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Effects of Crude Oil Contaminated Water on the Environment

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1. Introduction

With the development of oil industry, the general environment and in particular wetland ecosystem has become extremely vulnerable to damaging effects of oil pollution. Contamination of aquatic environment by crude oil and petroleum products constitute an additional source of stress to aquatic organisms (Omoregie *et al.*, 1997) and is of importance to the wetland environment. Oil contaminated water resulted in water becoming unsuitable for the growth of macrophytes (Edema, 2006) only scanty data are available for levels of chemical pollution of aquatic plants since most studies of biota are concentrated in fish (FAO, 1993).

2. The water environment

Water quality is one important factor of an aquatic environment. Water analysis consists of an assessment of the condition of water in relation to set goals. For example, water samples with decreased electrical conductivity measurement indicate a good measure of purity (Hoagland, 1972). During spillage, water supply becomes critical.

Toxic pollutants in water refer to a whole array of chemical which are leached into ground water or which are discharged directly into rivers. Contamination of aquatic environment by crude oil and petroleum products constitute an additional source of stress to aquatic organisms (Omoregie *et al.*, 1997) and is of importance to wetland environment.

Water pollutants can also include excessive amounts of heavy metals, radioactive isotopes, faecal coliform bacteria, phosphorus, nitrogen, sodium and other useful (even necessary) elements as well as certain pathogenic bacteria and viruses (Botkin and Keller, 1998).

The water environment experiences many dynamic changes induced by various natural events such as the spillage of toxic chemicals that may have significant impact on aquatic life (Camougis, 1981).

Even in Roman times, heavy metals from mining and pathogens from cities caused serious though local, water contamination (FAO, 1993). Some of the major factors associated with accelerating pace of fresh water pollution is accidental damage of pipes and tankers, major leaks and local spills. These cause varying degrees of aquatic toxicity and material damage. Industrial accidents involving spillage of long lasting pollutants such as persistent organic substances have the most serious effects on water quality. Many of these substances become concentrated in living tissue because organisms have no means of excreting them. They accumulate and are pass on at successively greater concentration of predators higher up the food chain.

This chapter is primarily focused on the biological impact of the exploration activities of oil companies in our water environment.

3. Crude oil

Crude oil is a colloidal mixture of huge number of hydrocarbon and non-hydrocarbon (Cadwallaer, 1993). The source material for nearly all petroleum products is crude oil. Spill, leaks and other releases of gasoline, diesel, fuels, heating oils and other petroleum products often result in the contamination of soil and water. Hydrocarbon form over 90 percent petroleum oil are grouped according to their chemical structures such as straight, branched and cyclic alkanes and aromatics. The non-hydrocarbon components of petroleum include (O_2, N, S ---) and some metals related porphyrin oxygen containing compounds e.g. naphthenic acid, carboxylic acid, esters, ketones, phenols etc (Odu, 1981). Oil pollution occurs when oil is introduced into the environment directly or indirectly by men's impacts resulting in unfavorable change in such a way that safety and welfare of any living organisms is endangered. Crude oil if spilled into the water spreads over a wide area forming a slick and oil in water immediately begins to undergo a variety of physical, chemical and biological changes including evaporation of high volatile fractions, dissolution of water-soluble fractions, photochemical oxidation, drill, emulsification, microbial degradation and sedimentation (Muller, 1987). Crude oil is a complex mixture of hydrocarbon and organic compounds of sulphur, nitrogen, oxygen and a certain quantity of water which varies in composition from place to place (Anoliefo, 1991). Crude oil is produced from decay of plants and animals over millions of years. It is also referred to as mineral oil. Crude oil, which is a mixture of hydrocarbons and inorganic compounds is drilled through rocks. Crude oil discharged on the sea surface undergoes physical, chemical and biological alteration. Rapid physical and chemical processes include spreading and movement by wind and currents, injection into the air, evaporation of volatile components, dispersion of small droplets into water, dissolution and chemical oxidation (Nelson Smith, 1972). Concurrent with these are relevant biological processes. They include degradation by micro-organisms and uptake by larger organisms followed by metabolism and storage or discharge (Nelson-Smith, 1972).

4. Water soluble fraction

Water and oil are usually considered to be non-miscible. However, crude oil contains a very small soluble portion referred to as the water soluble fraction (WSF) Kavanu, 1964. The soluble constituents are dispersed particulate oil, dissolved hydrocarbons and soluble contaminants such as metallic ions (Kauss and Hutchinson, 1975). Non-hydrocarbon components of crude oil include polar components containing nitrogen, sulphur and oxygen (Westlake, 1982). Oxygen containing compounds include esters and ketones, while nitrogen containing compounds include pyrimidine and quinoline (Obire, 1985).

The concentration of hydrocarbon and non-hydrocarbon components in crude oil from different sources differ greatly (Brunnock *et al.*, 1968). The components of crude oil that go into solution make up the WSF. They are taken up by living cells and metabolized. This is ecologically important because in the event of an oil spill or effluent discharge from engine oil vehicles or where there is deliberate discharge of petroleum products into aquatic habitats, these hydrocarbons are absorbed by living organisms, with serious effects on the ecosystem (Michael, 1977). The lower the molecular weight of the constituent hydrocarbon of crude oil, the higher is its concentration in the water-soluble fraction (Bohon and Clausen, 1951). Anderson *et al.* (1974) analyzed the water soluble extract of South Loisiana and Kuwait crude oils and reported that the WSF contained 20 aromatic compounds ranging from benzene to dimethyl phenothrenes and up to 14 saturated hydrocarbons ranging from C_{14} to parafins.

Adverse biological effects have been attributed to dissolved low molecular weight hydrocarbon particularly aromatics such as toluene. Anderson *et al.* (1974) and Winter (1976) considered naphthalene as a more important source of crude oil toxicity than low molecular weight aromatics. According to another source, the low boiling point unsaturated hydrocarbon such as benzene, toluene, xylene and naphthalene, are the most toxic components in crude oils, the toxicity can be said to be a function of the presence of these substances (Nelson-Smith, 1972).

When there is delay in clean up action for any reason, after spillage has occurred, the water soluble components of crude oil seep into the aquatic ecosystem. The components of crude oil that go into solution make up the WSF. Concave (1979) reported that pure hydrocarbon yield 4.2mgl^{-1} of WSF. Baker (1970a) observed that water soluble fraction (WSF) is produced during a long period of oil water contact.

5. Preparation of WSF

The Water Soluble Fraction was prepared according to the method of Anderson *et al.* (1974). A sample of crude oil (500ml) was slowly mixed in equal volume of deionized water in a 2 liter screw-cap conical flask. A Gallenkamp table top magnetic stirrer supplied with 7/1cm magnetic bar was used for mixing. Stirring was done for 20hrs and at room temperature (27^{0}C ± 2^{0}C). After mixing, the oil water mixture was allowed to stand overnight in a separating funnel. The lower phase was collected and used as the WSF. It was referred to as 100% or full- strength WSF. The stock WSF was diluted with water to give 50% and 25% strength WSF which were stored in crew-cap bottles prior to use. The WSF samples were applied at three levels, 25%, 50% and 100%.

6. Composition of WSF

Ionic components: These include the cations and anions.

Cation

Cations are positively charged ions. The four major cations of the total ionic salinity of water for all practical purposes are Ca^{++}, Mg^{++}, Na^+ and K^+ (Wetzel, 2001). These elements are required by plants in large amounts (Hopkins, 1999). Water soluble fraction of crude oil has been found to contain the following cations Na^+, Ca^{++}, Mg^{++}, Fe^{++}, Fe^{+++} , NH_4^+, K^+ (Edema, 2006)

Anions

Anions are negatively charged ions (Botkin and Keller, 1998). Anions, such as Cl^-, NO_3^- and SO_4^{2-} are soluble and are present in living plants largely as ions in solution (Hopkins, 1999). The major anions that constitute the ionic salinity of water for all practical purposes are Cl^-, SO_4^{2-}, HCO_3^- and CO^-_3 (Wetzel, 2001). Water soluble fraction of crude oil was found to contain, Cl^-, SO^{2-}_4, NO_3^-, PO_4^{2-} and HCO_3^- (Edema, 2006).

Heavy metals

The contamination of the aquatic system with heavy metals has been on the increase since the last century due to industrial activities (Ali and Mai, 2007). Heavy metals are taken up as cations. Among the heavy metals detected in WSF are Pb, Cu, Zn, Cd, Ni, Cr, and V (Edema, 2006). This is in agreement with the statement of Kauss and Hutchinson (1975) that the WSF of crude oil contains metallic ions among other soluble contaminants. Botkin and keller (1998) stated that Pb, Cr and V are among metals that pose hazard to living organisms. Heavy metals are non-biodegradable and are toxic under certain condition (Rana, 2005).

7. Physical composition

The physical components found to be present in WSF of crude oil include hydrogen ion concentration (pH), chemical oxygen demand (COD), total dissolved solids (TDs) and electrical conductivity (EC) (Edema, 2006). Chemical substances in WSF are capable of changing the hydrogen ion concentration (pH) of the medium (Neff and Anderson, 1981). Elevation of pH values after the introduction of macrophytes to WSF of crude oil were recorded by Edema *et al*. (2008). The pH values recorded were within the maximum permissible level (pH 6.5 – 9.8 values) (WHO, 1995). The values for electrical conductivity, total dissolved solids, chemical oxygen demand were significantly found to increase after exposure to plants. High EC, TDS and COD are signs of pollution. This means that more ions were available after the introduction of test macrophytes. Increase in EC indicates that most inorganic elements exist in abundance (Kadiri, 2006). Although the total dissolves solids (TDS) values were found to increase after exposure to plants were still within the highest desirable limit of WHO (500mg/l) and Talling and Talling (1965), classification Scheme of African water within conductivities of between 6,000 – 16,000μScm^{-1}. With continuous spillage, the values may rise and exceed the WHO values.

8. Salinity

The concentration of the 4 major cations Ca^{++}, Mg^{++}, Na^{++} and K^+ and 4 major anions, HCO_3^-, CO_3^-, SO_4^{2-} and Cl^- usually constitute the total ionic salinity of water for all practical purposes (Wetzel, 2001). Concentrations of ionized components of other elements such as N, P and Fe and numerous minor elements are of immerse biological importance but are usually minor contributors to total salinity (Wetzel, 2001). The sum of all ionic concentrations is the basis for salinity measurement (Covich, 1993). Total dissolved solids and ionic conductivity of water, are generally used measurement (Covich, 1993).

The values of ions increased with increase in concentration of WSF prior to used. This is in agreement with the report of McOliver (1981) that when there is oil spillage more salts are released into river. Thus, the amount of salts contained in aquatic ecosystem increased. These increases could be due to leakage of the cells brought about by salt (ionic) stress and associated oxidative damage (Burdon *et al.,* 1996). Salt stress refers to an excess of ions and is not limited to Na^+ and Cl^- ion (Hopkins, 1999). According to Hernandez *et al.* (1985) oxidative stress is influenced by environmental factors, metal ion deficiency and toxicity. The sum of ions in the WSF of crude oil studied had higher values than river waters of Africa as reported by Wetzel (2001).

WSF, %	Sum of all ionic contents (as the total salinity)		
	Before	After	Difference
25	123.33	245.50	121.17
50	151.25	263.70	112.43
100	206.26	385.80	197.54

Table Ia. Sum of all ionic contents of Amukpe well- head WSF before and after exposure to *Pistia stratiotes.* Source: Edema and Okoloko (2008)

WSF, %	Sum (EC+ TDS)		
	Before	After	Difference
25	145.83	191.10	45.27
50	167.62	263.40	95.79
100	220.35	374.56	154.21

Table Ib. Sum of EC and TDS (as total salinity) of the WSF of Amukpe well-head crude oil before and after exposure to *Pisitia stratiotes.* Source: Edema and Okoloko (2008)

WSF, %	Sum of all ionic concentration		
	Before	After	Difference
25	12.95	262.05	249.02
50	22.90	338.21	315.31
100	46.75	371.69	324.94

Table IIa. Sum of all ionic concentration of the WSF of Ogini well-head crude oil before and after exposure to *Azolla sp.*

WSF, %	Sum of (EC + TDS)		
	Before	After	Difference
25	14.60	287.28	264.68
50	21.40	340.38	318.94
100	36.02	455.00	418.98

Source: Edema (2009)

Table IIb. Sum of EC +TDS (as total salinity) of the WSF of Ogini well-head crude oil before and after exposure to *Azolla sp.*

9. Produced water

Almost all offshore oil produces large quantities of contaminated water that can have significant environmental effects if not handled appropriately (Will, 2000). Oil and gas reservoirs have natural water layer (called formation water). Because, it is denser is found under the hydrocarbons. Oil reservoirs frequently contain large volume of water. To achieve maximum oil recovery, additional water is usually injected into surface. The formation and injected water are eventually produced along with hydrocarbons. The product of the formation and injected water is referred to as produced water.

There is more in produced water than water and oil. Neff and Anderson (1981) described produced water for ocean discharge as containing up to 48ppm of petroleum. This is because it had usually been in contact with oil in the reservoir rock. There were also elevated concentration of barium, beryllium, cadmium, chromium, copper, Iron, lead, nickel, silver and zinc and "small amount of the neutral radionucleids radium 226 and radium 228 and non-volatile dissolved organic material of unknown composition". Due to rapid mixing with seawater, most physical – chemical features of produced water (low dissolved oxygen and pH, elevated salinity and metals) do not pose any hazard to water, elevated concentration of hydrocarbon may be detected in surface sediments up to about 1,000 from the discharge, that contains aromatic hydrocarbons and metals. These aromatic hydrocarbons and metals in produced water were reported by Neff and Anderson (1981) to be toxic to organisms.

10. Biological effects of crude oil

Baker (1970) reported that oil pollution effects vary according to the type and amount of oil involved, the degree of weathering, the time of the year, the plant species concerned and the age of the plant. Cowell (1977) include the physical and chemical properties of the oil as well as the quantity of the water being polluted. The water soluble fraction of crude oils has been found to reduce the growth rate of biomas turnover of some marcophytes (Gunlack and Hayes, 1977). Kauss and Hutchinson (1975) found that aquatic macrophytes population was reduced in the presence of water-soluble petroleum components. The inhibitory effects of petroleum components are known to be dependent upon the concentration of the crude oil as well as that of water soluble components (Shew, 1977).

Aquatic macrophytes e.g. water fern (*Azolla africana*) have been used to remove heavy metals from solution (Talor and Sela, 1992). Heavy metals (nickel, mercury, cadmium) are potential carcinogens from drinking water. These elements may become 4,000 – 20,000 times more concentrated in plants, than in water (Brix and Shierup, 1989., Horan, 1990., Mason, 1993) as a result of bioaccumulation. Duckweeds (*Spirodela polyrrhiza* and *Lemna* minor) have thus been used for the removal of excessive nutrients from polluted water (Culley and Epps, 1993). *Pistia stratiotes* has been similarly employed for the removal of nutrient from polluted bodies (Aoi *et al*., 1996). The plants absorb and incorporate the dissolved materials into their structure.

Studies with various species of organisms have demonstrated that the developmental stages of organisms are often more sensitive to toxicant than older stages (Alexander, 1977). Oil with aromatic content of 33 percent reduced the growth of maize plants to 31 percent.

Flowers and Haji bagheri (2001) reported that the effect of ion on the growth of leaves is determined by the ability of plants to accommodate the ions within compartments of the leaves cells where they will not do damage. If the ions are accommodated in the vacuole and concentration rises in the leaf apoplast then there will be osmotic effect on the leaf growth. Okoloko and Bewley (1982) reported the enhancement of protein synthesis in moss (*Tortula ruralis*) gametophytes exposed to 5mM aqueous SO_2. Higher levels were toxic. Some components, particularly compounds, are toxic to aquatic animals and plants (Odiete, 1999). They are acutely lethal and chronically lethal in sublethal concentration of part per billion (ppb). However, plants and animals vary widely in their sensitivity (Clark, 1982).

The soluble fraction of crude petroleum depress phytoplankton, photosynthesis, respiration and growth, and also kill or cause developmental abnormalities of young metallic ions present in the WSF may inhibit root growth (Winter *et al*. 1976).

Factors connected with phytotoxicity of oil as already mentioned, are the properties of the oil, the quantity of the oil applied and the environmental conditions. Other factors include the species of plants and the parts of the plant affected. Also of importance are the thickness of cuticle, number and structure of stomata, chloroplast physiology, CO_2 fixation pattern and photosynthetic electron transport system. Relatively low levels of pollution can cause rapid depression in the rate of net photosynthesis (Fitter and Hay, 1987).

The adverse effects of petroleum and its components on growth have earlier been recorded by Gill *et al.,* 1992. Oil contaminated water soluble fraction resulted in water becoming unsuitable for growth of aquatic macrophytes. Anoliefo (1991) reported that slight pollution with petroleum products or WSF makes carbonyl compounds available in the soil, hence the observed rapid increase in the growth of melon plants. Baker (1970b) reported that they inhibit metabolic processes. Edema and Okoloko (1997) showed increase in inhibition with increase in concentration of WSF. Studies on the effects of the water soluble fraction of Escravos hight and Odidi well oil on *Allium cepa* showed a “fertilizer effect” at 12.5% WSF level (Edema and Okoloko, 1997). Only higher levels of WSF are toxic. Also, growth enhancement and early flowering of *L. esculentus* at 0.25 x 10^{-3}ml/g concentration of crude oil treated soil was reported by Edema and Etioyibo (1999).

Edema (2010b) reported leaf bud formation in *Allium cepa* at 25% WSF and root initiation at 50% and 100% WSF treatments. Total inhibition of root was recorded for produced water at

100% which shows that produced water was more stressful to the plant than WSF of the same crude oil. Edema (2010b) also reported increase in catalase activity for WSF and decrease in catalase activity for produced water. Increased level of catalase activity is an indication of increased production of free radicals occasion by exposure of plants to crude oil. While decrease in activities of detoxification mechanisms of hydrogen peroxide can generate severe cell damage due to increase production of toxic oxygen radicals (Hernandez *et al;* 1995).

Salts influence the activities of aquatic plants resulting in the death of aquatic plants. Salt stress has been reported by Concave (1979) to reverse the condition that could make essential nutrients available to plants thereby resulting in mitoclondria damage (Cowell, 1977). The presence of ions in plants may block the oxidation of pyruvate for energy production (Anoliefo, 1991).

High salinity could be toxic to bacteria and may inhibit their activities. Besides, salinity may also affect the cellular infiltration pressure, leading to plasmolysis or even cell breakup (Ji *et al;* 2009).

Ajao *et al.* (1981) reported that undiluted formation water was toxic to millet at 1 – 100mg/l (1 – 100ppm) level. Edema (2010) also reported that produced water (PW) of crude oil was more toxic to *Allium cepa* than the water soluble fraction (WSF) of crude oil. Catalase activity could not be measured for *Allium cepa* exposed to produced water because of inhibition of growth (Edema, 2010).

The exposure of plants to metals results in the synthesis of phytochelatins, a metal binding polypeptide (Stern, 2000). Phytocheletins are known to sequester and detoxify metals through the formation of metals. Phytochelatin complexes (Stern, 2000; Clemens *et al*; 1999, Ha *et al*., 1999). Plant nutrient elements such as Ca, Mn, Fe and Zn for example may enter through Ca channels or by means of broad-range metal transporter previously identified as Fe transporter (Clemens *et al*., 1999). Edema (2006) reported that the levels of Fe in WSF before and after exposure to *Pistia* were far above the highest desirable limit for drinking water and still within the maximum permissible limit of 1.0mg/l of WHO value.

Edema and Asagba (2007) reported reduction in temperature and DO after exposure to the different levels of WSF. Reduction in the DO means reduction in the chemical oxygen demand and biological oxygen demand. An aquatic ecosystem with inadequate oxygen supply is considered polluted for organisms that require dissolved oxygen above the existing level (Botkin and Keller, 1998). Decrease in THC at 25% and 50% WSF after exposure to *Pistia* species was also reported by Edema (2007). This shows uptake or metabolism of THC by *Pistia stratiotes.* Odokuma and Dickson (2003) reported marked decrease in the percentage of THC in all the treatments applied in the bioremediation of crude oil in the tropical rainforest (using indigenous hydrocarbon utilizing bacteria) soil of the Niger-Delta except in the control treatment.

Thus, the introduction of WSF of crude oil into the aquatic system can increase the ionic, heavy metals and physical characteristics of aquatic ecosystem. And with continuous spillage there would be a build up of these ions in the aquatic environment. The need for government to implement measures to safeguard and reduce the effect of oil contaminated water on the environment cannot be overemphasized.

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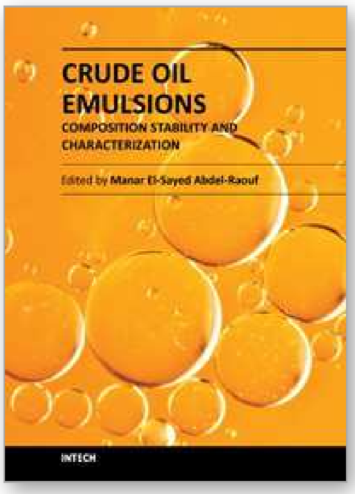

Crude Oil Emulsions- Composition Stability and Characterization

Edited by Prof. Manar El-Sayed Abdul-Raouf

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Petroleum "black gold" is the most important nonrenewable source of energy. It is a complex mixture of different phases and components. Refining it provides a vast number of organic compounds, all of them of which are used to produce petroleum based products for numerous applications, from industry to medicine, from clothing to food industries. We can find petroleum based products all around us. This book deals with some important topics related to petroleum such as its chemical composition and stability. It is well-known that the chemical composition of crude oil differs according to the site of production, and its grade varies from waxy to asphaltenic crude. Both of them are refined to produce different products. The stability of crude oil on aging and transportation is governed by several factors and these factors are included within this book. Some new technologies for petroleum characterization are also introduced. This book is aimed at researchers, chemical engineers and people working within the petroleum industry.

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