

Assessment of Lead (Pb) in Soil at Various Distances and Depths at Pb and Zn Mining Site in Ishiagu, Ebonyi State, Nigeria

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ABSTRACT

Pb in soil at various distance and depths was assessed at Pb and Zn mining site in Ishiagu Ebonyi State, Nigeria to determine the furthest distance travelled so far and the concentration at the distance. Pb ion in sampled soils at depth 0-10, 10-20, 20-30, 30-40 and 40-50 cm within pollution zones in 1 km x 1 km area of 100 m grid intervals were fitted with mathematical models for prediction using MATLAB. Pb ion change with distance was fitted into power model and linear polynomial models at distinct grid points. The models predictions showed decrease in Pb ion with distance. It revealed that the ion had travelled far into the soil with a furthest distance of 4760 cm but with no soil pollution signal because 64.54 mg/kg (concentration at 4760 cm) is less than 100 mg/kg specified as the maximum for soils. It showed a signal that the metal might threaten the ground water at some future date with an objectionable concentration above 0.01 mg/l specified for drinking water. Concentration at some intermediate distances is risk signal of food pollution through absorption of the metal by crops with root morphology and depth reaching these intermediate depths of objectionable concentration.

Keywords: Soils, Lead, Pollution Threat, Prediction

1.0. Introduction

Man, through transportation (Ogbonna and Okezie, 2011), solid waste (Ogbonna and Okeke, 2011), pesticides application (Ogbonna *et al.*, 2013), coal mining (Ogbonna *et al.*, 2018a), timber exploration (Ogbonna *et al.*, 2018b) and quarrying (Ogbonna *et al.*, 2020) have laden the environment with heavy metals (HMs). HMs are of sources of worry to man since they affect agricultural land and grown plants to contamination level and consequently impact negatively on fauna (including man) feeding on the grown crops (Kachenko and Singh, 2006; Tasrina *et al.*, 2015; Atikpo, 2016). This is because HMs do not biodegrade easily (Heidariehet *et al.*, 2013) and can be uptake by plants from soil (Ogbonna *et al.*, 2020). Some HMs are useful to plant at requisite concentrations but some like cadmium (Cd), mercury (Hg) and lead (Pb) are not of nutritional significance to fauna and flora (Fosmire, 1990; Ogbonna *et al.*, 2012).

Mining, a practice of immense economic significance is also simultaneously connected with reduction in environmental quality (Ogbonna *et al.*, 2012). Anthropogenic releases of HMs are of consequential damages to ecosystems near sources (Ogbonna and Okezie, 2011). Soil is a part of significant resources of ecology, environment and agriculture that needs protection from more quality reduction to make it adequately suitable for healthy food supply to meet the need of world's soaring population (Rashad and Shalaby, 2007; Ogbonna and Okezie, 2011). Consequently, environmental monitoring of HMs of anthropogenic input is an option of reducing soil pollution and associated food, water, and human contamination. For instance, Sweden initiated the application of sewage guideline to regulate HMs loads in soils, and other Scandinavian nations have embraced the policy to prevent high metals load in soil (Witter, 1996). Characterization and treatment are required for effective HMs contaminated soil ecosystem protection and restoration. Characterization furnishes speciation and bioavailability knowledge while remediation requires health risks, chemistry, contamination source

and environmental risk information (Wuana and Okieimen, 2011). These are necessary because of the toxicity of HMs, their potential health effect, bioaccumulation and bio-magnification in food chains (Ogbonna and Okezie, 2011).

Pb is among the pollutants of global recognition and concern (Ahamed and Siddiqui, 2007a; Ahamed and Siddiqui, 2007b). Pb is of high degree toxicity; and effects prolonged health problems even when its concentration is very low (Begum *et al.*, 2009; Daboor, 2014). Its intake or exposure could retard children mentally and substitute bone calcium (Adelekan and Abegunde, 2011; Badawy *et al.*, 2013); cause renal diseases (Fischbein, 1992); reduce hemoglobin synthesis and cause kidney problems (Okoronkwo, 2005). Exposure to high Pb amount has led to animals poisoning, incapacitation, and death (McDowell, 2003; Burki, 2012). Exposure to Pb is known to cause impaired cognitive functions, neuromuscular weakness, behavioral abnormalities, and hearing deficits in humans and animals used for experiments (Flora *et al.*, 2012). Seminal plasma Pb had a positive correlation with spermatozoa ROS level in a male reproductive system studied epidemiologically (Kiziler *et al.*, 2007). Pb acetate was reported by Elgawish and Abdelrazek (2014) to cause notable decrease in performance of reproductive organs in males; and change of testicular tissue. Pb poisoning of acute and chronic nature can induce hypertension, cause nephropathy disease, unwanted lead content in blood; and cardiovascular disease (Goyer, 1993; Ekong *et al.*, 2006; Navas-Acien *et al.*, 2007); and exposure to low Pb level may lead to hypertension in animals (including humans) (ATSDR, 2005).

Risk assessment furnishes decision makers an effective tool to handle contaminated sites to preserve the health of public and ecosystem in a manner that involves minimum cost (Zhao and Kaluarachchi, 2002). This, therefore, necessitated the investigation of Pb in agro soil at various distance and depths at Amaonye-Ishiagu, Ebonyi State, Nigeria. The results of this study will help to enlighten the people of Amaonye Community on the risk(s) associated with making use of the contaminated soil for agricultural purposes.

2.0. Methodology

2.1. Study area

The study location in Figure 1 falls between N5° 55'; N6° 00' and E7° 35'; E7° 35' (Atikpo, 2016). It has a low relief and undulated topography with dark shales and mudstones geology. The geologic colour is credited to sulphides and matter of organic nature formed in basins of stagnant marine (Ezepue, 1984). Lense of limestone and sandstone are also characteristic of the geology of calcareous and pyritic shales (Ezepue, 1984). The dominance by galena and sphalerite in Pb-Zn veins (Ezepue, 1984) created a huge galena market in the community (Atikpo, 2016). Availability of the stated minerals had midwived the activities of miners and consequent pollution menace in the community (Ezeh and Chukwu, 2011; Atikpo, 2016; Atikpo and Ihimekpen, 2018).

2.2. Materials

Perchloric acid, conical flasks, hot plate, nitric acid, atomic absorption spectrophotometer (AAS), sulphuric acid, machetes, volumetric flask, filter paper and augers.

2.3. Methods

2.3.1 Sampling

Samples of soils were abstracted from grids at depths 0 - 10, 10 - 20, 20 - 30, 30 - 40 and 40 - 50 cm (Figure 2) from the forest portion of (1km x 1km) and 100 m grid interval. Each sample was wrapped with nylon bag to prevent intrusion of external contaminant. The samples were kept in a cooler with ice blocks; and transported to laboratory at street 8, No. 5, Estate of Bendel, Ugborikoko, Warri, Nigeria for digestion using the method in (Atikpo, 2016; Atikpo and Ihimekpen, 2018); and analysis of lead ion in triplicates with AAS.

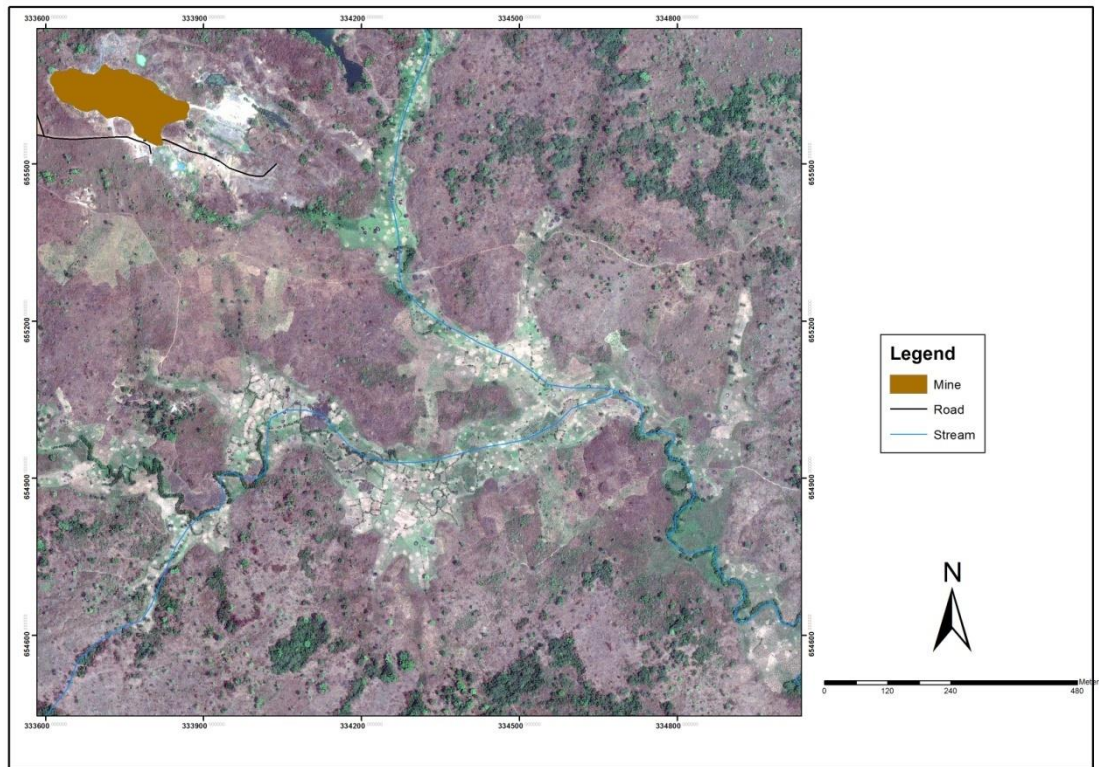


Figure 1: Image map of study area

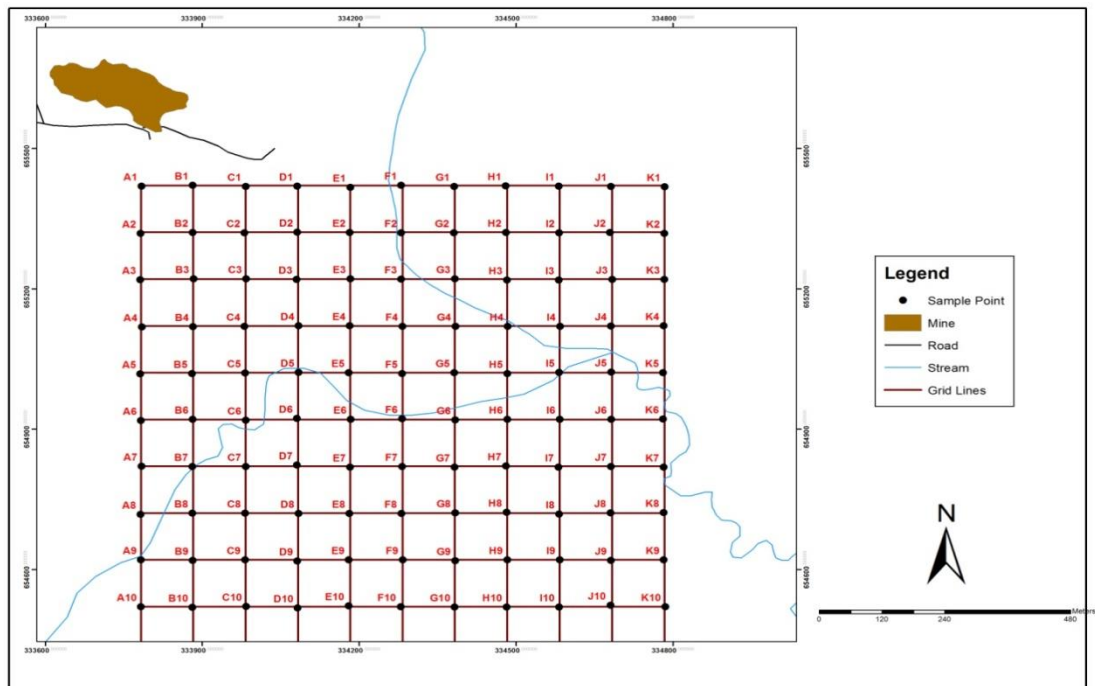


Figure 2: Points of sample collection

2.3.2 Soil digestion, Pb analysis and modelling

Following the approach in Atikpo (2016) and Atikpo and Ihimekpen (2018); 40 ml digestion solution (ratio1:2:2) from HNO_3 , HClO_4 and H_2SO_4 was combined with 2g, 2 mm dried soil in 250 ml flask and heated for 20 min and cooled, and mixed with water (20 ml) to effect further cooling prior filtration into a flask of 100 ml capacity and dilution to 100 ml mark. The overall solution was analyzed for Pb content with AAS (GBC SensAA Model no. A6358) (Atikpo and Micheal, 2018; Atikpo *et al.*, 2019; Ihimekpen *et al.*, 2020; Atikpo and Eboibi, 2020).

The ionic data of Pb was fitted into various models using the curve fitting tools of MATLAB to establish the descriptive models to determine the ionic change with distance down the soils layers in

the form of concentration, $f(x)$ versus vertical distance (x); and relying on some goodness of fit parameters as R^2 (coefficient of determination); SSE (sum of error square); RMSE (root-mean-square error); and trend of data at 95% confidence limit to establish the models reliabilities before use for predicting the lead ion change with distance down the soils layers beyond the maximum of 50 cm depth of sampling.

3.0. Results and Discussions

Field data collected at depth of 10 cm to 50 cm in the interval of 10 cm within the zone of highest pollution was fitted with mathematical models. The ionic data change with distance fits into power model at grid point (GP) H6 and linear polynomial at GPF3, GPD4, GPD7, GPE4, GPG7, GPG10, GPI8, GPJ7 and GPJ10.

Figures 3 and 4 are displays of models fitted for ionic change study at GH6 and GJ10 with the values of SSE (1.697); RMSE (0.7521); and R^2 (0.946) at GPH6 and SSE (19.25); RMSE (2.533); and R^2 (0.962) at GPJ10. These parameters and the data curves locations relative to the upper and lower bounds, and the curves trends at 95% confidence bound in Figures 5 and 6 justified prediction reliability of the models for prediction of the metal concentration beyond the highest depth of 50 cm in Tables 1 and 2. Information on the prediction reliabilities of models generated at other data study points are summarized in Table 3.

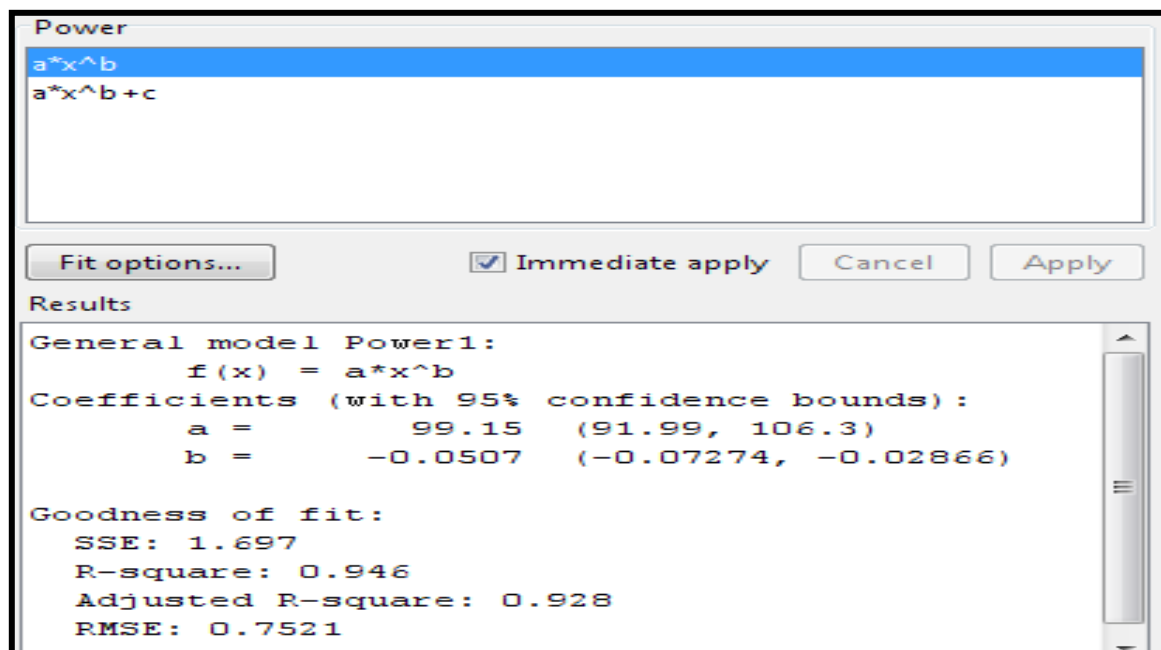


Figure 3: Fitted function at GPH6

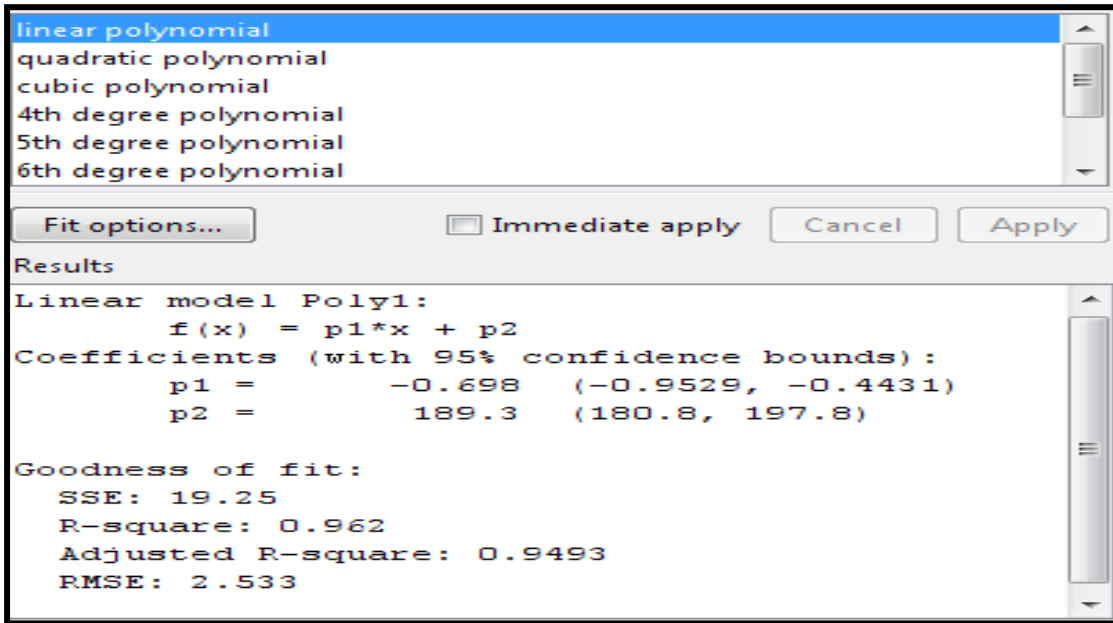


Figure 4: Fitted function at GPJ10

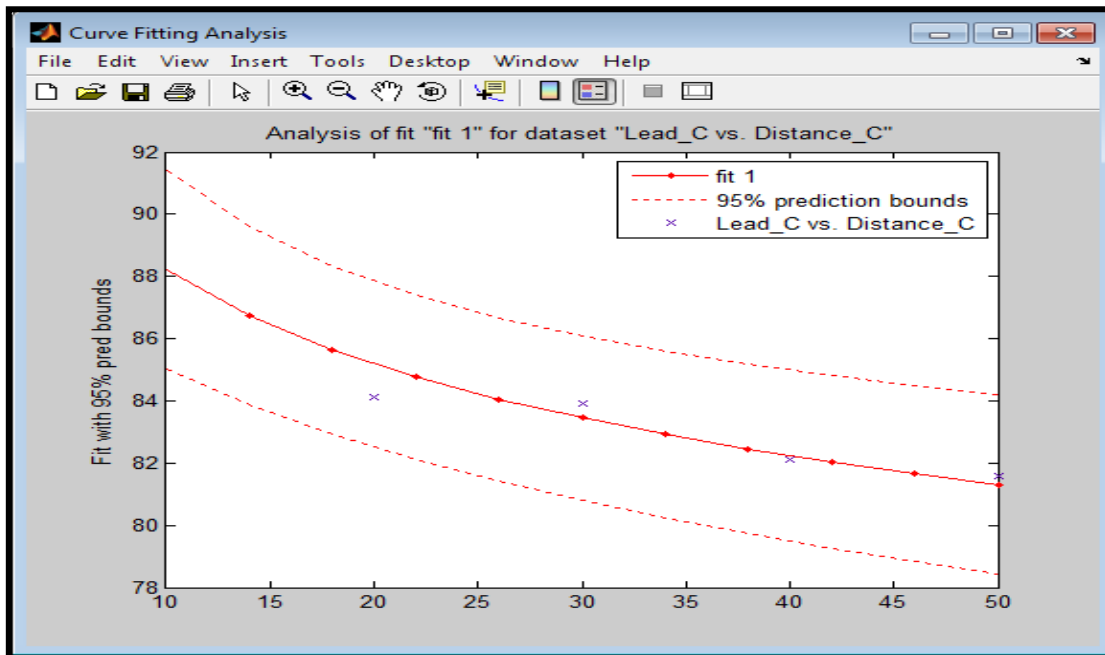


Figure 5: Bounds of Prediction at GPH6

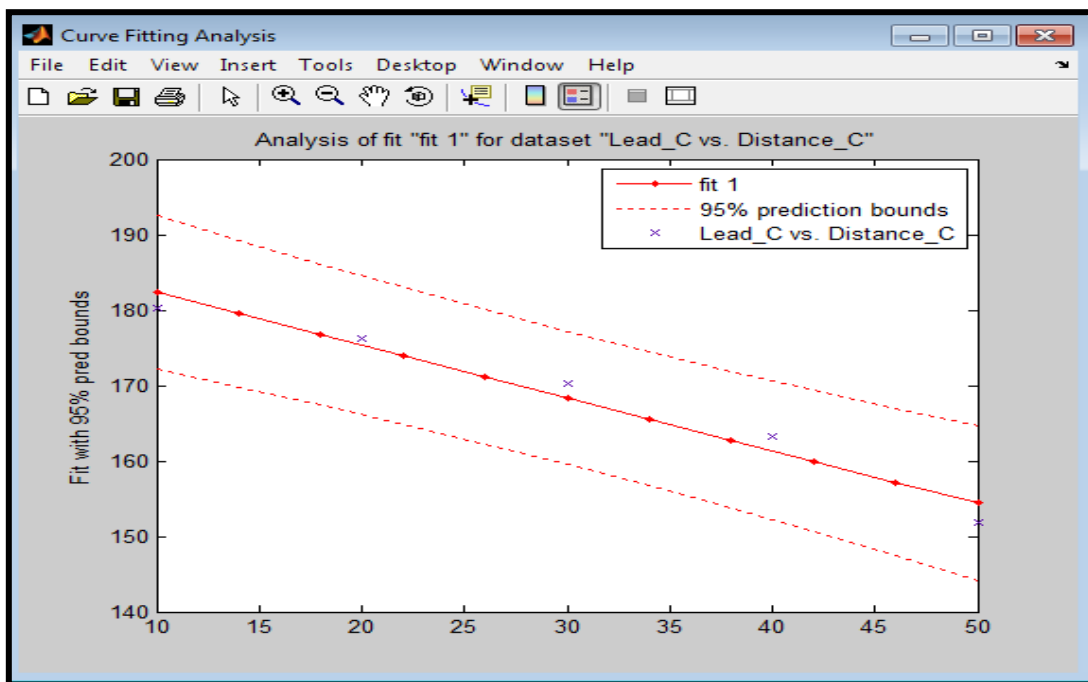


Figure 6: Bounds of Prediction at GPJ10

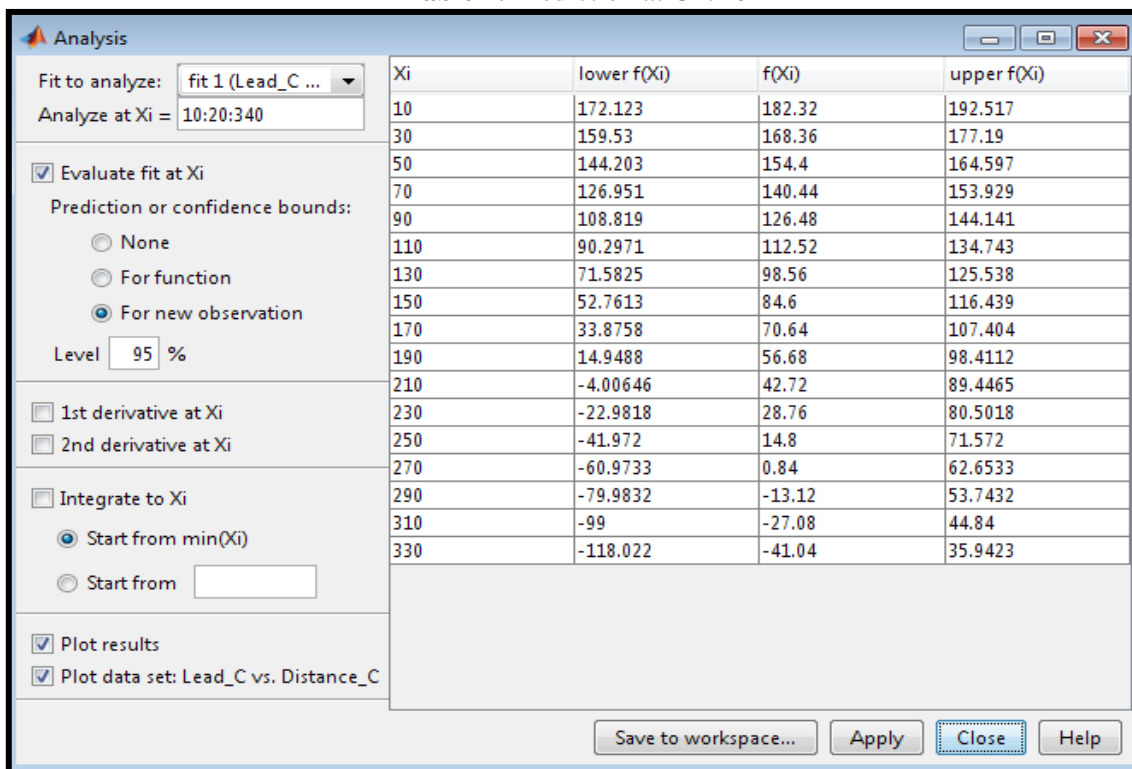
The generated models used as tools predicted ionic movement at depths greater than 50 cm of sampling. The ionic concentration and depths were 107.06 mg/kg and 70 cm at GPF3, 101.2 mg/kg and 60 cm at GPD4, 106.58 mg/kg and 60 cm at GPG7, 102.09 mg/kg and 59 cm at GPG10, 103.46 mg/kg and 85 cm at GPI8, 100.66 mg/kg and 80 cm at GPJ7; and 112.52 mg/kg and 110 cm at GPJ10. These are partly shown in Tables 1 and 2; and summarily in Table 3.

Table 1: Prediction at GPH6

The screenshot shows the "Analysis" dialog box with the following settings: "Fit to analyze: fit 1 (Lead_C ...)", "Analyze at Xi = 10:250:5000", "Evaluate fit at Xi" checked, "Prediction or confidence bounds: For new observation" selected, "Level: 95%", "1st derivative at Xi" unchecked, "2nd derivative at Xi" unchecked, "Integrate to Xi" unchecked, "Start from min(Xi)" selected, "Plot results" checked, and "Plot data set: Lead_C vs. Distance_C" checked. The table below contains the predicted values.

Xi	lower f(Xi)	f(Xi)	upper f(Xi)
10	85.0289	88.2257	91.4225
260	70.1615	74.7913	79.4211
510	66.8454	72.2795	77.7137
760	64.9314	70.8323	76.7333
1010	63.5915	69.8183	76.0451
1260	62.5642	69.0397	75.5153
1510	61.7331	68.409	75.085
1760	61.0366	67.8797	74.7229
2010	60.4378	67.4241	74.4104
2260	59.9133	67.0245	74.1358
2510	59.447	66.6689	73.8908
2760	59.0276	66.3487	73.6698
3010	58.6468	66.0577	73.4686
3260	58.2981	65.791	73.2838
3510	57.9768	65.545	73.1132
3760	57.6789	65.3167	72.9545
4010	57.4013	65.1039	72.8064
4260	57.1416	64.9045	72.6675
4510	56.8975	64.7171	72.5368
4760	56.6675	64.5403	72.4132

Table 2: Prediction at GPJ10



The model prediction results showed a decrease in Pb ion with distance. It revealed that the ion had travelled far into the soil with a furthest distance of 4760 cm at GPH6. However, at this distance of 4760 cm, the ionic concentration of 64.54 mg/kg was less than the maximum allowable of 100 mg/kg stipulated in standards contained in (Chiroma *et al.*, 2014). But this concentration value (64.54 mg/kg) at the distance (4760 cm) to which it had travelled at GPH6 is a signal that the metal might reach the ground water at some future date with an objectionable concentration above 0.01 mg/l specified for drinking water by (SON, 2007). Pollution level at some intermediate distances of 70 cm at GPF3, 60 cm at GPD4, 60 cm at GPG7, 59 cm at GPG1, 85 cm at GPI8, 80 cm at GPJ7, and 110 cm at GPJ10 with respective intermediate distance concentration levels of 107.06, 101.2, 106.58, 102.09, 103.46, 100.66 and 112.52 mg/kg are risk signals of food pollution through absorption of Pb by crops with root morphology and depth reaching this intermediate depths of soil pollution since one of the ways metals threatens lives is through food chain (Wong and Salvam, 2006; Ogabiela *et al.*, 2010; Singh and Kalamdhad, 2011).

Table 3: Models’ parameters and prediction summaries

Selected Grids within High Pollution Zone	Prediction Model	R ²	RMSE	SSE	Furthest Depth of Pollution Occurrence (FP) (cm)	Concentration (mg/kg) at FD	Furthest Depth of Pb Availability (FA) (cm)	Concentration (mg/kg) at FA	Depth at Which Pb was Absent (cm)
GPF3	LP	0.9949	0.9852	2.912	70	107.06	210	1.5	220
GPD4	LP	0.8959	4.394	57.91	60	101.2	200	2.36	210
GPD7	LP	0.9527	0.5453	0.892	-	-	660	0.46	710
GPE4	LP	0.7528	19.87	1184	35	104.43	85	9.48	90
GPG7	LP	0.9384	4.857	70.76	60	106.58	160	2.78	170
GPG10	LP	0.9952	1.935	11.24	59	102.09	122	5.82	129
GPH6	P	0.946	0.7521	1.697	-	-	4760	64.54	4760
GPI8	LP	0.9748	1.725	8.923	85	103.46	250	6.6	265
GPJ7	LP	0.9619	3.496	36.67	80	100.66	180	4.46	190
GPJ10	LP	0.962	2.533	19.25	110	112.52	270	0.84	290

*LP connotes linear polynomial, P connotes power.

4.0. Conclusions

This work is on lead movement in Amanye agro soils in Ebonyi State. Lead ion in soils at depth 0-10, 10-20, 20-30, 30-40 and 40-50 cm within pollution zones in 1 km x km area of 100 m grid intervals were fitted into mathematical models and used for prediction with the aid of MATLAB. The ionic field data change with distance fitted into power model at GPH6 and linear polynomial at other grid points.

The model prediction showed a decrease in Pb ion with distance. It revealed that the ion had travelled far into the soil, with a furthest distance of 4760 cm but with no soil pollution signal at 64.54 mg/kg less than 100 mg/kg specified as the maximum for soils. It showed a signal that the metal might reach the ground water at some future date with an objectionable concentration above 0.01 mg/l specified for drinking water. Concentration at some intermediate distances is risk signal of food pollution through absorption of the metal by crops with root morphology and depth reaching these intermediate depths of objectionable concentration.

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