# SORPTION OF PHENANTHRENE BY NATURAL ORGANIC MATTER FRACTIONS IN SELECTED ROCKS AND SOILS FROM SOUTHWESTERN NIGERIA

BY

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# ABSTRACT

Natural Organic Matter (NOM) fractions in rocks, sediments and soils are known to have good sorptive potentials for frequently occurring Hydrophobic Organic Contaminants (HOCs) such as phenanthrene. Despite widespread occurrence of organic matter-rich rocks, sediments and soils in Nigeria, there is limited information on the sorptive potentials of their NOM fractions for HOCs which may be useful in remediation and clean-up design. This study is aimed at investigating the sorption of phenanthrene by NOM fractions in selected rocks and soils from southwestern Nigeria.

Coal and mudstone, carbonaceous shale and sandy soils (500 g each) were purposively collected from Ute, Auchi and Lagos respectively. The rocks and soils (250 g each) were demineralised with 1M HCl and mixture of 1M HCl/10%HF (1:3) successively. Lipid and bound-lipid were extracted via solvent extraction and saponification methods respectively. Lignin was extracted from the soils with dioxane-acid hydrolysis method. Organic carbon, hydrogen and oxygen contents of demineralised, lipid free, bound-lipid free and lignin free (NOM fractions) were determined using bulk method. Organic matter type in the rocks and soils were determined from atomic ratios of the elements. Sorption parameters (nonlinearity and organic carbon normalised sorption coefficients, $K_{OC}$) of the bulk samples (control) and NOM fractions were determined from sorption experiments using phenanthrene concentrations ranging from 10 to 1250 ppb. The skeletal carbons of NOM fractions were determined using $^{13}$C Cross Polarisation Magic Angle SpinningNuclear Magnetic Resonance.

The ranges of organic carbon and oxygen contents of NOM fractions in the rocks were respectively: 53.0-70.8% and 11.6-23.1% (demineralised), 54.4-70.2% and 12.8-26.1% (lipid free), 33.4-51.6% and 28.3-38.6% (bound-lipid free). Those of NOM fractions in the soils were correspondingly: 27.8-63.1% and 7.0-21.4% (demineralised), 27.2-65.2% and 16.4-22.1% (lipid free), 9.2- 54.7% and 14.7-29.3% (bound-lipid free), 15.2-65.3% and 11.2-17.4% (lignin free). The bound-lipid free has the lowest organic carbon and highest oxygen. The H/C and O/C ratios in the NOM fractions were: 0.6-1.7, 0.6-1.3, 0.7-2.3, 0.5-1.3 and 0.1-0.5, 0.1-0.6, 0.3-1.2, 0.2-0.6 respectively, indicating increasing degree of maturity in NOM fractions with progressive extraction except in bound-lipid free. Higher O/C ratio in bound-lipid free indicates high polarity. The plot of H/C and O/C ratios indicated that the rocks contained type III kerogen while the soils contained type II/III kerogen. Phenanthrene sorption isotherms for bulk samples and NOM fractions were nonlinear ($n<1$). The nonlinearity increases with degree of maturity. The $K_{OC}$ range in bulk rocks, soils, demineralised, lipid free, bound-lipid free and lignin free were: 3305-21241, 751-3133, 570-2883, 2663-14084, 651-28751, 10459-63217 mL/g respectively, indicating higher sorption capacity in rocks than soils, and increasing sorption capacity in NOM fractions except in bound-lipid free. Single point $K_{OC}$ decreased with increasing concentration of phenanthrene in bulk samples and NOM fractions. The skeletal carbons in the NOM fractions showed that aliphatic carbon peak (0-93 ppm) decreased while aromatic carbon peak (93-165 ppm) increased, which further confirmed the degree of maturity.

The sorption of phenanthrene by natural organic matter fractions in the rocks and soils depended strongly on the degree of maturity and polarity.

**Keywords:** Natural phenanthrene, Sorption capacity, Natural organic matter, Degree of maturity.

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# CERTIFICATION

I certify that this work was carried out by Mr. A. M. Adeleye in the Department of Geology, University of Ibadan

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# DEDICATION

This research work is dedicated to my late grandparents who toiled hard to educate my parents. There is no doubt that the seeds you sowed have not only survived but have also started producing good fruits.

AND

To everyone who has been working hard to achieve one goal or the other in life, please do not relent, remain focused and be assured that your effort would soon be rewarded.

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# CHAPTER ONE

# INTRODUCTION

## 1.1 General Statement

Modern industrialized societies have developed thousands of synthetic organic compounds for many uses. Included are plastics, lubricants, refrigerants, fuels, solvents, pesticides and preservatives.While they have brought relief to human beings, they have also led to increasing organic contaminants in the environment. This has become threat to ecosystem and equally has adverse effect on the survival of man because the sources of his basic need of life such as land, water and air are seriously impacted. Several cases of organic contaminations have been reported in almost all parts of the world. Some of these cases have little or no adverse impact, while others have devastating impact on the earth exposures such as water bodies and land surfaces (ecosystem and its components). The likes of Exxon Valdex oil spill (on 24th March, 1989) and the recent Gulf of Mexico oil spill disaster (huge oil spill initiated by sea floor oil gusher that resulted from 20th April 2010 explosion of Deepwater horizon whichflow unabated for three months in 2010) etc are some of the major spills or organic contamination around the world. In Nigeria, cases of organic contaminations have been on the increase in recent years and they are mainly caused by problems associated with inefficient transportation or haulage and storage of petroleum products, improper handling and discharge of organic wastes, accidents on rig operations as well as vandalism of pipelinesoften described as*sabotage*. Generally, several methods have been used in solving problems of organic contaminants around the world. These include the use of chemical dispersants, booms to contain oil and contaminants from spreading, skimmer boats for skimming contaminants from water surface and bioremediation (use of microorganisms) among others depending on the nature and extent of the contamination.

Many environmental contaminants are hydrophobic organic contaminants (HOCs), which include polychlorobiphenyls (PCBs), polyaromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), dichlorodiphenyltrichloroethane (DDT) and other chlorinated insecticides, among others. Owing to their strong hydrophobicity, HOCs have their final destination in soil or sediment, where their ecotoxicological effects are closely regulated bysorption and thus bioavailability. Soils and sediments (rocks) are therefore priority sinks for these organic compounds because they repel or fail to dissolve in water (Kuster et al., 2004; Peck et al., 2004). Sorption of organic contaminants is directly related to natural organic matter (NOM) present in soils, sediments and rocks (Lambert, 1968).Therefore, sorption of hydrophobic organic compounds (HOCs) to sediment or soil organic matter (SOM) is a critical factor affecting their transport and fate in the environment. And as such, better understanding of the underlying sorption mechanism has been one of the major research focuses in geochemical and environmental studies.Sorption can be defined as physical and chemical process by which one substance becomes attached to another. Sorption involves absorption, adsorption and ion exchange processes. Absorption is the incorporation of a substance in one state into another of a different state (e.g. liquids being absorbed by a solid or gases being absorbed by a liquid). Adsorption is the physical adherence or bonding of ions and molecules onto the surface of another phase (e.g., reagents adsorbed to a solid catalyst surface). Ion exchange is exchange of ions between two electrolytes or between an electrolyte solution and a complex.

Sorption of organic compounds to soils and rocks is characterized by combination of absorption in amorphous organic matter and extensive adsorption to carbonaceous rocks or condensed organic matter. This is because organic matter was assumed to be composed of two domains; one showing linear and non competitive absorption and the other displaying nonlinear, extensive, and competitive adsorption (Weber et al., 1992; Xing and Pignatello and Xing, 1996;Xing and Pignatello Weber and Young, 1997). The absorption domain was proposed to consist of amorphous materials, such as partly degraded and or reconstituted biopolymers (e.g., polysaccharides, lignins), lipoproteins, amino acids, lipids, and humic or fulvic substances (Grathwohl, 1990; Young and Weber, 1995; Huang et al., 1997; Huang and Weber, 1997; Weber and Young, 1997; Huang and Weber, 1998; Kleineidam et al., 1999). The absorption process was regarded as simple diffusive dissolution in the organic matrix, analogous to dissolution of hydrophobic sorbates in rubbery polymers or organic solvents (Young and Weber, 1995; Pignatello and Xing, 1996;Weber and Young, 1997; Huang et al., 1997; Huang and Weber, 1997; Huang and Weber, 1998; Xia and Ball, 1999).Also, the adsorption domain was hypothesized to consist of glassy organic matter, in which molecular freedom of movement was restricted in condensed environments, analogous to the situation encountered in glassy polymers such as polystyrene (Grathwohl, 1990; Young and Weber, 1995; Pignatello and Xing, 1996;Huang et al., 1997; Huang and Weber, 1997; Weber and Young, 1997; Huang and Weber, 1998). Extensive and nonlinear sorption was recently observed for several inert, condensed and aromatic materials that physically and/or chemically are distinguishable and identifiable. These include unburned coal, kerogen, coke, cenosphere, soot, charcoal, etc.

Furthermore, nature of the organic matter in the rocks and soils determines the dominating sorption process. Rocks are formed over geological period of time and they are composed of aged and condensed organic matter (such as kerogen) which is characterized by adsorption domain with nonlinear, extensive sorption. While soils are commonly made up of young organic matter mainly composed of armorphous organic matter characterised by absorption domain with simple and linear sorption. Older soils and sediments that have also undergone significant diagenetic alterations typically have hard carbon dominated-NOMs that are physically condensed and chemically reduced. These soils exhibit more nonlinear, slower, and only partially reversible sorption of hydrophobic organic compounds (HOCs) and have greater sorption capacities for such contaminants. Conversely, younger soils that have undergone little or no diagenetic alteration have soft carbon dominated-NOMs that are more physically amorphous and chemically oxidized, and typically exhibit nearly linear, faster, and reversible HOCs sorption with lower sorption capacities for contaminants (Pignatello and Xing, 1996; Huang and Weber, 1997). In cases where amorphous and condensed organic matter occurred together in the soil or sediments, resultant sorption is nonlinear because of the higher sorption capacities of condensed organic matter (Huang and Weber, 1997; 1998).

Natural organic matter (NOM) is the remains of organic activities, which are often found in rocks, sediments and soils. They are the complex product resulting from the mixture of organic components (both plants and animals), which are found at different stages of decomposition and transformation. Natural organic matter has distinctive origin and history; the nature of the organic matter depends on the parental material (source) and other activities within the rocks, sediments and soils. Depending on the origin and diagenetic alteration history, NOM may be comprised of different types of organic materials ranging from biopolymer, humus to kerogen. Biopolymers (carbohydrates, lipids, protein, lignins, tannin, pigments, etc.) are often degraded and condensed to form geopolymers such as fulvic acid, humic acid, humin, and kerogen **(**Rashid, 1985). The stepwise disappearance of C=O and the formation of water and carbon dioxide result in a decrease of O/C ratio during diagenesis and catagenesis**(**Rullkotter, 1993). As alteration continues, the disappearance of saturated H-C functions causes a decrease in aliphatic content and a rise in aromaticity **(**Durand, 1980; Tissot and Welte, 1984**)**. Organic matter could be described as sedimentary organic matter orsediment or soil organic matter (SOM). Sedimentary organic matter is aged, resistant and condensed whileSOM is young and amorphous.

Sedimentary organic matter isthe preserved organic matter in sedimentary rocks having survivedbacterial degradation or decomposition processes. The organic matter associated with sedimentary rocks is commonly preserved under anoxic condition (Emerson, 1985). In addition to insufficient oxygen for degrading bacteria, lack of degrading bacteria andquick burial of sediments are major hindrances to degradation or loss of organic matter from sedimentary rocks (Demaison and Moore, 1980; Emerson, 1985).Major sources of sedimentary organic matter in order of importance include phytoplankton, higher plants, bacteria, zooplankton and fungi (least contribution).Sedimentary organic matter has been classified into two: kerogen and bitumen.Kerogen is the fraction of organic matter which is insoluble in organic solvent while the fraction of organic matter that is soluble in organic solvent is regarded as the bitumen **(**Durand, 1980). While some sedimentary rocks such as conglomerates and sandstones are completely devoid of organic matter, others like siltstones, mudstones and shales contain organic matter ranging from small quantity to as high as a quarter of a rock. Coals, carbonaceous shales and oil shales on the other hand composed almost entirely of organic matter. Sequel to primary deposition, organic matter in sedimentary rocks may be eroded and redeposited within more recent, geologically younger sediments as SOM. Therefore, SOM consists of a complex mixture of organic molecules with different origin and decomposability.SOM properties may also be influenced by the contribution of anthropogenic pollutants, such as fossil fuel derived carbon (Rumpel et al., 2003**).**

Organic matter associated with soils and sediments is commonly regarded as soils and sediments organic matter (SOM).SOM is an important factor in the global carbon cycle.It helps to maintain or improve the physical condition of the soils and sediments, thereby increasing their capacity for water infiltration and holding. A major part of the organic matter in soils and sediments are sourced from higher plants, phytoplanktons and zooplanktons. While higher plants dominate in the soils, phytoplanktons and zooplanktons dominate in marine sediments.SOM contains a range of physically and chemically different organic materials consisting of biopolymers such as lignin, polysaccharides, lipids and proteins; humic substances derived from biopolymers; and diagenetically matured kerogen and black carbon (Stevenson, 1994; Huang and Weber, 1997; Ran et al., 2002).

Since organic matter is the bye product of degradation of organisms,all organisms are composed of the same basic chemical classes; the most geochemically important among them are carbohydrates, proteins and lipids. In addition, higher plants contain significant quantities of lignin; a major component of their supportive tissue. Carbohydratesderives its name from the fact that it has the general formula $Cn(H_2O)n$, that is it contains only carbon, hydrogen and oxygen, with the hydrogen and oxygen atoms being in the same ratio as we have in water. They are polyhydroxy-substituted carbonyl compounds (i.e. aldehyde or ketone). The simplest molecules are monosaccharides, which are named according to the number of carbon atoms present; for example, tetroses, pentoses, hexoses and heptoses contain four, five, six and seven carbons, respectively. Others are Oligosaccharides (with two-ten units of monosaccharides) and Polysaccharides **(**with more units ofmonosaccharides such as cellulose). Carbohydrates can function as energy reserves, structural material and antidesiccants (MacGregor & Greenwood, 1980; Kennedy, 1988). The monosaccharides and disaccharides are commonly termed sugars while the polysaccharides can be termed glycans. Polysaccharides are major components in most cell walls, which provide a rigid, reinforcing layer around the cell membranes in plants,bacteria and fungi. Glucose is by far the most abundant monosaccharide. It is important as an energy source and it is the basic unit of the polysaccharide known as cellulose, the main structural building material of plants, a molecule which contains about104 glucose units.Cellulose is the most abundant natural organic compound, with higher plants containing the largest amounts, whereas some algae appear to have none. Carbohydrates are also important in the production of fats and proteins, as well as in generating energy;the citric acid cycle provides precursors for the biosynthesis of fatty acids, amino acids and terpenoids.

Proteinsaccount for most of the nitrogen containing organic materials in organisms. They are polymers (polypeptides) of aminoacids **(**i.e. the amino, $NH_2$ and carboxylic acid, COOH groups are attached to the same carbon atom). Amino acids can therefore be classified as neutral, acidic or basic depending on the ratio of carboxylic acid groups to amine groups in amino acids molecule. Proteins are made up of about 20 different amino acids. Sulphur is an important component in some amino acids (e.g. cysteine). In plants, amino acids are generally synthesized from glutamic acid by transfer of the amino group to other carbon skeletons (transamination). Animals cannot synthesize all the amino acids they need for protein formation and so must obtain these essential amino acids directly or indirectly from plants. An acid group on one amino acid molecule can undergo a condensation reaction with an amine group, with the elimination of water. The resulting amide group joins the two amino acids together to form a dipeptide usually called the peptide linkage. Condensation reactions can continue until large molecules, polypeptide**s** (polyamides) are built up.

Proteins are large polypeptides and they contain more than 8000 amino acid units with molecular weights greater than $10^6$. In such large molecules the types of amino acids incorporated and their order allow a multitude of different structural possibilities. The polypeptide chains often fold into regularly repeating structures especially when the primary structure (the amino acid sequence) is dominated by a few amino acids or has a repetitive sequence. Several helical strands can intertwine to form bundles of fibres, which are suitable for structural roles in organisms because the multiple intermolecular forces make the protein insoluble. These fibrous proteins serve as supportive tissues in animals, examples in skin and bone (collagen), hooves and claws (keratin), silk and sponge. This is in contrast to plants, where cellulose and lignin perform the structural role, although they can be associated with a collagen-like protein. There are also globular proteins that are folded up into compact globules and they generally perform important regulatory functions such as enzymes, hormones, antibodies, and transport and storage units.

Lipids are defined as geochemical substances produced by organisms which are extractable by non polar organic solvents such as hexane, benzene, or chloroform but effectively insoluble in water (Bergman, 1963). This broad definition encompasses a wide variety of compound classes, including photosynthetic pigments. However, application of the term lipid can vary, sometimes being restricted to fats, waxes, steroids and phospholipids, and sometimes to fats alone. Simple organic compounds like aliphatic, carboxylic acids and alcohols can be found among the lipids, but most lipids exist as combinations of these simple molecules with one another (e.g. wax esters, triglycerides, steryl esters and phospholipids) or with other compound classes such as carbohydrates (glycolipids) and proteins (lipoproteins). Lipids are oil soluble, but water insoluble organic compounds, including; fats, waxes, pigments, steroids, and terpenoids that are major precursors for petroleum (Peters and Moldowan, 1993).

Lipids are incorporated into kerogen during diagenesis, but many survive as free constituents in the bitumen. They are known as molecular fossils or biological marker or biomarkers (Eglinton and Calvin, 1967). Small amounts of bitumen originate from lipid components in once living organisms, but most bitumen is generated by cracking of the kerogen(Peters and Cassa, 1994). Organisms relatively rich in lipids, such as the plankton (with about10% lipids, dry wt), are quantitatively very important contributors to oil source rocks. Soil lipids are relatively stable organic carbon fractions that contain several biomarker compounds which can be related to the input of plant constituents to the soil and to their transformations (Lichtfouse et al., 1994, 1997; Bol et al., 1996; Van Bergen et al., 1997). Lipids represent 4–8% of SOM and they are assumed to be of high importance for SOM stabilization because of their influence on water retention capacity, structural ability, and biodegradation-humification balance in soils (Reveille et al., 2003). In soils, lipids are mainly derived from plants and microorganisms, but can be of anthropogenic origin (Gregorich et al., 1996; Lichtfouse et al., 1997; Rethemeyer et al., 2006).

Lignin is a high molecular weight higher plant component characterized by polyphenolic (hydroxy-aromatic) compounds formed by condensation reactions (involving dehydrogenation and dehydration) between three main building blocks: coumaryl, coniferyl and sinapyl alcohols (Adler, 1977). Such structures are derived originally from monosaccharides that are common in plant but not in animal tissue. Ligninis next to cellulose as the most abundant biopolymer. It is mostly found in cell walls, where it is intimately associated with hemicelluloses forming a network around cellulose fibres in maturing xylem (the channelled, woody core of terrestrial plants) and fulfilling an important supportive function (Isherwood, 1965; Kirk and Farrell, 1987; Stafford, 1988). It comprises of 20–30% of plant vascular tissue. They are biosynthesized from glucose (under enzymatic control) by a simplified reaction in which the shikimic acid which occur widely in plants (but not in animal tissue) is transformed into phenylalanine by a series of reactions, including $NH_3$ transfer from an amino acid (transamination). The phenylalanine then undergoes deamination and hydroxylation to form 4-hydroxycinnamate from which the three main lignin precursors are formed by reactions that include carboxyl reduction, ring hydroxylation and partial methylation of hydroxyl groups (Kirk and Farrell, 1987).

Figure 1.1 reflects a scheme of change in the composition of organic matter during sedimentation and burial. Naturally occurring biopolymers (carbohydrates, lipids, protein, lignins, tannin, pigments, etc.) are degraded and condensed to form geopolymers such as fulvic acid, humic acid, humin, and kerogen (Rashid, 1985). During diagenesis, catagenesis, and coalification (a process of biochemical and geochemical alteration of mostly terrestrial plant residues under semi aerobic or anaerobic conditions), the geopolymers are subjected to further alteration, and the final product may be graphite (crystalline carbon).

Humic materials are complex mixtures of polyelectrolytes produced by biotic and abiotic alteration of plant and animal derived organic matter (Meyers and Ishiwatari, 1993). These materials bear almost no resemblance to their precursors and cannot be classified into traditional organic compound classes (i.e., carbohydrates, proteins, lipids, etc.).Humic substances can be leached, particularly from acidic soils in cold wet upland regions and similar environments. They account for almost all the organic carbon in fresh waters, imparting the characteristic brown coloration to upland waters.  Most of the dissolved organic matter (DOM) in seawater is humic-like (Ishiwatari, 1985). The term humic substances describe three groups of material: fulvic acid, humic acid and humin (Weber et al., 1999). Treatment of bulk humic substances with dilute alkali dissolves the fulvic and humic acids, leaving a residue of insoluble humin. Acidification of

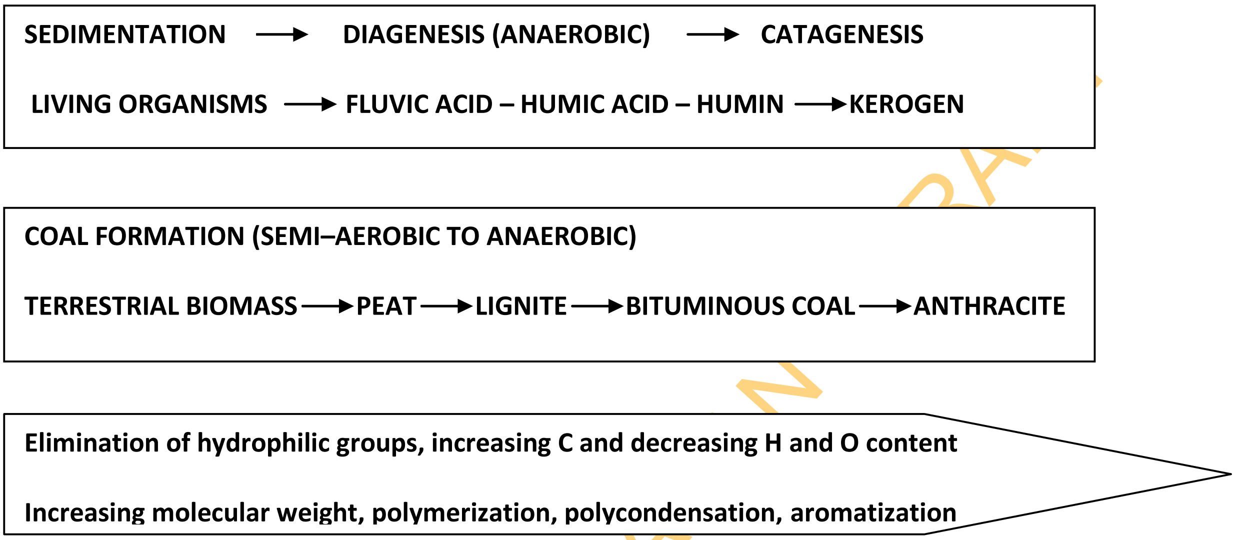


Figure 1.1: Scheme of the change in the composition of organic matter during sedimentation and burial (Rashid, 1985).

the alkaline extract precipitates humic acid, leaving fulvic acid in solution. Fulvic acid comprises smaller and more oxygenated units than humic acid (Weber et al., 1999). Both humic and fulvic acids are thought to be intermediates in the diagenetic formation of humin. Humic substances can occur in different physical states (e.g humic acids are found as solution in fresh water, as solids or gels in soil and as dry solids in coal). Rice and Maccarthy (1989) reported that humin could be further separated into lipid-bound-HA (BHA) and insoluble residue (IR). Humin in soils can be likened to kerogen in sedimentary rocks; meaning that humin may be operationally similar to kerogen.

It has been established that the chemical compositions and structures of soil or sediment organic matter (SOM) differ as functions of the characteristics of parental biological materials and the diagenetic alteration of those materials (Durand, 1980; Tissot and Welte, 1984; Engel and Macko, 1993). As earlier observed, as diagenetic alteration increases, SOM tends to become chemically more reduced and physically more condensed. As a result, SOM found in various geosorbents comprises a spectrum of organic materials having distinctly different chemical compositions, structures, and degrees of condensation. SOM chemical compositions, structures, and types change as a function of depth in sediment or soil profiles (Engel and Macko, 1993)**.** For example, organic matter associated with a given soil or sediment can be altered sequentially from fulvic acids to humic acids and humin (kerogen) as depth profile increases. Also a number of previous studies have proved that reworked kerogen may dominate NOM in several sediments and aquifers (Allen-King et al., 1997; Ran et al., 2003a, 2003b).

Since the reported case of organic contamination in Baruwa area of Lagos (contamination of water wells by refined petroleum products), government and many concerned agencies have made several attempts to assess the level of the contamination and provide short and long term solutions to the problem. A group of geoscientists were also commissioned to look into the problem using integrated geology and geophysical methods. This study therefore presents an enviromentally friendly technique or effort in solving some of the problems arising from organic contaminants in our environment. It is based on the following premises: (i) that soils and sediments (rocks) are priority sink for HOCs, (ii) that sorption of organic contaminants is directly related to NOM present in soils, sediments or rocks, and (iii) and that sorption of organic chemicals is an important process because it controls the fate and ecotoxicological risks of soil and sediment-bound chemicals. Therefore, this study attempts at solving problem of organic contaminants in our environment by studying the property of organic matter fractions and the sorption capacity of these organic matter fractions for organic contaminants such as phenanthrene, in order to understand the relationship between them. This would help in understanding the fate of these organic contaminants in our environment and may be useful in remediation and clean-up design.

## 1.2 Objectives and Scope of study

The main objectives of this study are:

i. to determine the properties (elemental composition and skeletal carbons) of the natural organic matter fractions in selected rocks and soils from Southwestern Nigeria,
ii. to determine the sorption capacity of the original rock and soil samples, as well as their natural organic matter fractions for phenanthrene (hydrophobic organic contaminant), and
iii. to establish a relationship between the sorption capacity and properties of natural organic matter fractions from the rocks and soils.

The scope of this study includes:

i. to isolate the different natural organic matter (NOM) fractions or components including lipid, bound-lipid, lignin and their residual fractions from selected rocks and soils,
ii. to determine the total organic carbon (TOC), hydrogen, oxygen and nitrogen (H, O, N) contents of the original soil and rock samples, as well as their natural organic matter fractions (residual and isolated organic matter fractions),
iii. to determine the skeletal carbons contained in the natural organic matter fractions (residual and isolated organic matter fractions) from the rocks and soils,
iv. to determine the sorption capacity of the original soil and rock samples, as well as their natural organic matter fractions (residual and organic matter fractions) for phenanthrene (hydrophobic organic contaminant),
v. to examine the contribution or impact of the different natural organic matter fractions to the overall sorption of the rocks and soils, and

vi. to relate the chemical properties of the organic matter fractions to their sorption capacities.

## 1.3. Research Justification

Several studies on sorption of organic contaminants from different parts of the world have shown that NOM fractions in rocks, sediments and soils are good sorbents for frequently occurring HOCs such as phenanthrene, pyrene, among others. Although there is an increasing understanding of the nature and property of organic matter associated with rocks, soils and sediments, and their sorption capacities or properties, but there is no consensus on the exact chemical properties of organic matter that control sorption of HOCs. This is due to the complex nature of soil and sediment organic matter (SOM). And partly to the fact that most sorption studies utilised humic substances and kerogen as geosorbent due to their abundance in SOM or NOM generally and there is little or no information on sorption of HOCs from a number of countries, even though the countries have widespread occurrence of organic matter containing rocks, sediments and soils. Therefore, there is need for studies on the sorption of organic contaminants by different organic matter fractions from countries like Nigeria because of her abundant organic matter containing rocks, sediments and soils to predict their roles in HOCs sorption. Nigeria is also an oil producing nation with high tendencies of being prone to HOCs.

## 1.4. Study Area

The study area is located in Lagos, Ute and Auchi in the southwestern Nigeria (Fig1.2). In Lagos, study area is confined to southeastern part of the city around Baruwa and its neighbouring environments. Lagos is an urban centre with a large population hosting about 50-70% of industries in Nigeria. It is bounded by Ogun state to north and north east. To the east and south is Ondo state and Atlantic sea, respectively. Ute is a relatively big town in Ondo state located between Owo, Okeluse and Ifon. Auchi on the other hand is an old commercial town in the southwestern to central part of Nigeria. Lagos is generally underlain by coastal plain sands and alluvium of the Benin Formation in the Eastern Dahomey Basin. Lagos was chosen for soils sampling because it is a commercial centre, prone to contamination by HOCs and generally underlain by soils (sandy to clayey sands). Rock samples were collected from outcrops of sedimentary rocks with appreciable organic matter content within the southwestern Nigeria.

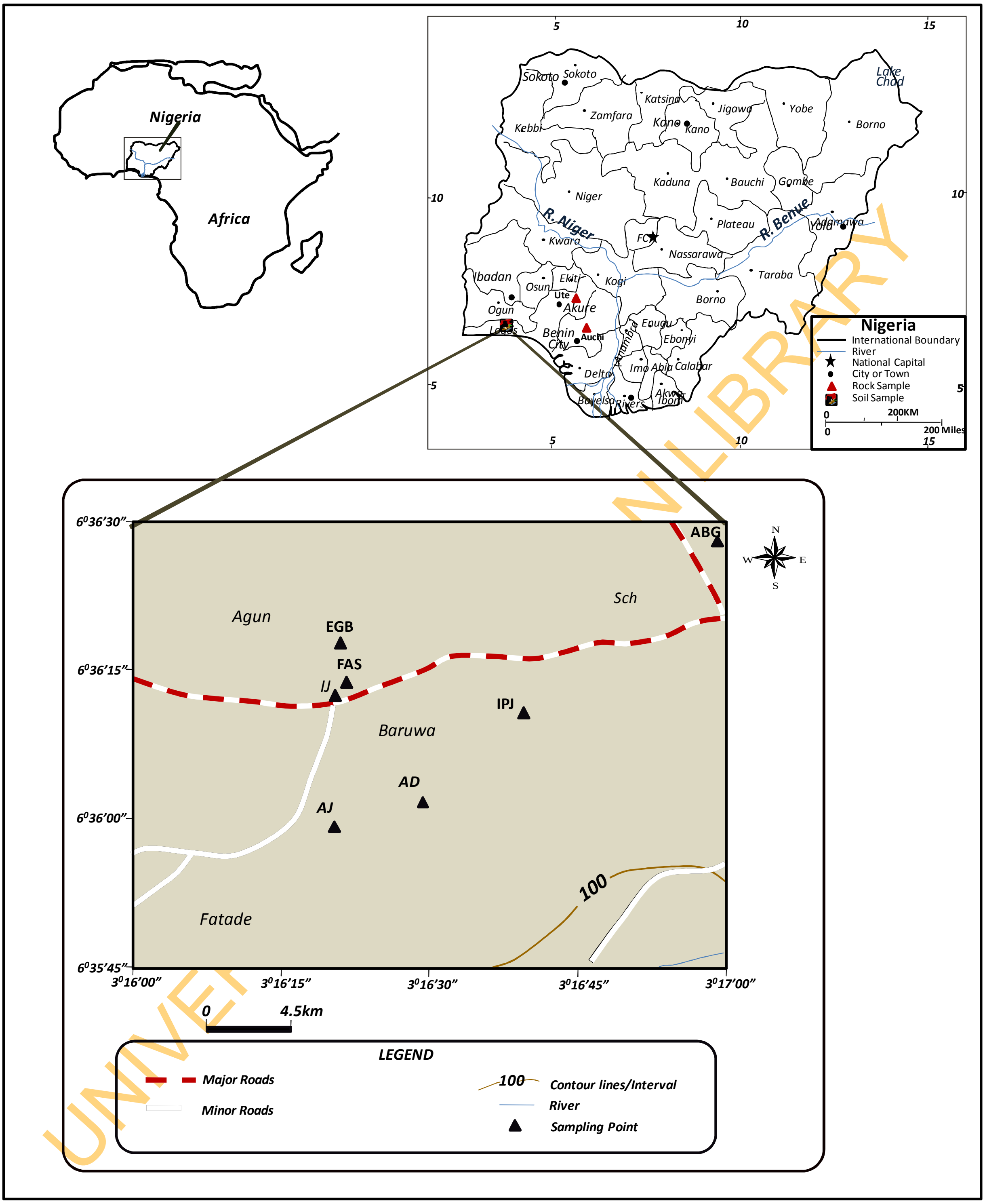


Figure 1.2: Location map of the study area.

Rock samples from Ute and Auchi belong to Araromi Formation of Dahomey Basin and Mamu Formation to the West of the Niger (western Flank of Anambra Basin) respectively.

## 1.5. Climate and Vegetation

The study area falls within the warm tropical climate which is characterized by relatively high temperature throughout the year. Average temperature ranges from 18$^{o}$C to 37$^{o}$C with mean value of 27$^{o}$C. It is relatively higher during the dry season, except during hammattan around December when temperature is sometimes as low as 15$^{o}$C. Mean annual rainfal ranges between 1500mm to 2000mm with two distinct seasons; the dry and the wet seasons.The dry season lasts from November till March/April while the rainy season lasts from March/April to October/November. The area is generally covered by lush green vegetation, predominantly of trees and shrubs, and there is no vegetation cover in some part of the area. Two distinct soil types characterized the study area; loose sandy soil in most part of the area and reddish brown soil or reddish lateritic soil in others. The land is used for several commercial purposes because the study area is an urban centre.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1. Literature Review on Sorption

Hydrophobic organic contaminants (HOCs) have attracted a great deal of research for more than four decades because of their persistence in the environment and tendency to bioaccumulate. The behaviour of HOCs in soils/sediments and rocks has been reviewed by several papers (Pignatello and Xing, 1996; Weber et al., 1999; Cornelissen et al., 2005, Pan et al., 2008). As early as 1968 it has been discovered that the organic matter (OM) in soils and sediments (rocks) was the principal factor controlling sorption of organic compounds (Lambert, 1968). Several studies have shown that the sorption of hydrophobic organic compounds in soils and sediments is strongly dependent on the organic carbon content of the soil (Lambert et al., 1965; Briggs, 1969; Karickhoff, 1979; Chiou et al., 1979: Karickhoff, 1980; Karickhoff, 1984) Consequently, sorption can be normalized to the soil organic carbon content (OC%).

$$\mathbf{Koc = K_d / OC\% \times 100} \qquad 1.1$$

whereKocis the concentration dependent distribution coefficient, $K_d$ is partition coeficient and OC % is organic carbon percentage in a given soil or sediment.

This concept appeared to function properly at that time, because most sorption measurements were carried out at relatively high concentrations of added organic compounds, employing limited sorbent-sorbate contact times. However, the concept of organic carbon having universal, homogeneous sorption properties with respect to organic compound sorption was challenged by several findings such as nonlinear sorption isotherms, multiphasic desorption kinetics, elevated TOC-water distribution coefficients (*K*TOC) in field sediments and soils, variable biota to sediment accumulation factors (BSAFs) that could not be explained by biological factors and limited bioremediation potential.

Numerous studies have also been carried out on the relationship between different organic mater in the soils, sediments and rocks, and sorption of organic contaminants. Study by Schwarzenbach and Westall, (1981) has shown that humic substances are the major content of SOM and dissolved organic matter (DOM) or nom generally, because the study concluded that chemical properties of humic substances control the sorption of HOC in soil and sediments especially when the organic content is higher than 0.1%. Humic substances are therefore of great importance for the sorption, bioavailability, and sequestration of xenobiotics in soils/sediments. However, several recent studies have also revealed that kerogen and black carbon materials can be important NOM components in soil and sediments (Nas et al., 1998; Karapanagioti and Sabatini, 2000; Ran et al., 2002; Accardi-Dey and Gschwend, 2002; Song et al., 2002; Ran et al., 2003a;), and these materials may dominate the overall HOC sorption by soils and sediments (Accardi-Dey and Gschwend, 2002; Jonker and Koelmans, 2002; Ran et al., 2003a; Xiao et al., 2004, Ran et al., 2007a; Sun et al., 2008).

Since sorption has been attributed to organic phase and disregarded contribution from inorganic phase (Kile et al., 1995; Huang and Weber, 1997), linear free energy models were proposed to predict concentration dependent distribution coefficient (Koc) from sorbate properties such as Kow-octanol water partitioning coeficients (Burkhard, 2000) Sw-solubility (Chiou et al., 1979), molecular connectivity index (Bahnick and Doucette, 1998), or a combination of polarity, polarizability, overall hydrogen-bond acidity, and basicity (Nguyen et al., 2005). This indicates that the behaviour of HOCs in soils, sediments and rocks could be easily predicted from their physicochemical properties and organic carbon content in the soils and sediments (rocks) regardless of the complexity of SOM or NOM, thus greatly facilitating the prediction of the environmental fate of HOCs. However, frequently reported large variations of Koc-concentration dependent distribution coefficients (Thomsen et al., 2002) and non ideal environmental behaviour of HOCs, such as nonlinear sorption, competition and sorption/desorption hysteresis, challenged further application of linear partitioning model. Thus dual-mode model and multi-domain reactivity models were proposed to explain the non ideal sorption behaviours. These models conceptualize SOM as an absorbent with sorption sites of distributed energy, where both linear and nonlinear sorption sites exist and interact with organic chemicals simultaneously. The nonlinear sorption site was attributed to relative compact or condensed fraction of organic matter or more specifically the glassy domain, while the linear sorption site was attributed to the amorphous organic matter fraction regarded as the rubbery domain (Weber et al., 1999). Although study of Accardi-Dey and Gschwend (2002) attributed the nonideal sorption to existence of black carbon, but strong evidence also indicates that SOM samples free of black carbon also exhibited distinct nonideal sorption for HOCs (Lu and Pignatello, 2004a; Wang and Xing, 2005b; Pignatello et al., 2006; Jeong et al., 2008; Sun et al., 2008). Carbonaceous geosorbents, such as coal and kerogen, have also been reported to have strong nonlinear sorption with HOCs (Allen-King et al., 2002; Ran et al., 2003a; Cornelissen et al., 2005; Ran et al., 2007a). Thus, SOM property is a crucial parameter affecting the fate of HOC (Weber et al., 1999; Kottler and Alexander, 2001).

Investigating the chemical characteristic of SOM using elemental composition and functional group analyses, and subsequent correlation with HOC sorption characteristics revealed a general observation that increasing nonlinearity and aromaticity are concurrent with diagenetic maturity (Xing, 2001b; Ding et al., 2002; Wang et al., 2005). Thus, nonlinear sorption is attributed to the contribution by aromatic carbon fractions in SOM because of their diagenetic maturity and condensed nature.There was also a positive relationship between aromaticity and sorption capacity (Gauthier et al., 1986; Chin et al., 1997; Chiou et al., 1998; Perminova et al., 1999; Ran et al., 2007a; Sun et al., 2008). Removal of aromatic carbon resulted in more linear isotherms, while removal of O-alkyl carbon resulted in more nonlinear isotherms (Gunasekara et al., 2003). All these results emphasized the importance of aromatic carbon fractions to HOC–SOM interactions. Using $^{13}$C Nuclear Magnetic Resonance, the amount of desorption-resistant phenanthrene was related to aromatic carbon (Golding et al., 2005). However, it was found out that not all the aromatic fractions have the same affinity for phenanthrene. Thus, aromatic carbon may not be the only parameter contributing to the high HOC–SOM affinities.

Weber et al. (1999) has reported that humic substance (HS) or SOM generally could be operationally separated into three fractions, namely fulvic acid (FA), humic acid (HA), and humin (HM). Aliphaticity, molecular weight, carbon content, density, cross-linking, HOC–HS interaction nonlinearity, and sorption/desorption hysteresis among other properties follow the order FA<HA<HM (Xing, 2001a; Pan et al., 2006). Therefore, aliphatic fraction increased with the successive extraction of humic acids from humic substances withthe highest aliphaticity in humin, thus indicating that aliphatic carbon is a major fraction in humin (Kang and Xing, 2005; Xing et al., 2005). Consistent with strong nonlinearity and a high capacity of HOC sorption in humin, the aliphatic fraction in SOM is also reported to dominate HOC sorption in soils or sediments (Chefetz et al., 2000; Mao et al., 2002; Salloum et al., 2002; Simpson et al., 2003; Sun et al., 2008). Therefore, amore realistic result could be that both aromatic andaliphatic carbons are important to the overall sorption.Thus there is need to relate other characteristics of the soil or sediment organic matter to sorption of HOCs. Attempts werealso made on the effects of polarity and molecular weight of SOM on its sorption properties.Study by Kang and Xing,(2005) revealed that polarity of SOM regulate its HOCs sorption rather than the structure.

Studies by Xing et al., (1994), Xing (1997,2001b),Chen and Xing (2005) havealso showed the relationship between SOM polarity and HOC–SOM interactions.Weber et al. (1999)established a semi-quantitative correlation method to predict isotherm linearity, single-pointconcentration dependent distribution coefficient (Koc) and sorption/desorptionhysteresis from SOM polarity. Molecular weight also has a positive relationship withKoc-concentration dependent distribution coefficient (Chin et al., 1994, 1997; Hur and Schlautman, 2004). So far, it has not been possible to establish a general model to predict SOM sorption characteristics from any individual chemical property (Salloum et al., 2001a; Thomsen et al., 2002; Hur and Schlautman, 2003; Bonin and Simpson, 2007), due to unpredictability (Pan et al., 2007).

However, further research revealed that SOM physical properties can also affect the accessibility of HOCs to SOM sorption sites and may be of great importance in altering HOC–SOM interactions.Physical conformation of glassy and rubbery states was originally used in polymer science. The rigidity of a polymer was described using glassy-rubbery transition temperature (Tg). When SOM is heated, its sorption nonlinearity decreased or even vanished over a critical temperature just like glassy polymers (Xing and Chen, 1999). The Tg for SOM has been reported to vary from 43°C to 79°C (Weber et al., 2001; Zhang et al., 2007). This phenomenon led to the analogy of SOM to polymers in terms of physical properties; thus, the methodology used for polymer science has been utilized to study SOM. The introduction of glassy/rubbery concept into SOM sorption characteristics has also helped in explaining the complicated nonideal sorption phenomenon and promoted the establishment of modern sorption theories such as the dual-mode model (Xing and Pignatello, 1997), distributed reactive model or dual reactive model (Weber et al., 1992), and extended dual-mode model (Xia and Pignatello, 2001). Consistently, these models recognize SOM having hard (glassy) and soft (rubbery) domains; where rubbery domain contributes to linear sorption, and glassy domain contributes to both linear and nonlinear sorption. Obviously these models emphasized the importance of physical state of SOM for HOC sorption.

Another evidence for the physical conformation effect on sorption is from SOM fractionation studies. SOM fractionation and subsequent examination of the properties of individual fractions have shown that the sum of sorption from the individual fractions is not equivalent to but normally higher than that by the original soils (Salloum et al.,2001b; Bonin and Simpson, 2007). The fractionation procedure may have altered the organization of SOM, thus making more sorption sites available to HOCs.

Braida et al. (2003) found out that desorption energy was much higher than sorption energy because sorption process enlarged or created pores inside SOM. Accordingly, the alteration of physical conformation could explain sorption/desorption hysteresis (Sander and Pignatello, 2005).This explanation is also applicable for the large difference between concentration dependent distribution coefficient (Koc) from laboratory sorption experiments and field-sampling measurements. This difference is attributed to the extended contact time or the presence of black carbon (Accardi-Dey and Gschwend, 2002; Sander and Pignatello, 2005). However, a generally neglected point is that the samples from the field could have undergone several sorption/desorption cycles; hence, the sorption process is not as clear as in any laboratory sorption experiment.

The physical state of SOM is also subjective to change in environmental conditions (such as temperature) without changing chemical compositions, thus the overall rigidity of SOM can give important information for HOC sorption (Ju and Young, 2004; Lu and Pignatello, 2004b).

Generally speaking, cross-linking, presence of unsaturated bonds and high molecular weight can decrease SOM molecular flexibility and, thus, favour a glassy state (Lu and Pignatello, 2004a). Aromatic structure is therefore inherently rigid, while aliphatic and oxygen substituted aliphatic fractions are flexible as indicated using two-dimensional homonuclear overhauser effect spectroscopy (Chien and Bleam, 1998).

Pore formation and deformation can change sorption nonlinearity and sorption/desorption hysteresis, therefore porosity mayalso be a more direct descriptor for SOM sorption. Traditional porosity measurement is based on nitrogen sorption, though the temperature in nitrogen sorption experiments is too low for nitrogen to penetrate into inner (nano-scale) pores in SOM (Pignatello,1998). The porosity measured by carbon dioxide sorption is more suitable for any correlation with SOM sorption characteristics (Pignatello, 1998; Mikutta and Mikutta, 2006).

It is therefore obvious from above account that there is a general knowledge and increasing understanding of the chemical characteristics and physical conformation of organic mater as well as the role of major content of organic matter to HOC sorption frommany parts of the world.However, there is no consensus on the exact chemical property of SOM that regulates HOC sorption and there is also no established relationship between the chemical property and physical condition of SOM that could serve as guide to HOCs sorption. Furthermore, there is limited or no information on the effects of chemical properties and physical conformation of organic matter fractions on HOCs sorption from Nigeria, despite the presence of widespread occurrence of organic matter-rich rocks, sediments and soils.

## 2.2 Literature Review on Geological Setting of Dahomey Basin

### 2.2.1 Regional Geology

Dahomey Basin is an extensive sedimentary basin on the continental margin of the Gulf of Guinea (Fig 2.1). It is a marginal sag basin (Kingston et al., 1983) or marginal pull-apart (Klemme, 1975) which developed in the Mesozoic Era as the African and South American lithospheric plates separated, while the continental margin foundered (Burke et al., 1971; Whiteman, 1982). It extends from the southeastern Ghana through Togo and Republics of Benin to the southwestern Nigeria. The Okitipupa Ridge separates the Dahomey Basin from the Niger Delta/Anambra Basin (Fig ). Dahomey Basin contains extensive wedges of sediments of about 3000m which thicken toward the offshore (Whiteman, 1982). Cretaceous sediments outcrop sediments in the basin vary markedly both in thickness and texture from place to place. The axis of the basin with the thickest sediments occurs at the western part between Nigeria and Republics of Benin (Slansky, 1962; Antolini, 1968; Billman, 1992). Early accounts on the basin were given by Jones and Hockey (1964) for the Nigeria's portion and Slansky (1962) for Togo and the Republics of Benin. Later synthetic treatments of the Nigerian portion were provided by Fayose (1970), Ogbe (1972), Omatsola and Adegoke (1981), Coker and Ejedawe (1987), Adediran and Adegoke (1987) and Okosun (1990). Later treatments of the offshore Benin Republic's portion were attributed to Billman (1992, 1996). The Nigerian portion of the basin known as the Eastern Dahomey Basin is covered by the Geological Survey of Nigeria (1:250,000) Series map sheets 59 (Ibadan), 68 (Lagos) and 69 (Okitipupa).

### 2.2.2 Tectonic Evolution of the Dahomey Basin

The evolution of the Dahomey Basin is attributed to the transcurrent movements on the oceanic fracture system, especiallythe Romanche, Chain and Charcot fractures, during the drifting stage of the separation of South America and Africa plates in the Campanian to Tertiary (Figure 2.1). The African and South American landmasses were separated as a result of the continental rifting and subsequent drifting leading to opening of the South Atlantic Ocean during the Mesozoic Era (Storey, 1995; Mpanda, 1997). Two major hypotheses have been developed for the evolution of the Dahomey Basin: the rift hypothesis of Equatorial Atlantic basins and the shearing hypothesis associated with Benue Trough. The rift hypothesis is widely supported based on the fact that Dahomey Basin is wrench modified with characteristic horsts and grabens underlying the basin (Mascle et al. 1887). Basement fracturing and initial separation between African and South American landmasses occurred in the Lower Jurassic to Early Cretaceous during the rifting stage. At this time, several marginal basins developed consequent to block faulting, fragmentation and subsidence on the central Basement rock (Asmus and Ponte, 1973; Omatsola and Adegoke, 1981; Ojeda, 1982; Adediran and Adegoke, 1987). The early movements were in

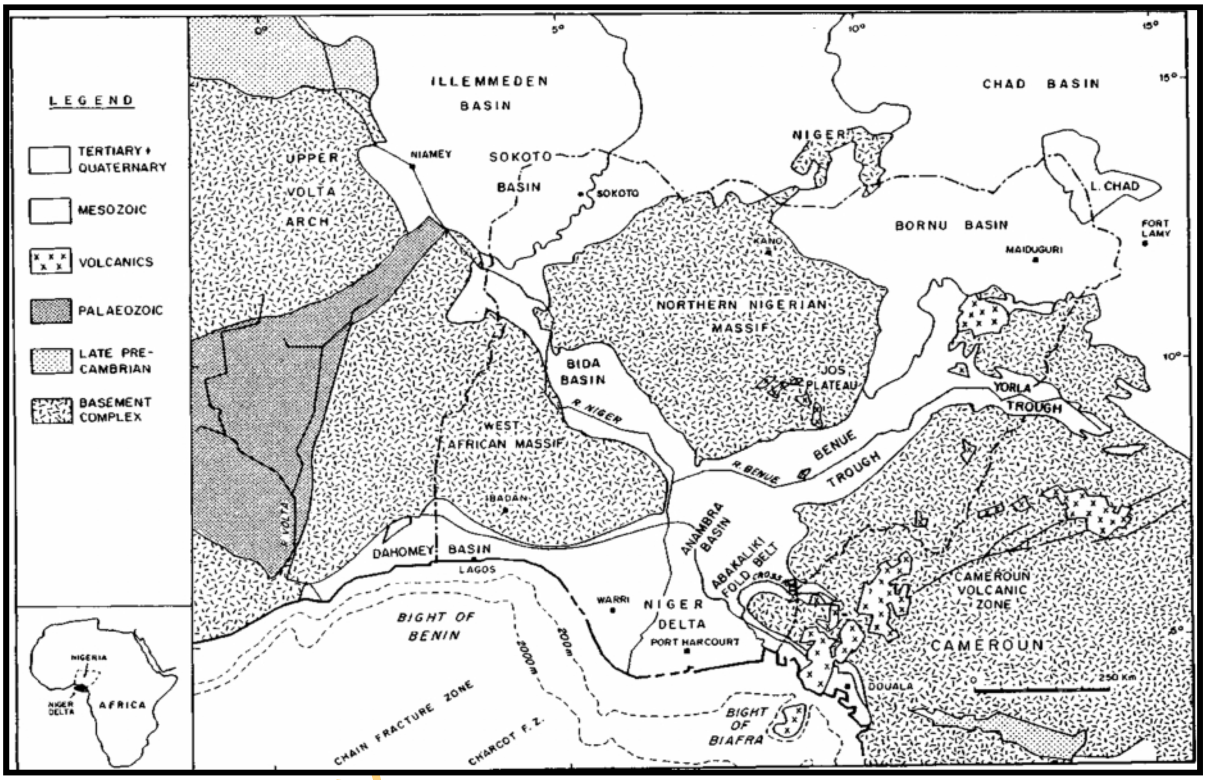


Figure 2.1: Geological mapof theDahomey Basin (AfterWhiteman, 1982**)**

the Lower Cretaceous when there was rifting (pulling apart) of the African and South American landmasses. Consequent to the opening of the South Atlantic Ocean, there was landward extension and transtensional movements (drift stage) during upper Cretaceous to Tertiary. Horizontal movements along the oceanic fracture zones were translated to vertical movements leading to block faulting and subsequent developments of horsts and grabens (Omatsola and Adegoke, 1981). Coker and Ejedawe (1987) identified three geoblocks, namely; the onshore geoblock (Bodashe, Ilepa – Ojo geoblock), the Okitipupa structure (Union–Gbekebo geoblock) and offshore geoblock. They emphasized that these three geoblocks have gone through the three main stages of basin evolution, which are initial graben (pre drift) phase, prolonged transitional stage and open marine (drift) phase.

### 2.2.3 Stratigraghy of the Dahomey Basin

Accounts of the stratigraphy and geology of the Dahomey Basin have been described by a number of authors, prominent among them are Jones and Hockey (1964), Reyment (1965), Adegoke (1969), Fayose (1970), Murat (1972), Ogbe (1972), Omatsola and Adegoke (1981), Whiteman (1982), Coker and Ejedawe (1987), Kogbe (1989), Okosun (1990), Billman (1992) and Hack et al., (2000). The stratigraphy of the entire Dahomey Basin has been divided into three chronostratigraphic packages: the pre-Lower Cretaceousfolded sediments, Cretaceous sediments and Tertiary sediments (Omatsola and Adegoke, 1981; Billman, 1992).However, the stratigraphy of the Nigerian portion of Dahomey basin is made up of the Cretaceous and Tertiary sediments (Figures 2.2 and 2.3). The Cretaceous sequence referred to as the Abeokuta Group was subdivided into three formational units, namely: Ise, Afowo, and Araromi (Omatsola and Adegoke, 1981). Ise Formation is the oldest unit and it overlies the Basement rocks (Fig 2.3). The Tertiary sediments consist of Ewekoro, Akinbo, Oshosun, Ilaro and Benin (Coastal Plain sands) Formations (Fig 2.3). Ewekoro Formation is made up of fossiliferous well bedded limestone. The Tertiary sediments are also overlain by Recent alluvium. The lithostratigraphy of the formations in the eastern Dahomey Basin is described as follows.

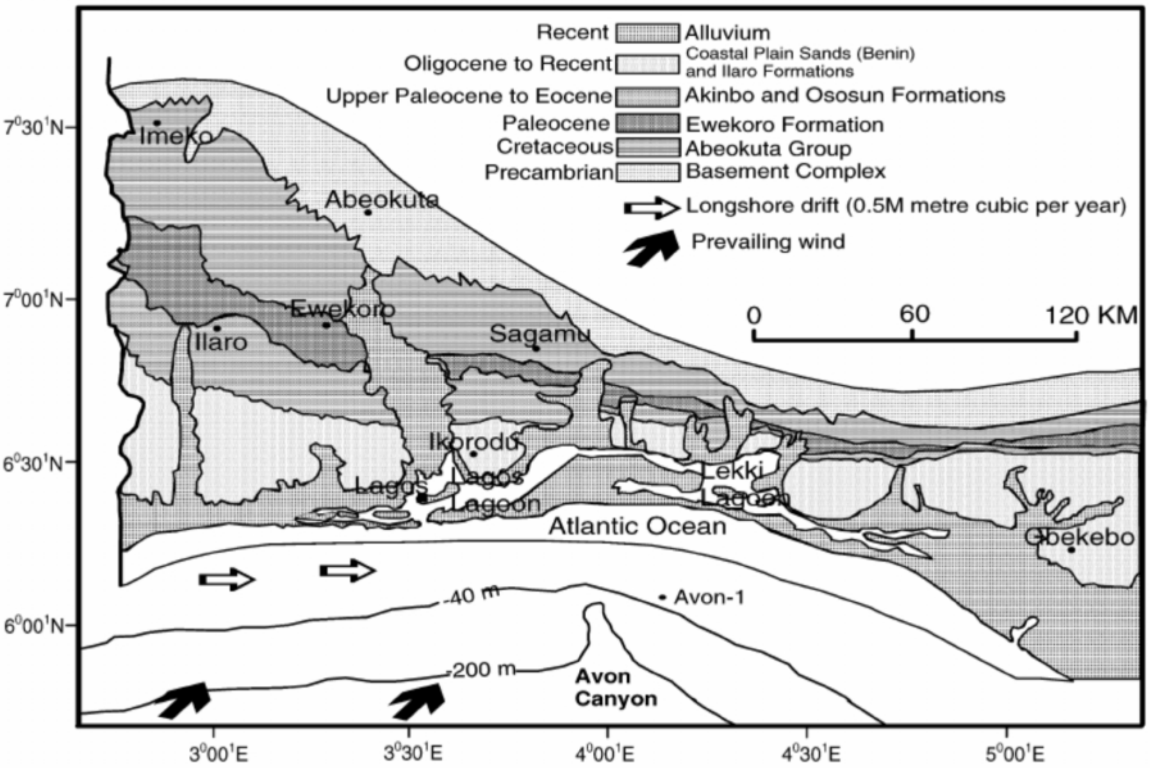


Figure 2.2: Geological mapof the Eastern Dahomey Basin (modified from Geological Survey of Nigeria map, sheets 59, 68 and 69)

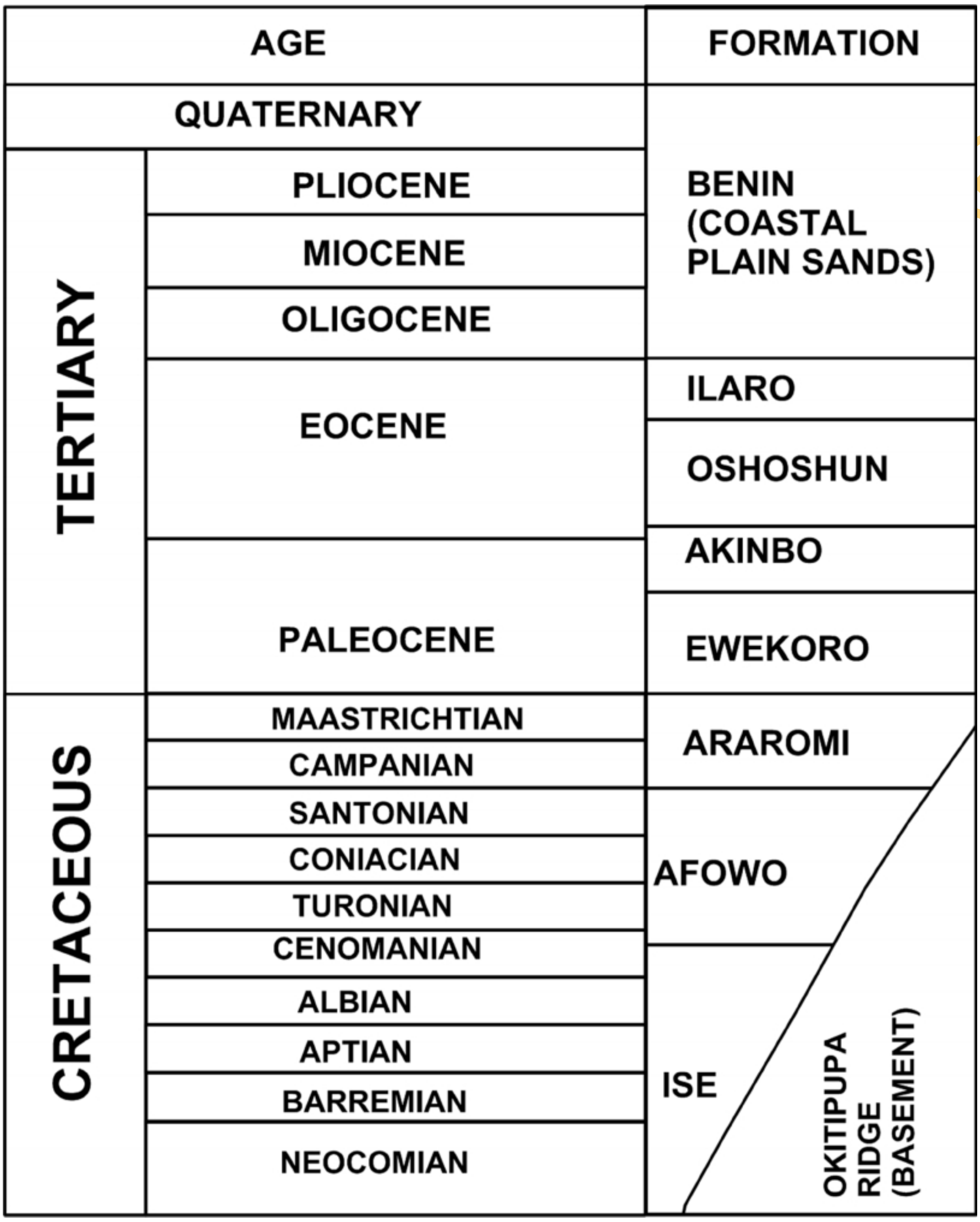


Figure 2.3: Stratigraphy of the Eastern Dahomey Basin showing the Cretaceous and TertiaryFormations (After Jones & Hockey, 1964; Omatsola and Adegoke, 1981)

#### 2.2.3.1 The Ise Formation

It overlies the Basement complex rocks and it is the oldest member of the Abeokuta Group of Omatsola and Adegoke (1981). It comprises of basal conglomerates and grits overlain by coarse to medium grained friable sandstones and grits with interbedded kaolinitic clays. Both the cross bedding azimuths of the sandstones and the pebble alignments indicated NE paleocurrent system (Nton, 2001). Omatsola and Adegoke (1981) suggested a Neocomian to Albian age for the Ise Formation on the basis of pollens and spores. Billman (1992) referred equivalent beds in the offshore Benin Republic to "the older folede sediments" which uncomformbly overlie "Albian sands". The formation has a non marine origin. The presence of basal conglomerates, coarse sandstones and kaolinitic clays pointed to initial deposits in an alluvial fan setting for the formation.

#### 2.2.3.2 The Afowo Formation

Afowo Formation conformably overlies the Ise Formation, although occasionally it oversteps basement in few places (Billman, 1976). The formation is composed of coarse to medium grained sandstones with an increasing proportion of siltstones, clays and shales in its upper part. The sandy facies are tar bearing around Okitipupa, while the shales are organic rich (Omatsola and Adegoke, 1981). The lower part of the formation is transitional with mixed brackish to marginal marine horizons that alternate with well sorted subrounded sands. This attributes indicated littoral or estuarine near-shore environmentin with flunctuating water level (Enu, 1990). Omatsola and Adegoke (1981) suggested an age ranging from Turonian toMaaastrichtian and believed the Afowo Formation to be the down dip lateral equivalents of the outcropping Abeokuta Formation of Jones and Hockey (1964). Okosun (1990) used the occurrence of argillaceous lithologies within the Afowo Formation to separate it from the underlying Ise Formation which were both originally referred to as the Abeokuta Formation by Jones and Hockey (1964). The sediments of this formation are bituminous at surface and subsurface sections.

#### 2.2.3.3 The Araromi Formation

Omatsola and Adegoke (1981) and Okosun (1990) both recognized the youngest Cretaceous rock of the Abeokuta Group as the Araromi Formation. It is equivalent to the Araromi shale of

Reyment (1965). It consists of fine and medium grained sandstone at the base and grades into siltstone and shale with intercalations of limestone, sandstone and lignite bands to the top (Omatsola and Adegoke, 1981). The shales are grey to black in colour, marine and rich in organic matter. It also bears abundant planktonic foraminifera, ostracods, pollen and spores. A Maastrichtian to Paleocene age is assigned to the formation by Omatsola and Adegoke (1981).

### 2.2.3.4 The Ewekoro Formation

Ewekoro Formation conformably overlies the Araromi Formation. It is predominantly made up of greyish white and occassionaly greenish limestone with marl forming the base of the group (Agagu, 1985). The limestone is extensive and traceable over a distance of about 320km continuously from East of Accra eastwards through the whole Dahomey Basin (Enu and Adegoke, 1988). The formation is Paleocene in age and was deposited in shallow marine environments (littoral to neritic conditions) because of the abundant microfossils and macrofauna such as coralline algae, gastropods, pelecypods, echinoids fragments and other skeletal debris associated with the limestone (Elueze and Nton, 2004). Although the formation is not folded but minor depositional structures have been reported by Jones and Hockey (1964). In Nigeria, the formation was affected by local crustal elevation which resulted in intensive erosion of the upper units of the limestone, with glauconitic shales and phosphathic materials accumulating on the erosional surface (Adegoke et al., 1980). Adegoke et al. (1980) established five microfacies of the Ewekoro limestone, these include; intrasparites, sandy algal biomicrites, shelly biomicrites, algal biomicrites and sandy algal biosparites.

### 2.2.3.5 The Akinbo Formation

Akinbo Formation conformably overlies the Ewekoro Formation and it is composed of greenish fossiliferous grey shale. It becomes siltier and sandy as it grades into the base of the overlying formation. The shale is thickly laminated towards the base but lost its lamination gradually upwards to massive mud and sand on top of the formation (Adegoke et al., 1980). The Akinbo Formation was deposited under marine conditions. Shallow marine clastic facies and a deeper facies have been recognized by Murat (1972). Reyment (1965) and Ogbe (1972) assigned

Paleocene age to the Akinbo Formation while Short and Stauble (1967) and Berggen (1960) ascribed the upper part to early Eocene.

### 2.2.3.6 The Oshosun Formation

The Osohsun Formation is overlain by marine phosphatic bearing shales and sandy beds. Agagu (1985) referred to this unit as Oshosun Member of the Imo Group. The Oshosun Formation consists of green to greenish grey clays and glauconitic shales interbedded with loose sand. The basal parts are arenaceous. Phosphatic material is present in the shales in nodular, vessicular, compact and granular textures (Okosun, 1998). Thin limestones and marls are locally or sporadically present. Pebbly mudstone occurs between the phosphatic horizons which are traceable laterally to a workable deposit in Togo (Reyment, 1965). Idowu et al (1993) inferred the deposiotional environment to have taken place in a marine–dominated transitional environment on the basis of organic matter content of the formation. The formation is middle to upper Eocene in age (Idowu et al., 1993).

### 2.2.3.7 The Ilaro Formation

Ilaro Formation was named by Jones and Hockey (1964). The sequence consists predominantly of coarse sandy estuarine, deltaic and continental bed, which displays rapid lateral facies changes. Ilaro Formation overlies the Oshosun Formation conformably and it is a lateral equivalent of the Ameki Formation in eastern Nigeria (Reyment, 1965; Adegoke, 1969; Fayose, 1970). The upper unit of the formation is made up of medium to coarse bedded sandstones and sandy clay sandstones with clays and shales intercalation. Pebble beds are also common. Bluish grey mudstone and glauconitic shales occur towards the base.The environment of deposition ranges from marine to continental (Jones and Hockey, 1964). Upper Eocene age has been assigned to it through chronological studies (Jones and Hockey, 1964).

### 2.2.3.8 The Benin Formation (Coastal Plain sands and Alluvium)

The Benin Formation is the youngest sedimentary unit in the Eastern Dahomey Basin and it is composed of coastal plain sands and alluvium sands. The Benin Formation probably lies on the Ilaro Formation unconformably, but convincing evidence as to this is lacking (Jones and Hockey, 1964). The coastal plain sand consists of soft, poorly sorted, in some cases unconsolidated clayey sands, pebbly sands, sandy clay and red thin band of lignite. Most of these sediments have been weathered to red pinkish or brown earth and clay grits in some cases. They are difficult to distinguish from Ilaro Formation on the field and from the basal beds of the Ise Formation. They lack fossil except for the plant remains. On the basis of the plant remains, the age ranges from Oligocene to Pliocene (Reyment, 1965). The clay sand which contains bitumen was formerly named Ijebu Formation by Reyment (1965). The alluvium sands are coarse clayey unsorted sand with clay lenses. They lie conformably on the coastal plain sands and the coarser pebbly sands that characterised the typical strata of the coastal plain sands.

### 2.2.4 The Geology of the Study Area

Lagos and Ute are within the Eastern Dahomey Basin while Auchi is within the western flank of Anambra Basin. Lagos is underlain by white to brownish, loose, poorly sorted coastal plain sands and alluvium belonging to the Benin Formation. The soil samples from Lagos are medium grained clayey sands to sand and brownish to dark brown in colour. Ute is underlain by reddish brown, fine and loose sandstones or alluvial sands of the Araromi Formation. The rocks encountered at Ute are coal and mudstones. The mudstone is grey to black coloured with occasional siltstone intercalations while the coal has a black colour and shining lustre. Auchi is underlain by white to reddish coloured, fine to medium grained, cross bedded, friable sandstones of Ajali Formation and carbonaceous shales and shales of Mamu Formation. The rocks sampled at Auchi are grey coloured fine grained shales and dark coloured fine grained carbonaceous shales

# CHAPTER THREE

# METHODOLOGY

## 3.1 Samples and Sampling

Four (4) organic matter associated sedimentary rocks and seven (7) soils were used for this study. The associated organic matter are commonly referred to as sediment or soil organic matter (SOM) or natural organic matter (NOM), though there may be variation in the type of organic matter found in sedimentary rocks and soils because they are essentially formed under different conditions and undergo different biochemical processes. The rocks from Ute and Auchi towns were chosen to cover major sedimentary rocks containing appreciable organic matter in the southwesten Nigeria. The soils were collected from Lagos because of its varied commercial activities which make it vulnerable to organic contamination, bearing in mind that the soils would have associated organic matter even if it is negligible. The need to find an environmentally friendly method of solving organic contaminantion problem such as that of Baruwa in Lagos also makes Lagos a suitable study location.

Prior to collection of the rock samples, the weathered surfaces were removed with cutlass and spade in order to collect fresh samples. Pitting was done with diggers and cutlass where the rocks are not well exposed.The rock samples were subsequently collected, kept in prepared sample bags, labeled and transferred to the laboratory. Coal and mudstones belonging to Araromi Formation were collected from Ute while shales and carbonaceous shales belonging to Mamu Formation were collected from Auchi. The Formations were sampled because they were known to be associated with organic matter and they were equally exposed at the two towns. Collected soil samples range from clayey sand to sandy soils were randomly collected by means of hand trowel from Baruwa and its environments where organic contaminant (refined petroleum products) was reported about fifteen years ago. The hand trowel was cleaned after each sampling. About 500g of each of the soil samples were randomly collected from major streets in

Baruwa and its environments. All samples collected were kept in a polythene bag, properly labeled and subsequently transported to the laboratory. The soil samples were air dried at room temperature before further processing.

### 3.2 Sample Preparation

Prior to isolation of the organic matter fractions from the rocks and soils, the soils were pulverised and sieved through a 0.18mm stainless sieve and demineralised (removal of carbonates and silicates) as follows: The soils were first dissolved in 1N HCl for 24 hours and subsequently centrifuged for 30 minutes at 4500rpm. After the supernatants were poured away, the residual fractions were treated with 1N HCl and 10% HF for 5 days, and this was repeated three (3) more times. The supernatants were finally removed by centrifugation at 4500rpm for 30 minutes. The residual fractions were rinsed with deionised water until the Ph of the supernatant was 7. The residues were dried in the oven at 50$^{o}$C. The rocks were also finely pulverised but not sieved like soils and demineralised in the same manner as the soils except that they were not treated with 1N HCl. The demineralised residues from the rocks were also oven dried at 50$^{o}$C. All demineralised samples (soils and rocks) were pulverised with a mortar and pestle and stored.

### 3.3 Laboratory Procedures and Experiments

#### 3.3.1 Isolation of Organic matter fractions

A flow chart showing the procedures involved in the extraction of the organic matter fractions (sorbents) is shown in the Figure 3.1. The details of the procedures for the extraction of SOM componenets such as lipid, bound lipid and lignin are discussed as follows.

##### 3.3.1.1 Isolation of lipid fraction

1. Demineralised sample was 5 times sequentially extracted with 2:1 (v/v) dichloromethane / methanol.
2. Each cycle consists of 3 minutes (1 minute interval) ultrasonication followed by centrifugation at 4500rpm for 30 minutes.
3. Lipids were concentrated from the pooled extract by rotatory evaporation and quantitatively transferred to quartz combustion tubes/glass bottles and lyophilized.

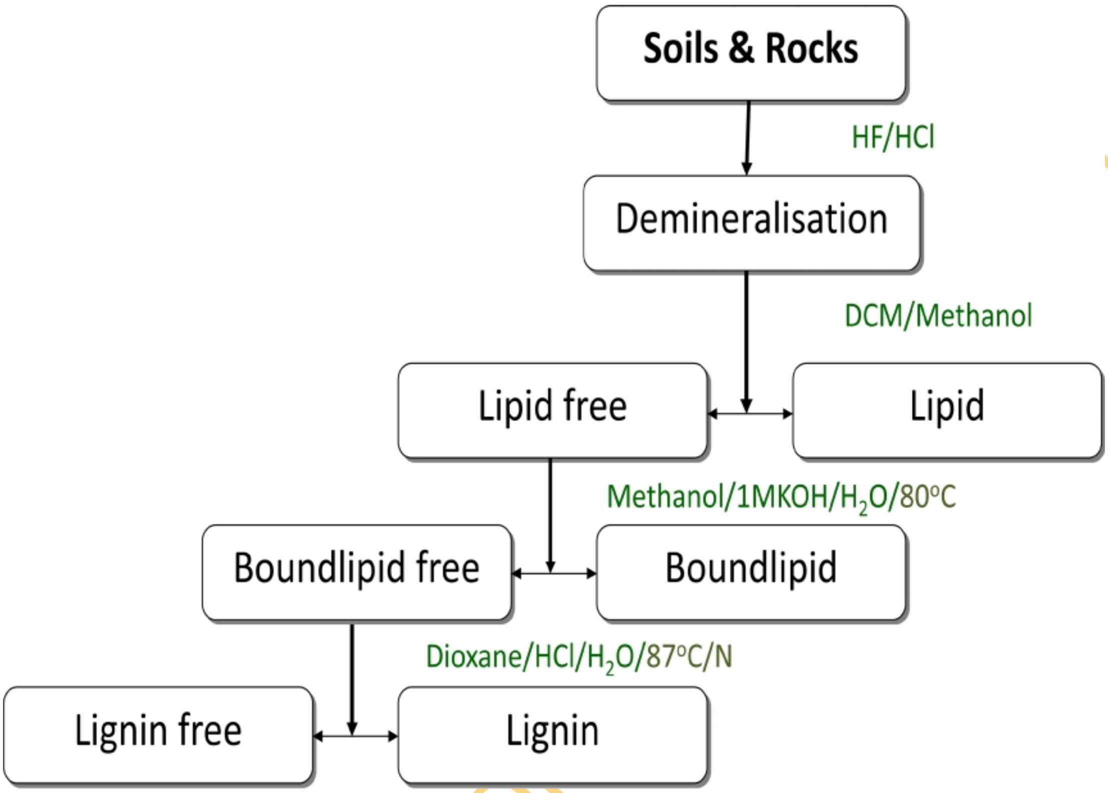


Figure 3.1: Flow Chart showing the procedures for extraction of organic matter fractions from rocks and soils

4. The lipids were dried (by nitrogen gas and in an oven at 45$^o$C) and weighed.
5. Lipid free samples were oven dried at 50$^o$C, weighed, finely pulverised and kept for isolation of bound-lipid fraction.

### 3.3.1.2 Isolation of bound-lipid fraction

1. Lipid free sample was put in a conical flask and a solution of 1N KOH, methanol and (15%) water was added to it.
2. The mixture was heated at 80$^o$C with a stirrer for 12 hours.
3. After cooling, the mixture was centrifuged at 4500rpm for 30 minutes and the supernatant was separated from the residue.
4. Dichloromethane was added to the supernatant in a separating funnel to extract the bound lipid fraction along with dichloromethane.
5. After 2-3 times extraction, 6N HCl was added to the remaining water and methanol to change the Ph to 1.
6. Then dichloromethane was added again to extract more bound-lipid from the remaining water and methanol in the separating funnel.
7. Anhydrous $Na_2SO_4$ salt was added to dichloromethane containing the extracted bound-lipid fraction and filtered to remove water from it.
8. The filtered bound-lipid fraction was concentrated from the pooled extract by rotatory evaporation and quantitatively transferred to quartz combustion tubes/glass bottles, and lyophilized.
9. Bound-lipid free samples were oven dried at 50$^o$C, weighed, finely pulverised and kept for isolation of lignin fraction.

### 3.3.1.3Isolation of lignin fraction

1. Bound-lipid free sample was put in a three necked, round bottom Pyrex flask, fitted with a reflux condenser, nitrogen inlet, dropping funnel, thermometer, and a three-way stopcock to a water pump and a solution of 0.1N HCl, dioxane-water (82:18) was added to it at a ratio of 1:20 (sample to solution).
2. The Ph was confirmed to be acidic or made acidic by adding few drops of 0.6N HCl.

3. The contents of the flask were gradually heated and continuously stirred to 87$^{o}$C ±2 and the temperature was maintained for 2 hours. A slow stream of nitrogen, at the rate of 80-100 bubbles/minute was maintained throughout the period of heating and subsequent cooling.
4. After thereaction mixturecooled down under the stream of nitrogen to 35-40$^{o}$C, it was centrifuged at 4500rpm for 30 minutes and the supernatant was separated from the residue.
5. The residue was washed with neutral dioxane-water until itwas colourless and thewashings were added.
6. The residue was further washed several times with a large excess of oxygen free-water until the washings were free from inorganic salts. It was then freeze dried as lignin freesample, transferred to a glass bottle, weighed, finely pulverised and kept.
7. The supernatant was concentrated by rotatory evaporation specifically to remove dioxane-water from it and oxygen free water was added to replace the evaporated dioxane-water.
8. The solution containing the extracted lignin was put in the refridgerator for at least 12 hours.After 12 hours in the refridgerator, the solution was centrifuged at 4500rpm for 20 minutes and the supernatant was separated from the residue.
9. The residue was washed several times with oxygen free water and the washings were added to the supernatant.
10. The residue was freeze dried as the lignin, and it was transferred to glass bottle, weighed, labeled, finely pulverised and kept.
11. The washings and the supernatant were also freeze dried as the lignin rest. And transferred to glass bottle, weighed, finely pulverised and stored.

A small fraction (approximately 2g) of the residual organic matter fractions including demineralised, lipid free, bound lipid free and lignin free fractions were weighed and separately kept in airtight bottle respectively beforethe next organic matter fraction was extracted.These small fractions were kept for sorption experiments and instrumental analyses. The isolated organic matter fractionssuch as lipid, bound-lipid and lignin were also weighed, finely pulverised and kept in airtight bottle for the sorption experiments and other instrumental analyses. Other products from the extraction processes such as bound-lipid supernatant, lignin supernatant were also weighed, kept and subjected to total organic carbon analysis for organic carbon mass balance.

### 3.3.2Sorption Procedures and Experiments

#### 3.3.2.1 Sorbent

Different organic matterfractions from thebulk rocks and soils which include demineralised, lipid free, bound-lipid free, lignin free, lipid and bound-lipid fractions were subjected to sorption experiments.These organic matter fractions are referred to as sorbents. It is important to note that among the organic matter fractions used for sorption experiments in this study, only 21 sorbents which included 5 bulk samples, 4 demineralised fractions, 4 lipid free fractions, 4bound-lipid free fractions, 3 lignin free fractions and a bound-lipid fraction generated good results or curves that were fitted to the Freundlich model. The total organic carbon content of the sorbent was used to determine the quantity of the sorbent that is required for sorption experiment.

#### 3.3.2.2Sorbate and background solution

14C-radiolabled and unlabeledPhenanthrene (Phen) obtained in spectrophotometric grades (<98%) from Sigma-Aldrich Chemical Company was used as the hydrophobic organic contaminant probe for this study. Its physicochemical propertiessuch as the octanol–water partition coefficient (log$K_{ow}$), aqueous solubility ($C_s$), and the $K_{oc}$valuesestimated from empirical correlations and reported in literatureis presented in Table 3.1.

Primary stock solutions were prepared by dissolving appropriate amounts of phenanthrene in methanol (high performance liquid chromatography [HPLC] grade), and sequentially diluted with methanol to make a series of stocks solutions of 100ppm, 1000ppm and 5000ppm concentrations. All stock solutions were stored at 4$^{o}$C in glass bottles sealed with Teflon-lined caps and then with Parafilm (Chicago, IL)to prevent vapour loss. A desired volume of stock solution was mixed with a background solution in a volumetric flask to make an initial aqueous solution for sorption experiments. Background solution (Ph=7) containing 0.005mol/L

Table 3.1: Physicochemical Properties of Phenanthrene

| Molecular Weight (g/mol) | Molar Volume ($cm^3$/mol) | Log $K_{ow}$ | $C_s$ (mg/L) | $K_{oc}$ estimated (L/g organic C) | | |
|---|---|---|---|---|---|---|
| | | | | (a) | (b) | (c) |
| 178.2 | 152 | 4.57 | 1.12 | 22.9 | 17.4 | 6.03 |

$C_s$, aqueous solubility; $K_{oc}$, organic carbon normalized sorption coefficient; $K_{ow}$, octanol-water partition coefficient.

(a) log $K_{oc}$ = log $K_{ow}$ – 0.21, from Karickhoff et al. (1979).

(b) log $K_{oc}$ = -0.686 log $C_s$ + 4.273, from Means et al. (1980).

(c) log $K_{oc}$ = 0.72 log $K_{ow}$ + 0.49, from Schwarzenbach and Westall (1981).

$CaCl_2$, 100mg/L $NaN_3$ as biocide (to prevent biological activity) and 5mg/L $NaHCO_3$ were prepared. 500 ml each of the background solution was spiked with the appropriate stock solutions to make initial aqueous solutions of the following concentrations; 10ppb, 20ppb, 40ppb, 80ppb, 150ppb, 300ppb, 500ppb, 750ppb, 1000ppb, and 1250ppb. Solute concentrations of the initial aqueous solutions were analysed with reverse phase high performance liquid chromatography (HPLC) (Model 1100; ODS,) with both diode array UV and fluorescence detection following procedures described in Ran et al. (2002).

#### 3.3.2.3 Sorption Experiments

A predetermined amount of sorbents which include bulk rock and soil samples, their demineralised, lipid free, bound lipid free, lignin free and bound lipid fractions were loaded into labeled glass ampoules. For a given sorbent, two samples were prepared for each of the different initial aqueous concentrations, thereby having 20 sorption experiment set up for a given sorbent type. The completely mixed batch reactors (CMBRs) consist of flame sealed ampoules (20 and 50 ml) containing the sorbents and initial aqueous solutions. The glass ampoules together with the sorbent were weighed and recorded. Each ampoule containing a predetermined amount of sorbent was filled with initial aqueous solution to the shoulder. The volume of the initial aqueous solution added to the sorbent in the glass ampoules were recorded, and the ampoules were immediately flame sealed. The reactors were mixed continuously in a rotatory shaker at 125rpm on a horizontal mode at 23$^{o}$C for 7 days. The manual mixing of the samples in the reactors was done at 4 hours interval per day for the period of seven days. After mixing in a rotary shaker, the ampoules were set upright for 2 days to allow suspended solids to settle. Preliminary tests showed that such a time period was sufficient to separate solids from solution.After settling, the ampoules were opened with flame and the supernatant was immediately withdrawn. A preliminary study had shown that, depending on solute concentration, about 1-7% of the aqueous-phase phenanthrene was lost by sorption to the glass walls of the GC vials during analysis. To eliminate this loss, 3 ml of the withdrawn supernatant from the ampoule was mixed with about 2 ml of methanol in a 5 ml vial capped with a Teflon top. Where it was observed that supernatant was still having suspended solids, the supernatant was centrifuged in the 5 mL vial at 10 rpm for 5 to 10 minutes. All withdrawn supernatants together with methanol were again thoroughly mixed and subsequently transferred into 2 ml vials for HPLC analyses. The 2 ml vials were capped with Teflon top and refrigerated to prevent loss of phenanthrene vapour. The quantity of supernatant and methanol were weighed, and the dilution factor for the supernatant was calculated from density data for mixtures of water and methanol. The dilution factor was then used to multiply the phenanthrene concentration analyzed for the mixture to obtain the concentration in the equilibrated aqueous solution. The result obtained from this procedure will be equivalent to analysis of a 1:1 (volume) liquid-liquid hexane extract of the same aqueous solution. Control experiments were also conducted using reactors containing no sorbent (sample) with a view to assessing loss of solutes to reactor components during sorption tests.Possible biodegradation of the solutes in the reactor systems were also checked by conducting four separate preliminary tests using a standard procedure as described in Huang and Weber (1998). No microorganism capable of degrading the target solutes was detected in the completely mixed batch reactors (CMBRs). Control experiments showed that average system losses were consistently less than 5% of initial concentrations of the phenanthrene which is within the standard deviations of the analyses given by the HPLC method. Hence, no correction was made during reduction of sorption data.

## 3.4 Instrumental Analyses

### 3.4.1 Elemental Analyses (C, H, O, N)

All samples including bulk and other fractions that were either extracted or products from the extraction processes were subjected to elemental analyses to determine the amount of the Organic Carbon, Hydrogen, Oxygen and Nitrogen in them. The samples include; bulk, demineralised, lipid free, bound-lipid free, lignin free, lipid, bound-lipid, bound-lipid rest, lignin, and lignin rest fractions. The analyses were carried out with the Elemental Vario EL III elemental analyser (Hanau, Germany) at the State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, China. It was carried out by injecting 2-20 mg of the samples wrapped in tiny aluminium foils into the elemental analyser. The samples for the organic carbon, hydrogen and nitrogen analyses were oven dried at 78$^{o}$C and allowed to cool prior to analyses. For oxygen analysis however, samples were oven dried at 105$^{o}$C for 4 hours and kept in airtight container before the analyses. This was to prevent the influence of the atmospheric oxygen on the results. Duplicate analyses were done for each sample and results were rejected where the standard deviation between the duplicates was greater than 5%. The mean value of the duplicate analyses was considered for each analysis and the elemental results were given in percentages. Theinstrument was calibrated with Acetalinide (standard sample) after every ten analyses. The Elemental analyses were carried out on other products (bound-lipid rest and lignin rest) from the extraction processes apart from the residual and extracted fractions in order to calculate the organic carbon mass balance. This equally helped in ensuring the effectiveness of the extraction procedures. The H/C, O/C and C/N atomic ratios were determined from the elemental analyses to characterise the natural organic matter fractions and determine the contamination factor.

### 3.4.2 Cross Polarisation/Magic Angle Spinning $^{13}$C Nuclear Magnetic Resonance Analyses.

Some of the NOM fractions from the rock and soil samples (mainly samples that underwent sorption experiment) were subjected to Cross-polarisation/magic angle spinning (CP/MAS) $^{13}$C Nuclear Magnetic Resonance (NMR) analysis to determine their structural composition and assign them to their different functional groups. The CP/MAS $^{13}$C NMR analyses were carried out at the Biogeochemical Laboratory of the University of Massachussets, U.S.A with a Bruker DSX400 Spectrometer and the NMR experiments were performed at 100 MHz in 4 mm rotors. The structural compositions of the residual organic matter fractions were determined and the different functional groups contained in these residual/isolated organic matter fractions were identified and expressed as percentages. The average percentages of the aliphatic carbons and aromatic carbons in the organic matter fractions were also determined.

### 3.4.3 High Performance Liquid Chromatography (HPLC) Analyses

HPLC analyses were carried out to determine concentrations of the phenanthrene in the prepared aqueous and equilibrated aqueous solutions before and after sorption experiments respectively. The High Performance Liquid Chromatography (HPLC) analyses were done at the State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, China. The phenanthrene concentrations in the mixture were analyzed using reverse-phase Shimadzu HPLC (ODS, 5mm, 2.1 _ 250 mm column on a Hewlett-Packard Model 1090) with a diode array UV detector (250-nm wavelength) for concentrations ranging from 20 to 1000 *u*g/L and a fluorescence detector (Model HP 1046A, 250-nm excitation wavelength, 364-nm emission wavelength) for concentrations ranging from 0.5 to 50 *u*g/L. External phenanthrene standards (in methanol) were used to establish both a linear calibration curve for the UV detector. The elute solvent used was a mixture of Acetonitrile (90%) and water (10%). The 2 ml vials containing the mixture of supernatant and methanol were put into the sample loading tray of the HPLC instrument. The tray facilitates the injection of the appropriate volume of the mixture needed for the analyses.

The phenanthrene concentrations in initial aqueous solution prior to sorption experiment and in the equilibrated aqueous solution withdrawn from glass ampoules after sorption experiments for the seven days period were determined. Duplicate analyses were done for each sample and the average constituted the final result where relative error between the results was not greater than 7%. The dilution factor obtained from the addition of methanol to the supernatant was then multiplied by the phenanthrene concentration analyzed for the mixture to obtain the actual phenanthrene concentrations in the analysed equilibrated aqueous, initial aqueous and control experiment aqueous solutions. The concentrations of phenanthrene in control experiments (ampoules without sample or sorbent) were also determined to know the loss of phenanthrene to the wall of the ampoules.

The concentrations of phenanthrene in the initial aqueous solution were compared with concentrations in the equilibrated aqueous solution to determine the concentrations of phenanthrene sorbed by the various organic matter fractions from the rocks and soils.The concentration of phenanthrene in the equilibrated aqueous solution ($C_e$) which is the liquid-phase equilibrium concentration was used to determine the solid-phase concentration ($q_e$) based on mass balance between the solid and the aqueous phases.

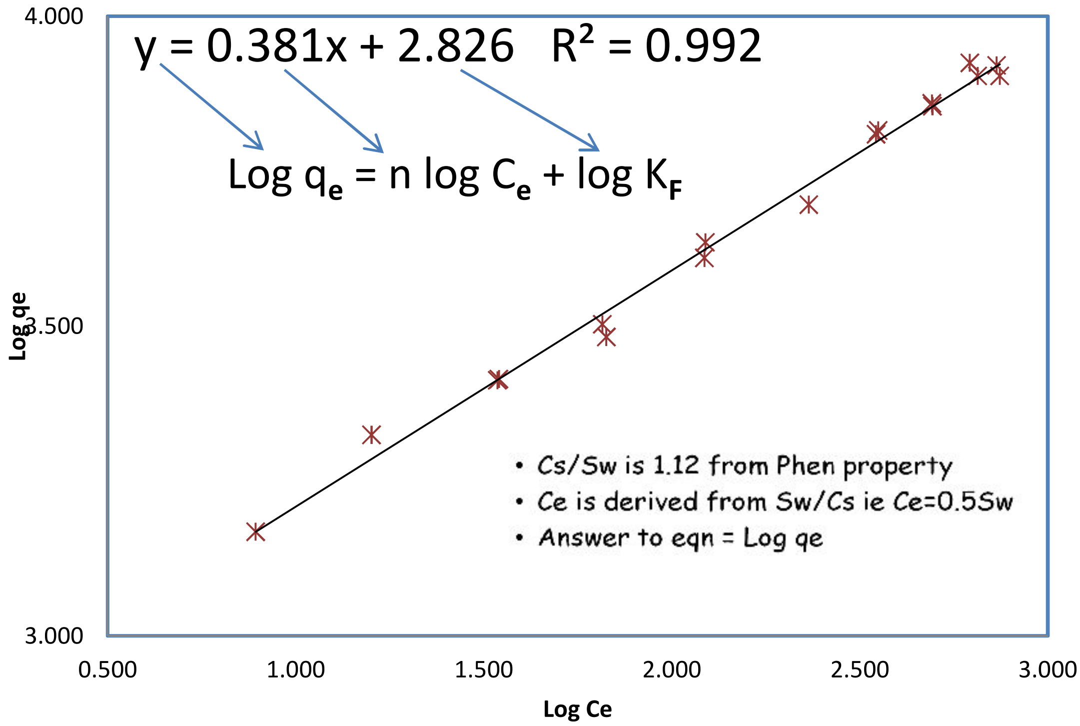
### 3.5 Sorption Model

Sorption isotherms for the different sorbents (organic matter fractions) generated from the HPLC results in combination with other sorption parameters such as the quantity of sorbent used and dilution factor among others. These isotherms were used to determine the sorption capacity parameters of the organic matter fractions through modeling as follows:

The sorption isotherms were fitted into the Freundlich model shown in the equation below:

$$\log q_e = \log K_F + n \log C_e \qquad 3.1$$

where $q_e$ is the solid-phase concentration ($u$g/g) and $C$e is the liquid-phase equilibrium concentration ($u$g/L). $K_F$ is the sorption capacity-related parameter (($u$g/g)/($u$g/L)$^n$) and $n$ is the isotherm nonlinearity index. A typical Freundlich model generated from sorption isotherm showing the sorption parameters is presented in Figure 3.2.



whereCs = Aqueous solubility (Phenanthrene property)

Sw = Water saturation

Ce is a function of Cs/Sw

Figure 3.2: A typical Freundlich model generated from sorption isotherm

# CHAPTER FOUR

# RESULTSINTERPRETATION AND DISCUSSIONS

## 4.1 Results Interpretation

### 4.1.1 Elemental Results

The results of the elementalanalysescarried outon the bulk samples (rocks andsoils),their residual and extracted organic matter fractions are given in Table 4.1. The tableshowsthe amounts of the Total Organic Carbon (TOC), Hydrogen (H), Nitrogen (N) and Oxygen (O), and atomic ratios of H/C, O/C and C/N. The residual fractions includedemineralised, lipid free, bound-lipid free andlignin free fractions, while the extracted fractions include lipid, bound-lipid and lignin fractions.All elemental results are in percentages. Each elemental result represents an average of duplicate analyses carried out on each sample for the above listed elements. The standard deviation between the duplicate analyses is less or equal to 5%.

The TOC contents of the bulk soils range from 0.13 to 10.12 % while the TOC values of the bulk rocks varied from 1.27 to 61.42 % (Table 4.1). The hydrogen (H) and nitrogen (N) values for the bulk soils vary from 0.09 to 1.44 % and 0.04 to 0.45 % respectively, while the value of the same parameters for the bulk rocks vary from 0.92 to 3.67 % and 0.09 to 1.21 % respectively (Table 4.1). The atomic C/N and H/C ratios of the bulk soils range from 3.79 to 59.03 and 0.96 to 8.31 respectively while the ratios for the bulk rocks vary from 4.02 to 59.22 and 0.72 to 9.54 respectively. The TOC range of the bulk soils indicates that some of the soils have very high organic matter content. The table showed that coal and the carbonaceous shale have TOC values of 61.42 and 13.82 % respectively while the mudstone and shale have comparatively lower organic matter content. Coal and carbonaceous shale of similar TOC values were referred to as carbonaceous geosorbents by Cornellisen et al. (2005). The organic carbon (OC), hydrogen (H), oxygen (O) and nitrogen (N) contents of the demineralised (dm) fractions from the soils range

Table 4.1 Elemental analyses results and atomic ratios of bulk samples and NOM fractions (dm, dlpd, dblpd, dlgn, lpd, blpd, lgn).

| Sample ID | Sample Type | C % | H % | O % | N % | H/C | O/C | C/N | Content wt% |
|---|---|---|---|---|---|---|---|---|---|
| IJ bulk | Soil | 10.12$^{a}$ | 0.81 | nd | 0.2 | 0.96 | nd | 59.03 | |
| IJ dm | NOM fract | 63.11 | 3.18 | 18.76 | 1.43 | 0.60 | 0.22 | 51.49 | 14.64 |
| IJ dlpd | NOM fract | 65.24 | 3.1 | 19.79 | 1.41 | 0.57 | 0.23 | 53.98 | 13.81 |
| IJ dblpd | NOM fract | 54.73 | 3.13 | 24.20 | 1.38 | 0.69 | 0.33 | 46.27 | 15.40 |
| IJ dlgn | NOM fract | 65.31 | 2.78 | 17.42 | 1.3 | 0.51 | 0.20 | 58.61 | 12.71 |
| IJ lpd | NOM fract | 66.4 | 8.92 | 13.87 | 2.71 | 1.61 | 0.16 | 28.59 | 0.77 |
| IJ blpd | NOM fract | 35.53 | 4.74 | 12.49 | 2.46 | 1.60 | 0.26 | 16.85 | 0.05 |
| IJ lgn | NOM fract | 60.89 | 5.91 | 33.48 | 3.68 | 1.16 | 0.41 | 19.30 | 0.23 |
| | | | | | | | | | |
| AD bulk | Soil | 1.06 | 0.51 | | 0.1 | 5.77 | nd | 12.37 | |
| AD dm | NOM fract | 31.62 | 3.1 | 21.43 | 2.26 | 1.18 | 0.51 | 16.32 | 2.28 |
| AD dlpd | NOM fract | 29.08 | 2.81 | 22.06 | 2.33 | 1.16 | 0.57 | 14.56 | 2.16 |
| AD dblpd | NOM fract | 9.23 | 1.78 | 14.72 | 0.46 | 2.31 | 1.20 | 23.46 | 5.51 |
| AD dlgn | NOM fract | 20.47 | 2.22 | 15.80 | 0.88 | 1.30 | 0.58 | 27.14 | 1.08 |
| AD lpd | NOM fract | 73.4 | 10.08 | 15.83 | 0.86 | 1.65 | 0.16 | 99.57 | 0.11 |
| AD bpd | NOM fract | 54.69 | 8.87 | 10.65 | 0.59 | 1.95 | 0.15 | 108.14 | 0.02 |
| AD lgn | NOM fract | 54.81 | 5.28 | 36.20 | 3.8 | 1.16 | 0.50 | 16.83 | 0.06 |
| | | | | | | | | | |
| AJ bulk | Soil | 0.92 | 0.61 | | 0.12 | 7.96 | 0.00 | 8.94 | |
| AJ dm | NOM fract | 27.85 | 2.62 | 19.23 | 1.79 | 1.13 | 0.52 | 18.15 | 2.01 |
| AJ dlpd | NOM fract | 27.16 | 2.55 | 19.39 | 1.9 | 1.13 | 0.54 | 16.68 | 1.84 |
| AJ dblpd | NOM fract | 20.21 | 1.96 | 29.34 | 0.88 | 1.16 | 1.09 | 26.79 | 2.04 |
| AJ dlgn | NOM fract | 15.24 | 1.57 | 11.27 | 0.57 | 1.24 | 0.55 | 31.18 | 1.32 |
| AJ lpd | NOM fract | 65.51 | 7.88 | 20.83 | 1.37 | 1.44 | 0.24 | 55.79 | 0.10 |
| AJ blpd | NOM fract | 54.53 | 5.74 | 27.19 | 3.59 | 1.26 | 0.37 | 17.72 | 0.04 |
| AJ lgn | NOM fract | 52.8 | 4.77 | 40.78 | 2.73 | 1.08 | 0.58 | 22.52 | 0.27 |
| | | | | | | | | | |
| FAS bulk | Soil | 0.98 | 0.64 | nd | 0.11 | 7.84 | nd | 10.39 | |
| FAS dm | NOM fract | 29.41 | 4.16 | 16.60 | 1.62 | 1.70 | 0.42 | 21.15 | 1.84 |
| FAS dlpd | NOM fract | 26.76 | 2.96 | 16.36 | 1.72 | 1.33 | 0.46 | 18.18 | 1.83 |
| FAS dblpd | NOM fract | 20.29 | 2.59 | 21.23 | 0.70 | 1.53 | 0.78 | 33.77 | 1.79 |
| FAS dlgn | NOM fract | 19.02 | 1.58 | 11.21 | 0.50 | 1.00 | 0.44 | 44.40 | 1.25 |
| FAS lpd | NOM fract | 75.15 | 10.57 | 13.42 | 2.41 | 1.69 | 0.13 | 36.38 | 0.16 |
| FAS blpd | NOM fract | 62.82 | 7.49 | 26.26 | 3.88 | 1.43 | 0.31 | 18.89 | 0.04 |
| FAS lgn | NOM fract | 58.57 | 5.22 | 35.65 | 3.65 | 1.07 | 0.46 | 18.72 | 0.12 |
| | | | | | | | | | |
| EGB bulk | Soil | 0.13 | 0.09 | nd | 0.04 | 8.31 | nd | 3.79 | |
| EGB dm | NOM fract | 9.08 | 1.05 | 6.99 | 0.42 | 1.39 | 0.58 | 25.22 | 0.60 |

| Sample ID | Sample Type | C % | H % | O % | N % | H/C | O/C | C/N | Content wt% |
|---|---|---|---|---|---|---|---|---|---|
| ABG bulk | Soil | 2.11 | 0.48 | nd | 0.1 | 2.73 | nd | 24.62 | |
| ABG dm | NOM fract | 51.78 | 5.93 | 15.26 | 1.08 | 1.37 | 0.22 | 55.81 | 3.64 |
| ABG dlpd | NOM fract | 49.39 | 4.87 | 17.16 | 1.36 | 1.18 | 0.26 | 42.42 | 2.69 |
| ABG dblpd | NOM fract | 33.94 | 4.03 | 22.84 | 0.50 | 1.42 | 0.50 | 79.00 | 2.93 |
| ABG dlgn | NOM fract | 41.14 | 3.44 | 11.74 | 0.41 | 1.00 | 0.21 | 115.89 | 2.08 |
| ABG lpd | NOM fract | 77.34 | 10.86 | 9.98 | 1.76 | 1.69 | 0.10 | 51.27 | 0.84 |
| ABG blpd | NOM fract | 63.21 | 8.26 | 25.23 | 2.95 | 1.57 | 0.30 | 25.00 | 0.06 |
| ABG lgn | NOM fract | 59.07 | 5.9 | 31.36 | 3.58 | 1.20 | 0.40 | 19.25 | 0.12 |
| | | | | | | | | | |
| IPJ bulk | Soil | 7.21 | 1.44 | nd | 0.45 | 2.40 | nd | 18.69 | |
| IPJ dm | NOM fract | 40.64 | 3.45 | 20.23 | 2.33 | 1.02 | 0.37 | 20.35 | 16.61 |
| IPJ dlpd | NOM fract | 34.63 | 2.83 | 19.42 | 2.32 | 0.98 | 0.42 | 17.41 | |
| IPJ dblpd | NOM fract | 23.04 | 2.24 | 15.59 | 0.83 | 1.17 | 0.51 | 32.39 | |
| IPJlpd | NOM fract | 73.39 | 8.11 | nd | 1.07 | 1.33 | nd | 80.02 | |
| IPJ blpd | NOM fract | 63.32 | 6.91 | nd | 1.38 | 1.31 | nd | 53.53 | |
| | | | | | | | | | |
| UT bulk | Rock | 61.42 | 3.67 | 24.28 | 1.21 | 0.72 | 0.30 | 59.22 | |
| UT dm | NOM fract | 68.06 | 5.13 | 23.10 | 1.08 | 0.90 | 0.25 | 73.52 | 77.06 |
| UT dlpd | NOM fract | 67.54 | 5.06 | 26.06 | 1.45 | 0.90 | 0.29 | 54.34 | 73.49 |
| UT dblpd | NOM fract | 50.71 | 4.73 | 37.40 | 1.08 | 1.12 | 0.55 | 54.78 | 90.68 |
| UT lpd | NOM fract | 72.39 | 7.46 | 17.08 | 0.86 | 1.24 | 0.18 | 98.20 | 3.61 |
| UT blpd | NOM fract | 68.83 | 6.66 | 22.35 | 1.07 | 1.16 | 0.24 | 75.05 | 1.21 |
| | | | | | | | | | |
| AB bulk | Rock | 13.82 | 1.66 | 8.96 | 0.33 | 1.44 | 0.49 | 48.86 | |
| AB dm | NOM fract | 70.78 | 5.34 | 11.57 | 1.88 | 0.91 | 0.12 | 43.92 | 17.90 |
| AB dlpd | NOM fract | 70.2 | 5.2 | 12.77 | 1.8 | 0.89 | 0.14 | 45.50 | 16.43 |
| AB dblpd | NOM fract | 51.58 | 4.48 | 28.29 | 1.36 | 1.04 | 0.41 | 44.25 | 22.43 |
| AB lpd | NOM fract | 76.32 | 3.34 | 9.69 | 0.87 | 0.53 | 0.10 | 102.34 | 0.80 |
| AB blpd | NOM fract | 64.04 | 6.49 | 19.26 | 1.36 | 1.22 | 0.23 | 54.94 | 0.11 |
| | | | | | | | | | |
| MDT bulk | Rock | 3.82 | 0.92 | 6.44 | 1.11 | 2.89 | 1.26 | 4.02 | |
| MDT dm | NOM fract | 52.99 | 3.84 | 17.36 | 1.56 | 0.87 | 0.25 | 39.63 | 6.18 |
| MDT dlpd | NOM fract | 54.38 | 4.23 | 18.69 | 1.54 | 0.93 | 0.26 | 41.20 | 5.65 |
| MDT dblpd | NOM fract | 33.41 | 3.31 | 38.65 | 0.96 | 1.19 | 0.87 | 40.60 | 3.97 |
| MDT lpd | NOM fract | 62.03 | 6.56 | 17.68 | 1.32 | 1.27 | 0.21 | 54.82 | 0.62 |
| MDT blpd | NOM fract | 47.53 | 5.62 | 22.11 | 1.06 | 1.42 | 0.35 | 52.31 | 0.26 |
| | | | | | | | | | |
| SH bulk | Rock | 1.27 | 1.01 | 7.61 | 0.09 | 9.54 | 4.49 | 16.46 | |
| SH dm | NOM fract | 55.28 | 3.78 | 16.94 | 2.08 | 0.82 | 0.23 | 31.01 | 2.15 |

**[a]Content is mass percentage of each fraction in bulk sample, [b]nd = not determined. NOM fract = Natural organic matter fraction. dm = demineralised, dlpd = lipid free, dblpd = bound lipid free, dlgn = lignin free, lpd = lipid, blpd = bound lipid, lgn = lignin.**

from 9.08 to 63.11 %, 1.05 to 5.93 %, 6.99 to 21.43 % and 0.42 to 2.33 % respectively, while the range of same parameters in demineralised (dm) fractions of the rocks are 52.99 to 70.78 %, 3.78 to 5.34 %, 11.57 to 23.10 % and 1.08 to 2.08 % respectively. The atomic H/C, O/C and C/N ratios of the soils' demineralised fractions range from 0.60 to 1.39, 0.22 to 0.58 and 16.32 to 55.81 respectively, while the values of same parameters for rocks' demineralised fractions range from 0.82 to 0.91, 0.12 to 0.25 and 31.01 to 73.52 respectively.

The lipid free (dlpd) fractions of the soils contained 27.16 to 65.24 % organic carbon, 2.55 to 4.87 % hydrogen, 16.36 to 22.06 % oxygen and 1.41 to 2.33 % nitrogen, while their atomic H/C, O/C and C/N ratios range from 0.57 to 1.33, 0.23 to 0.57 and 14.56 to 53.98 respectively. The organic carbon (OC), hydrogen (H), oxygen (O) and nitrogen (N) contents of the lipid free (dlpd) fractions from the rocks vary from 54.38 to 70.2 %, 4.23 to 5.2 %, 12.77 to 26.06 % and 1.45 to 1.8 % respectively, whiletheir atomic H/C, O/C and C/N ratios range from 0.89 to 0.93, 0.14 to 0.29 and 41.2 to 54.34 respectively. The organic carbon (OC), hydrogen (H), oxygen (O) and nitrogen (N) contents of the bound-lipid free (dblpd) fractions from the soils range from 9.23 to 54.73 %, 1.78 to 4.03 %, 14.72 to 29.34 % and 0.46 to 1.38 % respectively, while their the atomic H/C, O/C and C/N ratios range from 0.69 to 2.31, 0.33 to 1.20 and 23.46 to 79.00 respectively, Bound lipid-free (dblpd) fractions of the rocks contained 33.14 to 51.58% organic carbon, 3.31 to 4.73 % hydrogen, 28.29 to 38.65 % oxygen and 0.96 to 1.36 % nitrogen, while their atomic H/C, O/C and C/N ratios vary from 1.04 to 1.19, 0.41 to 0.87 and 40.6 to 54.78 respectively.The organic carbon (OC), hydrogen (H), oxygen (O) and nitrogen (N) contents of the lignin free (dlgn) fractions of the soils range from 15.24 to 65.31%, 1.57 to 3.44%, 11.21 to 17.42% and 0.41 to 1.30% respectively, whiletheiratomic H/C, O/C and C/N ratios range from 0.51 to 1.30, 0.20 to 0.58 and 27.14 to 115.89respectively.

The organic carbon (OC), hydrogen (H), oxygen (O) and nitrogen (N) contents of the lignin (lgn) fractions extracted from the soils vary from 52.80 to 60.89%, 4.77 to 5.91 %, 31.36 to 40.78% and 2.73 to 3.80% respectively, while their atomic H/C, O/C and C/N ratios vary from 1.07 to 1.20, 0.40 to 0.58 and 16.83 to 22.52 respectively. The lipid (lpd) fractions from the rocks contained 62.03 to 76.32% organic carbon, 3.34 to7.46% hydrogen, 9.69 to 17.68% oxygen and 0.86 to 1.32% nitrogen, while theiratomic H/C, O/C and C/N ratios range from 0.53 to1.27, 0.10

to 0.21 and 54.82 to 102.34 respectively. The organic carbon (OC), hydrogen (H), oxygen (O) and nitrogen (N) contents of the extracted lipid from the soils vary from 65.51 to 77.34%, 7.88 to 10.86%, 9.98 to 20.83% and 0.86 to 2.71% respectively, while theiratomic H/C, O/C and C/N ratios range from 1.33 to 1.69, 0.10 to 0.24 and 28.59 to 80.01 respectively.Bound-lipid (blpd) fractions extracted from the soils contained 35.53 to 63.32% organic carbon, 4.74 to 8.87% hydrogen, 10.65to 27.19% oxygen and 0.59 to 3.88% nitrogen, while theiratomic H/C, O/C and C/N ratios range from 1.26 to 1.95, 0.15 to 0.37 and 16.85 to 108.14 respectively. Also, organic carbon (OC), hydrogen (H), oxygen (O) and nitrogen (N) contents of bound-lipid (blpd) extracted from the rocks vary from 47.53 to 68.83%, 5.62 to 6.66%, 19.26 to 22.35% and 1.06 to 1.36% respectively, while their atomic H/C, O/C and C/N ratios range from 1.16 to 1.42, 0.23 to 0.35 and 52.31 to 75.05 respectively.

The organic carbon distribution in the bulk samples, demineralised, lipid free, bound-lipid free, lignin free, lipid, bound-lipid and lignin fractions of the soils and rocks samples are also presented in Table 4.2. The TOC value of the demineralised fractions varies from 9.08 to 63.11% and 52.99 to 70.78% in the soils and rocks respectively (Table 4.1). These values revealed that the demineralised fractions accounted for41.60 to 93.60% and 85.40 to 93.43% of the total organic carbon in the soils and rocks respectively (Table 4.2). The lipid free fractions of the soils and rocks also contained 27.16 to 65.24% and 54.38 to 70.2% organic carbon respectively (Table 4.1, and these accounted for 39.14 to 89.02% and 80.38 to 83.48% of the total organic carbon in the soils and rocks respectively (Table 4.2).The organic carbon in the bound-lipid free fractions of the soils and rocks ranged from 9.23 to 54.73% and 33.41 to 51.58% respectively and these accounted for 34.83 to 83.26% and 52.29 to 87.71% of the total organic carbon in the soils and rocks respectively (Table 4.2). The organic carbon in the lignin free fractions of the soils range from 15.24 to 65.31%, these accounted for 20.94 to 82.01% of the total organic carbon in the soils (Table 4.2).

In addition, lipid fractions extractedfrom the soils and rocks contained 62.03 to 76.32% and 65.51 to 77.34% organic carbon respectively (Table 4.1), these accounted for 5.08 to 30.63% and 4.21 to 10.01% of the total organic carbon in the soils and rocks respectively (Table 4.2). Bound

Table 4.2: Organic Carbon (OC) distribution in the bulk samples and NOM fractions(dm, dlpd, dblpd, dlgn, lpd, blpd and lgn).

| Samples | Bulk TOC wt % | DM/OC % | DLPD/OC % | DBLPD/OC % | DLGN/OC % | LPD/OC % | BLPD/OC % | LGN/OC % |
|---|---|---|---|---|---|---|---|---|
| SOILS | | | | | | | | |
| IJ | 10.12[a] | 91.3 | 89.02 | 83.26 | 82.01 | 5.08 | 0.19 | 1.37 |
| IPJ | 7.21 | 93.6 | 75.19 | 34.97 | ND[b] | 8.82 | 2.22 | ND |
| ABG | 2.11 | 89.34 | 63.07 | 59.19 | 40.62 | 30.63 | 1.87 | 3.49 |
| FAS | 0.98 | 55.34 | 49.97 | 36.99 | 24.3 | 12.04 | 2.29 | 7.46 |
| ADJ | 1.06 | 67.88 | 59.19 | 47.99 | 20.94 | 7.9 | 0.92 | 2.95 |
| AJ | 0.92 | 60.97 | 54.18 | 44.8 | 21.85 | 7.11 | 2.22 | 15.29 |
| EGB | 0.13 | 41.6 | ND | ND | ND | ND | ND | ND |
| Average | 3.22 | 71.43 | 65.1 | 51.2 | 37.9 | 11.93 | 1.62 | 6.11 |
| | | | | | | | | |
| ROCKS | | | | | | | | |
| UT | 61.42 | 85.4 | 80.81 | 74.87 | ND | 4.25 | 1.35 | ND |
| AB | 13.82 | 91.67 | 83.48 | 83.71 | ND | 4.41 | 0.52 | ND |
| MDT | 3.82 | 85.74 | 80.38 | 69.11 | ND | 10.01 | 3.26 | ND |
| SH | 1.27 | 93.43 | ND | ND | ND | ND | ND | ND |
| Average | 20.08 | 89.06 | 81.56 | 75.90 | | 6.22 | 1.71 | |

[a] Represents averages of total organic carbon. [b] ND: not determined

DM = demineralised
DLPD = lipid free
DBLPD = bound lipid free
DLGN = lignin free
LPD = lipid
BLPD = bound lipid
LGN = lignin

lipid fractions extracted from the soils and rocks contained 35.53 to 63.32% and 47.53 to 68.83% organic carbon respectively (Table 4.1), these accounted for 0.19 to 2.29% and 0.52 to 3.265 of the total organic carbon in the soils and rocks respectively (Table 4.2). The organic carbon contents in the extracted lignin from the soils vary from 52.80 to 60.89%, thus accounting for 1.37 to 15.29% of the total organic carbon in the soils.

### 4.1.2 $^{13}$C Cross Polarisation Magic Angle Spinning Nuclear Magnetic Resonance ($^{13}$C CPMAS NMR) Results

The selected results of the $^{13}$C Cross Polarisation Magic Angle Spinning Nuclear Magnetic Resonance ($^{13}$C CPMAS NMR) analyses are presented in Figures 4.1 to 4.5 and Table 4.3. The selected spectraof the natural organic matter fractions from the rocks and soils revealed their skeletal carbons or different structural components. It also shows marked difference in the functional groups associated with the natural organic matter fractions. Table 4.3 shows different functional groups of the natural organic matter fractions such as the alkyl carbon (0-45), methoxyl (45-63), O-alkyl/carbohydrate(63-93), aryl carbon (93-148), O aryl carbon (148-165), carboxyl (165-187) and Carbonyl/ketone (187-220) as well as their percentages. The cummulative percentages of totalaromatic and aliphatic carbons contained in the natural organic matter fractions are also shown in the table.

$^{13}$C NMR spectra for the residual organic matter fractions (including demineralised and lipid free) from coal and carbonaceous shale (samples UT and AB) shows a large contribution from alkyl carbon (0-45ppm) and the aryl carbon (93-148ppm) with small contribution from methoxyl carbon (45-63ppm) and O-aryl carbon (148-165 ppm) (Figures 4.4 to 4.5, Table 4.3). In addition to the above properties, the demineralised and lipid free fractions from the coal also contain minor contribution from carbohydrate (63-93ppm) and carboxyl carbon (165-187ppm). The bound-lipid free fraction from the coal has large contribution from alkyl carbon (0-45ppm) and the aryl carbon (93-148 ppm) with small contribution from methoxyl carbon (45-63 ppm), O-aryl carbon (148-165 ppm), carboxyl carbon (165-187 ppm), and minor contribution from carbohydrate (63-93 ppm) and carbonyl carbon (187-220 ppm) (Table 4.3).

The NMR spectra of the demineralised fractions from two soils (samples AD and AJ) showed a

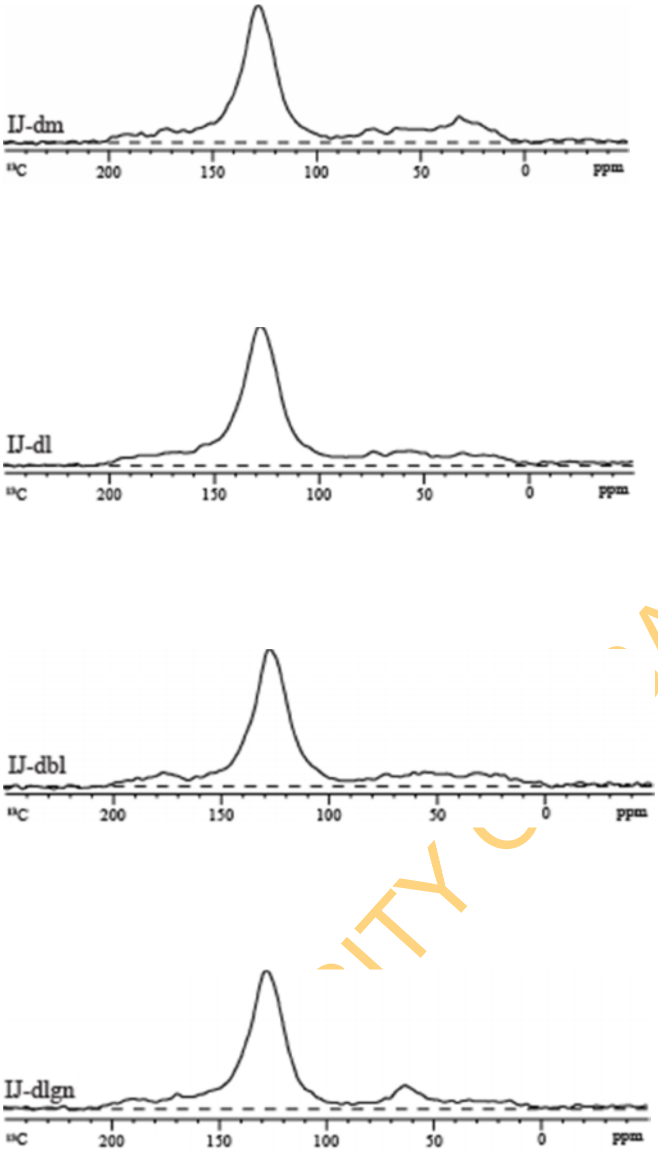


Figure 4.1: CPMAS NMR spectra of organic matter fractions in IJ soil sample

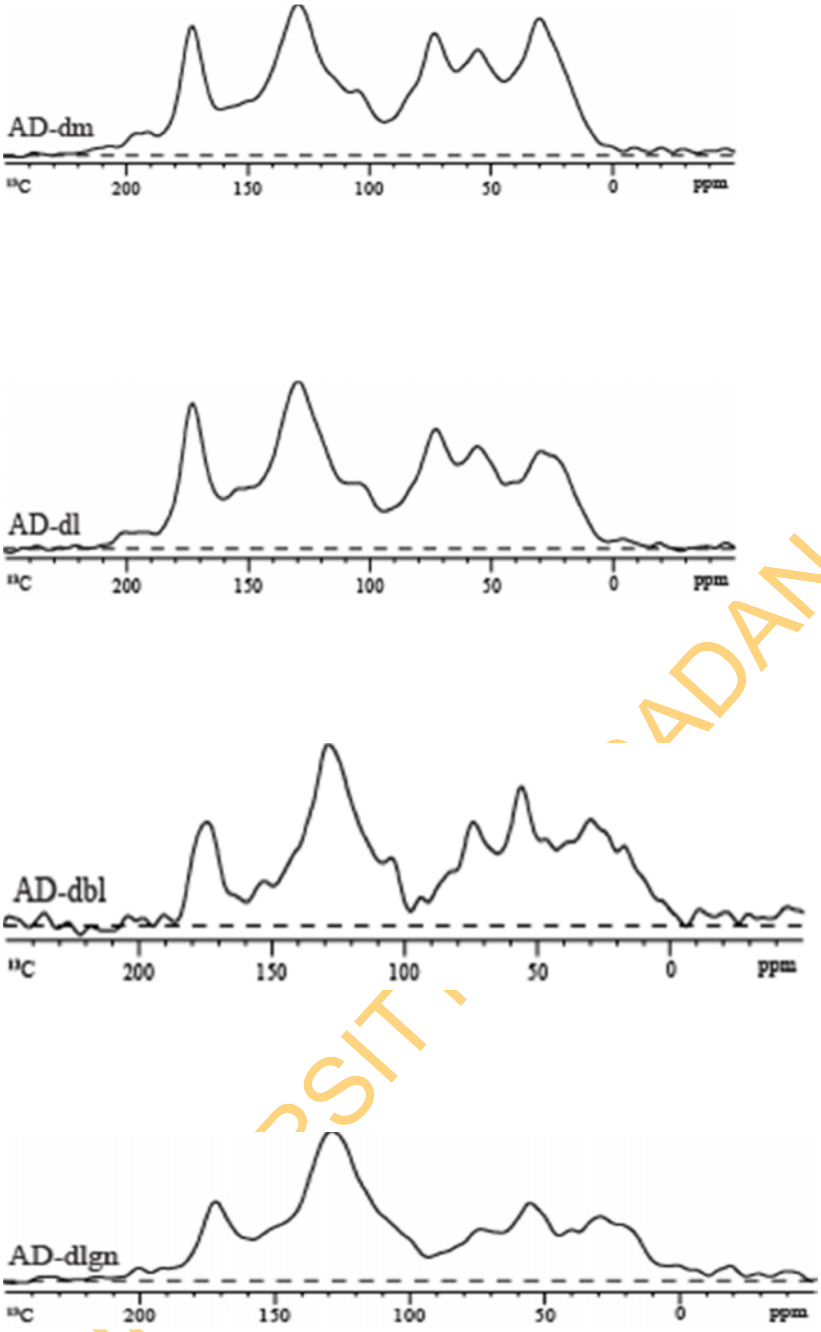


Figure 4.2: CPMAS NMR spectra of organic matter fractions in AD soil sample

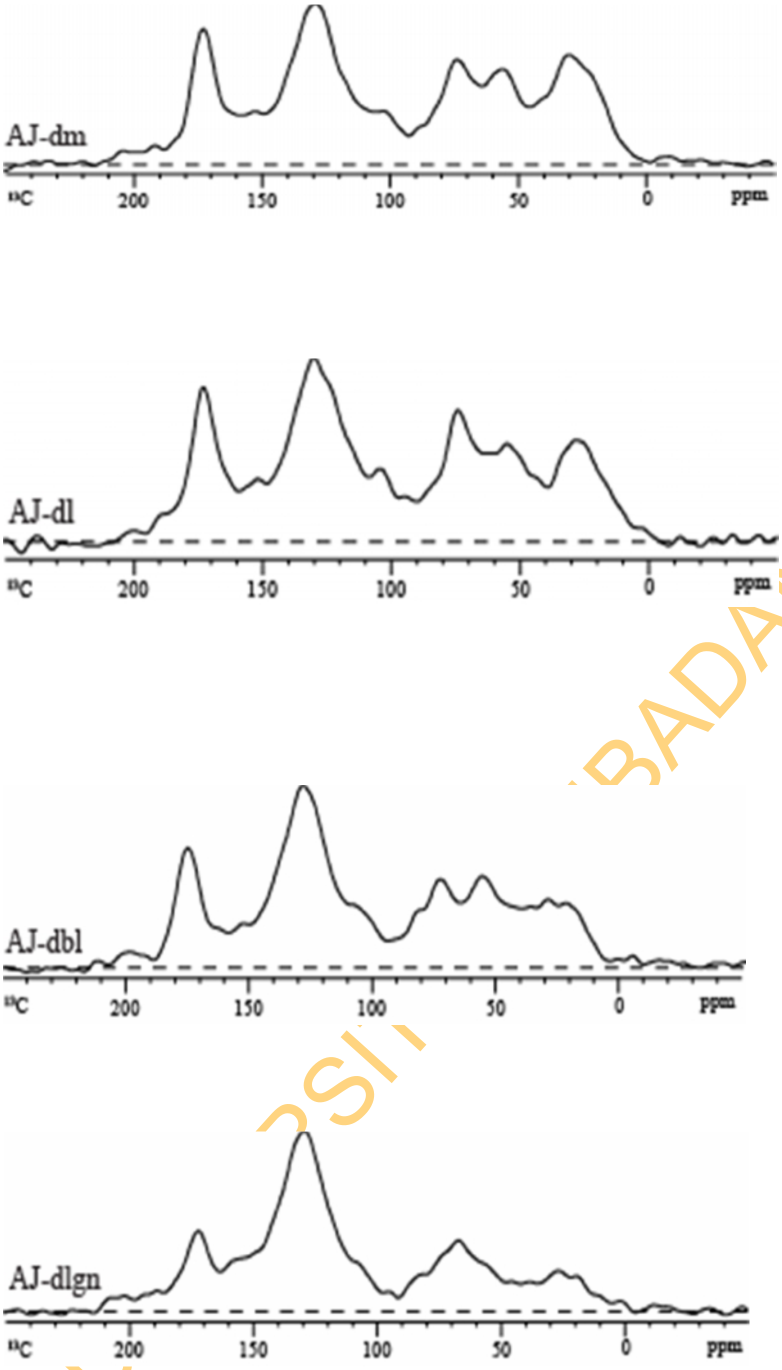


Figure 4.3: CPMAS NMR spectra of organic matter fractions in AJ soil sample

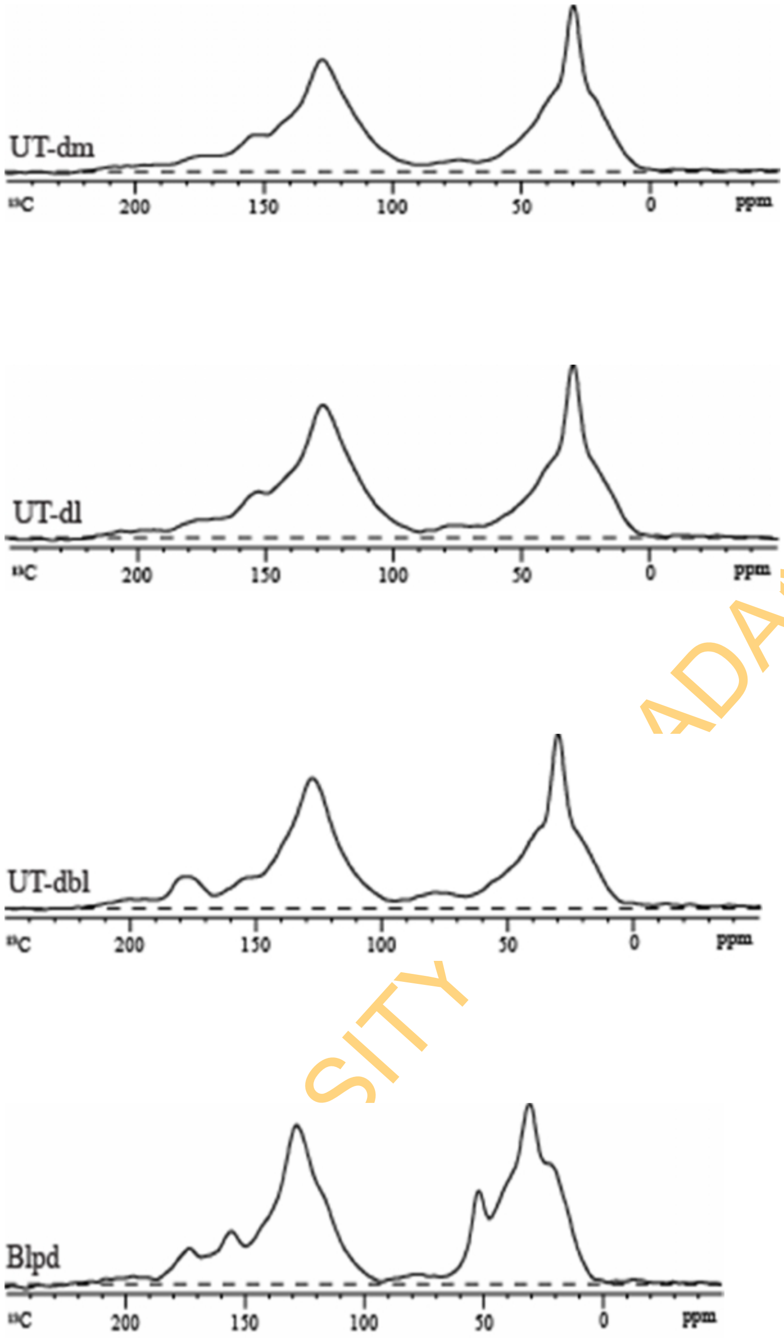


Figure 4.4: CPMAS NMR spectra of organic matter fractions in coal (sample UT)

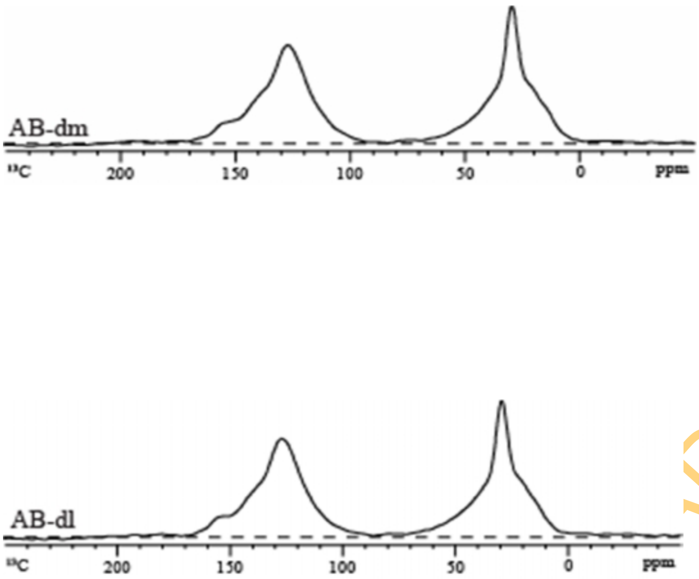


Figure 4.5: CPMAS NMR spectra of organic matter fractions in carbonaceous shale (sample AB)

Table 4.3: Skeletal carbons in the NMR Spectra of NOM fractions (dm, dl, dbl,dlgn and blpd)

| IJ (Soil) | 0-45 ppm alkyl | 45-64 ppm methoxyl | 64-94 ppm O-alkyl | 94-162 ppm aromatics | 162-190 ppm Carboxyl | 190-220 ppm Carbonyl | Aliphatic Carbons | Aromatic Carbons |
|---|---|---|---|---|---|---|---|---|
| IJ-dm | 13.2% | 5.4% | 5.3% | 68.9% | 5.8% | 1.3% | 23.9% | 68.9% |
| IJ-dl | 6.8% | 4.9% | 5.7% | 76.4% | 6.0% | 0.3% | 17.4% | 76.4% |
| IJ-dbl | 9.1% | 5.6% | 5.4% | 73.2% | 6.0% | 0.6% | 20.1% | 73.2% |
| IJ-dlgn | 5.3% | 6.0% | 5.1% | 76.6% | 5.9% | 1.0% | 16.4% | 76.6% |

| AJ (Soil) | 0-45 ppm alkyl | 45-64 ppm methoxyl | 64-94 ppm O-alkyl | 94-108 ppm DI O-alkyl | 108-160 ppm | 160-190 ppm Carboxyl | 190-220 ppm Carbonyl | 0-94 ppm Aliphatic | 94-160 ppm Aromatic |
|---|---|---|---|---|---|---|---|---|---|
| AJ-dm | 20.4% | 10.9% | 14.4% | 4.8% | 33.2% | 14.1% | 2.2% | 45.7% | 38.0% |
| AJ-dl | 17.4% | 10.5% | 15.6% | 5.4% | 34.7% | 15.1% | 1.4% | 43.5% | 40.1% |
| AJ-dbl | 16.0% | 11.2% | 13.7% | 4.8% | 38.8% | 13.8% | 1.7% | 40.9% | 43.6% |
| AJ-dlgn | 11.3% | 7.9% | 12.2% | 4.1% | 48.8% | 12.8% | 2.9% | 31.4% | 52.9% |

| AD (Soil) | 0-45 ppm alkyl | 45-64 ppm methoxyl | 64-94 ppm O-alkyl | 94-108 ppm DI-O-alkyl | 108-160 ppm | 160-186 ppm Carboxyl | 186-220 ppm Carbonyl /Ketone | 0-94 ppm Aliphatic | 94-160 ppm Aromatic |
|---|---|---|---|---|---|---|---|---|---|
| AD-dm | 22.4% | 11.7% | 15.5% | 4.8% | 30.8% | 12.1% | 2.7% | 49.6% | 35.6% |
| AD-dl | 18.1% | 11.3% | 15.7% | 5.2% | 33.8% | 13.6% | 2.4% | 45.1% | 39.0% |
| AD-dbl | 22.9% | 14.0% | 13.7% | 4.1% | 34.8% | 10.3% | 0.1% | 50.6% | 38.9% |
| AD-dlgn | 17.4% | 11.0% | 10.6% | 5.4% | 42.4% | 11.3% | 1.8% | 39.0% | 47.8% |

| AB (Rock) | 0-65 ppm | 65-93 ppm O-alkyl | 93-165 ppm aromatic | 165-190 ppm Carboxyl | 190-220 ppm Carbonyl | 0-93 ppm Aliphatic | 93-165 ppm Aromatic |
|---|---|---|---|---|---|---|---|
| AB-dm | 46.3% | 1.7% | 49.7% | 1.5% | 0.8% | 48.0% | 49.7% |
| AB-dl | 46.8% | 2.0% | 49.4% | 1.3% | 0.6% | 48.8% | 49.4% |

<table>
<tr><th>UT (Rock)</th><th>0-65 ppm</th><th>65-93 ppm O-alkyl</th><th colspan="2">93-165 ppm aromatic</th><th>165-190 ppm Carboxyl</th><th>190-220 ppm Carbonyl</th><th>0-93 ppm Aliphatic</th><th>93-165 ppm Aromatic</th></tr>
<tr><td>UT-dm</td><td>44.0%</td><td>3.5%</td><td colspan="2">46.3%</td><td>4.2%</td><td>2.0%</td><td>47.5%</td><td>46.3%</td></tr>
<tr><td>UT-dl</td><td>40.8%</td><td>3.5%</td><td colspan="2">48.9%</td><td>4.6%</td><td>2.2%</td><td>44.3%</td><td>48.9%</td></tr>
<tr><td>UT-dbl</td><td>43.1%</td><td>4.2%</td><td colspan="2">44.4%</td><td>6.3%</td><td>2.1%</td><td>47.3%</td><td>44.4%</td></tr>
<tr><td rowspan="2">UT blpd</td><td rowspan="2">47.5%</td><td rowspan="2">2.3%</td><td>93-149ppm aryl</td><td>149-168 ppmO-aryl</td><td rowspan="2">4.1%</td><td rowspan="2">1.9%</td><td rowspan="2">49.8%</td><td rowspan="2">44.2%</td></tr>
<tr><td>37.2%</td><td>7.0%</td></tr>
</table>

dm = demineralised fraction, dl = lipid free fraction, dbl = bound lipid free fraction,
dlgn = lignin free fraction, blpd = bound lipid fraction

large contribution from the alky carbon (0-45 ppm), methoxyl carbon (45-63 ppm), carbohydrate

large contribution from the alky carbon (0-45 ppm), methoxyl carbon (45-63 ppm), carbohydrate (63-93 ppm), aryl carbon (93-148 ppm), carboxyl carbon (165-187 ppm) and small contribution from O-aryl carbon (148-165 ppm) and minor contribution from carbonyl carbon (187-220 ppm). Lipid free fractions from two soils also showed large contribution from alky carbon (0-45 ppm), methoxyl carbon (45-63 ppm), carbohydrate (63-93 ppm), aryl carbon (93-148 ppm), carboxyl carbon (165-187 ppm) and small contribution from O-aryl carbon (148-165 ppm) and minor contribution from carbonyl carbon (187-220 ppm). Also, bound-lipid free fractions from the soils showed large contribution from aryl carbon (93-148 ppm), carboxyl carbon (165-187 ppm) and small contribution from alkyl carbon (0-45 ppm), methoxyl carbon (45-63 ppm), carbohydrate (63-93 ppm), O-aryl carbon (148-165 ppm) and little or no contribution from carbonyl carbon (187-220 ppm). While lignin free fractions from the two soils equally showed large contribution from aryl carbon (93-148 ppm), small contribution from alkyl carbon (0-45 ppm), methoxyl carbon (45-63 ppm), carbohydrate (63-93 ppm), O-aryl carbon (148-165 ppm), carboxyl carbon (165-187 ppm) and minor contribution from carbonyl carbon (187-220 ppm).

The NMR spectra from soil sample IJ revealed that all its residual organic matter fractions (demineralised, lipid free, bound-lipid free and lignin free) are characterised by large contribution from aryl carbon (93-148 ppm) with other functional groups differentiating one fraction from another. The demineralised fraction from the soil is dominated by large contribution from aryl carbon (93-148 ppm), very small contribution from alkyl carbon (0-45 ppm), and minor contribution from other functional groups. The lipid free and bound-lipid free fractions are characterised by minor contribution from all other functional groups in addition to a large contribution from aryl carbon (93-148 ppm). While the lignin free fraction of the soil is characterised by large contribution from aryl carbon (93-148 ppm), very small contribution from methoxyl carbon (45-63 ppm) and minor contribution from all other functional groups.

The spectra of the residual organic matter fractions from two soils (samples AD and AJ) show strong similarities and they are totally different from those of the soil sample IJ (Figures 4.1 to 4.3). This is because the two soils have strong resemblance in all the spectra of their residual organic matter fractions, thus suggesting that the two soils have similar organic matter properties.

Despite the observed differences in the properties of some of the NOM fractions from the soils and rocks, there are general similarities in the properties of the residual organic matter fractions in the samples with respect to their properties after extracting a particular component from them. For instance the spectra of lipid free fractions showed loss of alkyl carbon (0–45 ppm) compared to the spectra of their demineralised fractions in all the soils and rocks samples because the lipid fractions are composed essentially of alkyl carbon (0-45 ppm). Also, the spectra of bound-lipid free fractions in the coal and the soils are characterised by an increase in the contribution of carboxyl carbon (165-187 ppm) compared to the lipid free fractions. This shows that the contribution of carboxyl carbon (165-187 ppm) is quite significant in bound-lipid free fractions.

### 4.1.3High Performance Liquid Chromatography (HPLC) Results

The concentrations of the phenanthrene inthe initial aqueous solutions andthose of the equilibrated aqueous solutions after sorption experiment determinedby High Performance Liquid Chromatography Instrument are presented inthe appendices.All concentrations are given in ppb. The concentration of phenanathrene inthe equilibrated solution is the actual phenanthrene remaining in the solution after absorption by the geosorbents (organic matter fractions). Also, the concentration of phenanathrene in initial aqueous solution is thequantity of phenanthrene before sorption experiments. Therefore, a comparison of the phenanthrene concentrations in the initial aqueous solutions and those of the equilibrated aqueous solutions shows the concentration of the phenanthrene absorbed by the bulk samples and their NOMfractions. The phenanthrene concentrations in blank ampoules are also shown in appendices.

### 4.1.4Sorption Results

The modelled results of thesorption experiment regarded as sorption isothermparameters are presentedin Table 4.4. The entire sorption isotherms for phenanthrane on all the samples subjected to sorption experiment were nonlinear ($n<1$) and well fitted by the Freundlich equation (Table 4.4). The table equally showsthe single-point organic carbon-normalised distribution

Table 4.4: Sorption Isotherm Parameters and Single-point Organic Carbon Normalised Distribution Coefficient (Koc) Values for bulk samples and NOM fractions (dm, dlpd, dblpd, dlgn, blpd).

| | | | | | | | $K_{OC}$ (mL/g) | | |
|---|---|---|---|---|---|---|---|---|---|
| **Sample** | **log $K_F$** | **N** | **N[a]** | **$R^2$** | **$K_{FOC}$[b]** | **log$K_{FOC}$** | **Ce=0.005Sw** | **Ce=0.056Sw** | **Ce=0.56Sw** |
| **AJ bulk** | **-0.007** | **0.62** | **19** | **0.997** | **107** | **2.03** | **751** | **316** | **133** |
| **AJ dm** | **1.618** | **0.68** | **19** | **0.998** | **149** | **2.17** | **787** | **376** | **179** |
| **AJ dlpd** | **2.013** | **0.57** | **18** | **0.997** | **379** | **2.58** | **3619** | **1329** | **488** |
| **AJ dblpd** | **1.241** | **0.61** | **20** | **0.992** | **86** | **1.94** | **651** | **265** | **108** |
| **AJ dlgn** | **2.653** | **0.41** | **17** | **0.992** | **2951** | **3.47** | **63217** | **16212** | **4158** |
| | | | | | | | | | |
| **AD bulk** | **0.082** | **0.63** | **19** | **0.997** | **114** | **2.06** | **780** | **332** | **141** |
| **AD dm** | **1.616** | **0.72** | **19** | **0.997** | **131** | **2.12** | **570** | **296** | **154** |
| **AD dlpd** | **1.986** | **0.60** | **16** | **0.998** | **333** | **2.52** | **2663** | **1058** | **420** |
| **AD dblpd** | **1.233** | **0.52** | **19** | **0.993** | **185** | **2.27** | **2209** | **735** | **244** |
| **AD dlgn** | **2.243** | **0.52** | **16** | **0.994** | **855** | **2.93** | **10459** | **3440** | **1131** |
| | | | | | | | | | |
| **IJ bulk** | **1.418** | **0.52** | **19** | **0.991** | **259** | **2.41** | **3133** | **1035** | **342** |
| **IJ dm** | **1.848** | **0.64** | **18** | **0.994** | **112** | **2.05** | **733** | **318** | **138** |
| **IJ dlpd** | **2.736** | **0.46** | **16** | **0.994** | **835** | **2.92** | **14084** | **4015** | **1145** |
| **IJ dblpd** | **2.803** | **0.39** | **15** | **0.993** | **1161** | **3.06** | **28751** | **6913** | **1662** |
| **IJ dlgn** | **2.826** | **0.51** | **17** | **0.99** | **1026** | **3.01** | **13287** | **4260** | **1366** |
| | | | | | | | | | |
| **AB bulk** | **2.317** | **0.49** | **13** | **0.998** | **1501** | **3.18** | **21241** | **6549** | **2019** |
| | | | | | | | | | |
| **UT bulk** | **2.418** | **0.61** | **20** | **0.994** | **426** | **2.63** | **3305** | **1331** | **536** |
| **UT dm** | **2.597** | **0.69** | **18** | **0.996** | **581** | **2.76** | **2883** | **1416** | **695** |
| **UT dlpd** | **2.738** | **0.68** | **18** | **0.997** | **810** | **2.91** | **4345** | **2061** | **977** |
| **UT dblpd** | **2.134** | **0.71** | **18** | **0.996** | **268** | **2.43** | **1227** | **625** | **318** |
| **UT blpd** | **1.517** | **0.86** | **20** | **0.994** | **48** | **1.68** | **97** | **71** | **52** |

**[a] The number of observations**
**[b] $K_{FOC}$ = $K_F$/OC%**
**n = nonlinearity**
**$K^F$ = Freundlich capacity parameter**
**$R^2$ = coefficent of correlation**
**Ce = liquid phase concetration**
**Sw = water saturation**
**Koc = organic carbon distribution coeeficient**

coefficients$K_{oc}$ ($K_{oc} = q_e/C_e f_{oc}$)) in units of mL/g OC calculated at $C_e/S_w$ = 0.005, 0.05, and 0.5 for phenanthrene, in where $f_{oc}$ and $S_w$ are organic carbon content and phenanthrene solubility respectively.

## 4.2 Discussion

### 4.2.1 Properties of the Natural Organic Matter fractions

#### 4.2.1.1 Elemental Properties

The elemental results and organic carbon distribution in the NOM fractions (Tables 4.1 to 4.2) of the studied samples indicated that the rocks generally have higher concentrations of organic matter than the soils except for the two soils with 7.21 % and 10.12 % total organic carbon respectively. Primary deposition of organic matter is associated with the sedimentary rocks, while soils andgeologically younger sediments derived their organic matter from reworked and eroded kerogen from the rocks as a result of natural and man made processes(Allen-King et al., 1997; Ran et al., 2003a, 2003b).Since soilsare exposed to oxygen, their organic matter can be easily decomposed or leached away to nearby streams and rivers. Organic carbon distribution (Table 4.2) in the deminrealised fractions of the soils and rocks also indicates that the rocks contained higher percentage of organic matter.

The total organic carbon measured for the bulk rocks showed that the coal and the carbonaceous shale have higher TOC values (61.42 and 13.82 % respectively) while the mudstone and shale have comparatively lower TOCs (3.82 % and 1.27 % respectively). The coal sample in this study contained abundant palynomorphs (plant fossils) as reported by the study of Ola-buraimo and Adeleye (2010), thus indicating its higher organic matter content.Carbonaceous rocks (coal and carbonaceous shale) are generally known with higher TOCs ((Hunt, 1984; Tissot and Welte, 1984; Cornelissen et al., 2005).

Table 4.1 (elemental results)shows that the bound-lipid free fractions have the lowest organic carbon and the highest oxygen contents among the residual fractions, andtheaverage organic carbon of the extracted lipid and bound-lipid fractions from the soils and rocks are 71.86 % and

55.68%, 70.25 % and 60.13 % respectively. While the extracted lignin fraction from the soil contained 57.23% organic carbon and1.15 % nitrogen averagely.

Organic carbon distribution (Table 4.2)in lipid fractions extracted from thesoils range from 5.08 to 12.04 % (average 8.20%)except sample ABG with 30.63 %.Thelipid contents in thesoil samples are quite close to the lipid contents of SOM(4-8 %) reported by Lichtfouse et al. (1997). Therefore exceptionally higher lipid content of thesample ABG may be due to anthropogenic influence since lipid is also known to have anthropogenic origin (Gregorich et al., 1996; Lichtfouse et al., 1997). The possibility of contamination inthe soil sample was supported by the fact that Parsons et al. (1961) reported that lipid only accounted for 5-20% of the organic carbon in eleven phytoplankton species harvested during their exponential phase of cultural growth in the North Pacific. Therefore lipid content (30.63 %) in thesoil sample ABG must have been contaminated by lipid containing materials such as crude oil extracts, fats, wax excetrasincethe soil samplewas collected from a location where activities related to transportation and discharge of refined petroleum products by heavy trucks and tankers are prominent.

Table 4.2 shows that organic carbon content of bound-lipid components of the SOM are smaller than the lipid components. It was observed that where lipid content is high the bound-lipid content is also high, though the sample with the highest lipid fraction did not have the highest bound-lipid fraction. Total lipid extracts has been described as combination of lipids and bound-lipids Bee (1999).Table 4.2 further revealed that 4 out 5 lignin fractions extracted from the soils accounted for 1.37% to 7.46% of the SOM (average 3.81 %). This implies that lignin content of the soil organic matter is small. The soil sample AJwith lignin component of 15.29 % however, may suggests contamination with lignin derived materials possibly from higher plants materials and wasteproducts from wood processing industries.

Theatomic H/C and O/C ratios of the residual organic matter fractions(including demineralised, lipid free and bound-lipid free) from the rocks are consistently lower than those from the soils (Table 4.1). This indicates that the residual organic matter fractions from the rocksare more condensed than their counterparts from the soils.Although there was insignificant difference in the atomic H/C and O/C ratios between the demineralised fractions and lipid free fractions in the rocks after extracting the lipid fractions, the difference was significant betweenthe lipid free and bound-lipid free fractions after bound-lipid extraction, such that the atomic O/C ratios of the bound-lipid free fractions is twice as large as that of thelipid free fractions or even more (Table 4.1). The higher O/C atomic ratios in the bound-lipid free fractions indicate high polarity. Since the degree of maturation is a function of decreasein atomic H/C and O/C ratios,thebound-lipid free fractions have the lowest degree of maturation while the lipid free fractions havethe highest degree of maturation among the residual organic matter fractions in the rocks.Therefore the degree of maturation of the residual fractions in the rocks follows the order dlpd>dm>dblpd.

The atomic H/C and O/C ratios of the bulk soils show similar trend as observed in the residual organic matter fractions from the rocks (Table 4.1)such that the atomic H/C ratios of the lipid free fractions decrease slightly from those of the demineralised fractions while atomic O/C ratios increase slighty (Table 4.1). The extraction of bound-lipid fractions also causes a significant increase in the atomic H/C and O/C ratios (Table 4.1). On the other hand, the atomic H/C and O/C ratios decrease significantly after extracting the lignin fractions, such that they are as low as those of the demineralised fractions or even lower (Table 4.1). This shows that the atomic H/C and O/C ratios of the residual organic fractions in the soils follow the order dblpd>dm>dlpd>dlgn. Therefore, the lignin free fractions with the lowest atomic H/C and O/C ratios from the soils have the highest degree of maturation and are the most condensed. The bound-lipid freefractions with the highest atomic H/C and O/C ratios on the other hand have the lowest degree of maturation and are the least condensed. The bound-lipid free fractions have been described as high polarity materials because of their associated higher O/C ratios.

In addition, the atomic O/C ratios of the lignin free and lipid free fractions are lower than the average of 0.53 reported for typical humic substance extracted from soils and sediments (Wang and Xing, 2007) while those of the bound-lipid free fractions are higher than the average for humic substances. This shows that the lignin free and lipid free fractions from the soils in this study are more condensed than humic substances while bound-lipid fractions are less condensed than humic substances. Considering, the average atomic O/C ratios of 0.25 and 0.20 reported fornonhydrolysable carbon (NHC) from 6 sediments and 3 soils respectively (Ran et al., 2007a), the average O/C ratios of the lignin free and lipid free fractions in this study are slightly higher than the average O/C ratio of the NHC reported from the sediments and soils (Table 4.1). The closeness of their averages and almost equal values of O/C ratios in the NHC and some of the lignin free and lipidfree fractions implied that these fractions can be likened to kerogen isolatesas reported by Ran et al.(2007a) and Sun et al. (2008).

#### 4.2.1.2 NMR Properties

The NMR spectra for the selected samples revealed that there are similarities in the property of the residual organic matter fractions from the rocks and soils (Figures 4.1 to 4.5). The spectra further revealed that the residual organic matter fractions from the rocks (samples UT and AB) are totally different from those of the soils (samples IJ, AD and AJ). Also, the NMR spectra from soil sample IJ soil are totally different from the spectra of soil samples AD and AJ (Figures 4.1 to 4.3). This suggests that the studied soils display two major trends or organic matter types. There is also a consistent trend in the loss of particular group of skeletal carbons from the residual organic matter fractions from the soils and the rocks as more and more different organic matter components are extracted, despite differences in the organic matter properties of the samples (Figures 4.1 to 4.5).

Table 4.3 alsoshowsthat aliphatic carbon decreases in lipid free fractions while its aromatic carbon increases. This is because the extracted lipid fractions are mainly composed of aliphatic carbon hence the reduction in the aliphatic carbon of lipid free fractions while the aromatic carbon increases because of the system readjustment to loss of aliphatic carbon. In some of the samples, it was also observed in some of the samples that the aliphatic carbon of the bound-lipid free fractions increases after extracting bound-lipid while its aromatic carbon decreases. This is because bound-lipid fractions are composed of O aryl carbon of the aromatic carbon in addition to some aliphatic carbonsuch that its removal has caused an increase in carboxyl carbon of the residual fraction thus, leading to increased polarity of the bound-lipid free fractions. The spectra of the bound-lipid fraction in the coal sample also revealed the presence of aliphatic and aromatic carbons in the bound-lipid fraction (Figure 4.4 and Table 4.3). In the case of lignin free fractions, their aromatic carbon increases after extracting lignin fractions while their aliphatic carbon also decreases (Table 4.3). This is due to the fact that lignin fractions are composed of hydroxyl carbon and aryl carbon such that their removals introduce some methoxyl carbon and carbonyl carbons to the residual fraction. Their increasing aromaticcarbon is due to internal readjustment of the organic matter fractions sequel to reduction in aliphatic carbon.

The NMR results generally revealed that with progressive extraction of organic components from the soils, the aliphatic carbon decreases while the aromatic carbon increases such that the highest aromaticity and the lowest aliphaticity is attained in the lignin free fractions. However, there is an exception to this trend in the bound-lipid free fractions becausethe aliphatic carbon increases while the aromatic carbon decreases after extractingbound-lipid fraction, and this is contrary tothe observed trend with extraction of other organic components. Similar trend is also observed from the residualorganic matter fractions in the coal (sample UT)because the aliphatic carbon decreases and aromatic carbon increases with progressive extraction except for bound-lipid free fraction (Table 4.3). Therefore, lignin free fractions have the highest aromatic carbons and the lowest aliphatic carbons among residual organic matter fractions in the soils while lipid free fraction has the highest aromatic carbons and lowest aliphatic carbons among residual fractions in the coal sample. Also, the demineralised fractions have the lowest aromatic carbons and highest aliphatic carbons in the soils whilebound-lipid free fraction has the lowest aromatic carbon and nearly the highest aliphatic carbon in the coal sample (Table 4.3).

Since the lignin free fractions have the highest degree of maturation and the highest aromatic carbons in any given soil sample, and the lipid free fraction has the highest aromatic carbonsand highest degree of maturation in the coal sample, it therefore follows that aromatic carbon is directly related to degree of maturation within the residual organic matter fractions in the coal and soil samples. Therefore the higher the aromatic carbon contentwithin the organic matter fractions in a given coal or soil sample, the higher the degree of maturation.

### 4.2.2 Contamination Indices

The range of TOC values for the bulk soils (Table 4.1) revealed that some of the soils have high organic matter content. Since these soils are clayey sands and sandy soils, they may not be expected to have such higher organic matter content. The elemental results also revealed that the nitrogen contents are also high in some of the bulk soils (Table 4.1). This is equally unexpected of clayey sands or sandy soils. Higher organic carbon and nitrogen contents in the bulk soils may therefore indicate contamination. It is particularly interesting to note that the two bulk soils with about the highest TOC values also have about the highest nitrogen values (Table 4.1). Therefore, the observed organic carbon and nitrogen values from the soils are due to contamination. The contamination may probably results from human household waste, petroleum products, excetra since the soils samples were collected from a commercial centre with a lot of human activities. Table 4.1 also showed that the atomic C/N ratios of the bulk soils are highly varied and since the soils are generally similar (sandy soils to clayey sands), such wide variability is not expected. Higher atomic C/N ratios in some of the bulk soils strongly indicate contamination influence. The soils withhigher C/N ratios are also characterised by higher TOC and nitrogen values, hence can be regarded as contaminated soils. The values of atomic C/N ratios in four (4) of the seven (7) soils are higher than the typical C/N values of 6-10 reported for most sediments(McGroddy and Farrington, 1995; Wang et al., 2001) indicating that the organic matter in those soils was influenced by anthropogenic sources.Also, the soils are generally similar in nature;therefore tangible differences may not be expected in the NMR spectra of their organic matter. Therefore, IJ soil with characteristically different spectra from other soils may be considered as contaminated soil. Moreso, that its organic carbon and atomic C/N ratio are much higher than others.

However, the atomic C/N ratios in the bulk rocks (Table 4.1) are not related to contamination but perhaps to the properties and process of rock formation. The atomic C/N ratios of59.22, 49.86, and 16.46for bulk coal, carbonaceous shale and shale respectively indicated that were formed under similar environmental conditions, while the atomic C/N ratio of 4.02for the mudstone may indicate formation under a different environmental condition (Meyers, 1994). The NMR spectra of organic matter fractions from coal and carbonaceous shale also indicated that the rocks have similar organic matter formed under similar environments.

### 4.2.3 Organic matter Characterisation

The organic matter fractions from the soils and rocks are characterised by high percentage of H/C atomic ratios and low percentage of O/C atomic ratios (Table 4.1).Since the demineralised fractions represent the bulk of the organic matter after the inorganic materials have been removed, the demineralised fractions therefore containedthe bulkorganic matter in the rocks and soils. Van Krevelen plot (Figure 4.6) ofH/C and O/C atomic ratios from the demineralised fractions of the rocks and soils shows that the organic matter contained in the rocks is type III kerogen, and type II to III in the soils. This showsthat sedimentary rocks contain relatively stable organic matter that has been modified with time and burial. The soil organic matter shows variation in their source and type of organic matter perhaps because ofcontamination by different materials (organic and inorganic). The atomic H/C and O/C ratios (Figure 4.7) of the extracted organic matter fractions (lipid, bound-lipid and lignin) have also shown their closeness to similar extracts from sediments (Zhang et al., 2013),

Furthermore, C/N atomic ratios have also been used to distinguish between algal and terriginous plant origins of organic matter in shallow sediments and thermally immature sedimentary rocks (Silliman et al., 1996). Algae and vascular plants generally show atomic C/N ratios of 4-10 and >20 respectively (Meyers, 1994). Therefore the C/N ratios of the bulk rocks (Table 4.1) show that the organic matter in the coal and carbonaceous shale (samples UT and AB) are composed of terriginous or vascular plants remains while the organic matter in the mudstone sample (MDT) is made up of algal materials. Though, C/N ratio of the shale (sample SH) is less than 20 (Table 4.1) but its proximity to 20 indicates that the organic matter in the rock is from terriginous origin. The C/N ratio of the demineralised fraction of the shale sample also indicated organic matter of terriginious origin.

The NMR spectra show that the organic matter fractions from the rocks bear no similarities to those of the soils (Figure 4.8). Also, there are similarities in the NMR spectra of organic matter fractions from the rocks (Figure 4.8), despite the differences in the physical properties of the two rocks. Even with the differences in properties of the organic matter from the soils, none of the NMR spectra from the soils bear close similarities to those of the rocks (Figure 4.8). This further

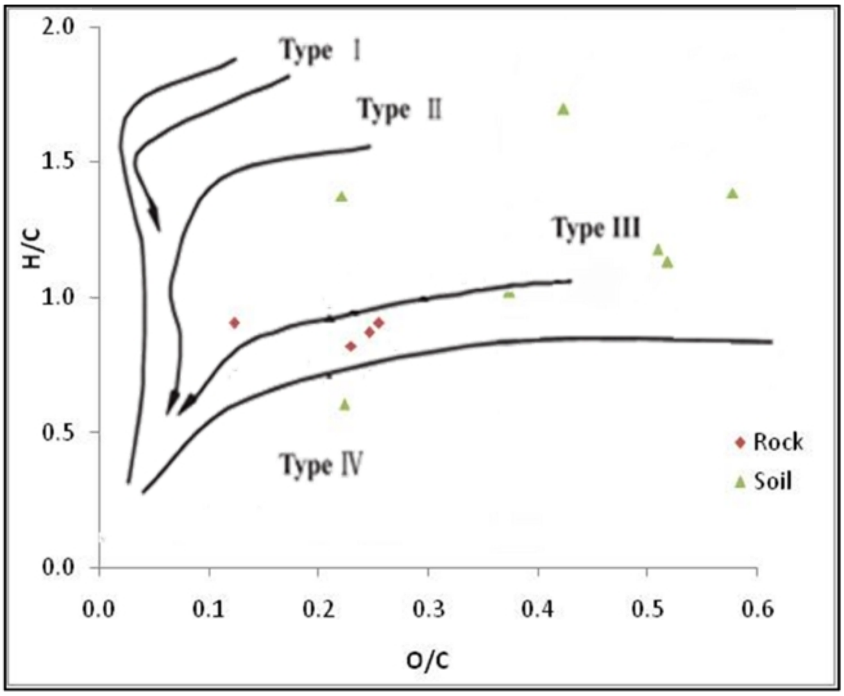


Figure 4.6: Van Krevelen plot showing organic matter type in the demineralised organic matter fractions from rocks and soils

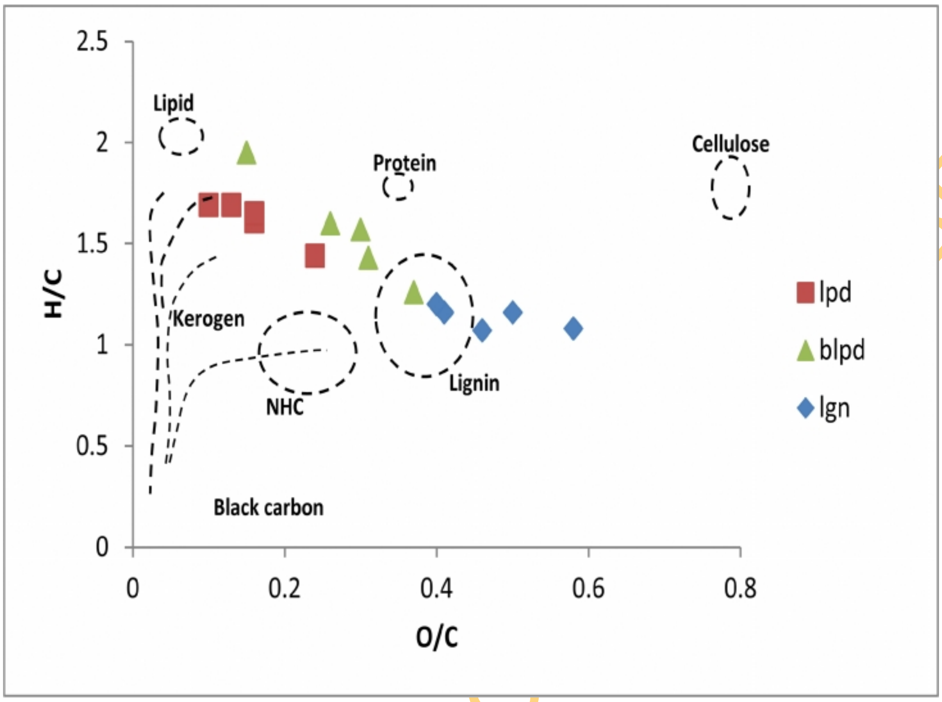


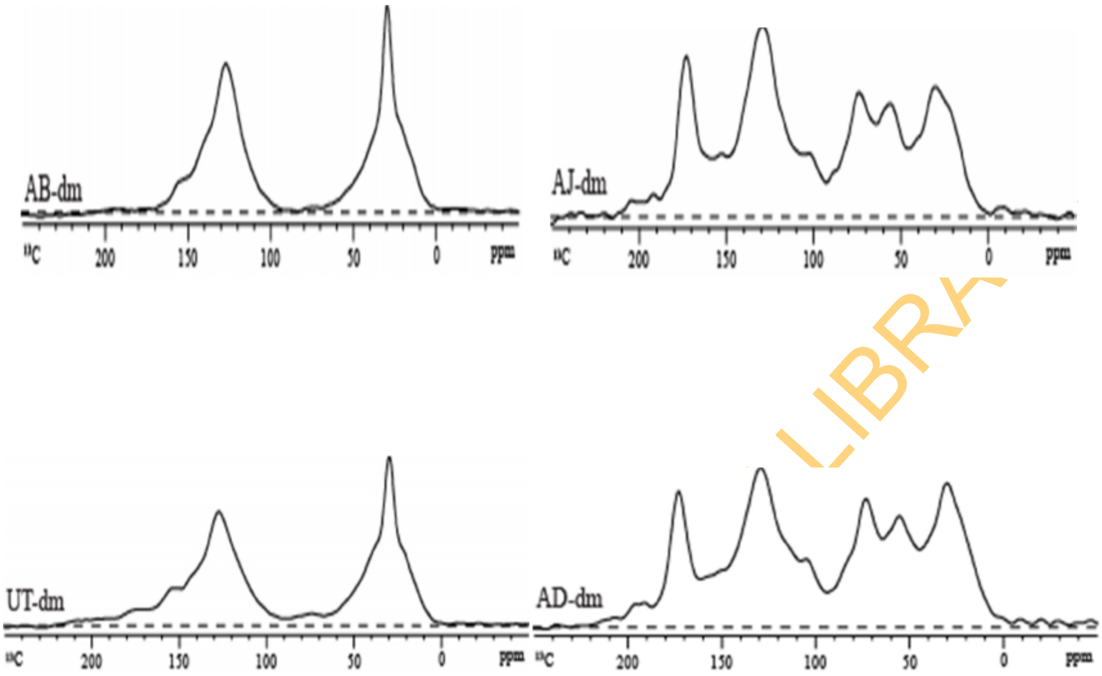
Figure 4.7: Van Krevelen plot of the extractedfractions showing resemblance to similar extracts.

confirms that the sedimentary organic matter is quite different from the young and recent soil organic matter.

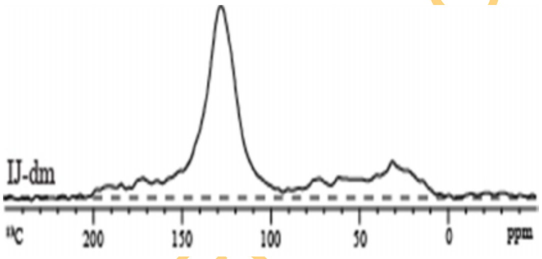
### 4.2.4 Sorption Isotherms

The data presented in Table 4.4 and Figures 4.9 to 4.13 indicated that all of the measured sorption isotherms for phenanthrene on the bulk samples and their organic matter fractions (including dm, dlpd, dblpd, dlgn and blpd) examined in this study are nonlinear and well fitted by the Freundlich equation. The *n* values in the bulk soil samples range from 0.52 to 0.63, while those of their demineralised and lipid free fractions vary from 0.64 to 0.72 and 0.46 to 0.60 respectively (Table 4.4). Also the *n* values of the soils' bound-lipid free and lignin free fractions range from 0.39 to 0.61 and 0.41 to 0.52 respectively (Table 4.4). The *n* values for bulk coal and carbonaceous (samples UT and AB) are 0.61 and 0.49 respectively, while for the coal's demineralised, lipid free, bound-lipid free and bound-lipid fractions are 0.69, 0.68, 0.71 and 0.86 respectively. The nonlinearity factor *n* is related to sorption site energy distribution and has also been related to heterogeneous glass, hard, or condensed NOM domain and to maturation degree of natural organic matter (Xiao et al., 2004; Ran et al., 2002, 2003a; Karapanagioti and Sabatini, 2000; Xing et al., 1996; Pignatello and Xing, 1996; Weber et al., 1992). The lower the *n* value, the more heterogeous is the sorption site energy distribution or the higher is the maturation degree of natural organic matter (Weber et al., 1992; Pignatello and Xing, 1996; Xing et al., 1996).

The lignin free (dlgn) fractions have the lowest*n* value compared to any other residual organic matter fractions from the soils generally except in the sample IJ (Table 4.4). This indicates that the lignin free fractions in these soils have the highest degree of maturation. Bound-lipid free (dblpd) fraction has the lowest *n* value in the IJ sample (Table 4.4), suggesting that it has the highest degree of maturation compared to other residual organic matter fractions. The nonlinearity (n) of the bulk coal sample is lower than those of its residual organic matter fractions (Table 4.4). Lipid free fraction has the lowest *n* value among the residual organicmatter fractions in the coal (sample UT) while bound-lipid free fraction (dblpd) has the highest *n* value. This shows that the lipid free fraction has the highest degree of maturation while the bound-lipid



Rocks



Soils

Figure 4.8: NMR spectra of the demineralised organic matter fractions from the rocks and soils showing the differencesbetween their organic matter properties

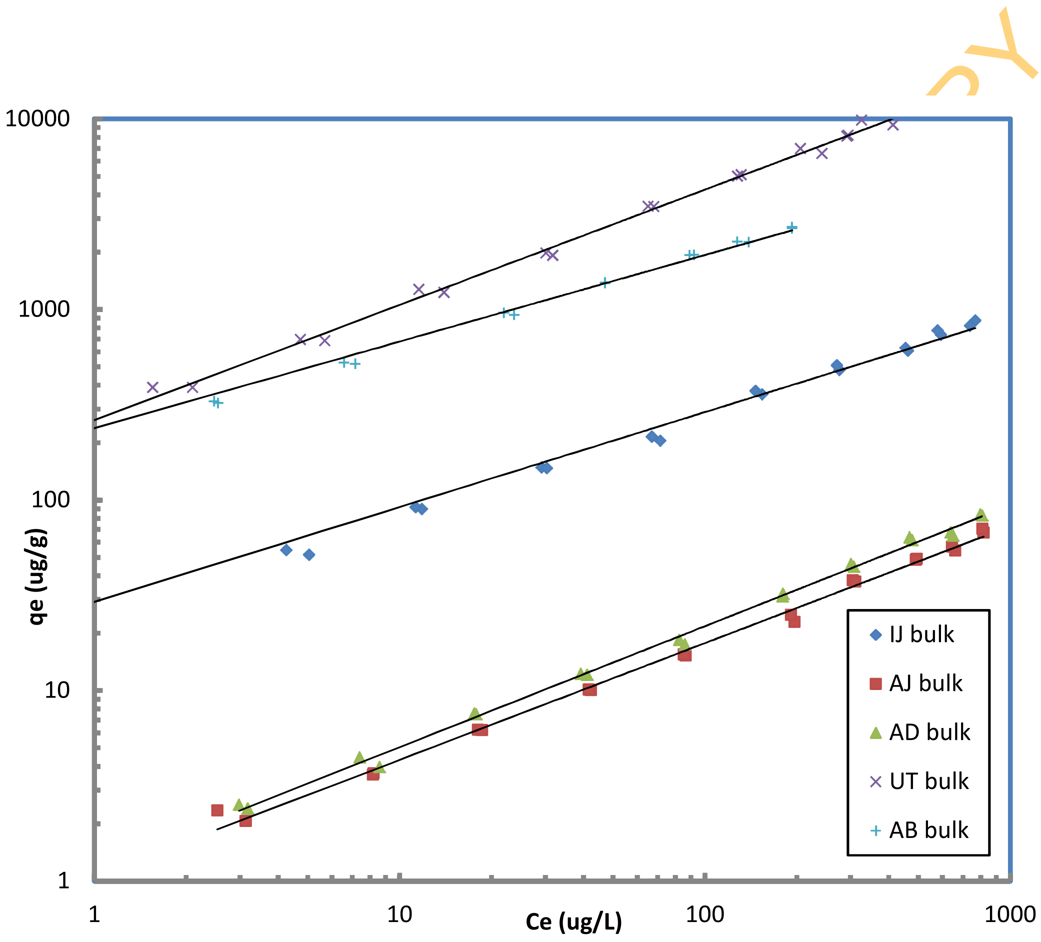


Figure 4.9: Sorption isotherm data and their fitting to freundlich equation line for bulk samples

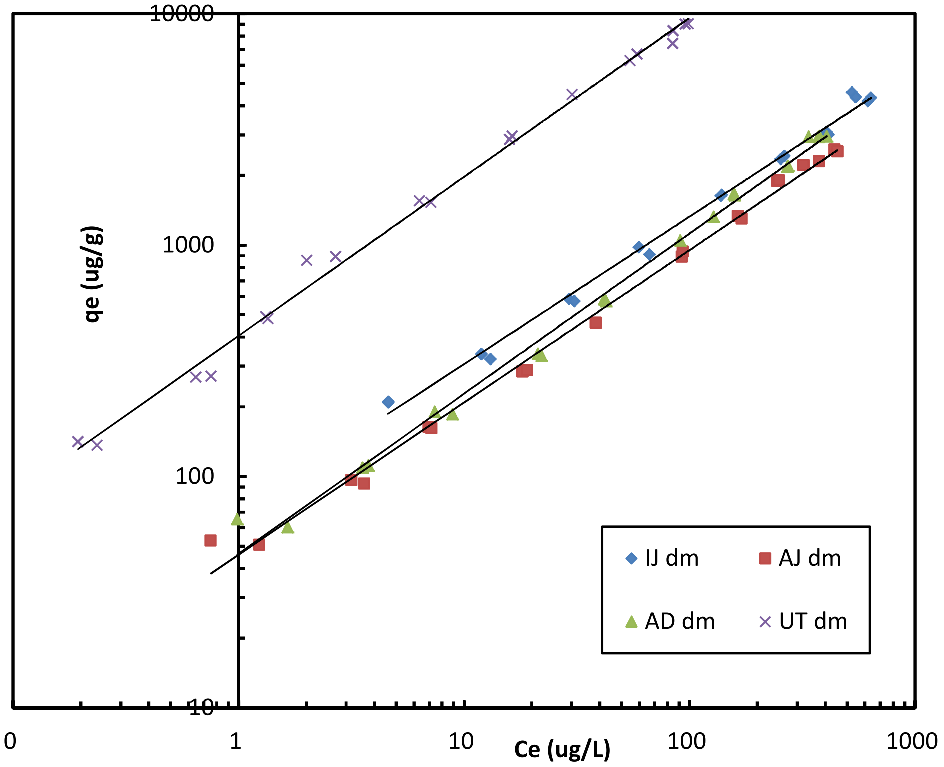


Figure 4.10: Sorption isotherm data and their fitting to freundlich equation line on demineralised (dm) fractions

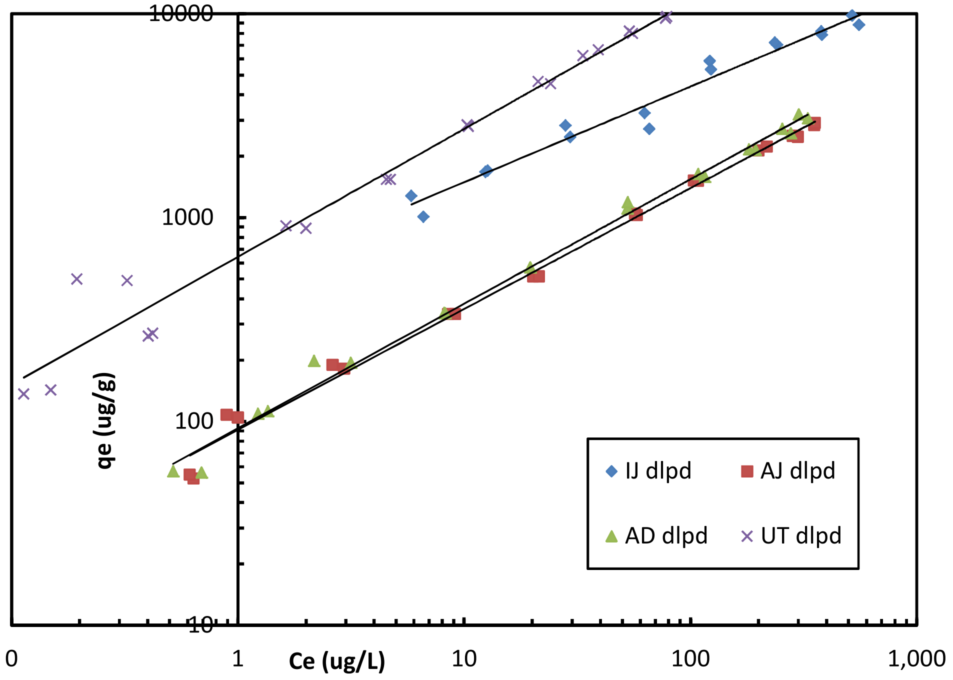


Figure 4.11: Sorption isotherm data and their fitting to freundlich equation line on lipid free (dlpd) fractions

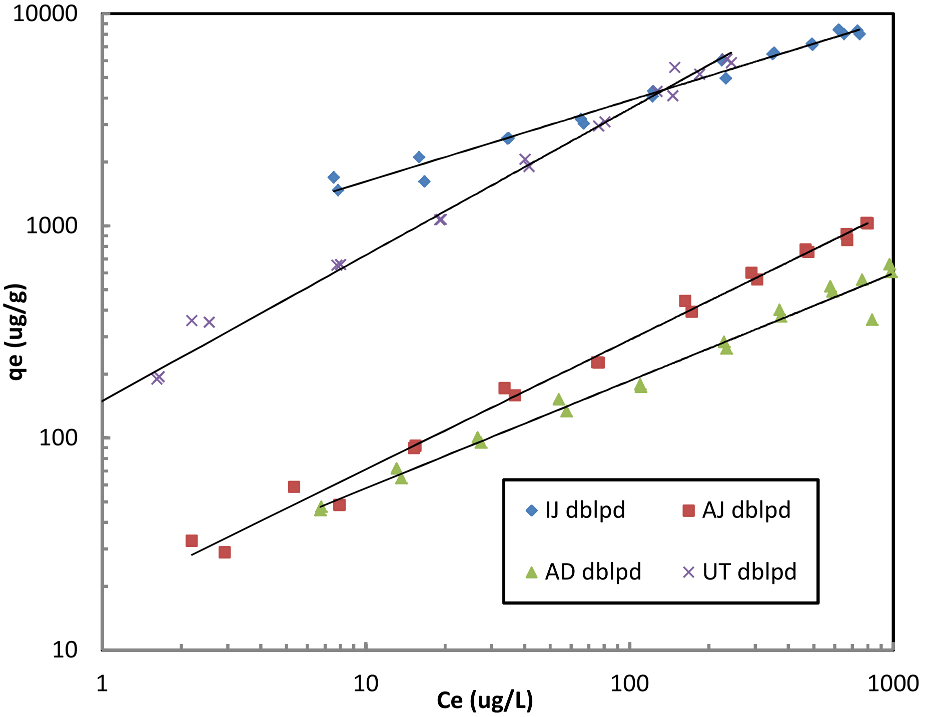


Figure 4.12: Sorption isotherm data and their fitting to freundlich equation line on bound lipid free (dblpd) fractions

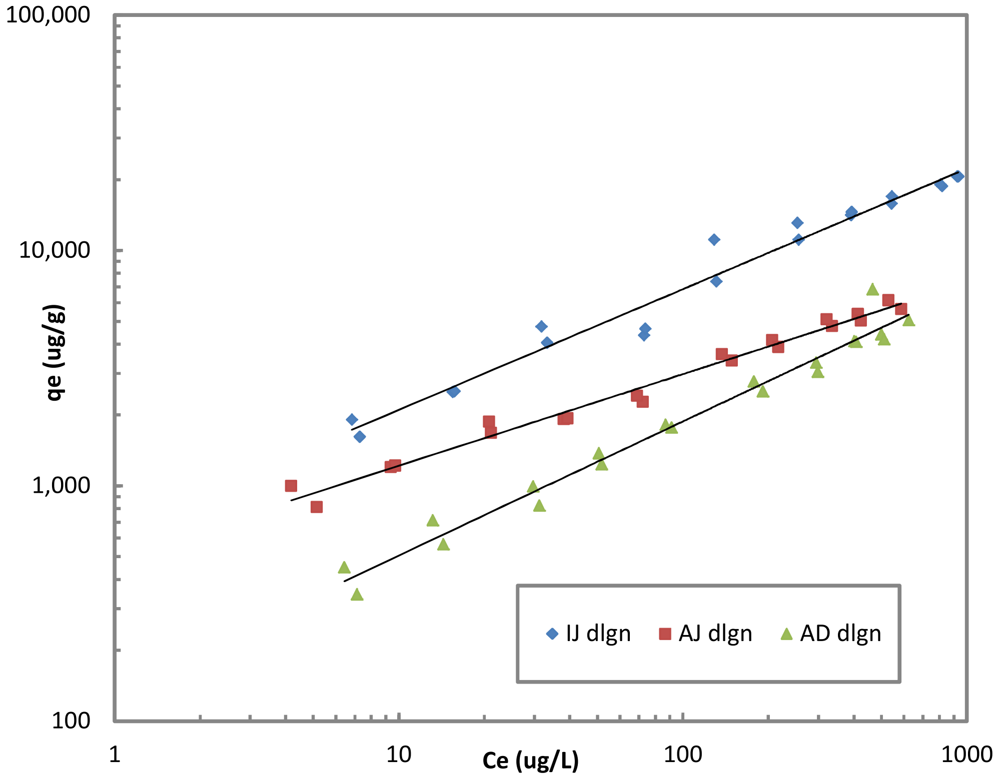


Figure 4.13: Sorption isotherm data and their fittings to Freundlich equation line on lignin free(dlgn) fractions.

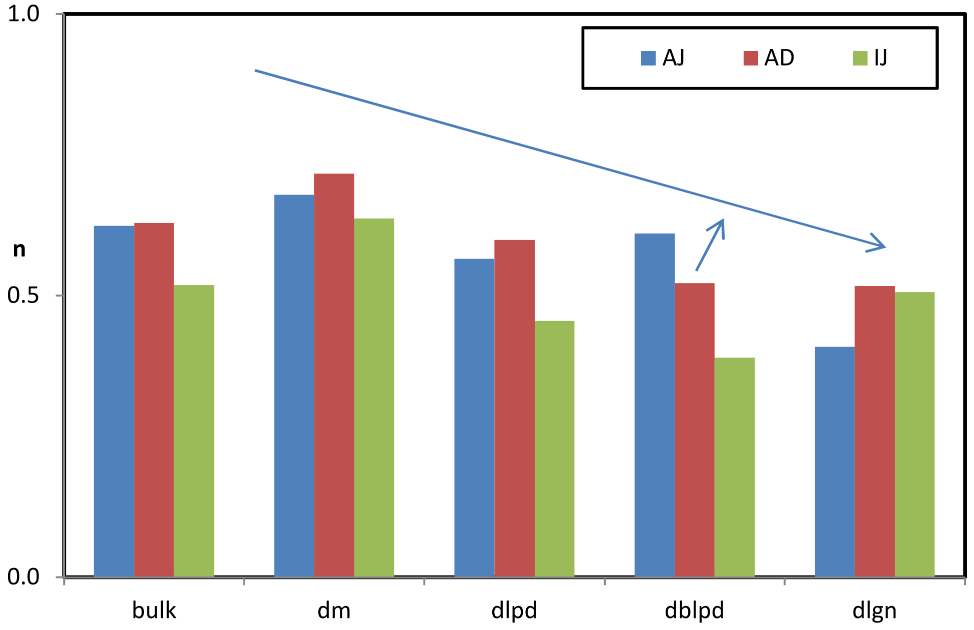


Figure 4.14: Diagram showing nonlinearity (n) value for phenanthrene sorption isotherm for the bulk soils andresidualorganic matter fractions

free fraction has the lowest degree of maturation. Therefore nonlinearity increases with progressive extraction in the coal and soil samples AJ and AD except for their bound-lipid free (dblpd) fractions (Table 4.4 and Figure 4.14).However, nonlinearity increases with extraction of lipid and bound-lipid and decreases with extraction of lignin in IJ sample, (Table 4.4 and Figure 4.14).

The OC-normalized Freundlich sorption capacity values (log $K_{FOC}$) range from 2.03 to 2.41, 2.05 to 2.17, 2.52 to 2.92, 1.94 to 3.06 and 2.93 to 3.47 (ug/g OC)/(ug/L)$^n$ for the bulk soil samples, their demineralised, lipid free, bound-lipid free and lignin free fractions respectively (Table 4.4). Also, the bulk coal (sample UT), its demineralised, lipid free, bound-lipid free and bound-lipid fractions have log $K_{FOC}$ value of 2.63, 2.76, 2.91, 2.43 and 1.68 respectively. The bulk carbonaceous shale (sample AB) has log $K_{FOC}$ value of 3.18 (Table 4.4). Previous investigation by Cornelissen et al. (2005) shows that log $K_{FOC}$ values range from 2.4 to 4.1, 1.7 to 3.8, and 2.5 to 3.5 for the sorption of phenanthrene on kerogen, coal and black carbon respectively. Log $K_{FOC}$ values of lipid free (dlpd) and lignin free (dlgn) fractions of the soils are within the Log $K_{FOC}$ values of kerogen reported by Cornelissen et al. (2005). Log $K_{FOC}$ values for bound-lipid free fractions from the soils are however not within the kerogen's Log $K_{FOC}$ values except for sample IJ. Therefore, lipid free and lignin free fractions in the soils may be likened to kerogen. For the coal sample however, the lipid free and bound-lipid free fractions may be likened to the kerogen since their Log $K_{FOC}$ values are within kerogen's Log $K_{FOC}$ values. The OC-normalized Freundlich sorption capacity values (log $K_{FOC}$) of the bulk coal and carbonaceous shale are also within the range of log $K_{FOC}$ of coal reported by Cornelissen et al. (2005). High log $K_{FOC}$ value indicates high sorption capacity of phenanthrene on natural organic matter (Cornelissen et al., 2005).

Generally, OC-normalized Freundlich sorption capacity values (log $K_{FOC}$) increases with progressive extraction in the soils except for bound-lipid free (dblpd) fractions (Table 4.4 and Figure 4.15). However, there is no exception in bound-lipid free fraction of IJ soil sample because its log $K_{FOC}$also increases and it is even slightly higher than that of lignin free fraction, indicating its higher sorption capacity (Figure 4.15).In the same manner, $K_{FOC}$ values increase with progressive extraction of organic matter components from the coal and soil samples except.

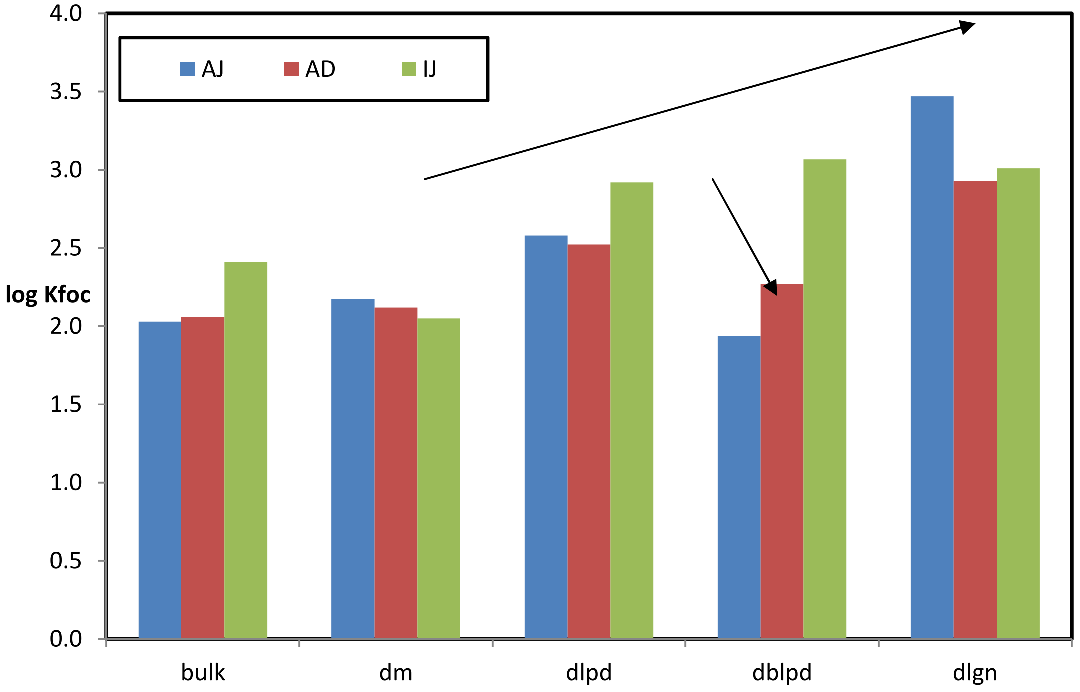


Figure 4.15: Diagram showing log $K_{FOC}$ values for phenanthrene sorption isotherm for the bulksoils andresidual organic matter fractions

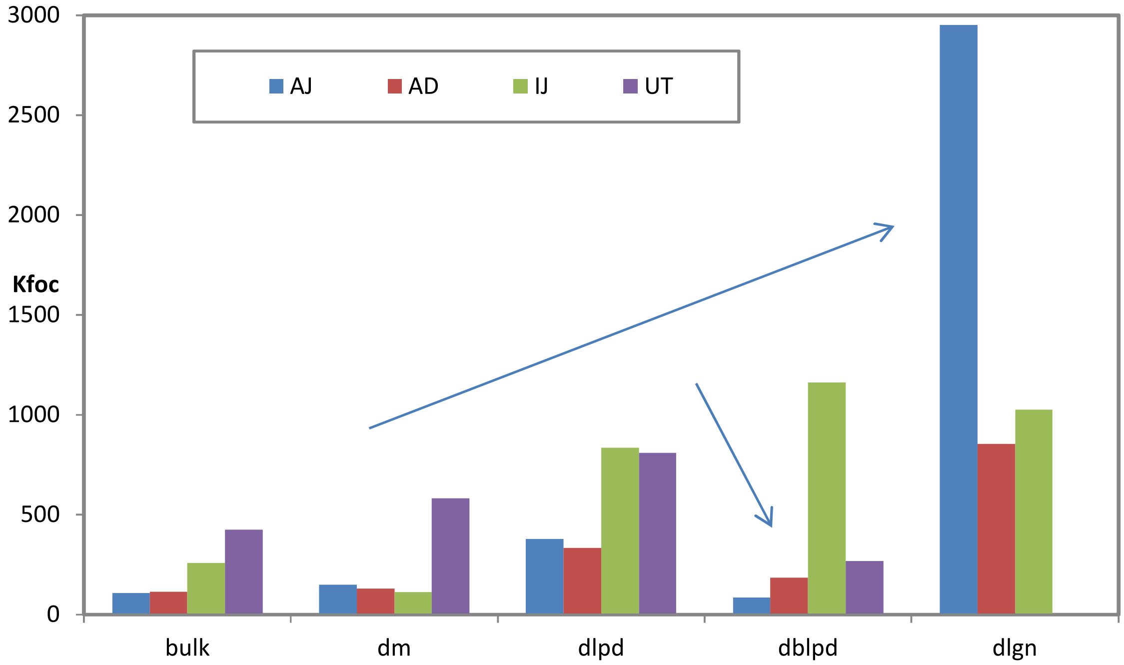


Figure 4.16: Diagram showing $K_{FOC}$ values for phenanthrene sorption isotherm for the bulk samples (coal and soils) andresidual organic matter fractions

for the bound-lipid free fractions (Table 4.4 and Figure 4.16). There is also no exception in the $K_{FOC}$ of bound-lipid free fraction from IJ soil with progressive extraction.

The $K_{OC}$ value measured for the phenanthrene decreases as a function of $C_e$ because of the isotherm nonlinearity (Table 4.4). Regardless of the $C_e$ levels, the bulk samples exhibited much lower sorption capacity than their lipid free and lignin free fractions, while lipid free fractions have lower sorption capacity compared to their lignin free equivalents except in IJ sample (Table 4.4). However, the sorption capacity parameters ($K_{FOC,}$ Log $K_{FOC}$ and $K_{OC}$) of the bulk samples (coal and soils) at any given $C_{e,}$ are close to their corresponding demineralised fractions with the exception of soil sample IJ, where there is a noticeable difference between the sorption capacity of the bulk sample and the demineralised fraction (Tabel 4.4, Figures 4.15 to 4.16). Similar pattern was observed in other sediments, soils, humic acid, humin and their demineralised fractions (Ran et al., 2007; Yang et al., 2011).This implies that the nonlinear sorption of phenanthrene is closely associated with organic phase rather than the inorganic phase (Kile et al., 1995; Huang and Weber, 1997). This further confirmed that organic matter in the bulk samples (rock and soils) has not been much affected by the dilute acid treatment of demineralisation (Wang et al., 1998). However, the scenario in soil sample IJ with a noticeable difference in the sorption capacity between the bulk sample and demineralised fraction may be a function of much higher TOC value, hence higher sorption capacity than the others soils. It may also be related to the presence of highly sorptive contaminants previously suggested on the basis of its C/N atomic ratio. The sorption capacity of the demineralised fraction of soil smaple IJ soil is therefore lower because some of the contaminants responsible for higher sorption in the bulk samples were removed during acid treatments. It is generally observed from Table 4.4 and Figures 4.10, 4.14 to 4.16 that the demineralised fractions in all the soils have very close sorption capacity values.

In addition, the values of the sorption capacity parameters (log $K_{FOC}$, $K_{FOC}$and $K_{OC}$) for the bulk rocks are significantly higher than those of the bulk soils and even higher than some of the NOM fractions from the soils (Table 4.4, Figures 4.9, 4.16). This shows that organic matter in the rocks have higher sorption capacity than their soil counterparts. The values of the sorption capacity parameters (log $K_{FOC}$, $K_{FOC}$ and $K_{OC}$) of the carbonaceous shale (sample AB) are higher than that of the coal (sample UT). However, the sorption isotherm of the coal is higher than that of the carbonaceous shale at higher concentrationswhile they are almost equal at lower concentrations (Figure 4.9). This may be attributed to the fact that log $K_F$ of the coal is higher than that of carbonaceous shale. Although, the sorption capacities of the demineralised fractions of the soil samples are quite similar (Table 4.4 Figure 4.10), the sorption capacity parameters (log $K_{F,}$ log $K_{FOC}$ and $K_{OC}$) for one of the bulk soils (IJ sample), its lipid free and bound-lipid free fractions are significantly higher than in the other soils (Table 4.4, Figures 4.14 to 4.16). The sorption isotherm of its lignin free fraction is also higher than those of the other soils (Figures 4.13). This shows that the sorption capacity of organic matter fractions in the IJ sample is higher than those of the samples AJ and AD. The NMR results (Table 4.3 and Figure 4.8) equally show a major difference in the properties of demineralised fraction of samples IJ and those of AD and AJ, thus supporting higher sorption capacity in the IJ soil sample.

Furthermore, the bulk samples and demineralised fractions of soil samples AJ and AD have almost the same Log $K_{FOC}$ values (i.e 2.03, 2.06 and 2.17, 2.12 respectively). This strongly suggests that the two soils have similar sorption capacities. Therefore, the closeness of their total organic carbon contents (0.92 % and 1.06 %) and similarities in the sorption capacity of almost all their residual organic matter fractions strongly suggest similarity in their organic matter properties. The two soils also have similar $K_{OC}$ at all $C_e$ levels of theirbulk samples and demineralised fractions and nearly parallel sorption isotherms in their bulk sample, demineralised and lipid free fractions (Table 4.4, Figures 4.9 to 4.11). The average Koc values for phenanthrene at Ce = 0.005 Sw is 12,272.72 mL/g for the two bulk rocks(samples UT and AB) as compared to the 1,554.78, 6,788.72, 11,058.04 and 28,987.79 mL/g for the three bulk soils, their lipid free, bound-lipid free and lignin free fractions respectively. The Koc values for phenanthrene at Ce = 0.005 Sw is 21,241, 3,305 and 4,345 mL/g for the carbonaceous shale, coal and coal's lipid free fraction respectively,while the values range from 751 to 3,133, 2,633 to 14,084,651 to 28,987.79 and 10,459 to 63,217 mL/g for the three bulk soils, their lipid free, bound-lipid free and lignin free fractions respectively. This shows that the average bulk rocks have sorption capacity within the range of bound-lipid free and lignin free fractions of the soils. When compared on individual basis, the bulk rocks can have sorption capacity ranging from those of lipid free fractions to as high as lignin free fractions. It can therefore be suggested from above that the organic matter in the rocks has stronger sorption capacity for phenanthrene than organic matter in the soils whether the polar organic matter or functional groups are removed or not

The sorption capacities of lipid free fractions in the soils are significantly higher than those of their demineralised fractions as reflected in their sorption parameters ($K_{FOC,}$ Log $K_{FOC}$ and $K_{OC}$). There is also an increase in sorption capacity of lipid free fraction of coal against its demineralised fraction (Table 4.4). The removal of lipid components considerably increased the sorption capacity by an average of 154 % in the soils and 39 % in the coal (Table 4.4, Figure 4.16). Free lipids mainly consisting of n-alkanes, saturated and unsaturated fatty acids, diols, as well as n-alkyl monoesters, occupy a set of sites with similar but different sorption energies in SOM. The removal of these compounds resulted in heterogeneous sites(Kohl and Rice, 1999; Wang and Xing, 2007b). It therefore means that the presence of lipid in SOM would be blocking the accessibility of sorption sites for HOCs. In this case, the competition could occur in a sorption system with aqueous solutes containing phenanthrene and free lipids(Kohl and Rice, 1999; Wang and Xing, 2007b). The linear sorption of phenanthrene by the lipids also supports the speculation that free lipid compounds exhibit partitioning domain in SOM(Wang and Xing, 2007b; Wen et al., 2007; Zhang et al., 2013). In addition, single Koc results show that the increase in sorption capacity of lipid free fractions occurred across both lower and higher aqueous concentrations of phenanthrene, though the increase in sorption reduces from lower to higher aqueous concentrations. This clearly indicates that the sites occupied by lipid components were with high energy for phenanthrene, and their removal lowered the sorption by partitioning phase at higher aqueous concentrations.

The sorption capacities of the bound-lipid free fractions are lower than those of their lipid free fractions in the coal and the two soil (samplesAJ and AD) as indicated by the decrease in log$K_{FOC}$ value from 2.91, 2.58 and 2.52 for the coal, sample AJ and sample AD lipid free fractions respectively to 2.43, 1.94 and 2.27 for the same samples' bound-lipid free fractions respectively (Table 4.4). This shows that the removal of bound-lipid components had a significant impact on the sorption of phenanthrene by thesoils and the coal sample. The removal of bound-lipid fraction in the coal and soil sample AJ is highly significant that their sorption capacity parameters are even lower than those of their bulk samples. The highly elevated ratios of O/C after bound-lipid removal (saponification) suggested a notable increase in the polarity for the bound-lipid free fractions, resulting in a decreasing sorption capacity compared to the lipid free fractions. More specific explanation could be that after saponification, there is an increase in hydrophilic groups (e.g., carboxyl and hydroxyl) which may block or obstruct the approach of hydrophobic phenanthrene to adsorption sites and partitioning domains in the SOM matrix(Cornelissen et al., 2005).

However, Log $K_{FOC}$ and $K_{OC}$ for the bound-lipid free fraction from soil sample IJ are higher than those of its lipid free fraction (Table 4.4, Figures 4.14 to 4.16). Even its nonlinearity (n) also increases from 0.46 to 0.39. This observed difference may in part be attributed to about 43 % elevated O/C ratio as compared to an average of about 100 % in the other soils and coal (Table.4.1). Thus, suggesting only small increase in polarity of the fraction. This may possibly explain the observed increase in the sorption capacity of the bound-lipid free fraction in the soil sample IJ relative to its lipid free fraction. Similar to lipid, removal of bound-lipid components caused an increase in nonlinearity of bound-lipid free fractions as observed in soil samples IJ and AD (Table 4.4) which equally indicates increase in heterogeneity of SOM probably due to release of sorption sites(Kohl and Rice, 1999). Although both samples IJ and AD have increased nonlinearity, theimpact is more in sample IJ, thus indicating that the reduced polarity in bound-lipid free fraction of sample IJis responsible for its higher sorption capacity.

The sorption capacities of lignin free fractions (Table 4.4) are significantly higher than those of the bound- lipid free fractions and even higher than the lipid free fractions in the two soils(samplesAJ and AD). This is indicated by the highest nonlinearity and significant increase in sorption capacity parameters ($K_{FOC,}$ Log $K_{FOC}$ and $K_{OC}$) of the lignin free (dlgn) fractions from the two soils (Table 4.4). A significant increase in $K_{OC}$ across all aqueous concentrations (Table 4.4) is also observed. Just like the case of lipid, the removed lignin components in SOM may yield a strong sorption competition with phenanthrene. This competition was further supported by the fact that both phenanthrene and lignin contain aromatic units. In the case of soil sample IJ, the sorption parameters ($K_{FOC,}$ Log$K_{FOC}$ and $K_{OC}$) of lignin free fraction are lower than those of its bound-lipid free fraction (Table 4.4). Also, the nonlinearity (*n)* decreases from 0.39 for bound-lipid free fraction to 0.51 for lignin free fraction, showing that nonlinearity decreases from bound-lipid free fraction to lignin free fraction in the sample IJ. However, Log $K_F$ and the sorption isotherm of the lignin free fraction are still higher than those of the bound-lipid free fraction in the sample (Table 4.4, Figure 4.17). Despite the observed difference in the IJ sample, the sorption parameters of lignin free (dlgn) fractions in all the soils are generally comparable to those of glass and hard, or condensed organic matter (Table 4.4). This is because previous studies have shown that *n* values of phenanthrene sorption by nonhydrolyzable organic carbon (NHC) range from 0.65 to 0.77, while those of black carbon (BC) range from 0.51 to 0.55(Ran et al., 2007a; Sun et al., 2008). Log $K_{Foc}$ values for black carbon also range from 2.5 to 3.6 (Cornelissen et al., 2004; Ran et al., 2007a).

In line with the statement of Weber et al. (1999), it has been observed that the sorption capacity of the bulk soils for Phenanthrene increases as the organic matter content of soil increases. This is the reason for the highest sorption capacity parameters or strogest sorption for phenanthrene in the bulk soil with the highest organic matter content (Figure 4.18). Log $K_F$ and $K_{OC}$ for the bulk soils at the three levels of relative solubility are also related to the organic carbon content of the bulk soils (Table 4.4). It was also observed that the sorption isotherms of the bulk rocks are reflections of their organic matter content. That accounted for the higher sorption isotherm of coal(sample UT) over that of the carbonaceous shale (sample AB)(Figure 4.19), despite the fact that the sorption parameters (Log $K_{FOC}$, $K_{FOC}$ & $K_{oc}$) of the carbonaceous shale are higher than those of the coal sample. For instance, At $C_e$ = 0.5Sw, the Koc values of the three original soils and two rock samples fall into a range of 133-342 mL/g and 536-2019 mL/g respectively. At $C_e$ = 0.005Sw, the Koc values of the same set of samples range from 751 to 3133 mL/g and 3305 to 21241 mL/g respectively.

The sorption capacity among the bulk samples follows the order: UT> AB> IJ> AD> AJ (Figure 4.9). This further shows that the sorption capacities of the bulk rocks (coal and carbonaceous shale) are higher than those of the bulk soils. Also among the soils, the sorption parameters and

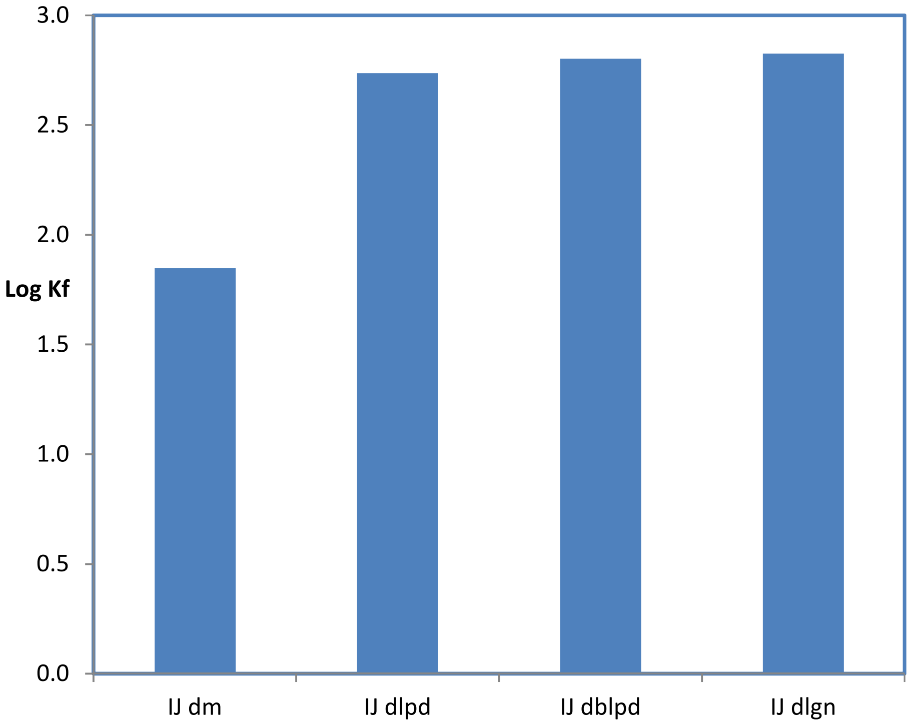


Figure 4.17: Diagram showing the distribution of Log $K_F$in the residual organic matter fractions of sample IJ

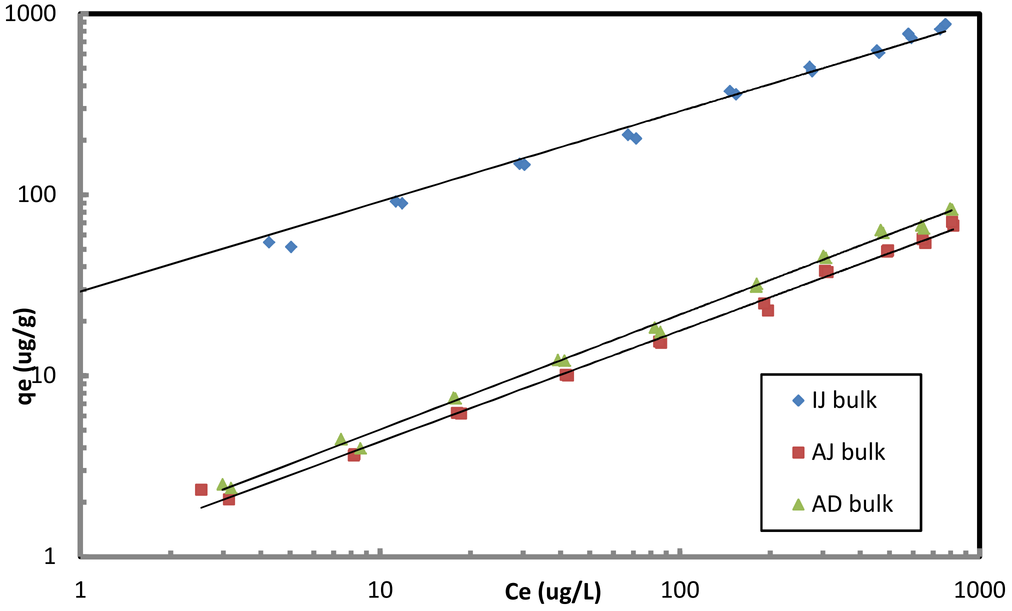


Figure 4.18: Diagram showingsorption isotherms of bulk soils with respect to theirorganic carbon content

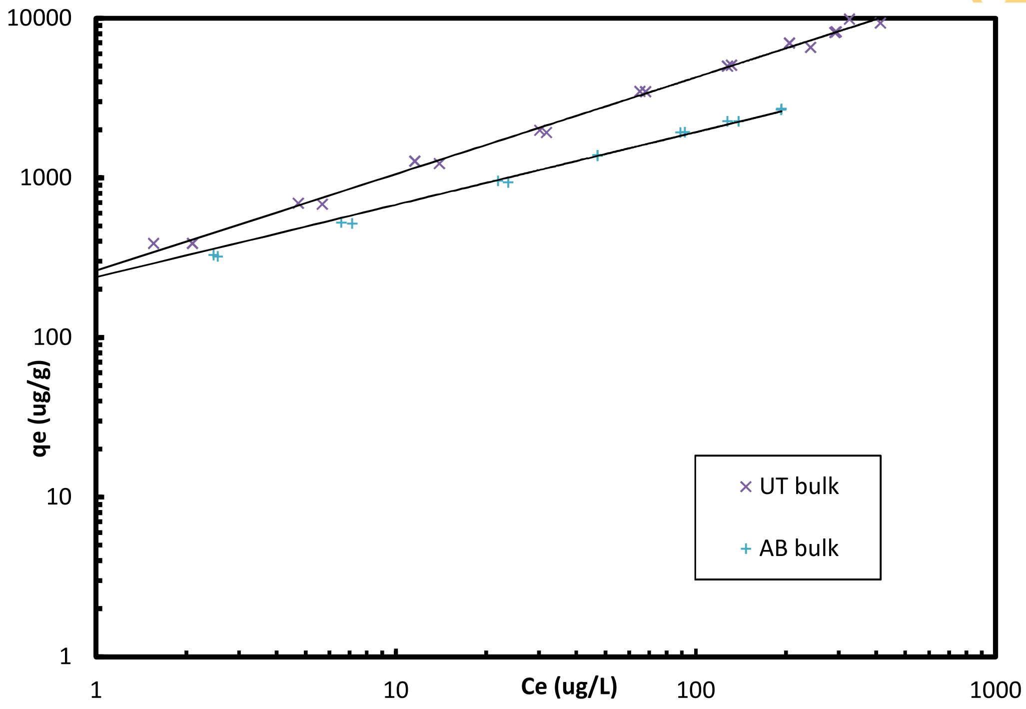


Figure 4.19: Diagram showing sorption isotherms of bulk rocks with respect to their organic carbon content

capacities of two bulk soils (samples AD and AJ) are low and similar, while those of sample IJ are higher and different from those of the two other soils.

Furthermore, lignin free (dlgn) fractions have the highest sorptioncapacitiesamong the residual organic matter fractions in the soils except in sample IJ where bound-lipid free (dblpd) fraction has the highest sorption parameters. The demineralised (dm) fractions have the least sorption capacities in the soils except in the sample AJ where bound-lipid free (dblpd) fraction has the least sorption capacity. Also, among the residual organic matter fractions in the coal (sample UT) where lignin was not extracted, the lipid free (dlpd) fraction has the highest sorption capacity while bound-lipid free (dblpd) fraction has the lowest sorption capacity. This therefore means that bound-lipid free (dblpd) fractions have the lowest sorption capacities in the sample AJ and coal (sample UT), while the demineralised fractions have the lowest sorption capacities in the soil samples IJ and AD. The least sorption capacity is actually associated with bound-lipid free (dblpd) fractions ofsample AJ and coal (sample UT) because they also exhibited lower sorption parameters than their bulk equivalents (Table 4.4). Among the two soilswith the least sorption capacity in their demineralised (dm) fractions, the sorption capacity of the IJbulk sample is higher than its demineralised fraction due to the presence of highly sorptive materials such as coal particles and degraded kerogen in the bulk sample, while the sorption capacity of the demineralised fraction in the sample AD is higher than that of its bulk sample. Although, sorption capacity of bound-lipid free fraction in the AD sample is higher than those of its demineralised and bulk counterparts, yet they are lower than those of the lipid free fraction in the soil.It can therefore be inferred that the removal of bound-lipid components could be responsible for the reduced sorption parameters of bound-lipid free fractions in the soils and coal since their removal has led to high polarity in their residual fractions except in sample IJ.

It is therefore concluded that fractionation procedures have altered the organization of natural organic matter or SOM in this study, thus making more sorption sites available to HOCs. This is because sorption of phenanthrane to most of the residual organic matter fractions is higher than that of their demineralised fraction. This observation is consistent with the fact that the sum of sorption from individual fractions is not equivalent but normally higher than that of the bulk or original soils (Salloum et al., 2001b; Bonin and Simpson, 2007).Therefore, sorption capacity follows the order dlgn>dlpd>dblpd>dm>bulk in soil sample AD and dlgn>dlpd>dm>bulk>dblpd in soil sample AJ with fairly low and similar organic carbon contents andsorption capacity. The sorption capacity follows the order dblpd>dlgn>dlpd>bulk>dm in soil sample IJ with higher organic carbon content and sorption capacity. Also,sorption capacityfollows the order dlpd>dm>bulk>dblpd in the coal (sample UT) withhigher organiccarbon and sorption capacity.The above sorption capacity patterns in the samplestherefore indicated that the coal and AJ soil have the same pattern of sorption capacity in their organic matter fractions except that lignin fraction was not extracted from the coal.

Although, it is expected that the bulk sample would have lower sorption capacity thantheir organic matterfractions because sorption sites of organic matter in bulk samples are not exposed (Salloum et al., 2001b; Bonin and Simpson, 2007),it was observed that this is not so in some of the samples. For instance, the bound-lipid free fractions have the lowest sorption capacity inthe sample AJand coal while demineralised fraction has the least sorption inthe soil sample IJ. The only samplewith the lowest bulk sorption capacity is the soilsample AD. Higher sorption capacity observed in the bulk soil sample IJ above its demineralised fraction is possibly linked to presence of highly sorptive materials (coal,degraded kerogen, etc) in the soil (Cornellisen et al., 2005).

The lowest sorption capacity observed in bound-lipid free fractions of coal (sample UT) and sample AJ is due to removal of bound-lipid component which also had great impact on the structure or property oftheir organic matter, thus resulting in exponential increase of their polarity. Removal of bound-lipid fractions from the coal and sample AJ is accompanied by approximately 100 % elevated O/C ratioin their bound-lipid free fractions (Table.4.1). Bound-lipid free fraction has the least sorption capacity amongall organic matter fractions in the coal sample (Table.4.4, Figure 4.20).Since bound-lipid is a small fraction isolated from the residual organic matter fraction, it is expected to have lower sorption capacity compared to other residual organic matter fractions. However, a comparison of the content of the bound-lipid fraction in the coal with its sorption isothermrevealed that its sorption capacity is relatively high and this is

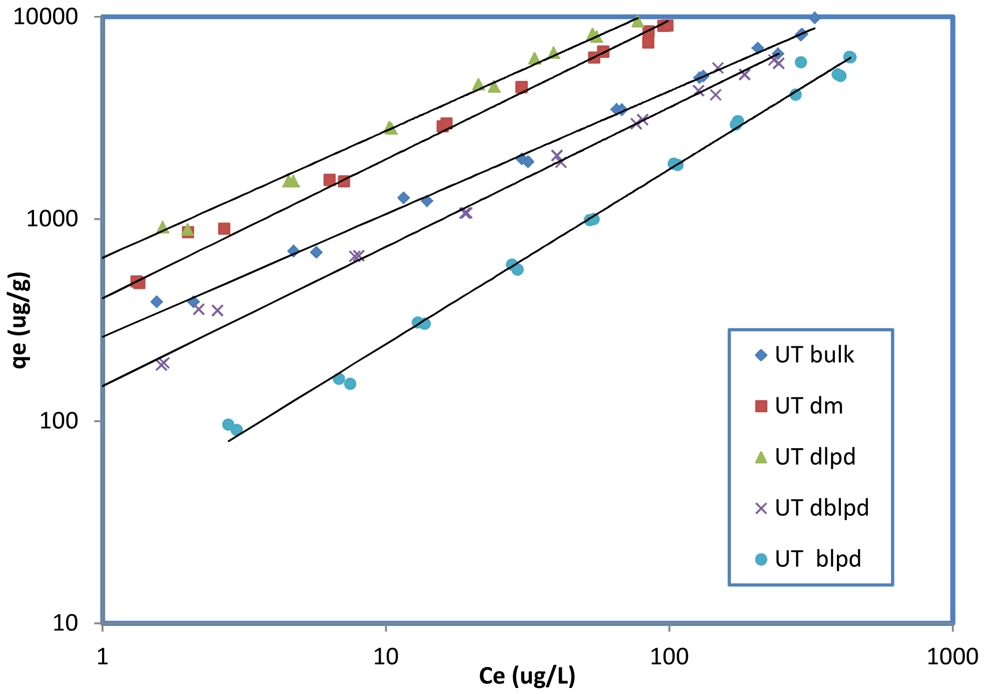


Figure 4.20: Diagram showing sorption isotherm of bound-lipid fraction of coal relative to the residual organic matter fractions rock

supported by the fact that its removal has led to significant decrease in the sorption capacity of the residual fraction.

### 4.2.5 Correlation between Sorption Isotherm Parameters and NOM Elemental Properties

The sorption nonlinearity factors (n) of the phenanthrene on the lignin free (dlgn) fractions have weak negative correlations with the O/C ratios and a weaker negative correlation with H/C ratios (Figures 4.21 and 4.22). These correlations strongly suggest that more aromatic (O/C ratios) and aliphatic (H/C ratios) carbons contributions to isotherm nonlinearity of the lignin free fractions, but thearomatic carbonshave higher contribution to increasing isotherm nonlinearity of the lignin free fractions than the aliphatic carbons. Sorption isotherm nonlinearity (n) of the phenanthrene on the lipid free fractions is also significantly correlated to the H/C and O/C ratios (Figures 4.23 and 4.24), but the correlation is weaker with H/C ratios than with O/C ratios. These correlations also suggested that structurally less aromatic and less aliphatic lipid free fractions exhibit greater isotherm nonlinearity but less aromatic contribute more to higher isotherm nonlinearity. This therefore means that more aliphatic lipid free fractions contribute more to isotherm nonlinearity.

Furthermore, the sorption isotherm nonlinearity (n) of the demineralised fractions is strongly correlated with H/C and O/C ratios (Figures 4.25 and 4.26), but the correlation is weaker with O/C ratios than H/C ratios. These correlations equally show that structurally less aromatic and and less aliphatic demineralised fractions contribute to increasing isotherm nonlinearity but less aliphatic contribute more to increasing nonlinearity of demineralised fraction. However, there exist a strong positive correlation between O/C ratio of bound-lipid free fractions and sorption isotherm nonlinearity (Figure 4.27) and a weak positive correlation between the isotherm nonlinearity and H/C ratios (Figure 4.28). These correlations strongly suggest that bound-lipid free fraction with lower O/C ratio has higher nonlinearity than bound-lipid free fraction with higher O/C ratio.

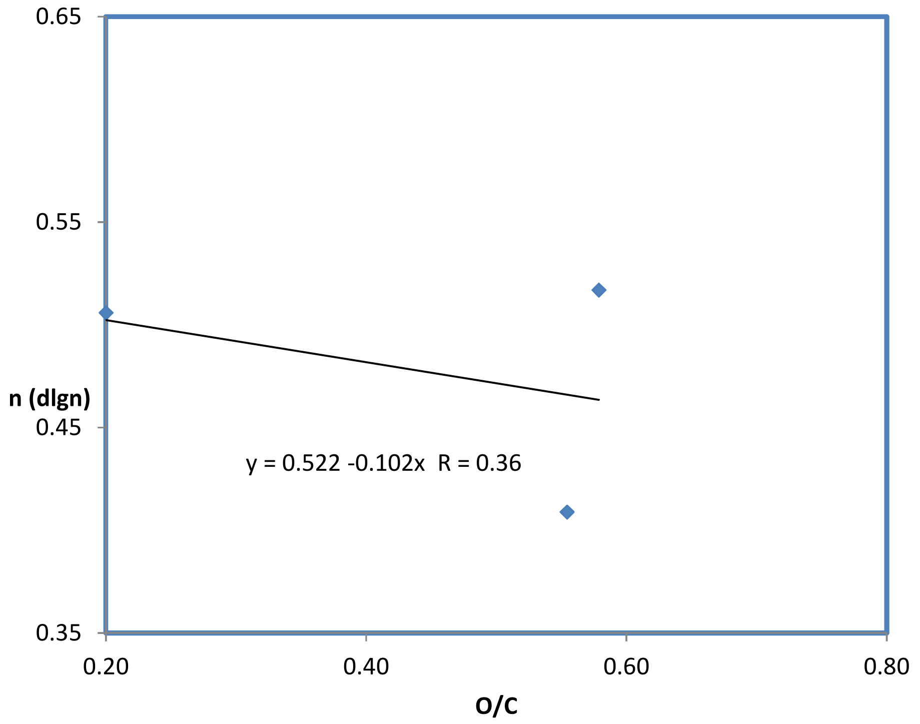


Figure 4.21: Correlation of nonlinearity and O/C ratios of lignin free fractions

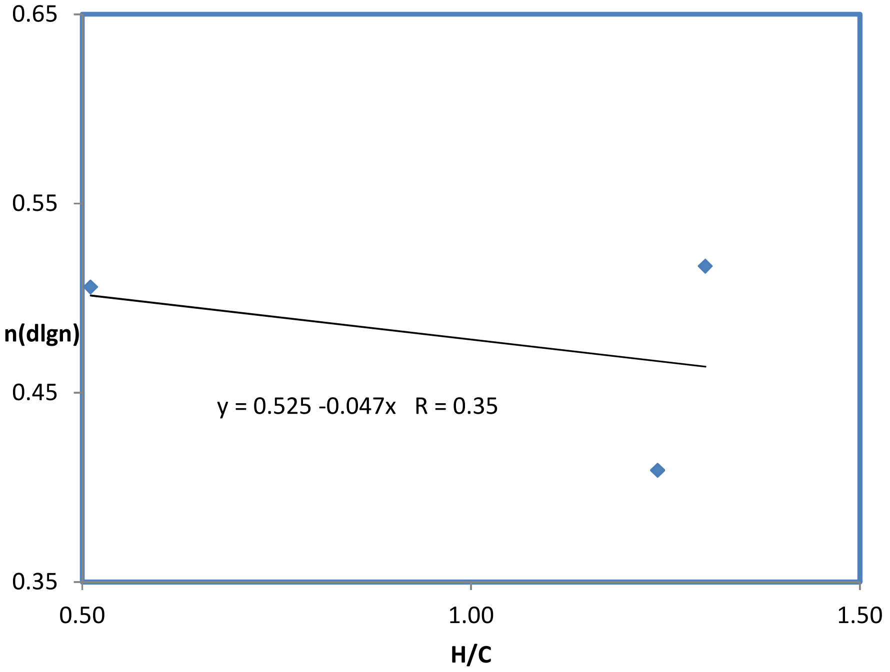


Figure 4.22: Correlation of nonlinearity and H/C ratios of lignin free fractions

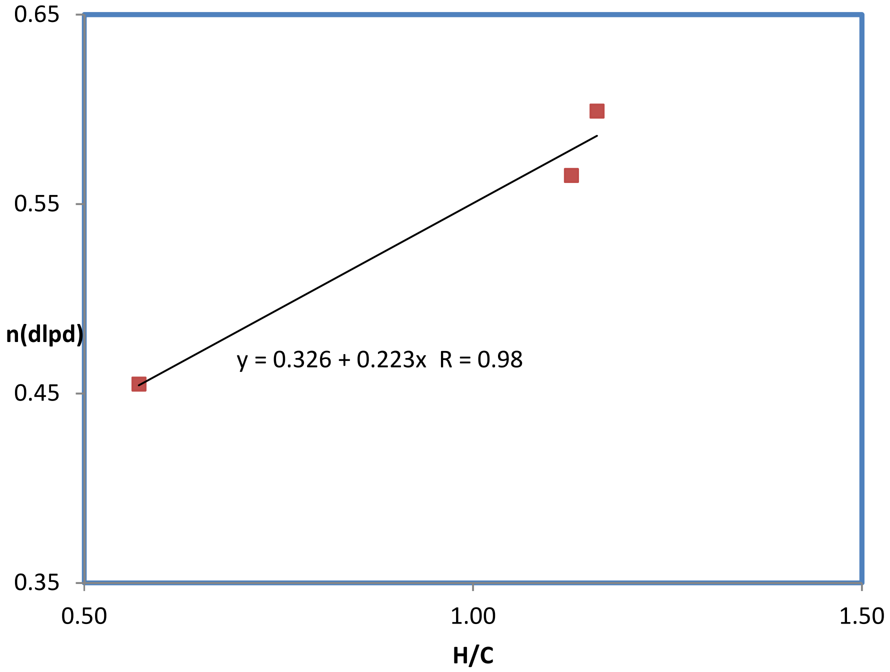


Figure 4.23: Correlation of nonlinearity and H/C ratios of lipid free fractions.

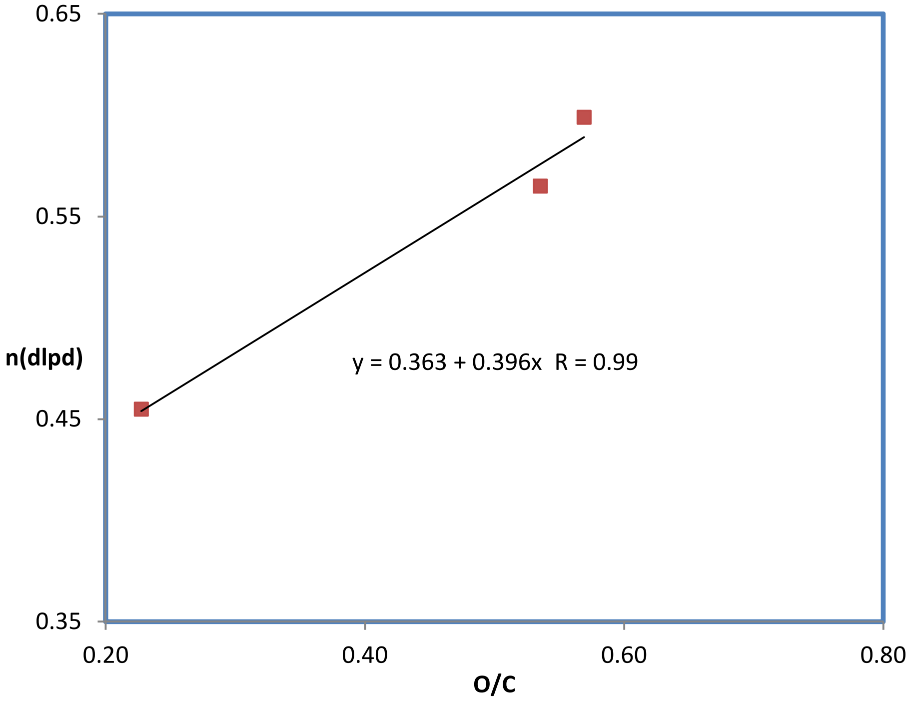


Figure 4.24: Correlation of nonlinearity and O/C ratios of lipid free fractions

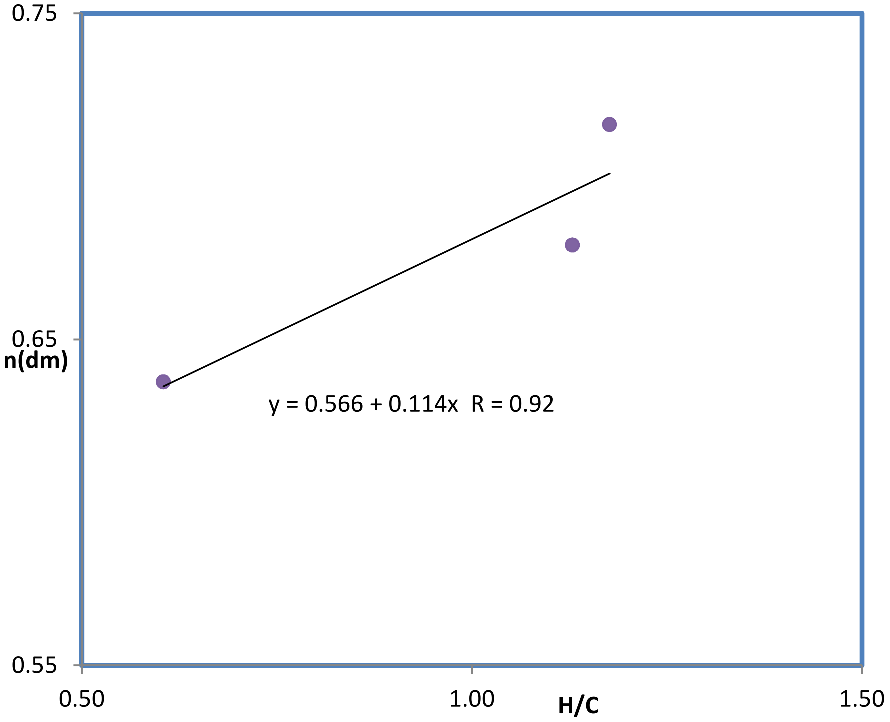


Figure 4.25: Correlation of nonlinearity and H/C ratios of demineralised fractions

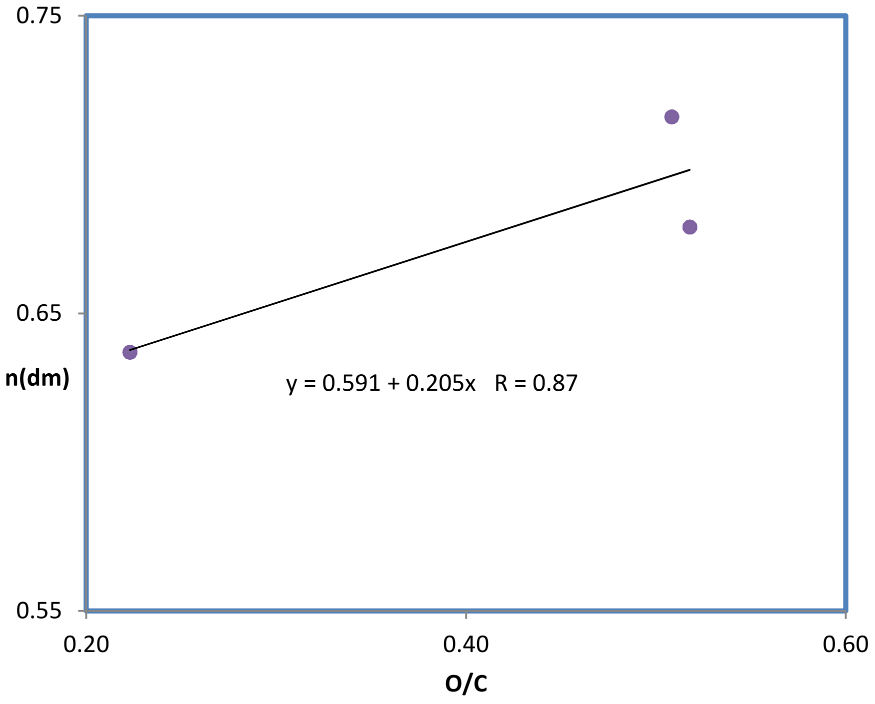


Figure 4.26: Correlation of nonlinearity and O/C ratios of demineralised fractions

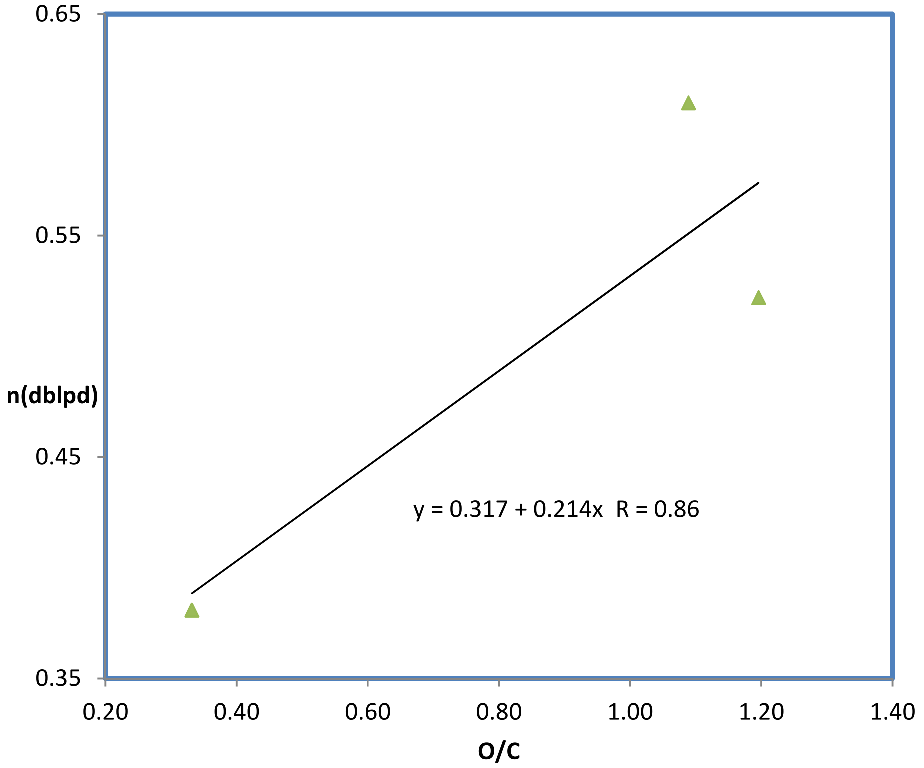


Figure 4.27: Correlation of nonlinearity and O/C ratios of bound-lipid free fractions

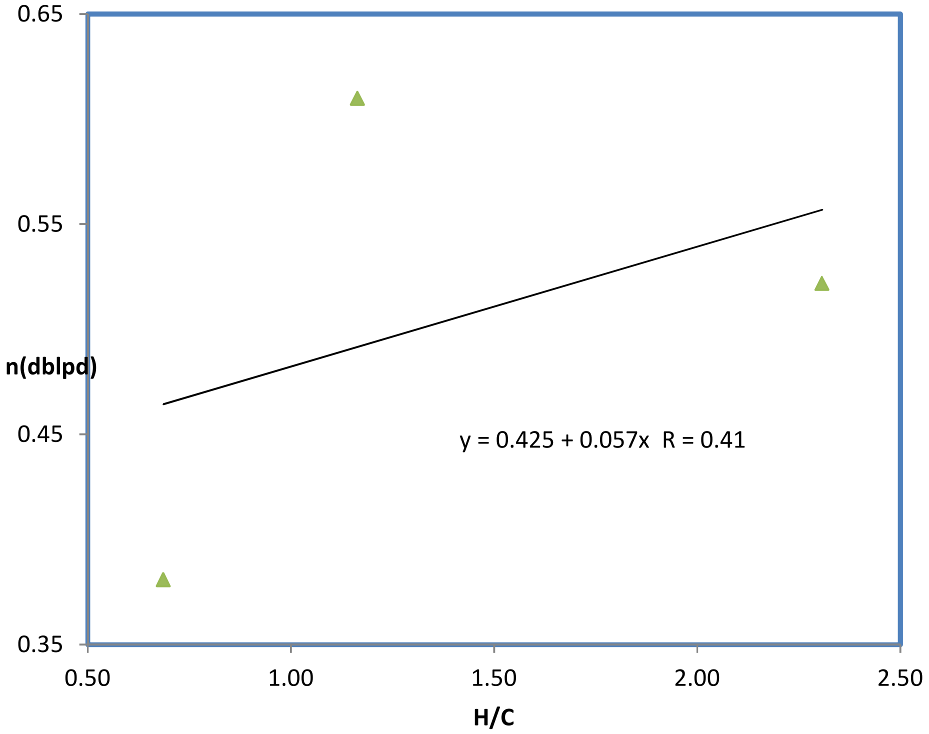


Figure 4.28: Correlation of nonlinearity and H/C ratios of bound-lipid free fractions

In addition, strong negative correlations exist between logKoc at each of the three phenanthrene concentrations and H/C ratios for the bulk soils and bulk rocks(Figures 4.29 and 4.30 respectively). These correlations show that sedimentary organic matter high in H/C ratios has stronger sorption capacity than soil organic matter with higher H/C ratios. Hence, it is concluded that organic matter in the rocks with higher H/C ratios has stronger sorption capacity for phenanthrene than soil organic matter with higher H/C ratios. There are also strong negative correlations between logKoc at each of the three phenanthrene concentrations and O/C ratios for the bound-lipid free fractions (Figure 4.31), and correspondingly weak negative correlations with H/C ratios (Figure 4.32). These show that high polarity (O/C ratios) in bound-lipid free fractions contributed to their lower sorption parameters.

Hence it is concluded that among the soil NOM fractions, bound-lipid free (dblpd) fractions are structurally different from lipid free (dlpd) and lignin free (dlgn) fractions. This is because the pattern displayed by the correlation of isotherm nonlinearity factors (n) and logKoc with H/C and O/C ratios respectively for lipid free and lignin free fractions are different from those of the bound-lipid free fractions. Moreso that sorption parameter (logKoc) decreases in bound-lipid free fractions while it increases in lipid free (dlpd) and lignin free (dlgn) fractions. It has also been observed that lignin free fractions in all the soils (except IJ sample) have the highest sorption parameters (sorption) and the highest aromaticity as well as the lowest aliphaticity. The organic matter fraction with the lowest sorption parameters (usually between demineralised and bound-lipid free fractions) has the highest aliphaticity as well as the lowest aromaticity. Therefore it is concluded that aromatic carbon in organic matter is positively correlated to sorption of hydrophobic organic contaminants while the aliphatic carbon is inversely or negatively correlated to HOCs sorption in the soils and rocks.

### 4.2.6 Contribution of the Natural Organic Matter Fractions to the Overall Sorption of Phenanthrene

The contribution of each of the natural organic matter or SOM fractions to total sorption was normalized to bulk sample by using the equation

$q_{e,i} = [K_{f,i}\,(C_e)^n\,\phi_{oc,i} f_{oc,bulk}]/f_{oc,i}$ 4.1

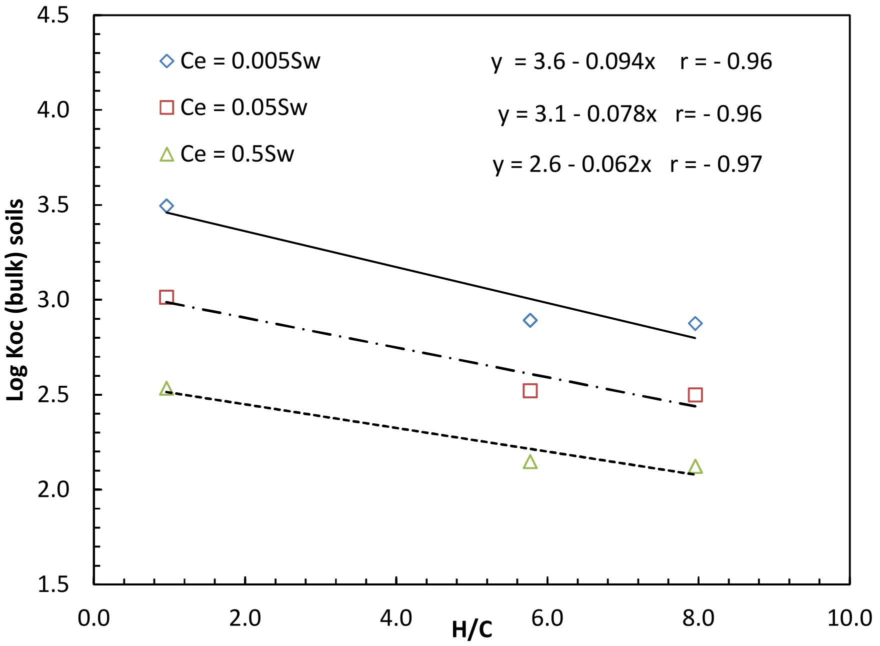


Figure 4.29: Correlation of LogKoc and H/C ratio of bulksoils

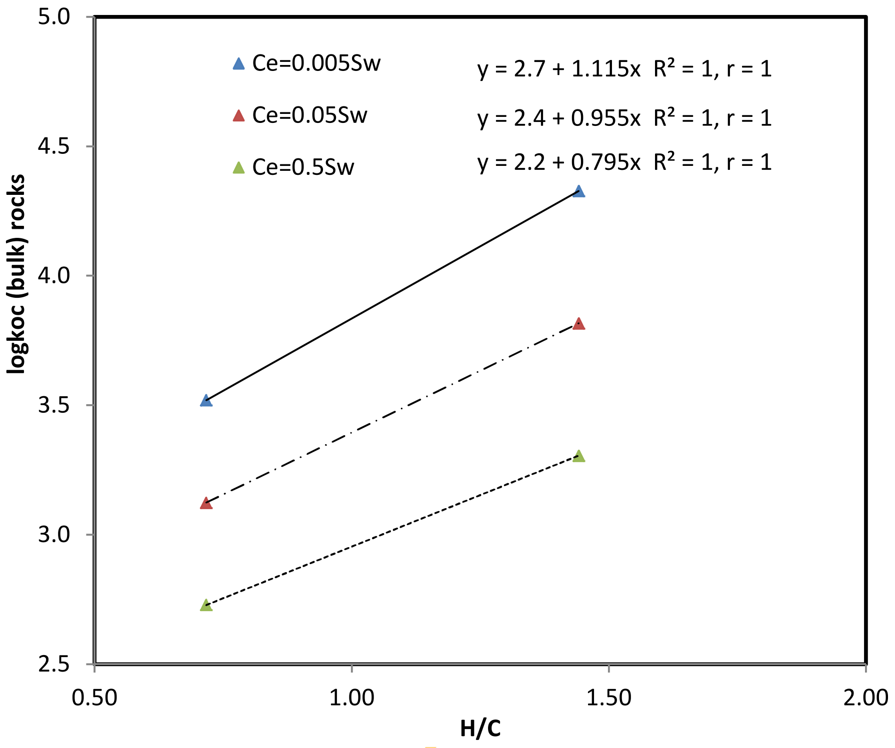


Figure 4.30: Correlation of LogKoc and H/C ratio of bulk rocks

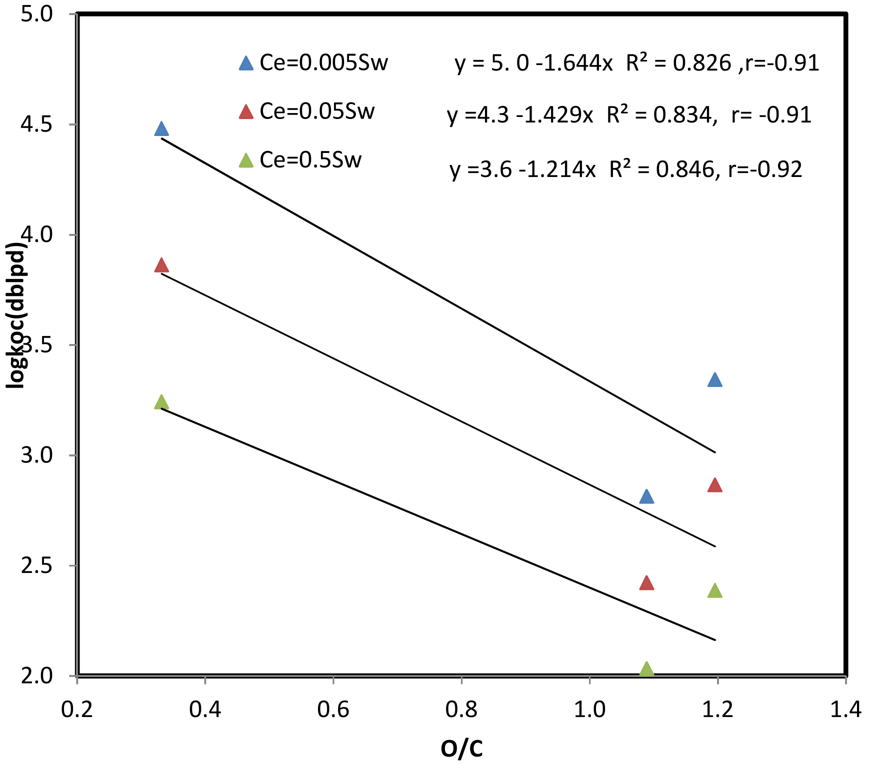


Figure 4.31: Correlation of LogKoc and O/C ratio of bound-lipid free fractions

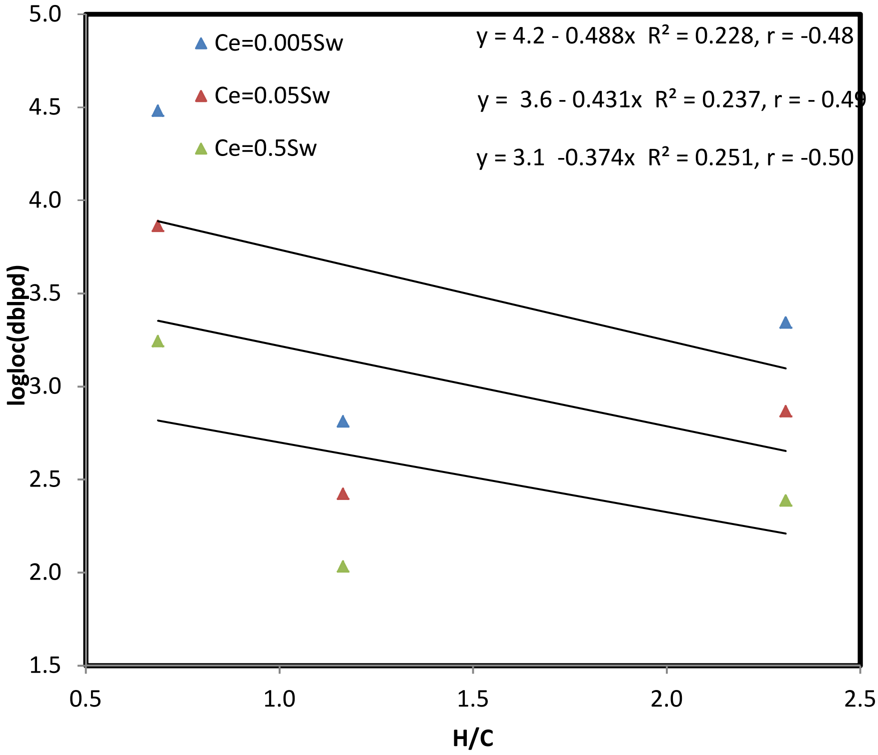


Figure 4.32: Correlation of LogKoc and H/C ratio of bound-lipid free fractions

where $K_{f,i}$and n are the phenanthrene Freundlich sorption coefficients listed in Table 4.4, $\phi_{oc,i}$ is the OC mass fraction (dlpd/OC, dblpd/OC and dlgn/OC), $f_{oc,bulk}$ is the fraction of organic carbon content of the bulk sample, and $f_{oc,i}$ is the fraction of organic carbon content in the NOM fractions in Table 4.1.

The contribution of the lipid free (dlpd) fraction in the coal sample exceeded the overall sorption capacity of the bulk and demineralised fraction while the contribution of its bound-lipid free (dblpd) fraction is below the overall sorption capacity of the bulk and demineralised fractions (Figure 4.33). The contributions of lignin free (dlgn) and lipid free (dlpd) fractions in the soil samples also exceeded the overall capacity of the bulk and demineralised fractions (Figures 4.34 to 4.36), thus indicating the dominance of the lignin free (dlgn) and lipid free (dlpd) fractions in the overall sorption of phenanthrene by bulk soil samples and the dominance of lipid free (dlpd) fraction in the overall sorption of the coal sample. The contributions of bound-lipid free (dblpd) fractions in all the soil samples exceeded the overall sorption capacity of the bulk samples (Figures 4.34 to 4.36) but their contributions are below the sorption capacity of the demineralised fractions except in soil sample IJ (Figures 4.34 to 4.36)where its contribution is above that of the demineralised fraction. These indicate that bound-lipid free fractions in the soils are relatively important in the overall sorption of these soils. These findings are consistent with several other studies that directly or indirectly demonstrated thatkerogen, polymethylene carbon, coal and black carbon are important sorbents in soils and sediments for HOCs (Karapanagioti et al., 2000; Jonker and Koelmans, 2002; Salloum et al., 2002; Chefetz et al., 2000; Nguyen et al., 2004 and Bucheli & Gustafsson, 2000, Ran et al., 2007a, Sun et al., 2008). Recent investigations also indicated that condensed SOM/NOM fractions including kerogen, nonhydrolysable carbon and black carbon can explain greater than 90% of the total sorption in soils and sediments (Ran et al., 2003a, 2007a and b; Cornellisen et al., 2005; Sun et al., 2008).

However, it is clear from the figures 4.33 to 4.36 that the contributions of lipid and lignin fractions to the overall sorption by the given soil or rock are significantly important. This is because the removal of lipid and lignin fractions from the coal and soils did not cause any significant reduction in the sorption capacity of their residual fractions but rather caused significant increase by removing the competitive sorption for phenanthrene by the lipid or lignin

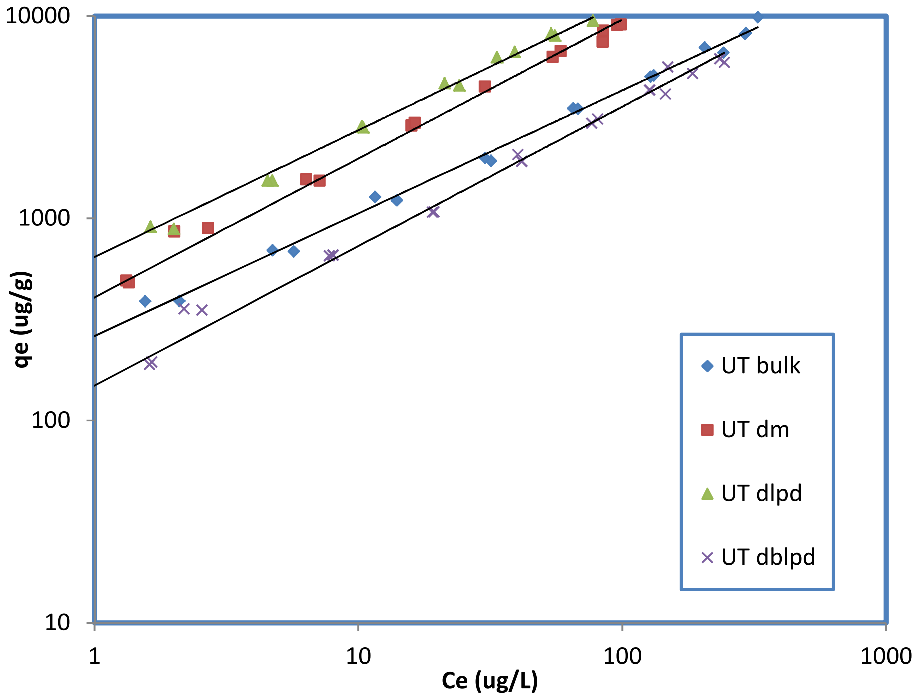


Figure 4.33: Sorption isotherms of Phenanthrene and the Freundlich modeling lines on the bulk coal (sample UT) and the contribution of its NOM fractions to the total sorption

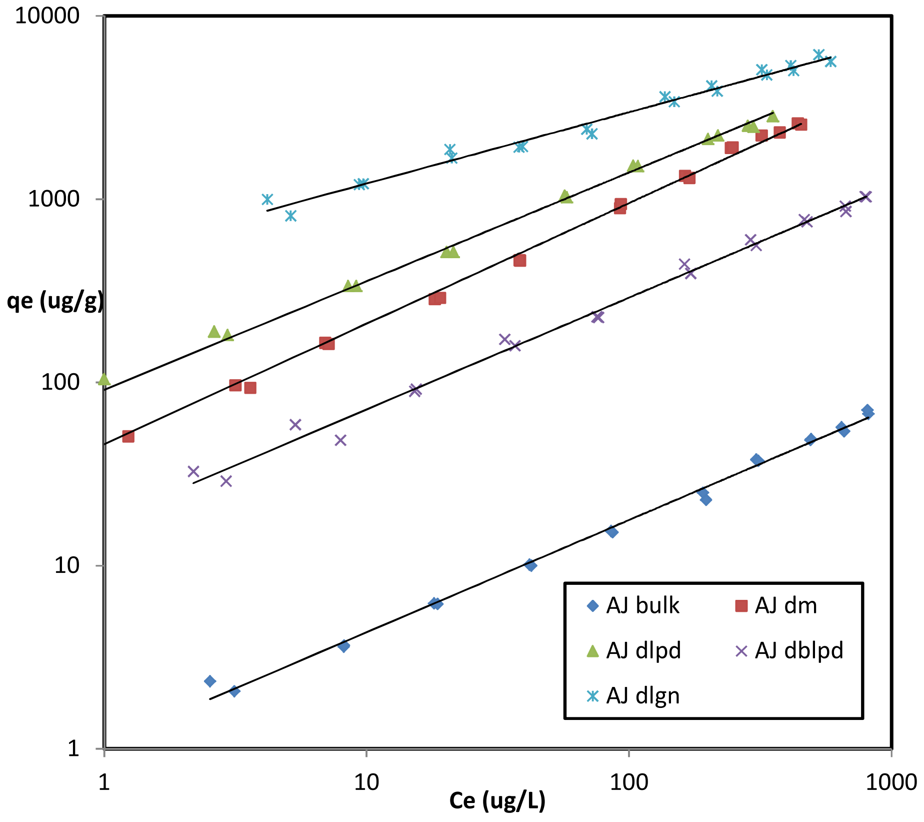


Figure 4.34: Sorption isotherms of Phenanthrene and the Freundlich modeling lines on the bulk AJ soil and the contribution of its NOM fractions to the total sorption

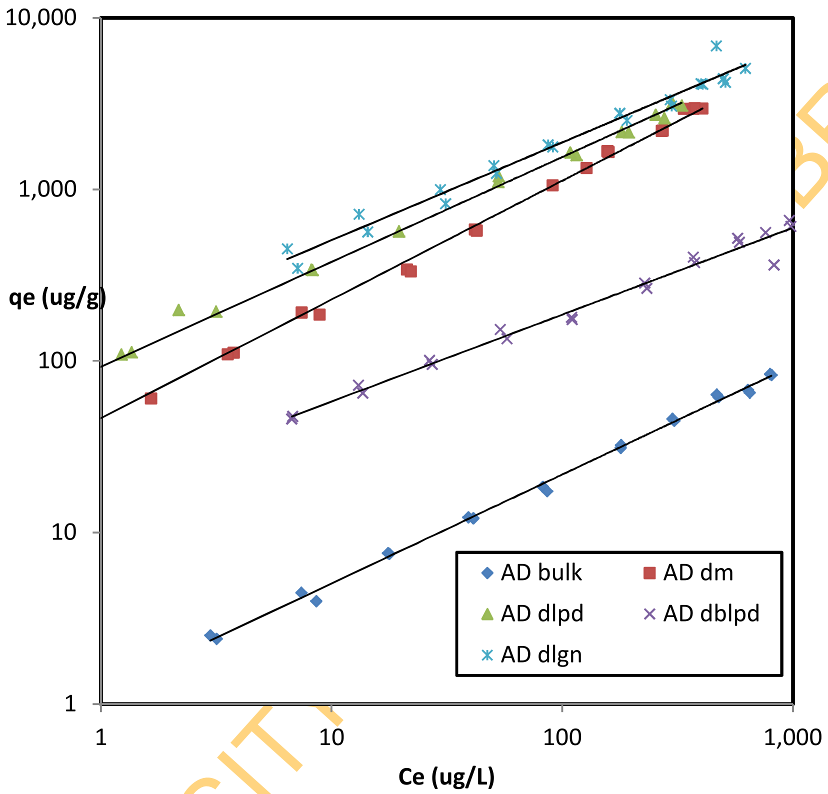


Figure 4.35: Sorption isotherms of Phenanthrene and the Freundlich modeling lines on the bulk AD soil and the contribution of its SOM fractions to the total sorption

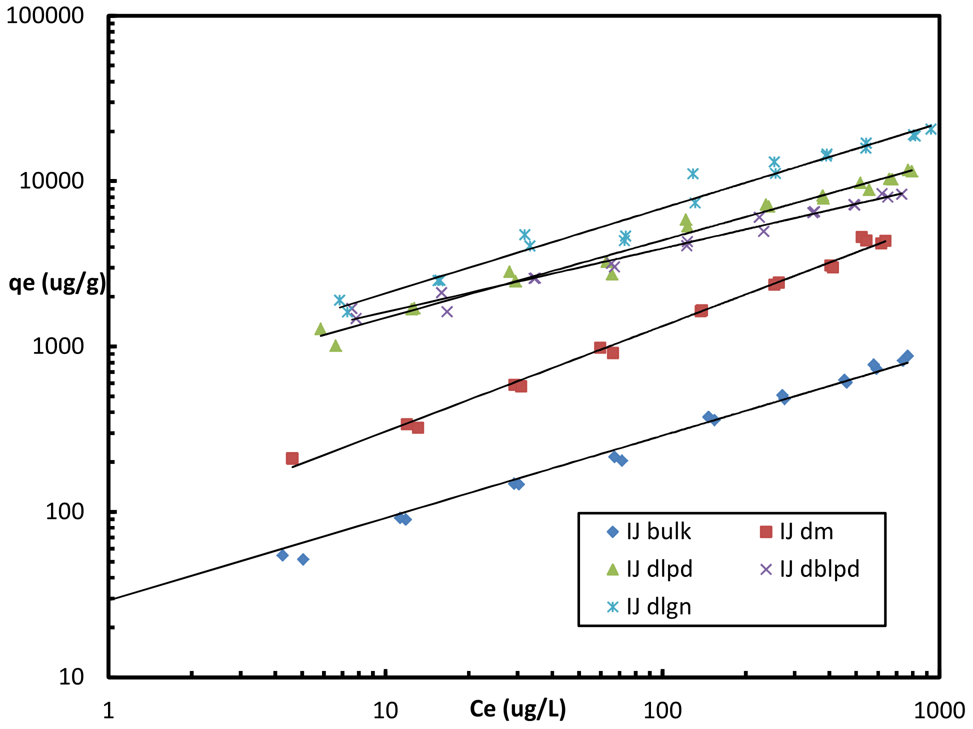


Figure 4.36: Sorption isotherms of Phenanthrene and the Freundlich modeling lines on the bulk IJ soil and the contribution of its SOM fractions to the total sorption

fractions. The contribution of bound-lipid fraction is also significant because its removal caused a significant reduction in the sorption capacity of the residual organic matter fractions in the coal and soils except in one soil. This clearly displays the contribution of bound-lipid fractions to the overall sorption in the coal and the soils because their removal made the residual organic matter fractions to have lower $K_{OC}$ values and also decreases their nonlinearity.

In addition, the sorption isotherm of the bound-lipid fraction from the coal sample is below the isotherms for all the residual organic matter fractions (Figure 4.20) possibly because it is an isolated organic matter fraction from lipid free fraction, yet its sorption capacity is nonlinear (Table 4.4) and considerably high for extracted fraction of the organiccarbon in the rock (Table 4.2). It has a sorption contribution of about 25 % to that of the bulk organic matter (demineralised fraction) at maximum and minimum aqueous equilibrium concentration of phenanthrene(Table 4.4and Figure 4.37). However, sorption capacities of lipid and lignin fractions extracted from riverine sediments using the same procedures were low, linear and almost linear respectively (Zhang et al., 2013). This study further shows that lignin(9.585 % of the sediments) has maximum sorption contribution of about 10 % at 1000 mg/L of aqueous equilibrium concentration of phenanthrene in two river sediments while lipid(19.94 % of the sediments) has about 12 % sorption contribution at minimum aqueous concentration. The sorption of HOCs by the lipids increase with increasing concentration to about 64 % at maximum concentration of phenanthrene for the two riverine sediments.

Also, the roles of the lignin free and lipid free fractions to the overall sorption in the soils is very high because the sorption capacities of the fractions are significantly increased after extracting lipid and lignin fractions from them (Figures 4.34 to 4.36). Their distributed sorption isotherms are also located well above the fractions that preceeded their extractions. The isotherms for lignin free fractions are the highest in all soils indicating their dominance in the overall soption by the bulk soils (Figures 4.34 to 4.36). Lipid free fraction equally has a significant contribution to overall sorption in the coal sample (Figure 4.33), their presence within the organic matter make them compete for phenanthrene sorption thereby blocking some of the sorption sites. The increased sorption in the lignin free fractions is also supported by the fact that lignin and

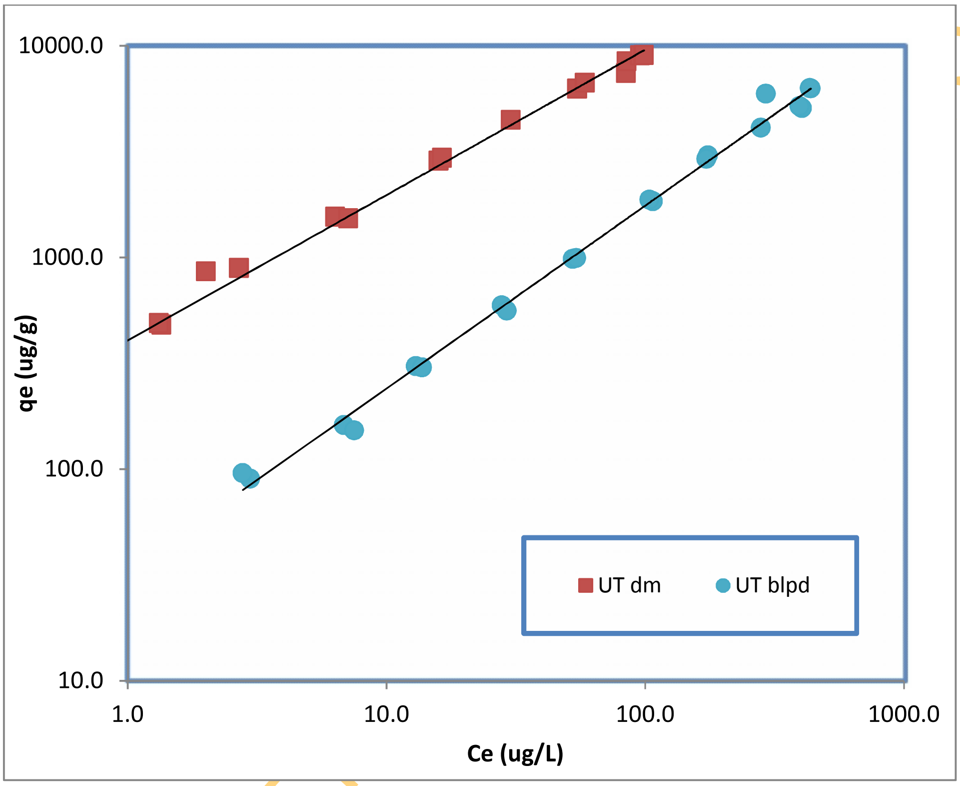


Figure 4.37: Sorption isotherms of Phenanthrene and the Freundlich modeling lines on the coal showing the contribution of bound-lipid fractions to demineralised fraction (bulk organic matter)

phenanthrene are both aromatic compounds, and when lignin is removed from the organic matter, the nannopores occupied by it would have strong affinity for phenanthrene, being another aromatic compound.

The role of the bound-lipid free fractions to the overall sorption inthe two soils (samples AD and AJ) is very small (Figures 4.34 and 4.35) because the distributed sorption isotherms of their bound-lipid free fractions occurred only above the sorption isotherms of the bulk samples but below all other residual organic matter fractions including the demineralised fraction. The role of the bound-lipid free fraction to the overall sorption in the coal is also small for almost the same reason (Figure 4.33). In the soil sample IJ however, thebound-lipid free fraction has a relatively significant contribution to the overall sorption since its sorption capacity was not reduced after extracting bound-lipid fraction from it (Table 4.4, Figure 4.36)Therefore, it can be suggested thatinsignificant or low sorption contribution from bound-lipid free fractions from the coal and the soils (samples AJ and AD) is due to removal of bound-lipid fraction from them which is accompanied by an increase in carbonyl and carboxyl groups (high polarity compounds) which block some sorption sites to phenanthrene. The significant contribution from bound-lipid free fraction in the soil sample IJ however, may be related to its relatively lower polarity when compared to other bound-lipid free fractions.

The sorption capacities of the individual lignin free and lipid free fractions were not fully assessed when they were within the bulk soils and coal sample because they have not been isolated (Figure 4.33 to 4.36). This is because inorganic mineral components may form complicated structures with condensed natural organic matter (NOM), and organic compositions may affect sorption of condensed NOM in rocks, sediments and soils (Xiao et al., 2004 and Ran et al., 2005). Once the inorganic components and organic compositions have been removed, the accessibility of sorption sites on the isolated NOM matrixes to sorbing molecules is significantly increased.

Finally, such a difference in sorption capacity between the isolated and the matrix-bound natural organic matter or soil organic matter (NOM/SOM) may bear very interesting implication for the rates of sorption and sequestration of HOC in soils and sediments. If the sorption capacity of the isolated NOM represents the ultimate HOC sorption capacity for a soil or sediment, the sorption measured in the laboratory could be far from a true equilibrium state (Xiao et al., 2004; Ran et al., 2005). This investigation shows that lipid free and lignin free fractions have similar sorption capacity for phenanthrene in the sense that they both have increased sorption capacity after removing lipid and lignin components from them respectively. The lignin fraction which is the difference between the bound-lipid free and lignin free fraction on one hand, and the lipid fraction which is also the difference between demineralised and lipid free fraction on the other hand would be significant sinks for hydrophobic organic contaminants (HOCs) in the soils and coal. The lipid and lignin fractions compete with HOCs for sorption sites, hence the reason for the increased sorption after their removal. However, removal of bound-lipid fraction has caused a significant reductionin sorption capacity of the coal and soils, thus indicating high sorption of bound-lipid fraction for phenanthrene and its large contribution to the sorption capacity before it removal. This investigation therefore revealed that bound-lipid free fractions have different sorption capacity from lipid free and lignin free fractions in the investigated coal and soil.

# CHAPTER FIVE

# CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

Coal and mudstone from Ute are black coloured with shinny lustre and grey to black coloured with occasional siltstone intercalations respectively. The rock units from Auchi are composed of fine grained, fissile, black coloured carbonaceous shale and fine grained, grey coloured shale. The soils from Lagos are essentially medium grained clayey sands to sands and brownish to dark brown in colour. The rocks and soils were demineralised and sequentially fractionated into NOM fractions including residual fractions (demineralised, lipid free, bound-lipid free and lignin free) and extracted fractions (lipid, bound-lipid and lignin).

Organic carbon contents of the bulk samples (rocks and soils) and their demineralised fractions indicated that the bulk rocks generally have higher organic matter contents than bulk soils except for some bulk soils. Coal and carbonaceous shale belonging have higher organic matter than the mudstone and shale. The bound-lipid free fractions have the lowest organic carbon and the highest oxygen contents among the residual fractions. Theaverage organic carbon content in the extracted lipid and bound-lipid fractions from the soils and rocks are 71.86 % and 55.68%, 70.25 % and 60.13 % respectively. While the average organic carbon in the extracted lignin fraction is 57.23%. The lipid fractions in the soils accounted for 5.08 to 12.04 % (except for one sample with 30.63 %) and 4.25 to 10.01 % in the rocks. Bound-lipid fractions accounted for 0.19 to 2.29 % and 0.52 to 3.26 % in the soils and rocks respectively. The lignin extracted from the soils also accounted for 1.37 % to 7.46 % except for one sample with 15.29 %. The lipid components of the rocks and soils are much higher than the bound-lipid and lignin components. Bound-lipid components seem to be related to lipid components. Higher lipid and lignin components in some of the soil samples are due to contamination.

The atomic H/C and O/C ratios indicated that the NOM fractions in the rocks are more condensed than those in the soils. The degree of maturity increases with progressive extraction in the residual fractions except in bound-lipid free fractions due to their higher polarity. The bound lipid free fractions have the lowest degree of maturation while the lipid free fractions have the highest degree of maturation in the rocks. The lignin free fractions also have the highest degree of maturation while bound-lipid free fractions have the lowest degree of maturation in the soils except in sample IJ. The lignin free and lipid free fractions in the soils are more condensed than bound-lipid free fractions except in IJ sample and they are likened to kerogen isolates. The lignin free fractions in the soils are also comparable to glassy, hard, or condensed organic matter.

The properties of NOM fractions from the rocks (samples UT & AB) are different from those of the soils (samples IJ, AD & AJ). The properties of NOM fractions from soil samples AJ and AD are similar and different from those of IJ soil sample suggesting that organic matter type in samples AJ and AD are different that of sample IJ. Similar properties of NOM fractions from coal and carbonaceous shale (UT and AB) suggested similar organic matter in them. The properties of NOM fractions indicated that lignin free fractions have the highest aromatic carbons and the lowest aliphatic carbons in the soils while lipid free fraction has the highest aromatic carbons and lowest aliphatic carbons in the coal. The demineralised fractions also have the lowest aromatic carbons and highest aliphatic carbons in the soils while bound-lipid free fraction has the lowest aromatic carbon and the highest aliphatic carbon in the coal.This indicated that aliphatic carbon decreases while the aromatic carbon increases with progressive extraction in the rocks and soils except in the bound-lipid free fractions, which further confirmed the degree of maturity.

Higher organic carbon and nitrogen contents in some bulk soils are due to contamination. The C/N atomic ratios in some of the bulk soils and marked differences in the properties of NOM fractions from the soils also confirmed anthropogenic influence in some soils. The C/N atomic ratios of the coal, carbonaceous shale and shale indicated that they were formed under similar environmental conditions while the mudstone was formed under different condition. The C/N atomic ratios also indicated that the coal, carbonaceous shale and shale contained vascular plants remains or terriginious organic matter while the mudstone is made up of algal materials. The rocks contained type III kerogen while the soils contained type II/III kerogen, suggesting that sedimentary organic matter is more stable than soil organic matter. Marked differences in the properties of NOM fractions from the rocks and soils further confirmed that sedimentary organic matter is different from soil organic matter. Van krevelen plot of the extracted fractions indicated their resemblance to similar extracts from sediments.

The phenanthrene sorption isotherms for the bulk samples and NOM fractions are nonlinear ($n>1$) and well fitted by the Freundlich equation. The nonlinearity increases with degree of maturity in the residual fractions with progressive extraction of the coal and soils except in bound-lipid free fractions of coal, AJ and AD samples, and lignin free fraction of IJ sample.The lignin free fractions have the highest degree of maturity in the soils except in IJ sample where bound-lipid free has the highest degree of maturity, and lipid free fraction has the highest degree of maturity in the coal sample.

Organic carbon normalized sorption capacity (log $K_{FOC}$) and $K_{FOC}$ values of residual fractions increases with progressive extraction in the coal and soils except in bound-lipid free fractions of the coal and samples AJ and AD, and lignin free fraction of sample IJ. These suggested that sorption capacity increases with progressive extraction in the coal and soils with exception in bound-lipid free fractions of the coal and samples AD and AJ, and the lignin free fraction of sample IJ. Single point Koc values decrease with increasing concentration of phenanthrene in the bulk samples and NOM fractions. The bulk samples exhibited much lower sorption capacity than the lipid free and lignin free fractions. The lipid free fractions also have lower sorption capacity than the lignin free fractions. The sorption capacity of the bulk coal and soil samples at any concentration are close to those of their demineralised fractions with exception in IJ sample indicating that sorption of phenanthrene is closely associated with organic phase. Higher sorption capacity in IJ bulk sample above its demineralised fraction is due to its higher TOC and contamination.

The sorption capacities of the bulk rocks are significantly higher than those of the bulk soils and some of their NOM fractions suggesting that organic matter in the rocks has higher sorption capacity than those in the soils. The sorption capacity of the carbonaceous shale is higher than that of the coal, but the sorption isotherm of the coal is higher than that of the carbonaceous shale at higher concentrations and they are almost equal at lower concentrations. The sorption capacities of all demineralised fractions in the soils are similar. Higher sorption capacities in IJ bulk soil and its NOM fractions compared other soils is due to marked difference in the properties of their NOM fractions. Similar sorption capacities of AJ and AD bulk samples, and almost all their NOM fractions is due to similarity in their organic matter properties and they also have nearly parallel sorption isotherms in their NOM fractions. The sorption capacities of the average bulk rocks are close to those of the lipid free to lignin free fractions in the soils suggesting that organic matter in the rocks has stronger sorption capacity for phenanthrene than those in the soils whether the polar organic matter or functional groups are removed or not.

The removal of lipid components increased the sorption capacity by average of 154 % in the soils and 39 % in the coal with increasing sorption capacity reducing from lower to higher concentrations, showing that sites occupied by lipids are with high energy for phenanthrene. The removal of bound-lipid components had a significant reduction in the sorption of phenanthrene by the coal and soil samples because of the elevated O/C ratios in bound-lipid free fractions suggesting notable increase in their polarity. However, there is an exception in bound-lipid free fraction of IJ sample because of its limited elevation of O/C ratio suggesting minute increament of its polarity. Just like the case of lipid, the removal of lignin components equally increased sorption capacity because of strong sorption competition with phenanthrene and the competition was further supported by the fact that both phenanthrene and lignin contain aromatic units.

The sorption capacity of the bulk samples is strongly related to their organic matter content, Sorption capacity in bulk samples therefore follows the order: UT> AB> IJ> AD> AJ. The sorption capacity follows the order dlgn>dlpd>dblpd>dm>bulk, dlgn>dlpd>dm>bulk>dblpd, dblpd>dlgn>dlpd>bulk>dm and dlpd>dm>bulk>dblpd in soil samples AD, AJ, IJ and coal sample respectively. This indicates that lignin free fractions have the highest sorption capacities among the NOM fractions in the soils except in sample IJ with highest sorption capacity in bound-lipid free, while demineralised fraction has the least sorption capacity in the soils except in sample AJ where bound-lipid free fraction has the least sorption capacity. The lipid free fraction has the highest sorption capacity while bound-lipid free fraction has the lowest sorption capacity among the NOM fractions in the coal. The sorption capacities of most of the NOM fractions in the soils are higher than that of their demineralised fractions because their sorption sites have been exposed. However, the sorption capacities of bound-lipid free fractions in the coal and sample AJ are lower than those of their demineralised fractions due to their higher polarity. The sorption capacity of bound-lipid fraction from the coal is also relatively high suggesting that its removal has caused significant decrease of sorption capacity.

The O/C atomic ratios of bound-lipid free fractions are inversely correlated to their sorption capacity. The bound-lipid free fractions are structurally different from lipid free and lignin free fractions. The degree of maturity and aromatic carbon in NOM fractions is positively correlated while the aliphatic carbon is inversely correlated to sorption of phenanthrene in the soils, rocks and their NOM fractions.

The lignin free and lipid free fractions dominated overall sorption of phenanthrene by bulk soil samples while lipid free fraction dominated overall sorption by the coal sample. The bound-lipid free fractions are less important in the overall sorption by the soils and coal except in IJ soil sample. The removal of lipid, bound-lipid and lignin fractions from NOM fractions shows that the contributions of lipid and lignin are vital in the sorption by NOM fractions because of reduced competition between them and phenanathrene making more sorption sites are available to phenanthrene. The contribution of bound-lipid is also significant in the sorption by NOM fractions because increased carbonyl and carboxyl groups blocking some sorption sites to phenanthrene.

The difference in sorption capacity between the isolated and the matrix-bound NOM or SOM may bear very interesting implication for the rates of sorption and sequestration of HOC in soils and sediments. This investigation showed that lipid free and lignin free fractions have similar sorption capacity for phenanthrene because sorption capacity increased after removing lipid and lignin components. However, sorption capacity of bound-lipid free fractions significantly reduced after removing bound-lipid components. The bound-lipid free fractions therefore have different sorption capacity from lipid free and lignin free fractions in the investigated rock and soils.

## 5.2 Recommendations

It is recommended that organic matter fractions subjected to sorption experiment in this studybe also subjected to desorption experiment to complement the findings from the sorption experiments. This will help in quatitatively determining the mechanism involved in the reverse process, since the fate of the organic contaminants is determined by their interaction with organic matter in soils and rocks. Further study should also be carried out on clay-rich soils especially laterites because of their abundance in this part of the world and their strong affinity for organic matter (interactions between theirclay minerals and organic matter). This will facilitate better understanding oforganic contaminants sorption mechanism in the presence of clay minerals and organic matter in Nigerianrocks and soils.

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# APPENDICES

## Appendix I: Concentrations of phenanthrene in initial aqueous solutions (10ppb to 1250ppb) before sorption experiments.

| Sample ID | Con1 | Con2 | Average | R.E. | Sample ID | Con1 | Con2 | Average | R.E. |
|---|---|---|---|---|---|---|---|---|---|
| 200ppb std25 | | | 201.702 | | 500ppb-std1 | | | 539.278 | |
| 10ppb | 5.997 | 6.051 | 6.024 | -0.90% | 10ppb | 6.512 | 6.349 | 6.431 | 2.53% |
| 20ppb | 12.713 | 12.512 | 12.613 | 1.59% | 20ppb | 13.212 | 13.116 | 13.164 | 0.73% |
| 40ppb | 25.453 | 25.553 | 25.503 | -0.39% | 40ppb | 27.507 | 27.813 | 27.66 | -1.11% |
| 80ppb | 52.903 | 54.108 | 53.506 | -2.25% | 80ppb | 57.676 | 58.891 | 58.284 | -2.08% |
| 150ppb | 95.51 | 97.787 | 96.649 | -2.36% | 150ppb | 99.826 | 102.561 | 101.194 | -2.70% |
| 200ppb std26 | | | 203.188 | | 500ppb std3 | | 539.895 | | |
| 300ppb | 177.335 | 182.359 | 179.847 | -2.79% | 300ppb | 214.999 | 211.192 | 213.096 | 1.79% |
| 500ppb | 290.993 | 299.009 | 295.001 | -2.72% | 500ppb | 352.244 | 353.667 | 352.956 | -0.40% |
| 750ppb | 457.176 | 475.575 | 466.376 | -3.95% | 750ppb | 529.392 | 535.138 | 532.265 | -1.08% |
| 1000ppb | 648.1 | 655.17 | 651.635 | -1.08% | 1000ppb | 609.252 | 638.11 | 623.681 | -4.63% |
| 1250ppb | 748.147 | 761.643 | 754.895 | -1.79% | 1250ppb | 852.016 | 879.076 | 865.546 | -3.13% |

## Appendix II: Concentrations of phenanthrene inampoules without geosorbents (samples) for the period of sorption experiments.

| Sample ID | Con1 | Con2 | Average | R.E. | Sample ID | Con1 | Con2 | Average | R.E. |
|---|---|---|---|---|---|---|---|---|---|
| 200ppb std27 | | 201.745 | | | 500ppb-std2 | | | 539.278 | |
| KB10ppb | 5.016 | 5.106 | 5.061 | -1.78% | KB10ppb | nd | nd | | |
| KB20ppb | 11.904 | 12.147 | 12.026 | -2.02% | KB20ppb | 11.926 | 12.076 | 12.001 | -1.25% |
| KB40ppb | 22.808 | 23.187 | 22.998 | -1.65% | KB40ppb | 24.146 | 24.496 | 24.321 | -1.44% |
| KB80ppb | 48.287 | 48.902 | 48.595 | -1.27% | KB80ppb | 48.994 | 49.636 | 49.315 | -1.30% |
| KB150ppb | 86.47 | 87.146 | 86.808 | -0.78% | KB150ppb | 92.128 | 92.736 | 92.432 | -0.66% |
| 200ppb std10 | | | 201.015 | | 200ppb-std31 | | 202.603 | | |
| KB300ppb | 171.429 | 172.28 | 171.855 | -0.50% | KB300ppb | 185.384 | 186.977 | 186.181 | -0.86% |
| KB500ppb | 264.966 | 274.702 | 269.834 | -3.61% | KB500ppb | 315.964 | 319.957 | 317.961 | -1.26% |
| KB750ppb | 443.432 | 457.065 | 450.249 | -3.03% | KB750ppb | 460.701 | 465.255 | 462.978 | -0.98% |
| KB1000ppb | 553.208 | 570.208 | 561.708 | -3.03% | KB1000ppb | 630.09 | 630.486 | 630.288 | -0.06% |
| KB1250ppb | 690.395 | 723.866 | 707.131 | -4.73% | KB1250ppb | 742.068 | 756.695 | 749.382 | -1.95% |

**Appendix III: Concentrations of phenanthrene in equilibrated aqueous solutions after sorption experiments in ampouleswith geosorbents or samples (1=10ppb, 2=20ppb, 3=40ppb, 4=80ppb, 5= 150ppb, 6=300ppb, 7=500ppb, 8=750ppb, 9=1000ppb, 10=1250ppb).**

| Sample ID | Con1 | Con2 | Average | R.E. | Sample ID | Con1 | Con2 | Average | R.E. |
|---|---|---|---|---|---|---|---|---|---|
| 500ppb std3 | | | 539.895 | | 200ppb-std27 | | | 201.745 | |
| IJ dm3 | 3.04 | 2.957 | 2.9985 | -2.77% | IJ dlpd1 | 3.565 | 3.736 | 3.651 | -4.68% |
| IJ dm4 | 3.191 | 2.976 | 3.0835 | -6.97% | IJ dlpd2 | 4.262 | 4.267 | 4.265 | -0.12% |
| IJ dm5 | 7.81 | 7.753 | 7.7815 | -0.73% | IJE dlpd3 | 7.780 | 8.102 | 7.941 | -4.05% |
| IJ dm6 | 8.417 | 8.669 | 8.543 | 2.95% | IJ dlpd4 | 7.820 | 7.918 | 7.869 | -1.25% |
| IJ dm7 | 17.816 | 18.019 | 17.9175 | 1.13% | IJ dlpd5 | 18.618 | 18.725 | 18.672 | -0.57% |
| 500ppb std4 | | | 545.148 | | IJ dlpd6 | 17.932 | 18.824 | 18.378 | -4.85% |
| IJ dm8 | 18.647 | 19.01 | 18.8285 | 1.93% | IJ dlpd 6 | 40.287 | 40.696 | 40.492 | -1.01% |
| IJ dm9 | 37.056 | 37.995 | 37.5255 | 2.50% | IJ dlpd8 | 38.629 | 39.709 | 39.169 | -2.76% |
| IJ dm10 | 41.391 | 41.678 | 41.5345 | 0.69% | IJ dlpd9 | 75.049 | 75.637 | 75.343 | -0.78% |
| IJ dm11 | 83.386 | 84.951 | 84.1685 | 1.86% | IJ dlpd10 | 76.049 | 77.117 | 76.583 | -1.39% |
| IJ dm12 | 83.752 | 85.606 | 84.679 | 2.19% | 200ppb-std28 | | | 201.424 | |
| 500ppb std5 | | | 543.932 | | IJ dlpd11 | 145.581 | 149.045 | 147.313 | -2.35% |
| IJ dm13 | 168.741 | 170.444 | 169.5925 | 1.00% | IJ dlpd12 | 142.829 | 145.691 | 144.260 | -1.98% |
| IJ dm14 | 159.534 | 160.008 | 159.771 | 0.30% | IJ dlpd13 | 228.450 | 232.721 | 230.586 | -1.85% |
| IJ dm15 | 241.214 | 241.609 | 241.4115 | 0.16% | IJ dlpd14 | 237.606 | 237.751 | 237.679 | -0.06% |
| IJ dm16 | 253.088 | 253.318 | 253.203 | 0.09% | IJ dlpd15 | 344.608 | 350.740 | 347.674 | -1.76% |
| IJ dm17 | 330.113 | 332.861 | 331.487 | 0.83% | IJ dlpd16 | 324.291 | 327.454 | 325.873 | -0.97% |
| 500ppb std6 | | | 545.927 | | IJ dlpd17 | 414.842 | 414.934 | 414.888 | -0.02% |
| IJ dm18 | 331.161 | 337.366 | 334.2635 | 1.86% | IJ dlpd18 | 409.645 | 417.211 | 413.428 | -1.83% |
| IJ dm19 | 390.69 | 397.938 | 394.314 | 1.84% | IJ dlpd19 | 480.775 | 488.004 | 484.390 | -1.49% |
| IJ dm20 | 390.728 | 397.826 | 394.277 | 1.80% | IJ dlpd20 | 501.124 | 507.820 | 504.472 | -1.33% |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 200ppb-std29 | | | 201.888 | | 200ppb-std31 | | | 202.603 | |
| IJ dblpd1 | 4.731 | 4.994 | 4.863 | -5.41% | IJ dlgn1 | 4.308 | 4.421 | 4.365 | -2.59% |
| IJ dblpd2 | 4.859 | 5.037 | 4.948 | -3.60% | IJ dlgn2 | 4.553 | 4.663 | 4.608 | -2.39% |
| IJ dblpd3 | 9.809 | 10.126 | 9.968 | -3.18% | IJ dlgn3 | 9.255 | 9.637 | 9.446 | -4.04% |
| IJ dblpd4 | 10.707 | 10.973 | 10.840 | -2.45% | IJ dlgn4 | 9.809 | 9.884 | 9.847 | -0.76% |
| IJ dblpd5 | 21.672 | 22.087 | 21.880 | -1.90% | IJ dlgn5 | 19.889 | 20.430 | 20.160 | -2.68% |
| IJ dblpd6 | 21.651 | 21.710 | 21.681 | -0.27% | IJ dlgn6 | 19.740 | 20.188 | 19.964 | -2.24% |
| IJ dblpd7 | 40.742 | 41.622 | 41.182 | -2.14% | IJ dlgn7 | 45.576 | 46.555 | 46.066 | -2.13% |
| IJ dblpd8 | 40.875 | 41.385 | 41.130 | -1.24% | IJ dlgn8 | 43.675 | 44.125 | 43.900 | -1.03% |
| IJ dblpd9 | 75.020 | 77.068 | 76.044 | -2.69% | IJ dlgn9 | 77.070 | 78.914 | 77.992 | -2.36% |
| IJ dblpd10 | 74.433 | 77.200 | 75.817 | -3.65% | IJ dlgn10 | 81.853 | 82.926 | 82.390 | -1.30% |

| Sample ID | Con1 | Con2 | Average | R.E. | Sample ID | Con1 | Con2 | Average | R.E. |
|---|---|---|---|---|---|---|---|---|---|
| 200ppb-std31 | | | 202.603 | | 200ppb-std16 | | | 201.857 | |
| IJ bulk1 | 0.590 | 0.600 | 0.595 | -1.68% | IJ bulk11 | 94.978 | 97.549 | 96.264 | -2.67% |
| IJ bulk2 | 0.460 | | 0.460 | | IJ bulk12 | 100.900 | 102.520 | 101.710 | -1.59% |
| IJ bulk3 | 3.286 | 2.993 | 3.140 | 9.33% | IJ bulk13 | 168.944 | 173.887 | 171.416 | -2.88% |
| IJ bulk4 | 2.706 | 2.721 | 2.714 | -0.55% | IJ bulk14 | 168.349 | 173.565 | 170.957 | -3.05% |
| IJ bulk5 | 6.989 | 7.468 | 7.229 | -6.63% | IJ bulk15 | 290.995 | 300.147 | 295.571 | -3.10% |
| 200ppb-std15 | | | 199.998 | | 200ppb-std17 | | | 201.809 | |
| IJ bulk6 | 7.258 | 7.230 | 7.244 | 0.39% | IJ bulk16 | 283.433 | 290.195 | 286.814 | -2.36% |
| IJ bulk7 | 19.018 | 18.329 | 18.674 | 3.69% | IJ bulk17 | 376.158 | 381.171 | 378.665 | -1.32% |
| IJ bulk8 | 19.223 | 20.127 | 19.675 | -4.59% | IJ bulk18 | 368.224 | 380.696 | 374.460 | -3.33% |
| IJ bulk9 | 45.085 | 46.795 | 45.940 | -3.72% | IJ bulk19 | 499.853 | 504.863 | 502.358 | -1.00% |
| IJ bulk10 | 42.061 | 41.887 | 41.974 | 0.41% | IJ bulk20 | 459.394 | 465.409 | 462.402 | -1.30% |
| 200ppb-std33 | | | 201.138 | | 200ppb-std14 | | | 202.277 | |
| AJ bulk1 | 1.534 | 1.610 | 1.572 | -4.83% | AJ bulk11 | 126.501 | 125.691 | 126.096 | 0.64% |
| AJ bulk2 | 2.059 | 2.010 | 2.035 | 2.41% | AJ bulk12 | 122.042 | 124.301 | 123.172 | -1.83% |
| AJ bulk3 | 4.918 | 5.154 | 5.036 | -4.69% | AJ bulk13 | 190.967 | 203.379 | 197.173 | -6.29% |
| AJ bulk4 | 5.141 | 5.258 | 5.200 | -2.25% | AJ bulk14 | 194.447 | 198.741 | 196.594 | -2.18% |
| AJ bulk5 | 11.343 | 11.824 | 11.584 | -4.15% | AJ bulk15 | 312.298 | 312.439 | 312.369 | -0.05% |
| 200ppb-std13 | | | 202.087 | | 200ppb-std15 | | | 199.998 | |
| AJ bulk6 | 11.268 | 11.612 | 11.440 | -3.01% | AJ bulk16 | 304.353 | 310.019 | 307.186 | -1.84% |
| AJ bulk7 | 25.325 | 26.058 | 25.692 | -2.85% | AJ bulk17 | 422.285 | 420.469 | 421.377 | 0.43% |
| AJ bulk8 | 26.142 | 26.637 | 26.390 | -1.88% | AJ bulk18 | 408.043 | 417.777 | 412.910 | -2.36% |
| AJ bulk9 | 54.132 | 55.718 | 54.925 | -2.89% | AJ bulk19 | 516.169 | 525.341 | 520.755 | -1.76% |
| AJ bulk10 | 52.633 | 53.578 | 53.106 | -1.78% | AJ bulk20 | 519.027 | 532.906 | 525.967 | -2.64% |
| 500ppb-std16 | | | 544.491 | | 500ppb-std20 | | | 542.363 | |
| AJ dm1 | 0.905 | 0.862 | 0.884 | 4.87% | AJL dlpd1 | 2.188 | 2.157 | 2.173 | 1.43% |
| AJ dm2 | 0.653 | | | | AJ dlpd2 | 2.023 | 2.069 | 2.046 | -2.25% |
| AJ dm3 | 2.547 | 2.372 | 2.460 | 7.12% | AJ dlpd3 | 5.513 | 5.558 | 5.536 | -0.81% |
| AJ dm4 | 2.153 | 2.092 | 2.123 | 2.87% | AJ dlpd4 | 0.628 | 0.659 | 0.644 | -4.82% |
| AJ dm5 | 4.529 | 4.882 | 4.706 | -7.50% | AJ dlpd5 | 2.046 | 2.033 | 2.040 | 0.64% |
| 500ppb-std17 | | | 544.519 | | 500ppb-std21 | | | 543.096 | |
| AJ dm6 | 4.893 | 4.946 | 4.920 | -1.08% | AJ dlpd6 | 1.7 | 1.707 | 1.704 | -0.41% |
| AJ dm7 | 11.866 | 12.098 | 11.982 | -1.94% | AJ dlpd7 | 5.565 | 5.625 | 5.595 | -1.07% |
| AJ dm8 | 12.698 | 13.156 | 12.927 | -3.54% | AJ dlpd8 | 6.082 | 6.286 | 6.184 | -3.30% |
| AJ dm9 | 60.301 | 62.071 | 61.186 | -2.89% | AJ dlpd9 | 39.658 | 41.025 | 40.342 | -3.39% |
| AJ dm10 | 67.282 | 68.673 | 67.978 | -2.05% | AJ dlpd10 | 37.053 | 38.201 | 37.627 | -3.05% |

| Sample ID | Con1 | Con2 | Average | R.E. | Sample ID | Con1 | Con2 | Average | R.E. |
|---|---|---|---|---|---|---|---|---|---|
| 500ppb-std18 | | | 544.086 | | 500ppb-std22 | | | 540.699 | |
| AJ dm11 | 26.411 | 26.109 | 26.260 | 1.15% | AJ dlpd11 | 13.707 | 13.956 | 13.832 | -1.80% |
| AJ dm12 | 24.319 | 25.018 | 24.669 | -2.83% | AJ dlpd12 | 13.481 | 13.978 | 13.730 | -3.62% |
| AJ dm13 | 112.821 | 114.795 | 113.808 | -1.73% | AJ dlpd13 | 71.465 | 72.902 | 72.184 | -1.99% |
| AJ dm14 | 110.603 | 112.380 | 111.492 | -1.59% | AJ dlpd14 | 69.486 | 69.852 | 69.669 | -0.53% |
| AJ dm15 | 168.025 | 170.630 | 169.328 | -1.54% | AJ dlpd15 | 137.099 | 137.954 | 137.527 | -0.62% |
| 500ppb-std19 | | | 543.406 | | 500ppb-std23 | | | 542.233 | |
| AJ dm16 | 170.946 | 170.591 | 170.769 | 0.21% | AJ dlpd16 | 145.779 | 147.377 | 146.578 | -1.09% |
| AJ dm17 | 203.878 | 210.984 | 207.431 | -3.43% | AJ dlpd17 | 187.395 | 192.513 | 189.954 | -2.69% |
| AJ dm18 | 260.166 | 263.235 | 261.701 | -1.17% | AJ dlpd18 | 201.845 | 203.187 | 202.516 | -0.66% |
| AJ dm19 | 296.299 | 302.598 | 299.449 | -2.10% | AJ dlpd19 | 237.581 | 234.767 | 236.174 | 1.19% |
| AJ dm20 | 308.005 | 310.884 | 309.445 | -0.93% | AJ dlpd20 | 232.214 | 228.467 | 230.341 | 1.63% |
| 500ppb-std21 | | | 543.096 | | 200ppb-std33 | | | 201.138 | |
| AJ dblpd1 | 6.942 | 6.867 | 6.905 | 1.09% | AJ dlgn1 | 5.019 | 5.277 | 5.148 | -5.01% |
| AJ dblpd2 | 9.265 | 9.109 | 9.187 | 1.70% | AJ dlgn2 | 4.114 | 4.254 | 4.184 | -3.35% |
| AJ dblpd3 | 16.155 | 15.985 | 16.070 | 1.06% | AJ dlgn3 | 9.250 | 9.501 | 9.376 | -2.68% |
| AJ dblpd4 | 21.778 | 21.401 | 21.590 | 1.75% | AJ dlgn4 | 9.795 | 9.630 | 9.713 | 1.70% |
| AJ dblpd5 | 10.306 | 10.489 | 10.398 | -1.76% | AJ dlgn5 | 20.904 | 21.346 | 21.125 | -2.09% |
| 500ppb-std22 | | | 540.699 | | 200ppb-std8 | | | 200.186 | |
| AJ dblpd6 | 9.517 | 9.713 | 9.615 | -2.04% | AJ dlgn6 | 20.544 | 21.009 | 20.777 | -2.24% |
| AJ dblpd7 | 23.189 | 22.687 | 22.938 | 2.19% | AJ dlgn7 | 37.688 | 38.642 | 38.165 | -2.50% |
| AJ dblpd8 | 24.657 | 24.519 | 24.588 | 0.56% | AJ dlgn8 | 38.946 | 39.720 | 39.333 | -1.97% |
| AJ dblpd9 | 48.293 | 48.131 | 48.212 | 0.34% | AJ dlgn9 | 71.816 | 72.671 | 72.244 | -1.18% |
| AJ dblpd10 | 47.388 | 47.856 | 47.622 | -0.98% | AJ dlgn10 | 67.698 | 70.282 | 68.990 | -3.75% |
| 500ppb-std23 | | | 542.233 | | 200ppb-std9 | | | 201.176 | |
| AJ dblpd11 | 106.563 | 107.506 | 107.035 | -0.88% | AJ dlgn11 | 148.657 | 148.978 | 148.818 | -0.22% |
| AJ dblpd12 | 110.853 | 108.900 | 109.877 | 1.78% | AJ dlgn12 | 134.455 | 139.825 | 137.140 | -3.92% |
| AJ dblpd13 | 188.629 | 193.605 | 191.117 | -2.60% | AJ dlgn13 | 203.599 | 208.974 | 206.287 | -2.61% |
| AJ dblpd14 | 185.709 | 190.010 | 187.860 | -2.29% | AJ dlgn14 | 215.247 | 218.557 | 216.902 | -1.53% |
| AJ dblpd15 | 303.388 | 308.275 | 305.832 | -1.60% | AJ dlgn15 | 329.887 | 339.851 | 334.869 | -2.98% |
| 500ppb-std24 | | | 539.728 | | 200ppb-std10 | 201.015 | | 200ppb-std10 | 201.015 |
| AJ dblpd16 | 293.436 | 297.400 | 295.418 | -1.34% | AJ dlgn16 | 319.403 | 322.521 | 320.962 | -0.97% |
| AJ dblpd17 | 408.235 | 416.309 | 412.272 | -1.96% | AJ dlgn17 | 404.715 | 421.642 | 413.179 | -4.10% |
| AJ dblpd18 | 440.420 | 456.387 | 448.404 | -3.56% | AJ dlgn18 | 417.249 | 429.892 | 423.571 | -2.98% |
| AJ dblpd19 | 511.621 | 523.408 | 517.515 | -2.28% | AJ dlgn19 | 521.161 | 536.335 | 528.748 | -2.87% |
| AJ dblpd20 | 529.906 | 540.443 | 535.175 | -1.97% | AJ dlgn20 | 580.854 | 592.215 | 586.535 | -1.94% |
| 500ppb-std1 | | | 601.658 | | 500ppb-std2 | | | 539.278 | |

| Sample ID | Con1 | Con2 | Average | R.E. | Sample ID | Con1 | Con2 | Average | R.E. |
|---|---|---|---|---|---|---|---|---|---|
| 200ppb-std15 | | | 199.998 | | 500ppb-std13 | | | 542.447 | |
| AD bulk1 | 2.010 | 1.955 | 1.983 | 2.77% | ADJ dm1 | 0.508 | nd | | |
| AD bulk2 | 1.887 | 1.872 | 1.880 | 0.80% | ADJ dm2 | 0.977 | 1.055 | 1.016 | 7.68% |
| AD bulk3 | 5.417 | 5.605 | 5.511 | -3.41% | ADJ dm3 | 2.398 | 2.213 | 2.306 | -8.02% |
| AD bulk4 | 4.676 | 4.724 | 4.700 | -1.02% | ADJ dm4 | 2.233 | 2.239 | 2.236 | 0.27% |
| AD bulk5 | 11.176 | 11.698 | 11.437 | -4.56% | ADJ dm5 | 5.557 | 5.565 | 5.561 | 0.14% |
| 200ppb-std19 | | | 202.269 | | 500ppb-std14 | | | 542.395 | |
| AD bulk6 | 11.222 | 11.782 | 11.502 | -4.87% | ADJ dm6 | 4.64 | 4.684 | 4.662 | 0.94% |
| AD bulk7 | 25.422 | 26.455 | 25.939 | -3.98% | ADJ dm7 | 13.312 | 13.413 | 13.363 | 0.76% |
| AD bulk8 | 25.222 | 26.117 | 25.670 | -3.49% | ADJ dm8 | 13.947 | 14.107 | 14.027 | 1.14% |
| AD bulk9 | 53.138 | 55.032 | 54.085 | -3.50% | ADJ dm9 | 24.686 | 25.123 | 24.905 | 1.75% |
| AD bulk10 | 53.257 | 54.831 | 54.044 | -2.91% | ADJ dm10 | 27.992 | 28.107 | 28.050 | 0.41% |
| 200ppb-std20 | | | 202.462 | | 500ppb-std26 | | | 542.227 | |
| AD bulk11 | 112.315 | 115.286 | 113.801 | -2.61% | ADJ dm11 | 54.005 | 55.040 | 54.523 | 1.90% |
| AD bulk12 | 115.083 | 116.674 | 115.879 | -1.37% | ADJ dm12 | 81.115 | 82.491 | 81.803 | 1.68% |
| AD bulk13 | 192.065 | 198.563 | 195.314 | -3.33% | ADJ dm13 | 101.412 | 101.917 | 101.665 | 0.50% |
| AD bulk14 | 180.472 | 189.248 | 184.860 | -4.75% | ADJ dm14 | 94.609 | 94.901 | 94.755 | 0.31% |
| AD bulk15 | 299.862 | 306.367 | 303.115 | -2.15% | ADJ dm15 | 178.826 | 180.331 | 179.579 | 0.84% |
| 200ppb-std21 | | | 201.684 | | 500ppb-std27 | | | 544.204 | |
| AD bulk16 | 292.443 | 306.102 | 299.273 | -4.56% | ADJ dm16 | 154.563 | 155.766 | 155.165 | 0.78% |
| AD bulk17 | 407.886 | 416.836 | 412.361 | -2.17% | ADJ dm17 | 210.077 | 210.212 | 210.145 | 0.06% |
| AD bulk18 | 415.670 | 418.520 | 417.095 | -0.68% | ADJ dm18 | 230.354 | 234.061 | 232.208 | 1.60% |
| AD bulk19 | 491.478 | 500.140 | 495.809 | -1.75% | ADJ dm19 | 222.338 | 223.759 | 223.049 | 0.64% |
| AD bulk20 | 514.669 | 515.888 | 515.279 | -0.24% | ADJ dm20 | 246.669 | 246.555 | 246.612 | -0.05% |
| 500ppb-std22 | | | 540.699 | | 500ppb-std24 | | | 539.728 | |
| AD dlpd1 | 1.677 | nd | 1.677 | | AD dlpd11 | nd | | | |
| AD dlpd2 | 2.327 | 2.355 | 2.341 | -1.20% | AD dlpd12 | 13.141 | 13.136 | 13.139 | 0.04% |
| AD dlpd3 | 4.038 | 4.092 | 4.065 | -1.33% | AD dlpd13 | 76.509 | 76.981 | 76.745 | -0.62% |
| AD dlpd4 | 4.499 | 4.454 | 4.477 | 1.01% | AD dlpd14 | 74.141 | 74.475 | 74.308 | -0.45% |
| AD dlpd5 | 1.442 | 1.510 | 1.476 | -4.61% | AD dlpd15 | 122.259 | 123.795 | 123.027 | -1.25% |
| 500ppb-std23 | | | 542.233 | | 500ppb-std25 | | | 539.983 | |
| AD dlpd6 | 2.081 | 2.156 | 2.119 | -3.54% | AD dlpd16 | 130.755 | 131.329 | 131.042 | -0.44% |
| AD dlpd7 | 5.391 | 5.537 | 5.464 | -2.67% | AD dlpd17 | 184.528 | 184.952 | 184.740 | -0.23% |
| AD dlpd8 | 5.308 | 5.348 | 5.328 | -0.75% | AD dlpd18 | 167.432 | 169.374 | 168.403 | -1.15% |
| AD dlpd9 | 35.102 | 35.287 | 35.195 | -0.53% | AD dlpd19 | 212.374 | 219.792 | 216.083 | -3.43% |
| AD dlpd10 | 35.361 | 35.650 | 35.506 | -0.81% | AD dlpd20 | 223.758 | 228.113 | 225.936 | -1.93% |

| Sample ID | Con1 | Con2 | Average | R.E. | Sample ID | Con1 | Con2 | Average | R.E. |
|---|---|---|---|---|---|---|---|---|---|
| 200ppb-std15 | | | 199.998 | | 200ppb-std16 | | | 201.857 | |
| AD dblpd1 | 4.137 | 4.230 | 4.184 | -2.22% | AD dlgn1 | 4.108 | 4.235 | 4.172 | -3.04% |
| AD dblpd2 | 4.373 | 4.471 | 4.422 | -2.22% | AD dlgn2 | 4.497 | 4.681 | 4.589 | -4.01% |
| AD dblpd3 | 8.895 | 9.274 | 9.085 | -4.17% | AD dlgn3 | 9.485 | 9.802 | 9.644 | -3.29% |
| AD dblpd4 | 8.534 | 8.847 | 8.691 | -3.60% | AD dlgn4 | 8.193 | 8.250 | 8.222 | -0.69% |
| AD dblpd5 | 16.799 | 17.311 | 17.055 | -3.00% | AD dlgn5 | 18.336 | 18.558 | 18.447 | -1.20% |
| 200ppb-std17 | | | 201.809 | | 200ppb-std11 | | | 201.134 | |
| AD dblpd6 | 17.696 | 17.580 | 17.638 | 0.66% | AD dlgn6 | 19.751 | 20.764 | 20.258 | -5.00% |
| AD dblpd7 | 35.896 | 36.293 | 36.095 | -1.10% | AD dlgn7 | 32.344 | 32.858 | 32.601 | -1.58% |
| AD dblpd8 | 37.673 | 37.910 | 37.792 | -0.63% | AD dlgn8 | 33.009 | 33.930 | 33.470 | -2.75% |
| AD dblpd9 | 71.078 | 71.586 | 71.332 | -0.71% | AD dlgn9 | 57.383 | 57.450 | 57.417 | -0.12% |
| AD dblpd10 | 72.644 | 72.727 | 72.686 | -0.11% | AD dlgn10 | 58.300 | 59.154 | 58.727 | -1.45% |
| 200ppb-std18 | | | 200.078 | | 200ppb-std12 | | | 200.652 | |
| AD dblpd11 | 147.335 | 150.339 | 148.837 | -2.02% | AD dlgn11 | 122.110 | 125.512 | 123.811 | -2.75% |
| AD dblpd12 | 155.147 | 156.738 | 155.943 | -1.02% | AD dlgn12 | 107.939 | 111.893 | 109.916 | -3.60% |
| AD dblpd13 | 241.609 | 243.708 | 242.659 | -0.87% | AD dlgn13 | 190.607 | 197.581 | 194.094 | -3.59% |
| AD dblpd14 | 240.023 | 248.269 | 244.146 | -3.38% | AD dlgn14 | 191.246 | 195.164 | 193.205 | -2.03% |
| AD dbl1pd5 | 359.033 | 355.177 | 357.105 | 1.08% | AD dlgn15 | 261.812 | 266.857 | 264.335 | -1.91% |
| 200ppb-std19 | | | 202.269 | | 200ppb-std13 | | | 202.087 | |
| ADdblpd16 | 367.149 | 373.219 | 370.184 | -1.64% | AD dlgn16 | 256.198 | 258.539 | 257.369 | -0.91% |
| AD dblpd17 | 478.150 | 492.073 | 485.112 | -2.87% | AD dlgn17 | 306.025 | 320.270 | 313.148 | -4.55% |
| AD dblpd18 | 526.639 | 520.802 | 523.721 | 1.11% | AD dlgn18 | 332.739 | 327.932 | 330.336 | 1.46% |
| AD dblpd19 | 604.906 | 621.187 | 613.047 | -2.66% | AD dlgn19 | 294.542 | 293.429 | 293.986 | 0.38% |
| AD dblpd20 | 612.405 | 617.102 | 614.754 | -0.76% | AD dlgn20 | 395.363 | 407.492 | 401.428 | -3.02% |
| 200ppb-std13 | | | 202.087 | | 200ppb-std22 | | | 203.156 | |
| AB bulk1 | | | nd | | AB bulk11 | 14.927 | 14.675 | 14.801 | 1.70% |
| AB bulk2 | | | nd | | AB bulk12 | 13.539 | 14.362 | 13.951 | -5.90% |
| AB bulk3 | | | nd | | AB bulk13 | 30.382 | 30.622 | 30.502 | -0.79% |
| AB bulk4 | | | nd | | AB bulk14 | 29.232 | 29.823 | 29.528 | -2.00% |
| AB bulk5 | | | nd | | AB bulk15 | 58.704 | 59.257 | 58.981 | -0.94% |
| 200ppb-std21 | | | 201.684 | | 200ppb-std23 | | | 202.569 | |
| AB bulk6 | 0.202 | 0.200 | 0.201 | 1.00% | AB bulk16 | 57.120 | 57.210 | 57.165 | -0.16% |
| AB bulk7 | 1.648 | 1.657 | 1.653 | -0.54% | AB bulk17 | 89.959 | 89.795 | 89.877 | 0.18% |
| AB bulk8 | 1.508 | 1.580 | 1.544 | -4.66% | AB bulk18 | 80.813 | 82.651 | 81.732 | -2.25% |
| AB bulk9 | 4.212 | 4.261 | 4.237 | -1.16% | AB bulk19 | 123.328 | 129.056 | 126.192 | -4.54% |
| AB bulk10 | 4.447 | 4.528 | 4.488 | -1.81% | AB bulk20 | 117.774 | 121.375 | 119.575 | -3.01% |