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Accumulation of Heavy Metals in the Seeds of *Zea mays* L. from Crude Oil Impacted Soils in Kom-Kom, Rivers State, Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. Author IMO wrote the first draft of the manuscript. Authors LCO and EON designed the study. All authors read and approved the final manuscript.

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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 200 m 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 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 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.

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Keywords: Seed Accumulation Factor (SAF); regression model; Total Petroleum Hydrocarbon (TPH); heavy metals; zinc; contamination; soil; Kom-Kom.

1. 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 [1]. 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 span several million kilometres and this is growing yearly due to inter-regional trade in petroleum products [2]. Pipelines usually have a life span and are subject to ''tear and wear'', thus can fail with time [3]. Spilled petroleum hydrocarbons in the environment are usually drawn into the soil due to gravity until an impervious horizon is met, for example bedrock, watertight clay or an aquifer [4].

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

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

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

2. MATERIALS AND METHODS

2.1 Study Area

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 (*Zea mays*),cassava (*Manihot esculenta*)and native pear (ube) (*Dacryodes edulis*).

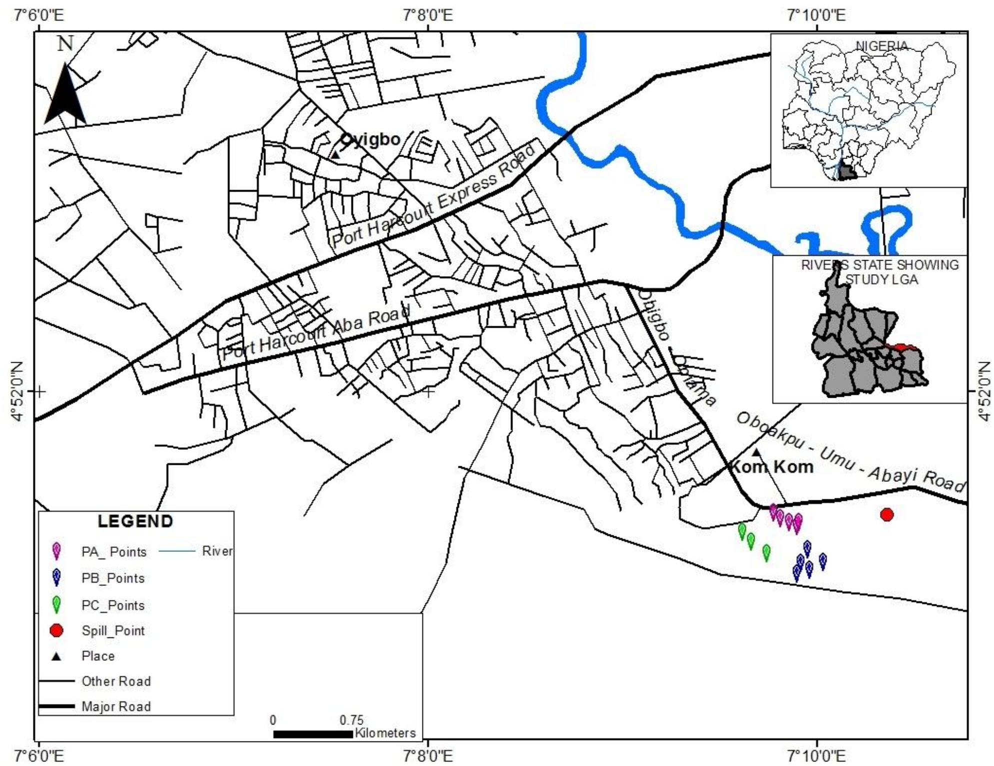

Fig. 1. Map of study area showing the spill point and sampling plots

2.2 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 200 m away from the spill impacted area. At each spot in a plot, the sample was collected using hand auger at 0-15 cm and 15-30 cm depth then bulked to form a composite sample. All soil samples were taken immediately to the laboratory for analysis.

2.3 Laboratory Analysis

Laboratory analyses were done in line with the United States Environmental Protection Agency (USEPA) analytical protocol. Parameters analyzed wereTotal 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.

2.4 Maize Produce Collection

Zea mays L. (Maize)seeds were 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 [18].

2.5 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 20 ml 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 100 ml standard flask. Then made up to mark and the content transferred into 100 ml plastic container. Each metal was run using an AAS calibrated daily with specific metallic standard [18].

2.6 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 analyses.

2.7 Seed Accumulation Factor

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

$$SAF = \frac{C_{seed}}{C_{soil}} \quad (1)$$

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

$C_{soil}$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 Equation 2.

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

Where, β is coefficient of regression, β_0 is the intercept, x are the independent variable, k is number of independent variable andi ranges from 1 to n where n is number of observations.

3. 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 [15]. 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.

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

The seed accumulation factors (SAFs) 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.,[16] (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.

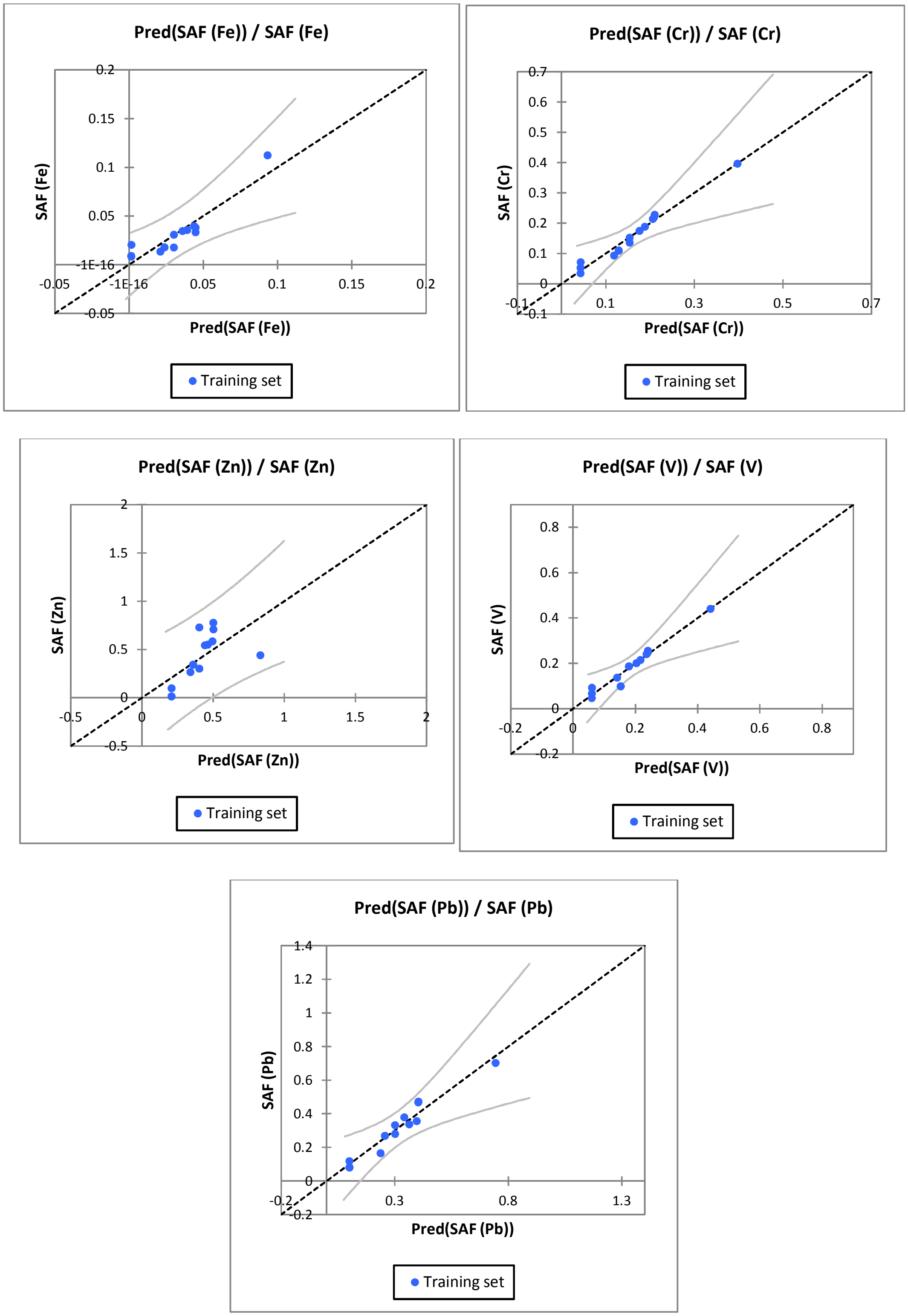

Fig. 2a-e. SAF Models for the heavy metals

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 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

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

Where Y = SAF and X_1 = TPH

4. 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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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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