MODELING AND VERTICAL PREDICTIONS OF HEAVY METALS CONCENTRATIONS IN AMAONYE FOREST IN ISHIAGU OF EBONYI STATE IN NIGERIA

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Abstract:

This study centers on the modeling and vertical prediction of heavy metals such as lead (Pb), cadmium (Cd), zinc (Zn) and arsenic (As) in the polluted forest soil of Amaonye community of Ishiagu clan of Ebonyi State in Nigerias. Systematic soil sampling was carried out in the field. Soil samples were collected with the aid of depth calibrated urgers, at the depths of 10cm, 20cm, 30cm, 40cm and 50cm. Each sample was immediately placed in a fresh plastic bag and tightly sealed and then kept in a cooler containing ice cubes. The samples were transported to the laboratories for heavy metals analysis using Atomic Absorption Spectrophotometer (**GBC SensAA** Model no.**A6358**) to determine the baseline data. Using the baseline data, the vertical downward concentrations of the metals within some selected points F3, D4, D7, E4, G7, G10, H6, I8, J7 and J10 within the zone of high concentration were modeled and predicted using curve fitting tool from MATLAB. The curve fitting with MATLAB showed the best fitted models to be linear and quadratic polynomials, power function and cubic polynomial. The model prediction at 95% confidence bounds revealed the deepest downward vertical distance travelled to be 4760cm by lead at point H6, 460cm by cadmium at point D7, 960cm by zinc at I8 and 370cm by arsenic at D7. The respective concentrations of these metals at these depths are 64.54mg/kg, 0.72mg/kg, 5.12mg/kg and 0.46mg/kg. At these furthest distances, none of these metals was found to be above the maximum allowable limit. At some intermediate distances of 435cm, 610cm and 250cm, the respective concentration were of 3.97 mg/kg for Cd, 346.72 mg/kg for Zn and 20.26 mg/kg for As and were found to be above the maximum allowable limits. This information is vital in determining the extent to which deep rooted crops can come in contact with these metals, and how safe is the ground water is from metals contamination.

Keywords: Modeling, Models, Prediction, Goodness of fit, Lead, Cadmium, Arsenic and Zinc.

Introduction

Soil has complex functions which are beneficial to man and other living organisms (Atar and Vohora, 2006). Though its volume and mass are very small, in comparison to the lithosphere, it is of vast importance to man (Narayanan, 2007).

Narayanan (2007) pointed out that the soil fulfills a wide range of inter-related functions such as forming a crucial link the atmosphere, geology, water resources and use; acts as a reservoir of carbon, which is a key factor in determining concentrations of green house gases; regulates the flow of water from rainfall to water bodies, aquifers, vegetation and the atmosphere; acts as the medium for vegetation, crops and forests and plays a major role in determining the nature and distribution of life; and forms the basis for terrestrial ecosystems. Therefore, the sustainable use of such a versatile resource like soil implies that we minimize damage to it so that it can continue to be used and can support the widest range of functions (Narayanan, 2007).

Soil pollution deals primarily with topsoil and aquifers. Soil pollution occurs due to climatic and geological changes, human activities, and agriculture, mining and industrial operations. All those activities add considerable quantity of particulate pollutants, mineral wastes, and wide range of inorganic and organic compounds, petrochemicals and toxic substances to the soil. Mining and construction operations lead to land deteriorations. Trip mining is ecologically destructive to land surface and vegetation (Narayanan, 2007).

Heavy metal contamination of soil is a worldwide problem that affects a large number of sites (Gray et al., 2005). Soil contamination by heavy metals is increasing (Galiulin et al., 2002). Heavy metals entre agroecosystem through both natural and anthropogenic processes (Yang and Stoffella, 2005). According to Galiulin et al. (2002), the anthropogenic enrichment or contamination of the environment by heavy metals is caused by their dispersion.

Heavy metal pollution refers to cases where the quantities of these elements in soils are higher than the maximum allowable concentrations, and this is potentially harmful to biological life at such locations (Adelekan and Abegunde, 2011). At these concentrations, heavy metals are considered serious pollutants because of toxicity, persistence and non degradable conditions in the environment, thereby constituting threat to human beings and other forms of biological life (Tam and Wong, 2000; Yuan et al., 2004; Nwuche and Ugozi. 2008; Aina et al., 2009; Mohiuddin et al., 2010).

Ishiagu is an important economic (mining) community. Mining is important in the community because of Pb-Zn lodes in the area (Ezeh and Chukwu, 2011; Onyedika and Nwosu, 2008).

Like in many other places in the world, heavy metal interaction with environment occurs in Ishiagu. As reported by (Ezeh and Chukwu, 2011; Onyedika and Nwosu, 2008; Obiekezie et al., 2006; Nwaugo et al., 2008), some areas in Ishiagu are polluted with some heavy metals. This is because, the wastes resulting from their mining and use liter many places (Nwaugo et al., 2008).

Heavy metal contamination in soil

is a major concern because of their toxicity and threat to human life, the environment and ground water (Begum et al., 2009).

Due to the world wide experiences of the serious ecological consequences of soils contaminated with heavy metals, there is a need to take preventive and attenuation measures (Galiulin et al., 2002), and understanding of the sub soil distribution and vertical concentration of heavy metals in soil is an important pre requisite (Hua et al., 2012).

Materials and Methods

To obtain the baseline data for modeling and prediction of these metals in the soil, systematic soil sampling was carried out in the field. Soil samples were collected with the aid of depth calibrated urgers, at the depths of 10cm, 20cm, 30cm, 40cm and 50cm. Each sample was immediately placed in a fresh plastic bag and tightly sealed and then kept in a cooler containing ice cubes. The samples were transported to the laboratories for heavy metals analysis.

In the laboratory, three different acids were mixed in the ratio of perchloric 1, Nitric acid 2; and sulphuric acid 2 (i.e., 1:2:2). After air drying the soil samples and passing it through 2mm sieve, 2g of air dried samples were weighed into a 250ml conical flask; 40ml of digestion mixture was added. The conical flask containing the soil samples and acid were placed on a hot plate in a fume-hood and digested for 15-20 minutes until a clear solution appeared. The solution was allowed to cool and 20ml of distilled water was added and allowed to cool. The solutions were filtered using a Whatman filter paper into a 100ml volumetric flask and diluted to mark. The digested soil was then analyzed for heavy metals concentrations by using Atomic Absorption Spectrophotometer (**GBC SensAA** Model no. **A6358**) to determine the baseline data.

Using the baseline data, the vertical downward concentrations of the metals within some selected points F3, D4, D7, E4, G7, G10, H6, I8, J7 and J10 within the zone of high concentration were predicted using curve fitting tool from MATLAB.

The field data for metal concentration against the vertical distance were validated by studying the relationship between the variables f(x) (metal concentration) and x (vertical downward distance) using a best fit distribution model. To justify the suitability of the fitted model and the adequacy of the field data, some selected goodness of fit such as sum of error square (SSE), coefficient of determination (R^2), adjusted R-square (Adj R^2) and Root Mean Square Error (RMSE) were employed.

To further justify the adequacy of the data collected, a 95% confidence limit was employed to predict data using the fitted model. Graphical variation of the field data and the predicted data were obtained; and the trend patterns of the plots were used to justify the adequacy of the field data collected.

Based on validated mathematical model generated, vertical downward series predictions were carried out to ascertain the concentration of metals outside the experimental range of 10-50cm.

Results and Discussion

Cadmium (Cd) Modeling and Prediction at Grid Point D7

The vertical downward concentration of cadmium within the zone of high concentration as indicated by grid point D7 fit into a linear polynomial distribution as shown in Figure 1. The optimal values of model coefficients P1 and P2 are (-0.13) and 60.52 respectively. The high value of R^2 which is 0.9053 reveals a high correlation between cadmium concentration and vertical downward distance.

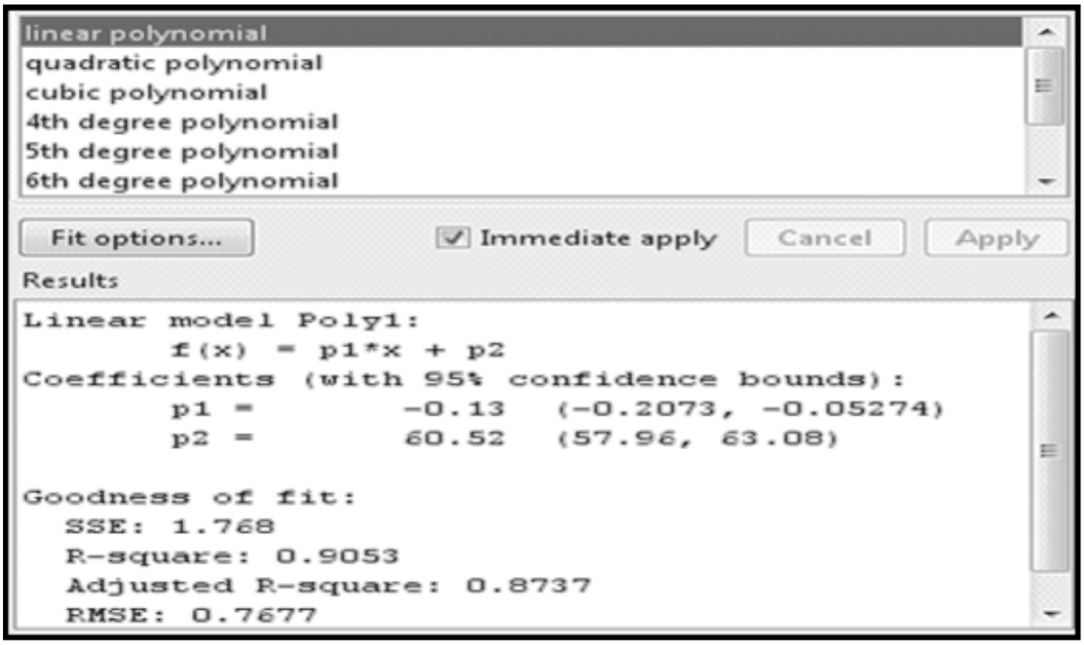

Figure 1: Fitted Function for Cardmium Concentration Against Distance at Point D7

The values of SSE=1.768, RMSE= 0.7677, R^2=0.9053 and Adj-R^2= 0.8737 justify the suitability of the fitted model and the adequacy of the field data. The location of the field data curve between the upper and the lower bounds and the curves trend pattern at 95% confidence bound further validates the model and also justify the adequacy of the field data collected as shown in Figure 2.

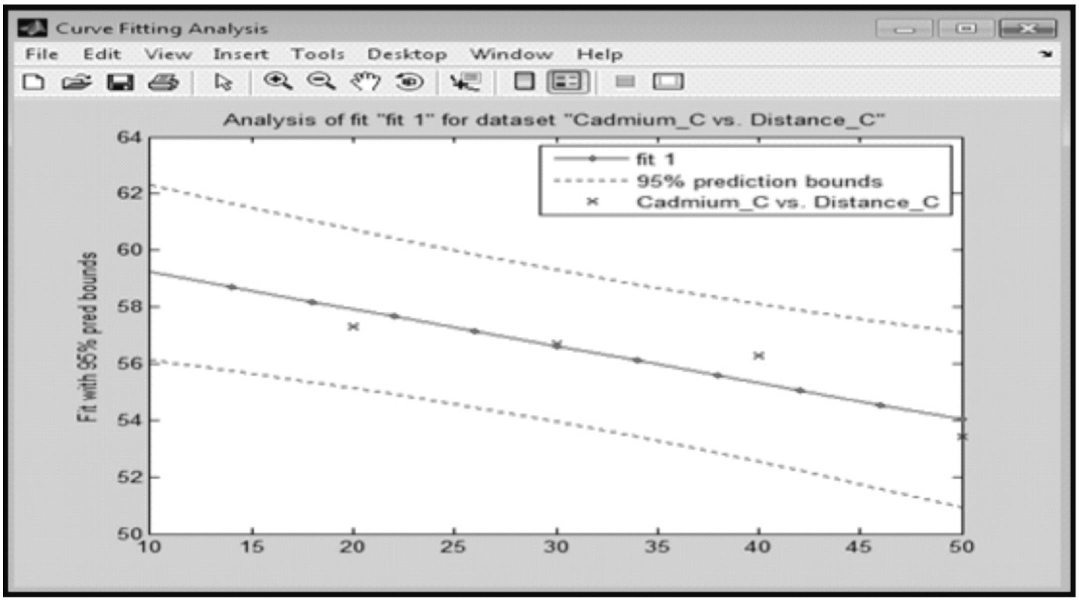

Figure 2: Prediction Bounds for Cadmium Concentration Against Distance at Point D_7

The mathematical model generated is adequate and was used in prediction. The model prediction of the vertical downward series of the concentration of cadmium outside the experimental range of 10-50cm, at 95% confidence bound and at vertical interval of 25cm is shown in Table 1.

Table 1: Downward Prediction of Cadmium Concentration at Point D7

Xi	lower f(Xi)	f(Xi)	upper f(Xi)
10	56.1297	59.22	62.3103
35	53.266	55.97	58.674
60	49.1796	52.72	56.2604
85	44.4483	49.47	54.4917
110	39.4848	46.22	52.9552
135	34.4279	42.97	51.5121
160	29.326	39.72	50.114
185	24.1996	36.47	48.7404
210	19.0584	33.22	47.3816
235	13.9076	29.97	46.0324
260	8.75033	26.72	44.6897
285	3.58834	23.47	43.3517
310	-1.57707	20.22	42.0171
335	-6.74508	16.97	40.6851
360	-11.9151	13.72	39.3551
385	-17.0867	10.47	38.0267
410	-22.2596	7.22	36.6996
435	-27.4336	3.97	35.3736
460	-32.6084	0.72	34.0484
485	-37.784	-2.53	32.724
510	-42.9601	-5.78	31.4001
535	-48.1368	-9.03	30.0768

The prediction shows that the concentration of cadmium decreases with increasing vertical distance downward up to a concentration value of 460 mg/kg at a distance of about 460cm and finally fades from the soil at a distance of about 485cm.

Arsenic (As) Modeling and Prediction at Grid Point D7

The fitted linear polynomial distribution model describing the vertical downward concentration of arsenic within the zone of high pollution as indicated by grid point D7 is shown in Figure 3. The model shows optimal values of coefficients P1 and P2 to be (-0.165) and 61.51 respectively, and R^2 value of 0.9313 which indicates a high correlation between the variables.

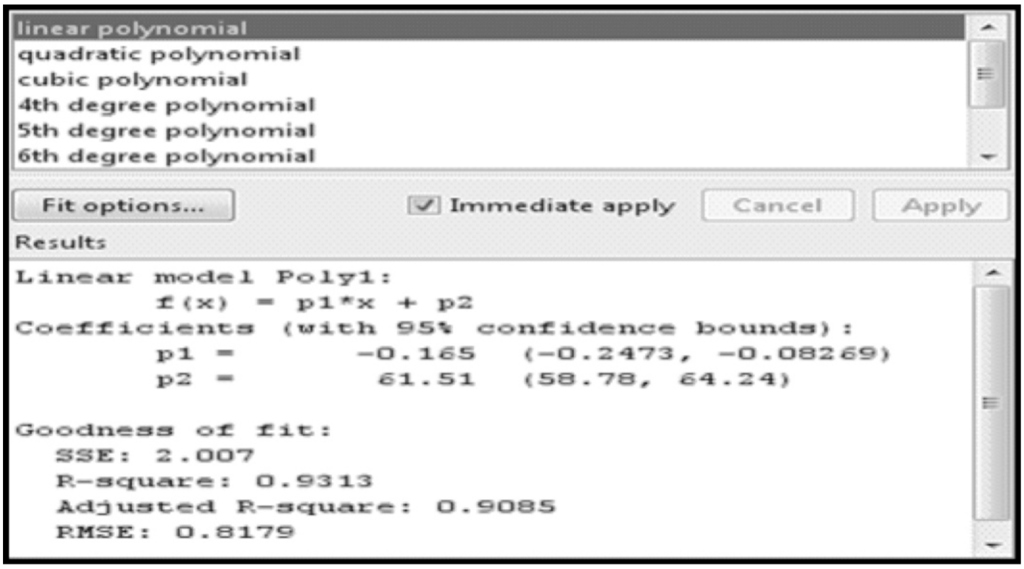

Figure 3: Fitted Function for Arsenic Concentration Against Distance at Point D7

The lower values of SSE=2.007, RMSE= 0.8179 and the high values of R^2=0.9313 and Adj-R^2= 0.9085 justify the suitability of the fitted model and the adequacy of the field data. The location of the field data curve between the upper and the lower bounds and the curves trend pattern at 95% confidence bound further validates the model and also justify the adequacy of the field data collected as shown in Figure 4.

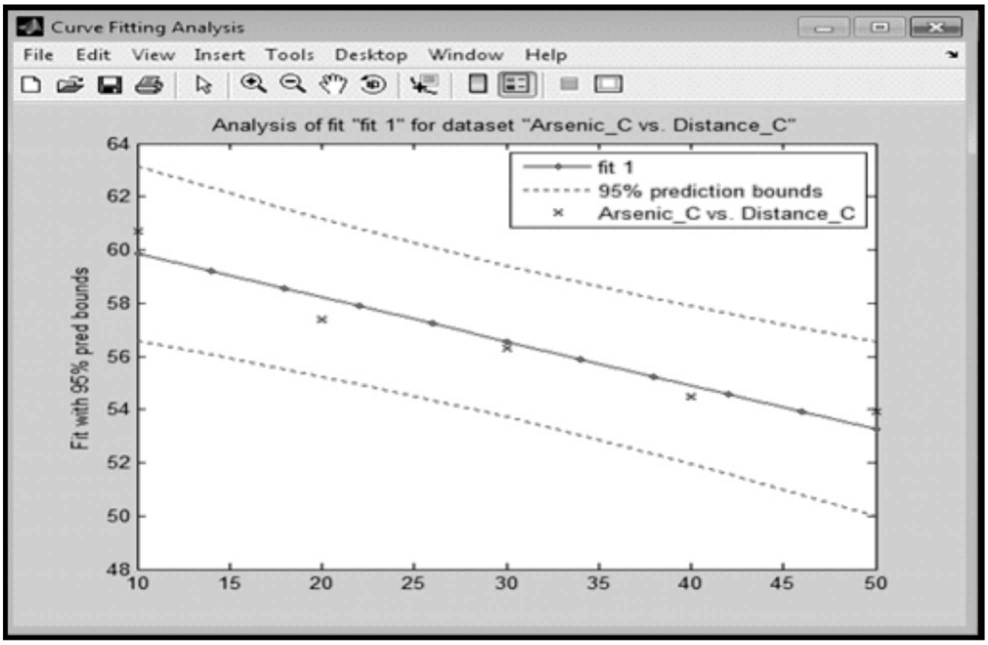

Figure 4: Prediction Bounds for Arsenic Concentration Against Distance at Point D7

The mathematical model predicted the vertical downward change in arsenic concentration outside the experimental range of 10-50cm, at 95% confidence bound and at vertical interval of 20cm as shown in Table 2.

Table 2: Downward Prediction of Arsenic Concentration at Point D7

Analysis

Fit to analyze: fit 1 (Arsenic...

Analyze at Xi = 10:20:450

Evaluate fit at Xi

Prediction or confidence bounds:

None

For function

For new observation

Level 95 %

1st derivative at Xi

2nd derivative at Xi

Integrate to Xi

Start from min(Xi)

Start from

Plot results

Plot data set: Arsenic_C vs. Distance_C

Xi	lower f(Xi)	f(Xi)	upper f(Xi)
10	56.5674	59.86	63.1526
30	53.7086	56.56	59.4114
50	49.9674	53.26	56.5526
70	45.6043	49.96	54.3157
90	40.9571	46.66	52.3629
110	36.184	43.36	50.536
130	31.3487	40.06	48.7713
150	26.479	36.76	47.041
170	21.5885	33.46	45.3315
190	16.6846	30.16	43.6354
210	11.7716	26.86	41.9484
230	6.85207	23.56	40.2679
250	1.92778	20.26	38.5922
270	-3.0001	16.96	36.9201
290	-7.93078	13.66	35.2508
310	-12.8637	10.36	33.5837
330	-17.7983	7.06	31.9183
350	-22.7344	3.76	30.2544
370	-27.6717	0.46	28.5917
390	-32.6099	-2.84	26.9299
410	-37.5491	-6.14	25.2691
430	-42.4889	-9.44	23.6089

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From prediction, the concentration of arsenic decreases with increasing vertical distance downward up to a concentration value of 0.46 mg/kg at a distance of about 370cm and finally faded from the soil at 390cm.

Lead (Pb) Modeling and Prediction at Grid Point H6

The vertical downward change in the concentration of lead within the zone of high concentration at grid point H6 fit into a power distribution model shown in Figure 5. The model shows the values of the coefficients 'a' and 'b' to be 99.15 and -0.0507 respectively, and a value of 0.946 for R^2 indicates a very high correlation between the variables.

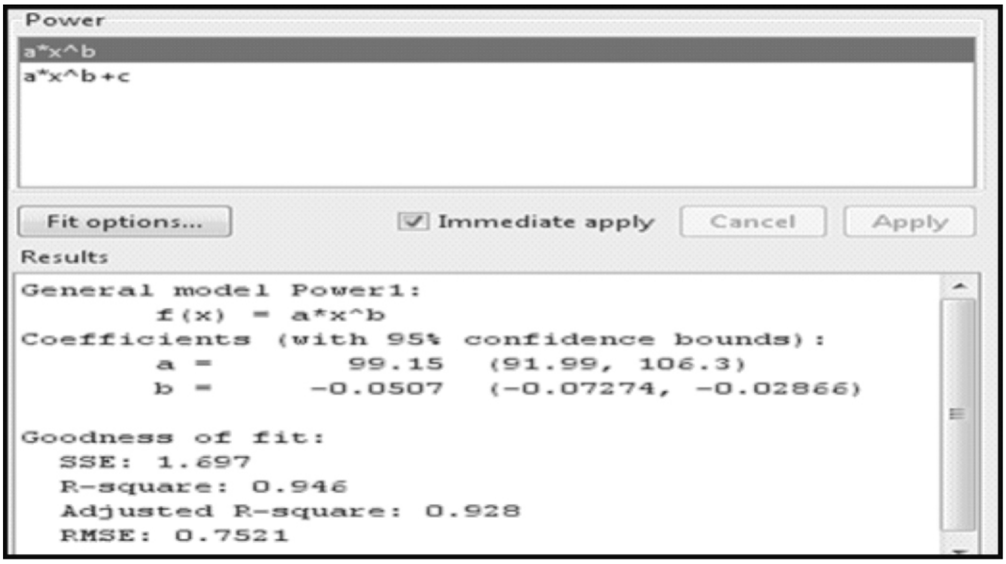

Figure 5: Fitted Function For Lead Concentration Against Distace at Point H6

The lower values of SSE=1.697, RMSE= 0.7521 and the high values of R^2=0.946 and Adj-R^2= 0.928 justify the suitability of the fitted model and the adequacy of the field data.

The location of the field data curve between the upper and the lower bounds and the curves trend pattern at 95% confidence bound further validates the model and also justify the adequacy of the field data collected as shown in Figure 6.

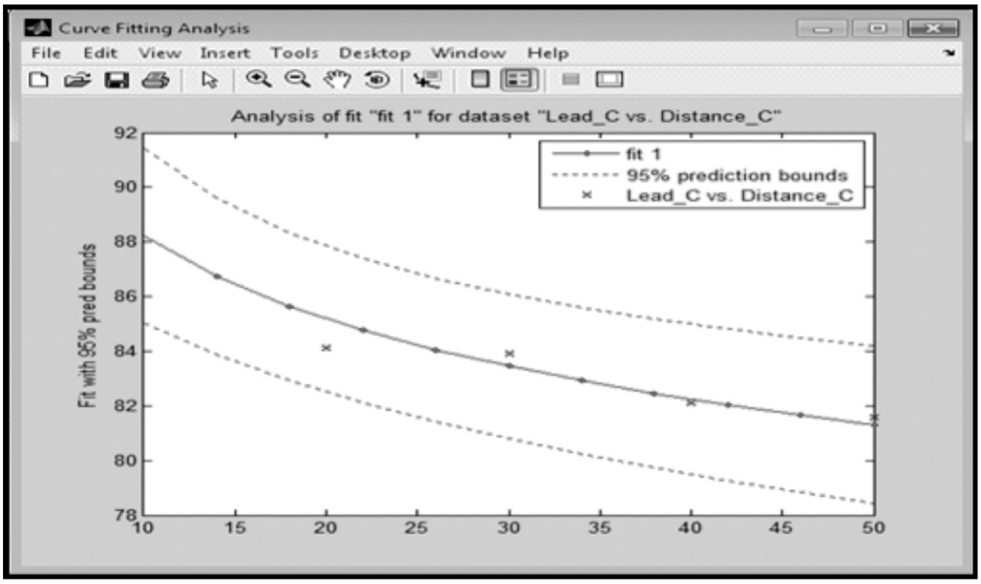

Figure 6: Prediction Bounds for Lead Concentration Against Distance at Point H6

Model prediction of the concentration of lead outside the experimental downward vertical distance range of 10-50cm, at 95% confidence bound and vertical interval of 250cm is shown in Table 3.

Table 3: Downward Prediction of Lead Concentration at Point H6

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

Predicted result reveals that the concentration of lead decreases with increasing vertical distance downward to a concentration value of 64.5403mg/kg a distance of 4760cm in the soil.

Zinc (Zn) Modeling and Prediction at Grid Point I8

The vertical downward concentration change of zinc within the zone of high concentration at grid point I8 fits into a linear polynomial distribution model in Figure 7. The model shows the values of its coefficients P1 and P2 to be -2.591 and 960.1, with a R^2 value of 0.9912 which shows a very high correlation between zinc concentration and vertical distance downward.

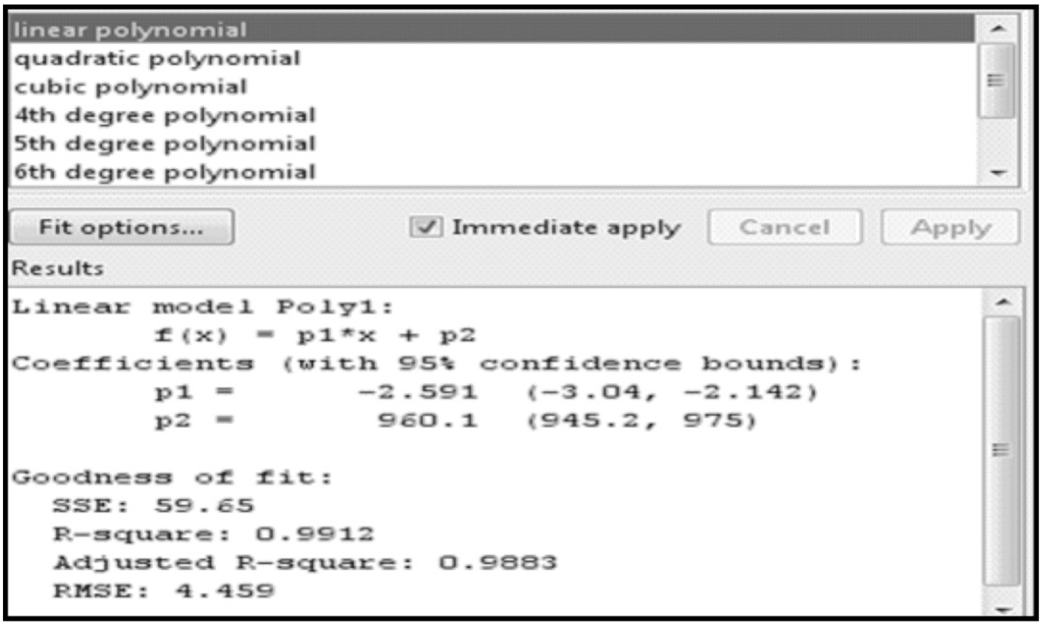

Figure 7: Fitted function for Zinc Concentration Against Distance at Point I8

The lower values of SSE=59.65, RMSE= 4.459 and the high values of R^2=0.9912 and Adj-R^2= 0.9883 justify the suitability of the fitted model and the adequacy of the field data.

The location of the field data curve between the upper and the lower bounds and the curves trend pattern at 95% confidence bound further validates the model and also justify the adequacy of the field data collected as shown in Figure 8.

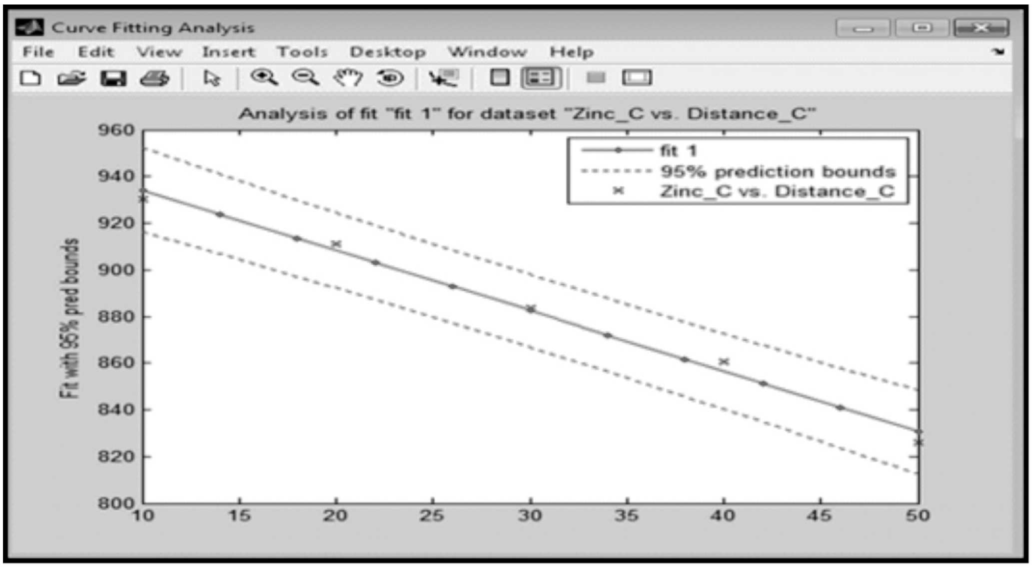

Figure 8: Prediction Bounds for Zinc Concentration Against Distance at Point I8

Model prediction of the concentration of zinc outside the experimental range of 10-50cm, at 95% confidence bound and vertical interval of 20cm is shown in Table 4.

Table 4: Downward Prediction of Zinc Concentration at Point I8

Xi	lower f(Xi)	f(Xi)	upper f(Xi)
10	916.21	934.16	952.11
30	866.795	882.34	897.885
50	812.57	830.52	848.47
70	754.954	778.7	802.446
90	695.789	726.88	757.971
110	635.938	675.06	714.182
130	575.748	623.24	670.732
150	515.371	571.42	627.469
170	454.88	519.6	584.32
190	394.316	467.78	541.244
210	333.702	415.96	498.218
230	273.053	364.14	455.227
250	212.378	312.32	412.262
270	151.683	260.5	369.317
290	90.9727	208.68	326.387
310	30.2506	156.86	283.469
330	-30.481	105.04	240.561
350	-91.2206	53.22	197.661
370	-151.967	1.4	154.767
390	-212.718	-50.42	111.878

The predicted result shows that the concentration of zinc decreases with increasing vertical distance downward up to a concentration value of 1.4mg/kg at a distance of 370cm and then finally fades from the soil at a distance of 390cm.

Conclusion

The curve fitting with MATLAB showed the best fitted models to be linear and quadratic polynomials, power function and cubic polynomial. The model prediction at 95% confidence bounds revealed the deepest downward vertical distance travelled to be 4760cm by lead at point H6, 460cm by cadmium at point D7, 960cm by zinc at I8 and 370cm by arsenic at D7. The respective concentrations of these metals at these depths are 64.54mg/kg, 0.72mg/kg, 5.12mg/kg and 0.46mg/kg. At these furthest distances, none of these metals was found to be above the maximum allowable limit. At some intermediate distances of 435cm, 610cm and 250cm, the respective concentration were of 3.97 mg/kg for Cd, 346.72 mg/kg for Zn and 20.26 mg/kg for As and were found to be above the maximum allowable limits. This information is vital in determining the extent to which deep rooted crops can come in contact with these metals, and how safe is the ground water is from metals contamination.

Table 5: Maximum concentration limits of some trace elements in soils

Chemical Element	Maximum Allowable Limits in Soils (µg/g)
As	20
Cd	3
Co	50
Cr	100
Cu	100
Fe	50000
Mn	2000
Ni	50
Pb	100
Se	10
Zn	300

Source: *Ewers (1991), Pendias (1992) and WHO (2001).*

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