Raw Materials. Van Nostrand, Princeton, N.J.

Al-Bahrani, K.S., Martin ,R. J., 1976. Adsorption studies using gas-liquid chromatography. I. Effect of molecular structure. Water Res. 10, 731-736.

Alemany, L., Pugmire, R. J. 1984. The fate of cellulose and lignin in peats: an exploratory study of the input to coalification. Org. Geochem. 6, 399-407.

Allen, J. R. L., Fulford, M. G. 1986. The Wentlooge Level: a Romano-British saltmarsh reclamation in southeast Wales. Britannia, 17, 91 – 117.

Allen, J. R. L., Rae, J. E., 1988. Vertical salt marsh accretion since the Roman period in the Severn Estuary, southwest Britain. Mar. Geol., 83: 225 – 235.

Allen, J. R. L., 1990. The Severn Estuary in southwest Britain: its retreat under the marine transgression, and fine sediment regime. Sedimentary Geology., 66: 13 – 28.

Alshafie, M., Ghoshal, S., 2004. The role of interfacial films in the mass transport of naphthalene from creosotes to water. Journal of Contaminant Hydrology 74. 283 – 298.

Anderson, W. G., 1986. Wettability literature survey, Part 1. Rock/Oil/Brine interactions, and the effect of core handling on wettability. J. Pet. Technol., Oct 1986, p. 1125-1149.

Andrade, F. A., Qureshi, H. A., Hotza, D. 2001. Measuring the plasticity of clays. Applied Clay Science 51, 1 – 7.

Atkins, P., Jones, L., 2002. Chemical Principals: The Quest for Insight. W. H. Freeman and Company Publishers, New York.

ATSDR. (September 2002). Toxicological Profile for Wood Creosote, Coal Tar Creosote, Coal Tar, Coal Tar Pitch, and Coal Tar Pitch Volatiles. U.S. Department of Health and Human Services. Public Health Service Agency for Toxic Substances and Disease Registry.

Azevedo, A. S., Kanwar, R. S., Horton, R., 1998. Effect of cultivation on hydraulic properties of an Iowa soil using tension infiltrometers. Soil Science 163, 22 – 29.

Baird, A. J., 1997. Field estimation of macropore functioning and surface hydraulic conductivity in a fen peat. Hydrologicla Processes 11 (3), 287 – 295.

Ball, W. P., Roberts, P. V., 1991. Long-term sorption of halogenated organic chemicals by aquifer material: 2. Intraparticle diffusion. Environ. Sci. Technol. 25 (7), 1237-1249.

Barnes, G. 2010. Soil Mechanics: Principles and Practice. Third Edition. Palgrave McMillan Publishers

Barranco, F. T., Dawson, H. E., 1999. Influence of aqueous pH on the interfacial properties of coal tar. Environmental Science and Technology 33 (10), 1598-1603.

Baudu, M., Raveau, D., Guibaud, G., 2004. Application of the IAS theory combining to a three compartments description of natural organic matter to the adsorption of Atrazine or Diuron on activated carbon. Environ. Technol. 25, 763.

Bayard, R., Barna, L., Mahjoub, B., Gourdon, R., 2000. Influence of the presence of PAHs and coal tar on naphthalene sorption in soils. Journal of Contaminant Hydrology 46 61-80

Bear, J., 1972. Dynamics of Fluids in Porous Media. Dover Publications, Inc., New York.

Birak, P. S., Miller, C. T., 2009. Dense non-aqueous phase liquids at former manufactured gas plants: Challenges to modelling and remediation. Journal of Contaminant Hydrology 105. 81 – 98.

Blodau, C., Moore, T. R., 2002. Macroporosity affects water movement and pore water sampling in peat soils. Soil Science 167, 98 – 109.

Bolster, C., H., Hornberger, G., M., 2007. On the use of Linearized Langmuir Equations. Soil Sci. Soc. Am. J. 71.1796 – 1806.

British Geological Survey (1986), Sheet 263 Cardiff, 1:50,000 Series Geological Survey of England and Wales.

British Geological Survey (1980), Sheet 279 Weston-super-Mare, 1:50,000 Series Geological Survey of England and Wales.

British Geological Survey (1975), Sheet 249 Newport, 1:50,000 Series Geological Survey of England and Wales.

British Geological Survey. Lexicon of Named Rock Units website - http://www.bgs.ac.uk/lexicon/lexicon_intro.html

British Standards Institute: BS 5930:1999. *Code of Practice for site investigation*. British Standard Institute. ISBN 0 580 33059 1.

British Standards Institute: BS 10175: 2001: Investigation of Potentially Contaminated Sites: Code of Practice. ISBN 978 0 580 681 98 1.

British Standards Institute: BS 1377: 1990. Methods of test for soil for civil engineering purposes. Parts 5 & 6: *Consolidation and permeability tests in hydraulic cells and with pore pressure measurement.* British Standards Institute. ISBN 0 580 185885.

Broholm, K., Jorgensen, P. R., Hansen, A. B., Arvin, E., Hansen, M., 1999. Transport of creosote compounds in a large, intact, macroporous clayey till column. Journal of Contaminant Hydrogeology 39. 309 - 329.

Brown, D. G., Gupta, L., Moo-Young, H.K., Coleman, A., 2005. Raoult's law-based method for determination of coal tar average molecular weight. Environ. Toxicol. Chem. 28, 1886 – 1892.

Brown, D. G., Gupta, L., Kim, T., Young, H. K., Coleman, A. J., 2006. Comparative assessment of coal tars obtained from 10 former manufactured gas plant sites in the Eastern United States. Chemosphere 65 1562-1569.

Bucheli, T.D., Gustafsson, O., 2000. Quantification of the soot-water distribution coefficient of PAHs provides mechanistic basis for enhanced sorption observations. Environ. Sci. Technol. 34, 5144-5151.

Carter, M.C., Weber Jr., W.J., 1994. Modeling adsorption of TCE by activated carbon preloaded by background organic matter. Environ. Sci. Technol. 28, 614.

Cohen, R. M., Mercer, J. W., Slenska, M., Brourman, M., 2007. Creosote wettability review and evaluation at a portion of the Cabot Carbon/Koppers Superfund site. In *The Proceedings of the 2nd International Conference on DNAPL Characterisation and Remediation, Niagara Falls, NY., September 24-27,2007.* Available at http://www.geotransinc.com/publications.html

Cornelissen, G., Kukulska, Z., Kalaitzidis, S., Christanis, K., Gustafsson, O., 2004. Relations between environmental black carbon sorption and geochemical sorbent characteristics. Environ. Sci. Technol. 38, 3632-3640.

Cornelissen, G., Gustafsson, O., 2006. Effetcs of added PAHs and precipitated humic acid coatings on phenanthrene sorption to environmental Black carbon. Environmental Pollution 141. 526-531.

Coulon, F., Orsi, R., Turner, C., Walton, C., Daly, P., Pollard, S. (2009). Understanding the fate and transport of petroleum hydrocarbons from coal tar within gasholders. Environmental International 35, 248-252.

Craig, R. F., 1978. Soil Mechanics (2nd Edition).

Department of the Environment (DoE) Industry Profile (1995). Gas works, coke works and other Coal carbonisation plants.

Department for Environment, Food and Rural Affairs, Environment Agency and Institute for Environment and Health., 2000. *Guidelines for Environmental Risk Assessment and Management*. The Stationery Office, PO Box 29, Norwich NR3 1GN.

Devitt, D. A., Smith, S. D. 2002. Root channel macropores enhance downward movement of water in Mojave Desert ecosystem. Journal of Arid Environments 50, 99 – 108.

Dickens, A. F., Gelinas, Y., Masiello, C. A., Wakeham, S., Hedges, J. I. , 2004. Reburial of fossil organic carbon in marine sediment.

Dong, J., Chowdhry, B., Leharne, S., 2004. Investigation of the wetting behaviour of coal tar in three phase systems and its modification by poloxamine block copolymeric surfactants. ES&T, 38 (2), 594-602.

Douglas, J., T., 1986. Macroporosity and permeability of some soil cores from England and France. Geoderma, 37, 221 – 231.

Edwards, W. M., Shipitalo, M. J., Norton, L., D., 1988. Contributions of macroporosity on infiltration into a continuous corn no-tilled watershed: Implications for contaminant movement. Journal of Contaminant Hydrology, 3, 193-205.

Edwards W., M., Shipitalo, M. J., Owens L., B., 1993. Gas, water and solute transport in soils containing macropores: a review of methodology. Geoderma, 57, 1993, 31-49.

Environment Agency, 2003a. An illustrated handbook of DNAPL transport and fate in the subsurface. R&D Publication 133.

Environment Agency, 2003b. Draft Technical Report P5- 079/TR1. Review of the Fate and Transport of Selected Contaminants in the Soil Environment.

Environment Agency, 2004. Model Procedures for the Management of Land Contamination. Contaminated Land Report 11.

Environment Agency 2006. Remedial Target Methodology: Hydrogeological Risk Assessment for Land Contamination.

Environment Agency 2010. Environment Agency Website. http://maps.environment-agency.gov.uk/wiyby/wiybyController?x=357683.0&y=355134.0&scale=1&layerGroups=default&ep=map&textonly=off&lang=_e&topic=drinkingwater

Fetter, C., 1993. Contaminant Hydrogeology. Mac Millan Publishing Co.

Gentry, F. M. ,1927. The Technology of Low Temperature Carbonisation.

Goldberg, E. D., 1985. Black Carbon in the Environment: Properties and Distribution. John Wiley & Sons. New York.

Goring, C. A. I., Soil Sci., 93, 211(1962)

Grathwohl, P., 1990. Influence of organic matter from Soils and Sediments from Various Origins on the Sorption of Some Chlorinated Aliphatic Hydrocarbons: Implications on Koc Correlations. Environ. Sci. Technol., 24, No. 11, p1687-1693.

Gustafson, J. B., Tell, J. G., Orem, D., 1997. Total Petroleum Hydrocarbon Criteria Working Group Series. Volume 3; Selection of Representative TPH Fractions Based on Fate and Transport Considerations.

Hamper, M.J., 2006. Manufactured gas history and processes. Environmental Forensics 7 (1), 55 – 64.

Hassett, J. J., Means, J. C., Banwart, W. L., Wood, S. G., 1980. Sorption Properties of Sediment in Energy Related Pollutants. Report No.EPA-600/3-80-041, U.S. Environmental Protection Agency, Athens, Ga.

Haudek, H. W., Viti, E., 1978. Textilfasern. Verlag Johann L. Bondi & Sohn, Wein-Perchtoldsdorf, Austria.

Holden, J., Burt, T. P., Cox N. J., 2001. Macroporosity and infiltration in blanket peat: the implications of tension disc infiltrometer measurements. Hydrological Processes 15, 289 – 303.

Holden, J., Burt, T. P., 2002. Piping and pipeflow in a deep peat catchment. Catena 48 (3) 163 – 199.

Holden, J. 2009. Flow through macropores of different size classes in blanket peat. Journal of Hydrology. 364, 342 – 348.

Howard, P.H., 1991. Handbook of Environmental Degradation Rates. Lewis Publishers.

Huang, W., Weber, W. J. Jr., 1997a. A distributed reactivity model for sorption by soils and sediments. 10 Relationships Between Desorption, Hysteresis, and Chemical Characteristic. Environ. Sci. Tech., V. 31, No. 9, p.2562-2569.

Huang, W., Weber, W. J. Jr., 1997b. A distributed reactivity model for sorption by soils and sediments. 9. General isotherm non-linearity and applicability of the dual reactive domain model. Environ. Sci. Tech., V. 31 (6) p.1703-1710.

Huang , W., Weber, W. J. Jr., 1997c. A Distributed Reactivity Model for Sorption by Soils and Sediments. 11. Rate of diffusion within organic matter domains. Environ. Sci. Technol., in review.

Hugaboom, D. A., Powers, S. E., 2002. Recovery of coal tar and creosote from porous media: The influence of wettability. Groundwater Monitoring and Remediation, 22 (4), 83-90.

Ikarashi, I., Kaniwa, M., Tsuchiya, T.,2005. Monitoring of polycyclic aromatic hydrocarbons and water extractable phenols in creosotes and creosote treated woods made and procured in Japan. Chemosphere 60. 1279–1287.

International Programme on Chemical Safety (IPCS) operated by the World Health Organisation (WHO). www.who.int/ipcs/en/

Iuliano, M., Ciavatta, L., Gaetano, T., 2007. Protolytic behaviour of hydroxylated Pyrex glass surface in NaCl media. Journal of Colloid and Interface Science 319, 402 – 410.

Jackson, R. E., Ewing, J. E., Avis, J. (Undated). The migration of viscous NAPLS in alluvium: Implications for brownfield redevelopment and surface-water contamination.

Jonker, M. T. O., Koelmans, A. A., 2002. Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment. Mechanistic Considerations. Environ. Sci. Technol. 36. 3725-3734.

Jonker, M.T.O., Hawthorne, S.B., Koelmans, A. A., 2005. Extremely slowly desorbing polycyclic aromatic hydrocarbons from soot and soot like materials. Evidence by supercritical fluid extraction. Environ. Sci. Technol.

Jonker, M.T.O., 2008. Absorption of polycyclic aromatic hydrocarbons to cellulose. Chemosphere. 70, 778-782.

Jones, J., C., Godefrey, J. (2002). Stages in the Coalification Sequence reflected in oxidation reactivities. International Journal on Engineering Performance Fire Codes. 4, 10 – 12.

Jones, R. L., Keen, D. H., 1993. Pleistocene Environments in the British Isles.

Karapanagioti, H. K., Sabatini, D. A., Kleineidam, S., Grathwohl, P., Ligouis, B., 1999. Phenanthrene Sorption with Heterogenous Organic Matter in a Landfill Aquifer Material. Phys. Chem. Earth (B), Vol. 24, No. 6, pp. 535-541.

Karickhoff, S. W., 1981. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediment and soils. Chemosphere Vol.10, No.8., pp.833 – 846.

Kellaway, G. A., Welch, F. B. A., (1993). Geology of the Bristol District. *Memoir of the British Geological Survey*. HMSO.

Kleineidam, S., Schuth, C., Grathwohl, P. 2002. Solubility-normalised combined adsorption-partitioning sorptionisotherms for organic pollutants. Environ. Sci. Technol. 36, 4689-4697.

Koelmans, A. A., Jonker, M. T. O., Cornelissen, G., Bucheli, T. D., Van Noort, P. C. M., Gustafsson, O., 2006. Black carbon: The reverse of its dark side. Chemosphere 63, 365-377.

Kopp, O. C., Bennett, M. E., Clark, C. E. (2000). Volatiles lost during coalification. Internation Journal of Coal Geology. 44, 69 – 84.

Lapidus, D. F., (1990). Collins Dictionary of Geology.

LeBoeuf, E. J., Weber, W. J. Jr., 1997. A distributed reactivity model for sorbtion by soils and sediments: 8. Sorbent organic domains: Discovery of a humic acid glass transition and an argument for polymer-based model. Environ. Sci. Technol. 31 (6) 1687-1702.

Lesiatoi, A. L., 2007. The Development of a Method for the Analysis of Creoste Compounds in Groundwater to Assess the Lamella Clarifier Efficiency in Removing Creosote Contamination from Groundwater. M.S.C. Dissertation, School of Mechanical Engineering, Cardiff University.

Levine, G. D., Schlosberg, R.H., Silbernagel, B.G., 1982. Understanding the chemistry and physics of coal structure (a review). Proc. Natl. Acad. Sci. USA 79, 3365-3370.

Liu, Y., 2006. Some consideration on the Langmuir isotherm equation. Colloids and Surfaces A: Physiochem. Eng. Aspects 274. 34 – 36.

Liu, S. Q., Li, J. G., Mei, M., Dong, D. 2007. Groundwater pollution from Underground Coal Gasification. Journal of China University of Mining and Technology 17 (4) 467 – 472.

Lou, L., Zhang, S., Ma, Y., 2008. Evaluation of impacts of soil fraction on phenanthrene sorption. Chemosphere 72 (6) 891 - 896

Mackay, D., Shui, W. Y., Ma, K. C., 1992. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Lewis Publishers.

Mercer, J. W., Cohen, R. M., 1990. A review of immiscible fluids in the subsurface: properties, models, characterisation and remediation. Journal of Contaminant Hydrology. 6. 107-163.

Mitra, S., Bianchi, T.S., McKee, B. A., Sutula, M., 2002. Black carbon from the Mississippi river: quantities, sources, and potential implications for the global carbon cycle.Environ. Sci. Technol. 36. 2296-2302.

Mooney, S. J., Tams, A. R., Berry, P. M., 2006. A reliable method for preserving soil structures in the field for subsequent morphological examination. Geoderma 133, 338 – 344.

Murphy, B. L., Sparacio, T., Shields, W. J., 2005. Manufactured gas plants – processes, historical development, and key issues in insurance coverage disputes. Environmental Forensics 6 (2), 161 – 173.

Oades, J., M., 1993. The role of biology in the formation, stabilisation and degradation of soil structure. Geoderma, 56, 377-400.

Pindoria, R., Megaritis, A., Chatzakis, I., Vasanthakumar, L., Zhang, S., Lazaro, M., Herod, A., Garcia, X., Gordon, A., Kandiyoti, R. (1996) Structural characterisation of tar from a coal gasification plant. Fuel 76, 101 – 113.

Powers, S. E., Ancker, W.H., Seacord, T. F., 1996. Wettability of NAPL-contaminated sands. Journal of Environmental Engineering, October 1996, 889-896.
Rhodes, E., 1945. The chemical nature of coal tar. In: Lowry, H. (Ed.), Chemistry of Coal Utilisation, vol. 2. John Wiley & Sons, New York, pp. 1287 1370 (U.S.).

Priddle, M. W., MacQuarrie T. B., 1993. Dissolution of creosote in groundwater: an experimental and modelling investigation. Journal of Contaminant Hydrology, 15, 27 – 56.

Rhodes, E., 1966. Water-gas tars and oil-gas tars. In: Hoiberg, A. (Ed.), Bituminous Materials: Asphalts, Tars and Pitches. Vol. 3 of Coal Tars and Pitches. Interscience Publishers, New York, pp. 33-35.

RUTGERS Chemicals. 2003. Creosote. Preservative for Industrial Wood Impregnation. Technical Information Sheet.

Salloum, M.J., Chefetz, B., Hatcher, P.G., 2002. Phenanthrene sorption by aliphatic-rich natural organic matter. Environ. Sci. Technol. 36, 1953-1958.

Shinari, A., 2008. Ph.D. researcher, University of Wales, Cardiff. Pers. comm.

Site A. D. (2000). Factors Affecting the Sorption of Organic compounds in Natural Sorbent/Water Systems and Sorption Coefficients for Selected Pollutants. A Review. Journal of Physical Chemistry, 30, 187 – 439.

Smetten, K., R., J., 1992. The relation of Earthworms to soil hydraulic properties. Soil. Biol. Biochem. Vol 24. No. 12, 1539 – 1543.

Squirrell, H. C., Downing, R. A., 1969. Geology of the South Wales Coalfield, Part 1, The Country around Newport (3rd Edition). Natural Environmental Research Council, Institute of Geological Science. HMSO.

Staples, T. L., Shaffer, D. G., 2001. Wicking flow in irregular capillaries. Colloids and Surfaces. A: Physiochemical and Engineering Aspects 204, 239 – 250.

Suthersan, S. S. (1999). In-situ Bioremediation. CRC Press LLC.

Tavisto, M., Kuisma, R., Pasila, A., Hautala, M. 2003. Wetting and wicking of fibre plant straw fractions. Industrial Crops Products, 18, 25 – 35.

Taylor P., Gagan M., Alkenes and Aromatics. S205, Book 7. The Open University. 2002.

Taylor, G. H., Teichmuller, M., Davis, A., Diessel, C. F. K., Littke, R., Robert, P., (1998).Organic Petrology. Gebruder Borntraeger, Berlin.

Terzaghi, K. and Peck, R.B. (1967) "Soil Mechanics in Engineering Practice," John Wiley, NewYork. 729.

Tiruta-Barna, L., Mahjoub, B., Faure, L., Hanna, K., Bayard, R., Gourdon, R. 2006. Assessment of the multi-compound non-equilibrium dissolution behaviour of a coal tar containing PAHs and phenols into water. Journal of Hazardous Materials. B132, 277 – 286

TOXNET Hazardous Substances Data Bank, National Library of Medicine, Bethesda, MD (2004) http://toxnet .nlm.nih.gov/

Traxler, R., 1964. Rheology and rheological modifiers other than elastomers: structure and time. In: Hoiberg, A. (Ed). Bituminous Materials. Asphalts, Tars, and Pitches. Vol 1 of Asphalts Tars and Pitches. Interscience Publishers, New York, pp. 143-211.

Tschinkel W. R., 2010. Methods for casting subterranean ant nests. Journal of Insect Science 10:88 available online: insectscience.org/10.88.

United States Environmental Protection Agency, Document EPA/600/R-06/035A (2006). Application of Equilibrium Partitioning Theory to Soil PAH Contamination.

Walker, R., Mastalerz, M., Brassesell, S., Elswick, E., Hower, J.C., Schimmelmann, A., 2007. Chemistry of thermally altered high volatile bituminous coals from southern Indiana. International Journal of Coal Geology 71, 2-14.

Wang, X., Yang, K., Tao, S., Xing, B., 2007. Sorption of aromatic organic contaminants by biopolymers: effects of pH, copper (II) complexation, and cellulose coating. Environ. Sci. Technol. 41, 185-191.

Weber, W. J., McGinley, P. M., Katz, L. E., 1991. Sorption phenomena in subsurface systems:concepts, models and effects on contaminant fate and transport. Water Res. 25 (5) 499-528.

Weber, W. J., Huang, W., 1998. Hysteresis in the sorption and desorption of hydrophobic organic contaminants by soils and sediments. 2. Effects of soil organic matter heterogeneity. Journal of Contaminants Hydrogeology 31 p. 149-165.

Wilson, J. L., Conrad, S. H., Mason, W. R., Peplinski, W., Hagan, E., 1990. Laboratory investigation of residual liquid organics from spills, leaks, and the disposal of hazardous wastes in groundwater. EPA/600/6-90/004, U.S. Environmental Protection Agency, Ada, Oklahoma.

Xing, B., Pignatello, J., J., 1997. Dual-Mode Sorption of Low Polarity Compounds in Glassy Poly(Vinyl Chloride) and Soil Organic Matter. Environ. Sci. Technol., V. 31, No 3, p. 792-799.

Yang, C., Huang, W., Xiao, B., Yu, Z., Peng, P., Fu, J., Sheng, G., 2004. Intercorelations among degree of geochemical alterations, physiochemical properties, and organic sorption equilibria of kerogen. Environ. Sci. Technol. 38. 4396-4408.

Yang, Y., Hoffman, T., Pies, C., Grathwohl, P., 2008. Sorption of polycyclic aromatic hydrocarbons (PAHs) to carbonaceous materials in a river floodplain soil. Environmental Pollution 29. (2008) 1–7.

Young, T. M., Weber, W. J., 1995. A Distributed Reactivity Model for Sorption by Soils and Sediments. 3. Effects of Diagenetic Processes on Sorption Energetics. Environ. Sci. Tech., 29, No. 1, p.92-97.

Zamfirescu, D., Grathwohl, P., 2001. Occurence and attenuation of specific organic compounds in the groundwater plume at a former gasworks site. Journal of Contaminant Hydrology 53. 407 – 427.

Zapf-Gilje, R., O'Hara, G., Rankin, M. (2003). Capping of creosote contaminated sediment protects aquatic habitat in the Fraser River, Vancouver, BC. 2nd Symposium on Contaminated Sediments, Quebec City, Canada.

Zheng, C., Wang, P.,P., 1998. MT3DMS. A modular three-dimensional multispecies transport model for simulation of advection, dispersion and chemical reactions of contaminantsin groundwater systems. Reference Manual . Waterloo Hydrogeological Software.

Zheng, J. Z., Powers, S.E., 1999. Organic bases in NAPLs and their impact on wettability. Journal of Contaminant Hydrology. 39 (1-2). 161 – 181.

Zheng, J. Z., Shoa, J. H., Powers, S. E., 2001. Asphaltenes from coal tar and creosote: their role in reversing the wettability of aquifer systems. Journal of Colloid and Interface Science 244 (2), 365 - 371.

Zheng, J. Z., Powers, S. E., 2003. Identifying the effect of polar constituents in coal derived NAPLs on interfacial tension. Environmental Science and Technology 37 (14), 3090 – 3094.

Physicochemical Data for Selected Components of Coal Tar

Source	Compound	Molecular Weight	Aqueous Solubility (mg/l) (Temp)	Vapour Pressure (Pa) (Temp)	Henry's Law Constant (Pa-m3/mol) (Temp)	Log Kow	Log Koc
	BTEX						
1	Benzene	78.11	1770 (25 C)	9970 (20 C)	442.5 (20 C)	2.13	2.13
1	Toluene	92.15	535 (25 C)	3000 (20 C)	537 (20 C)	2.65	2.25
1	Ethylbenzene	106.16	169 (25 C)	950 (20 C)	663.5 (20 C)	3.13	2.64
1	o-Xylene	106.16	173 (25 C)	660 (20 C)	534 (25 C)	3.12	2.63
1	m-Xylene	106.16	160 (25 C)	790 (20 C)	493.3 (20 C)	3.20	2.69
1	p-Xylene	106.16	180 (25 C)	860 (20 C)	699 (25 C)	3.15	2.65
	PAH						
1	Naphthalene	128.17	31 (25 C)	36.81 (25 C)	43.01 (25 C)	3.37	3.11
1	Acenaphthylene	152.2	16.1 (25 C)	4.14 (25 C)	8.40 (25 C)	4.00	3.40
1	Acenaphthene	154.2	3.8 (25 C)	1.52 (25 C)	12.17 (25 C)	3.92	3.85
1	Fluorene	166.22	1.9 (25 C)	0.72 (25 C)	7.87 (25 C)	4.18	4.14
1	Phenanthrene	178.23	1.1 (25 C)	0.113 (25 C)	3.24 (25 C)	4.57	4.36
1	Anthracene	178.23	0.045 (25 C)	0.0778 (25 C)	3.96 (25 C)	4.54	4.47
1	Fluoranthene	202.26	0.26 (25 C)	8.7 E-03 (25 C)	1.04 (25 C)	5.22	5.03
1	Pyrene	202.26	0.13 (25 C)	0.0119 (25 C)	0.92 (25 C)	5.18	5.02
1	Chrysene	228.3	0.0016 (25 C)	1.07 E-04 (25 C)	0.065 (25 C)	5.70	3.66
1	Benzo(a)anthracene	228.3	0.011 (25 C)	6.06 E-04 (25 C)	0.581 (25 C)	5.91	4.00
1	Benzo(b)fluoranthene	252.32	0.0015 (25 C)	6.67 E-05 (25 C)	0.43 (25 C)	5.80	5.74
1	Benzo(k)fluoranthene	252.32	8.0 E-04 (25 C)	4.12 E-06 (25 C)	0.084 (25 C)	6.00	6.09
1	Benzo(a)pyrene	252.32	0.0038 (25 C)	2.13 E-05 (25 C)	0.046 (25 C)	6.04	6.01
1	Indeno(123-cd)pyrene	276.34	2.2 E-05 (25 C)	1.30 E -08 (25 C)	0.162 (25 C)	6.65	6.54
1	Benzo(ghi)perylene	276.34	2.6 E-04 (25 C)	2.25 E-05 (25 C)	0.075 (25 C)	6.50	5.61
1	Dibenzo(ah)anthracene	278.36	6.0 E-04 (25 C)	9.16 E-08 (25 C)	1.49 e-03 (25 C)	6.75	6.58
1	Coronene	300.36	1.40 E-04 (25 C)	2.00 E-10 (25 C)		6.75	5.00
	PHENOL						
1	Phenol	94.11	84000 (20 C)	47.59 (20 C)	0.040 (25 C)	1.47	1.46
2	3,5 - Xylenol	122.16	5000 (20 C)				
2	2,4 - Xylenol	122.16	7900 (20 C)				
2	Naphthols	144.17	7000 (20 C)				
2	p-Cresol	108.14	19000 (20 C)	0.147 (25 C)		1.94	
2	o-Cresol	108.14	25000 (20 C)				
2	m-Cresol	108.14	24000 (20 C)	0.147 (25 C)		1.96	
	HETEROCYCLICS						
2	Quinoline	129.2	6100 (20 C)	8 (20 C)		2.06	

1. Environment Agency Technical Report P5-079/TR1 (2003)
2. International Programme on Chemical Safety

Location: Weston Super Mare

Borehole No: WS1

Date of Borehole: 03/06/2008

Sample Depth: 0.70 m

Sample Type: WINDOWLESS SAMPLER

Soil Description: MADE GROUND: Soft, grey, very sandy SILT/CLAY.

Photo:

Geotechnical Data:

Location: Weston Super Mare

Borehole No: WS1

Date of Borehole: 03/06/2008

Sample Depth: 2.00 – 2.50 m

Sample Type: WINDOWLESS SAMPLER

Soil Description: Soft, grey to brown, thinly laminated, CLAY/SILT.

6 bio-casts noted in 87mm diameter sample: 0.4mm open clean, 0.5mm fibre-filled, 0.5mm open clean, 0.7mm fibre filled, 1.1mm open clean, 1.2mm open clean

Photo:

Geotechnical Data:

Chemical Data: (STL COV/520958/2008)
WS1 2.60m
Total Aliphatic C6 – C40 -88 mg/kg, Total Aromatic C6 – C40 – 770 mg/kg
Total PAH – 240 mg/kg

Location: Weston Super Mare

Borehole No: WS1

Date of Borehole: 03/06/2008

Sample Depth: 3.00 – 3.40 m

Sample Type: WINDOWLESS SAMPLER

Soil Description: Soft, grey to brown, thinly laminated, CLAY/SILT.

4 bio-casts noted in 87mm diameter sample: 0.3mm open containing hydrocarbon free-product, 0.5mm fibre-filled and hydrocarbon stained, 0.7mm open containing hydrocarbon free-product, 0.8mm open containing hydrocarbon free-product and 1.5mm stain.

Photo:

Geotechnical Data:

Chemical Data: (STL COV/520958/2008)
WS1 2.80m
Total Aliphatic C6 – C40 -21 mg/kg, Total Aromatic C6 – C40 – 75 mg/kg
Total PAH – 31 mg/kg

Location: Weston Super Mare

Borehole No: WS1

Date of Borehole: 03/06/2008

Sample Depth: 4.50 – 5.00 m

Sample Type: WINDOWLESS SAMPLER

Soil Description: Very soft, grey, SILT/CLAY.

4 bio-casts noted in 50mm diameter sample: 0.4mm open containing hydrocarbon free-product, 0.5mm open containing hydrocarbon free-product and staining to 1.1mm, 0.7mm open containing hydrocarbon free-product, 0.7mm open containing hydrocarbon free-product and 1.3mm stain.

Photo:

Geotechnical Data:

Chemical Data: (STL COV/520958/2008)
WS1 4.60m
Total Aliphatic C6 – C40 -340 mg/kg, Total Aromatic C6 – C40 – 1200 mg/kg
Total PAH – 770 mg/kg

Location: Portishead

Borehole No: BH1

Date of Borehole: 07/10/2008

Sample Depth: 0.50 – 1.00m

Sample Type: BULK

Soil Description: MADE GROUND: Firm, brown, gravelly CLAY. Gravel comprises tarmac.

Photo:

Geotechnical Data:

Location: Portishead

Borehole No: BH1

Date of Borehole: 07/10/2008

Sample Depth: 1.50 – 2.00m

Sample Type: BULK

Soil Description: MADE GROUND: Firm, grey, very gravelly CLAY. Gravel comprises fragments of angular brick with very occasional coal.

Photo:

Geotechnical Data:

Location: Portishead

Borehole No: BH1

Date of Borehole: 07/10/2008

Sample Depth: 2.50 – 3.00m

Sample Type: BULK

Soil Description: Firm, grey to brown, thinly laminated CLAY/SILT.

Very strong coal tar odour and pockets of hydrocarbon free-product in silt lenses and fossil biocasts.

Photo:

Geotechnical Data: NA

Chemical Data: (DETS 09-32144)

Ammoniacal Nitrogen	200 mg/kg
Total Aliphatic C5 – C35	180 mg/kg
Total Aromatic C5 – C35	2400 mg/kg
Total PAH	1600 mg/kg
Monohydric Phenol	7.6 mg/kg

Location: Portishead

Borehole No: BH1

Date of Borehole: 07/10/2008

Sample Depth: 3.50 – 4.00m

Sample Type: BULK

Soil Description: Firm, grey to occasionally brown, thinly laminated CLAY/SILT.
Fossil bio-casts present – open and in filled or with trace of plant fibre with coal tar free-product.

Photo:

Geotechnical Data: NA
Chemical Data:

Location: Portishead

Borehole No: BH1

Date of Borehole: 07/10/2008

Sample Depth: 4.70 – 5.00m

Sample Type: BULK

Soil Description: Soft, grey, thinly laminated CLAY passing into dark brown, soft, pseudo-fibrous peat. Bio-casts in clay open or containing plant fibres. Weak hydrocarbon odour.

Photo:

Geotechnical Data: NA
Chemical Data: NA

Location: Portishead

Borehole No: BH1

Date of Borehole: 07/10/2008

Sample Depth: 10.45 – 10.55m

Sample Type: U100 Shoe

Soil Description: Soft to very soft, grey, very sandy CLAY/silt. Only large casts preserved, fibre filled – Sand may represent higher energy environment which may account for less preserved casts.

Photo:

Geotechnical Data: NA
Chemical Data: NA

Location: Portishead

Borehole No: BH1

Date of Borehole: 07/10/2008

Sample Depth: 11.00 – 11.50m

Sample Type: Bulk

Soil Description: Very soft, grey, sandy CLAY. Too soft to preserve soil structure. Some lamination and plant material apparent.

Photo:

Geotechnical Data: NA
Chemical Data: NA

Location: Portishead

Borehole No: BH1

Date of Borehole: 07/10/2008

Sample Depth: 13.45 – 13.55m

Sample Type: U100 Shoe

Soil Description: Black, fibrous peat with laminated structure.

Photo:

Geotechnical Data: NA
Chemical Data: NA

Location: Portishead

Borehole No: BH1

Date of Borehole: 07/10/2008

Sample Depth: 16.00 – 16.50m

Sample Type: Bulk

Soil Description: Very soft, red-brown, very gravelly sandy CLAY to very clayey sandy GRAVEL.

Photo:

Apex Drilling 01656 749149
LOCATION HARBOUR RD PORTSHEAD
JOB No 8 10 2009
DEPTH 1600/650
BOREHOLE No 1
SAMPLE No 329

Geotechnical Data: NA
Chemical Data: NA

Location: Portishead

Borehole No: BH2

Date of Borehole: 13/10/2008

Sample Depth: 0.50 – 1.00m

Sample Type: BULK

Soil Description: MADE GROUND: Firm to stiff, brown, gravelly CLAY including fragments of concrete and brick.

Photo:

Geotechnical Data: N/A

Chemical Data: N/A

Location: Portishead

Borehole No: BH2

Date of Borehole: 13/10/2008

Sample Depth: 1.50 – 2.00m

Sample Type: BULK

Soil Description: MADE GROUND: Stiff, brown, reworked thinly laminated CLAY with occasional gravel of brick. Mild hydrocarbon odour noted.

Photo:

Geotechnical Data: N/A

Chemical Data: N/A

Location: Portishead

Borehole No: BH2

Date of Borehole: 13/10/2008

Sample Depth: 2.50 – 3.00m

Sample Type: BULK

Soil Description: Soft, grey, thinly laminated CLAY. Soil structure destroyed during recovery.

Photo:

Geotechnical Data: N/A

Chemical Data: N/A

Location: Portishead

Borehole No: BH2

Date of Borehole: 13/10/2008

Sample Depth: 3.50 – 4.00m

Sample Type: BULK

Soil Description: Firm, grey to brown, thinly laminated CLAY. Hydrocarbon stained bio-casts noted – Open or fibre filled.

Photo:

Geotechnical Data: N/A

Chemical Data: N/A

Location: Portishead

Borehole No: BH2

Date of Borehole: 13/10/2008

Sample Depth: 4.50 – 5.00m

Sample Type: BULK

Soil Description: Soft, grey to brown, SILT/CLAY. Hydrocarbon stained bio-casts noted, fibre filled. Very weak hydrocarbon odour noted.

Photo:

Geotechnical Data: N/A

Chemical Data: N/A

Location: Portishead

Borehole No: BH2

Date of Borehole: 13/10/2008

Sample Depth: 6.00 – 6.50m

Sample Type: BULK

Soil Description: Very soft clay. Structure lost during recovery.

Photo:

Geotechnical Data: N/A

Chemical Data: N/A

Location: Portishead

Borehole No: BH2

Date of Borehole: 13/10/2008

Sample Depth: 7.50 – 8.00m

Sample Type: BULK

Soil Description: Very soft, grey to brown, CLAY with laminae of very soft fibrous peat.

Photo:

Geotechnical Data: N/A

Chemical Data: N/A

Location: Portishead

Borehole No: BH2

Date of Borehole: 13/10/2008

Sample Depth: 9.00 – 9.50m

Sample Type: BULK

Soil Description: Extremely soft CLAY. Structure lost during sampling.

Photo:

Geotechnical Data: N/A

Chemical Data: N/A

Location: Portishead

Borehole No: BH2

Date of Borehole: 13/10/2008

Sample Depth: 10.50 – 11.00m

Sample Type: BULK

Soil Description: Extremely soft CLAY. Structure lost during sampling.

Photo:

Geotechnical Data: N/A

Chemical Data: N/A

Location: Portishead

Borehole No: BH2

Date of Borehole: 13/10/2008

Sample Depth: 13.60 – 14.00m

Sample Type: BULK

Soil Description: Soft, grey, thinly laminated, CLAY with abundant fossil wood fragments and bio-casts.

Photo:

Geotechnical Data: N/A

Chemical Data: N/A

Location: Portishead

Borehole No: BH2

Date of Borehole: 13/10/2008

Sample Depth: 15.00 – 15.50m

Sample Type: BULK

Soil Description: Soft to firm, brown, sandy gravelly CLAY .

Photo:

Apex Drilling 01656 749149
LOCATION HARBOUR RD PORTISHEAD
JOB No 14 10 209
DEPTH 1500 1550
BOREHOLE No 2
SAMPLE No B23.

Geotechnical Data: N/A

Chemical Data: N/A

Location: Portishead

Borehole No: BH2

Date of Borehole: 13/10/2008

Sample Depth: 16.50 – 17.00m

Sample Type: BULK

Soil Description: Recovered as angular GARVEL to COBBLES of marl .

Photo:

Geotechnical Data: N/A

Chemical Data: N/A

Location: Portishead

Borehole No: BH2

Date of Borehole: 13/10/2008

Sample Depth: 18.00 – 18.50m

Sample Type: BULK

Soil Description: Recovered as clayey, very sandy GRAVEL to COBBLE of marl .

Photo:

Geotechnical Data: N/A

Chemical Data: N/A

Location: Portishead

Borehole No: BH2

Date of Borehole: 13/10/2008

Sample Depth: 19.30 – 19.60m

Sample Type: BULK

Soil Description: Recovered as clayey, very sandy GRAVEL to COBBLE of marl .

Photo:

Geotechnical Data: N/A

Chemical Data: N/A

Location: Newport

Borehole No: BH101

Date of Borehole: 15/09/2008

Sample Depth: 0.5m

Sample Type: Bulk Bag

Soil Description: Made Ground: Black, sandy gravelly SILT/CLAY with fine to medium gravel fragments of coal, ash and rounded sandstone.

Photo:

Geotechnical Data: N/A

Location: Newport

Borehole No: BH101

Date of Borehole: 15/09/2008

Sample Depth: 1.5m

Sample Type: Bulk Bag

Soil Description: Made Ground: Black, sandy gravelly SILT/CLAY with fine to medium gravel fragments of coal, ash and rounded sandstone.

Photo:

Geotechnical Data: N/A

Location: Newport

Borehole No: BH101

Date of Borehole: 15/09/2008

Sample Depth: 2.5m

Sample Type: Bulk Bag

Soil Description: Made Ground: Soft (wet) black, gravelly, very sandy CLAY/SILT with fine to medium gravel fragments of coal, ash, clinker, occasional brick and rounded sandstone.

Photo:

Geotechnical Data: N/A

Location: Newport

Borehole No: BH101

Date of Borehole: 15/09/2008

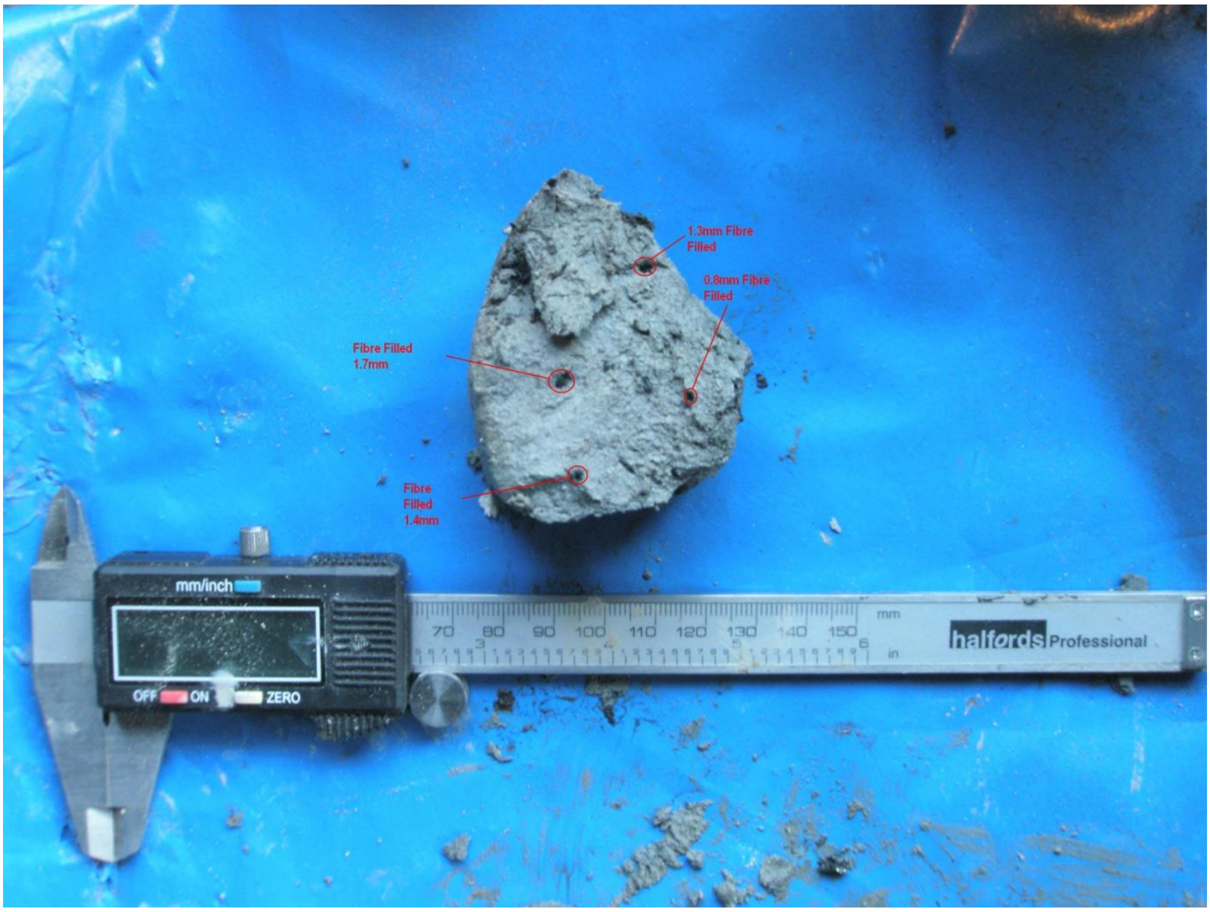
Sample Depth: 4.0m

Sample Type: Bulk Bag

Soil Description: Soft to firm, grey to very occasionally orange-brown, very thinly laminated, SILT with clay. Includes very thin lenses of orange silt up to 0.5mm thick and of limited horizontal extent.

Clay Cutter Fragment (Cross Sectional Area 0.00126m^2) Fibre Filled Pores (diameter = 0.8mm, 1.3mm, 1.4mm and 1.7mm)

Photo:



Geotechnical Data:

PSD Analysis – 81% Silt, 19% Clay.

Moisture Content – 33%

Organic Carbon Content – 0.01930%

Location: Newport

Borehole No: BH101

Date of Borehole: 15/09/2008

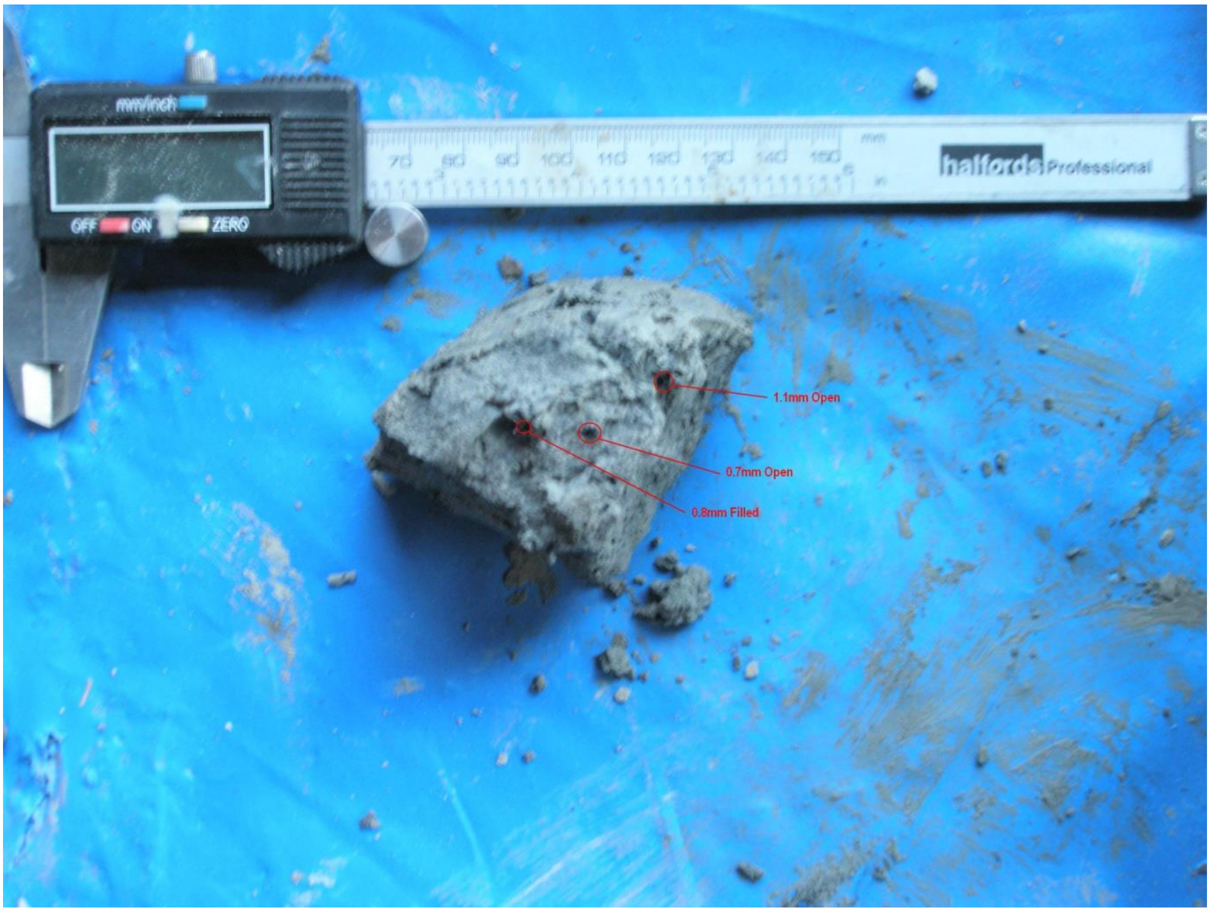
Sample Depth: 5.0m

Sample Type: Bulk Bag

Soil Description: Soft, grey to very occasionally orange-brown, very thinly laminated, very slightly sandy SILT with clay. Includes very thin discontinuous lenses of orange silt.

Clay Cutter cross-section (cross-sectional area 0.00126m^2) 1.1mm pore (open), 0.7mm pore (open), 0.8mm pore (filled with fibre).

Photo:



Geotechnical Data:
PSD Analysis – 1% Sand, 69% Silt, 30% Clay.
Moisture Content – 38%

Location: Newport

Borehole No: BH101

Date of Borehole: 15/09/2008

Sample Depth: 6.0m

Sample Type: Bulk Bag

Soil Description: Very soft, grey to very occasionally orange-brown, very thinly laminated, very slightly gravelly, very slightly sandy SILT with clay. Contains black, non-fibrous, mineral dominated peat/organic layers. Contains very thin, discontinuous silt lenses.

Sample too disturbed to discern bio-casts.

Photo:

Geotechnical Data:
PSD Analysis – 1% Gravel, 2% Sand, 75% Silt, 22% Clay.
Moisture Content – 38%

Location: Newport

Borehole No: BH101

Date of Borehole: 15/09/2008

Sample Depth: 6.0m

Sample Type: Bulk Bag

Soil Description: Very soft, grey to very occasionally orange-brown, very thinly laminated, very slightly gravelly, very slightly sandy SILT with clay. Contains black, non-fibrous, mineral dominated peat/organic layers. Contains very thin, discontinuous silt lenses.

Sample too disturbed to discern bio-casts.

Photo:

Geotechnical Data:
PSD Analysis – 1% Gravel, 2% Sand, 75% Silt, 22% Clay.
Moisture Content – 52%

Location: Newport

Borehole No: BH101

Date of Borehole: 15/09/2008

Sample Depth: 6.6m – 6.8m

Sample Type: Bulk Bag

Soil Description: Very soft, very dark brown to dark red-brown, occasionally grey, pseudo-fibrous to slightly fibrous, PEAT .

Photo:

Geotechnical Data:
PSD Analysis – Not applicable on peat.
Moisture Content – N/A
Organic Carbon Content – 29.10%
Inorganic Carbon Content – 0.0000%
XRD Analysis – Carbon (as graphite) and Silicate ($Si0_2$)

Location: Newport

Borehole No: BH101

Date of Borehole: 15/09/2008

Sample Depth: 7.0 – 7.45m

Sample Type: U100

Soil Description: Very soft, grey to very occasional brown, very thinly laminated, very slightly sandy SILT/CLAY.

U100 Sample (cross sectional area 0.0079m^2). Open Pores (0.9mm, 0.9mm, 1.5mm, 1.6mm diameter).

Photo:

Geotechnical Data: N/A

Location: Newport

Borehole No: BH101

Date of Borehole: 15/09/2008

Sample Depth: 8.0m

Sample Type: Bulk Bag

Soil Description: Very soft, grey to red-brown, thinly laminated, very slightly sandy SILT with clay. Very occasional iron oxide staining noted.

Clay Cutter Fragment (cross sectional area apprx. 0.00126m^2) Open Pore (1.1mm and 1.4mm diameter).

Photo:

Geotechnical Data:
PSD 1% Sand, 72% Silt, 27% Clay
Moisture Content 47%
Organic Carbon Content – 0.02981%

Location: Newport

Borehole No: BH101

Date of Borehole: 15/09/2008

Sample Depth: 9.0m

Sample Type: Bulk Bag

Soil Description: Very soft, grey to occasionally orange-brown, thinly laminated, very slightly gravelly, very slightly sandy SILT with clay.

Clay Cutter Fragment (Cross Sectional Area 0.00126m^2) Open Pore (0.8mm and 1.9mm diameter)

Photo:

Geotechnical Data:
PSD 1% Gravel, 6% Sand, 69% Silt, 24% Clay
Moisture Content 43%
Liquid Limit 48%, Plastic Limit 50%, Plasticity Index 24%

Location: Newport

Borehole No: BH101

Date of Borehole: 15/09/2008

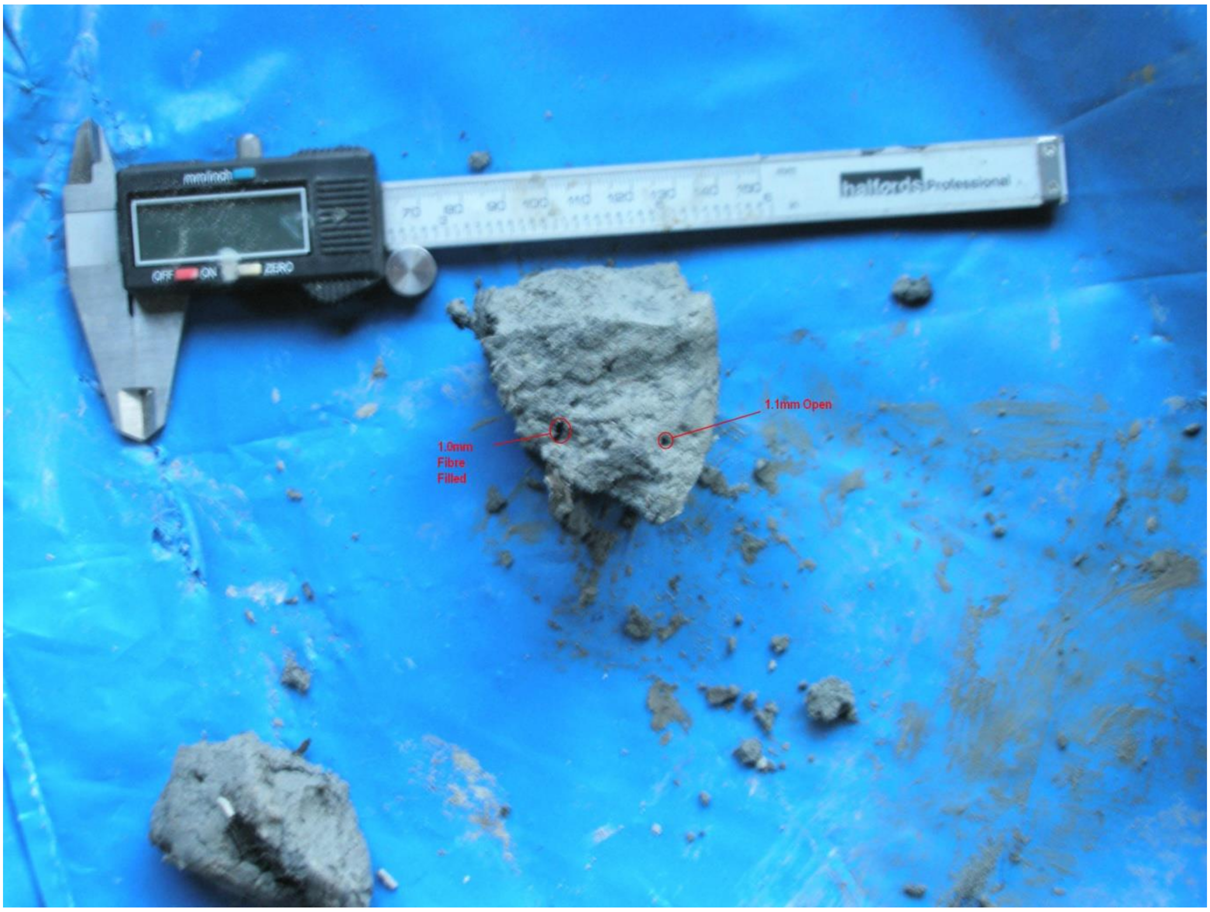
Sample Depth: 10.0m

Sample Type: Bulk Bag

Soil Description: Very soft, grey, thinly laminated, very slightly sandy SILT with clay.

Clay Cutter Fragment (Cross Sectional Area 0.00125 m^2) Open Pore (1.1mm diameter), Fibre Filled Pore (1.0mm diameter)

Photo:



Geotechnical Data:
PSD 4% Sand, 78% Silt, 18% Clay
Moisture Content 52%

Location: Newport

Borehole No: BH101

Date of Borehole: 15/09/2008

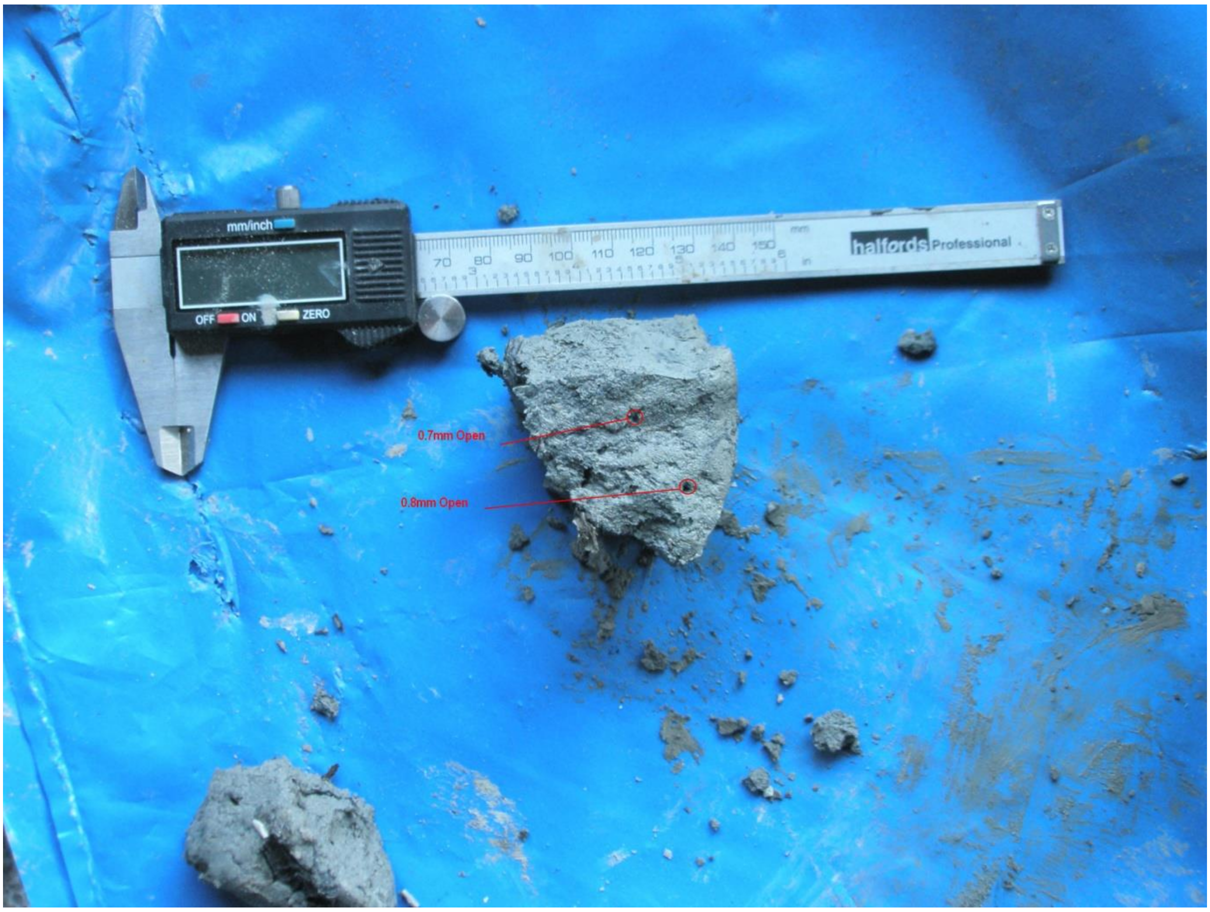
Sample Depth: 11.0m

Sample Type: Bulk Bag

Soil Description: Very soft, grey, thinly laminated, slightly sandy SILT with clay. Contains occasional very thin beds (<1mm) of black, mineral dominated peat.

Clay Cutter Fragment (Cross Sectional Area 0.00126m^2) Open Pore 0.7mm diameter, Open Pore 0.8mm diameter.

Photo:



Geotechnical Data:
PSD 8% Sand, 68% Silt, 24% Clay
Moisture Content 52%

Location: Newport

Borehole No: BH101

Date of Borehole: 15/09/2008

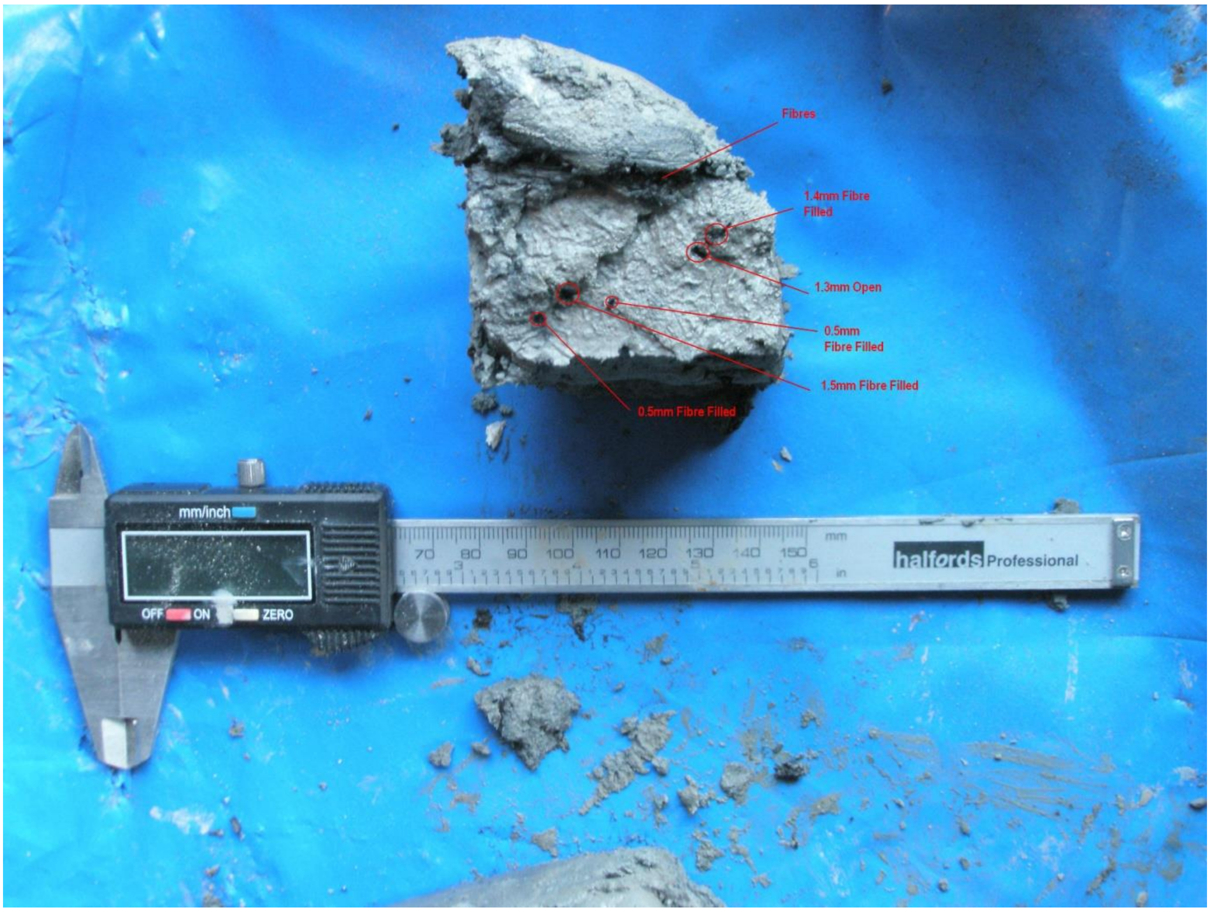
Sample Depth: 12.0m

Sample Type: Bulk Bag

Soil Description: Very soft, grey, thinly laminated, slightly sandy SILT with clay.

Clay Cutter Fragment (Cross Sectional Area 0.00125m^2) Open Pore (1.3mm diameter) Fibre Filled Pores (d = 0.5mm, 0.5mm, 1.3mm, 1.4mm and 1.5mm).

Photo:



Geotechnical Data:
PSD 6% Sand, 76% Silt, 18% Clay
Moisture Content 46%
Organic Carbon Content – O.O7999%

Location: Newport

Borehole No: BH101

Date of Borehole: 15/09/2008

Sample Depth: 13.0m

Sample Type: Bulk Bag

Soil Description: Very soft, grey, very slightly sandy SILT with clay.

Sample too disturbed to determine structure.

Photo:

Geotechnical Data:
PSD 5% Sand, 72% Silt, 23% Clay
Moisture Content 57%

Location: Newport

Borehole No: BH101

Date of Borehole: 15/09/2008

Sample Depth: 13.3m

Sample Type: Bulk Bag

Soil Description: Dense to very dense, grey to brown, very slightly sandy, slightly silty/clayey GRAVEL of fine to coarse GRAVEL of rounded to sub-rounded carboniferous with occasional angular fragment of mercia mudstone.

Photo:

Geotechnical Data:
PSD 90% Gravel, 2% Sand, 8% Silt & Clay
Moisture Content 2.6%

Location: Newport

Borehole No: BH101

Date of Borehole: 15/09/2008

Sample Depth: 14.5m

Sample Type: Bulk Bag

Soil Description: Dense to very dense, grey to brown to occasionally red-brown, slightly sandy, very slightly silty/clayey GRAVEL of fine to coarse GRAVEL of rounded to sub-rounded Carboniferous with occasional angular fragment of Mercia Mudstone.

Photo:

Geotechnical Data:
PSD 91% Gravel, 7% Sand, 2% Silt & Clay
Moisture Content 7%

Location: Newport

Borehole No: BH102

Date of Borehole: 17/09/2008

Sample Depth: 0.6m

Sample Type: Bulk Bag

Soil Description: MADE GROUND: Black, Gravelly, very sandy CLAY to clayey SAND. Contains fragments of ash and slag. Weak hydrocarbon odour.

Photo

Geotechnical Data: N/A

Location: Newport

Borehole No: BH102

Date of Borehole: 17/09/2008

Sample Depth: 2.0m

Sample Type: Bulk Bag

Soil Description: MADE GROUND: Firm, grey to occasionally brown and black, SILT/CLAY with inclusions of timber.

Hydrocarbon odour noted

Photo

Geotechnical Data: N/A

Location: Newport

Borehole No: BH102

Date of Borehole: 17/09/2008

Sample Depth: 3.0m

Sample Type: Bulk Bag

Soil Description: Soft to very soft, grey, sandy SILT with clay.

Sample very disturbed but bio-pores noted up to 0.16mm diameter.

Mild hydrocarbon odour noted. Sample possibly reworked ground.

Photo

Geotechnical Data: N/A

Location: Newport

Borehole No: BH102

Date of Borehole: 17/09/2008

Sample Depth: 4.0m

Sample Type: Bulk Bag

Soil Description: Soft to very soft, grey, sandy SILT with clay.

Sample very disturbed but bio-pores noted up to 0.14mm diameter.

Very mild hydrocarbon odour noted. Sample possibly reworked ground.

Photo

Geotechnical Data: N/A

Location: Newport

Borehole No: BH102

Date of Borehole: 17/09/2008

Sample Depth: 5.0m

Sample Type: Bulk Bag

Soil Description: Firm, grey to occasionally orange-brown, thinly laminated SILT with clay.

Clay cutter sample (cross-sectional area approximately 0.00126m^2) Open Pores (0.8mm, 1.0mm, 1.1mm) Fibre Filled Pores (1.1mm, 1.2mm). Hydrocarbon free-product noted in pores.

Photo

Geotechnical Data: N/A

Location: Newport

Borehole No: BH102

Date of Borehole: 17/09/2008

Sample Depth: 5.5m

Sample Type: Bulk Bag

Soil Description: Firm, grey to occasionally orange-brown, thinly laminated SILT with clay. Contains pockets of sandy silt.

Clay cutter sample (cross-sectional area approximately 0.00126m^2) Open Pores (1.0mm, 1.0mm, 1.8mm) Fibre Filled Pores (1.2mm, 1.6mm). Hydrocarbon free-product noted in pores.

Photo

Geotechnical Data: N/A

Location: Newport

Borehole No: BH102

Date of Borehole: 17/09/2008

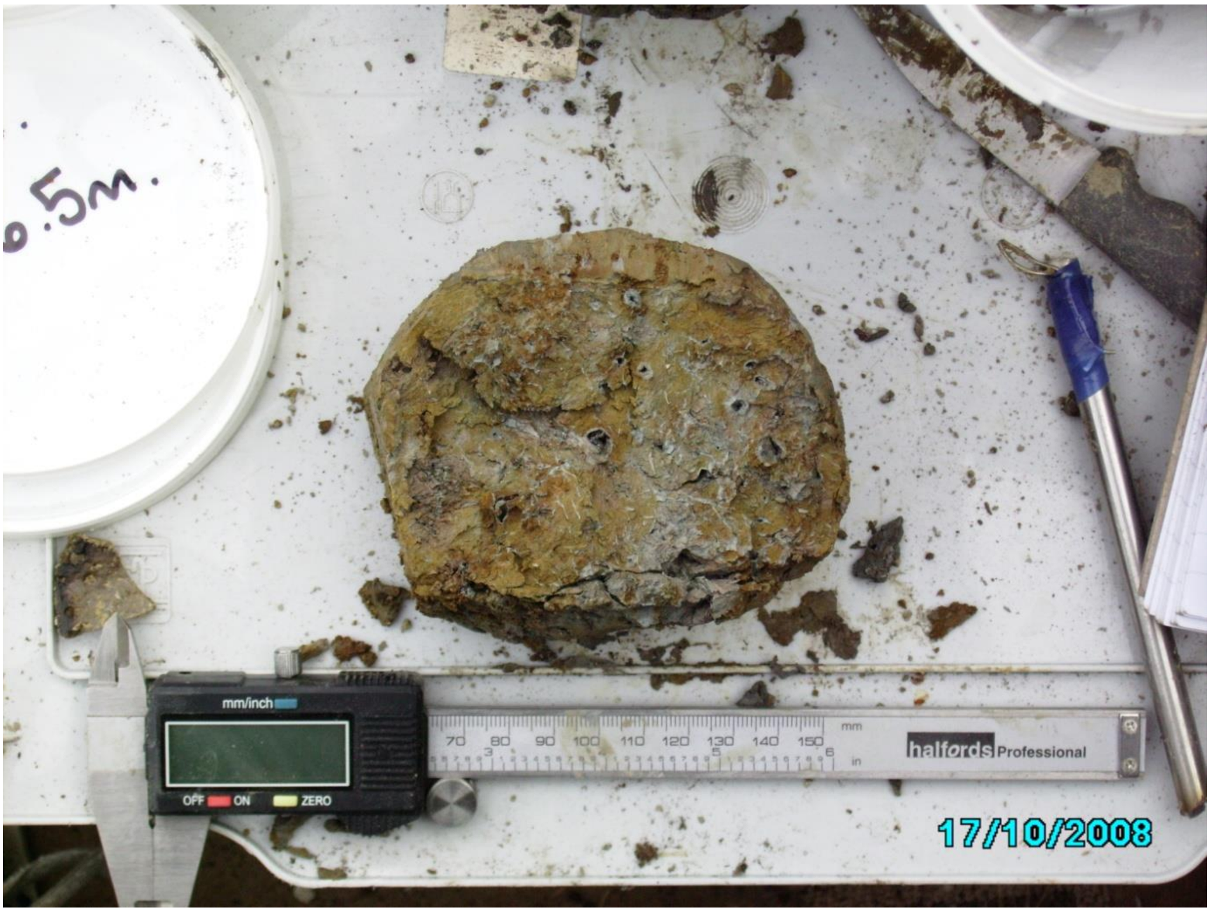
Sample Depth: 6.0 – 6.5m

Sample Type: U100

Soil Description: Soft, grey to orange-brown, thinly laminated SILT with clay.

100mm cross section (CS area of 0.0079m^2). Ten bio-pores noted with diameters - 0.2mm, 0.4mm, 0.9mm, 1.0mm, 1.1mm, 1.4mm, 1.5mm, 1.5mm. 1.5mm and 2.5mm.

Photo



Geotechnical Data: N/A

Location: Newport

Borehole No: BH102

Date of Borehole: 17/09/2008

Sample Depth: 6.5m

Sample Type: tub

Soil Description: Soft, grey to orange-brown, thinly laminated SILT with clay.

100mm shoe sample (cross-sectional area approximately 0.0079m^2) Open Pores (0.2mm, 0.5mm, 0.5mm, 0.9mm, 0.9mm, 1.1mm) Fibre Filled Pores (1.1mm, 1.6mm). Hydrocarbon free-product noted in pores.

Photo

Geotechnical Data: N/A

Location: Newport

Borehole No: BH102

Date of Borehole: 17/09/2008

Sample Depth: 8.00 – 8.50m

Sample Type: U100

Soil Description: Soft, grey to orange-brown, thinly laminated SILT with clay. Contains open and in filled root-casts.

U100 Sample (Cross-section 0.0079m^2) Open pores (0.5mm, 0.5mm, 0.6mm) Fibre filled pores (0.9mm, 1.0mm, 1.2mm, 1.2mm, 1.4mm, 1.5mm, 1.6mm, 1.9mm, 2.1mm).

Photo

Geotechnical Data: N/A

Location: Newport

Borehole No: BH102

Date of Borehole: 17/09/2008

Sample Depth: 10.00m

Sample Type: BULK

Soil Description: Soft, grey to orange-brown, thinly laminated SILT with clay. Hydrocarbon staining and odours noted.

Clay Cutter Sample (Cross-section approximately 0.00126m^2) Open Pores (0.5mm, 0.6mm) Fibre Filled Pores (0.8mm, 0.8mm, 1.2mm, 1.4mm, 1.6mm) and horizontal fibres present.

Photo

Geotechnical Data: N/A

Location: Newport

Borehole No: BH102

Date of Borehole: 17/09/2008

Sample Depth: 13.00m

Sample Type: BULK

Soil Description: Very soft, grey to orange-brown, thinly laminated SILT with clay. Hydrocarbon staining and odours noted within bio-casts.

Clay Cutter Sample (Approx. Cross-sectional area 0.00126m^2) Open Pores (0.4mm, 0.5mm) and Fibre Filled (0.6mm, 0.7mm, 0.7mm, 0.9mm, 1.0mm, 1.4mm, 1.5mm) and horizontal plant fibres present.

Photo

Geotechnical Data: N/A

Location: Newport

Borehole No: BH102

Date of Borehole: 17/09/2008

Sample Depth: 14.00m

Sample Type: BULK

Soil Description: Dense, brown, sandy rounded GRAVEL to COBBLES of sandstone. Hydrocarbon staining noted.

Photo

Geotechnical Data: N/A

Location: Weston Super Mare

Borehole No: BH1

Date of Borehole: 16/06/2008

Sample Depth: 0.40 m

Sample Type: BULK

Soil Description: MADE GROUND: Grey, sandy GRAVEL of crushed limestone.

Photo:

Geotechnical Data:

Location: Weston Super Mare

Borehole No: BH1

Date of Borehole: 16/06/2008

Sample Depth: 1.00 – 1.45 m

Sample Type: SPT Spoon Sample (35mm diameter)

Soil Description: Soft, grey to brown, CLAY/SILT.

4 No. root-casts noted. 0.4mm open, 0.4mm open, 0.9mm open, 1.1 mm open.

Photo:

Geotechnical Data:

Location: Weston Super Mare

Borehole No: BH1

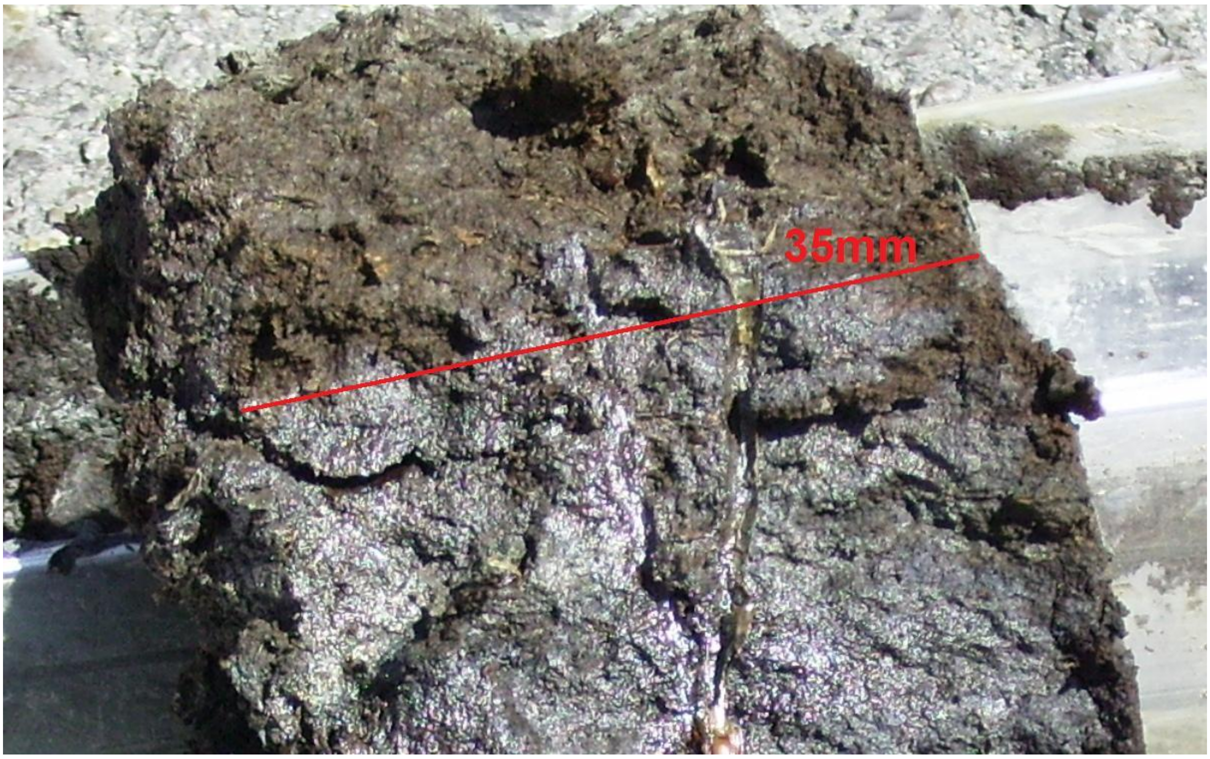
Date of Borehole: 16/06/2008

Sample Depth: 2.00 – 2.45 m

Sample Type: SPT Spoon Sample (35mm diameter)

Soil Description: Spongy, fibrous to pseudo-fibrous PEAT with clay inclusions. Hydrocarbon odour noted and hydrocarbon sheen apparent in regions of open structure.

Photo:



Geotechnical Data:

Location: Weston Super Mare

Borehole No: BH1

Date of Borehole: 16/06/2008

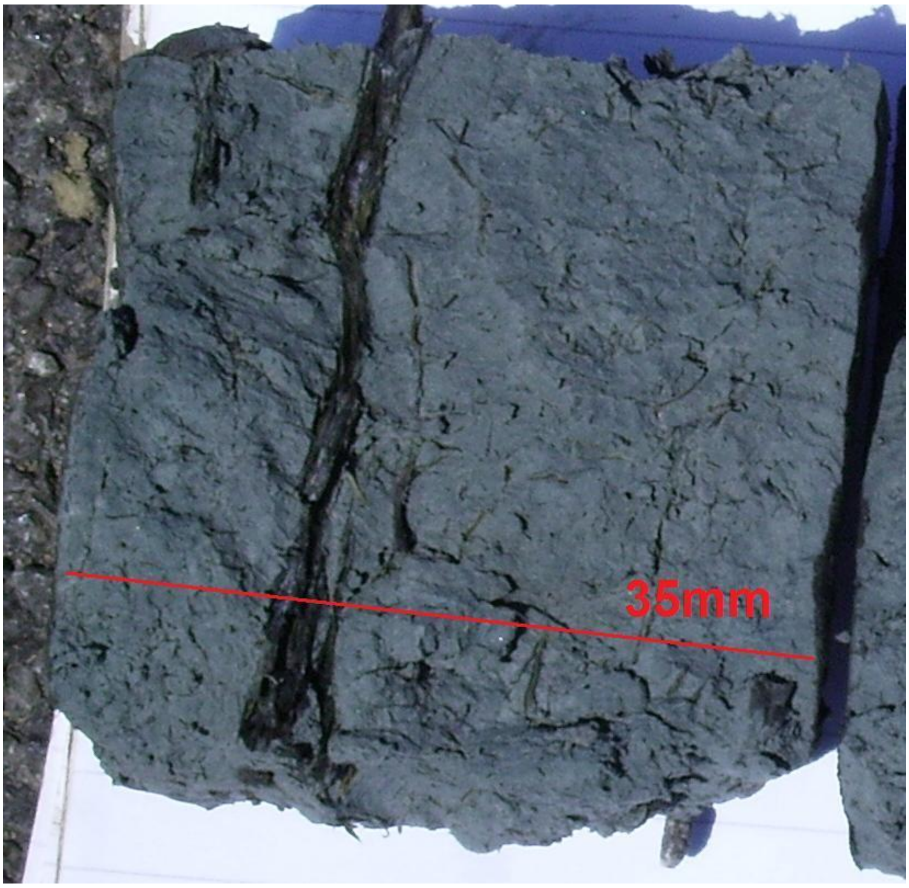
Sample Depth: 3.00 – 3.45 m

Sample Type: SPT Spoon Sample (35mm diameter)

Soil Description: Very soft, thinly laminated, grey to brown, SILT/CLAY. Hydrocarbon odour noted and free-product observed in open bio-casts.

Three bio-casts noted – 0.4mm open and filled with hydrocarbon free-product, 0.8mm open and filled with hydrocarbon free-product, 2.3mm filled with fibres – Hydrocarbon odours noted.

Photo:



Geotechnical Data:

Chemical Data:

Location: Weston Super Mare

Borehole No: BH1

Date of Borehole: 16/06/2008

Sample Depth: 5.00 – 5.45 m

Sample Type: SPT Spoon Sample (35mm diameter)

Soil Description: Very soft, thinly laminated, grey to brown, SILT/CLAY.

Photo:

Geotechnical Data:

Chemical Data:

Location: Weston Super Mare

Borehole No: BH1

Date of Borehole: 16/06/2008

Sample Depth: 9.50 – 9.95 m

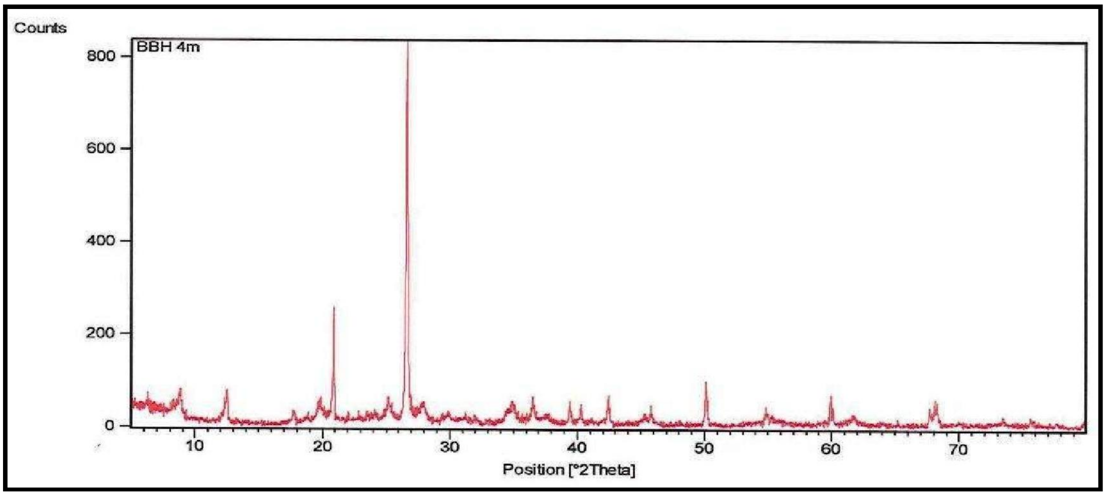
Sample Type: SPT Spoon Sample (35mm diameter)

Soil Description: Loose to very loose, light grey to brown, silty fine SAND to sandy SILT with occasional clay pockets.

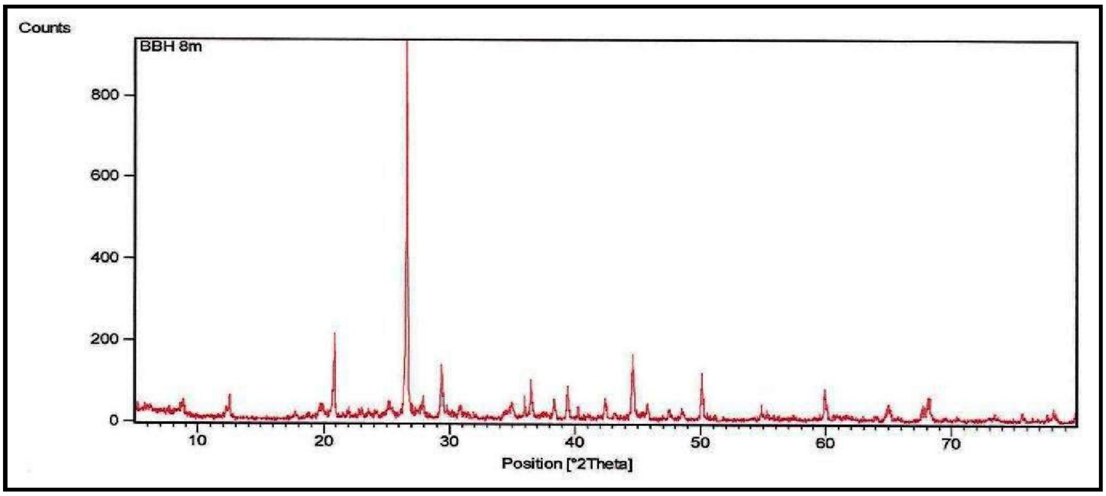
Photo:

Geotechnical Data:

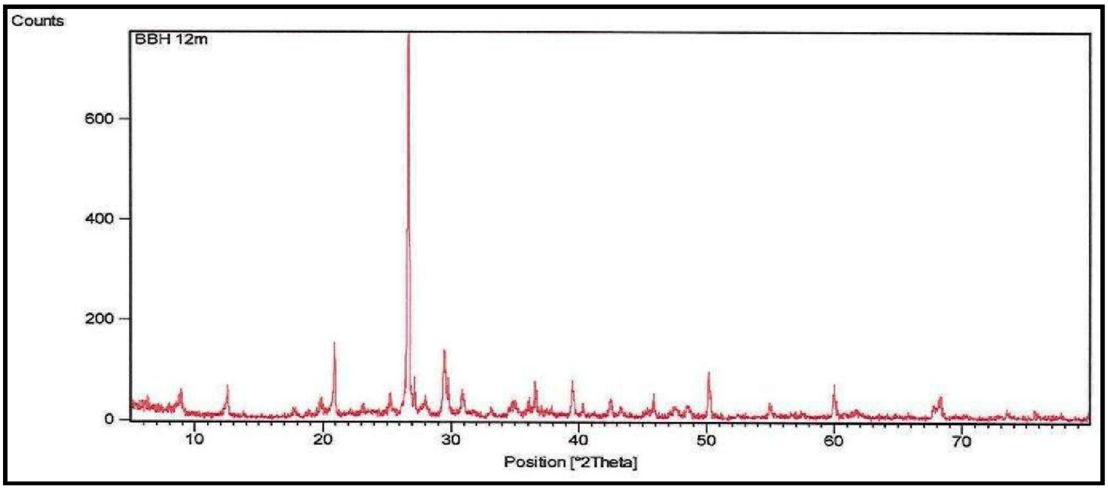
Chemical Data:



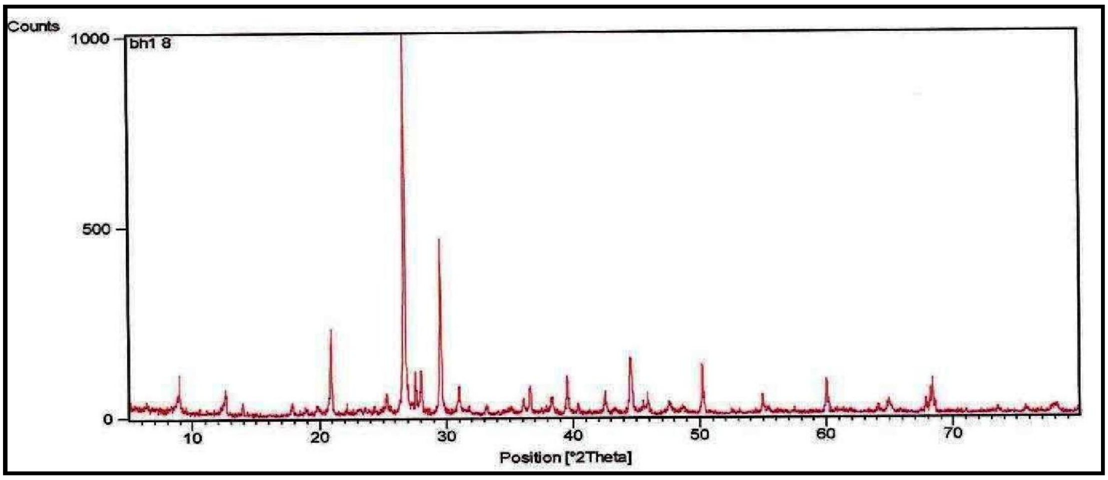
1: X-Ray Diffraction trace for alluvial clay/silt from BH101 4.0m, Newport.



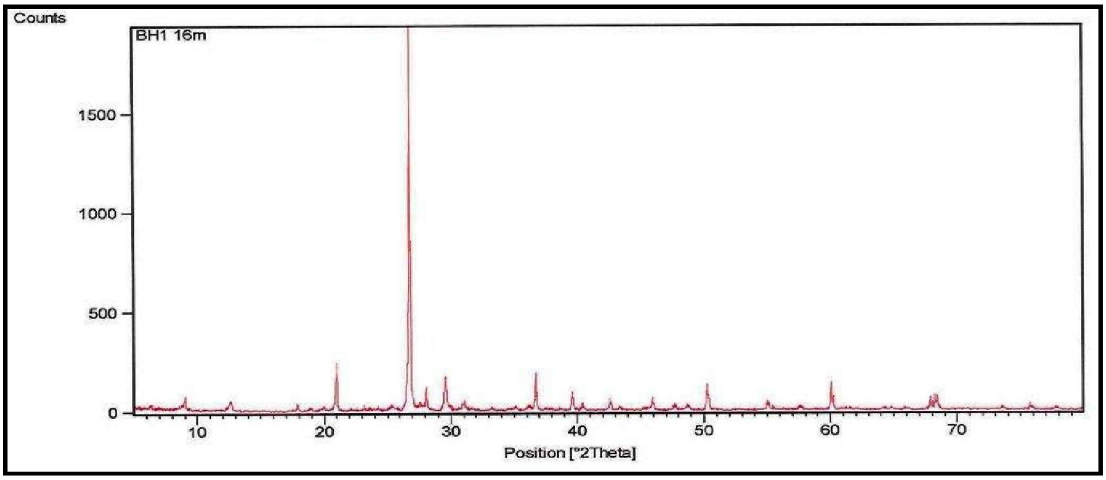
2: X-Ray Diffraction trace for alluvial clay/silt from BH101 8.0m, Newport.



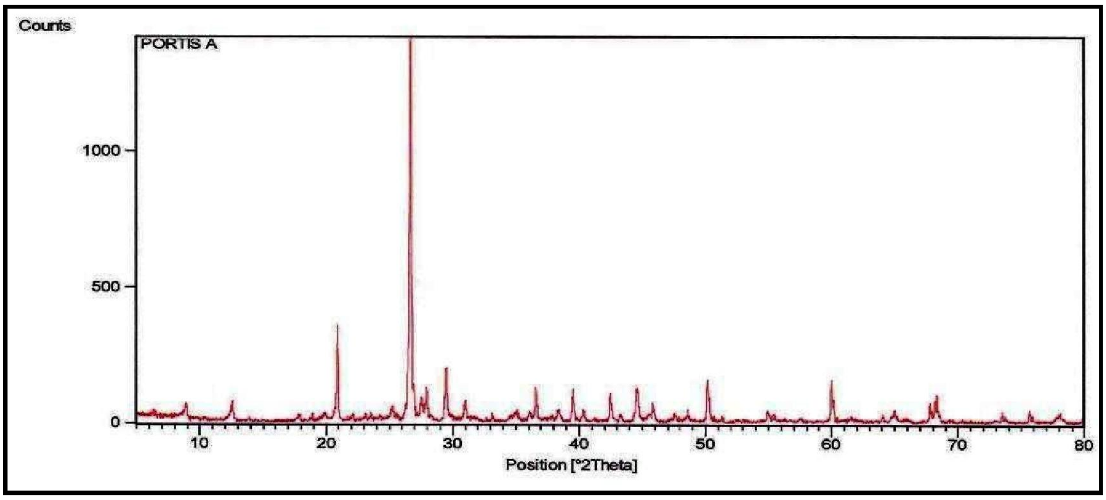
3: X-Ray Diffraction trace for alluvial clay/silt from BH101 12.0m, Newport.



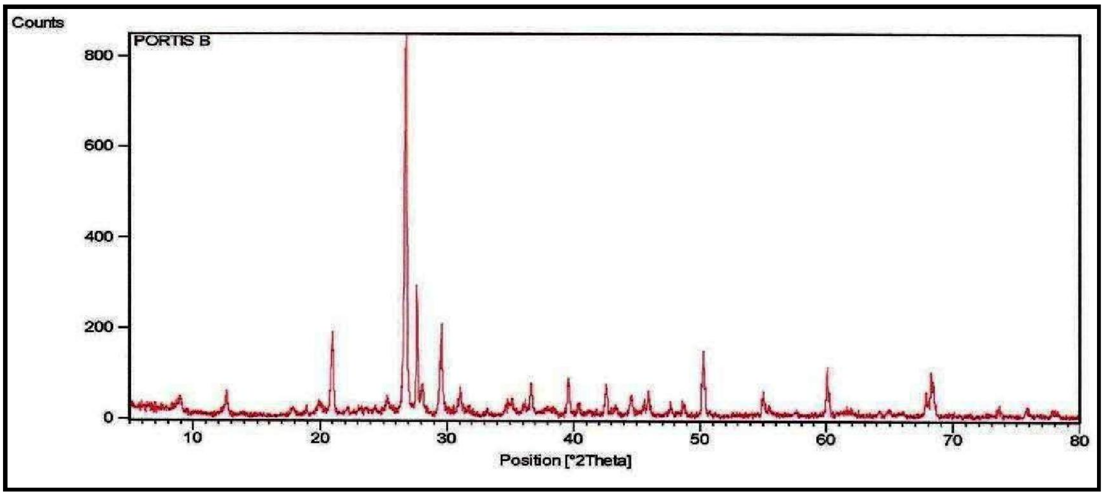
4: X-Ray Diffraction trace for alluvial clay/silt from BH1 8.0m, Cardiff.



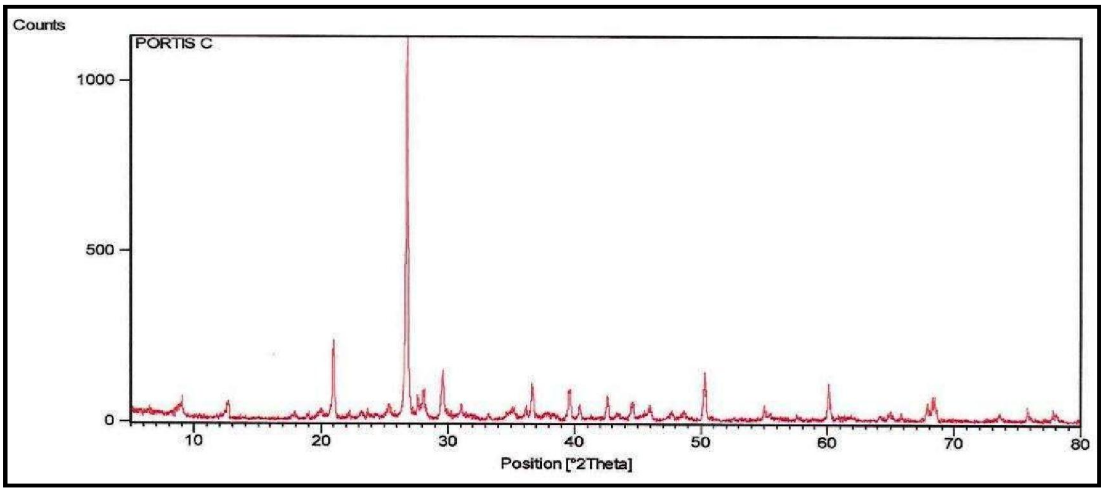
5: X-Ray Diffraction trace for alluvial clay/silt from BH1 16.0m, Cardiff.



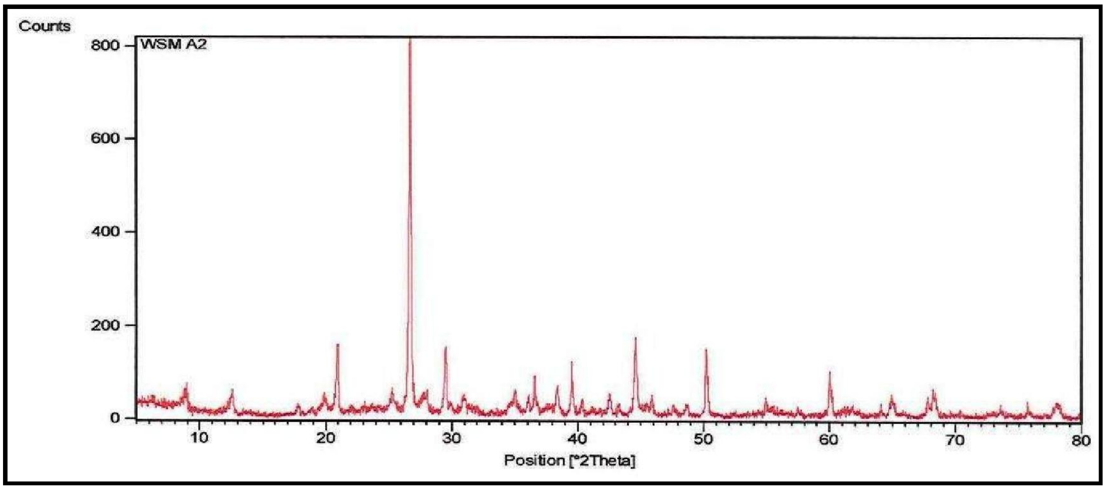
6: X-Ray Diffraction trace for alluvial clay/silt from BH1 8.0m, Portishead.



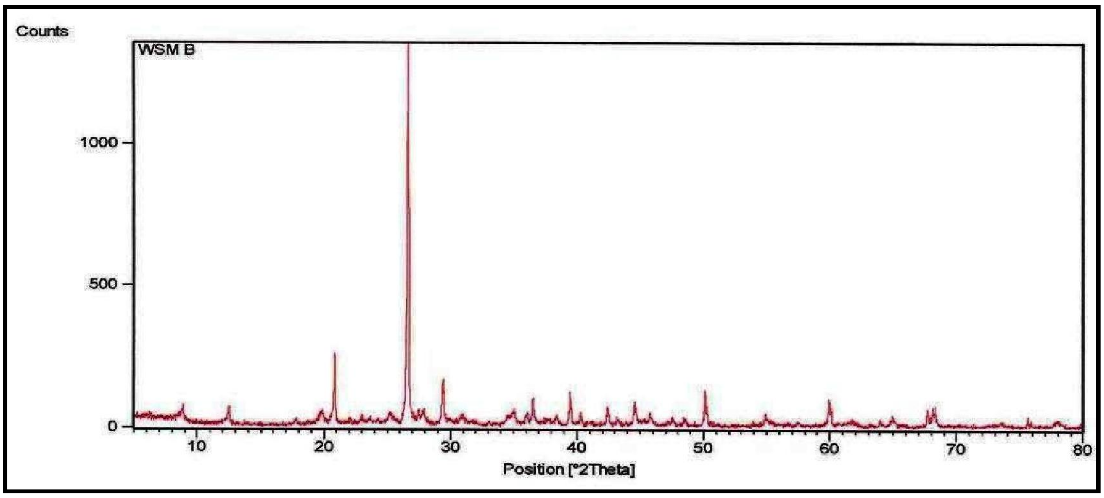
7: X-Ray Diffraction trace for alluvial clay/silt from BH1 12.0m, Portishead.



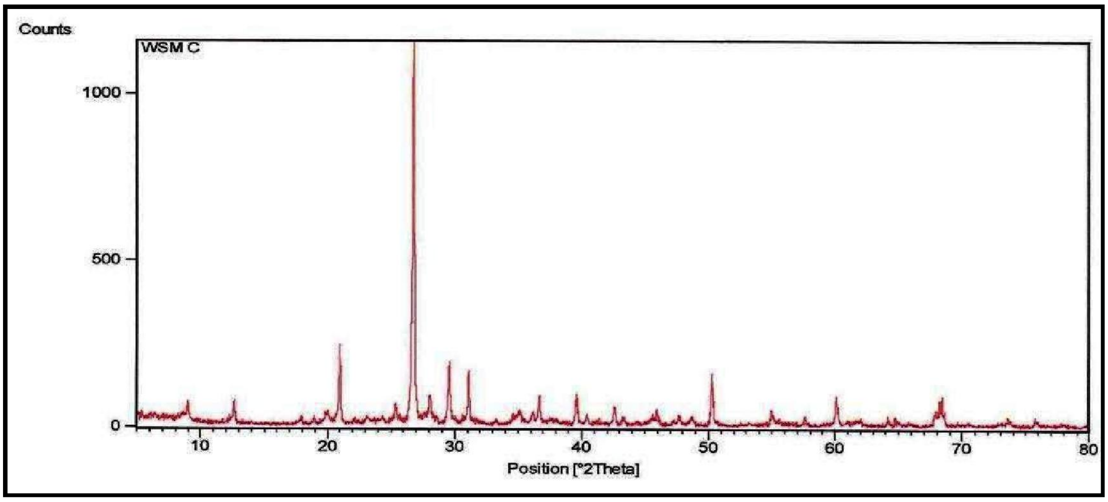
8: X-Ray Diffraction trace for alluvial clay/silt from BH1 14.0m, Portishead.



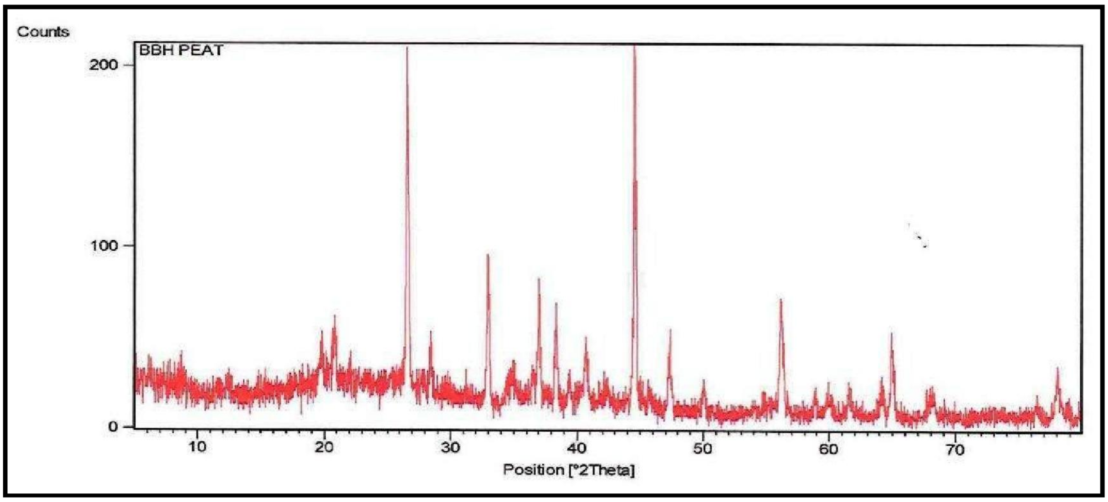
9: X-Ray Diffraction trace for alluvial clay/silt from BH1 8.0m, Weston Super Mare.



10: X-Ray Diffraction trace for alluvial clay/silt from BH1 12.0m, Weston Super Mare.



11: X-Ray Diffraction trace for alluvial clay/silt from BH1 8.0m, Weston Super Mare.



12: X-Ray Diffraction trace for alluvial peat from BH101 6.6m, Newport.

Summary of Laboratory Sample Descriptions

Hole Number	Sample Number	Type	Depth m	Description of Sample*
101			4.00	Grey clayey SILT.
101			5.00	Grey slightly sandy (fine to coarse) clayey SILT.
101			6.00	Grey slightly gravelly (fine) slightly sandy (fine to coarse) very clayey SILT.
101			6.70	Grey gravelly (fine) very sandy (fine to coarse) SIL/CLAY.
101			8.00	Grey slightly sandy (fine to coarse) very clayey SILT.
101			9.00	Grey slightly gravelly (fine) sandy (fine to coarse) very clayey SILT.
101			10.00	Grey slightly sandy (fine to coarse) clayey SILT.
101			11.00	Grey sandy (fine to coarse) very clayey SILT.
101			12.00	Grey sandy (fine to coarse) clayey SILT.
101			13.00	Grey sandy (fine to coarse) very clayey SILT.
101			13.30	Grey slightly sandy (fine to coarse) silty fine to coarse GRAVEL.
101			14.50	Grey sandy (fine to coarse) slightly silty fine to coarse GRAVEL.

Note: Results on this table are in summary format and may not meet the requirements of the relevant standards, additional information is held by the laboratory

Checked by Date 27/10/08

Approved by Date 27/10/08

LABORATORY TESTING SERVICES LIMITED

BBH

Contract No.:
GEO/6802/08
Client ref:
N/A

Summary of Soil Classification Tests

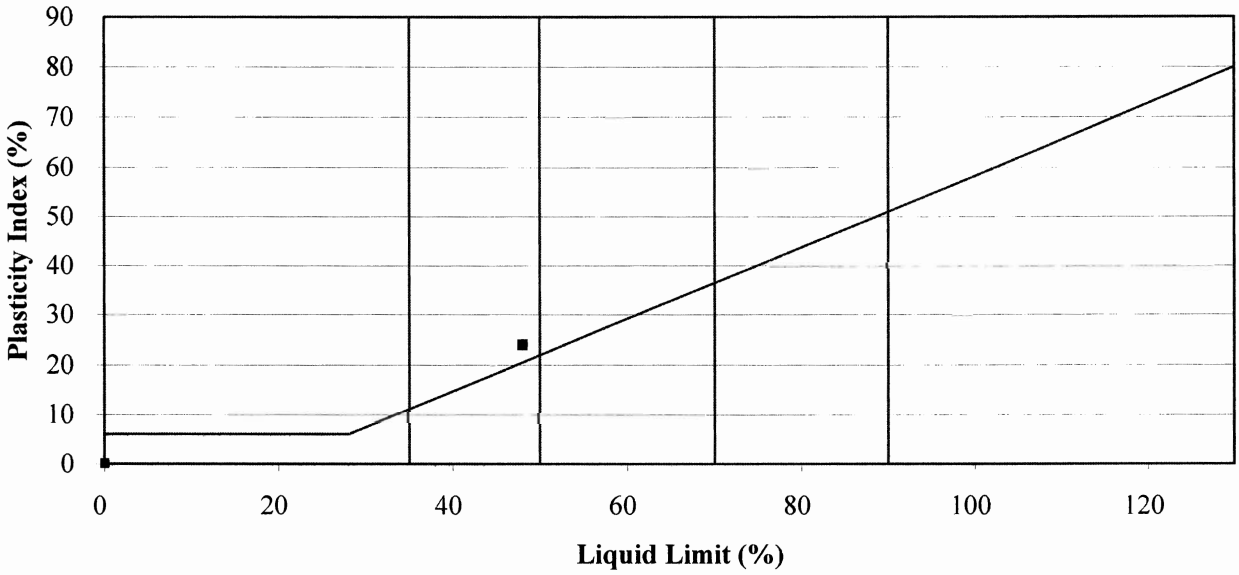
BS 1377:Part 2:1990

Hole/ Sample Number	Sample Type	Depth m	Moisture Content % Cl. 3.2	Liquid Limit % Cl. 4.3/4.4	Plastic Limit % Cl. 5.	Plasticity Index % Cl. 6.	% Passing .425mm	Remarks
BH1		4.00	33					
BH1		5.00	38					
BH1		6.00	52					
BH1		6.70	186					
BH1		8.00	47					
BH1		9.00	43	48	50	24	97	CI Intermediate Plasticity
BH1		10.00	52					
BH1		11.00	52					
BH1		12.00	46					
BH1		13.00	57					
BH1		13.30	2.6					
BH1		14.50	7.0					

Symbols: NP : Non Plastic # : Liquid Limit and Plastic Limit Wet Sieved

PLASTICITY CHART FOR CASAGRANDE CLASSIFICATION.

BS 5930:1999



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GEO/6802/08
Client Ref No:
N/A

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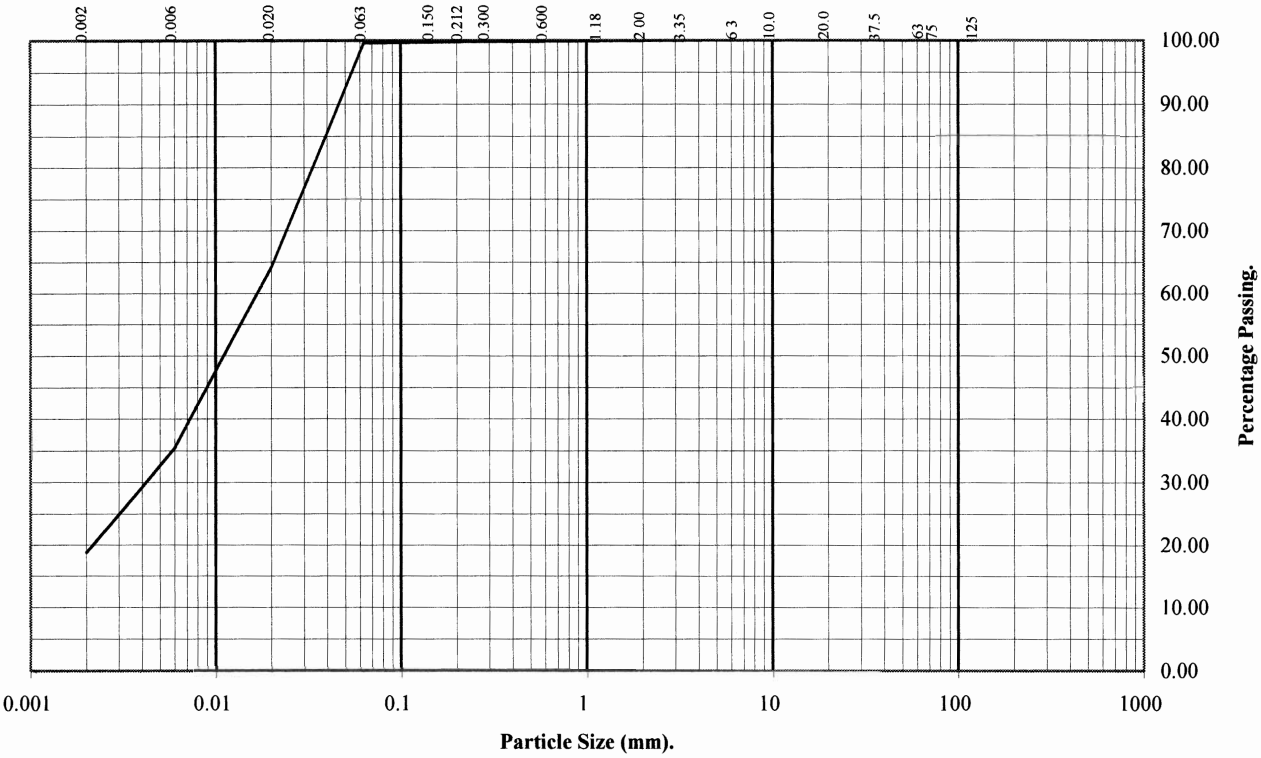
PARTICLE SIZE DISTRIBUTION TEST

BS 1377 Part 2:1990.

Wet sieve Pipette analysis Clause 9.2 9.4

Hole Number: **BH101** **Depth (m)** **4.00**



BS Test Sieve	Percentage Passing
125	100
75	100
63	100
37.5	100
20	100
10	100
6.3	100
3.35	100
2	100
1.18	100
0.6	100
0.3	100
0.212	100
0.15	100
0.063	100

Particle Diameter	Percentage Passing
0.02	64
0.006	35
0.002	19

Soil Fraction	Total Percentage
Cobbles	0
Gravel	0
Sand	0
Silt	81
Clay	19

Remarks:

Cl 9.4.8 - Sample has not been pretreated

7/10/08

Checked by **Date**

7/10/08

Approved by **Date**

LABORATORY TESTING SERVICES LIMITED

BBH

Contract No.:
GEO/6802/08
Client Ref No:
N/A

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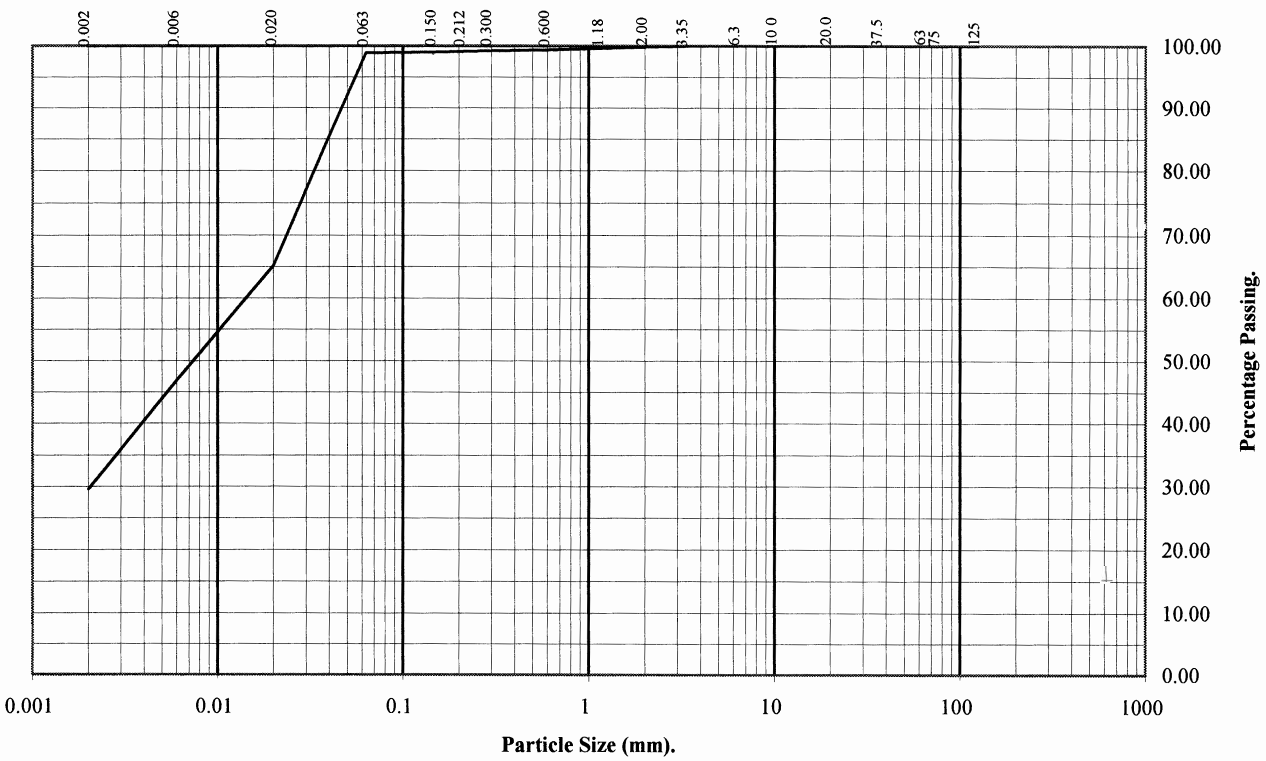
PARTICLE SIZE DISTRIBUTION TEST

BS 1377 Part 2:1990.

Wet sieve Pipette analysis Clause 9.2 9.4

Hole Number: **BH101** **Depth (m)** **5.00**



BS Test Sieve	Percentage Passing
125	100
75	100
63	100
37.5	100
20	100
10	100
6.3	100
3.35	100
2	100
1.18	100
0.6	99
0.3	99
0.212	99
0.15	99
0.063	99

Particle Diameter	Percentage Passing
0.02	65
0.006	47
0.002	30

Soil Fraction	Total Percentage
Cobbles	0
Gravel	0
Sand	1
Silt	69
Clay	30

Remarks:

Cl 9.4.8 - Sample has not been pretreated

24/10/08

Checked by **Date**

24/10/08

Approved by **Date**

LABORATORY TESTING SERVICES LIMITED

BBH

Contract No.:
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Client Ref No:
N/A

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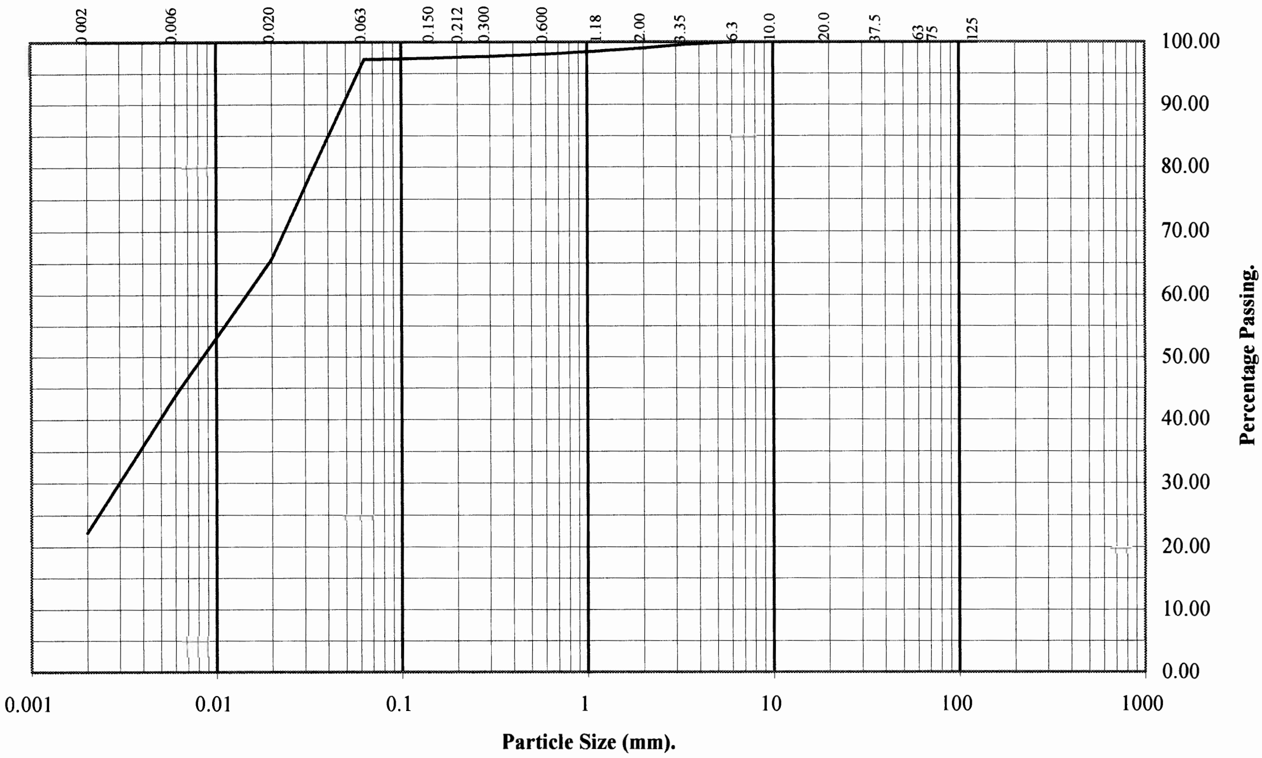
PARTICLE SIZE DISTRIBUTION TEST

BS 1377 Part 2:1990.

Wet sieve Pipette analysis Clause 9.2 9.4

Hole Number: **BH101** **Depth (m)** **6.00**



BS Test Sieve	Percentage Passing
125	100
75	100
63	100
37.5	100
20	100
10	100
6.3	100
3.35	100
2	99
1.18	99
0.6	98
0.3	98
0.212	98
0.15	97
0.063	97

Particle Diameter	Percentage Passing
0.02	66
0.006	44
0.002	22

Soil Fraction	Total Percentage
Cobbles	0
Gravel	1
Sand	2
Silt	75
Clay	22

Remarks:

Cl 9.4.8 - Sample has not been pretreated

24/10/08

Checked by **Date**

24/10/08

Approved by **Date**

LABORATORY TESTING SERVICES LIMITED

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Contract No.:
GEO/6802/08
Client Ref No:
N/A

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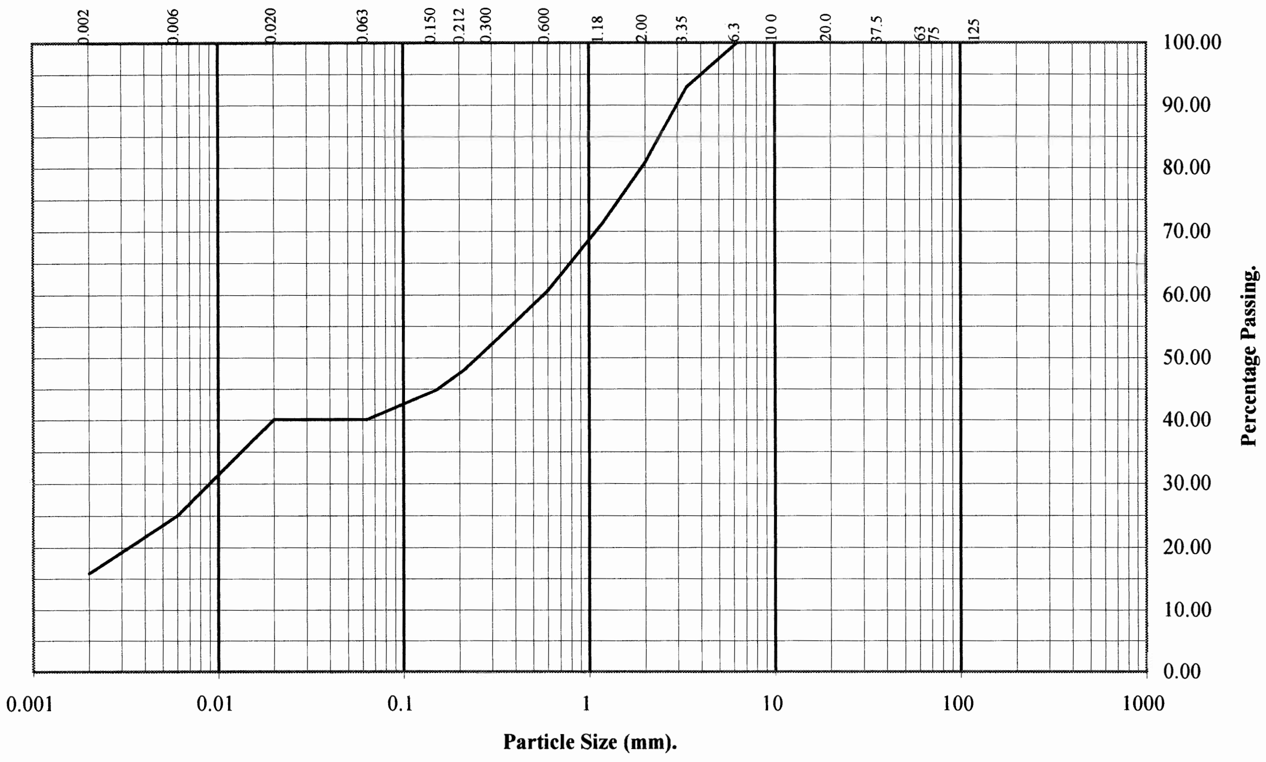
PARTICLE SIZE DISTRIBUTION TEST

BS 1377 Part 2:1990.

Wet sieve Pipette analysis Clause 9.2 9.4

Hole Number: **BH101** **Depth (m)** **6.70**



BS Test Sieve	Percentage Passing
125	100
75	100
63	100
37.5	100
20	100
10	100
6.3	100
3.35	93
2	81
1.18	71
0.6	61
0.3	52
0.212	48
0.15	45
0.063	40

Particle Diameter	Percentage Passing
0.02	40
0.006	25
0.002	16

Soil Fraction	Total Percentage
Cobbles	0
Gravel	19
Sand	41
Silt	24
Clay	16

Remarks:

Cl 9.4.8 - Sample has not been pretreated

24/10/08

Checked by **Date**

24/10/08

Approved by **Date**

LABORATORY TESTING SERVICES LIMITED

BBH

Contract No.:
GEO/6802/08
Client Ref No:
N/A

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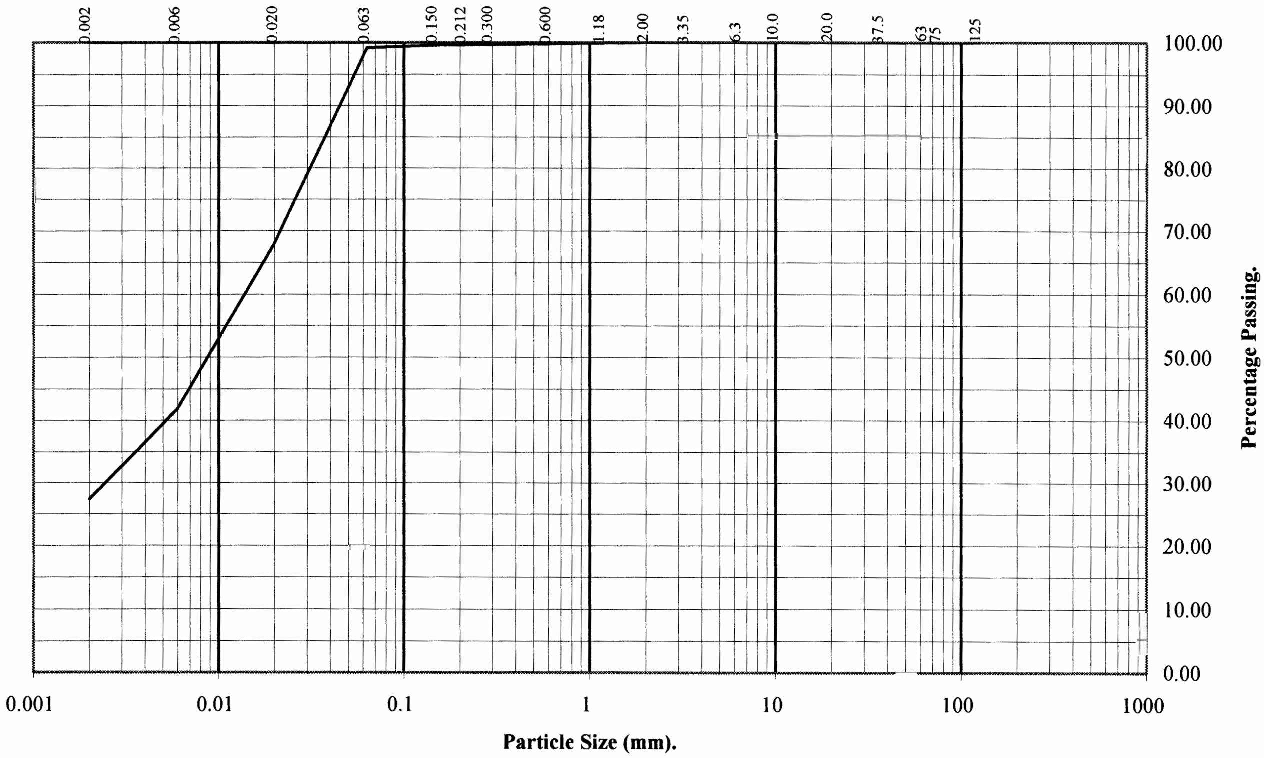
PARTICLE SIZE DISTRIBUTION TEST

BS 1377 Part 2:1990.

Wet sieve Pipette analysis Clause 9.2 9.4

Hole Number: **BH101** **Depth (m)** **8.00**



BS Test Sieve	Percentage Passing
125	100
75	100
63	100
37.5	100
20	100
10	100
6.3	100
3.35	100
2	100
1.18	100
0.6	100
0.3	100
0.212	100
0.15	100
0.063	99

Particle Diameter	Percentage Passing
0.02	68
0.006	42
0.002	27

Soil Fraction	Total Percentage
Cobbles	0
Gravel	0
Sand	1
Silt	72
Clay	27

Remarks:

Cl 9.4.8 - Sample has not been pretreated

24/10/08
Checked by **Date**

24/10/08
Approved by **Date**

LABORATORY TESTING SERVICES LIMITED

BBH

Contract No.:
GEO/6802/08
Client Ref No:
N/A

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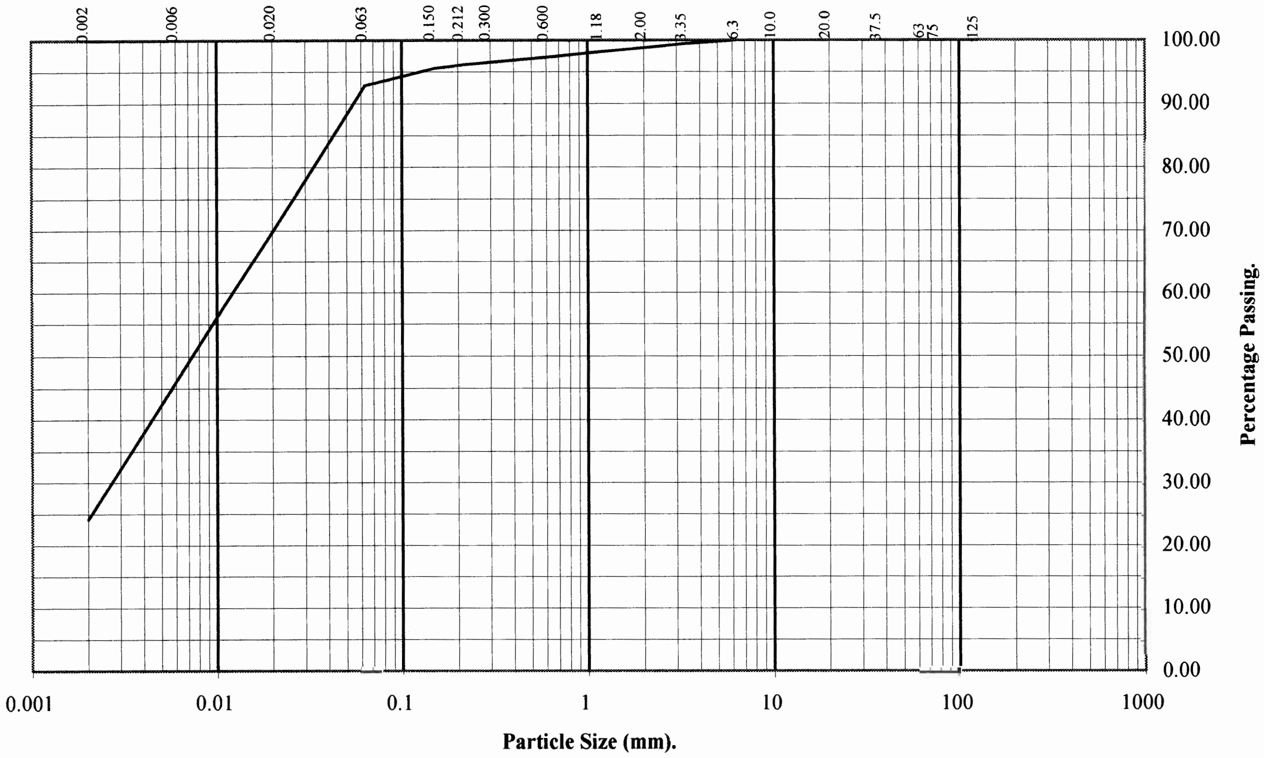
PARTICLE SIZE DISTRIBUTION TEST

BS 1377 Part 2:1990.

Wet sieve Pipette analysis Clause 9.2 9.4

Hole Number: **BH101** **Depth (m)** **9.00**



BS Test Sieve	Percentage Passing
125	100
75	100
63	100
37.5	100
20	100
10	100
6.3	100
3.35	99
2	99
1.18	98
0.6	97
0.3	96
0.212	96
0.15	96
0.063	93

Particle Diameter	Percentage Passing
0.02	70
0.006	46
0.002	24

Soil Fraction	Total Percentage
Cobbles	0
Gravel	1
Sand	6
Silt	69
Clay	24

Remarks:

Cl 9.4.8 - Sample has not been pretreated

24/10/08

Checked by **Date**

24/10/08

Approved by **Date**

LABORATORY TESTING SERVICES LIMITED

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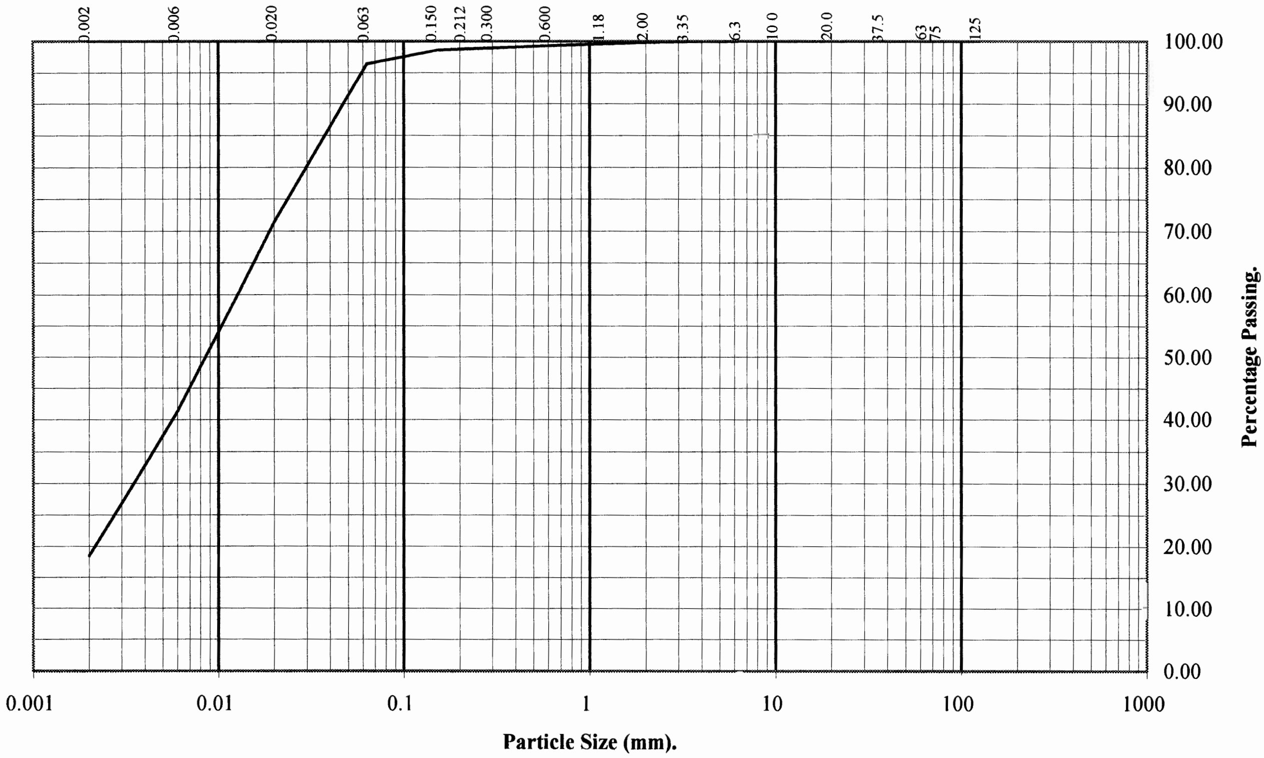
Contract No.:
GEO/6802/08
Client Ref No:
N/A

PARTICLE SIZE DISTRIBUTION TEST

BS 1377 Part 2:1990.

Wet sieve Pipette analysis Clause 9.2 9.4

Hole Number: **BH101** **Depth (m)** **10.00**



BS Test Sieve	Percentage Passing
125	100
75	100
63	100
37.5	100
20	100
10	100
6.3	100
3.35	100
2	100
1.18	100
0.6	99
0.3	99
0.212	99
0.15	99
0.063	96

Particle Diameter	Percentage Passing
0.02	71
0.006	41
0.002	18

Soil Fraction	Total Percentage
Cobbles	0
Gravel	0
Sand	4
Silt	78
Clay	18

Remarks:

Cl 9.4.8 - Sample has not been pretreated

24/10/08

Checked by **Date**

24/10/08

Approved by **Date**

LABORATORY TESTING SERVICES LIMITED

BBH

Contract No.:
GEO/6802/08
Client Ref No:
N/A

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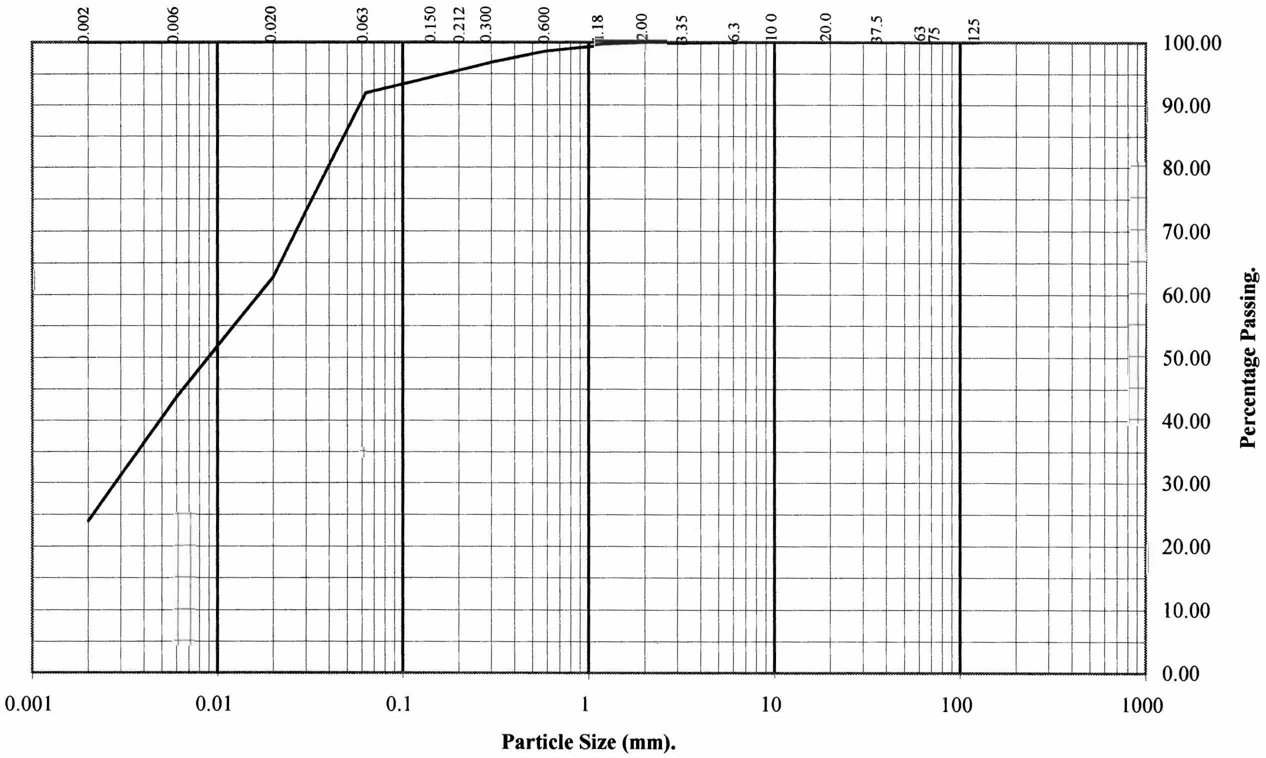
PARTICLE SIZE DISTRIBUTION TEST

BS 1377 Part 2:1990.

Wet sieve Pipette analysis Clause 9.2 9.4

Hole Number: **BH101** **Depth (m)** **11.00**



BS Test Sieve	Percentage Passing
125	100
75	100
63	100
37.5	100
20	100
10	100
6.3	100
3.35	100
2	100
1.18	100
0.6	99
0.3	97
0.212	96
0.15	95
0.063	92

Particle Diameter	Percentage Passing
0.02	63
0.006	44
0.002	24

Soil Fraction	Total Percentage
Cobbles	0
Gravel	0
Sand	8
Silt	68
Clay	24

Remarks:

Cl 9.4.8 - Sample has not been pretreated

24/10/08

Checked by **Date**

24/10/08

Approved by **Date**

LABORATORY TESTING SERVICES LIMITED

BBH

Contract No.:
GEO/6802/08
Client Ref No:
N/A

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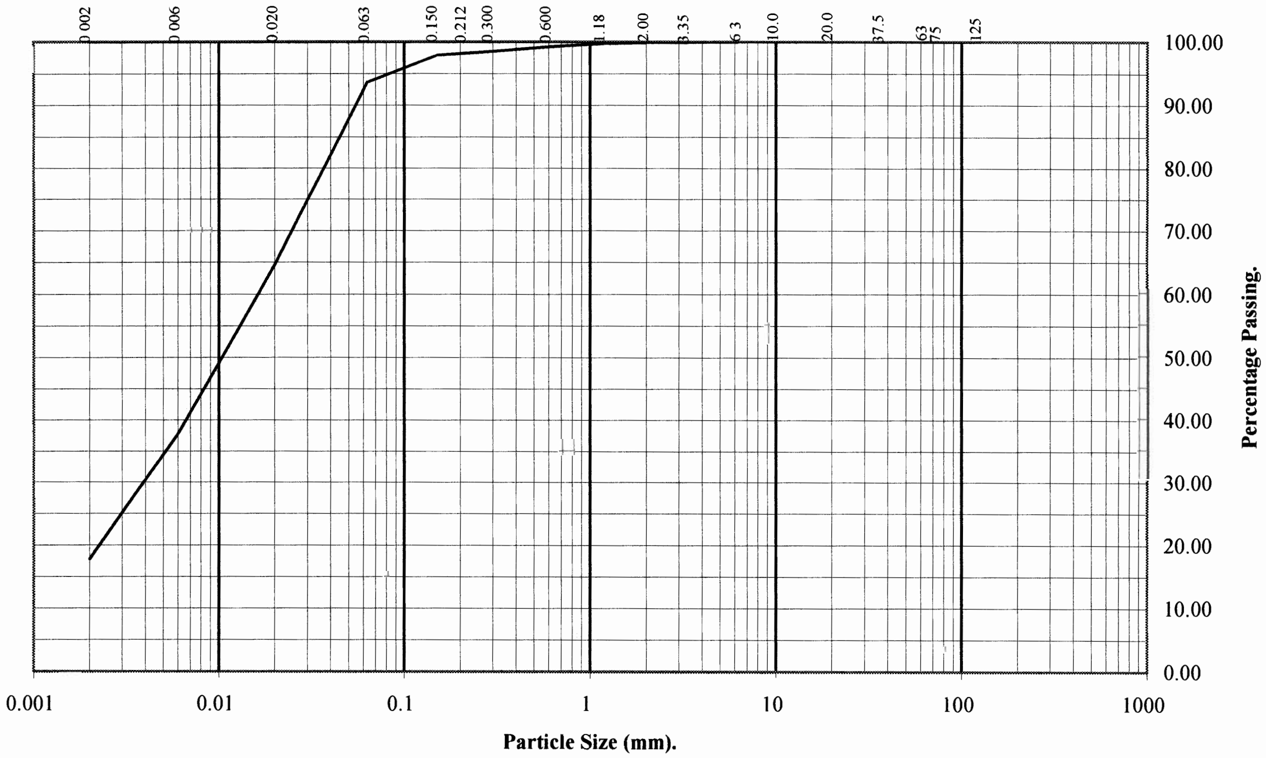
PARTICLE SIZE DISTRIBUTION TEST

BS 1377 Part 2:1990.

Wet sieve Pipette analysis Clause 9.2 9.4

Hole Number: **BH101** **Depth (m)** **12.00**



BS Test Sieve	Percentage Passing
125	100
75	100
63	100
37.5	100
20	100
10	100
6.3	100
3.35	100
2	100
1.18	100
0.6	99
0.3	99
0.212	98
0.15	98
0.063	94

Particle Diameter	Percentage Passing
0.02	65
0.006	38
0.002	18

Soil Fraction	Total Percentage
Cobbles	0
Gravel	0
Sand	6
Silt	76
Clay	18

Remarks:

Cl 9.4.8 - Sample has not been pretreated

Checked by **Date**

24/10/08

Approved by **Date**

LABORATORY TESTING SERVICES LIMITED

BBH

Contract No.:
GEO/6802/08
Client Ref No:
N/A

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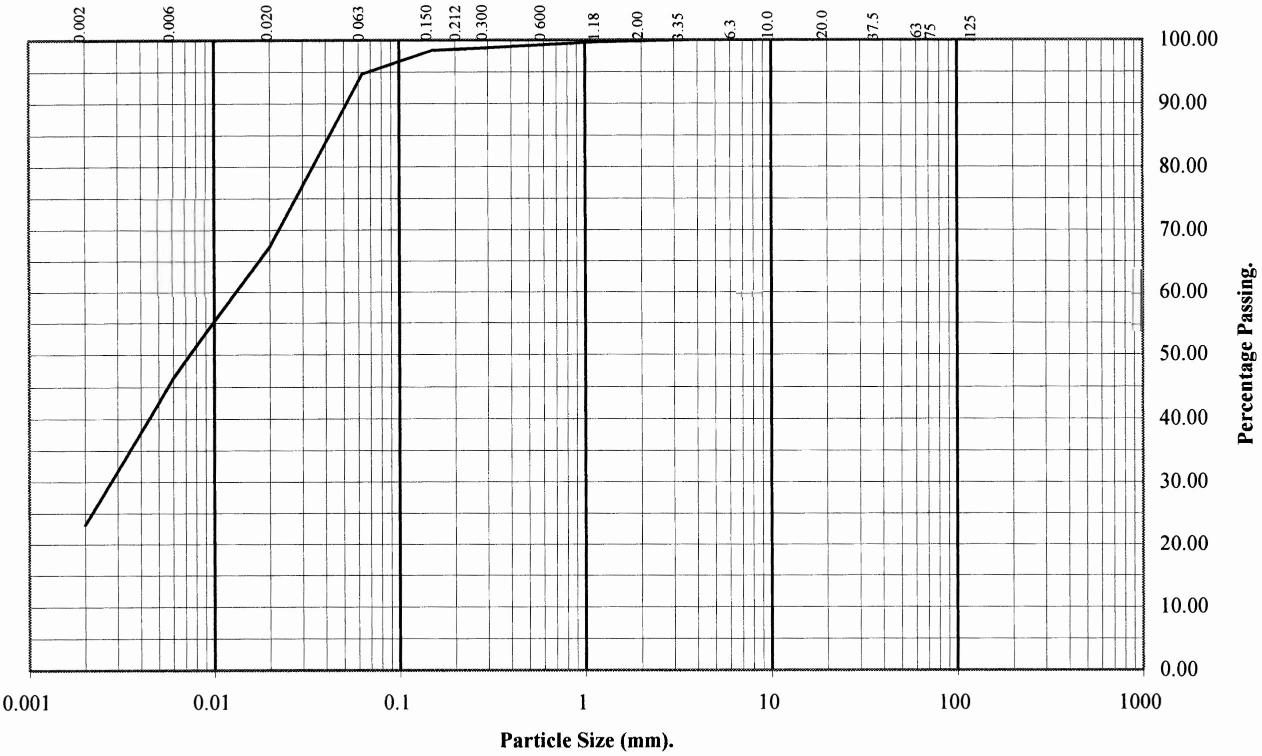
2788

PARTICLE SIZE DISTRIBUTION TEST

BS 1377 Part 2:1990.

Wet sieve Pipette analysis Clause 9.2 9.4

Hole Number: **BH101** **Depth (m)** **13.00**



BS Test Sieve	Percentage Passing
125	100
75	100
63	100
37.5	100
20	100
10	100
6.3	100
3.35	100
2	100
1.18	100
0.6	99
0.3	99
0.212	99
0.15	98
0.063	95

Particle Diameter	Percentage Passing
0.02	67
0.006	46
0.002	23

Soil Fraction	Total Percentage
Cobbles	0
Gravel	0
Sand	5
Silt	72
Clay	23

Remarks:

Cl 9.4.8 - Sample has not been pretreated

AhWalton 24/10/08

Checked by **Date**

AhWalton 24/10/08

Approved by **Date**

LABORATORY TESTING SERVICES LIMITED

BBH

Contract No.:
GEO/6802/08
Client Ref No:
N/A

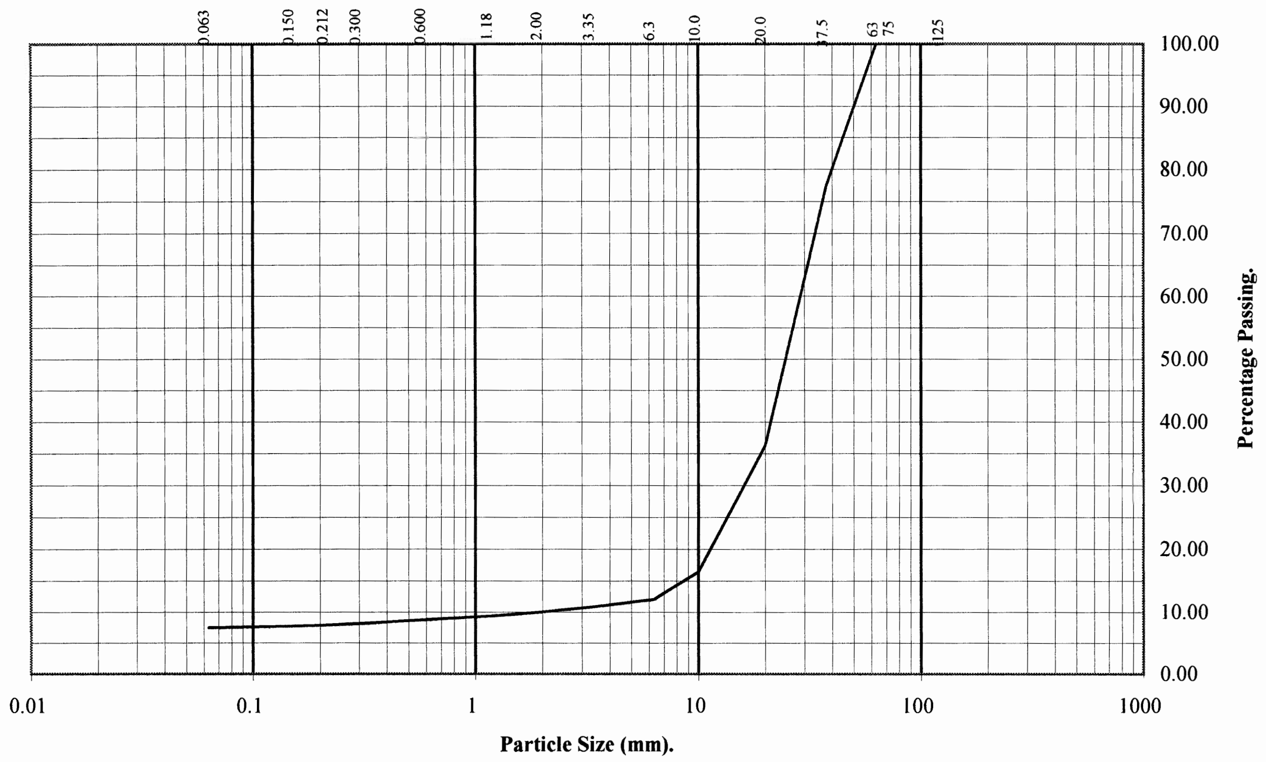
UKAS TESTING 2788

PARTICLE SIZE DISTRIBUTION TEST

BS 1377:Part 2:1990.

Wet sieve Clause 9.2

Hole Number: **BH101** **Depth (m):** **13.30**



BS Test Sieve	Percentage Passing
125	100
75	100
63	100
37.5	77
20	36
10	16
6.3	12
3.35	11
2	10
1.18	9
0.6	9
0.3	8
0.212	8
0.15	8
0.063	8

Soil Fraction	Total Percentage
Cobbles	0
Gravel	90
Sand	2
Silt and Clay	8

Remarks:

24/10/08

Checked by **Date**

24/10/08

Approved by **Date**

LABORATORY TESTING SERVICES LIMITED

BBH

Contract No.:
GEO/6802/08
Client Ref No:
N/A

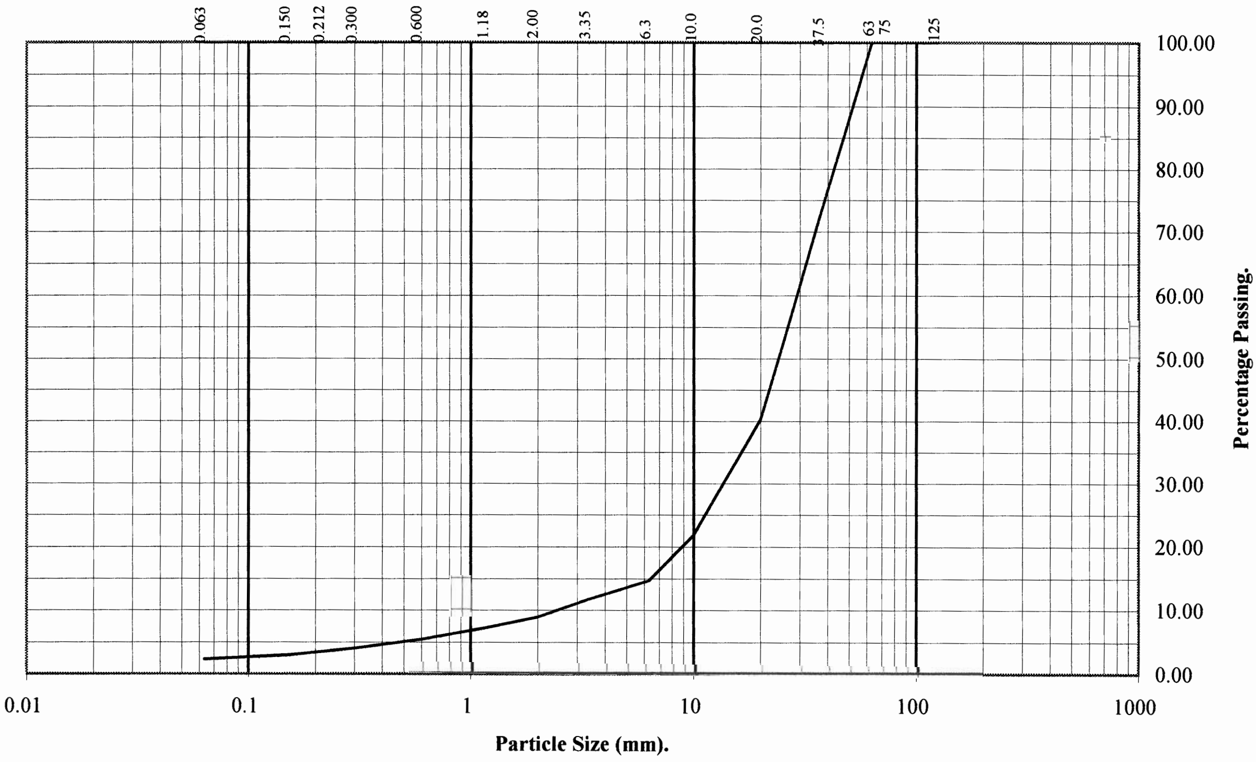
UKAS
TESTING
2788

PARTICLE SIZE DISTRIBUTION TEST

BS 1377:Part 2:1990.

Wet sieve Clause 9.2

Hole Number: **BH101** **Depth (m):** **14.50**



BS Test Sieve	Percentage Passing
125	100
75	100
63	100
37.5	73
20	40
10	22
6.3	15
3.35	12
2	9
1.18	7
0.6	5
0.3	4
0.212	3
0.15	3
0.063	2

Soil Fraction	Total Percentage
Cobbles	0
Gravel	91
Sand	7
Silt and Clay	2

Remarks:

24/10/08

Checked by **Date**

24/10/08

Approved by **Date**

LABORATORY TESTING SERVICES LIMITED

BBH

Contract No.:
GEO/6802/08
Client Ref No:
N/A

UKAS TESTING 2788

Determination of a Permeability

Falling Head in Permeameter
K.H. Head Volume 2 : Section 10.7

Date:	29-Sep-08
Contract Number:	GEO/6802/08
Client Ref Number:	
Borehole/Sample Number:	BH101
Depth:	14.50
Sample Type:	Bulk
Sample Preparation:	Recompacted with 2.5 kg rammer
Start Date:	27/09/2008
Completion Date:	29/09/2008
Test Duration (Days):	2
Operator:	P Evans

Soil Description

Grey sandy GRAVEL

Test Results

Initial Conditions:

Diameter (mm):	101.30
Length (mm):	116.70
Bulk Density (Mg/m3):	1.97
Moisture Content (%):	7
Dry Density (Mg/m3):	1.84

Permeability:

Initial Time	0.03
Initial Height Above datum (mm)	556
Final Time	0.07
Final Height above datum (mm)	157
Coefficient of Permeability @ 20oC:	**0.68x 10-3**

Remarks:
All remaining samples shall be retained for a period of one month from the above date, after which time all samples shall be disposed of.

	24\10\08		24\10\08
Checked by	**Date**	**Approved by**	**Date**

Contract No.
GEO/6802/08

Client Ref No.

LABORATORY TESTING SERVICES LIMITED

GEO Laboratory Testing Services Ltd,
Unit 1a, Bynea Business Park,
Heol , Bwlch
Bynea, Llanelli, Carmarthenshi
SA14 9SU

WSP
Environmental Laboratories

Certificate of Analysis

Job Number: 08-04913

Report Date:	17-Oct-08
Project Number:	12191773 001
Customer:	GEO Laboratory Testing Limited
Site Address:	Terra Firma Wales LTD
Date of Sampling:	Unspecified
Date of Analysis:	14 October 2008 - 17 October 2008

Dear Vaughan

Please find attached your results for the above project.
This report includes the samples we received at WSP Environmental Laboratories on 14/10/2008.

Your feedback is critical to the evolution and improvement of our business, so please feel free to email us you comments to: ideas_lab@wspgroup.com.

Results authorised by:

Mark Beastall
Geotechnical Laboratory Manager

WSP Environmental Laboratories
The Laboratory, 4/5 Lakeview, Lakeview Drive, Sherwood Park, Nottingham NG15 0ED.

Solid Samples

Job No: 08-04913
Site: Terra Firma Wales LTD
Report Date: 17/10/2008

			Lab No.	**65162**	**65163**	**65164**	**65165**
			Sample Date	/ /	/ /	/ /	/ /
			Sample Ref	**BH101**	**BH101**	**BH101**	**BH101**
			Other ID				
			Depth (m)	**6.7**	**9**	**13.3**	**14.5**
Determination	**LOD**	**Units**	**Method**				
Solid Description				LOAM	LOAM	CLAY	SAND
Moisture	0.1	%		51.6	10.3	25.5	5.9
Fraction of Organic Carbon	0.0012			0.12	0.0023	0.0064	< 0.0012

SUMMARY OF SOIL COMPACTION RELATED TESTS

(B.S. 1924 : PART 2 : 1990)

Hole Number	Sample Number	Depth m	Initial Moisture Content %	% Passing 37 mm BS Sieve	% Passing 20 mm BS Sieve	Particle Density Mg/m^3	Method of compaction (kg Rammer)	Bulk Density Mg/m^3	Dry Density Mg/m^3	Saturated Density Mg/m^3	Porosity (n)	C.B.R Value Base %	Remarks
BH101		9.00	45			2.56	2.5kg	1.71	1.17	1.72	0.54		
BH101		14.00	7.0			2.64	2.5kg	2.17	2.03	2.13	0.023		

*: Assumed Particle Density.

Checked by 24/10/08 Date

Approved by 24/10/08 Date

Contract No.
GEO/6802/08

Client Ref No.
N/A

BBH

LABORATORY TESTING SERVICES LIMITED

terrafirma

Terra Firma (Wales) Limited
Wharfedale Road, Pentwyn
Cardiff
CF23 7HB

Tel: 029 20 735 354
Fax: 029 20 735 433
Email: info@terrafirmawales.co.uk

Borehole No	**BH101**
	Sheet 1 of 2
Project Name	[redacted]
Project No.	[redacted]
Co-ords:	-
Hole Type	Cable
Location:	Newport
Level:	-
Scale	1:50
Client:	
Dates:	-
Logged By	

Well	Water Strikes	Samples & In Situ Testing Depth (m)	Type	Results
		1.00	CPT	N=6 N=6 (2,2,2,1,2,1)
		2.00	CPT	N=7 N=7 (2,1,2,2,1,2)
		3.00	SPT	N=3 N=3 (1,0,1,0,1,1)
		4.00	SPT	N=3 N=3 (1,0,1,1,0,1)
		5.00 5.00-5.45	SPT D	N=3 N=3 (1,0,1,1,0,1)
		6.50	SPT	N=3 N=3 (1,0,1,1,1,0)
		8.00	SPT	N=1 N=1 (1,0,0,0,1,0)
		9.50 9.50-9.95	SPT D	N=1 N=1 (1,0,0,1,0,0)

Depth (m)	Level (m AOD)	Legend	Stratum Description
		▩	MADE GROUND: Grey, GRAVEL aggregate
0.30		▩	MADE GROUND: Loose black, slightly clayey sandy GRAVEL. Includes fragments of brick, concrete, sandstone and ash
2.80		× × × ×	Soft to very soft, grey to occasionally orange brown, mottled, occasionally very slightly sandy, clayey SILT.
6.60		᯽	Very soft, dark grey to brown to black, fibrous, mineral dominated PEAT
6.80		× × × ×	Very soft, grey to occasionally brown, slightly sandy , clayey SILT. Contains root casts

Continued next sheet

Remarks:

HoleBASE III (Bld 426.48) Standard Borehole Log v2 dated 27th Nov 03

terrafirma

Terra Firma (Wales) Limited
Wharfedale Road, Pentwyn
Cardiff
CF23 7HB

Tel: 029 20 735 354
Fax: 029 20 735 433
Email: info@terrafirmawales.co.uk

Borehole No
BH101
Sheet 2 of 2

Project Name [redacted]	Project No. [redacted]	Co-ords: -	Hole Type Cable
Location: Newport		Level: -	Scale 1:50
Client:		Dates: -	Logged By

Well	Water Strikes	Samples & In Situ Testing Depth (m)	Type	Results	Depth (m)	Level (m AOD)	Legend	Stratum Description
							× × × ×	Very soft, grey to occasionally brown, slightly sandy , clayey SILT. Contains root casts
		11.00	SPT	N=2 N=2 (1,0,1,0,0,1)			× × × ×	
		12.50	SPT	N=1 N=1 (1,0,0,1,0,0)			× × × ×	
					13.20		∴	Dense to very dense, sandy silty GRAVEL. Predominantly comprises rounded clasts of carboniferous sandstone and subordinate clasts of red marl
		13.50	CPT	N=43 N=43 (6,8,8,9,12,14)			∴	
		15.50	SPT	50/10mm 10mm - Abandoned	15.50			End of Borehole at 15.50 m

11
12
13
14
15
16
17
18
19

Type Results

Remarks:

Compilation Terra Firma Wales

STL Laboratory Number				**318962**	**318963**	**318964**	**318965**	**318966**	**318967**
Customer Sample Ref				**BH15A @ 5.50m**	**BH15A @ 6.10m**	**BH15A @ 6.70m**	**BH15A @ 7.30m**	**BH15A @ 7.90m**	**BH15A @ 8.50m**
Analyte	**Method**	**Units**	**Acc**						
Stones BG 2.6/3.0	Stones	%	*	44	34	44	49	48	46
Moisture content at 30 C	33A	%	*	16	18	18	19	13	21
catechol	322	mg/kg		<0.10	0.23	0.15	0.2	<0.10	0.28
resorcinol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
phenol	322	mg/kg		17	15	23	19	25	38
cresols	322	mg/kg		29	23	39	32	33	58
xylenols	322	mg/kg		37	28	45	40	40	62
naphthols	322	mg/kg		6.8	7.1	7.4	6.2	6.3	9.2
trimethylphenol	322	mg/kg		8.9	4.8	8.4	9.8	6.8	15
Total Phenol	322	mg/kg		98	78	122	106	113	177
TPH by GC (>C6-C10)	317	mg/kg		<50	<50	<50	<50	<50	<50
TPH by GC (>C10 - C20)	317	mg/kg		1548	1220	1951	1728	1494	2278
TPH by GC (>C20-C40)	317	mg/kg		369	244	488	395	299	506
TPH by GC (>C6 - C40)	317	mg/kg		1905	1463	2439	2099	1724	2785
>C6 to C8 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aliphatic	317R	mg/kg		2.7	<1.0	2.2	<1.0	<1.0	2.9
>C10 to C12 Aliphatic	317R	mg/kg		5	<1.0	4.5	4	4.1	7.1
>C12 to C16 Aliphatic	317R	mg/kg		14	2.4	13	12	14	30
>C16 to C21 Aliphatic	317R	mg/kg		15	<5.0	15	14	18	38
>C21 to C40 Aliphatic	317R	mg/kg		23	<10	16	14	126	46
Total Aliphatic	317R	mg/kg		60	<20	50	43	161	123
>C5 to C7 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C7 to C8 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aromatic	317R	mg/kg		33	8.2	30	26	30	53
>C10 to C12 Aromatic	317R	mg/kg		393	159	390	494	448	772
>C12 to C16 Aromatic	317R	mg/kg		405	85	390	395	368	810
>C16 to C21 Aromatic	317R	mg/kg		571	122	512	568	552	1152
>C21 TO C40 Aromatic	317R	mg/kg		167	33	146	160	172	304
Total Aromatic	317R	mg/kg		1548	415	1463	1605	1609	3038
Total EPH Aliphatic/Aromatic	317R	mg/kg		1667	415	1463	1728	1724	3165
naphthalene	LPH307	ug/kg	*	150000	190000	200000	230000	170000	220000
acenaphthylene	LPH307	ug/kg	*	3400	3400	3400	3500	3700	4000
acenaphthene	LPH307	ug/kg	*	46000	40000	44000	51000	64000	64000

Key

N/S - Not Scheduled
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To Follow - analysis incomplete (interim reports only)

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STL Laboratory Number				**318962**	**318963**	**318964**	**318965**	**318966**	**318967**
Customer Sample Ref				**BH15A @ 5.50m**	**BH15A @ 6.10m**	**BH15A @ 6.70m**	**BH15A @ 7.30m**	**BH15A @ 7.90m**	**BH15A @ 8.50m**
Analyte	**Method**	**Units**	**Acc**						
fluorene	LPH307	ug/kg	*	64000	55000	58000	63000	95000	81000
phenanthrene	LPH307	ug/kg	*	170000	140000	160000	180000	240000	230000
anthracene	LPH307	ug/kg	*	68000	73000	71000	66000	210000	94000
fluoranthene	LPH307	ug/kg	*	64000	50000	58000	71000	91000	87000
pyrene	LPH307	ug/kg	*	37000	28000	33000	41000	53000	50000
benzo(a)anthracene	LPH307	ug/kg	*	10000	7600	8100	12000	17000	13000
chrysene	LPH307	ug/kg	*	11000	8500	8900	13000	19000	14000
cyclopenta(cd)pyrene	LPH307	ug/kg	*	540	140	100	140	200	3000
benzo(b)fluoranthene	LPH307	ug/kg	*	2700	1900	2200	2500	4800	3500
benzo(k)fluoranthene	LPH307	ug/kg	*	2900	1800	2100	3000	4500	3500
benzo(e)pyrene	LPH307	ug/kg	*	2100	1300	1500	1900	3300	2500
benzo(a)pyrene	LPH307	ug/kg	*	2400	1600	1800	2600	3800	2900
dibenzo(ah)anthracene	LPH307	ug/kg	*	290	280	220	270	480	200
benzo(ghi)perylene	LPH307	ug/kg	*	630	380	460	640	900	730
indeno(123cd)pyrene	LPH307	ug/kg	*	810	500	610	810	1200	970
anthanthrene	LPH307	ug/kg	*	180	120	150	190	300	850
PAH (Total)	LPH307	ug/kg	*	630000	610000	650000	740000	980000	880000

Key

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Compilation Terra Firma Wales

STL Laboratory Number				**318968**	**318969**	**318970**	**318971**	**318972**	**318973**
Customer Sample Ref				**BH15A @ 9.10m**	**BH15A @ 9.60m**	**BH15A @ 10.70m**	**BH15A @ 11.40m**	**BH15A @ 12.00m**	**BH15A @ 12.60m**
Analyte	**Method**	**Units**	**Acc**						
Stones BG 2.6/3.0	Stones	%	*	45	30	45	48	32	45
Moisture content at 30 C	33A	%	*	17	17	14	15	35	25
catechol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
resorcinol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
phenol	322	mg/kg		116	13	24	16	0.31	0.2
cresols	322	mg/kg		181	28	34	24	<0.10	<0.10
xylenols	322	mg/kg		120	52	30	26	<0.10	<0.10
naphthols	322	mg/kg		12	7.1	3.8	4.7	<0.10	<0.10
trimethylphenol	322	mg/kg		25	16	5.1	6.8	<0.10	<0.10
Total Phenol	322	mg/kg		458	114	97	79	<0.50	<0.50
TPH by GC (>C6-C10)	317	mg/kg		<50	<500	<50	<50	<50	<50
TPH by GC (>C10 - C20)	317	mg/kg		747	4699	942	1412	<50	<50
TPH by GC (>C20-C40)	317	mg/kg		120	771	221	435	<50	<50
TPH by GC (>C6 - C40)	317	mg/kg		867	5542	1163	1882	<50	<50
>C6 to C8 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aliphatic	317R	mg/kg		<1.0	9.3	2.3	2.5	<1.0	<1.0
>C10 to C12 Aliphatic	317R	mg/kg		<1.0	20	4	4.5	<1.0	<1.0
>C12 to C16 Aliphatic	317R	mg/kg		<1.0	84	10	11.5	<1.0	<1.0
>C16 to C21 Aliphatic	317R	mg/kg		<5.0	90	9.7	11.1	<5.0	<5.0
>C21 to C40 Aliphatic	317R	mg/kg		<10	69	22	15	<10	<10
Total Aliphatic	317R	mg/kg		<20	277	48	45	<20	<20
>C5 to C7 Aromatic	317R	mg/kg		<1.0	<1.0	5.8	<1.0	<1.0	<1.0
>C7 to C8 Aromatic	317R	mg/kg		<1.0	<1.0	3.7	<1.0	<1.0	<1.0
>C8 to C10 Aromatic	317R	mg/kg		11.9	89	17	18	<1.0	<1.0
>C10 to C12 Aromatic	317R	mg/kg		96	976	163	176	<1.0	<1.0
>C12 to C16 Aromatic	317R	mg/kg		102	1325	244	306	<1.0	<1.0
>C16 to C21 Aromatic	317R	mg/kg		82	1687	326	506	<5.0	<5.0
>C21 TO C40 Aromatic	317R	mg/kg		18	518	106	165	<10	<10
Total Aromatic	317R	mg/kg		313	4578	872	1176	<20	<20
Total EPH Aliphatic/Aromatic	317R	mg/kg		313	4819	919	1176	<40	<40
naphthalene	LPH307	ug/kg	*	67000	140000	27000	73000	42000	34000
acenaphthylene	LPH307	ug/kg	*	1600	6400	1400	3700	160	230
acenaphthene	LPH307	ug/kg	*	25000	100000	22000	62000	2700	1800

Key

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Compilation Terra Firma Wales

STL Laboratory Number				**318968**	**318969**	**318970**	**318971**	**318972**	**318973**
Customer Sample Ref				**BH15A @ 9.10m**	**BH15A @ 9.60m**	**BH15A @ 10.70m**	**BH15A @ 11.40m**	**BH15A @ 12.00m**	**BH15A @ 12.60m**
Analyte	**Method**	**Units**	**Acc**						
fluorene	LPH307	ug/kg	*	25000	130000	29000	93000	620	1500
phenanthrene	LPH307	ug/kg	*	63000	340000	85000	230000	630	3600
anthracene	LPH307	ug/kg	*	9000	110000	23000	150000	190	2200
fluoranthene	LPH307	ug/kg	*	13000	150000	35000	91000	260	1300
pyrene	LPH307	ug/kg	*	7000	84000	20000	52000	170	740
benzo(a)anthracene	LPH307	ug/kg	*	1200	26000	5500	16000	110	410
chrysene	LPH307	ug/kg	*	1300	27000	6100	17000	100	310
cyclopenta(cd)pyrene	LPH307	ug/kg	*	67	1600	73	470	<10	<10
benzo(b)fluoranthene	LPH307	ug/kg	*	300	7800	1500	4700	41	100
benzo(k)fluoranthene	LPH307	ug/kg	*	330	7500	1500	4600	39	100
benzo(e)pyrene	LPH307	ug/kg	*	220	5500	1000	3100	37	78
benzo(a)pyrene	LPH307	ug/kg	*	280	6700	1200	3900	33	77
dibenzo(ah)anthracene	LPH307	ug/kg	*	45	770	170	500	<10	<10
benzo(ghi)perylene	LPH307	ug/kg	*	110	1600	380	1000	43	42
indeno(123cd)pyrene	LPH307	ug/kg	*	120	2200	440	1300	29	38
anthanthrene	LPH307	ug/kg	*	33	490	120	330	<10	<10
PAH (Total)	LPH307	ug/kg	*	210000	1200000	260000	800000	47000	47000

Key

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Compilation Terra Firma Wales

STL Laboratory Number				**318974**	**318975**	**318976**	**318977**	**318978**	**318979**
Customer Sample Ref				**BH15A @ 13.10m**	**BH15A @ 13.70m**	**BH15A @ 14.20m**	**BH16A @ 3.50m**	**BH16A @ 4.10m**	**BH16A @ 4.70m**
Analyte	**Method**	**Units**	**Acc**						
Stones BG 2.6/3.0	Stones	%	*	36	35	50	28	25	38
Moisture content at 30 C	33A	%	*	16	28	19	20	24	21
catechol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
resorcinol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
phenol	322	mg/kg		0.31	0.5	0.22	<0.10	0.28	0.3
cresols	322	mg/kg		<0.10	0.14	<0.10	<0.10	<0.10	<0.10
xylenols	322	mg/kg		<0.10	0.38	<0.10	<0.10	<0.10	<0.10
naphthols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
trimethylphenol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Total Phenol	322	mg/kg		<0.50	1.01	<0.50	<0.50	<0.50	<0.50
TPH by GC (>C6-C10)	317	mg/kg		<50	<50	<50	<50	<50	<50
TPH by GC (>C10 - C20)	317	mg/kg		<50	<50	<50	<50	125	<50
TPH by GC (>C20-C40)	317	mg/kg		<50	<50	<50	<50	1316	<50
TPH by GC (>C6 - C40)	317	mg/kg		<50	<50	<50	<50	1447	<50
>C6 to C8 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C10 to C12 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C12 to C16 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C16 to C21 Aliphatic	317R	mg/kg		<5.0	<5.0	<5.0	<5.0	184	<5.0
>C21 to C40 Aliphatic	317R	mg/kg		<10	<10	<10	<10	1263	<10
Total Aliphatic	317R	mg/kg		<20	<20	<20	<20	1447	<20
>C5 to C7 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C7 to C8 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C10 to C12 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C12 to C16 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C16 to C21 Aromatic	317R	mg/kg		<5.0	<5.0	<5.0	<5.0	57	<5.0
>C21 TO C40 Aromatic	317R	mg/kg		<10	<10	<10	<10	513	<10
Total Aromatic	317R	mg/kg		<20	<20	<20	<20	579	<20
Total EPH Aliphatic/Aromatic	317R	mg/kg		<40	<40	<40	<40	1974	<40
naphthalene	LPH307	ug/kg	*	12000	30000	31000	10000	13000	13000
acenaphthylene	LPH307	ug/kg	*	320	400	330	290	340	300
acenaphthene	LPH307	ug/kg	*	800	870	850	1300	1300	980

Key

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Compilation Terra Firma Wales

STL Laboratory Number				**318974**	**318975**	**318976**	**318977**	**318978**	**318979**
Customer Sample Ref				**BH15A @ 13.10m**	**BH15A @ 13.70m**	**BH15A @ 14.20m**	**BH16A @ 3.50m**	**BH16A @ 4.10m**	**BH16A @ 4.70m**
Analyte	**Method**	**Units**	**Acc**						
fluorene	LPH307	ug/kg	*	810	720	540	1000	750	570
phenanthrene	LPH307	ug/kg	*	1100	640	480	2500	800	590
anthracene	LPH307	ug/kg	*	500	120	140	490	180	160
fluoranthene	LPH307	ug/kg	*	260	87	100	1800	350	220
pyrene	LPH307	ug/kg	*	170	62	67	1100	230	190
benzo(a)anthracene	LPH307	ug/kg	*	67	14	41	120	21	30
chrysene	LPH307	ug/kg	*	89	32	42	170	45	41
cyclopenta(cd)pyrene	LPH307	ug/kg	*	<10	<10	<10	<10	<10	<10
benzo(b)fluoranthene	LPH307	ug/kg	*	32	20	16	87	29	21
benzo(k)fluoranthene	LPH307	ug/kg	*	36	15	21	93	28	21
benzo(e)pyrene	LPH307	ug/kg	*	27	19	18	85	22	15
benzo(a)pyrene	LPH307	ug/kg	*	25	18	13	75	21	20
dibenzo(ah)anthracene	LPH307	ug/kg	*	<10	<10	<10	11	<10	<10
benzo(ghi)perylene	LPH307	ug/kg	*	21	19	20	52	23	17
indeno(123cd)pyrene	LPH307	ug/kg	*	20	12	13	51	18	15
anthanthrene	LPH307	ug/kg	*	<10	<10	<10	11	<10	<10
PAH (Total)	LPH307	ug/kg	*	16000	33000	34000	20000	17000	16000

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STL Laboratory Number				**318980**	**318981**	**318982**	**318983**	**318984**	**318985**
Customer Sample Ref				**BH16A @ 5.30m**	**BH16A @ 5.90m**	**BH16A @ 6.50m**	**BH16A @ 7.10m**	**BH16A @ 7.70m**	**BH16A @ 8.30m**
Analyte	**Method**	**Units**	**Acc**						
Stones BG 2.6/3.0	Stones	%	*	53	60	26	48	30	36
Moisture content at 30 C	33A	%	*	19	21	23	24	20	18
catechol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
resorcinol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
phenol	322	mg/kg		0.28	0.57	0.3	0.43	0.43	0.49
cresols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	0.13
xylenols	322	mg/kg		<0.10	<0.10	<0.10	0.18	<0.10	0.29
naphthols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
trimethylphenol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Total Phenol	322	mg/kg		<0.50	<0.50	<0.50	<0.50	<0.50	0.91
TPH by GC (>C6-C10)	317	mg/kg		<50	<50	<50	<50	<50	<50
TPH by GC (>C10 - C20)	317	mg/kg		<50	304	<50	<50	95	<50
TPH by GC (>C20-C40)	317	mg/kg		<50	228	<50	<50	250	<50
TPH by GC (>C6 - C40)	317	mg/kg		<50	532	<50	<50	338	<50
>C6 to C8 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C10 to C12 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	2.4	1.6
>C12 to C16 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	20	15
>C16 to C21 Aliphatic	317R	mg/kg		<5.0	6.5	<5.0	<5.0	263	232
>C21 to C40 Aliphatic	317R	mg/kg		42	16	<10	<10	1200	1061
Total Aliphatic	317R	mg/kg		42	<20	<20	<20	1500	1341
>C5 to C7 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C7 to C8 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C10 to C12 Aromatic	317R	mg/kg		<1.0	3.4	<1.0	<1.0	<1.0	<1.0
>C12 to C16 Aromatic	317R	mg/kg		3.2	94	<1.0	<1.0	2.1	3.3
>C16 to C21 Aromatic	317R	mg/kg		<5.0	266	<5.0	<5.0	8.1	10.5
>C21 TO C40 Aromatic	317R	mg/kg		<10	57	<10	<10	46	54
Total Aromatic	317R	mg/kg		<20	418	<20	<20	56	67
Total EPH Aliphatic/Aromatic	317R	mg/kg		<40	443	<40	<40	1500	1341
naphthalene	LPH307	ug/kg	*	7300	26000	10000	10000	4900	3200
acenaphthylene	LPH307	ug/kg	*	250	1400	650	280	170	120
acenaphthene	LPH307	ug/kg	*	3900	87000	30000	1300	840	1000

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Compilation Terra Firma Wales

STL Laboratory Number				**318980**	**318981**	**318982**	**318983**	**318984**	**318985**
Customer Sample Ref				**BH16A @ 5.30m**	**BH16A @ 5.90m**	**BH16A @ 6.50m**	**BH16A @ 7.10m**	**BH16A @ 7.70m**	**BH16A @ 8.30m**
Analyte	**Method**	**Units**	**Acc**						
fluorene	LPH307	ug/kg	*	3000	71000	26000	700	510	360
phenanthrene	LPH307	ug/kg	*	9200	230000	88000	1600	1400	540
anthracene	LPH307	ug/kg	*	2100	24000	6000	470	240	130
fluoranthene	LPH307	ug/kg	*	8800	240000	77000	770	1400	810
pyrene	LPH307	ug/kg	*	4900	130000	39000	460	870	430
benzo(a)anthracene	LPH307	ug/kg	*	570	3000	690	120	63	27
chrysene	LPH307	ug/kg	*	620	4100	960	140	72	39
cyclopenta(cd)pyrene	LPH307	ug/kg	*	<10	140	<10	<10	<10	<10
benzo(b)fluoranthene	LPH307	ug/kg	*	220	2700	520	64	54	19
benzo(k)fluoranthene	LPH307	ug/kg	*	240	2300	500	53	34	<10
benzo(e)pyrene	LPH307	ug/kg	*	200	1900	430	50	45	16
benzo(a)pyrene	LPH307	ug/kg	*	220	1900	380	46	32	<10
dibenzo(ah)anthracene	LPH307	ug/kg	*	39	440	84	<10	<10	<10
benzo(ghi)perylene	LPH307	ug/kg	*	110	1100	280	49	42	16
indeno(123cd)pyrene	LPH307	ug/kg	*	130	1200	300	39	32	16
anthanthrene	LPH307	ug/kg	*	22	110	30	<10	<10	<10
PAH (Total)	LPH307	ug/kg	*	42000	820000	280000	16000	11000	6800

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Compilation Terra Firma Wales

STL Laboratory Number				**318986**	**318987**	**318988**	**318989**	**318990**	**318991**
Customer Sample Ref				**BH16A @ 9.00m**	**BH16A @ 9.70m**	**BH16A @ 10.30m**	**BH16A @ 10.90m**	**BH16A @ 11.50m**	**BH16A @ 12.10m**
Analyte	**Method**	**Units**	**Acc**						
Stones BG 2.6/3.0	Stones	%	*	44	30	57	35	38	44
Moisture content at 30 C	33A	%	*	18	19	25	20	24	18
catechol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
resorcinol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
phenol	322	mg/kg		<0.10	<0.10	<0.10	1.05	0.41	0.3
cresols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
xylenols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
naphthols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
trimethylphenol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Total Phenol	322	mg/kg		<0.50	<0.50	<0.50	1.05	<0.50	<0.50
TPH by GC (>C6-C10)	317	mg/kg		<50	<50	<50	<50	<50	<50
TPH by GC (>C10 - C20)	317	mg/kg		63	<50	<50	<50	<50	<50
TPH by GC (>C20-C40)	317	mg/kg		341	<50	307	<50	<50	<50
TPH by GC (>C6 - C40)	317	mg/kg		402	<50	307	<50	<50	<50
>C6 to C8 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C10 to C12 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C12 to C16 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C16 to C21 Aliphatic	317R	mg/kg		<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
>C21 to C40 Aliphatic	317R	mg/kg		22	<10	<10	<10	<10	<10
Total Aliphatic	317R	mg/kg		<20	<20	<20	<20	<20	<20
>C5 to C7 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C7 to C8 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C10 to C12 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C12 to C16 Aromatic	317R	mg/kg		<1.0	<1.0	5.1	<1.0	<1.0	<1.0
>C16 to C21 Aromatic	317R	mg/kg		<5.0	<5.0	293	<5.0	<5.0	<5.0
>C21 TO C40 Aromatic	317R	mg/kg		<10	<10	800	<10	<10	<10
Total Aromatic	317R	mg/kg		<20	<20	1093	<20	<20	<20
Total EPH Aliphatic/Aromatic	317R	mg/kg		<40	<40	1093	<40	<40	<40
naphthalene	LPH307	ug/kg	*	5000	6000	16000	6100	12000	5500
acenaphthylene	LPH307	ug/kg	*	98	90	150	120	130	110
acenaphthene	LPH307	ug/kg	*	1000	910	1200	480	740	340

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Compilation Terra Firma Wales

STL Laboratory Number				**318986**	**318987**	**318988**	**318989**	**318990**	**318991**
Customer Sample Ref				**BH16A @ 9.00m**	**BH16A @ 9.70m**	**BH16A @ 10.30m**	**BH16A @ 10.90m**	**BH16A @ 11.50m**	**BH16A @ 12.10m**
Analyte	**Method**	**Units**	**Acc**						
fluorene	LPH307	ug/kg	*	220	260	280	180	190	130
phenanthrene	LPH307	ug/kg	*	250	360	250	520	170	250
anthracene	LPH307	ug/kg	*	90	91	69	74	59	83
fluoranthene	LPH307	ug/kg	*	250	390	130	180	58	120
pyrene	LPH307	ug/kg	*	180	240	100	130	39	80
benzo(a)anthracene	LPH307	ug/kg	*	43	40	17	31	15	18
chrysene	LPH307	ug/kg	*	43	40	33	47	18	47
cyclopenta(cd)pyrene	LPH307	ug/kg	*	<10	<10	<10	<10	<10	<10
benzo(b)fluoranthene	LPH307	ug/kg	*	22	17	16	13	<10	20
benzo(k)fluoranthene	LPH307	ug/kg	*	19	16	15	20	<10	16
benzo(e)pyrene	LPH307	ug/kg	*	16	18	19	15	<10	12
benzo(a)pyrene	LPH307	ug/kg	*	14	22	15	11	<10	11
dibenzo(ah)anthracene	LPH307	ug/kg	*	<10	<10	<10	<10	<10	<10
benzo(ghi)perylene	LPH307	ug/kg	*	17	16	15	14	10	12
indeno(123cd)pyrene	LPH307	ug/kg	*	16	12	15	<10	<10	12
anthanthrene	LPH307	ug/kg	*	<10	<10	<10	<10	<10	<10
PAH (Total)	LPH307	ug/kg	*	7300	8600	18000	8000	13000	6800

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Compilation Terra Firma Wales

STL Laboratory Number				**318992**	**318993**	**318994**	**318995**	**318996**	**318997**
Customer Sample Ref				**BH16A @ 12.90m**	**BH17A @ 4.50m**	**BH17A @ 5.10m**	**BH17A @ 5.60m**	**BH17A @ 6.15m**	**BH17A @ 6.70m**
Analyte	**Method**	**Units**	**Acc**						
Stones BG 2.6/3.0	Stones	%	*	57	47	26	44	38	36
Moisture content at 30 C	33A	%	*	17	24	19	18	23	22
catechol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
resorcinol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
phenol	322	mg/kg		0.42	0.68	0.67	0.55	0.77	0.63
cresols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
xylenols	322	mg/kg		<0.10	1.4	0.83	0.41	<0.10	0.24
naphthols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
trimethylphenol	322	mg/kg		<0.10	0.8	<0.10	0.38	<0.10	0.32
Total Phenol	322	mg/kg		<0.50	3	1.5	1.3	0.77	1.19
TPH by GC (>C6-C10)	317	mg/kg		<50	<50	<50	<50	<50	<50
TPH by GC (>C10 - C20)	317	mg/kg		<50	132	<50	<50	<50	1154
TPH by GC (>C20-C40)	317	mg/kg		<50	92	<50	<50	<50	321
TPH by GC (>C6 - C40)	317	mg/kg		<50	224	<50	<50	<50	1410
>C6 to C8 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aliphatic	317R	mg/kg		<1.0	1.7	<1.0	<1.0	<1.0	<1.0
>C10 to C12 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	1.9
>C12 to C16 Aliphatic	317R	mg/kg		2.4	3.9	<1.0	2	<1.0	6
>C16 to C21 Aliphatic	317R	mg/kg		59	6.6	<5.0	<5.0	<5.0	35
>C21 to C40 Aliphatic	317R	mg/kg		253	22	<10	<10	<10	256
Total Aliphatic	317R	mg/kg		313	34	<20	<20	<20	295
>C5 to C7 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C7 to C8 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aromatic	317R	mg/kg		<1.0	3.9	<1.0	2.8	<1.0	6.8
>C10 to C12 Aromatic	317R	mg/kg		<1.0	26	<1.0	13	<1.0	71
>C12 to C16 Aromatic	317R	mg/kg		2.7	96	<1.0	45	<1.0	154
>C16 to C21 Aromatic	317R	mg/kg		6.7	130	<5.0	56	<5.0	167
>C21 TO C40 Aromatic	317R	mg/kg		20	63	<10	34	<10	85
Total Aromatic	317R	mg/kg		29	316	<20	146	<20	474
Total EPH Aliphatic/Aromatic	317R	mg/kg		349	355	<40	159	<40	782
naphthalene	LPH307	ug/kg	*	3700	6300	3200	3600	6500	31000
acenaphthylene	LPH307	ug/kg	*	95	140	120	97	90	1500
acenaphthene	LPH307	ug/kg	*	830	520	2400	1200	1400	46000

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Compilation Terra Firma Wales

STL Laboratory Number				318992	318993	318994	318995	318996	318997
Customer Sample Ref				**BH16A @ 12.90m**	**BH17A @ 4.50m**	**BH17A @ 5.10m**	**BH17A @ 5.60m**	**BH17A @ 6.15m**	**BH17A @ 6.70m**
Analyte	**Method**	**Units**	**Acc**						
fluorene	LPH307	ug/kg	*	480	490	2400	1200	420	50000
phenanthrene	LPH307	ug/kg	*	1700	2300	9500	4700	540	160000
anthracene	LPH307	ug/kg	*	240	340	960	440	66	17000
fluoranthene	LPH307	ug/kg	*	1400	860	2900	1700	180	58000
pyrene	LPH307	ug/kg	*	830	540	1900	1200	140	37000
benzo(a)anthracene	LPH307	ug/kg	*	38	190	570	330	39	8000
chrysene	LPH307	ug/kg	*	76	180	510	340	46	8600
cyclopenta(cd)pyrene	LPH307	ug/kg	*	<10	<10	<10	<10	<10	150
benzo(b)fluoranthene	LPH307	ug/kg	*	30	48	100	89	14	2200
benzo(k)fluoranthene	LPH307	ug/kg	*	28	46	150	88	21	2600
benzo(e)pyrene	LPH307	ug/kg	*	28	49	100	74	20	1900
benzo(a)pyrene	LPH307	ug/kg	*	23	45	130	84	15	2300
dibenzo(ah)anthracene	LPH307	ug/kg	*	<10	<10	13	<10	<10	240
benzo(ghi)perylene	LPH307	ug/kg	*	20	21	48	37	14	840
indeno(123cd)pyrene	LPH307	ug/kg	*	19	19	54	38	11	980
anthanthrene	LPH307	ug/kg	*	<10	<10	<10	<10	<10	140
PAH (Total)	LPH307	ug/kg	*	9500	12000	25000	15000	9500	420000

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Compilation Terra Firma Wales

STL Laboratory Number				**318998**	**318999**	**319000**	**319001**	**319002**	**319003**
Customer Sample Ref				**BH17A @ 7.30m**	**BH17A @ 7.90m**	**BH17A @ 8.50m**	**BH17A @ 9.10m**	**BH17A @ 9.70m**	**BH17A @ 10.30m**
Analyte	**Method**	**Units**	**Acc**						
Stones BG 2.6/3.0	Stones	%	*	22	33	71	43	28	13
Moisture content at 30 C	33A	%	*	21	29	24	30	23	24
catechol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
resorcinol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
phenol	322	mg/kg		0.24	0.37	0.26	0.31	0.42	0.18
cresols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
xylenols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
naphthols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
trimethylphenol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Total Phenol	322	mg/kg		<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
TPH by GC (>C6-C10)	317	mg/kg		<500	<50	<50	<50	<50	<50
TPH by GC (>C10 - C20)	317	mg/kg		2532	254	724	214	<50	<50
TPH by GC (>C20-C40)	317	mg/kg		16456	89	158	443	<50	<50
TPH by GC (>C6 - C40)	317	mg/kg		18987	338	882	657	<50	<50
>C6 to C8 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C10 to C12 Aliphatic	317R	mg/kg		2.7	1.4	3	<1.0	<1.0	<1.0
>C12 to C16 Aliphatic	317R	mg/kg		11.5	5.4	11.4	<1.0	<1.0	<1.0
>C16 to C21 Aliphatic	317R	mg/kg		177	10.4	16	<5.0	<5.0	<5.0
>C21 to C40 Aliphatic	317R	mg/kg		747	34	16	<10	<10	<10
Total Aliphatic	317R	mg/kg		937	51	46	<20	<20	<20
>C5 to C7 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C7 to C8 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aromatic	317R	mg/kg		5.7	5.5	9.3	<1.0	<1.0	<1.0
>C10 to C12 Aromatic	317R	mg/kg		43	59	158	<1.0	<1.0	1.6
>C12 to C16 Aromatic	317R	mg/kg		99	169	368	<1.0	<1.0	2.9
>C16 to C21 Aromatic	317R	mg/kg		108	197	408	<5.0	<5.0	<5.0
>C21 TO C40 Aromatic	317R	mg/kg		67	82	145	<10	<10	<10
Total Aromatic	317R	mg/kg		316	521	1079	<20	<20	<20
Total EPH Aliphatic/Aromatic	317R	mg/kg		1253	563	1132	<40	<40	<40
naphthalene	LPH307	ug/kg	*	43000	33000	24000	14000	2700	7200
acenaphthylene	LPH307	ug/kg	*	2100	380	900	100	100	200
acenaphthene	LPH307	ug/kg	*	76000	11000	34000	2100	340	6100

Key

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Compilation Terra Firma Wales

STL Laboratory Number				**318998**	**318999**	**319000**	**319001**	**319002**	**319003**
Customer Sample Ref				**BH17A @ 7.30m**	**BH17A @ 7.90m**	**BH17A @ 8.50m**	**BH17A @ 9.10m**	**BH17A @ 9.70m**	**BH17A @ 10.30m**
Analyte	**Method**	**Units**	**Acc**						
fluorene	LPH307	ug/kg	*	85000	8300	36000	1500	220	7900
phenanthrene	LPH307	ug/kg	*	270000	20000	110000	5700	480	30000
anthracene	LPH307	ug/kg	*	23000	2300	10000	780	89	2200
fluoranthene	LPH307	ug/kg	*	97000	6800	40000	2100	120	10000
pyrene	LPH307	ug/kg	*	61000	4300	25000	1400	88	6500
benzo(a)anthracene	LPH307	ug/kg	*	14000	1100	5500	400	44	1500
chrysene	LPH307	ug/kg	*	15000	1000	6200	360	50	1700
cyclopenta(cd)pyrene	LPH307	ug/kg	*	780	85	160	<10	<10	40
benzo(b)fluoranthene	LPH307	ug/kg	*	3900	320	1500	120	28	410
benzo(k)fluoranthene	LPH307	ug/kg	*	4600	340	1700	120	16	450
benzo(e)pyrene	LPH307	ug/kg	*	3300	220	1300	90	21	340
benzo(a)pyrene	LPH307	ug/kg	*	4000	310	1500	110	19	380
dibenzo(ah)anthracene	LPH307	ug/kg	*	490	45	200	14	<10	37
benzo(ghi)perylene	LPH307	ug/kg	*	1500	130	580	56	15	170
indeno(123cd)pyrene	LPH307	ug/kg	*	1700	140	650	58	13	200
anthanthrene	LPH307	ug/kg	*	190	23	92	<10	<10	20
PAH (Total)	LPH307	ug/kg	*	700000	90000	300000	29000	4400	76000

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Compilation Terra Firma Wales

STL Laboratory Number				**319004**	**319005**	**319006**	**319007**	**319008**
Customer Sample Ref				**BH17A @ 10.80m**	**BH17A @ 11.30m**	**BH17A @ 11.80m**	**BH17A @ 12.40m**	**BH17A @ 13.00m**
Analyte	**Method**	**Units**	**Acc**					
Stones BG 2.6/3.0	Stones	%	*	27	26	48	25	37
Moisture content at 30 C	33A	%	*	25	29	27	32	26
catechol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10
resorcinol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10
phenol	322	mg/kg		0.41	0.48	0.68	0.94	0.54
cresols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10
xylenols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10
naphthols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10
trimethylphenol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10
Total Phenol	322	mg/kg		<0.50	<0.50	0.68	0.94	<0.50
TPH by GC (>C6-C10)	317	mg/kg		<50	<50	<50	<50	<50
TPH by GC (>C10 - C20)	317	mg/kg		<50	<50	<50	<50	<50
TPH by GC (>C20-C40)	317	mg/kg		<50	310	<50	<50	<50
TPH by GC (>C6 - C40)	317	mg/kg		<50	310	<50	<50	<50
>C6 to C8 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0
>C10 to C12 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0
>C12 to C16 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	6.1
>C16 to C21 Aliphatic	317R	mg/kg		<5.0	<5.0	<5.0	<5.0	120
>C21 to C40 Aliphatic	317R	mg/kg		15	<10	15	<10	784
Total Aliphatic	317R	mg/kg		<20	<20	<20	<20	919
>C5 to C7 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0
>C7 to C8 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0
>C10 to C12 Aromatic	317R	mg/kg		2.3	<1.0	<1.0	<1.0	<1.0
>C12 to C16 Aromatic	317R	mg/kg		13	<1.0	2.7	<1.0	2
>C16 to C21 Aromatic	317R	mg/kg		21	<5.0	<5.0	<5.0	10
>C21 TO C40 Aromatic	317R	mg/kg		<10	<10	<10	<10	14
Total Aromatic	317R	mg/kg		37	<20	<20	<20	<20
Total EPH Aliphatic/Aromatic	317R	mg/kg		<40	<40	<40	<40	932
naphthalene	LPH307	ug/kg	*	7900	5800	10000	3200	4700
acenaphthylene	LPH307	ug/kg	*	340	130	570	250	300
acenaphthene	LPH307	ug/kg	*	12000	1500	14000	560	590

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Compilation Terra Firma Wales

STL Laboratory Number				**319004**	**319005**	**319006**	**319007**	**319008**
Customer Sample Ref				**BH17A @ 10.80m**	**BH17A @ 11.30m**	**BH17A @ 11.80m**	**BH17A @ 12.40m**	**BH17A @ 13.00m**
Analyte	**Method**	**Units**	**Acc**					
fluorene	LPH307	ug/kg	*	17000	1700	16000	470	650
phenanthrene	LPH307	ug/kg	*	75000	4500	45000	840	2100
anthracene	LPH307	ug/kg	*	7200	2200	7300	160	140
fluoranthene	LPH307	ug/kg	*	29000	1800	20000	210	980
pyrene	LPH307	ug/kg	*	18000	1100	13000	160	740
benzo(a)anthracene	LPH307	ug/kg	*	4100	480	2800	44	230
chrysene	LPH307	ug/kg	*	4700	400	3000	68	190
cyclopenta(cd)pyrene	LPH307	ug/kg	*	110	19	150	<10	<10
benzo(b)fluoranthene	LPH307	ug/kg	*	1100	120	880	23	58
benzo(k)fluoranthene	LPH307	ug/kg	*	1300	120	870	23	63
benzo(e)pyrene	LPH307	ug/kg	*	980	86	680	21	54
benzo(a)pyrene	LPH307	ug/kg	*	960	84	780	<10	62
dibenzo(ah)anthracene	LPH307	ug/kg	*	140	<10	120	<10	<10
benzo(ghi)perylene	LPH307	ug/kg	*	420	47	290	18	33
indeno(123cd)pyrene	LPH307	ug/kg	*	440	50	320	15	36
anthanthrene	LPH307	ug/kg	*	60	<10	46	<10	<10
PAH (Total)	LPH307	ug/kg	*	180000	20000	140000	6000	11000

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STL Laboratory Number				**319009**	**319010**	**319011**	**319012**	**319013**	**319014**
Customer Sample Ref				**BH17A @ 13.80m**	**BH17A @ 14.10m**	**BH18A @ 5.00m**	**BH18A @ 5.70m**	**BH18A @ 6.30m**	**BH18A @ 6.90m**
Analyte	**Method**	**Units**	**Acc**						
Stones BG 2.6/3.0	Stones	%	*	52	55	56	57	38	44
Moisture content at 30 C	33A	%	*	24	25	20	19	21	24
catechol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
resorcinol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
phenol	322	mg/kg		0.71	0.75	0.65	0.58	1.06	1.12
cresols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
xylenols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
naphthols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
trimethylphenol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Total Phenol	322	mg/kg		0.71	0.75	0.65	<0.50	1.06	1.12
TPH by GC (>C6-C10)	317	mg/kg		<50	<50	<50	<50	<50	<50
TPH by GC (>C10 - C20)	317	mg/kg		<50	<50	99	<50	<50	<50
TPH by GC (>C20-C40)	317	mg/kg		<50	<50	89	<50	<50	<50
TPH by GC (>C6 - C40)	317	mg/kg		<50	<50	188	<50	<50	<50
>C6 to C8 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C10 to C12 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C12 to C16 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C16 to C21 Aliphatic	317R	mg/kg		<5.0	28	7.1	<5.0	<5.0	<5.0
>C21 to C40 Aliphatic	317R	mg/kg		<10	147	26	15	<10	<10
Total Aliphatic	317R	mg/kg		<20	173	34	<20	<20	<20
>C5 to C7 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C7 to C8 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C10 to C12 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C12 to C16 Aromatic	317R	mg/kg		<1.0	<1.0	15	6.2	<1.0	<1.0
>C16 to C21 Aromatic	317R	mg/kg		<5.0	<5.0	55	9.1	<5.0	<5.0
>C21 TO C40 Aromatic	317R	mg/kg		<10	<10	30	<10	<10	<10
Total Aromatic	317R	mg/kg		<20	<20	99	<20	<20	<20
Total EPH Aliphatic/Aromatic	317R	mg/kg		<40	173	138	<40	<40	<40
naphthalene	LPH307	ug/kg	*	2500	6900	3000	3500	3100	5400
acenaphthylene	LPH307	ug/kg	*	280	400	270	210	99	130
acenaphthene	LPH307	ug/kg	*	370	490	580	780	390	1100

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Compilation Terra Firma Wales

STL Laboratory Number				**319009**	**319010**	**319011**	**319012**	**319013**	**319014**
Customer Sample Ref				**BH17A @ 13.80m**	**BH17A @ 14.10m**	**BH18A @ 5.00m**	**BH18A @ 5.70m**	**BH18A @ 6.30m**	**BH18A @ 6.90m**
Analyte	**Method**	**Units**	**Acc**						
fluorene	LPH307	ug/kg	*	500	570	800	990	170	700
phenanthrene	LPH307	ug/kg	*	1400	900	2700	3200	270	2300
anthracene	LPH307	ug/kg	*	370	150	930	1300	54	450
fluoranthene	LPH307	ug/kg	*	360	220	1800	1600	90	1100
pyrene	LPH307	ug/kg	*	260	180	1200	1100	66	680
benzo(a)anthracene	LPH307	ug/kg	*	79	48	440	390	30	85
chrysene	LPH307	ug/kg	*	110	80	390	330	210	140
cyclopenta(cd)pyrene	LPH307	ug/kg	*	<10	<10	<10	<10	<10	<10
benzo(b)fluoranthene	LPH307	ug/kg	*	25	22	150	82	<10	41
benzo(k)fluoranthene	LPH307	ug/kg	*	29	21	140	120	<10	46
benzo(e)pyrene	LPH307	ug/kg	*	23	21	85	69	280	43
benzo(a)pyrene	LPH307	ug/kg	*	22	17	88	82	280	41
dibenzo(ah)anthracene	LPH307	ug/kg	*	<10	<10	<10	<10	<10	<10
benzo(ghi)perylene	LPH307	ug/kg	*	14	11	49	34	<10	26
indeno(123cd)pyrene	LPH307	ug/kg	*	13	<10	49	33	<10	23
anthanthrene	LPH307	ug/kg	*	<10	<10	10	<10	<10	<10
PAH (Total)	LPH307	ug/kg	*	6400	10000	13000	14000	5000	12000

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STL Laboratory Number				319015	319016	319017	319018	319019	319020
Customer Sample Ref				**BH18A @ 7.50m**	**BH18A @ 8.10m**	**BH18A @ 8.70m**	**BH18A @ 9.25m**	**BH18A @ 9.80m**	**BH18A @ 10.40m**
Analyte	**Method**	**Units**	**Acc**						
Stones BG 2.6/3.0	Stones	%	*	38	41	50	43	29	28
Moisture content at 30 C	33A	%	*	23	19	21	16	22	25
catechol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
resorcinol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
phenol	322	mg/kg		0.77	0.43	0.34	0.38	0.35	0.45
cresols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
xylenols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
naphthols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
trimethylphenol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Total Phenol	322	mg/kg		0.77	<0.50	<0.50	<0.50	<0.50	<0.50
TPH by GC (>C6-C10)	317	mg/kg		<50	<50	<50	<50	<50	<50
TPH by GC (>C10 - C20)	317	mg/kg		<50	<50	<50	<50	<50	<50
TPH by GC (>C20-C40)	317	mg/kg		<50	<50	<50	<50	<50	<50
TPH by GC (>C6 - C40)	317	mg/kg		<50	<50	<50	<50	<50	<50
>C6 to C8 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C10 to C12 Aliphatic	317R	mg/kg		4.5	<1.0	<1.0	<1.0	<1.0	<1.0
>C12 to C16 Aliphatic	317R	mg/kg		22	2.3	<1.0	<1.0	<1.0	<1.0
>C16 to C21 Aliphatic	317R	mg/kg		338	37	<5.0	<5.0	<5.0	<5.0
>C21 to C40 Aliphatic	317R	mg/kg		1688	198	<10	<10	<10	<10
Total Aliphatic	317R	mg/kg		2078	235	<20	<20	<20	<20
>C5 to C7 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C7 to C8 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C10 to C12 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C12 to C16 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
>C16 to C21 Aromatic	317R	mg/kg		14	6.5	<5.0	<5.0	<5.0	<5.0
>C21 TO C40 Aromatic	317R	mg/kg		34	<10	<10	<10	<10	<10
Total Aromatic	317R	mg/kg		48	<20	<20	<20	<20	<20
Total EPH Aliphatic/Aromatic	317R	mg/kg		2078	247	<40	<40	<40	<40
naphthalene	LPH307	ug/kg	*	3500	2800	2200	1000	950	4700
acenaphthylene	LPH307	ug/kg	*	180	340	510	360	360	590
acenaphthene	LPH307	ug/kg	*	330	570	450	270	200	500

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Compilation Terra Firma Wales

STL Laboratory Number				**319015**	**319016**	**319017**	**319018**	**319019**	**319020**
Customer Sample Ref				**BH18A @ 7.50m**	**BH18A @ 8.10m**	**BH18A @ 8.70m**	**BH18A @ 9.25m**	**BH18A @ 9.80m**	**BH18A @ 10.40m**
Analyte	**Method**	**Units**	**Acc**						
fluorene	LPH307	ug/kg	*	230	570	900	600	580	1000
phenanthrene	LPH307	ug/kg	*	410	1200	1800	630	540	1200
anthracene	LPH307	ug/kg	*	210	500	490	130	92	230
fluoranthene	LPH307	ug/kg	*	660	1000	750	96	45	64
pyrene	LPH307	ug/kg	*	490	740	540	87	34	57
benzo(a)anthracene	LPH307	ug/kg	*	95	170	89	15	<10	17
chrysene	LPH307	ug/kg	*	91	180	150	25	<10	34
cyclopenta(cd)pyrene	LPH307	ug/kg	*	<10	<10	<10	<10	<10	<10
benzo(b)fluoranthene	LPH307	ug/kg	*	33	67	43	<10	<10	11
benzo(k)fluoranthene	LPH307	ug/kg	*	32	69	51	<10	<10	<10
benzo(e)pyrene	LPH307	ug/kg	*	39	50	41	12	<10	11
benzo(a)pyrene	LPH307	ug/kg	*	37	50	39	<10	<10	<10
dibenzo(ah)anthracene	LPH307	ug/kg	*	<10	<10	<10	<10	<10	<10
benzo(ghi)perylene	LPH307	ug/kg	*	23	34	27	<10	<10	<10
indeno(123cd)pyrene	LPH307	ug/kg	*	26	32	24	<10	<10	<10
anthanthrene	LPH307	ug/kg	*	<10	<10	<10	<10	<10	<10
PAH (Total)	LPH307	ug/kg	*	6400	8400	8100	3200	2800	8400

Key

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I/S - Insufficient Sample
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Acc = Accreditation codes: * = not UKAS accredited.

STL Laboratory Number				**319021**	**319022**	**319023**	**319024**	**319025**
Customer Sample Ref				**BH18A @ 11.10m**	**BH18A @ 11.70m**	**BH18A @ 12.30m**	**BH18A @ 12.90m**	**BH18A @ 13.50m**
Analyte	**Method**	**Units**	**Acc**					
Stones BG 2.6/3.0	Stones	%	*	56	41	54	32	30
Moisture content at 30 C	33A	%	*	20	23	31	21	23
catechol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10
resorcinol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10
phenol	322	mg/kg		0.31	0.26	1.04	0.57	0.53
cresols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10
xylenols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10
naphthols	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10
trimethylphenol	322	mg/kg		<0.10	<0.10	<0.10	<0.10	<0.10
Total Phenol	322	mg/kg		<0.50	<0.50	1.04	<0.50	<0.50
TPH by GC (>C6-C10)	317	mg/kg		<50	<50	<50	<50	<50
TPH by GC (>C10 - C20)	317	mg/kg		<50	<50	<50	<50	<50
TPH by GC (>C20-C40)	317	mg/kg		<50	<50	<50	<50	<50
TPH by GC (>C6 - C40)	317	mg/kg		<50	<50	<50	<50	<50
>C6 to C8 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0
>C10 to C12 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0
>C12 to C16 Aliphatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0
>C16 to C21 Aliphatic	317R	mg/kg		<5.0	<5.0	<5.0	<5.0	<5.0
>C21 to C40 Aliphatic	317R	mg/kg		<10	<10	<10	<10	<10
Total Aliphatic	317R	mg/kg		<20	<20	<20	<20	<20
>C5 to C7 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0
>C7 to C8 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0
>C8 to C10 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0
>C10 to C12 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0
>C12 to C16 Aromatic	317R	mg/kg		<1.0	<1.0	<1.0	<1.0	<1.0
>C16 to C21 Aromatic	317R	mg/kg		<5.0	<5.0	<5.0	<5.0	<5.0
>C21 TO C40 Aromatic	317R	mg/kg		<10	<10	<10	<10	<10
Total Aromatic	317R	mg/kg		<20	<20	<20	<20	<20
Total EPH Aliphatic/Aromatic	317R	mg/kg		<40	<40	<40	<40	<40
naphthalene	LPH307	ug/kg	*	3100	1500	5700	4400	5300
acenaphthylene	LPH307	ug/kg	*	390	490	460	350	310
acenaphthene	LPH307	ug/kg	*	480	360	1500	550	1200

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Compilation Terra Firma Wales

STL Laboratory Number				**319021**	**319022**	**319023**	**319024**	**319025**
Customer Sample Ref				**BH18A @ 11.10m**	**BH18A @ 11.70m**	**BH18A @ 12.30m**	**BH18A @ 12.90m**	**BH18A @ 13.50m**
Analyte	**Method**	**Units**	**Acc**					
fluorene	LPH307	ug/kg	*	630	810	1500	660	1400
phenanthrene	LPH307	ug/kg	*	960	890	4100	1100	3600
anthracene	LPH307	ug/kg	*	160	170	630	220	1300
fluoranthene	LPH307	ug/kg	*	280	220	2900	170	1300
pyrene	LPH307	ug/kg	*	190	140	1600	110	740
benzo(a)anthracene	LPH307	ug/kg	*	32	33	130	44	380
chrysene	LPH307	ug/kg	*	59	60	180	66	320
cyclopenta(cd)pyrene	LPH307	ug/kg	*	<10	<10	<10	<10	<10
benzo(b)fluoranthene	LPH307	ug/kg	*	16	23	78	13	66
benzo(k)fluoranthene	LPH307	ug/kg	*	20	24	74	12	71
benzo(e)pyrene	LPH307	ug/kg	*	15	17	69	15	56
benzo(a)pyrene	LPH307	ug/kg	*	13	11	71	14	58
dibenzo(ah)anthracene	LPH307	ug/kg	*	<10	<10	<10	<10	<10
benzo(ghi)perylene	LPH307	ug/kg	*	<10	24	55	16	24
indeno(123cd)pyrene	LPH307	ug/kg	*	<10	19	54	<10	21
anthanthrene	LPH307	ug/kg	*	<10	<10	<10	<10	<10
PAH (Total)	LPH307	ug/kg	*	6300	4800	19000	7700	16000

Key

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To Follow - analysis incomplete (interim reports only)

Acc = Accreditation codes: * = not UKAS accredited.

Summary of Chemical Analysis
Soil Samples

Our Ref: 13-80386

Client Ref: 11802-45

Contract Title: Alluvium

			Lab No.	508572
			Sample ID	S A 1
			Depth	
			Sample Ref	
			Sample Type	
			Sampling Date	/ /
			Sampling Time	
Test	**Units**	**DETSxx**	**LOD**	
Aluminium	mg/kg	DETS 042*	1	18000
Calcium	mg/kg	DETS 042*	1	7600
Iron	mg/kg	DETS 042	1200	37000
Potassium	mg/kg	DETS 042*	1	7600
Magnesium	mg/kg	DETS 042*	1	5700

				Approx 95 % confidence limits	
Parameters	*Initial estimates **	*Fitted Values*	*Standard errors*	*Lower bound*	*Upper bound*
K (L/kg)	-2.368	***0.005***	*6.0342*	*-14.7600*	*14.7704*
Smax (mg/kg)	-207.6	***101247.3***	*118185366.1344*	*-289087925.20*	*289290419.73*

* Enter these values into the blue colored cells prior to running Solver

Color Coding

🟦	Changing cells
🟩	Target cell
🟧	Data entry cells

GOVERNING EQUATION

$$S = \frac{S_{\max} KC}{1 + KC}$$

Goodness of fit statistics

SSE	***2.864E+00***
E	***0.978***
AIC	***3.78***

Approximate Correlation Matrix

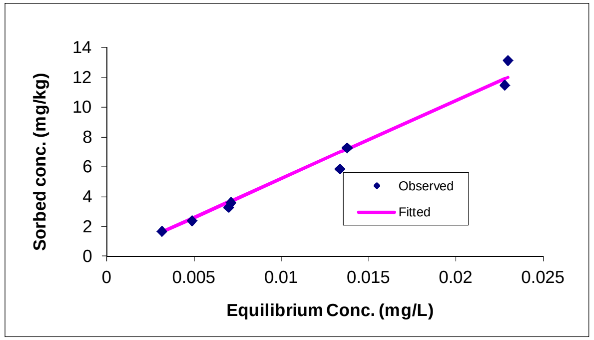
	K	***Smax***
K	*1*	*-1.000*
Smax	*-1.000*	*1*

Measured C **mg/L**	***Measured S*** **mg/kg**	***Modeled S*** **mg/kg**	***Weights*** ***wi***
0.022964365	13.16614103	12.02	
0.02278115	11.49860517	11.92	
0.013747818	7.29377826	7.19	
0.013340229	5.881339496	6.98	
0.007089652	3.625397793	3.71	
0.006966181	3.302831599	3.65	
0.004869821	2.412908486	2.55	
0.003131927	1.691159659	1.64	

If data are weighted by the inverse of their variance select "yes" in red box below

no

CAUTION
To allow Solver to work, cells are NOT write-protected. Therefore, only enter data into the appropriate cells (i.e.the tan and blue colored cells). Making changes to any other cells may result in modifying the calculations leading to erroneous results



Langmuir Isotherm - Test 6 (Peat)

Approx 95 % confidence limits

Parameters	*Initial estimates **	*Fitted Values*	*Standard errors*	*Lower bound*	*Upper bound*
K (L/kg)	4.040	***0.109***	*3.8893*	*-8.5571*	*8.7749*
Smax (mg/kg)	2979.3	***106208.6***	*3787499.7259*	*-8332866.63*	*8545283.88*

* Enter these values into the blue colored cells prior to running Solver

Color Coding

🟦	Changing cells
🟩	Target cell
🟧	Data entry cells

GOVERNING EQUATION

$$S = \frac{S_{\max} KC}{1+KC}$$

Goodness of fit statistics

SSE	***1.716E+03***
E	***0.966***
AIC	***68.55***

Approximate Correlation Matrix

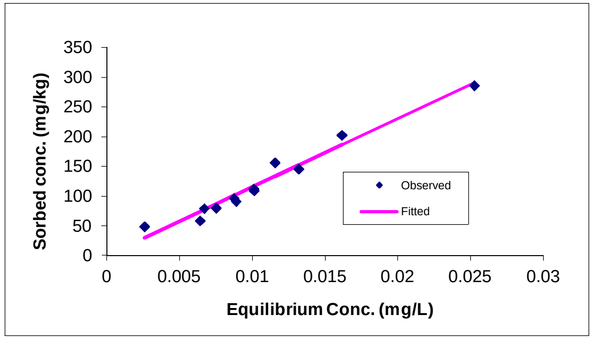
	K	***Smax***
K	*1*	*-1.000*
Smax	*-1.000*	*1*

Measured C mg/L	***Measured S*** mg/kg	***Modeled S*** mg/kg	***Weights*** *wi*
0.025247707	286.2011022	291.13	
0.016143113	202.6811669	186.33	
0.011547502	156.5517295	133.35	
0.013180438	145.9952864	152.18	
0.01008349	112.4547543	116.46	
0.010118141	109.5983367	116.86	
0.008723432	96.84339198	100.77	
0.008883693	91.44452684	102.62	
0.007497646	80.30550278	86.62	
0.006683344	79.62823151	77.22	
0.00639314	58.88153853	73.87	
0.002577181	48.97568772	29.79	

If data are weighted by the inverse of their variance select "yes" in red box below

no

CAUTION
To allow Solver to work, cells are NOT write-protected. Therefore, only enter data into the appropriate cells (i.e.the tan and blue colored cells). Making changes to any other cells may result in modifying the calculations leading to erroneous results

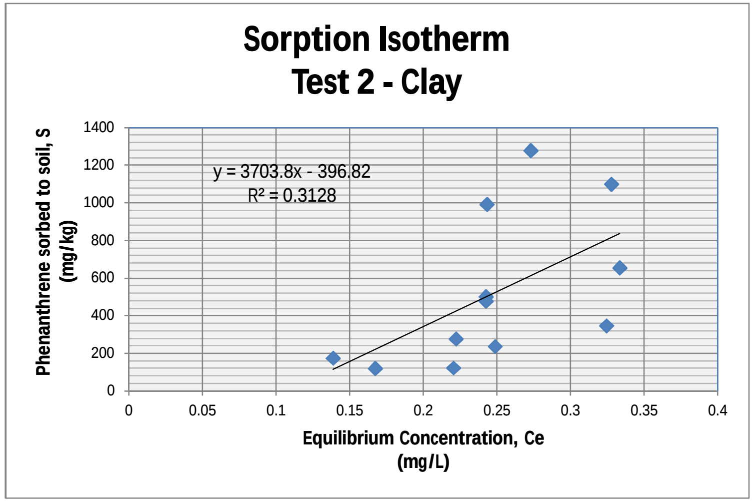


Langmuir Isotherm - Test 1 (Peat)

Results of Sorption Testing

Soil Type	Clay
Contaminant	Phenanthrene

TEST 2	**Initial Conc., Co. mg/L**	0.477445449		
Sample No.	**Soil Sample Weight, M, (g/ltr)**	**Equilibrium Conc., Ce, (mg/L)**	**Sorbed Mass of Pheneanthrene per unit mass soil, S**	**Sorbed Mass of Pheneanthrene (mg) per unit mass soil (kg/L), S**
3	0.136	0.327764523	1.100595043	1100.595043
6	0.16	0.272899455	1.278412463	1278.412463
7	0.22	0.333338728	0.655030549	655.0305489
5	0.236	0.243182979	0.992637583	992.6375828
1	0.44	0.324433249	0.347754999	347.754999
10	0.468	0.242422717	0.502185324	502.1853244
9	0.492	0.242419562	0.477694891	477.6948911
8	0.92	0.222176396	0.277466361	277.4663613
12	0.964	0.248694092	0.237293939	237.2939385
13	1.936	0.138575938	0.175035904	175.0359043
15	2.084	0.22038142	0.123351261	123.3512613
14	2.568	0.167166216	0.120825246	120.8252464



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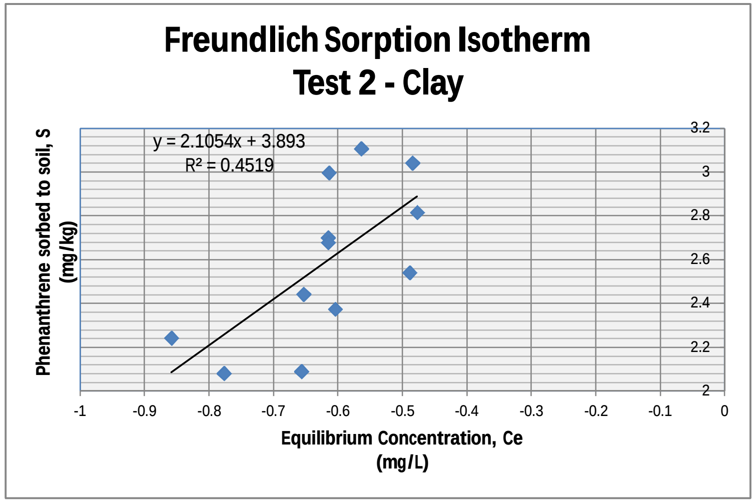
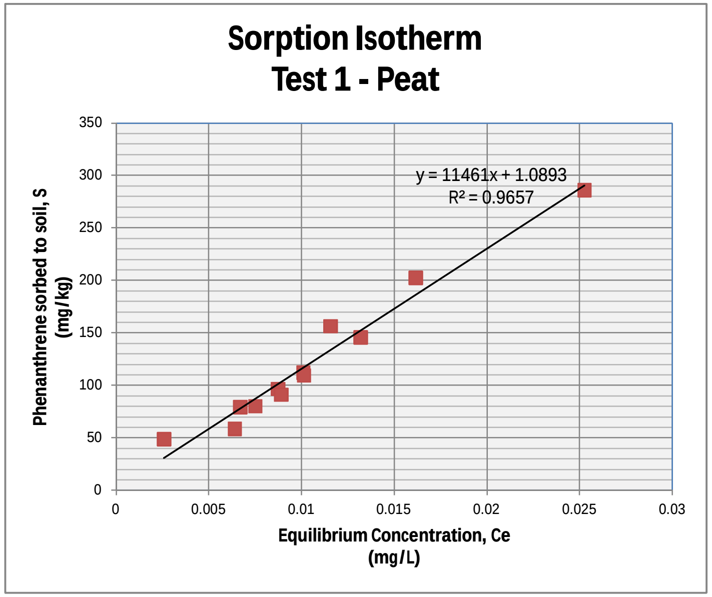
TEST 2	Initial Conc. (Co) ppm	0.477445449
Sample No.	**Log Equilibrium Conc, Log Ce. (mg/L)**	**Log Sorbed Mass of Phenanthrene (mg) per unit mass soil (kg/L), Log S.**
3	-0.484438056	3.041627553
6	-0.563997332	3.106670996
7	-0.477114226	2.816261555
5	-0.614066825	2.996790714
1	-0.488874644	2.541273382
10	-0.615426686	2.700864017
9	-0.615432337	2.679150597
8	-0.653302082	2.443210339
12	-0.604334532	2.375286645
13	-0.858312173	2.243127143
15	-0.656825022	2.091143594
14	-0.776851488	2.08215769

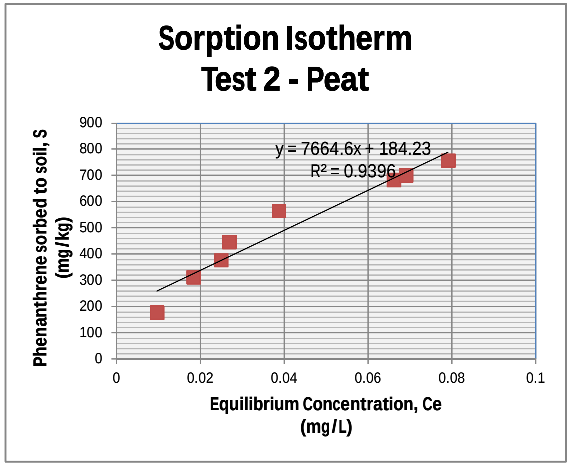


Results of Sorption Testing
Soil Type Peat
Contaminant Phenanthrene

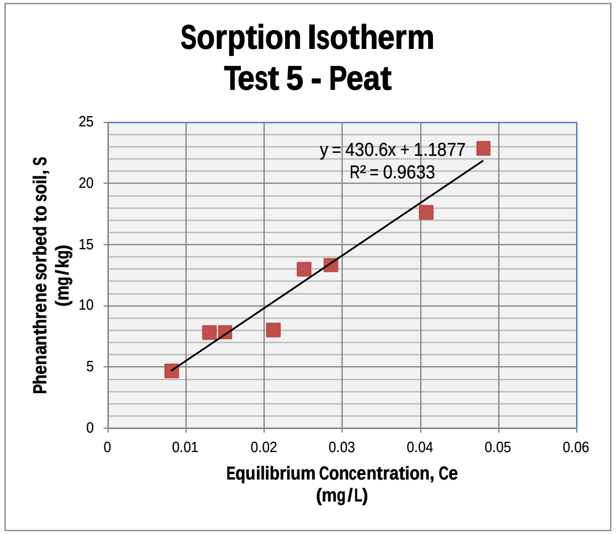
TEST 1	**Initial Conc., Co. mg/L**	0.477445449		
Sample No.	**Soil Sample Weight, M, (g/ltr)**	**Equilibrium Conc., Ce, (mg/L)**	**Sorbed Mass of Pheneanthrene per unit mass soil, S**	**Sorbed Mass of Pheneanthrene (mg) per unit mass soil (kg/L), S**
A8	1.58	0.025247707	0.286201102	286.2011022
A11	2.276	0.016143113	0.202681167	202.6811669
A14	2.976	0.011547502	0.15655173	156.5517295
A12	3.18	0.013180438	0.145995286	145.9952864
A13	4.156	0.01008349	0.112454754	112.4547543
A15	4.264	0.010118141	0.109598337	109.5983367
A17	4.84	0.008723432	0.096843392	96.84339198
A16	5.124	0.008883693	0.091444527	91.44452684
A18	5.852	0.007497646	0.080305503	80.30550278
A19	5.912	0.006683344	0.079628232	79.62823151
A20	8	0.00639314	0.058881539	58.88153853
A21	9.696	0.002577181	0.048975688	48.97568772



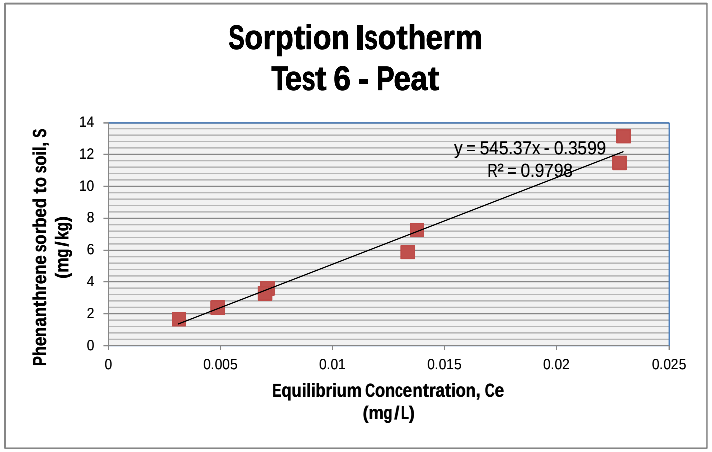
TEST 2	Initial Conc., Co. mg/L	0.4774		
Sample No.	**Soil Sample Weight, M, (g/ltr)**	**Equilibrium Conc., Ce, (mg/L)**	**Sorbed Mass of Pheneanthrene per unit mass soil, S**	**Sorbed Mass of Pheneanthrene (mg) per unit mass soil (kg/L), S**
B22	0.9	0.009662586	0.178152682	178.1526817
B24	0.484	0.018356706	0.313312591	313.3125908
B23	0.384	0.024975089	0.37766904	377.6690396
B19	0.32	0.02688994	0.447218937	447.2189367
B18	0.232	0.038751294	0.565727183	565.727183
B17	0.152	0.066104962	0.683519985	683.5199853
B21	0.144	0.069010363	0.701316925	701.3169245
B16	0.12	0.079060967	0.757825275	757.825275



TEST 5	**Initial Conc., Co. mg/L**	0.139547984		
Sample No.	**Soil Sample Weight, M, (g/ltr)**	**Equilibrium Conc., Ce, (mg/L)**	**Sorbed Mass of Pheneanthrene per unit mass soil, S**	**Sorbed Mass of Pheneanthrene (mg) per unit mass soil (kg/L), S**
S4	28	0.008111943	0.004694144	4.694144346
S1	16.16	0.012947245	0.007834204	7.834204188
S3	15.84	0.014937392	0.00786683	7.866830305
S6	14.72	0.021109638	0.008046083	8.046083306
S2	8.8	0.025071346	0.013008709	13.00870887
S7	8.32	0.028490046	0.01334831	13.34830996
S8	5.6	0.04068053	0.017654903	17.65490263
S5	4	0.047999865	0.02288703	22.8870298



TEST 6	**Initial Conc., Co. mg/L**	0.065096017		
Sample No.	**Soil Sample Weight, M, (g/ltr)**	**Equilibrium Conc., Ce, (mg/L)**	**Sorbed Mass of Pheneanthrene per unit mass soil, S**	**Sorbed Mass of Pheneanthrene (mg) per unit mass soil (kg/L), S**
S14	3.2	0.022964365	0.013166141	13.16614103
S10	3.68	0.02278115	0.011498605	11.49860517
S12	7.04	0.013747818	0.007293778	7.29377826
S15	8.8	0.013340229	0.005881339	5.881339496
S13	16	0.007089652	0.003625398	3.625397793
S11	17.6	0.006966181	0.003302832	3.302831599
S16	24.96	0.004869821	0.002412908	2.412908486
S17	36.64	0.003131927	0.00169116	1.691159659



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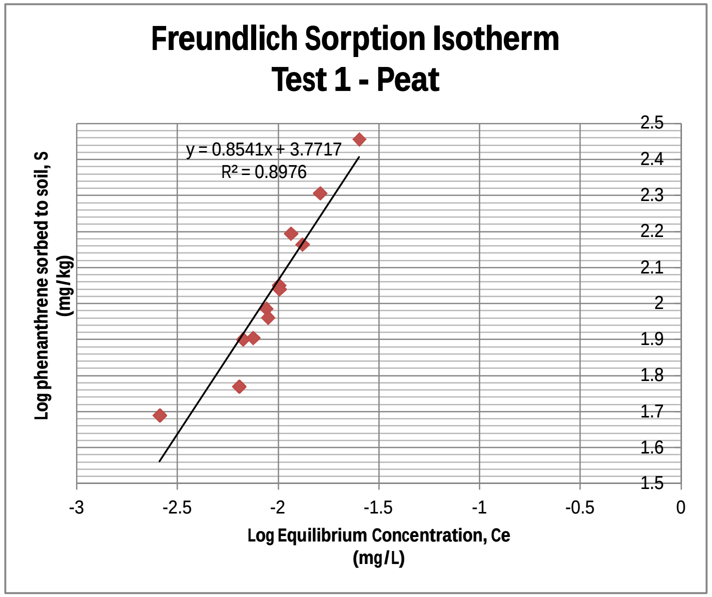
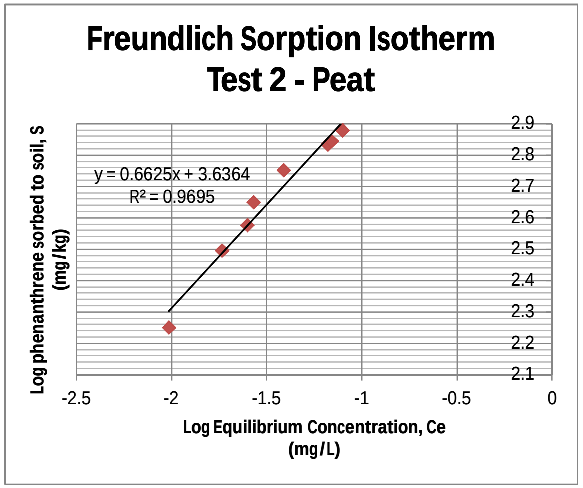
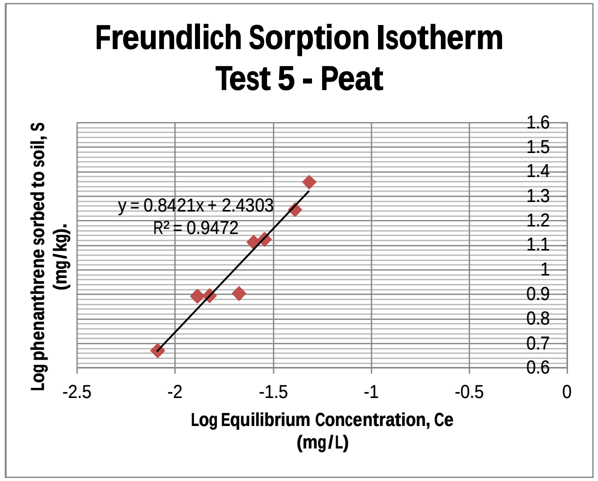
TEST 1	Initial Conc. (Co) ppm	0.477445449
Sample No.	**Log Equilibrium Conc, Log Ce. (mg/L)**	**Log Sorbed Mass of Phenanthrene (mg) per unit mass soil (kg/L), Log S.**
A8	-1.597778054	2.456671302
A11	-1.792012717	2.306813396
A14	-1.937511965	2.19465787
A12	-1.880070157	2.164338834
A13	-1.996389134	2.050977821
A15	-1.994899271	2.039803963
A17	-2.059312644	1.986069992
A16	-2.051406449	1.961157717
A18	-2.125075042	1.904745305
A19	-2.175006184	1.90106707
A20	-2.194285752	1.769979149
A21	-2.588855144	1.689980543



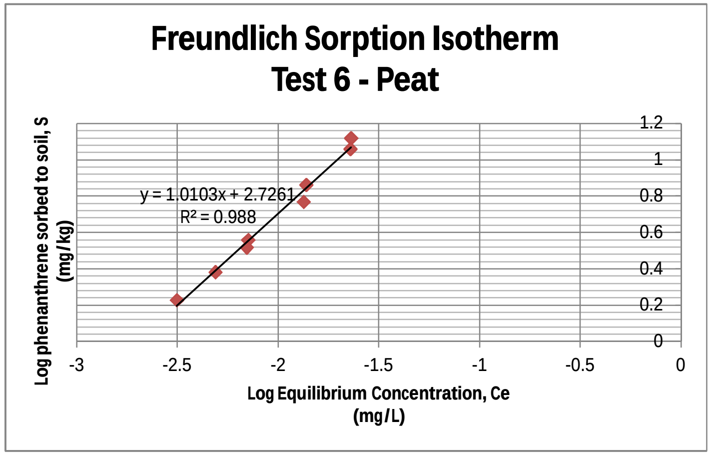
TEST 2	Initial Conc. (Co) ppm	0.4774
Sample No.	**Log Equilibrium Conc, Log Ce. (mg/L)**	**Log Sorbed Mass of Phenanthrene (mg) per unit mass soil (kg/L), Log S.**
B22	-2.014906607	2.250792364
B24	-1.736205247	2.495977848
B23	-1.602492959	2.577111384
B19	-1.570410163	2.650520185
B18	-1.411713796	2.752607047
B17	-1.179765939	2.834751217
B21	-1.161085689	2.84591432
B16	-1.102037878	2.879569086



TEST 5	Initial Conc. (Co) ppm	0.139547984
Sample No.	**Log Equilibrium Conc, Log Ce. (mg/L)**	**Log Sorbed Mass of Phenanthrene (mg) per unit mass soil (kg/L), Log S.**
S4	-2.090875126	0.67155644
S1	-1.887822644	0.893994887
S3	-1.825725212	0.895799782
S6	-1.675519212	0.905584525
S2	-1.600822345	1.114234195
S7	-1.545306857	1.125426283
S8	-1.390613401	1.246865327
S5	-1.318759983	1.359589435



TEST 6	Initial Conc. (Co) ppm	0.065096017
Sample No.	Log Equilibrium Conc, Log Ce. (mg/L)	Log Sorbed Mass of Phenanthrene (mg) per unit mass soil (kg/L), Log S.
S14	-1.638945551	1.119458503
S10	-1.642424362	1.060645162
S12	-1.861766233	0.862952556
S15	-1.87483671	0.769476249
S13	-2.149375079	0.559355666
S11	-2.157005272	0.518886431
S16	-2.312487009	0.382540851
S17	-2.504188395	0.22818461



Parameters	*Initial estimates **	*Fitted Values*	*Standard errors*	*Approx 95 % confidence limits* *Lower bound*	 *Upper bound*
K (L/kg)	-2.130	***53687091.200***	###############	############	############
Smax (mg/kg)	-294.5	***200.0***	*596.9543*	*-1130.10*	*1530.10*

* Enter these values into the blue colored cells prior to running Solver

Color Coding

🟦	Changing cells
🟩	Target cell
🟧	Data entry cells

GOVERNING EQUATION

$$S = \frac{S_{\max} KC}{1 + KC}$$

Goodness of fit statistics

SSE	***3.020E+06***
E	***-0.716***
AIC	***158.23***

Approximate Correlation Matrix

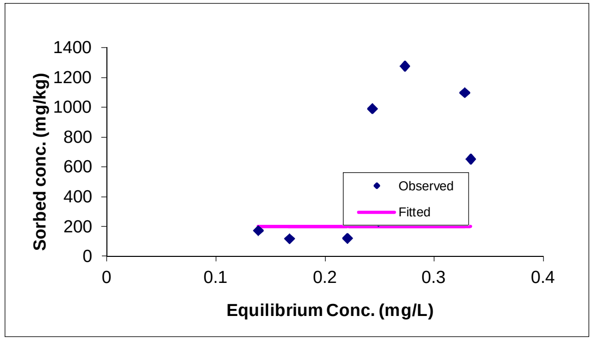
	K	***Smax***
K	*1*	*-0.964*
Smax	*-0.964*	*1*

If data are weighted by the inverse of their variance select "yes" in red box below

no

Measured C mg/L	***Measured S*** mg/kg	***Modeled S*** mg/kg	***Weights*** *wi*
0.327764523	1100.595043	200.00	
0.272899455	1278.412463	200.00	
0.333338728	655.0305489	200.00	
0.243182979	992.6375828	200.00	
0.324433249	347.754999	200.00	
0.242422717	502.1853244	200.00	
0.242419562	477.6948911	200.00	
0.222176396	277.4663613	200.00	
0.248694092	237.2939385	200.00	
0.138575938	175.0359043	200.00	
0.22038142	123.3512613	200.00	
0.167166216	120.8252464	200.00	

CAUTION
To allow Solver to work, cells are NOT write-protected. Therefore, only enter data into the appropriate cells (i.e.the tan and blue colored cells). Making changes to any other cells may result in modifying the calculations leading to erroneous results



Langmuir Isotherm - Test 2 (Clay)

				Approx 95 % confidence limits	
Parameters	*Initial estimates **	*Fitted Values*	*Standard errors*	*Lower bound*	*Upper bound*
K (L/kg)	17.504	***18.902***	*2.4133*	*12.9973*	*24.8075*
Smax (mg/kg)	1301.2	***1255.7***	*82.4331*	*1053.94*	*1457.36*

* Enter these values into the blue colored cells prior to running Solver

Color Coding

🟦	Changing cells
🟩	Target cell
🟧	Data entry cells

GOVERNING EQUATION

$$S = \frac{S_{\max} KC}{1 + KC}$$

Goodness of fit statistics

SSE	***3.085E+03***
E	***0.990***
AIC	***59.64***

Approximate Correlation Matrix

	K	***Smax***
K	*1*	*-0.974*
Smax	*-0.974*	*1*

Measured C mg/L	***Measured S*** mg/kg	***Modeled S*** mg/kg	***Weights*** ***wi***
0.009662586	178.1526817	193.92	
0.018356706	313.3125908	323.46	
0.024975089	377.6690396	402.68	
0.02688994	447.2189367	423.15	
0.038751294	565.727183	530.89	
0.066104962	683.5199853	697.47	
0.069010363	701.3169245	710.77	
0.079060967	757.825275	752.27	

If data are weighted by the inverse of their variance select "yes" in red box below

no

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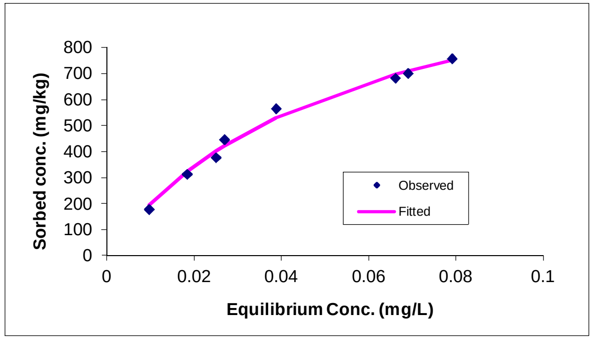


Langmuir Isotherm - Test 2 (Peat)

				Approx 95 % confidence limits	
Parameters	*Initial estimates **	*Fitted Values*	*Standard errors*	*Lower bound*	*Upper bound*
K (L/kg)	6.306	***2.442***	*3.6460*	*-6.4797*	*11.3630*
Smax (mg/kg)	89.7	***208.9***	*286.8023*	*-492.93*	*910.63*

* Enter these values into the blue colored cells prior to running Solver

Color Coding

🟦	Changing cells
🟩	Target cell
🟧	Data entry cells

GOVERNING EQUATION

$$S = \frac{S_{\max} KC}{1+KC}$$

Goodness of fit statistics

SSE	***1.094E+01***
E	***0.957***
AIC	***14.51***

Approximate Correlation Matrix

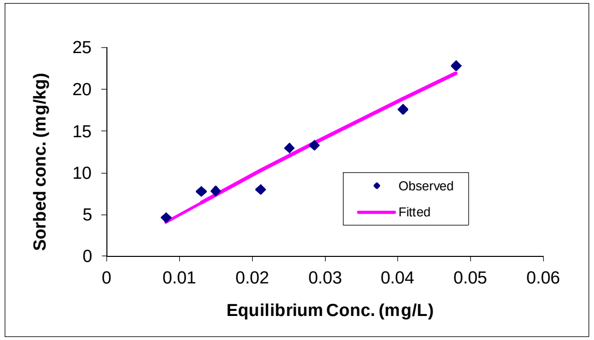
	K	***Smax***
K	*1*	*-1.000*
Smax	*-1.000*	*1*

Measured C mg/L	***Measured S mg/kg***	***Modeled S mg/kg***	***Weights wi***
0.008111943	4.694144346	4.06	
0.012947245	7.834204188	6.40	
0.014937392	7.866830305	7.35	
0.021109638	8.046083306	10.24	
0.025071346	13.00870887	12.05	
0.028490046	13.34830996	13.58	
0.04068053	17.65490263	18.87	
0.047999865	22.8870298	21.91	

If data are weighted by the inverse of their variance select "yes" in red box below

no

CAUTION
To allow Solver to work, cells are NOT write-protected. Therefore, only enter data into the appropriate cells (i.e.the tan and blue colored cells). Making changes to any other cells may result in modifying the calculations leading to erroneous results



Langmuir Isotherm - Test 5 (Peat)