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Prediction Patterns of Cr and Ni in soils

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Abstract:- Correlation and regression analyses were conducted on the data generated from the analysis of soils samples from Bauchi state, in order to comparehow two metals (Cr and Ni) in these soils can be predicted by some soil physico-chemical properties (pH, electrical conductivity, EC; and soil moisture contents, MC). Resulting coefficient of correlation established a linear relationship between the study metals and one or more physico – chemical parameters in all the study sites. Test results of the suitability of the models to the data obtained indicated that linear, logarithmic and quadratic models were found suitable for both metals in the study sites, although quadratic models gave better predictions. The Regression equations obtained showstriking similarities in the prediction pattern of both metals with respect to their predictor variables. The models obtained could be used to predict approximately between 41.0 – 84.0% Cr and 50.0 – 82.0% Ni.

***Keyword**: Chromium, Nickel, soil moisture contents,soil pH, electrical conductivity, regression equations.*

I. INTRODUCTION

The quality of soils has been compromised by several anthropogenic activities such as mining, use of agricultural inputs, emissions from industrial processes, burning fossil fuel, emissions from automobile exhaust, waste disposal and incineration. These activities have contributed to increased levels of heavy metals, including chromium (Cr) and nickel (Ni) in soils [1-3]. These heavy metals are non-biodegradable and as such highly persistent in soil, with residence times as long as thousands of years [4].

Chromium has been reported, after lead, as the second most common metal found in contaminated sites. It is less common and does not occur naturally in elemental form but in compounds [5]. Its concentrationin the environment has steadily increased due to industrial growth especially release from electroplating processes and the disposal of Cr – containing wastes [4-6]. Cr has been classified as priority pollutants with a carcinogenicity classification A (human carcinogen) by the United States Environmental Protection Agency [7]. Its accumulation in the environment should be checked aslocal permeation of this metal to soil, water or the atmosphere might result in excessive amounts of this pollutant in biogeochemical circulation [6].

Sources of Nickel in the environment are both naturaland anthropogenic. It is hardly found in its elemental form.Igneous rock is the primary source of Ni [8] It accumulatesanthropogenicallydue to its application in stainless steels production, paint making, chemical and catalysts production, electroplating, nickel- cadmium batteries,refining and petroleum industries, manufacturing of motor vehicles, cables and wire, coins and electronic products [9,10,11,12].Nickel is an essential element only in small doses but at doses above the maximum tolerable amount, it can cause various kinds of cancers [5,8].Other health risks of Niinclude fibrosis, respiratory tract infections, impaired pulmonary function and emphysema [13].

The concentration of heavy metals in the soil is affected by many factors including the soil pH, moisture levels of soil, electrical conductivity and soil organic matter. Soil pH is a major factor influencing metal chemistry. It has a major effect on metal dynamics because it controls adsorption, movement, retention andprecipitation [14,15].At low pH levels, the solubility and availability of micronutrients in soils increases significantly. The rate of adsorption and bioavailability of these metals also decreases. The mobility of the metals thus increases [16,17]. Soil moisture content places vital a role on the availability of metals in soil. It can significantly alter the properties of soils. Soil moisture easily fluctuates with temperature and rainfall and could therefore regulate the availability of nutrients in soil. Studies have shown that most metals, including Ni are in most cases less available at high soil moisture due to the effect of reducing conditions on the metal ion. In waterlogged soils, most metals, including Zn, Cd, and Ni exhibit complicated solubility with generally reduced solubility due to low redox potential and formation of sparingly soluble sulphides [18]. Significant positive correlations have been reported between heavy metals and moisture content and water holding capacity [19]. Soil electrical conductivity is also an important property of the soil that affects soil chemistry. It offers a very quick and convenient way for determining the total amount of ionisable salt and the existence of some ions in the soil changes soil electrical conductivity value. The nature of various substances, their concentration and ionic strengths vitally affect the conductance [20,21].In the physio-chemical sense, high heavy metal concentration upsets salinity and electrical conductivity (EC) balance of the soil [22].

Owing to the continuous reclamation of contaminated sites such as dumpsites, mechanic facilities and their surroundings for residential and other purposes like digging of wells, farming etc., it has become imperative to regularly monitor the level of heavy metal within the vicinitiesof these sites. Continuous monitoring of these metals will be very rigorous and would therefore need adequate tools such as mathematical models for easy assessment. Regression analysis is a statistical technique usually used to estimate the relationships between a dependent variable and one or more independent variable. The goal in the regression procedure is to create a model where the predicted and observed values of the variable to be predicted are as similar as possible [23]. Regression analysis technique has attracted the attentions of researchers' community. The applicability of linear regressions models, which depends mainly on the equation

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for estimation, prediction and hypothesis testing has been proven efficient and has received attention in the fields of environmental sciences [24,25]. In order to monitor these metals on a continual basis, mathematical models can be used. Regression models which are predictive in nature can be used to forecast the level of heavy metal in an environment using the soil physicochemical parameters. The aim of the study is to generate regression models with data from soil analysis to investigate the prediction pattern of Cr and Ni in these soils. Models generated may assist concerned government agencies to formulate adequate policy to allow more accurate risk assessments and management decisions on managing metal contaminants in our environment.

II. METHODOLOGY

A. *Study Area*

Soil samples from the vicinities of three different auto-repair facilities and their dumpsitesin Fadamamada(FM), YelwaTudun (YT) and Jos Road (JR), all in Bauchi Statewere collected. The area under investigation have soils which have been affected by activities associated with the repairs and servicing of vehicles such as dumping of waste engine oil, antifreeze, metal and batteries scrap, and other refuse.

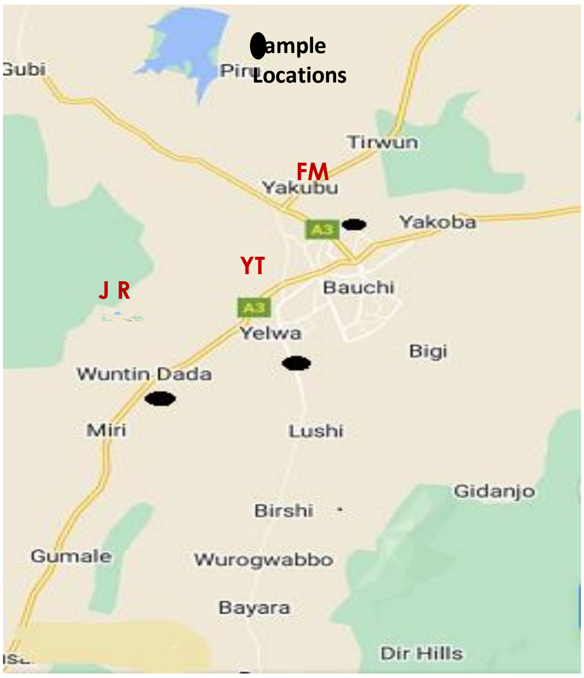

Fig. 1: Location Map of the Study Area

B. *Sample Collection and Preparation*

Each of the study area was divided into tenstrata based on the nature of activities carried out by the artisan, in order to capture the variation in the concentration of the metals in the sites. A total of 200 soil samples were collected at a depth of 0 – 30 cm in each of the sites. 20 soil samples collected per strata in each site were then homogenized to form ten composite samples for each contaminated site [22,26]. Soil samples were air dried, pulverisedand sieved through 2 mm meshand stored in labelled polythene[27].

C. *Sample analysis*

The pulverised samples were digested with aqua regia according to standard procedures. The digested samples were analyzed for Cr and Mn content using the atomic absorption spectrophotometer [28,29].

D. *Physicochemical Properties of Soil*

Soil pH was measured with a pH meter at a ratio of 2.5:1 water/soil suspension. [30]. Soil moisture content was determined by gravimetric method involving drying in an oven at 110ºC for 6 hours until constant weight was obtained. The Electrical conductivity of the soil was measured with an EC meter calibrated to a 1412 μScm^{-1} calibration standard at 25ºC at a ratio of 1:5 soil/water suspension [31].

E. *Data Analysis*

The SPSS was used to analyse the data generated and to develop the models in the study. The statistical variations were considered significant at $p<0.05$.

III. RESULTS AND DISCUSSION

A. *Correlation Analysis of study Parameters*

In Table 1, very strong significant correlations were established at both at $p < 0.01$ and $p < 0.05$ between the Cr/Ni and predictor variables: pH, electrical conductivity (EC), and % moisture content (MC) in the soils in the study sites. This is a strong indication that some sort of relationship exists between these metals and the soil properties and the relationship can therefore be estimated using regression analysis.

B. *Regression Analysis of Cr and Mn in the study site*

In YelwaTudun, the linear model (Figure 1a) suited the data for Cr in this site is expressed thus:

$$Cr = -50.18 + 72.57\ pH.$$

$$Adj.\ R^2 = 0.407.$$

For this model, only approximately 41.0% of the variation in the concentration of Cr in the soil can be accounted for by soil pH. Although the model is significant at $p < 0.05$, it may not really do a good job in explaining the variance in predicting the concentration of Cr in this site (Figure 1a).

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		Cr	Ni	pH	EC	MC
				YelwaTudun		
Cr	R	1				
Ni	R	.736*	1			
pH	R	.688*	.754*	1		
EC	R	.534	.593	.942**	1	
MC	R	.439	.403	.782**	.882**	1
				Jos Road		
Cr	R	1				
Ni	R	.930**	1			
pH	R	.838**	.832**	1		
EC	R	.057	.082	.141	1	
MC	R	.640*	.615	.594	.469	1
				Fadamamada		
Cr	R	1				
Ni	R	.446	1			
pH	R	.739*	.724*	1		
EC	R	.882**	.755*	.772**	1	
MC	R	.694*	.754*	.792**	.810**	1

Table 1: Correlation between Trace Metals and Physico–Chemical Parameters in the study sites

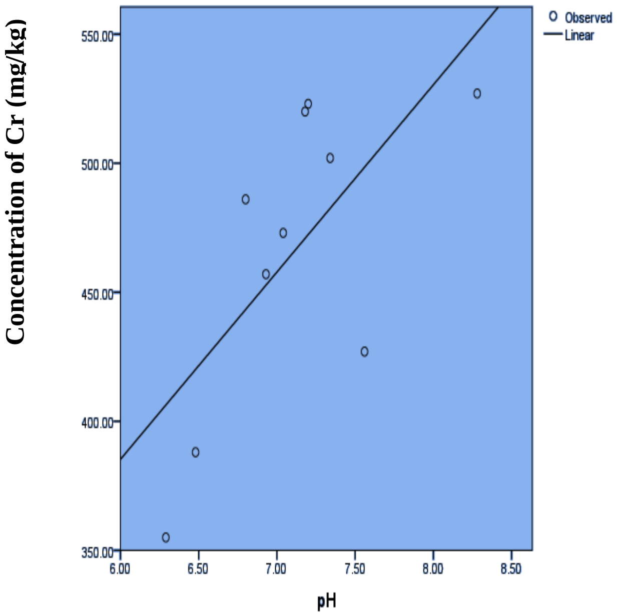

Fig. 1a: Regression Curve Estimate for Cr in YelwaTudun

pH also correlates significantly with Ni in YT and was used to generate the linear equation (Figure 1b) for Ni given as:

Ni = - 53.04 +9.430 Ph

and a logarithmic model:

Ni = 67.331 ln(pH) – 117.88.

Both models and predictors for Ni in this site are significant at $p < 0.05$ and can account for approximately 50.0% of the variance in the concentration of soil Ni in this site.

Soil pH also highly correlated with Cr (pH: r = 0.838; $p < 0.01$) in JR and three regression models for Cr emerged (Figure 2a).

Linear: Cr = -1586.5 + 243.3pH Adj. $R^2 = 0.666$

Logarithmic:
Cr = 1645.7 ln(pH) – 3085.80 Adj. $R^2 = 0.650$

Quadratic:
$Cr = 18093.2 – 5517.68pH + 421.21pH^2$ Adj. $R^2 = 0.823$

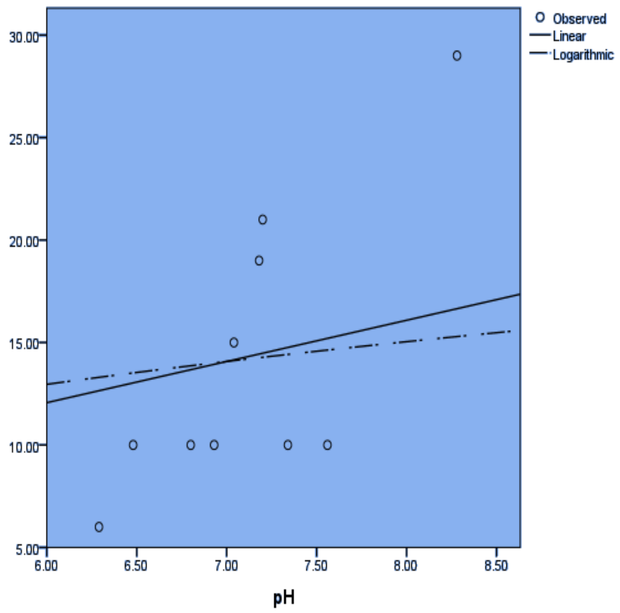

Fig. 1b: Regression Curve Estimate for Ni in YelwaTudun

Of all these models, the quadratic model with adjusted R-Square value of 0.823, explains not less than 80% of the variance in the concentration of Cr in this site (Table 2), making it an excellent and the most preferred model. The significance levels of the models and their predictors are high at $p < 0.05$.

Ni in JR was predicted by pH (r = 0.832). In Figure 2b, the three regression equations that emerged for Ni are:

Linear:
Ni = -485.3 + 75.76pH Adj. $R^2 = 0.654$

Logarithmic:
Ni = 512.40 ln(pH) – 952.10 Adj. $R^2 = 0.638$

Quadratic:
$Ni = 5656.49 - 1722.18pH + 131.46pH^2$ $Adj.R^2 = 0.807$

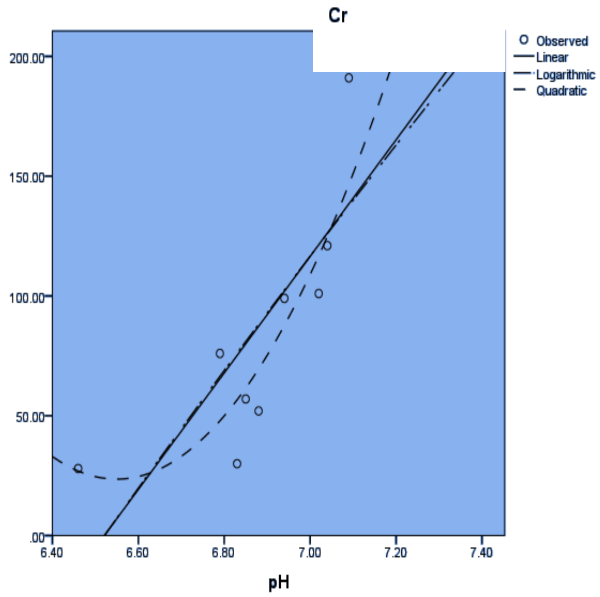

Fig. 2a: Regression Curve Estimate for Cr in Jos Road

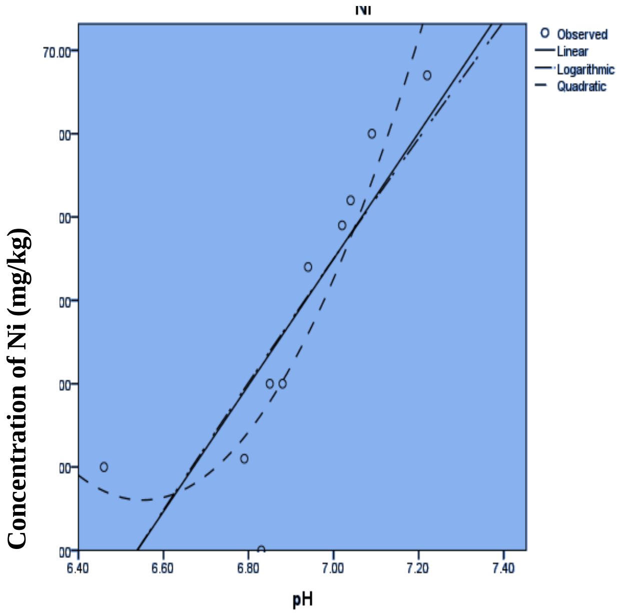

Figure 2b Regression Curve Estimate for Ni in Jos Road

Sites	Metals	Regression Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
	Cr	Linear	0.688	0.473	0.407	45.663
YT	Ni	Linear	0.754	0.569	0.515	4.892
		Logarithmic	0.746	0.557	0.501	4.960
	Cr	Linear	0.838	0.703	0.666	34.743
		Logarithmic	0.830	0.689	0.650	35.535
JR		Quadratic	0.929	0.862	0.823	25.296
	Ni	Linear	0.832	0.692	0.654	11.101
		Logarithmic	0.824	0.678	0.638	11.344
		Quadratic	0.922	0.850	0.807	8.295
	Cr	Linear	0.882	0.778	0.750	84.164
		Logarithmic	0.921	0.848	0.829	69.681
FM		Quadratic	0.934	0.873	0.837	67.975
	Ni	Linear	0.755	0.570	0.516	7.140
		Logarithmic	0.697	0.485	0.421	7.809

Table 2: Summary of the regression model for Cr and Mn in the study locations

Although the models and their predictor variables are statistically significance at $p < 0.05$, only the quadratic model does the best job of accounting for 80% of the variance in the concentration of soil Ni in this site.

From the correlation table, only EC ($r = 0.882$) significantly and better predicted the concentration of Cr for FM, even though the other independent variables (pH and MC) could individually predict it. This is because all the variables highly correlated with eachother andindividually with Cr. In Figure 3a, three regression equations obtained for Cr using EC are expressed thus:

Linear:
$Cr = 6.259 + 1.423EC$
Logarithmic:
$Cr = 298.12 \ln(EC) - 1251.40$
Quadratic:
$Cr = 5.687EC - 0.009EC^2 - 376.53$

The linear, logarithmic and quadratic model, have an adjusted R-Square values of 0.750, 0.829 and 0.837 respectively. Therefore approximately 80% of the variance in theconcentration of Cr in this site is explained by the model (Table 20). With the significance levels of the models and their predictors less than alpha ($p < 0.05$), the models with EC significantly predicted Cr in this site.

In Figure 3b, the regression line for Ni – EC pairs in FM are given in the equations below.

Linear: Ni = 1.05 + 0.074EC

Logarithmic:

Ni = 13.75 ln(EC) – 155.29

The models and predictor variables are statistically significance at $p < 0.05$. With adjusted R^2 values of 0.516 and 0.421, the linear and logarithmic models can account for only 52% and 42% of the variance in the concentration of soil Ni in this site respectively. The linear model better explains the variation in the concentration of Ni.

Regression models in this study are consistent with other works.The R^2 values for the relationship between the distance from a mine and Cu and Ni concentration in the soils indicates that between 70.0 and 77.0% of the variations in concentrations of Cu and Ni respectively in the soils can be explained by distance from the mine [1] In a study that explores the relationship between heavy-metal concentrations in the roadside soils on the heavy-metal uptake capabilities of the corresponding local grasses, the linear, logarithmic and quadratic models were developed to predict the transfer ratio of Cd, Cu and Pb in grasses of roadside farmlands [32]. In their study, Atulegwu[22] reported that the Linear, logarithmic and quadratic models were suitable for the data generated for pH, Cr and Ni in soils and as such these regression models can predicted the concentrations of Cr and Ni in the soil using pH.

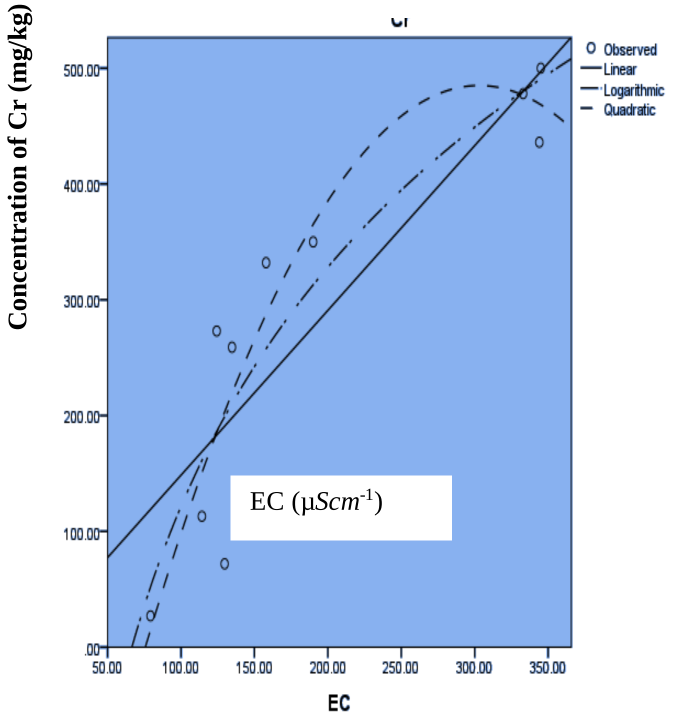

Fig. 3a: Regression Curve Estimate for Cr in Fadamamada

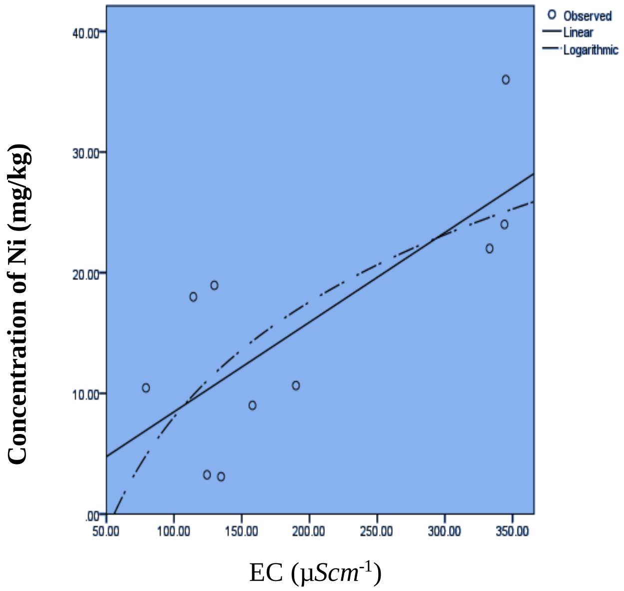

Fig. 3b: Regression Curve Estimate for Ni in Fadamamada

All models in this work are consistent with their findings, except those for Cr in YT and FM and Ni in FM, accounting for less than 65.0 % variability in the concentration of the metals in these sites.

The variations in the ability of pH and EC to adequately predict these metals in the various sites could be attributed to the dynamic system of the soil and its types. Changes in soil pH, moisture content and redox conditions normally occur in soils. The gradual alterations of soil in response to changes in its management and environmental factors affect the rate of adsorption and release of metals in the soil [4,16]. These changes in the soil properties could be responsible for the prediction patterns observed inthe models developed.

IV. CONCLUSION AND RECOMMENDATION

Cr and Ni show similar prediction patterns in terms of their predictor variables. In YT and JR, pH was the independent variable for both metals while EC predicted these metals in FM.The quadratic models (with Adj. $R^2 >$ 0.800) fitted the data generated for pH, Ni and Cr better than the other models in JR and FM. While both pH and EC could not adequately predict the levels of the metals in YT, pH was the best predictor variablefor Cr and Ni in JR, EC could only predict Cr very well in FM.The models can also be used to generate data on a monthly, quarterly or yearly basis for periodical assessment of these metal content levels of the soils and for forecasting. As a way of improving the coefficients of explanatory variables and the significance of some of the model, non-linear regression may be carried out to test data pairs that are non – linearly related in the work. Also, othersoil physico – chemical properties besides those in this study should be studied in order to improve on the models or develop better models for metals predictions.

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