Original Research Article

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

Abstract

The 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 from plot A (PA), five samples from plot B (PB) and three samples from plot C (PC) which acted as control situated about 200m away from the spill impacted area and 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.

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

Introduction

Oil production has continued to play a dominant role 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 accidental spills, third party interference (sabotage) and spills from ruptured oil pipelines. Today the international oil and gas-pipelines span several

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

42 Contamination of soil by oil spills is a wide spread environmental problem that often requires
43 cleaning up of the contaminated sites, which calls for an effective technological solution. Many
44 affected sites around the world remain contaminated, because it is expensive to clean them up by
45 available technologies (Ezeonu et *al.*, 2012). Human activities have led to the release of liquid
46 petroleum hydrocarbon (also known as crude oil) into the environment, causing the pollution of
47 marine/coastal waters, shorelines and land as well. Liquid petroleum hydrocarbons are a
48 naturally-occurring fossil fuel, formed from dead organic materials in the earth's crust (Kingston,
49 2002). These petroleum hydrocarbons adversely affect the germination and growth of plants in
50 soils (Agbogidi et *al.*, 2007). Oil spills affect plants by creating conditions which make essential
51 nutrients like nitrogen and oxygen needed for plant growth unavailable to them (Adam and
52 Duncan, 2002). Oil spill on the land may penetrate underground and move downward reaching
53 eventually groundwater. However, such vertical movement may be slowed done if not prevented
54 by the presence of paved surfaces, natural clay layers or other natural or anthropogenic barriers.
55 Oil may also move laterally along less permeable layers (including surface pavements) or with
56 groundwater and surface waters. (EPC, 2010).

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

65 Maize is a multipurpose crop because every part of its plant has economic value. The seed, cob,
66 tassel, leaves and stalk can be used to produce a huge variety of food and non-food product
67 (IITA, 2001). Maize seed is a major source of food. It can be eaten roasted, cooked and its flour
68 form is used in many food products. Maize is ubiquitously planted in the Niger Delta region of
69 Nigeria both for subsistent and commercial purpose. Accumulation of heavy metals in soil due to
70 crude oil spillage in the Niger Delta has been well reported in literature (Osuji and Adesiyan,
71 2005; Adami et *al.*, 2007; Iwegbue et *al.*, 2008; Akporido and Ipeaiyeda, 2014; Umoren. and
72 Udousoro, (2009). Adeniyi and Owoade, 2010; Sojinu et *al.,* 2010; Ekpo et *al.*, 2012; Nwaichi
73 et *al*, 2016) thus this study asssesed and modelled the accumulation of heavy metals in the seeds
74 maize planted in a crude oil contaminated soil.

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76 **Materials and Methods**

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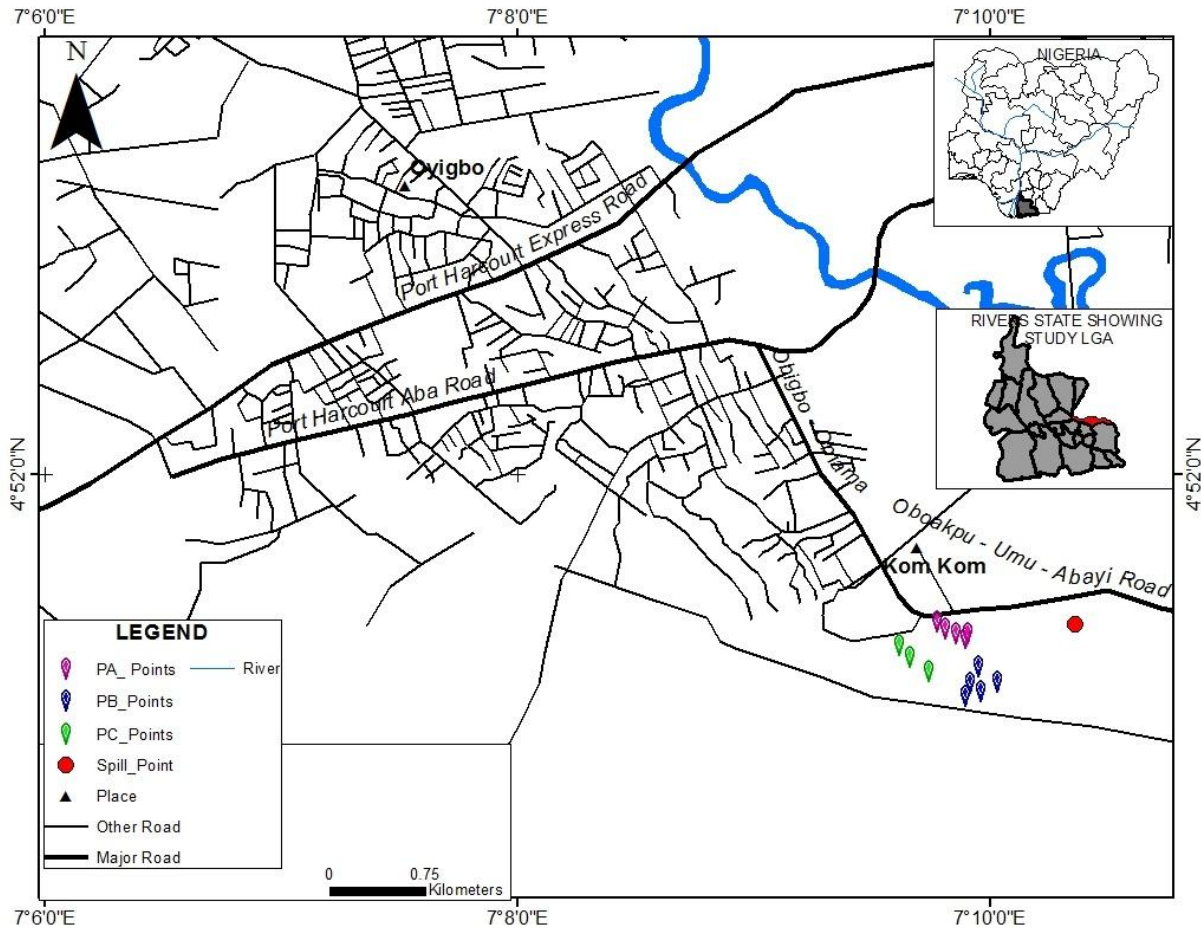
Figure 1: Map of Study Area showing the spill point and sampling plots

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

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

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

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

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

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

Data Analysis

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

Seed Accumulation Factor

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

$$SAF = \frac{C_{seed}}{C_{soil}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 1$$

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

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

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

$$Y_i = \beta_o + \beta_1 x_{1i} + \beta_2 x_{2i} + \cdots + \beta_k k_i + \varepsilon_i \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (2)$$

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

Results and Discussion

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

128 **Table 1: Result of Analysis for Heavy Metals in Soil and Heavy Metals in Maize Seed and the Seed**
129 **Accumulation Factor**

| Plot	TPH and Heavy metal in Soil						Heavy metal in seed					Seed accumulation factor				
	TPH	Fe	Zn	Pb	Cr	V	Fe	Zn	Pb	Cr	V	SAF (Fe)	SAF (Zn)	SAF (Pb)	SAF (Cr)	SAF (V)
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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131 TPH in the soil had mean values of 3003.65±1017.96 mg/kg, 4125.40±2408.89 mg/kg and
132 17.61±4.53 mg/kg for PA, PB and PC respectively. According to Osuji et *al*., (2004), high
133 hydrocarbon levels (3400–6800 mg/kg) affect both above-ground and subterranean flora and
134 fauna, which are essential indices in the biogeochemical cycle that affects availability of
135 plant nutrients. The soil values for Iron in PA, PB and PC had mean values of 33.52±14.74
136 mg/kg, 24.67±7.78 mg/kg and 16.01±4.59 mg/kg respectively. Zinc values in PA, PB and PC
137 had mean values of 1.45±0.52 mg/kg, 0.37±0.81 mg/kg and 0.92±0.29 mg/kg respectively. Soil
138 analysis results for Lead in PA, PB and PC had mean values of 0.134±0.02 mg/kg, 0.121±0.02
139 mg/kg and 0.022±0.01 mg/kg respectively. Chromium results had mean values for PA, PB and
140 PC as 0.362±0.06 mg/kg, 0.170±0.04 mg/kg and 0.057±0.001 mg/kg respectively. Results of soil
141 analysis for Vanadium for PA, PB and PC had mean values of 0.564±0.09 mg/kg, 0.367±0.04
142 mg/kg and 0.039±0.01 mg/kg respectively. There are residential building with subsistence farms
143 around the spill impacted area and as such could be exposed to the contamination. From the
144 observed plant (Maize) growth, TPH had an effect as the plot with the highest TPH level had no
145 seed in the harvested fruit. Aside the low plant yield, crops planted around this impacted area
146 may be harvested and eaten or sold in a local market. Zinc had relatively the highest seed
147 accumulation factor (SAF) with a mean SAF of 0.413 this was followed by Lead, Vanadium,
148 Chromium and Iron with mean SAF of 0.312, 0.186, 0.160 and 0.032 respectively. Heavy metals
149 have deleterious effects in health however are usually chronic thus accumulation of heavy metals
150 poses great risk. Lead has been reported as neurotoxic and can accumulate in the bone marrow
151 (Murphy, 1981). Lead affects membrane permeability of kidney, liver and brain cells thus
152 resulting in either reduced functioning or complete breakdown of these tissues, as lead is a
153 cumulative poison (Forstner and Wittmann, 1981). Cadmium (Cd) and mercury compete
154 with and displace in a number of Zn-containing metalloenzymes by irreversibly binding to
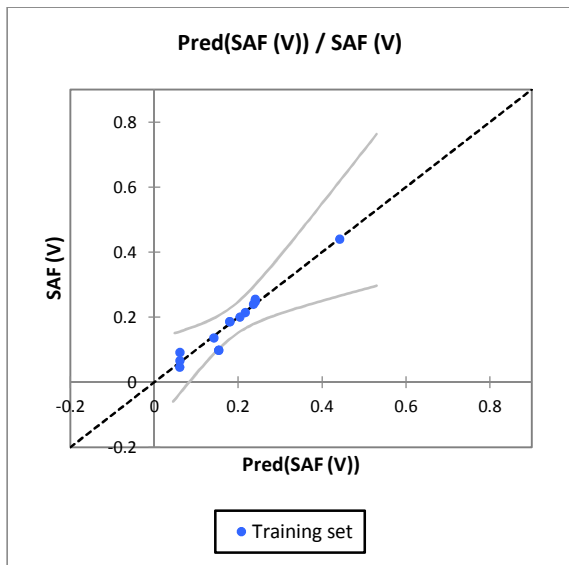155 active sites thereby destroying normal metabolism.

156 **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

157 Where Y = SAF and X_1 = TPH

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Pred(SAF (V)) / SAF (V)
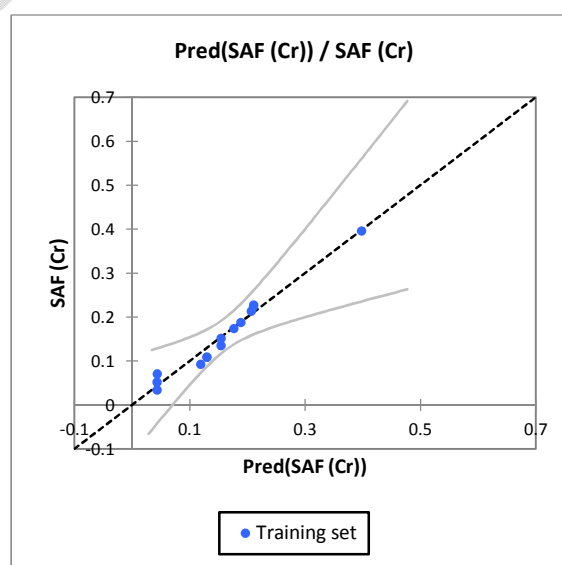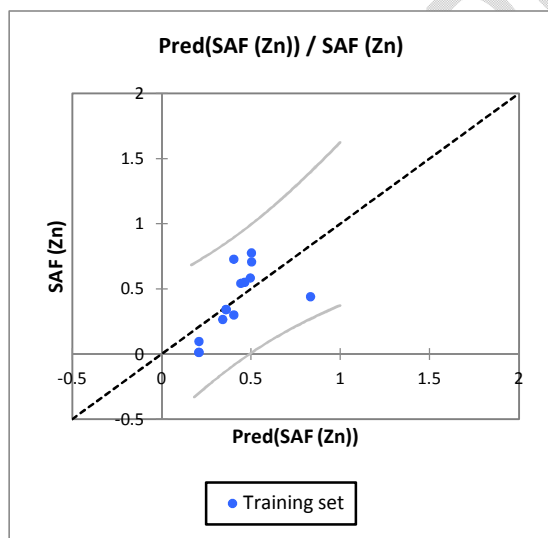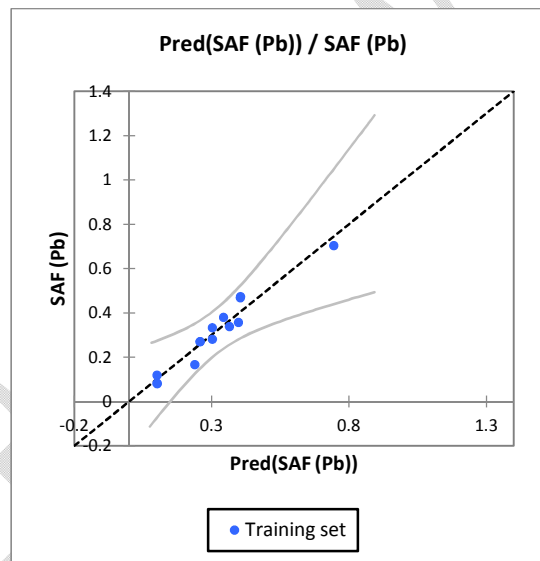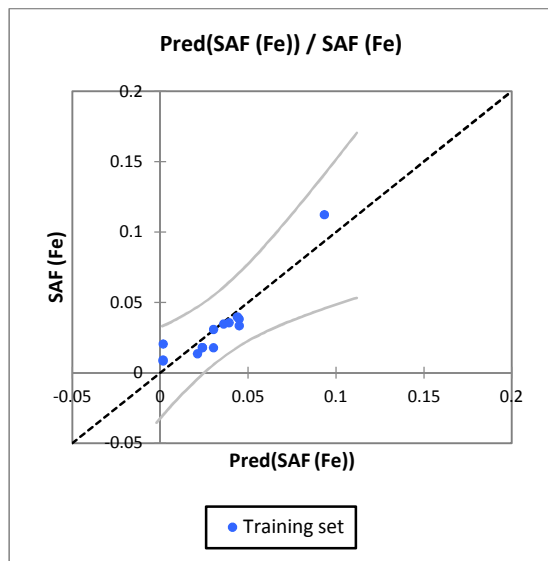
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164 **Figure 2a-e: SAF Models for the Heavy**
165 **Metals**

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The seed accumulation factors (SAF) 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 (Table 2; Figure 2a-e). The SAF as explained by the TPH level suggest that the chemical property of the soil could be responsible for the accumulation of heavy metals in the seeds of the Maize. This is complemented by the report by Aktaruzzaman *et al*., (2013) that mobility of metals from soil to plants is a function of the physical and chemical properties of the soil and is altered by several environmental and human factors. However, with the relatively high SAF value for Zinc but with relatively poor model performance suggest that Zinc accumulation in the seeds may not be influenced by TPH level.

Conclusion

Total Petroleum Hydrocarbon (TPH) was able to model the heavy metal parameters in the maize seed with relatively high model performance for the heavy metals 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. The models were all linear and as such, linear relationship exist among the maize seed parameters and the soil data before planting thus suggesting that the changes in the oil contaminants are not changing abruptly or in a nonlinear fashion.

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