

ACCUMULATION OF HEAVY METAL IN THE SEEDS OF *ZEA MAYS* L. FROM CRUDE OIL IMPACTED SOILS IN KOM-KOM, RIVERS STATE, NIGERIA.

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ABSTRACT

This study assessed and modelled the accumulation of heavy metals in the seeds of *Zea mays* L. (maize) planted in a crude oil impacted soil. A total of thirteen soil samples were randomly collected. Five samples each were obtained from plot A (PA) and plot B (PB); the crude oil impacted plots. Three samples were obtained from plot C (PC); the control plot which was about 200m away from the spill impacted area. All samples were analysed for Total Petroleum Hydrocarbon (TPH) and Heavy Metals [iron (Fe), lead (Pb), zinc (Zn), chromium (Cr) and vanadium (V)]. Maize was planted on each of the thirteen plots and the seeds upon harvest was analysed for heavy metals (Fe, Pb, Zn, Cr and V). The seed accumulation factors for each heavy metal was modelled using TPH as the independent variable. Aside the Zn regression model with R² value of 0.399, other models performed well with R² values of 0.994, 0.942, 0.974 and 0.964 for Fe, Pb, Cr and V respectively. TPH was able to model the seed parameters with relatively high model performance except for Zinc. This suggests that accumulation of some heavy metals in the seed of the *Zea mays* L. planted is dependent on TPH. These models can be useful in predicting accumulation of heavy metals in the seeds of Maize planted in a crude oil polluted soil.

Keywords: *Seed Accumulation Factor (SAF), Regression Model, Total Petroleum Hydrocarbon (TPH), Heavy Metals, Zinc, Contamination, Soil, Kom-Kom*

29

1. INTRODUCTION

30 Oil production has continued to play dominant roles in the Nigerian economy, ranging from generation of
31 foreign exchange to serving as a source of energy to run the nation's Economy. Most industry's operation
32 is made possible with the use of refined petroleum products. Today, the quicker and easier means of
33 transportation would have been difficult without the products from hydrocarbon. Oil spills are a frequent
34 occurrence, particularly because of the extensive use of oil and petroleum products in our daily lives [1].
35 Production of other necessary needs of man derived from crude oil would not have been
36 possible if crude oil was not discovered and exploited.

37 Sources of oil spill on land includes amongst others accidental spills, third party interference (sabotage)
38 and spills from ruptured oil pipelines. Today the international oil and gas pipelines span several million
39 kilometres and this is growing yearly due to inter-regional trade in petroleum products [2]. Pipelines usually
40 have a life span and are subject to "tear and wear", thus can fail with time [3]. Spilled petroleum
41 hydrocarbons in the environment are usually drawn into the soil due to gravity until an impervious horizon
42 is met, for example bedrock, watertight clay or an aquifer [4].

43 Contamination of soil by oil spills is a wide spread environmental problem that often requires cleaning up
44 of the contaminated sites, which calls for an effective technological solution. Many affected sites around
45 the world remain contaminated, because it is expensive to clean them up by available technologies [2].
46 Human activities have led to the release of liquid petroleum hydrocarbon (also known as crude oil) into
47 the environment, causing the pollution of marine/coastal waters, shorelines and land as well. Liquid
48 petroleum hydrocarbons are a naturally-occurring fossil fuel, formed from dead organic materials in the
49 earth's crust [5]. These petroleum hydrocarbons adversely affect the germination and growth of plants in
50 soils [6]. Oil spills affect plants by creating conditions which make essential nutrients like nitrogen and
51 oxygen needed for plant growth unavailable to them [7]. Oil spill on the land may penetrate underground
52 and move downward reaching eventually groundwater. However, such vertical movement may be slowed
53 done if not prevented by the presence of paved surfaces, natural clay layers or other natural or
54 anthropogenic barriers. Oil may also move laterally along less permeable layers (including surface
55 pavements) or with groundwater and surface waters [8].

56 Oil spills have degraded most agricultural lands and have turned previously productive areas into
57 wastelands. With increasing soil infertility due to the destruction of soil micro-organisms, and
58 dwindling agricultural productivity, farmers have been forced to abandon their land, to seek non-
59 existent alternative means of livelihood. Also, numerous human health complications are traceable to
60 contamination by endocrine-disrupting chemicals of which petroleum and its products are principal
61 examples. These health issues include DNA damage, birth defects, lowering of the white blood cell count
62 in humans, miscarriages, infertility and sterility, and cancers of different parts (organs) of the body [9].

63 Maize is a multipurpose crop because every part of its plant has economic value. The seed, cob, tassel,
64 leaves and stalk can be used to produce a huge variety of food and non-food products [10]. (IITA, 2001).
65 Maize seed is a major source of food. It can be eaten roasted, cooked and its flour form is used in many
66 food products. Maize is ubiquitously planted in the Niger Delta region of Nigeria both for subsistent and
67 commercial purpose. Accumulation of heavy metals in soil and in plants, due to crude oil spillage in the
68 Niger Delta has been reported in literatures [11, 12, 6, 13, 4, 14, 15 16, 17], thus this study assessed and
69 modelled the accumulation of heavy metals in the seeds of maize (*Zea mays* L.) planted in a crude oil
70 contaminated soil.

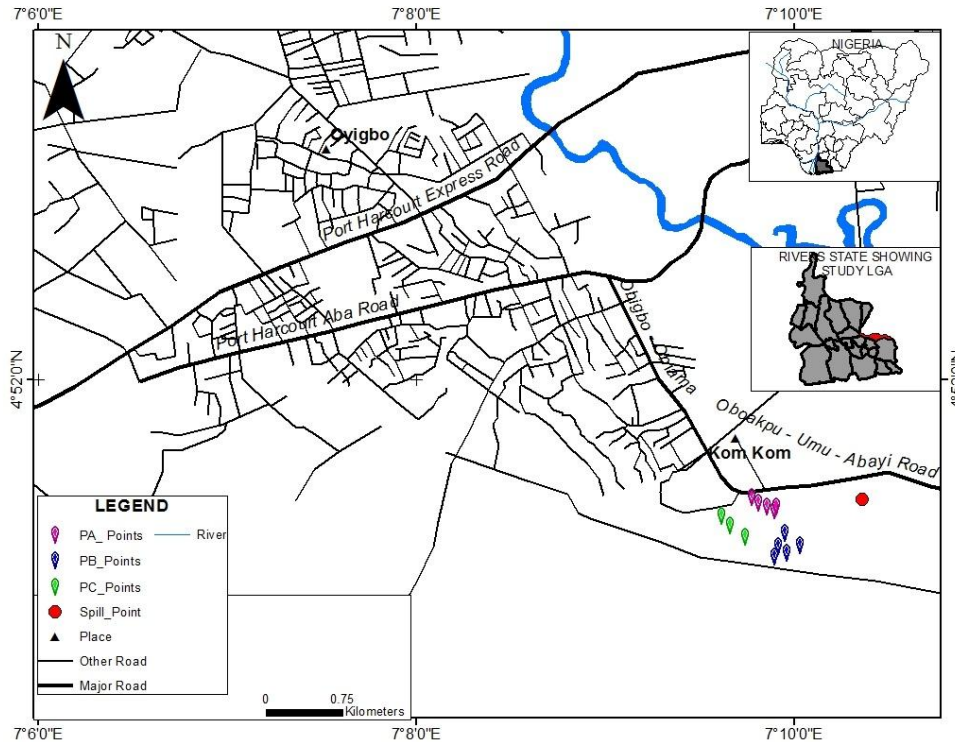
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74 **2. MATERIALS AND METHODS**

75 **2.1 Study area**



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77 **Figure 1: Map of Study Area showing the spill point and sampling plots**

78 This study was carried out in a crude oil impacted area at Kom-Kom, Oyigbo, Rivers State, Nigeria. The
79 area bears the Trans-Delta Bonny Light Line of an oil company. Kom-Kom is a small settlement with
80 farmers and traders. The soil type in the area is loamy thus the presence of various food crops like maize
81 (*Zea mays*), cassava (*Manihotesculenta*) and native pear (ube) (*Dacryodes edulis*).

82 **2.2 Soil Sample Collection:** A total of thirteen soil samples were randomly collected. Five samples from
83 plot A (PA), five samples from plot B (PB) and three samples from plot C (PC) which acted as control
84 situated about 200m away from the spill impacted area. At each spot in a plot, the sample was collected
85 using hand auger at 0-15cm and 15-30 cm depth then bulked to form a composite sample. All soil
86 samples were taken immediately to the laboratory for analysis.

87 **2.3 Laboratory analysis:** Laboratory analyses were done in line with the United States Environmental
88 Protection Agency (USEPA) analytical protocol. Parameters analyzed were Total Petroleum Hydrocarbon
89 (TPH) and Heavy Metals (Iron, Lead, Zinc, Chromium, and Vanadium).

90 TPH was analysed using gas chromatograph flame ionization detector system while heavy metals were
91 analysed using a properly calibrated Atomic Absorption Spectrometer (AAS) with specific metallic
92 standards.

93 **2.4 Maize Produce Collection:** *Zea mays* L. (Maize) seeds were planted on each of the thirteen plots.
94 After harvesting, the produce (cobs) were collected, weighed and deseeded. The seeds were weighed,
95 air dried and grounded with home blender to avoid powder waste and contamination. Then the powder
96 was wrapped in foil and taken to the laboratory for heavy metal analysis [18].

97 **2.5 Maize Powder Analysis:** The heavy metal analysis method adopted for analysing the maize powder
98 was in line with the API analytical protocol. One gram of air-dried ground maize powder sample was

99 weighed and 10ml of well mixed Perchloric, nitric and sulphuric acid were added to the soil sample. It was
100 passed through a heating mantle for 10-20 minutes. Allowed to cool and 20ml of distilled water added to
101 it, then boiled to bring the metals into solution. The solution was allowed to cool and filtered through
102 Whatmann filter paper into 100ml standard flask. Then made up to mark and the content transferred into
103 100ml plastic container. Each metal was run using an AAS calibrated daily with specific metallic
104 standard[18].

105 2.6 Data Analysis

106 The results collected from the laboratory were statistically analysed using Descriptive analysis and
107 Multiple linear regression (MLR). Xcel Stat was used to process these statistical analyses.

108 2.7 Seed Accumulation Factor

109 The seed accumulation factor (SAF) was calculated for each heavy metal using Equation 1

$$110 SAF = \frac{C_{seed}}{C_{soil}} \dots\dots\dots(Equation 1)$$

111 Where, C_{seed} is the concentration of heavy metal in the seed

112 C_{soil} is the concentration of heavy metal in the soil

113 Multiple linear regression (MLR) models were generated for each heavy metal analysed using TPH as the
114 independent variable. MLR is given byEquation 2

$$115 Y_i = \beta_0 + \beta_1x_{1i} + \beta_2x_{2i} + \dots + \beta_kk_i + \varepsilon_i \dots\dots\dots(Equation 2)$$

116 Where, β is coefficient of regression, β_0 is the intercept, x are the independent variable. and k ranges
117 from 1 to n.

119 3. RESULTS AND DISCUSSION

120 Heavy metals are accumulated in soils as well as in plants. Heavy metals are accumulated in tissues and
121 on the surface of organs thus possible availability across food chain[15]. Results of Total Petroleum
122 Hydrocarbon (TPH), Heavy metals in Soil and Heavy metals in the Maize seed as well as the seed
123 accumulation factor are presented in Table 1.

124 **Table 1: Heavy Metals accumulated in Soil, Maize Seed and the Seed Accumulation Factor**

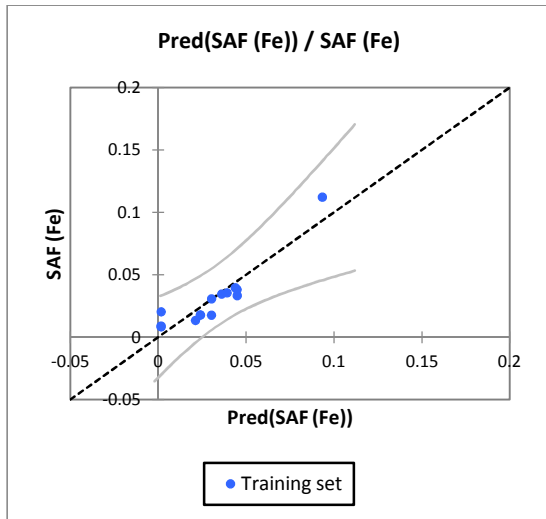
Plot	TPH and Heavy metal in Soil						Heavy metal in seed					Seed accumul		
	TPH	Fe	Zn	Pb	Cr	V	Fe	Zn	Pb	Cr	V	SAF (Fe)	SAF (Zn)	SAF
PA 1	3931	33.578	0.891	0.032	0.317	0.596	2.221	0.692	0.015	0.071	0.148	0.038	0.777	0
PA 2	2038	31.617	1.396	0.037	0.292	0.577	0.565	0.478	0.01	0.032	0.057	0.018	0.342	0
PA 3	1788.26	22.289	1.828	0.024	0.343	0.577	0.301	0.486	0.004	0.032	0.079	0.014	0.266	0
PA 4	3842	21.980	2.111	0.014	0.430	0.658	0.873	1.234	0.005	0.092	0.158	0.040	0.585	0
PA 5	3419	58.141	1.022	0.065	0.430	0.414	1.195	0.563	0.022	0.081	0.089	0.036	0.551	0
PB1	2614	16.920	0.425	0.032	0.138	0.310	0.521	0.083	0.009	0.021	0.058	0.031	0.301	0
PB2	2612	23.942	2.166	0.050	0.184	0.424	0.425	0.392	0.003	0.025	0.067	0.018	0.729	0
PB3	3139	17.750	0.243	0.027	0.126	0.368	0.615	0.132	0.019	0.022	0.074	0.035	0.543	0
PB4	8324	35.122	0.538	0.009	0.232	0.359	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0
PB5	3938	29.627	0.276	0.019	0.171	0.375	0.989	0.301	0.009	0.039	0.096	0.033	0.708	0
PC1	22.25	12.046	0.615	0.025	0.056	0.043	0.246	0.06	0.002	0.001	0.004	0.020	0.098	0
PC2	17.37	14.945	1.208	0.024	0.058	0.030	0.125	0.017	0.002	0.002	0.002	0.008	0.014	0
PC3	13.20	21.037	0.937	0.017	0.057	0.043	0.191	0.012	0.002	0.003	0.002	0.009	0.013	0

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 126 TPH in the soil had mean values of 3003.65±1017.96 mg/kg, 4125.40±2408.89 mg/kg and 17.61±4.53
 127 mg/kg for PA, PB and PC respectively. According to Osuji et al. [11], high hydrocarbon levels (3400–
 128 6800 mg/kg) affect both above-ground and subterranean flora and fauna, which are essential
 129 indices in the biogeochemical cycle that affects availability of plant nutrients. The soil values for
 130 Iron in PA, PB and PC had mean values of 33.52±14.74 mg/kg, 24.67±7.78 mg/kg and 16.01±4.59 mg/kg
 131 respectively. Zinc values in PA, PB and PC had mean values of 1.45±0.52 mg/kg, 0.37±0.81 mg/kg and
 132 0.92±0.29 mg/kg respectively. Soil analysis results for Lead in PA, PB and PC had mean values of
 133 0.134±0.02 mg/kg, 0.121±0.02 mg/kg and 0.022±0.01 mg/kg respectively. Chromium results had mean
 134 values for PA, PB and PC as 0.362±0.06 mg/kg, 0.170±0.04 mg/kg and 0.057±0.001 mg/kg respectively.
 135 Results of soil analysis for Vanadium for PA, PB and PC had mean values of 0.564±0.09 mg/kg,
 136 0.367±0.04 mg/kg and 0.039±0.01 mg/kg respectively. There are residential building with subsistence
 137 farms around the spill impacted area and as such could be exposed to the contamination. From the
 138 observed plant (Maize) growth, TPH had an effect as the plot with the highest TPH level had no seed in
 139 the harvested fruit. Aside the low plant yield, crops planted around this impacted area may be harvested
 140 and eaten or sold in a local market. Zinc had relatively the highest seed accumulation factor(SAF) with a
 141 mean SAF of 0.413 this was followed by Lead, Vanadium, Chromium and Iron with mean SAF of 0.312,
 142 0.186, 0.160 and 0.032 respectively. Heavy metals have deleterious effects in health however are usually
 143 chronic thus accumulation of heavy metals poses great risk. Lead has been reported as neurotoxic and
 144 can accumulate in the bone marrow [19]. Lead affects membrane permeability of kidney, liver and brain
 145 cells thus resulting in either reduced functioning or complete breakdown of these tissues, as lead
 146 is a cumulative poison [20]. Cadmium (Cd) and mercury compete with and displace in a number of
 147 Zn-containing metalloenzymes by irreversibly binding to active sites thereby destroying normal
 148 metabolism.

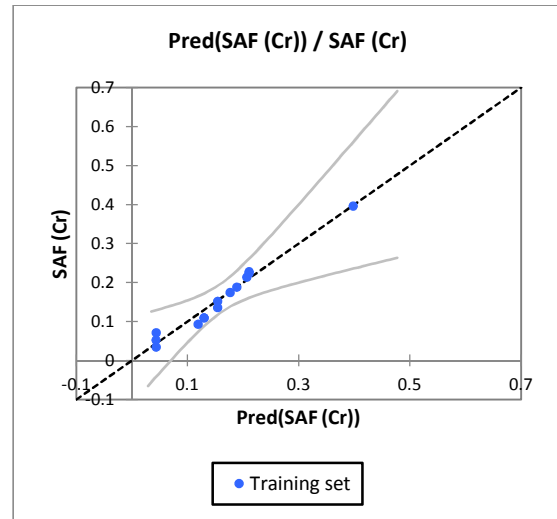
149 **Table 2: SAF Regression Models**

SN	Heavy metal	Model equation	R ²
1	Fe	Y = 0.001342 – 0.00001104X ₁	0.994
2	Zn	Y = 0.2064 – 0.00007517X ₁	0.399
3	Pb	Y = 0.09930 – 0.00007745X ₁	0.942
4	Cr	Y = 0.04244 + 0.00004268X ₁	0.974
5	V	Y = 0.05978 + 0.00004589X ₁	0.964

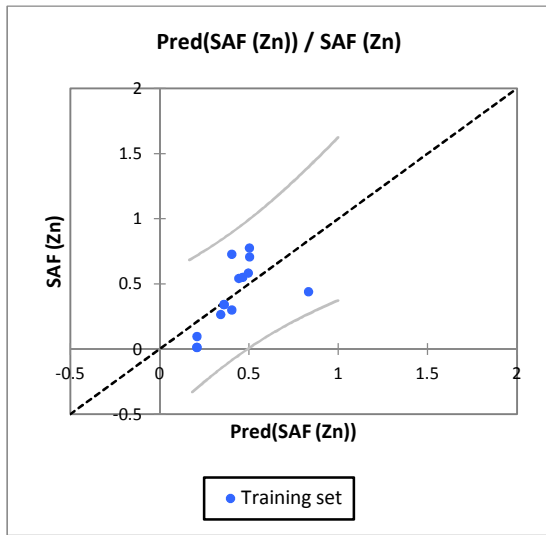
150 Where Y = SAF and X₁ = TPH



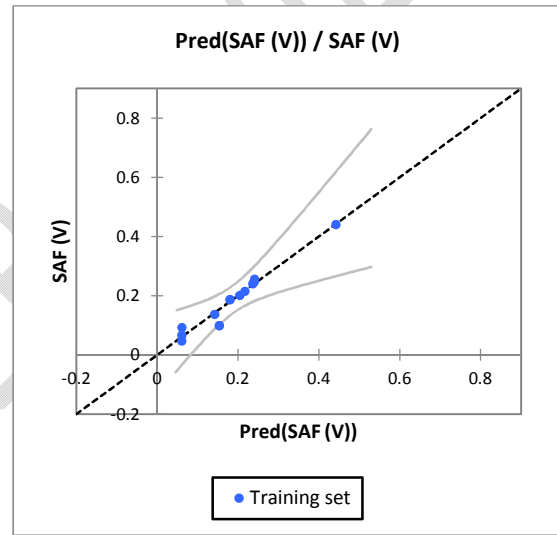
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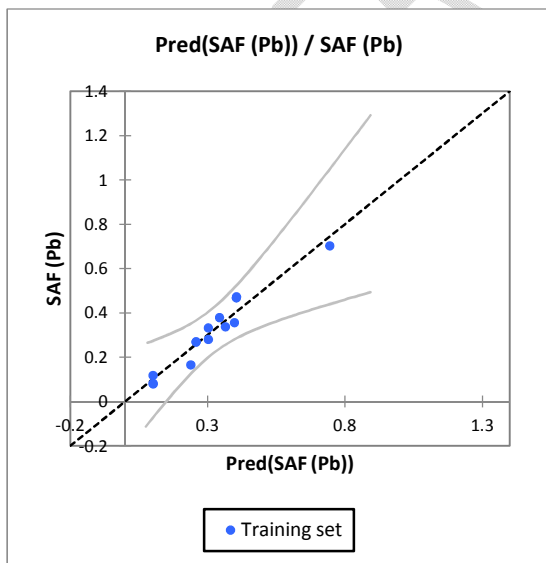
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156 **Figure 2a-e: SAF Models for the Heavy Metals**

157 The seed accumulation factors (SAFs) for each heavy metal was modelled using TPH as the independent
158 variable. Aside the Zinc regression model with R² value of 0.399, other models performed well with R²
159 values of 0.994, 0.942, 0.974 and 0.964 for Fe, Pb, Cr and V respectively (Table 2; Figure 2a-e). The
160 SAF as explained by the TPH level suggest that the chemical property of the soil could be responsible for
161 the accumulation of heavy metals in the seeds of the Maize. This is complemented by the report by
162 Aktaruzzaman et al., [16] (2013) that mobility of metals from soil to plants is a function of the physical and
163 chemical properties of the soil and is altered by several environmental and human factors. However, with
164 the relatively high SAF value for Zinc but with relatively poor model performance suggest that Zinc
165 accumulation in the seeds may not be influenced by TPH level.

166 **4. CONCLUSION**

167 Total Petroleum Hydrocarbon (TPH) was able to model the heavy metal parameters in the maize seed
168 with relatively high model performance for the heavy metals except for Zinc. This suggests that
169 accumulation of some heavy metals in the seed of the *Zea mays* L. planted is dependent on TPH. These
170 models can be useful in predicting accumulation of heavy metals in the seeds of Maize planted in a crude
171 oil polluted soil. The models were all linear and as such, linear relationship exist among the maize seed
172 parameters and the soil data before planting thus suggesting that the changes in the oil contaminants are
173 not changing abruptly or in a nonlinear fashion.

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176 statistical knowledge of Dr. Ramson Enotoriuwa and for the encouragement, suggestions and support.

177 **Competing Interests**

178 Authors have declared that no competing interests exist.

179 **Authors' contributions**

180 This research was carried out in collaboration with all authors. Author OIM wrote the first draft of the
181 manuscript. Authors OLC and NEO designed the study. All authors read and approved the final
182 manuscript

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195 **REFERENCES**

- 196 1. Michel J, Fingas M. Oil Spills: Causes, Consequences, Prevention, and Countermeasures. In
 197 book: Fossil Fuels, Chapter 7: 159-201. 2016. Researchgate. DOI
 198 10.1142/9789814699983_0007
- 199 2. Ezeonu CS, Onwurah INE, Oje OA. Comprehensive Perspectives in Bioremediation of Crude Oil
 200 Contaminated Environments. Edited by Dr. Laura Romero-Zerón, Introduction to Enhanced Oil
 201 Recovery (EOR) Processes and Bioremediation of Oil-Contaminated Sites. Chapter 6:143-
 202 184.2012. ISBN 978-953-51-0629-6.
- 203 3. Beller M., Schoenmaker H, Huuskonen E. Pipeline inspection environmental protection through
 204 on-line inspection, proceeding of the NNPC seminar: Oil industry and the Nigerian Environment,
 205 Port Harcourt, Nigeria.1996; 233-241.
- 206 4. OgbonnaJF,Amajuoyi CA.Physicochemical Characteristics and Microbial Quality of an Oil
 207 Polluted Site in Gokana, Rivers State. Journal of Applied Sciences & Environmental
 208 Management.2009; 13(3): 99-103.
- 209 5. Kingston P. Long-term environmental impact of oil spills. Spill Science & Technology
 210 Bulletin.2002; 7: 53-61.
- 211 6. Agbogidi OM, Erutor PG,Akparobi SO. Effects of Time of Application of Crude Oil to Soil on the
 212 Growth of Maize (*Zea mays* L.). Research Journal of Environmental Toxicology.2007; 1: 116-123.
- 213 7. Adam G, Duncan HJ. Influence of Diesel Fuel on Seed Germination. Environmental Pollution.
 214 2002; 120: 363-370
- 215 8. EPC (Environmental Pollution Centers). Oil Spill Pollution. May,
 216 2010.<https://www.environmentalpollutioncenters.org/oil-spill/>
- 217 9. Briggs L, Briggs C. Petroleum Industry Activities and Human Health. In Prince E. Ndimele of The
 218 Political Ecology of Oil and Gas Activities in the Nigerian Aquatic Ecosystem Pages 143-147.
 219 2018.<https://doi.org/10.1016/B978-0-12-809399-3.00010-0>
- 220 10. IITA. Annual Report on Maize Production. International Institute of Tropical Agriculture, Ibadan,
 221 Oyo State.2001
- 222 11. Osuji LC, Adesiyon SO, Obute GC. Post impact assessment of oil pollution in the Agbada
 223 west plain of Niger Delta Nigeria: Field reconnaissance and total extractable hydrocarbon
 224 content. Chemistry & Biodiversity. 2004; 1 (10): 1569-1578.
- 225 12. Adami G, Cabras I, Predonzani S, Barbiei P, Reisenhofer E. Metal pollution assessment of
 226 surface sediments along a new gas pipeline in the Niger Delta (Nigeria). Environmental
 227 Monitoring and Assessment. 2007; 125, (1–3): 291–299
- 228 13. Umoren IU, Udousoro II.Fractionation of Cd, Cr, Pb and Ni in roadside soils of Uyo, Niger
 229 Delta Region, Nigeria using the optimized BCR sequential extraction technique .
 230 Environmentalist. 2009; 29 (3): 280 – 286
- 231 14. Adeniyi AA, Owoade OJ. Total petroleum hydrocarbons and trace heavy metals in roadside
 232 soils along the Lagos-Badagry expressway, Nigeria. Environmental Monitoring and
 233 Assessment. 2010; 167, (1 – 4): 625 – 630.
- 234 15. Singh J, Kalamdhad AS. Effects of Heavy Metals on Soil, Plants, Human Health and Aquatic Life.
 235 International Journal of Research in Chemistry and Environment.2011; 1 (2):15-21.
- 236 16. Aktaruzzaman M, Fakhruddin ANM, Chowdhury MAZ, Fardous, Z, Alam, MK. Accumulation of
 237 Heavy Metals in Soil and their Transfer to Leafy Vegetables in the Region of Dhaka Aricha
 238 Highway, Savar, Bangladesh, Pakistan Journal of Biological Sciences. 2013; 16(7):332-338.
 239 DOI: 10.3923/pjbs.2013.332.338
- 240 17. Nwaichi EO, Chuku LC, Igboavwogan E. Polycyclic Aromatic Hydrocarbons and Selected Heavy
 241 Metals in Some Oil Polluted Sites in Delta State Nigeria. Journal of Environmental
 242 Protection.2016;7:1389-1410. <http://dx.doi.org/10.4236/jep.2016.710120>

- 243 18. API (American Petroleum Institute). Inter Laboratory Study of Three Methods for Analyzing
244 Petroleum Hydrocarbons in Soil, Diesel Range Organics (DRO), Gasoline Range Organics
245 (GRO) and Petroleum Hydrocarbon (PHC).Publication Number 4599:1994.
246 19. Murphy CB. "Bioaccumulation and toxicity of heavy metals and related trace elements. Research
247 Journal of the Water Pollution Control Federation.1981; 53, (6): 993–999
248 20. Forstner U,Wittman GTW. Metal Pollution in the Aquatic Environment. Springer-Verlag, Berlin,
249 Germany,1981; Pages: 488. ISBN-13: 9783642693854.

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