

## Original Research Article

### 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 polluted soil. A total of thirteen soil samples were randomly collected. Five samples was obtained from plot A (PA) and plot B (PB). Three samples was also obtained from plot C (PC); PC acted as the control, obtained 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 Zinc regression model with  $R^2$  value of 0.399, other models performed well with  $R^2$  values of 0.994, 0.942, 0.974 and 0.964 for Fe, Pb, Cr and V respectively. TPH was able to model plant 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.

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

#### Introduction

Oil production has continued to play dominant roles in the Nigerian economy, ranging from generation of foreign exchange to serving as a source of energy to run the nation's Economy. Most industry's operation is made possible with the use of refined petroleum products. Today, the quicker and easier means of transportation would have been difficult without the products from hydrocarbon.

Oil spills are a frequent occurrence, particularly because of the extensive use of oil and petroleum products in our daily lives (Michel and Fingas, 2016). Production of other necessary needs of man derived from crude oil would not have been possible if crude oil was not discovered and exploited.

Sources of oil spill on land includes amongst others accidental spills, third party interference (sabotage) and spills from ruptured oil pipelines. Today the international oil and gas pipelines

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47 span several million kilometres and this is growing yearly due to inter-regional trade in  
48 petroleum products. Pipelines usually have a life span and are subject to “tear and wear”, thus  
49 can fail with time. Spilled petroleum hydrocarbons in the environment are usually drawn into the  
50 soil due to gravity until an impervious horizon is met, for example bedrock, watertight clay or an  
51 aquifer.

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52 Contamination of soil by oil spills is a wide spread environmental problem that often requires  
53 cleaning up of the contaminated sites, which calls for an effective technological solution. Many  
54 affected sites around the world remain contaminated, because it is expensive to clean them up by  
55 available technologies (Ezeonu et al., 2012). Human activities have led to the release of liquid  
56 petroleum hydrocarbon (also known as crude oil) into the environment, causing the pollution of  
57 marine/coastal waters, shorelines and land as well. Liquid petroleum hydrocarbons are a  
58 naturally-occurring fossil fuel, formed from dead organic materials in the earth's crust (Kingston,  
59 2002). These petroleum hydrocarbons adversely affect the germination and growth of plants in  
60 soils (Agbogidi et al., 2007). Oil spills affect plants by creating conditions which make essential  
61 nutrients like nitrogen and oxygen needed for plant growth unavailable to them (Adam and  
62 Duncan, 2002). Oil spill on the land may penetrate underground and move downward reaching  
63 eventually groundwater. However, such vertical movement may be slowed down if not prevented  
64 by the presence of paved surfaces, natural clay layers or other natural or anthropogenic barriers.  
65 Oil may also move laterally along less permeable layers (including surface pavements) or with  
66 groundwater and surface waters (EPC, 2010).

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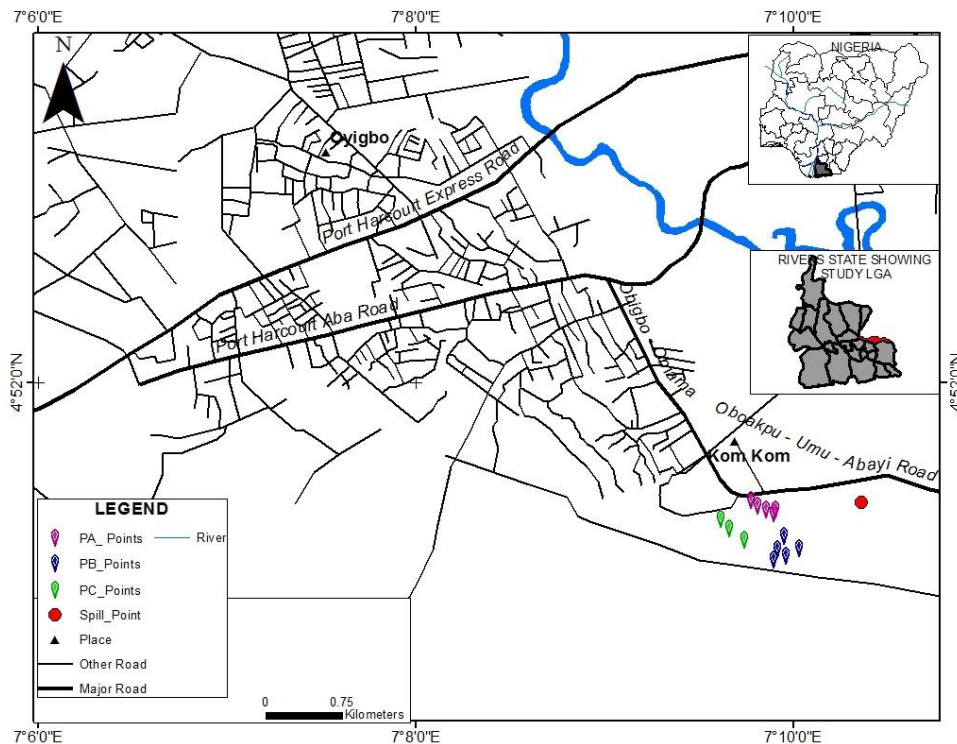
67 Oil spills have degraded most agricultural lands and have turned previously productive areas into  
68 wastelands. With increasing soil infertility due to the destruction of soil micro-organisms,  
69 and dwindling agricultural productivity, farmers have been forced to abandon their land, to  
70 seek non-existent alternative means of livelihood. Also, numerous human health complications  
71 are traceable to contamination by endocrine-disrupting chemicals of which petroleum and its  
72 products are principal examples. These health issues include DNA damage, birth defects,  
73 lowering of the white blood cell count in humans, miscarriages, infertility and sterility, and  
74 cancers of different parts (organs) of the body. (Briggs and Briggs, 2018).

75 Maize is a multipurpose crop because every part of its plant has economic value. The seed, cob,  
76 tassel, leaves and stalk can be used to produce a huge variety of food and non-food product  
77 (IITA, 2001). Maize seed is a major source of food. It can be eaten roasted, cooked and its flour  
78 form is used in many food products. Maize is ubiquitously planted in the Niger Delta region of  
79 Nigeria both for subsistent and commercial purpose. Accumulation of heavy metals in soil due to  
80 crude oil spillage in the Niger Delta has been well reported in literature (Osuji and Adesiyani,  
81 2005; Adami et al., 2007; Iwegbue et al., 2008; Akporido and Ipeaiyeda, 2014; Umoren. and  
82 Udousoro, (2009). Adeniyi and Owoade, 2010; Sojinu et al., 2010; Ekpo et al., 2012; Nwaichi  
83 et al, 2016) thus this study assessed and modelled the accumulation of heavy metals in the seeds  
84 maize planted in a crude oil contaminated soil.

85

## 86 **Materials and Methods**

### 87 **Study area**



89  
90 **Figure 1: Map of Study Area showing the spill point and sampling plots**

91 This study was carried out in a crude oil impacted area at Kom-Kom, Oyigbo, Rivers State,  
92 Nigeria. The area bears the Trans-Delta Bonny Light Line of an oil company. Kom-Kom is a  
93 small settlement with farmers and traders. The soil type in the area is loamy thus the presence of  
94 various food crops like maize, cassava and native pear (ube).

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

100 **Laboratory analysis:** Laboratory [analyses were](#) done in line with the United States  
101 Environmental Protection Agency (USEPA) analytical protocol. Parameters analyzed were Total  
102 Petroleum Hydrocarbon (TPH) and Heavy Metals (Iron, Lead, Zinc, Chromium, and Vanadium).

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

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

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112 **Maize Powder Analysis:** The heavy metal analysis method adopted for analysing the maize  
113 powder was in line with the API analytical protocol. One gram of air-dried ground maize powder  
114 sample was weighed and 10ml of well mixed Perchloric, nitric and sulphuric acid were added to  
115 the soil sample. It was passed through a heating mantle for 10-20 minutes. Allowed to cool and  
116 20ml of distilled water added to it, then boiled to bring the metals into solution. The solution was  
117 allowed to cool and filtered through Whatmann filter paper into 100ml standard flask. Then  
118 made up to mark and the content transferred into 100ml plastic container. Each metal was run  
119 using an AAS calibrated daily with specific metallic standard (API, 1994).

### 120 Data Analysis

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

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### 123 Seed Accumulation Factor

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

125 
$$SAF = \frac{C_{seed}}{C_{soil}} \dots\dots\dots (Equation 1)$$

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

127  $C_{soil}$  is the concentration of heavy metal in the soil

128 Multiple linear regression (MLR) models were generated for each heavy metal analysed using  
129 TPH as the independent variable. MLR is given by

130 
$$Y_i = \beta_0 + \beta_1 x_{1i} + \beta_2 x_{2i} + \dots + \beta_k k_i + \varepsilon_i \dots\dots\dots (Equation 2)$$

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131 Where,  $\beta$  is coefficient of regression,  $\beta_0$  is the intercept, x are the independent variable. i and k  
132 ranges from 1 to n.

### 134 Results and Discussion

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

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

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Plot	TPH and Heavy metal in Soil						Heavy metal in seed					Seed accumulation factor				SAF (V)
	TPH	Fe	Zn	Pb	Cr	V	Fe	Zn	Pb	Cr	V	SAF (Fe)	SAF (Zn)	SAF (Pb)	SAF (Cr)	
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	0.469	0.224	0.248
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	0.270	0.110	0.099
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	0.167	0.093	0.137
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	0.357	0.214	0.240
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	0.338	0.188	0.215
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	0.281	0.152	0.187
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	0.333	0.136	0.186
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	0.380	0.175	0.201
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	0.00	0.00	0.00
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	0.474	0.228	0.256
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	0.081	0.071	0.092
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	0.083	0.035	0.067
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	0.119	0.053	0.047

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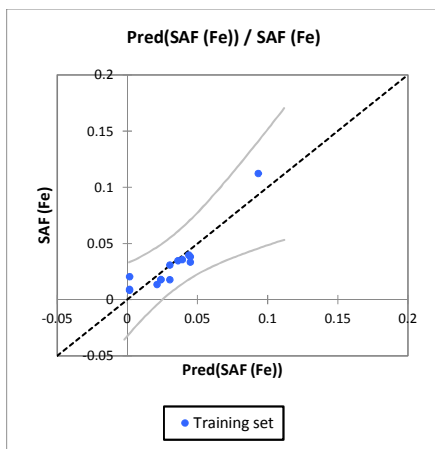
146 TPH in the soil had mean values of  $3003.65 \pm 1017.96$  mg/kg,  $4125.40 \pm 2408.89$  mg/kg and  
 147  $17.61 \pm 4.53$  mg/kg for PA, PB and PC respectively. According to Osuji et al., (2004), high  
 148 hydrocarbon levels (3400–6800 mg/kg) affect both above-ground and subterranean flora and  
 149 fauna, which are essential indices in the biogeochemical cycle that affects availability of  
 150 plant nutrients. The soil values for Iron in PA, PB and PC had mean values of  $33.52 \pm 14.74$   
 151 mg/kg,  $24.67 \pm 7.78$  mg/kg and  $16.01 \pm 4.59$  mg/kg respectively. Zinc values in PA, PB and PC  
 152 had mean values of  $1.45 \pm 0.52$  mg/kg,  $0.37 \pm 0.81$  mg/kg and  $0.92 \pm 0.29$  mg/kg respectively. Soil  
 153 analysis results for Lead in PA, PB and PC had mean values of  $0.134 \pm 0.02$  mg/kg,  $0.121 \pm 0.02$   
 154 mg/kg and  $0.022 \pm 0.01$  mg/kg respectively. Chromium results had mean values for PA, PB and  
 155 PC as  $0.362 \pm 0.06$  mg/kg,  $0.170 \pm 0.04$  mg/kg and  $0.057 \pm 0.001$  mg/kg respectively. Results of soil  
 156 analysis for Vanadium for PA, PB and PC had mean values of  $0.564 \pm 0.09$  mg/kg,  $0.367 \pm 0.04$   
 157 mg/kg and  $0.039 \pm 0.01$  mg/kg respectively. There are residential building with subsistence farms  
 158 around the spill impacted area and as such could be exposed to the contamination. From the  
 159 observed plant (Maize) growth, TPH had an effect as the plot with the highest TPH level had no  
 160 seed in the harvested fruit. Aside the low plant yield, crops planted around this impacted area  
 161 may be harvested and eaten or sold in a local market. Zinc had relatively the highest seed  
 162 accumulation factor (SAF) with a mean SAF of 0.413 this was followed by Lead, Vanadium,  
 163 Chromium and Iron with mean SAF of 0.312, 0.186, 0.160 and 0.032 respectively. Heavy metals  
 164 have deleterious effects in health however are usually chronic thus accumulation of heavy metals  
 165 poses great risk. Lead has been reported as neurotoxic and can accumulate in the bone marrow  
 166 (Murphy, 1981). Lead affects membrane permeability of kidney, liver and brain cells thus  
 167 resulting in either reduced functioning or complete breakdown of these tissues, as lead is a  
 168 cumulative poison (Forstner and Wittmann, 1981). Cadmium (Cd) and mercury compete  
 169 with and displace in a number of Zn-containing metalloenzymes by irreversibly binding to  
 170 active sites thereby destroying normal metabolism.

173 **Table 2: SAF Regression Models**

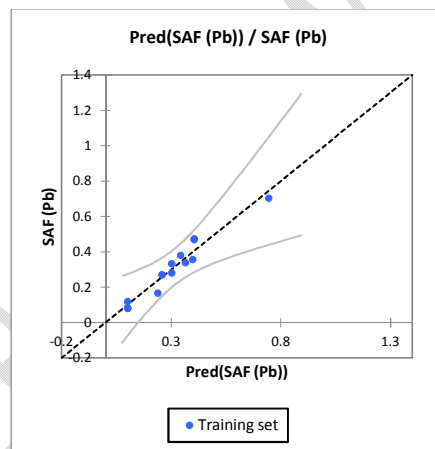
SN	Heavy metal	Model equation	R <sup>2</sup>
1	Fe	$Y = 0.001342 - 0.00001104X_1$	0.994
2	Zn	$Y = 0.2064 - 0.00007517X_1$	0.399
3	Pb	$Y = 0.09930 - 0.00007745X_1$	0.942
4	Cr	$Y = 0.04244 + 0.00004268X_1$	0.974
5	V	$Y = 0.05978 + 0.00004589X_1$	0.964

174 Where Y = SAF and X<sub>1</sub> = TPH

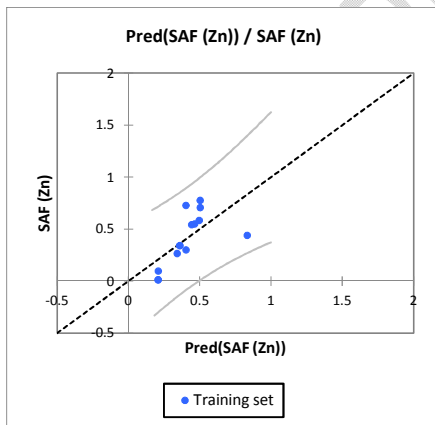
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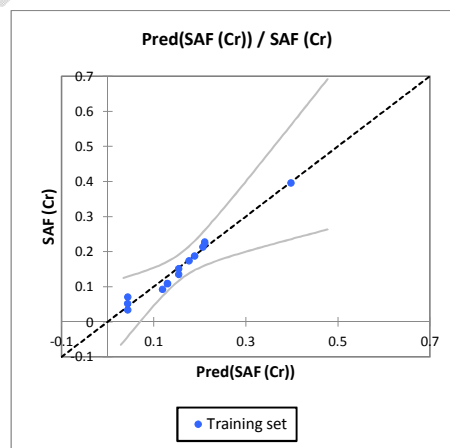
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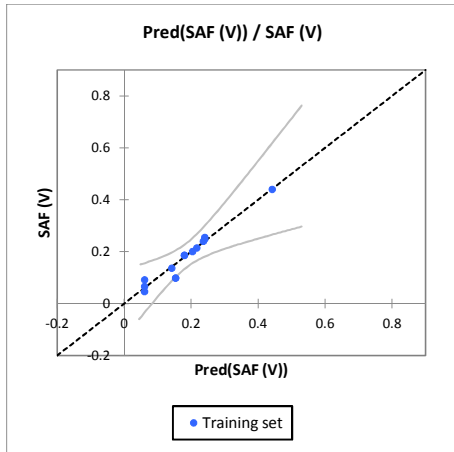
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181 **Figure 2a-e: SAF Models for the Heavy**  
182 **Metals**

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UNDER PEER REVIEW

184

185 The seed accumulation factors (SAF) for each heavy metal was modelled using TPH as the  
186 independent variable. Aside the Zinc regression model with  $R^2$  value of 0.399, other models  
187 performed well with  $R^2$  values of 0.994, 0.942, 0.974 and 0.964 for Fe, Pb, Cr and V respectively  
188 (Table 2; Figure 2a-e). The SAF as explained by the TPH level suggest that the chemical  
189 property of the soil could be responsible for the accumulation of heavy metals in the seeds of the  
190 Maize. This is complemented by the report by Aktaruzzaman *et al.*, (2013) that mobility of  
191 metals from soil to plants is a function of the physical and chemical properties of the soil and is  
192 altered by several environmental and human factors. However, with the relatively high SAF  
193 value for Zinc but with relatively poor model performance suggest that Zinc accumulation in the  
194 seeds may not be influenced by TPH level.

### 195 **Conclusion**

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

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### 206 **References**

207 Adam, G. and Duncan, H. J. (2002): Influence of Diesel Fuel on Seed Germination.  
208 *Environmental Pollution*, 120: 363-370

209 Adami G, Cabras I, Predonzani S, Barbieri P, Reisenhofer E (2007). Metal pollution  
210 assessment of surface sediments along a new gas pipeline in the Niger Delta (Nigeria).  
211 *Environmental Monitoring and Assessment*, 125, (1-3): 291-299

212 Adeniyi, A. A., and Owoade, O. J. (2010). Total petroleum hydrocarbons and trace heavy  
213 metals in roadside soils along the Lagos-Badagry expressway, Nigeria.  
214 *Environmental Monitoring and Assessment*, 167, (1 - 4): 625 - 630.

215 Agbogidi, O.M., Eruotor, P.G. and Akparobi, S.O. (2007). Effects of Time of Application of  
216 Crude Oil to Soil on the Growth of Maize (*Zea mays* L.). *Research Journal of*  
217 *Environmental Toxicology*, 1: 116-123.

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- 218 Akporido, S. O. and Ipeaiyeda, A. O. (2014). An assessment of the oil and toxic heavy metal  
219 profiles of sediments of the Benin River adjacent to a lubricating oil producing factory,  
220 Delta State, Nigeria. *International Research Journal of Public and Environmental*  
221 *Health, 1* (2): 40-53.
- 222 Aktaruzzaman, M., Fakhruddin, A. N. M., Chowdhury, M. A. Z., Fardous, Z. and Alam, M. K.  
223 (2013): Accumulation of Heavy Metals in Soil and their Transfer to Leafy Vegetables in  
224 the Region of Dhaka Aricha Highway, Savar, Bangladesh, *Pakistan Journal of Biological*  
225 *Sciences* 16 (7) 332-338 / DOI: 10.3923/pjbs.2013.332.338
- 226 API (American Petroleum Institute) (1994) Inter Laboratory Study of Three Methods for  
227 Analyzing Petroleum Hydrocarbons in Soil, Diesel Range Organics (DRO), Gasoline  
228 Range Organics (GRO) and Petroleum Hydrocarbon (PHC). Publication Number 4599.
- 229 Briggs, L. and Briggs, C. (2018). Petroleum Industry Activities and Human Health. In Prince E.  
230 Ndimele of *The Political Ecology of Oil and Gas Activities in the Nigerian Aquatic*  
231 *Ecosystem* Pages 143-147 <https://doi.org/10.1016/B978-0-12-809399-3.00010-0>
- 232 Ekpo, B. O., Oyo-Ita, O. E., Oros, D. R. and Simoneit, B. R. T., (2012). Distribution and  
233 sources of Polycyclic aromatic hydrocarbons in surface sediments from Cross River  
234 estuary S. E. Niger Delta. *Environmental Monitoring and Assessment, 184* (2):1037–  
235 1047
- 236 EPC (Environmental Pollution Centers) (May, 2010). Oil Spill Pollution.  
237 <https://www.environmentalpollutioncenters.org/oil-spill/>
- 238 Ezeonu, C. S., Onwurah, I. N. E. and Oje, O. A., (2012). Comprehensive Perspectives in  
239 Bioremediation of Crude Oil Contaminated Environments. Edited by Dr. Laura Romero-  
240 Zerón, *Introduction to Enhanced Oil Recovery (EOR) Processes and Bioremediation of*  
241 *Oil-Contaminated Sites*. Chapter 6:143-184. ISBN 978-953-51-0629-6
- 242 Forstner, U. and Wittman, G. T. W., (1981). Metal Pollution in the Aquatic Environment.  
243 Springer-Verlag, Berlin, Germany, ISBN-13: 9783642693854, Pages: 488.
- 244 IITA (2001). International Institute of Tropical Agriculture, Ibadan, Oyo State. Annual Report  
245 on Maize Production.
- 246 Iwegbue, C. M. A., William, E. S. and Nwajei, G. E. (2008). Characteristic levels of total  
247 petroleum hydrocarbon in soil profiles of mechanic waste dumps. *International Journal*  
248 *of Soil Science, 3*: 48–51.
- 249 Kingston, P., (2002). Long-term environmental impact of oil spills. *Spill Science & Technology*  
250 *Bulletin, 7*: 53-61.

- 251 Michel, J. and Fingas, M., (2016). Oil Spills: Causes, Consequences, Prevention, and  
252 Countermeasures. In book: *Fossil Fuels*, Chapter 7: 159-201. Researchgate. DOI  
253 10.1142/9789814699983\_0007
- 254 Murphy, C. B., (1981). "Bioaccumulation and toxicity of heavy metals and related trace  
255 elements. *Research Journal of the Water Pollution Control Federation*, 53, (6): 993–999
- 256 Osuji, L. C. and Adesiyan, S. O., (2005). The Isiokpo Oil-Pipeline Leakage: Total Organic  
257 Carbon/Organic Matter Contents of Affected Soils. *Chemistry & Biodiversity* 2: 1079-  
258 1085.
- 259 Sojinu, O. S. S., Wang, J. Z., Sonibare, O. O. and Zeng, E. Y., (2010). Polycyclic aromatic  
260 hydrocarbons in sediments and soils from oil exploration areas of the Niger Delta,  
261 Nigeria. *Journal for Hazardous Materials*, 174, (1-3):641-647
- 262 Umoren, I. U. and Udousoro, I. I., (2009). Fractionation of Cd, Cr, Pb and Ni in roadside soils  
263 of Uyo, Niger Delta Region, Nigeria using the optimized BCR sequential  
264 extraction technique. *Environmentalist*. 29 (3): 280 – 286.  
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