



# INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

## CITRUS PARADISE

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### ABSTRACT

Citrus paradise (grape fruit) curative effects on haemorrhage of the interstitium in kidney tissues of rats exposed to very high volumes of Bonny light crude oil was investigated. Albino rats weighing 180-200g were placed into control and test groups which consisted of 4(four) cages carrying 5(five) animals. The animals (albino rats) were used to test effects of high volumes of Bonny light crude oil on the interstitium of the kidneys. The feeding pattern employed for control animals was unpolluted feed and water while test animals were fed crude oil polluted feed and water in the ratio of 3kg feed mixed with 500ml Bonny light crude oil and water for 21days. Histological studies on rats given polluted feed and water revealed haemorrhage in the kidney interstitium. With more studies incorporating grape fruit and grape fruit juice, into the feed and water of experimental animals, 2kg feed in 1kg dried grape fruit with 480ml water and 20ml grape fruit juice, experimental animals not “sacrificed” in the previous experiment were re-used in this experiment. On day 21 of the second experiment test and control animals were “sacrificed” with further examination on the kidney tissue. Haemorrhage was completely non existent and inferences made directly that Citrus paradisi stopped bleeding in the interstitium of the kidney.

### INTRODUCTION

#### ENVIRONMENTAL DEGRADATION:

Environmental degradation is a process through which the natural environment is compromised in some way reducing bio-diversity and the overall health of the environment.

The process can either be natural, accelerated or caused by human activities.

Oil spillage is the release of crude oil hydrocarbons into the environment. It is a disaster of global proportions and concern and it usually occurs intentionally or accidentally and results most times from our day to day human activities which release crude oil into our coastal waters

and land. Environmental degradation arising from oil prospecting and exploration has negatively impacted on the biological diversity of affected regions in the Niger Delta of Nigeria.

Major problems arise from leakage of pipes carrying crude oil, gas flaring and escapee chemicals that are involved in the production process. Since crude oil consists of many toxic compounds that have the potentials of causing grave health challenges, which include immune system effects and eventually coma and death, it is important for remediation of the areas spills occur even to surrounding areas miles away because the oil travels long distances and is also known to bio accumulate.

Most records kept on oil spills don't relate the true situation since there always exist a code of silence by Government agencies to enable the major oil companies in the areas to keep exploring and exploiting to the detriment of the inhabitants of the areas. Still, estimated values are being reported because of interference of heavy current that often times "sweep" off the oil to other areas.

The Nigerian National Petroleum Corporation places the quantity of crude oil spilled into the environment on a yearly basis at 2,300 cubic meters with average annual spills of 300. In Nigeria oil spills are becoming more rampant with most spills occurring due to accidents on pipelines and tankers.

One major bottle neck is sabotage, where youths in oil producing communities seek to get rich by all means possible and break these pipelines in order to steal crude oil and other products.

On the 26<sup>th</sup> of December, 2006 a pipeline explosion in Abule Egba in Lagos State, Nigeria killed hundreds of people with number of deaths initially reported at 500. This number was

later reported as more than the number of casualties. This occurred due to puncture marks deliberately inflicted on an elevated pipeline carrying petroleum products.

## **CRUDE OIL (General Feature)**

Crude oil is a naturally occurring fossil fuel and this means it originates from the remains of dead organisms. It is made up of a mixture of hydrocarbons: compounds composed of hydrogen and carbon. It exists in liquid form underground in tiny spaces that are found within sedimentary rocks (rocks formed from pre-existing rocks).

Crude oil is extracted through drilling and refined to products that can be used which include gasoline, different forms of petrochemicals and diesel. It is made up of hydrocarbons.

Approximately 62-97% of crude oil is composed of hydrocarbons, with about 6-10% being nitrogen, sulfur, and oxygen. Metals make up less than 1% of crude oil. Crude oil consists of the remains of algae and planktons which fell to the bottom of the ocean with a mixing of crude with mud which was later covered by layers of sediments. With high pressures, the remains over several millennia become a wax substance known as kerogen which becomes liquid oil with great heat and pressure.

Crude oil is a combination of compounds of varying degrees of volatility. The compounds are mainly composed of hydrogen and carbon with trace amounts of nitrogen, sulfur and oxygen. The difference notwithstanding, almost all crude oil range from 82-97% carbon by weight and about 11-15% hydrogen by weight. Characterization of crude oils are considerably done

according to the type of hydrocarbon compound found in greater weight in them. Examples include: paraffins, aromatics and naphthenes.

## PARAFFINS

Are waxy crystalline and flammable substances. It is a common name for alkane hydrocarbons which have the formula  $C_nH_{2n+2}$ . The simplest paraffin molecule is methane  $CH_4$ , it is a gas at room temperature. Paraffin is derived from Latin parum meaning barely plus affinis meaning lacking reactivity or affinity the reason for this is that alkanes are non-polar and also lack functional groups which makes them highly unreactive.

Paraffins are major components of petroleum and natural gas. Gaseous paraffins contain fewer than 5 carbon atoms per molecule at room temperature. Liquid paraffins usually have 5-15 atoms with straight chain paraffins having more than 15 carbon atoms per molecule being solids. There is a much higher octane number rating compared to straight chain paraffins and this makes them better components of gasoline. All paraffins are colorless.

The octane number also known as anti-knock rating is a measure of the ability of a fuel to resist knocking when ignited in a mixture with air in the cylinder of an internal combustion engine. It is the percentage by volume of iso-octane in a mixture called the iso-octane-heptane flow which matches fuel that is tested in an engine that is standard.

## NEPHTHENES

Nephthenes are cyclic aliphatic hydrocarbons that are derived from petroleum. The nephthenes have a general formula  $C_nH_{2n}$  and are characterized by possessing one or more rings of saturated hydrocarbons. Nephthenes are essential components of liquid petroleum products. A primary difference between naphthenic crude oil is that it is more readily

converted into gasoline than paraffin-rich crudes. Naphthenes can also be called cycloalkanes or cycloparaffins. Examples include cyclohexane and cyclopropane.

## AROMATICS

Aromatic compounds are named based on the number and kind of substituents found on the ring aromatic compounds are ring compounds that have unusual stability because of the pi electron density which is not localized and is shared between all carbon atoms found in the ring. Examples methylbenzene known as toluene and dimethylbenzene called xylene. Aromatic compounds are produced from petroleum and coal tar. Aromatic compounds have a closed ring of alternate single and double bonds with delocalized electrons.

## CONSEQUENCES OF OIL SPILLS

Oil spills are detrimental to marine organisms, bird and mammals. Oil destroys the capacity of animals that bear furs to conserve heat and what this directly entails is that the animals are at the mercy of harsh elements.

With the occurrence of spills, thousands of tons of oil find their way into the ecosystem and seep into the soil. These spills are grave causing death of plants and animals, pollute the air and the water, cause a huge upset in salinity values. With spills that occur in large bodies of water like the oceans and fresh water bodies it travels fast, thinning out on the surface of the water and eventually blocks sunlight from reaching the oceanic environments thereby disabling producers and the whole food chain when this happens, death occurs leading to a complete disruption of the oceans food chain.

**Plankton:** producers that dwell at the bottom of the food chain are often killed by an oil spill due to changes in the water and lack of sunlight. Other sea animals like mussels that feed on

the planktons can't get food and die off. If oil cakes the feathers of a bird, it inhibits flight and if the bird is not cleaned of the oil, it may die because in an attempt to clean their feathers, many birds ingest large amounts of oil.

Oil spills also affect human health and these effects depend largely on the kind of oil spilled on the area spilled; land or water, the kind of exposure and extent of exposure. Effects on humans are more common on those that carry out remediation procedures. Most common problems seen are skin and eye irritation, breathing (respiratory insufficiency) and weakness.

Oil spills have a major effect on the ecosystem into which spilled crude is released and may therefore constitute what is known as ecoside. Ecoside is basically a criminalized human activity that violates the principles of environmental justice by causing extensive damage destroying ecosystems or harming the health and well-being of a species humans inclusive.

The effects of oil spill basically depend on various factors which include the quality and type of oil spilled and its interactions with the marine environment. Weather conditions at the time also influence the physical characteristics of the oil. Still other factors like biological and ecological attributes of the area, importance of major species and their sensitivity to oil pollution and the time of year.

## **CRUDE OIL COMPOSITION**

Crude oil is a mixture of comparatively volatile liquid hydrocarbon compounds composed mainly of hydrogen and carbon. It also contains some nitrogen, sulphur and oxygen. The elements form diverse groups of complex molecular structures with some not being readily identified. Variations notwithstanding, almost all crude oil range from 82-87% carbon by weight and 12– 15% hydrogen by weight.

Customarily, classification is done by the type of hydrocarbon compound that is most prevalent in them.

These are paraffins, naphthenes and aromatics, with paraffin being the most common hydrocarbon found in crude oil. Certain liquid paraffins are the major constituents of gasoline and are therefore of very great importance. Naphthenes are a crucial part of all liquid refinery products and also form some of the heavy asphalt like residues of refinery processes. The hydrocarbon structures found in oil include saturates, aromatics and polar compounds which include resins and asphaltenes.

Resins and asphaltenes are largely refractory in the environment. They evaporate, dissolve and degrade poorly and end up accumulating as residues especially after a crude oil spill. The percentage of saturates and aromatics called the light compounds in comparison to the heavy residue forming resins and asphaltenes vary with type of crude oil.

Aromatics generally constitute only a small percentage of most crude with the most common aromatic in crude oil being benzene, a popular building block in the petrochemical industry. Because crude oil is a mixture of such widely varying constituents and proportions, its physical properties also vary widely. In appearance, crude oil ranges from colourless to “black”. The most important physical property probably is specific gravity; which is the ratio of the weight of equal volumes of the crude oil and pure water at standard conditions.

In laboratory measurements of specific gravity, it is customary to assign pure water a measurement of one (1). Substances lighter than water such as crude oil receive a measurement less than one (1). The petrochemical industry however uses the American Petroleum Institute (API) gravity scale in which pure water has been arbitrarily assigned an API gravity of  $10^0$ .

Liquids lighter than water such as oil have API gravities numerically greater than 10. On the basis of API gravities, crude oil can be classified as heavy, medium and light as follows;

Heavy 10 – 20<sup>0</sup> API gravity

Medium 20 – 25<sup>0</sup> API gravity

Light above 25<sup>0</sup> API gravity

Crude oil is also categorized as “sweet” or “sour” depending on the level of sulphur which occurs whether as elemental sulphur or in compounds such as hydrogen sulphide. Sweet crudes have sulphur contents of 0.5% or less by weight while “sour” crudes have sulphur contents of 1% or more by weight.

Generally, the heavier the crude oil, the more its sulphur content. Excess sulphur is often removed from crude oil during refining because sulphur oxides released to the atmosphere during combustion of oil is a major pollutant. Petroleum in Nigeria is often classified as “light” and “sweet” since the oil is largely free of sulphur.

Most crude oils are named according to export terminals; for example there is Bonny light, Qua iboe, Escravos blend, Brass river, Forcados and Pennington Anfan. The major and minor classes of crude oil come from various export terminals in Nigeria. Bonny light was so named because its export terminal is located in the city of Bonny in Rivers State, South-South Nigeria.

Another classification into light, medium and heavy oil is based on their densities and toxicity levels which also depend on their volatilities. The purification of crude oil focuses first on the use of industrialized fractional distillation to separate crude oil into primary products which is followed by different cracking and refining processes to generate secondary products from the primary products whose purification is outsmarted by their utilization locally or whose



utilization by the Nigerian populace is well reduced as compared to their level of production.

Crude oil is not a single indistinguishably homogenous substance without differences that are unique. There are many different types of crude oil.

In its natural unrefined state, crude oil ranges in density and consistency from very thin light weight and volatile fluidity to an extremely thick semi-solid heavy weight oil. There also exists a gradation in colour that the oil extracted from the ground exhibits ranging from a light golden yellow to the very deepest black.

## TYPES OF CRUDE OIL

### BRENT BLEND

This blend is actually a mixture of different oils. Its API gravity is 38.8<sup>0</sup> which makes it light crude oil. It also contains about 0.37% sulphur and this makes it a “sweet” crude oil.

Brent blend is excellent in making gasoline and middle distillates, it remains a major benchmark for other crude oils in Europe and Africa.

### OPEC BASKET

The OPEC basket is a collection of seven (7) different crude oils from Algeria, Saudi Arabia, Indonesia, Nigeria, Dubai, Venezuela and the Mexican Isthmus. Because OPEC oil has a much higher percentage of sulphur within its natural make up and therefore is not nearly as “sweet” as Brent blend it is also not naturally as light as Brent blend.

The bulk of the compounds present in crude oil are hydrocarbons. Crude oil generally contains classes of hydrocarbons and other compounds.

## HYDROCARBON COMPOUNDS

### Alkanes (Paraffins)

Alkanes are straight chain normal alkanes and branched iso-alkanes with general formula  $C_nH_{2n+2}$ . The major paraffinic components of most crude oils are in the range  $C_1 - C_{35}$ , although small quantities of alkanes up to  $C_{60}$  or higher may be present. Crude oils vary widely in alkane content.

### CYCLOALKANES (Naphthenes)

Cycloalkanes, cycloparaffins or naphthenes are saturated hydrocarbons containing structures with carbon atoms linked in a ring. The cycloalkane composition in crude oil worldwide typically varies from 30-60%.

The predominant monocycloalkanes in crude oil are in the cyclopentane series having 5 (five) carbon atoms in the ring and cyclohexane having a six (6) membered ring.

### AROMATIC HYDROCARBONS

Aromatic hydrocarbons are those which contain one or more benzene rings. The name of the class comes from the fact that many of them have strong pungent aromas. The most common aromatic compounds in crude oil are benzene. The concentration of benzene in crude oil is estimated to be between 0.01% and 1%, Aromatic hydrocarbons also include benzene active metabolites.

### ALIPHATIC HYDROCARBONS

Aliphatic stems from the Greek word meaning fat or oil. It refers to hydrocarbons that are straight chained, branched or non aromatic. Hydrocarbons which do not contain a benzene

ring are called aliphatic hydrocarbons. Some of the most common flammable and volatile compounds are aliphatic hydrocarbons. They can either be saturated or unsaturated.

## NON HYDROCARBON COMPOUNDS

Vanadium, nickel, nitrogen and sulphur are known to be the most significant non hydrocarbon constituents of crude oil. Non hydrocarbon compounds provide fundamental answers in petroleum geo-chemistry.

They may be small in quantity but some have considerable influence on the quality of products. They have harmful effects in most cases and must be removed or converted to less harmful compounds during the refining process. The most common occurring non-hydrocarbons are sulphur, nitrogen and oxygen.

### SULPHUR COMPOUNDS

Sulphur is common in crude oil but varies from 0.2-6% by weight. There are corrosive and non corrosive sulphur compounds. One corrosive compound is hydrogen sulphide ( $H_2S$ ). Fortunately, sulphides have highly obnoxious smell that gives some warning of their danger.

If one hydrogen atom is replaced by a hydrocarbon group, the compound is called a Mercaptan or thiol. Such compounds are formed during the distillation of crude oils. They can cause severe corrosion of the processing units and the addition of chemicals; proper temperature control and the use of special alloys in refinery equipment are required to control them. If both of the two hydrogen atoms are replaced by hydrocarbon groups, the compound is called a sulphide or thio-ether. An example is thiophene ( $C_4H_4S$ ). Thiophenes have a relatively pleasant odour.

## **NITROGEN COMPOUNDS**

Nitrogen compounds in crude oil are complex. They may cause discolouration in gasoline and kerosene or may produce a lacquer quality there by reducing the effectiveness of lubricating oils. Almost all crude oils contain nitrogen usually in quantities less than 0.1% by weight.

## **OXYGEN COMPOUNDS**

Some crude oils contain oxygen compounds. Their structures have not been established but on distillation of the crude, the oxygen compounds decompose to form ring compounds with a carboxylic acid group in the side chain. The oxygen content of crude oil is usually less than 2% in weight with heavier oils containing the most oxygen.

## **OTHER COMPOUNDS**

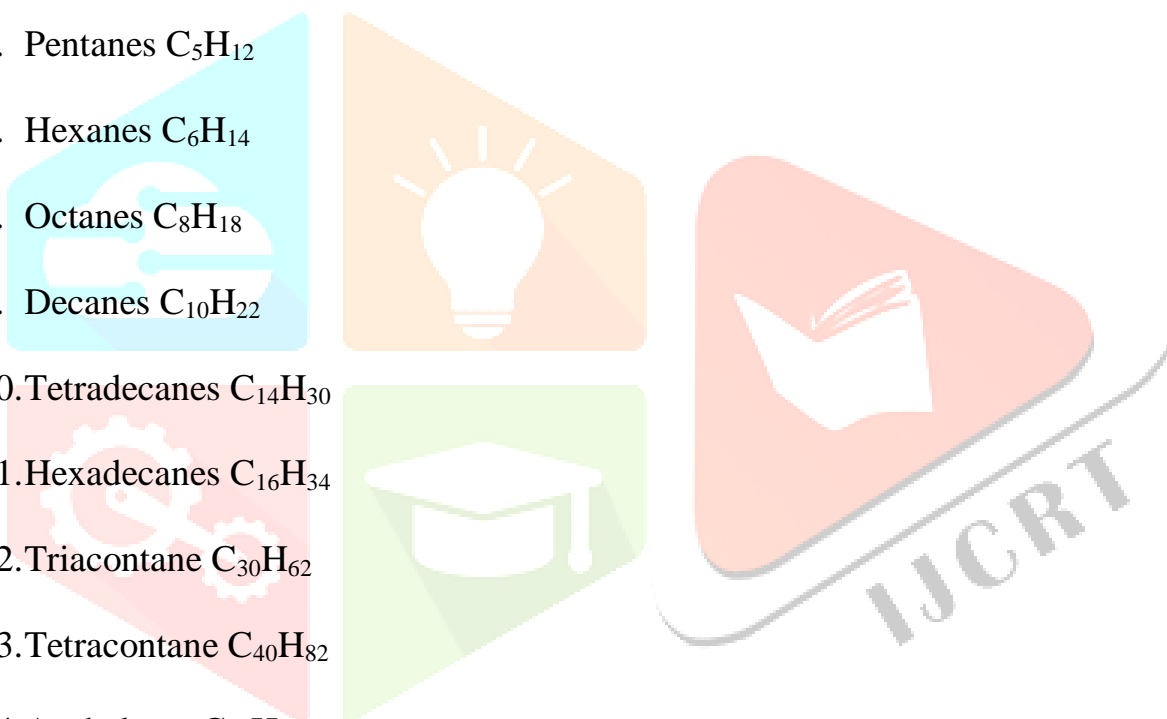
Several other organic and inorganic compounds occur in crude oil. An example is the metal vanadium which is an important component in the manufacture of specialty steels and can be recovered from the residue of the refining process. Many metallic elements are found in crude oils including most of those that occur in sea water probably because of the close association between sea water and the organic forms from which oil is generated.

Vanadium is the most common metallic element in oil followed by nickel. They probably occur in organic combinations as they do in living plants and animals. Crude oil also contains a small amount of decay resistant organic remains such as siliceous skeletal fragments, wood, spores, resins, coal and various other remnants of former life.

## CONSTITUENTS OF NIGERIA CRUDE OIL

The following are found in Nigeria crude oil;

1. Methane  $\text{CH}_4$
2. Ethane  $\text{C}_2\text{H}_6$
3. Propane  $\text{C}_3\text{H}_8$
4. Iso-butane I- $\text{C}_4\text{H}_{10}$
5. N-butane N- $\text{C}_4\text{H}_{10}$
6. Pentanes  $\text{C}_5\text{H}_{12}$
7. Hexanes  $\text{C}_6\text{H}_{14}$
8. Octanes  $\text{C}_8\text{H}_{18}$
9. Decanes  $\text{C}_{10}\text{H}_{22}$
10. Tetradecanes  $\text{C}_{14}\text{H}_{30}$
11. Hexadecanes  $\text{C}_{16}\text{H}_{34}$
12. Triacontane  $\text{C}_{30}\text{H}_{62}$
13. Tetracontane  $\text{C}_{40}\text{H}_{82}$
14. Asphaltane  $\text{C}_{80}\text{H}_{162}$



There are hydrocarbons of simple, short chains, long chains and branched chains. These hydrocarbons are also called simple paraffins (alkanes), branched paraffins (cycloalkanes), Naphthenes, aromatics, benzene, naphthalene and alkyl derivatives, polynuclear aromatic hydrocarbons (PAHs) which contain two or more fused rings. Essentially, some of these paraffins are gasoline and kerosene.

Crude oil also contains small but significant amounts of impurities such as formation sand and water, sediments, trace metals especially lead (Pb), iron (Fe), copper (Cu), asphalt (As) and Vanadium (V). Compounds of sulphur(s), chlorine(cl), oxygen(o) and Nitrogen(N) are present as mercaptans, salts, phenols and anilines respectively.

In addition to the constituent compounds that are derived from the crude which result from the interaction of crude oil constituents and living cells also exist when crude oil is spilled or taken into a living cell.

The compounds are;

1. 3, 4 benzo(a) pyrene
2. 20 methylcholanthrene (2methylcholanthrene)
3. 7, 12 dimethyl benzanthracene
4. Polycyclic aromatic hydrocarbons
5. Dibenz (a, b) acridine
6. 5-methyl chrysene
7. Dibenz (a, b) anthracene
8. Toluene

A significant effect resulting from crude oil spillage is the emission into the atmosphere some of the gases of non-metallic origin and discharge into the air of volatile hydrocarbons. The emission of these gases constitutes air pollution.

The direct consequence of air pollution is the oxidation of the non-metallic gases to form gaseous compounds which produce harmful effects in the environment. The gases include;

1. Hydrogen sulphide
2. Nitrogen oxides
3. Carbon monoxide
4. Ozone
5. Sulphur oxides
6. Particulate sulphates

## **TOXIC EFFECTS OF THE CHEMICALS IN THE NIGERIAN PETROLEUM CRUDE OIL.**

1. **ALIPHATIC HYDROCARBONS:** The  $C_1$ - $C_4$  aliphatic hydrocarbons are simple asphyxiants and their effects are observed when they are highly concentrated in air leading to reduction in the amount of oxygen
2. The  $C_5$ - $C_8$  aliphatic hydrocarbons depress the central nervous system causing dizziness and in-coordination.

### **Paraffin, gasoline and Kerosene**

These contain aliphatic, aromatic and a variety of branched chain and unsaturated hydrocarbons. Ingestion or exposure of humans to these agents produce unpleasant signs and symptoms which include in-coordination, restlessness, excitement, confusion, disorientation, ataxia, delirium and coma. Paraffinic vapour sensitizes the myocardium such that small amounts of circulating epinephrine may precipitate ventricular fibrillations.

High concentrations of paraffinic vapour may lead to rapid depression of the central nervous system and finally death from respiratory insufficiency. Poisoning from these hydrocarbons result either from inhalation of the vapours or from ingestion of the liquid. Ingestion is known to be more hazardous. Ingestion of the substances can be easily aspirated into the respiratory tract by vomiting or eructation.

Chemical pneumonitis complicated by secondary bacterial pneumonia and pulmonary edema is the most serious sequel to aspiration. Death usually occurs by haemorrhagic pulmonary edema within 16-18 hours.

### **AROMATIC HYDROCARBONS**

Aromatic hydrocarbons example benzene is very toxic. After acute exposure to large amounts to benzene either by ingestion or breathing concentrated vapours, the major toxic effects is on the central nervous system (CNS). Symptoms from mild exposure include headache, nausea, vomiting, tightness in the chest and staggering. With more severe exposures, symptoms progress to blurred vision, tremors, shallow and rapid respiration, ventricular irregularities, paralysis and unconsciousness. Chronic exposure to benzene is usually due to inhalation of vapour.

Signs and symptoms include effects on the central nervous system and the gastrointestinal tract which include nervousness, headache, and loss of appetite, drowsiness and palor. Aplastic anaemia is the major manifestation of toxicity. The most sensitive to benzene are bone marrow cells in early stages of development with arrest of maturation leading to gradual depletion of circulating cells.



## GENOTOXICITY OF AROMATIC HYDROCARBON DERIVATIVES

### BENZENE

The major effect of benzene from long term exposure is on the blood. Long term exposure could be a year or more. Benzene causes harmful effects on the bone marrow causing a decrease in red blood cells thereby leading to anaemia. Epidemiological studies demonstrate that benzene is a human leukenogen. Benzene has also been shown to be a multi organ carcinogen in animals, high levels of benzene can cause eye, skin and respiratory irritation, difficulty breathing, cardiovascular effects such as ventricular fibrillations, gastritis, kidney congestion and neurological effects such as distal neuropathy, abnormality in nerve conduction velocity, difficulty sleeping and memory loss.

At high levels of exposure, confusion, convulsive movements, paralysis and death can occur.

Intermediate and chronic exposure to benzene cause a variety of pathological states which include cytopenia (anaemia, leukopenia or thrombocytopenia).

Central nervous system effects such as headache, dizziness, fatigue, anorexia, visual disturbances, hearing loss and respiratory irritation evidenced by difficulty in breathing.

Benzene has also been shown to be an immune suppressive agent. Critical effect of chronic exposure to benzene is an increased risk of cancer.

Benzene can also cause chromosomal aberrations in humans. Chromosomal analyses have been used in investigations of benzene exposures.

## ARENE OXIDE

Arene oxide is a metabolite of benzene and two important families of arene oxides are benzene oxides and naphthalene oxides which are intermediates in the oxidative degradation of benzene and naphthalene which are two common pollutants.

Arene oxide causes leukemia and its threshold value is set at 1ppm (parts per million). Other metabolites of aromatic hydrocarbons such as benzo (a) pyrene, 3 methycholanthrene, benza anthracene dibenz, anthracene and toluene are carcinogenic.

## OZONE AND NITROGEN DIOXIDE

### OZONE

Ozone is found in very high amounts during a prolonged spillage of crude petroleum. It is a lung irritant capable of causing death from respiratory edema. Long term exposure to ozone may cause thickening of the terminal respiratory bronchioles, chronic bronchitis, fibrosis and emphysematous changes are observed in a variety of species exposed to ozone at concentrations slightly above 1ppm.

The ozone layer or ozone shield is a region of the earth's stratosphere that absorbs most of the sun's ultraviolet radiation. It contains high concentration of ozone relative to other parts of the atmosphere.

The ozone layer contains less than 10parts per million of ozone while the average ozone concentration in earth's atmosphere as a whole is only about 0.3 parts per million. The ozone layer absorbs 97-99% of the sun's medium frequency ultra violet light from (about 200nm – 500nm) wave length which otherwise would potentially damage exposed life from near the surface.

The ozone molecule is unstable and is created in the earth's stratosphere by ultra violet light striking ordinary oxygen molecules containing two oxygen atoms (atomic oxygen). It then combines with unbroken oxygen to form ozone; the molecule is unstable and when ultra violet light hits ozone it splits into a molecule of  $O_2$  and an individual atom of  $O_2$  (oxygen) in a process known as the ozone-oxygen cycle.

The ozone-oxygen cycle is the process by which ozone is continually regenerated in earth's stratosphere, converting ultraviolet radiation (UV) into heat. Sydney Chapman resolved the chemistry involved in 1930. The process is commonly called the Chapman cycle. He discovered the photochemical mechanisms that give rise to the ozone layer.

Ozone is also known tri-oxygen is composed of 3(three) oxygen atoms. That is to say one molecule of ozone is made up of 3 oxygen atoms and averages 3 molecules of ozone for every 10million air molecules. The ozone layer was discovered by Charles Fabey and Henri Buisson in 1913. The British meteorologist G.M.B Dobson developed a simple spectrophotometer (the Dobson meter) for use in measuring atmospheric ozone. September 16<sup>th</sup> has been designated for the preservation of the ozone layer by the United States general assembly.

## **NITROGEN OXIDE**

Nitrogen dioxide is a pollutant that is capable of causing pulmonary edema and is a particular risk to farmers. Chronic exposure results in emphysematous changes. Nitrogen dioxide can irritate the lungs and also lower resistance to respiratory infections such as influenza.

Effects are not clear with short term exposures but frequent exposure to concentrations that are typically much higher than what is found in ambient air may likely cause increased incidence of acute respiratory illness in children.

## CARBON MONOXIDE

Carbon monoxide is a major pollutant that results from crude oil spillage because its natural source is atmospheric oxidation of methane, a gas that is found in abundance in petroleum crude oil.

It reduces the oxygen carrying capacity of blood. Signs and symptoms of carbon monoxide poisoning include headache, weakness, dizziness, nausea, vomiting, syncope, increased respiration and pulse, depressed cardiac function, respiratory failure, coma and death.

The pathology of acute carbon monoxide poisoning indicates that the tissues most affected are the brain and heart and lesions are predominantly hemorrhagic. During prolonged and low-level exposure to carbon monoxide, the heart is highly susceptible since there is a shift in metabolism from aerobic to anaerobic. Foetuses have been observed to be extremely susceptible to effects of carbon monoxide during prolonged exposure with the gas readily crossing the placenta. Women that survived short term exposures to high concentrations of the gas while pregnant delivered infants that often-displayed neurological sequelae with possibilities of gross damage to the brain.

Polycythemia develops with long term exposures to carbon monoxide. Poisoning occurs after much inhalation of the gas. It is a toxic gas but since it is colourless, odourless and tasteless and initially non-irritating, it is very difficult to detect.

Carbon monoxide is a product of incomplete combustion of organic matter due to insufficient oxygen supply to enable a complete oxidation to carbon dioxide. Carbon monoxide is frequently produced in domestic or industrial settings by motor vehicles that run on gasoline,

diesel, methane or other carbon-based fuels. Poisoning occurs when carbon monoxide builds up in the blood stream.

When there is too much carbon monoxide in the air, the body replaces the oxygen in the red blood cells with carbon monoxide which can lead to serious tissue damage or death.

## **SULPHUR DIOXIDE AND SULPHURIC ACID**

Because crude oil contains sulphur, oxidation may occur from sulphur oxides and sulphuric acid during a spill of great magnitude. Oxides and sulphates of sulphur primarily cause bronchial constriction and increase in airway resistance which leads to a decrease in pulmonary function particularly with sulphur dioxide. Particulate sulphates also have similar effects to those of sulphur oxide and sulphuric acid. Sulphur dioxide is a gas with a suffocating odour that is similar to a just struck match. It has an acidic taste and is a liquid when under pressure.

Sulphur dioxide is formed when fuels containing sulphur such as coal and oil are burned. The chemical symbol for sulphur dioxide is  $\text{SO}_2$ . Most sulphur dioxide in the air comes from burning of coal and oil at electric power plants. Other sources of sulphur dioxide in the air are industrial facilities that use coal or oil, petroleum refineries, cement manufacturing, metal processing, paper pulp manufacturing and copper smelting, trains, large ships and some equipments burn high sulphur fuel which releases sulphur dioxide into the air. Volcanic eruptions also release sulphur.

## Signs and symptoms of poisoning

Breathing difficulties and obstruction of airways especially for patients with lung disease. Long term exposures to persistent levels of sulphur dioxide can cause chronic bronchitis, emphysema and respiratory illness.

It can also exacerbate existing heart disease. Short term exposure can also cause stomach pain, menstrual disorders, and watery eyes, inhibition of thyroid function, nausea, vomiting, fever, convulsions and dizziness. Prolonged industrial exposure to sulphur dioxide may decrease fertility in men and women.

Breathing sulphur dioxide can irritate the nose, throat and lungs and cause coughing and shortening of breath.

## SULPHURIC ACID

Sulphuric acid is a highly corrosive, strong mineral with a molecular formula  $H_2SO_4$  and molecular weight 98.079g/mol. It is a pungent ethereal colourless, slightly yellow viscous liquid which is soluble in water at all concentrations. It is sometimes dyed dark brown during production to alert people to its hazards. Sulphuric acid shows different properties depending on its concentration.

It has strong dehydrating and oxidizing properties. At high concentrations, sulphuric acid can cause very serious damage upon contact since not only does it cause chemical burns via hydrolysis, it also causes secondary thermal burns through dehydration. It can lead to permanent blindness if splashed into the eyes and irreversible damage if swallowed. It is hygroscopic readily absorbing water vapour from the air.

Applications of sulphuric acid include: Domestic acidic drain cleaner, electrolyte in lead acid batteries.

## **CITRUS PARADISI (GRAPE FRUIT)**

Grape fruit is a citrus hybrid, a natural cross between pomelo and orange: an accidental cross between sweet orange (*Citrus sinensis*) and the pomelo or shaddock (*Citrus maxima*) varieties of grapefruits are differentiated according to their flesh and colour of fruit produced with very common varieties being pink or yellow in colour.

Grapefruits are highly acidic with some having sour to sweet and tart that result from the composition of sugars basically sucrose, organic acids; basically, citric acid and terpenes consisting of monoterpenes and sesquiterpenes that function in aroma compounds, that influence the odour and taste of grape fruit in comparison to other citrus fruits.

The main chemical compound of grape fruit essential oil is d-limonene. Limonene is in the monoterpenes group and possesses strong aromatic properties. Grape fruit provides small amounts of B vitamins, zinc, copper and iron which all work together in the body to promote immune system function. It also contains fiber and water which both increase fullness thereby reducing intake of calories.

## SCIENTIFIC CLASSIFICATION

<b>KINGDOM</b>	<b>PLANTAE</b>
Clade	Tracheophytes
Clade	Angiosperms
Clade	Eudicots
Clade	Rosids
Order	Sapindales
Family	Rutaceae
Genus	Citrus
Species	C. paradisi

**Binomial name: Citrus paradisi**

Grapefruit is thought to improve heart health and does this by reducing the risk factors for heart disease such as cholesterol and high blood pressure. In a study, people that ate grapefruit three (3) times a day for 2(two) months experienced observable reduction in blood pressure. Improvement was also evident in total cholesterol LDL or bad cholesterol levels.

Grapefruit is probably effective in cardio protection and this is due to its high potassium content since potassium is a mineral noted for its roles in heart health.

Some constituents in grapefruit includes;

- 1. Flavonones:** The anti-inflammatory properties of flavonones have been known to reduce blood pressure and cholesterol.
- 2. Reduction in risk of kidney stones:** Grapefruit consumption may reduce risk of developing kidney stones. The citric acid in grapefruit may help reduce the formation of calcium oxalate kidney stones. Grapefruit is known to perform other functions such as diabetes management, improvement of digestion and sleep.



Grapefruit and its constituents have been studied for their radical scavenging, anti-microbial and proliferation inhibition abilities of several cancer cells. Health wise, grapefruit is one of the most useful citrus fruits. Grapefruit also contains furanocoumarins which are known to suppress cancer cell growth basically through apoptosis.

Quercetin found in grapefruits has anti-oxidant and anti-inflammatory effects which might help reduce inflammation, control blood sugar, kill cancer cells and also prevent heart disease and osteoporosis. The active chemical compounds found in grapefruit include flavones, flavonoids, isoflavones, furanocoumarins and anthocyanin. They have all been found to have anti-oxidant, anti-microbial and anti-inflammatory activities.

**3. FLAVONOIDS:** Flavonoids also known as bio flavonoids derived from that Latin word flavus which means yellow are a class of polyphenolic secondary metabolites that are found in plants. Flavonoids are the most important pigments in plants which produce yellow or blue/red pigmentation which solely aims at attracting animals for pollination. Flavonoids are involved in ultra violet filtration, floral pigmentation and symbiotic nitrogen fixation. Flavonoids particularly the catechins make up the most common group of polyphenolic compounds in human diet. Dietary sources include the following blue berries, black and green tea, all citrus fruits grapes inclusive, buck wheat, Ginkgo biloba etc.

**4. FURANOCOUMARINS:** Furanocoumarins also called furocoumarins are a class of organic chemical compounds produced by different plants. Most of the species of plants which contain furanocoumarins belong to the plant families Apiaceae and Rutaceae, they are most common in plants that have flowered and also in ripe seeds and fruits. They may be produced by plants as a defense mechanism against insects and mammals, they are also

thought to be a plants natural defense against attacks by fungi. Dietary sources include sap of plants, parsnip and giant hogweed.

**5. NARINGIN:** Naringin is a flavanone-7-0-glycoside. It is a naturally occurring flavanone in citrus fruits especially grapefruit where it is responsible for the fruits bitter taste. Naringinase materbolises naringin in humans to an aglycone known as naringenin which is not bitter. Naringenin has been shown to posses anti-inflammatory, anti-cancer effects, effects on bone regeneration, genetic damage, central nervous system diseases and metabolic syndrome. It also modulates signaling pathways and interacts with signaling molecules. Dietary sources of naringin: the skin of oranges and grapefruit. It occurs naturally in citrus foods. It is also found in tomatoes skin.

### **OBJECTIVE OF THE STUDY**

A major spill in the Niger Delta region of Nigeria occurred on the 1<sup>st</sup> of May 2010. It was the Exxon Mobil Oil spill which occurred at an Exxon Mobil offshore oil platform. It was approximately 20-25 miles from the shore.

More than a million gallons of crude was spilled into the Delta. This spill contributed to major environmental problems in the Niger Delta region of Akwa Ibom State, Nigeria. The leakage discharged approximately 323 barrels of crude oil into the Atlantic ocean thereby contaminating the waters and coastal settlements in areas known predominantly for fishing. The consequence of this leak was attested by locals who claimed a huge environmental damage as a result of the leak.

Fish allegedly killed from the Exxon Mobil were brought in from locations about 20km from the shore line. The spill increased the problems of pollution already suffered by the region. Great expanse of the Delta was covered with tar in addition to stagnant lakes of crude oil resulting from oil spills of the past. The effects of this spill are seen as air pollution, soil and water pollution. Toxicity was also expressed in the inhabitants such as man, aquatic animals and plants of Qua Iboe area.

This informed a study into pathological effects of this spill. Laboratory animals (albino rats) were fed with crude oil concentrations below that at the oil spill sites. The rats established signs and symptoms similar to those in human of the Qua Iboe area. The signs and symptoms include reduced ability to run across bars placed in cage, aversion for mating, restlessness before they finally died. Furthermore, 28days after the crude oil exposure to the rats extracts of *Garcinia kola* (bitter kola) was administered to the experimental (test) animals with observations of recovery of rats being recorded.

With these observations, it was significant to carryout studies into histopathology of affected organs in the rats which resulted to their deaths due to re-exposure to Nigerian crude oil.

## **HISTOLOGY STUDY**

The organs obtained from the rats were “cut” into sections and dehydrated with a range of concentrations of ethyl alcohol, later cleared with xylem and embedded in molten paraffin wax. The embedded tissue blocks were sectioned with a Shandon as 325 rotatory microtome and slides prepared with the sections. Lillie’s method of staining was doing using Ehrlich’s Haematoxylin and Eosin blue.

## METHODOLOGY

### Material I

Twenty albino rats were obtained from the University of Port Harcourt animal house Choba, Rivers State Nigeria. The rats were fed ad libitum (as desired). They were acclimatized to the test environment for seven (7) days. There were four (4) each cages “housing” five (5) rats. Petroleum crude oil was obtained from Nigerian National Petroleum Corporation (NNPC), Port Harcourt, Rivers State Nigeria.

### Preparation of food and water

The crude oil polluted food and water were prepared by mixing 250ml of crude oil to 500ml of tap water and stirred vigorously for two (2) hours. The crude was later decanted and the water (decant) used as the animals drinking water. The other part of decanted crude oil was mixed with the animal feed in the ration of 3kg of feed per 500ml of decanted crude oil, the feed and crude were mixed manually.

### Method 1

Male and female albino rats weighing 200 - 220g were used.

The study was made up of: (i) The control group (ii) The test group.

Each test group consisted of 2males and 3female. The same applied to the control group. Normal (unpolluted) feed and water was given to the control group rats and as desired (ad libitum). The test (experimental) animals were given crude oil polluted food and water for 21days. Strength was measured by animal’s ability to cross graded bars. Appetite was

measured by quantity of feed consumed by the animals. Appetite was scored on a daily basis as 0 means absences of feeding 2 which means consumption of 25percent of feed, 3 means consumption of 75percent of feed and 100percent consumption of all feed.

## **METHODOLOGY II**

**MATERIALS:** Rats that were previously poisoned with crude oil.

Grapefruit (*Citrus paradisi*) grapefruit – Sun dried, Juice extractor, Bowls, water.

### **Preparation of *Citrus paradisi* for inclusion into animal feed.**

The grapefruit was sun dried, 2kg feed was mixed with 1kg dried grape fruit. Water for experimental animals was 480ml with 20ml grape fruit juice. The grapefruit was purchased from Swali market, Bayelsa State, Nigeria. Peeled, sun dried for 3 days and blended with 2kg animal feed.

On day 21 of second experiment, the animals were again “sacrificed” using the same methods and histological procedures. From observations, there was no sign of haemorrhage in the kidney interstitium of experimental animals.

### **EFFECTS OF NIGERIAN CRUDE OIL ON THE INTERSTITIUM OF KIDNEY**

Investigations were carried out on the effects of Nigerian crude oil on the interstitium of the Kidney. Initial reports had evidence of haemorrhage in the interstitial spaces of the kidney. Control group animals were not administered crude oil feed and water. With the addition of grapefruit and grape fruit juice, the blood in the interstitium was completely non-evident. This simply means *Citrus paradisi* cleared the interstitium of the kidney of blood.

## DISCUSSION

The study confirms speculations of the toxicity suffered by humans, animals and plants when exposed to high volumes of crude oil like the one seen in huge oil spills.

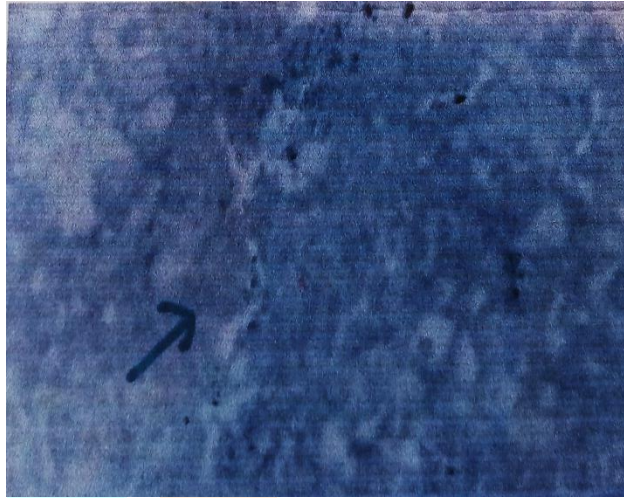
Effects on the interstitium of the kidney shows that when exposed to crude oil, blood is seen in the interstitium of the kidney and this can possibly lead to renal failure. Toxic manifestations are like the ones found in areas of massive oil spills like was found in Qua Iboe region of Akwa Ibom state, Nigeria.

The effects on kidney interstitium are in line with other related reports of Crude oil toxicity B. Ziworitin, O.A Georgewill and R.N.P Nwakwoala Jan, 2006: Histopathological effects of prolonged exposure of Nigerian crude oil to rats. With subsequent experiments in which grape fruit (*Citrus paradisi*) was added in the water and feed of the test animals, haemorrhage in the interstitium was completely non evident.

This absence of blood is possibly due to the presence of anti-oxidants like vitamin C, Beta carotene, lycopene, quercetin, limonoids, naringin, furanocoumarins. In summary, *Citrus paradisi* fruit and juice extract stopped haemorrhage in the kidney interstitium.



Rats were fed with 3kg of feed per 500ml water ad libitum for 21days. Organs were excised from the animals and preserved in 10% formaldehyde, sliced and dehydrated with ethyl alcohol and embedded in molten paraffin wax. The embedded tissue blocks were sectioned and stained as described in the methods.



**Kidney: Interstitial Haemorrhage**

**Figure 1b**

Rats were fed with crude oil polluted feed and water in the ratio of 3kg/500ml crude oil ad libitum for 21days. Organs were excised from the animals and preserved in 10% formaldehyde, sliced and dehydrated with ethyl alcohol and embedded in molten paraffin wax. The embedded tissue blocks were sectioned and stained as described in the methods.



**Kidney – Normal**

**Figure 1c**

Experimental rats were fed with 2kg feed in 1kg dried grapefruit with 480ml water and 20ml grape fruit juice ad libitum for 21days. Organs were excised from the animals and preserved in 10% formaldehyde, sliced and dehydrated with ethyl alcohol and embedded in molten paraffin wax. The embedded tissue blocks were sectioned and stained as described in the methods.

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