

# Investigation into the Characteristic of Chloride and Phosphate on Industrial Area Soil Pollution

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**Abstract** – Research was conducted on industrial area of Niger Delta zone upon the influence of effluent discharge into the environment. An experimental approach was applied to monitor and predict the rate of contamination and variation on the physiochemical properties of chloride and phosphate of the soil characteristics of the environment. The concentration of chloride and phosphate was monitored using both experimental and theoretical techniques. The concept of least square method was applied using the necessary mathematical tools as presented in the research article. The experimental data was used in formulating the theoretical concept putting in mind the necessary functional parameters that influence the characteristics of chloride and phosphate diffusion in soil environment. It observed that the concentration of the chloride and phosphate varies with depth as well upon the rate of effluent discharge within the environment.

**Keywords** – Investigation, Characteristic, Chloride, Phosphate, Industrial, Soil Pollution.

## I. INTRODUCTION

Diffusion is the process by which a contaminant in water will move from an area of greater concentration toward an area where it is less concentrated. Diffusion will occur as long as a concentration gradient exists, even if the fluid is not moving, and as a result, contaminant may spread away from the place where it is introduced into a porous medium. Diffusion may also occur when the concentration of a contaminant is higher in one stratum than in an adjacent stratum [1-30] provided that the adjacent stratum has the requisite porosity.

Diffusion occurs due to the random movement of chemical molecules. This motion is due to non-uniform, random collisions of molecules. Compared with other transport processes, diffusion is a relatively slow process [31-40].

Convection is fluid motion caused by external forces. An example of convection is water flowing along a stream bed. This flow occurs when water moves from higher elevation to lower elevation. This flow is due to a difference in energy levels at the two elevations. Water at the higher elevation (point A) has a greater potential energy than water at the lower elevation (point B). This potential energy difference causes the water to move from point A to point B. When the potential energy difference is large and occurs over a short distance, the water moves quickly. We see this in rapidly flowing surface runoff water, streams and waterfalls. When the gradient of the soil surface elevation is small, the flow of water down a stream is fairly slow [16-20].

Movement of water and chemicals in soil occurs due to differences in the potential energy of water in the soil. The potential energy level is usually due to gravity and attractive forces associated with small pores between soil particles. Whether it moves rapidly or slowly, this flow of

soil water is called **convection**. The transport of chemicals in soil water is called **advection** [20-55].

When water moves through soil, it travels around soil particles and rocks, following flow paths that act like a bundle of capillary tubes of different lengths. Water and chemicals following these tortuous paths create a phenomenon called hydrodynamic dispersion. Two water molecules may follow different flow paths, so the actual distances they travel may be quite different. So, they may arrive at the same destination at substantially different times. Since the actual water flow paths in most soils must curve around solid soil particles and air space, water and dissolved chemicals follow a tortuous path [20-40].

Chemical characteristics influence the ability of substances to be transported. Characteristics of particular interest include solubility, sorption and density. Chemicals that are more soluble at the soil's pH tend to move more easily with water than chemicals that are less water soluble. In contrast, chemicals with lower water solubility's will tend to attach to clay particles and organic matter near the soil surface. Some of these will form chemical precipitates. If soil particles are moved by water or wind erosion, attached chemicals will move with them. In this way, chemicals are carried across the soil surface away from their point of application, and sometimes into surface water. Chemicals that are only slightly water soluble can still reach surface or ground waters. However, their rates of movement will tend to be slowed through interactions with soil particles. Often refers to the process where molecules are attracted to the surface of soil particles. True adsorption occurs when molecular layers form on a soil particle surface. When molecules commingle with another substance, we refer to the process as absorption. Most soils absorb water and chemicals, although in amounts much less than those sorbed. In practice, it is difficult to distinguish between absorption, adsorption and other processes [33-50].

Desorption is the process by which molecules are detached from the surface of soil particles. Adsorption and desorption usually occur simultaneously. Molecules and ions are continually transferred between the soil solution and soil particle surface. Since the specific process is difficult to measure, the more general term, sorption, can be used to describe how a chemical is held in the soil. Clay particles and organic matter are the most chemically active soil solids. They are the major soil components to which chemicals absorb. Most chemicals are subject to forces of sorption. Examples include simple inorganic ions such as calcium, sodium, and ammonium. Complex organic chemicals such as humus, many pesticides and industrial solvents are also absorbed onto soil.

Chemicals such as phosphorus that are strongly absorbed to soil particles near the surface of most soils will tend to contaminate surface water if erosion is a problem. Chemicals, such as nitrate, that are more water soluble and less strongly absorbed to soil particles, will tend to contaminate ground water if rainfall or irrigation exceeds plant water use. Positively charged ions (called cations) are attracted to a negatively charged site on clay or organic particles. The movement of cations between clay or organic particles and the surrounding soil water is called cation exchange. It is an important process. It controls the mobility of many chemicals through the soil profile. Cation exchange is seldom observed with most organic chemicals that might be added to the soil, because few organic chemicals carry positive charges at a normal soil pH. However, some examples do exist. The pesticides Parquet and Diquat are examples of cationic pesticides that can be absorbed onto soil particles through cation exchange. A number of other bonding mechanisms exist by which organic compounds are absorbed to soil surfaces. For any given compound (organic or inorganic), it is likely that a combination of mechanisms is responsible for sorption onto soil. Whatever the mechanism is, soil organic matter is the principal sorbent for many nonionic organic chemicals. It is important to know a particular chemical's attraction to organic matter, and the amount of organic matter available in a particular soil [15-30].

One interesting aspect of chemical transport involves whether chemicals are more or less dense than water. This demonstration shows a chemical developing finger because it is denser than water. These fingers of concentrated chemical sink to the bottom of the water column before they appreciably mix with the water. Spilled chemicals that are denser than water will tend to sink to the lower depths of a ground water aquifer. Chemicals that are less dense than water (for example, gasoline) will tend to float near the top of a ground water aquifer

## II. MATERIALS AND METHODS

### Sample Collection:

Soil samples were collected within the vicinity of the H & H Asphalt Plant Company Located at Enito 3, a village

in Ahoada West Local Government Area, River State, Nigeria.

Soil samples were obtained from the surface (top soil) to a depth of 60cm. A total of five (5) soil samples were collected within the interval of 15cm depth, top soil 0-0.5cm, 15cm, 30cm, 45cm and 60cm. The samples were transported to the Chemical Sciences Research Laboratory of the Niger Delta University for analysis, for the determination of the Physio-chemical Parameters.

### Soil Samples Ready for Analysis:



Fig.1a. Soil samples obtained from the vicinity of the Asphalt plant Company, Enito 3, Ahoada west LGA, ready for analysis in the Chemical Sciences Research Laboratory of the Niger Delta University, Wilberforce Island, Bayelsa State.

### Chloride (Cl<sup>-</sup>):

The Chloride content of the soil was determined by titrimetric method. 100g of soil was weighed in a 750ml reagent bottle and 500ml of distilled water added and shaken on the shaker for 30minutes. The suspension was transferred into a titration flask, 1ml of potassium Chromate was added as an indicator. This was titrated with 0.1M AgNO<sub>3</sub> [10] three titration were made and the amount of chloride was calculated in ppm.

$$(A - B) * M * 70,900$$

$$Cl^- (mg) = \frac{\text{ml of Sample}}$$

Where, A is ml of AgNO<sub>3</sub>; B is Blank titer; M is the Molarity of AgNO<sub>3</sub>

### Phosphate (PO<sub>4</sub>) (Bray Kurtz and Jackson, 1975)

Preparation of extraction solution of phosphate, 15ml of 1.0M Ammonium Fluorides solution and 25ml of 0.5M Hydrochloric acid were added into a 500ml volumetric flask. 460ml of distilled water was also added to make up to the mark.

1.0g of air-dried soil sample were weighed into a centrifuged at 2000rpm for 10min. 2ml aliquots of the clear supernatant were transferred into boiling tubes, 5ml distilled water and 2ml of ammonia solution were also added and well mixed. Finally 1ml of aliquot of stannous chloride were added and mixed. The spectrophotometer was then set at 660nm, the absorbance values were taken. The amount of phosphate in the soil was determined from

the standard curve prepared with the standard phosphate solution.

The Figure 1 shows a control volume in a soil environment describing the behavior of contaminants in the soil environment

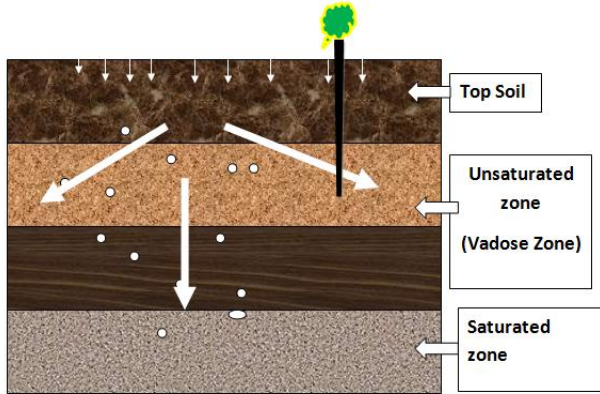


Fig.1. Systematic distribution of contaminants in subsurface soil environment.

The model was developed by considering the illustration as shown in figure 3.1. Then, the Concentration term can be expressed by the following differential equation. The material balance expression for the system is as shown in equation (1a), thus:

$$\text{Rate of contaminant accumulation} = \text{Diffusion} - \text{Convection (Advection)} - \text{rate of adsorption} - \text{irreversible decay rate} \dots (1a)$$

The mathematical representation of equation (1a) is shown below:

$$\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C - vC) - R - f \quad (1b)$$

$$\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C) - \nabla \cdot (vC) - \frac{\partial Ca}{\partial t} - f \quad (3.2a)$$

Where, **C** is the concentration, **v** is the average water velocity, **D** is the dispersion coefficient (diffusivity), **Ca** is the concentration of the adsorbed chemical contaminant and **f** is the irreversible reaction decay rate.

By expanding the equation (2) into three coordinates

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) - v \frac{\partial C}{\partial x} - \frac{\partial Ca}{\partial t} - f + \frac{\partial}{\partial y} \left( D \frac{\partial C}{\partial y} \right) - v \frac{\partial C}{\partial y} - \frac{\partial Ca}{\partial t} - f + \frac{\partial}{\partial z} \left( D \frac{\partial C}{\partial z} \right) - v \frac{\partial C}{\partial z} - \frac{\partial Ca}{\partial t} - f \quad (2b)$$

1. Assuming one-dimensional flow. Then, the y- and z-coordinates are neglected and assumed to be zero, the equation becomes:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) - v \frac{\partial C}{\partial x} - \frac{\partial Ca}{\partial t} - f \quad (3)$$

The equation 1 can be rearranged as

$$\frac{\partial C}{\partial t} - \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) + v \frac{\partial C}{\partial x} = -\frac{\partial Ca}{\partial t} - f \quad (4)$$

2. Assuming that contaminant are transported at a steady state within the soil environment.

Then, equation 2 reduces to a second order differential equation

$$-D \frac{d^2 C}{dx^2} + v \frac{dC}{dx} + f = 0 \quad (5a)$$

Since diffusion is taking place the negative sign is insignificant to the system.

$$D \frac{d^2 C}{dx^2} + v \frac{dC}{dx} + f = 0 \quad (5b)$$

Equation (5b) is expressed as a quadratic equation of the form

$$DX^2 + vX + f = 0 \quad (6)$$

Where  $X^2 = \frac{d^2 C}{dx^2}$  and  $X = \frac{dC}{dx}$ , The variable X is the depth.

The concentration is expressed as a function of depth

$$C(X) = DX^2 + vX + f \quad (7)$$

### Empirical Model Approach

Empirical modeling depends on the availability of representative data for model development and validation of already existing models. Its function includes approximation of unknown functional relationship by some mathematical functions based on the experimentally gather data from the physical system.

The resultant quadratic equation relates the Diffusivity (D), water Velocity (v) and the irreversible decay rate (f). Using the least square method the experimental data are fitted to the above equation (3.7) for all the parameters that were analyzed as:

$$C(X) = DX^2 + vX + f \quad (8)$$

$$Cl^- (X) = DX^2 + vX + f \quad (9)$$

$$PO_4 (X) = DX^2 + vX + f \quad (10)$$

### III. RESULTS AND DISCUSSION

The results obtained from the research work are presented in Tables and Figures for the various investigations conducted on the empirical model approach to the evaluation for the degree of pollutant deposition and diffusion in soil environment. The experimental and the theoretical results obtained from investigation are presented in Table 1 to 6 for chloride and phosphate concentration.

Table 1: Results of Experimental Determination of Physio-chemical Parameters

Parameter	Unit	Depth (cm)					DPR Limit/ Intervention level
		0.00-5.00	15.00	30.00	45.00	60.00	
Chloride (Cl <sup>-</sup> )	ppm	12.90	16.70	14.50	13.40	15.50	
Phosphate (PO <sub>4</sub> )	mg/kg	0.48	0.42	0.38	0.36	0.45	

Table 2: Theoretical Computation of Chloride (Cl<sup>-</sup>) values Investigated

Depth (cm) (Dp)	Chloride (ppm) (Cl <sup>-</sup> ) <sub>EV</sub>	Dp* Cl <sup>-</sup>	Dp <sup>2</sup>	Dp <sup>2</sup> * Cl <sup>-</sup>	Dp <sup>3</sup>	Dp <sup>4</sup>
0.00-5.00	12.90	0.00	0.00	0.00	0.00	0.00
15.00	16.70	250.50	225.00	3757.50	3375.00	50625.00
30.00	14.50	435.00	900.00	13050.00	27000.00	810000.00
45.00	13.40	603.00	2025.00	27135.00	91125.00	4100625.00
60.00	15.50	930.00	3600.00	55800.00	216000.00	12960000.00
∑ Dp	∑(Cl <sup>-</sup> ) <sub>EV</sub>	∑ Dp* Cl <sup>-</sup>	∑ Dp <sup>2</sup>	∑ Dp <sup>2</sup> * Cl <sup>-</sup>	∑ Dp <sup>3</sup>	∑ Dp <sup>4</sup>
=150.00	=73.00	=2218.50	=6750.00	=99742.50	=337500.00	=17921250.00

Table 3: Comparison of Experimental, Theoretical and validated values for Chloride (Cl<sup>-</sup>) investigation.

Depth (cm) (Dp)	Chloride (ppm) (Cl <sup>-</sup> ) <sub>EV</sub>	Chloride (ppm) (Cl <sup>-</sup> ) <sub>TDM</sub>	Chloride (ppm) (Cl <sup>-</sup> ) <sub>VM</sub>
0.00-5.00	12.90	13.89	14.22
15.00	16.70	14.57	14.40
30.00	14.50	14.91	14.58
45.00	13.40	14.93	14.76
60.00	15.50	14.62	14.94

Table 4: Theoretical Computation of Phosphate (PO<sub>4</sub>) values Investigated

Depth (cm) (Dp)	Phosphate (mg/kg)(PO <sub>4</sub> ) <sub>EV</sub>	Dp*PO <sub>4</sub>	Dp <sup>2</sup>	Dp <sup>2</sup> *PO <sub>4</sub>	Dp <sup>3</sup>	Dp <sup>4</sup>
0.00-5.00	0.48	0.00	0.00	0.00	0.00	0.00
15.00	0.42	6.30	225.00	94.50	3375.00	50625.00
30.00	0.38	11.40	900.00	342.00	27000.00	810000.00
45.00	0.36	16.20	2025.00	729.00	91125.00	4100625.00
60.00	0.45	27.00	3600.00	1620.00	216000.00	12960000.00
∑ Dp	∑ (PO <sub>4</sub> ) <sub>EV</sub>	∑ Dp*PO <sub>4</sub>	∑ Dp <sup>2</sup>	∑ Dp <sup>2</sup> *PO <sub>4</sub>	∑ Dp <sup>3</sup>	∑ Dp <sup>4</sup>
=150.00	=2.09	=60.90	=6750.00	=2785.50	=337500.00	=17921250.00

Table 5: Comparison of Experimental, Theoretical and validated values for Phosphate (PO<sub>4</sub>) investigation.

Depth (cm) (Dp)	Phosphate (mg/kg) (PO <sub>4</sub> ) <sub>EV</sub>	Phosphate (mg/kg) (PO <sub>4</sub> ) <sub>TDM</sub>	Phosphate (mg/kg) (PO <sub>4</sub> ) <sub>VM</sub>
0.00-5.00	0.48	0.49	0.44
15.00	0.42	0.41	0.44
30.00	0.38	0.37	0.44
45.00	0.36	0.38	0.44
60.00	0.45	0.44	0.44

Table 6: Theoretical Computation of Total Hydrocarbon (THC) values Investigated

Depth (cm) (Dp)	Total Hydrocarbon (ppm) (THC) <sub>EV</sub>	Dp*THC	Dp <sup>2</sup>	Dp <sup>2</sup> *THC	Dp <sup>3</sup>	Dp <sup>4</sup>
0.00-5.00	3.50	0.00	0.00	0.00	0.00	0.00
15.00	4.65	69.75	225.00	1046.25	3375.00	50625.00
30.00	3.86	115.80	900.00	3474.00	27000.00	810000.00
45.00	4.85	218.25	2025.00	9821.25	91125.00	4100625.00
60.00	3.76	225.60	3600.00	13536.00	216000.00	12960000.00
∑ Dp	∑(THC) <sub>EV</sub>	∑ Dp*THC	∑ Dp <sup>2</sup>	∑ Dp <sup>2</sup> *THC	∑ Dp <sup>3</sup>	∑ Dp <sup>4</sup>
=150.00	=20.62	=629.40	=6750.00	=27877.50	=337500.00	=17921250.00

Figure 2 shows a good match, indicating the reliability of the developed model when compared with the experimental values. The model can be used to predict Sulphate concentration at various depths as expected.

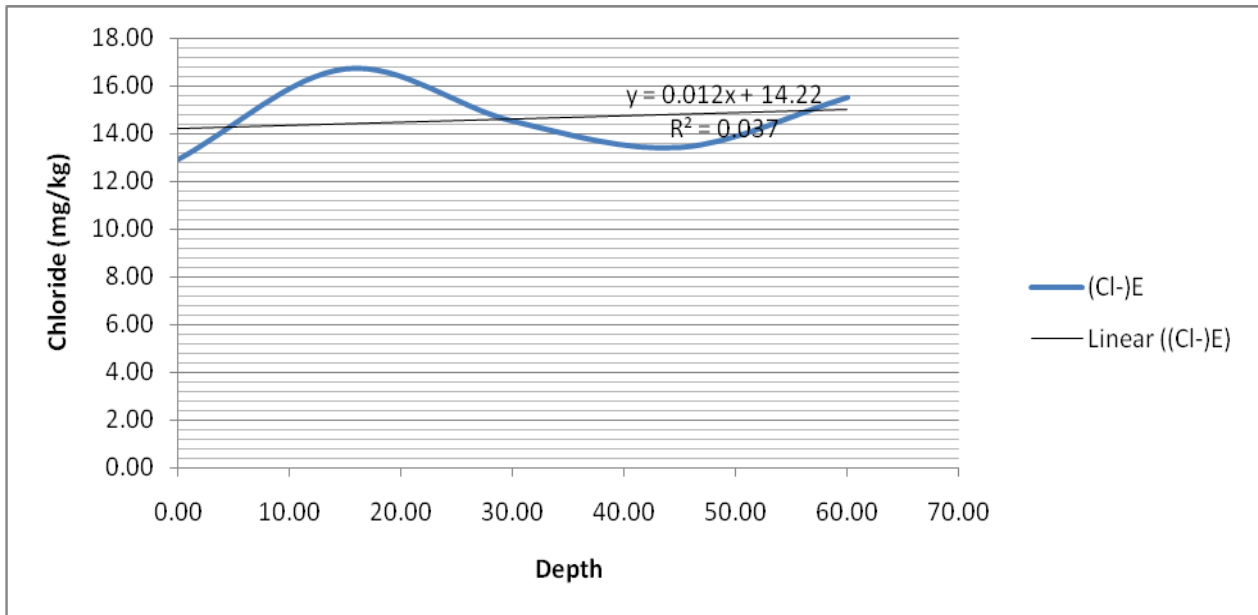


Fig.2. Graph of Experimental Chloride (Cl<sup>-</sup>) values against Depth.

The Figure 4.9 illustrates the relationship between the experimental Chloride concentrations against Depth. The relationship is sinusoidal in nature due to the fluctuation of the values of the Chloride ions. The polynomial of the

curve is established as  $(Cl^-)_{VM} = 0.012Dp + 14.22$ . And the coefficient of determination is given as  $R^2 = 0.037$ . The theoretical developed model is given as  $(Cl^-)_{TDM} = -0.00073Dp^2 + 0.056Dp + 13.89$

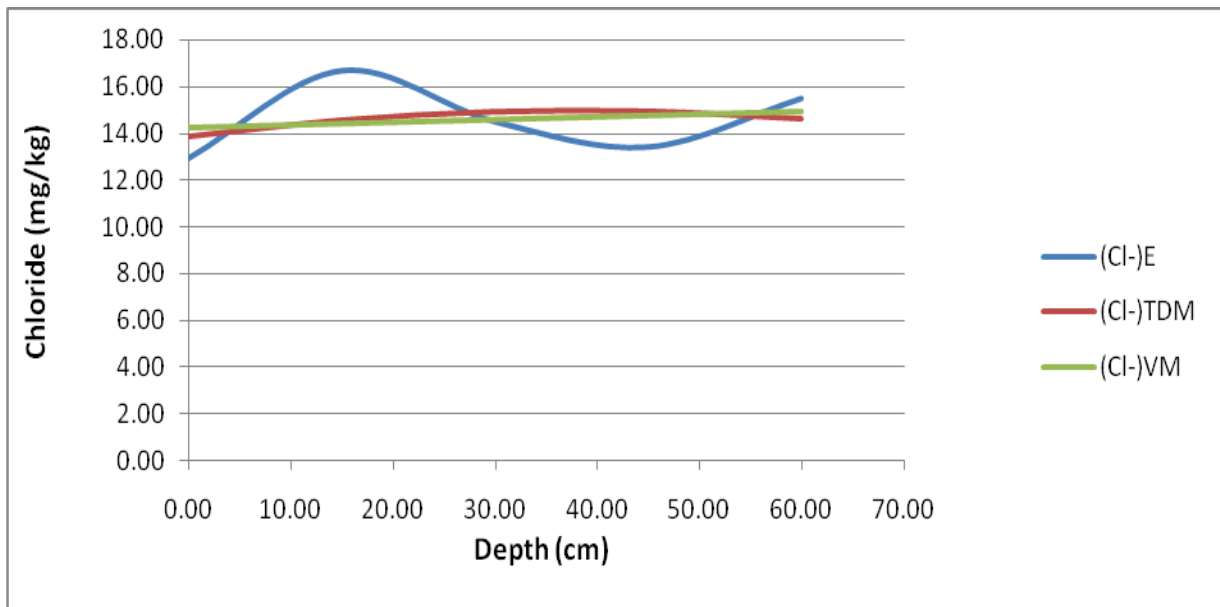


Fig.3. Comparison of Experimental, Theoretical model and Validated model Nitrate values against Depth.

From figure 3 Points of interception were obtained at various regions, at a depth of 8.00cm, 28cm and 55cm for experimental, theoretical and validated values. It therefore

indicates that the model is reliable for the prediction of other depths.

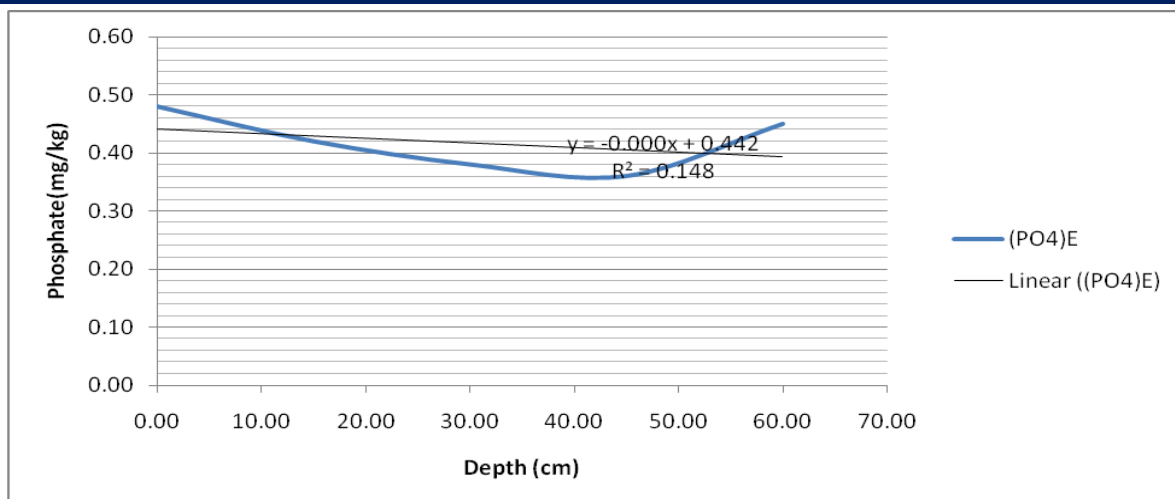


Fig.4. Graph of Experimental Phosphate (PO<sub>4</sub>) values against Depth.

From the Figure 4 the result presented is a hyperbolic curve, which describes the relationship between the experimental Phosphate concentrations against depth. The polynomial of the curve was established as  $(PO_4)_{VM} = -$

$0.00001Dp+0.442$  and the coefficient of determination is given as  $R^2=0.148$ . The theoretical developed model is given as  $(PO_4)_{TDM} = 0.000102Dp^2-0.0069Dp+0.488$ .

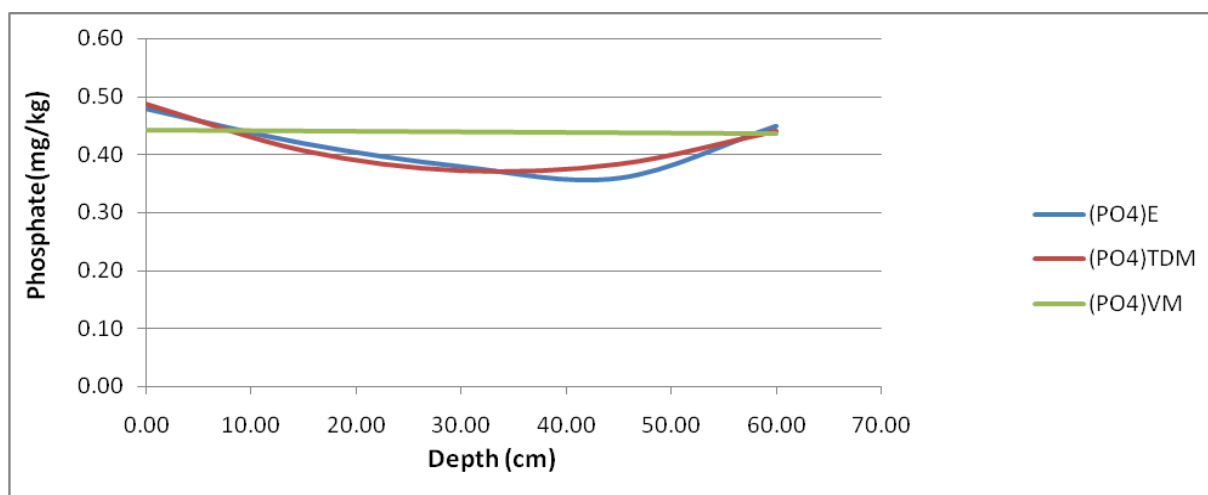


Fig.5. Comparison of Experimental, Theoretical model and Validated model Phosphate (PO<sub>4</sub>) values against Depth.

From the Figure 5 the comparison of the Experimental, Theoretical model and Validated model Phosphate (PO<sub>4</sub>) values against Depth. The theoretical developed model values and the Experimental values show the same behaviour, indicating the reliability of the model.

#### IV. CONCLUSION

From the comparison of the results shown there's a reasonable level of agreement between the experimented theoretical and validated model, indicating the viability of the developed model. The concentration of the parameters analyzed can be predicted and various depths, the coefficient of diffusivity (D), the water velocity (v) and the irreversible decay rate (f) can as well be obtained from the equation developed.

The following conclusion was drawn from the investigation

- The industrial activity influence the deposition of chloride and phosphate in the soil environment
- The concentration of chloride and phosphate varies with depth indicating the diffusion of the component to different soil layers.
- The experimental comparison with theoretical data obtain shows a good match.
- Chloride and phosphate component are major important soil parameter that need to be monitored since plants needs high percentage of nitrate component for their growth.
- The application of least square method was apply to the values presented in table 1 to enable us establish the theoretical data which was compared with the experimental data.

f) The comparison of the theoretical and experimental data shows a good match indicating the use fullness of the approach used in this investigation.

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