

Research article

MODEL STUDIES OF HEAVY METALS TO MONITOR THE RATE OF CONTAMINATED SOIL AND WATER IN PORT HARCOURT: RIVERS STATE OF NIGERIA

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Abstract

Model studies of heavy metal to monitor the rate of contaminated soil and water has been carried out. This paper addresses the risk assessment of heavy metal in a waste dump site, numerous sample were collected, the samples were subjected to standard laboratory analysis to assess the rate of heavy metals contaminant, the metal analyzed are copper, lead, and zinc, results from the study area generated model equations, this model equations are $Y = 0.007x^2 - 0.313x + 3.85$ and $R^2 = 0.980$ (cu), $Y = -0.000X^3 + 0.036X^2 - 0.766X + 7.1$ and $R^2 = 1$ (Zn) $Y = -0.000x^3 + 0.0012x^2 - 0.338x + 3.15$ and $R^2 = 1$ (Pb), $Y = 0.005X^2 - 0.190X + 1.967$ and $R^2 = 0.097$ (Cu), $Y = 0.011x^2 - 0.366x + 3.13$ and $R^2 = 0.995$,(Zn), $Y = 8E-06X^3 - 0.000X^2 + 0.005$ and $R^2 = 1$ (Pb), $Y = -8E-05X^3 + 0.005X^2 - 0.0115X + 0.78$ and $R^2 = 1$ (Pb), $Y = 0.001x^2 - 0.139x + 3.39$ and $R^2 = 0.983$ (Cu), $Y = -0.00x^3 - 0.031x^2 + 0.659x - 1.7$ and $R^2 = 1$ (Zn), $Y = -0.000X^2 + 0.018X - 0.164$ and $R^2 = 0.997$ (Pb), $Y = 0.000X^3 - 0.022X^2 + 0.446X - 2.04$ and $R^2 = 1$ (Cu), $Y = -0.000X^3 + 0.015X^2 - 0.323X + 2.319$ and $R^2 = 1$ (Zn), $Y = 2E-05X^3 - 0.001X^2 + 0.39X - 0.12$ and $R^2 = 1$ (Pb), $Y = 0.000X^3 - 0.007X^2 + 0.150X - 0.68$ and $R^2 = 1$ (Cu), $Y = 0.000X^2 - 0.012X + 0.395$ and $R^2 = 0.987$ (Zn) and $Y = -3E-05X^3 + 0.002X^2 - 0.046X + 0.53$ and $R^2 = 1$ (Pb). These model equations generated theoretical values for model prediction in the study area, variation from various heavy metals deposited on organic soils is in a continuous process at the waste dump site, this will definitely increase the pollution from heavy metals. Thus Transporting through the influence of porosity and permeability on the soil to ground water aquifers, Hence on the process of transport, the contaminant will definitely experience dispersion and diffusion, the contaminant will spread to a large area, the study area is deltaic in nature, therefore there should be thorough risk assessment on the study area to accommodate other environmental pollution, the results should be integrated in design and construction of ground water to avoid abortive wells and water related diseases from heavy metals.

Keywords: heavy metals, soil, water, copper, lead, zinc

1 Introduction

Numerous ex-situ and in-situ options exist to remove toxic heavy metal contamination from soil. Ex-situ processes such as incineration and land filling are traditional methods, which require the soil to be physically removed from the site. Excavation and land farming are traditional alternatives for the removal of heavy metals. In-situ recovery processes, such as chemical degradation and soil washing are often difficult. Recovery processes include using flocculants to separate the metals from soil, adding resins to absorb the effluents, or the mixing of clay amendments [13]. Excavation traditionally, excavation and transport of contaminated soil to an off-site landfill has been a commonly selected alternative, often due to regulatory agency pressure. However, the cost can exceed \$300 per cubic yard making large disposal efforts very expensive. This alternative also is restrained by the physical limitation of the excavation equipment. Excavations deeper than approximately 20 feet have increased equipment cost, sheeting, and risk of undermining nearby structures; therefore excavation is usually limited to small contaminated soil cleanup projects. Increased contaminated soil volume generally warrants research into treatment alternatives. The physical removal of the soils from the ground through mechanical manipulation may change the physical characteristics of the soils]. In land farming applications contaminated soil is removed and treated at an offsite location (ex-situ). The soil is spread over a large area until remediation processes are completed. Several remediation options exist. Chemical additives, soil washing, and phytoremediation methods can be applied to the contaminated soil. Remediation is able to regulate cleaning efforts at a greater efficiency due to the controlled environment present at land farming sites. However, the cost of land farming is high and it is a labor-intensive process. Contamination of the remediation site is also a drawback to land farming applications.

Chemical Degradation Chemical degradation is a process where oxidizing or reducing agents are injected into the contamination zone to degrade the contaminant into other chemicals. This oxidation-reduction reaction is performed to degrade the chemical to a by-product that has more favorable characteristics, including lower toxicity, increased mobility, volatility, or absorption. The most Common chemical degradation is capable of oxidizing many compounds in the following classes: halogenated hydrocarbons, halogenated aromatics, pesticides, and heavy metals [3,3 and 5]. The chemical reactivity of a contaminant, and its mobility within the soil during application of the oxidizing-reducing agent, will be a factor of the ultimate fate of a chemical. The interaction between dissolution and sorption at a site complicates the remedial design and frequently gives reason to eliminate this technology as a remedial alternative. In addition, unfavorable by-products are often the result of chemical degradation. These by-products may have decreased volatility or adsorption characteristics, making them more difficult to remove following chemical degradation [3, 4]. Soil washing utilizes the solubility of a substance in water to transfer it from the soil matrix into the groundwater. Typically, an underground piping network or aboveground bermed area or pit is constructed spanning the dimensions of the contaminated area. A water flow is maintained through groundwater recovery wells [2]. The groundwater is recovered through groundwater recovery wells. The groundwater is then pumped to the surface and treated. Subsequently, the treated groundwater may be reinjected into the contaminated soil area. Water was commonly used as the flushing solution. Recently, other agents, such as acids, chelating agents and phosphates, have been used to enhance the flushing rate of a chemical from the soil matter. Soil washing may be described as an accelerated precipitation and percolation process. This description is based on large quantities of water generally required to remove the contaminants from the soil matrix, compared to the low quantities of precipitation rates received in most locations. If a soil washing system is designed properly, the overall length of time for groundwater recovery and treatment can be reduced significantly [3]. A major consideration is the capacity of the groundwater recovery system. Measures must be established to verify that the groundwater recovery system will recover all the contaminants that are flushed from the soil. Additionally, the treatment system must be designed to handle the added contaminant loading [2].

Heavy metal contamination of soil is one of the most important environmental problems throughout the world [6, 9]. The ability of heavy metals to accumulate and cause toxicity in biological systems humans, animals, microorganisms and plants has been reported [6, 7, and 10]. As chemical hazards, heavy metals are non-biodegradable and can remain almost indefinitely in the soil environment. However, their availability to biota can change considerably depending on their chemical speciation in the soil. The adequate protection and restoration of the soil ecosystems, therefore, require the characterization and remediation of soils that are contaminated with heavy metals [11, 13]. Remediation techniques include: (i) *ex-situ* (excavation) or *in-situ* (on-site) soil washing/leaching/ flushing with Chemical agents, (ii) chemical immobilization/stabilization method to reduce the solubility of heavy metals by adding some non-toxic materials into the soils, (iii) Electrokinetics (electromigration), (iv) covering the original polluted soil surface with clean soils, (v) dilution method (mixing polluted

soils with surface and subsurface clean soils to reduce the concentration of heavy metals), (vi) phytoremediation by plants such as woody trees [8,11,and 15]. Soil washing is particularly frequently used in soil remediation because it: (i) completely removes the contaminants, hence ensures the rapid cleanup of a contaminated site [1,5], (ii) meets specific criteria, (iii) reduces or eliminates long-term liability (iv) may be the most cost-effective solution and (v) may produce recyclable material or energy [8]. Since heavy metals are sparingly soluble and occur predominantly in a sorbed state, washing the soils with of cations in the leachates, chemical agents have to be added to the washing water [4, 5]. With chemical soil washing soil particles are cleaned by selectively transferring the contaminants from the soil into solution [1, 5]. The effectiveness of washing is closely related to the ability of the extracting solution to dissolve the metal contaminants in soils. However, the strong bonds between the soil and metals make the cleaning process difficult. Therefore, only extractants capable of optimally dissolving the metals must be carefully sought during soil washing. Several classes of chemicals used for soil washing include surfactants, co solvents, cyclodextrins, chelating agents and organic acids [1, 2, 8, 13, and 15]. All these soil washing extractants have been developed on a case-by-case basis depending on the contaminant type at a particular site. A few studies have indicated that the solubilization/exchange/extraction of heavy metals by washing solutions differs considerably for different soil types. Strong acids attack and degrade the soil crystalline structure at extended contact times. For less damaging washes, organic acids and chelating agents are often suggested as alternatives to straight mineral acid use [14, 15].

2. Materials and Method

Heavy Metals Determination (AAS):

A measured quantity of the samples were transferred into a Kjeldahl flask; 20ml of concentrated nitric acid (HNO_3) was added and the sample pre-digested by heating gently for 20mins. More acid was thereafter added and digestion was continued for 30-40mins. Digestion was stopped when a clear digest was obtained. The flask was cooled and the content transferred into a 50ml volumetric flask and made to the mark with distilled water.

The equipment was conditioned by auto-zeroing it with distilled water and with 2% HNO_3 . The pre-treated sample was analyzed for heavy metals using the appropriate hollow cathode element of each metal of interest at the appropriate wavelength, lamp current, band-pass, and background correction. The results were plotted, it produce model equations. The model will produce theoretical values for model prediction

3. Results and Discussion

Different type heavy metals deposited on the study area are presented in tables and figure below

Table: 1 of different type of heavy metals deposited from waste dump site

| Depth | conc copper (Cu) | conc copper (Cu) location 2 | Conc (Cu) Location 3 |
|-------|------------------|-----------------------------|----------------------|
| 10 | 1.5 | 0.52 | 5.93 |
| 20 | 0.31 | 0.79 | 5.92 |
| 30 | 1.15 | 1.06 | 3.5 |
| 40 | 2.86 | 3.62 | 1.59 |
| Depth | conc copper (Zn) | Conc (Zn) Location 2 | Conc (Zn) Location 3 |
| 10 | 2.08 | 0.52 | 5.93 |
| 20 | 2.36 | 0.54 | 5.92 |
| 30 | 1.15 | 2.08 | 3.5 |
| 40 | 2.86 | 6.62 | 1.59 |

| | | | |
|-------|------------------|----------------------|----------------------|
| Depth | conc copper (Pb) | Conc (Pb) Location 2 | Conc (Pb) Location 3 |
| 10 | 0.9 | 0.001 | 0.13 |
| 20 | 0.31 | 0.07 | 0.15 |
| 30 | 0.46 | 0.14 | 0.33 |
| 40 | 0.43 | 0.27 | 0.16 |
| Depth | conc copper (Cu) | Conc (Cu) location 2 | Conc (Cu) loation 3 |
| 10 | 2.14 | 0.52 | 0.17 |
| 20 | 1.41 | 0.79 | 0.18 |
| 30 | 0.68 | 1.06 | 0.05 |
| 40 | 0.65 | 3.62 | 0.48 |
| Depth | Conc (Zn) | Conc (Zn)Location 2 | Conc (Zn)) loation 3 |
| 10 | 2.14 | 0.4 | 0.28 |
| 20 | 2.11 | 0.22 | 0.21 |
| 30 | 0.68 | 0.51 | 0.14 |
| 40 | 0.32 | 0.001 | 0.13 |
| Depth | Conc (Pb) | Conc (Pb) location 2 | Conc (Pb)) loation 3 |
| 10 | 0.007 | 0.15 | 0.26 |
| 20 | 0.13 | 0.24 | 0.24 |
| 30 | 0.24 | 0.24 | 0.26 |
| 40 | 0.29 | 0.24 | 0.11 |

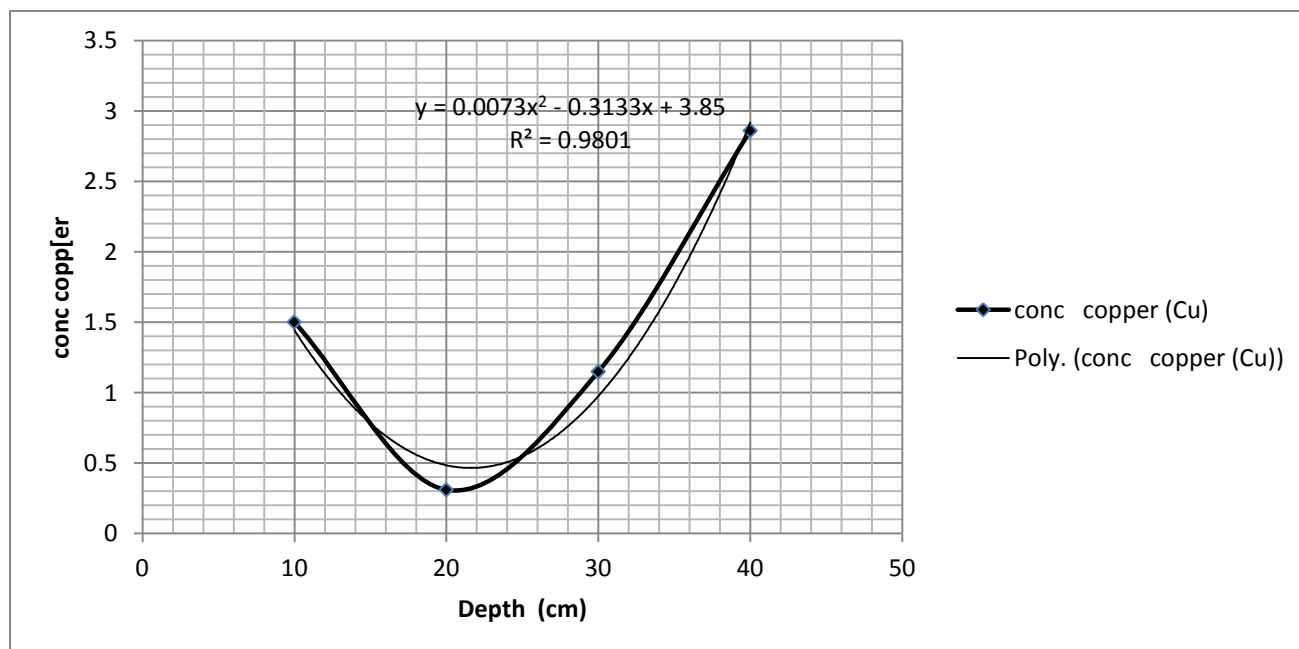


Figure 1: heavy metal deposition at different depth

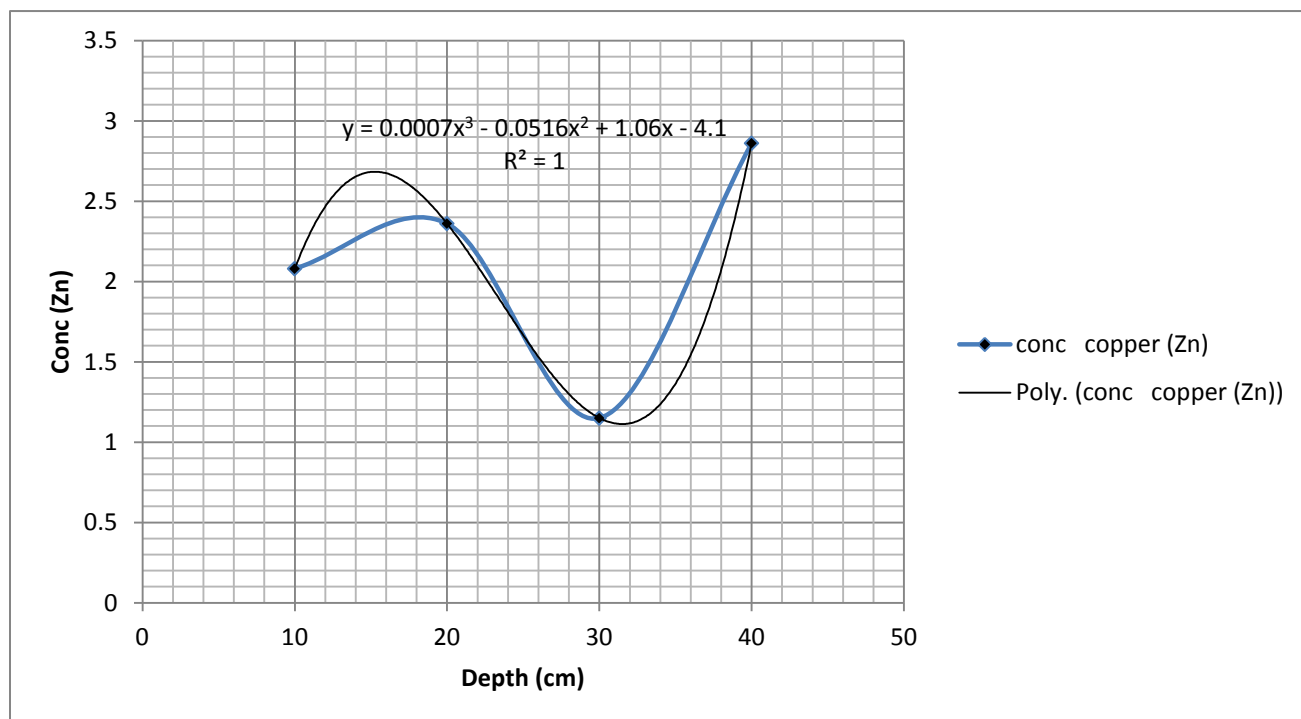


Figure 2: heavy metal deposition at different depth

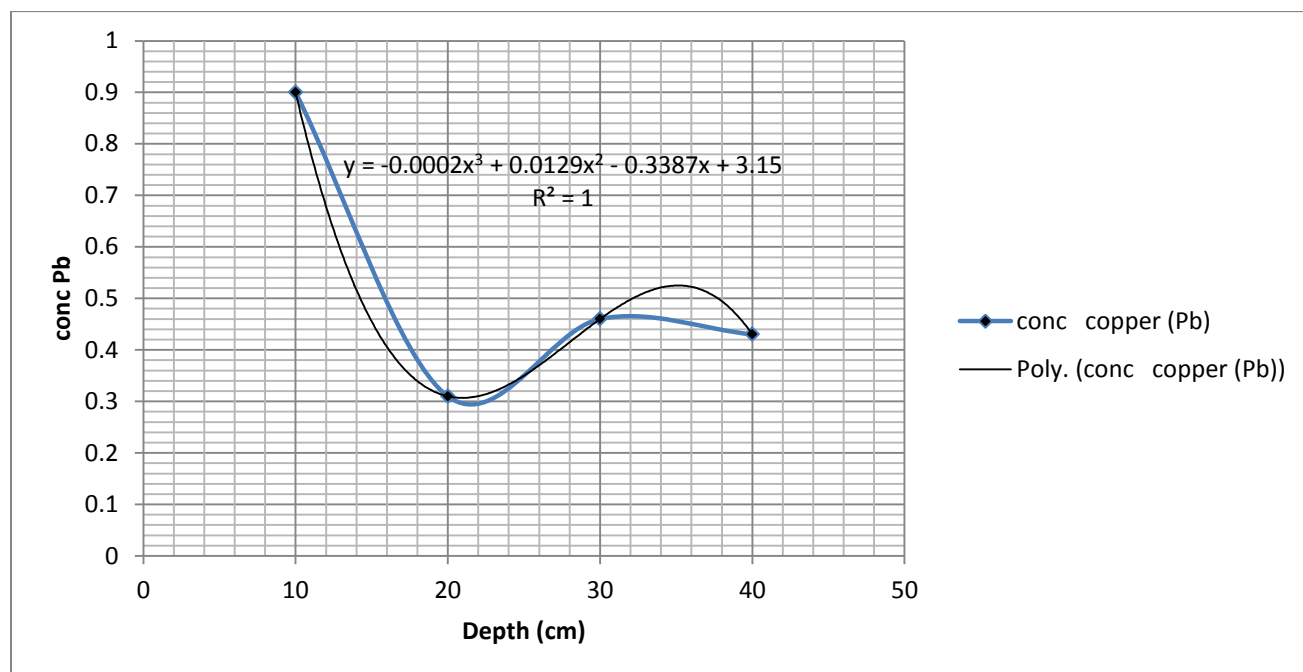


Figure 3: heavy metal depositions at different depth

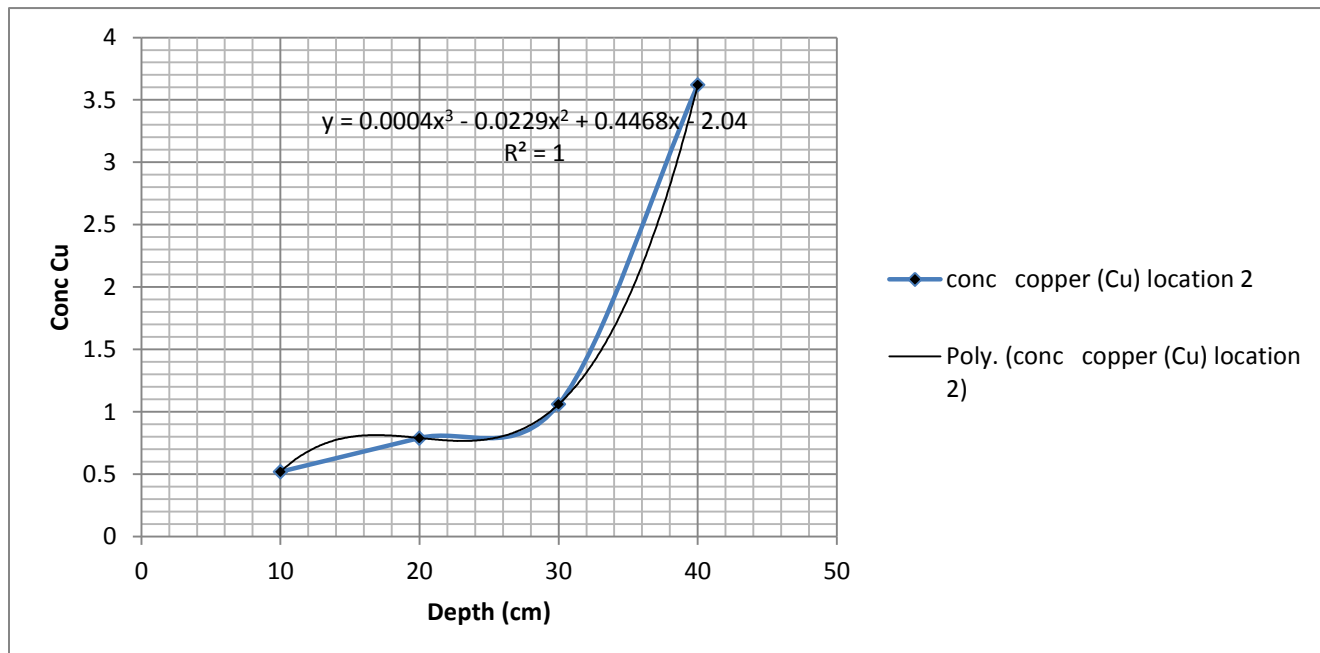


Figure 4 : heavy metal depositions at different depth

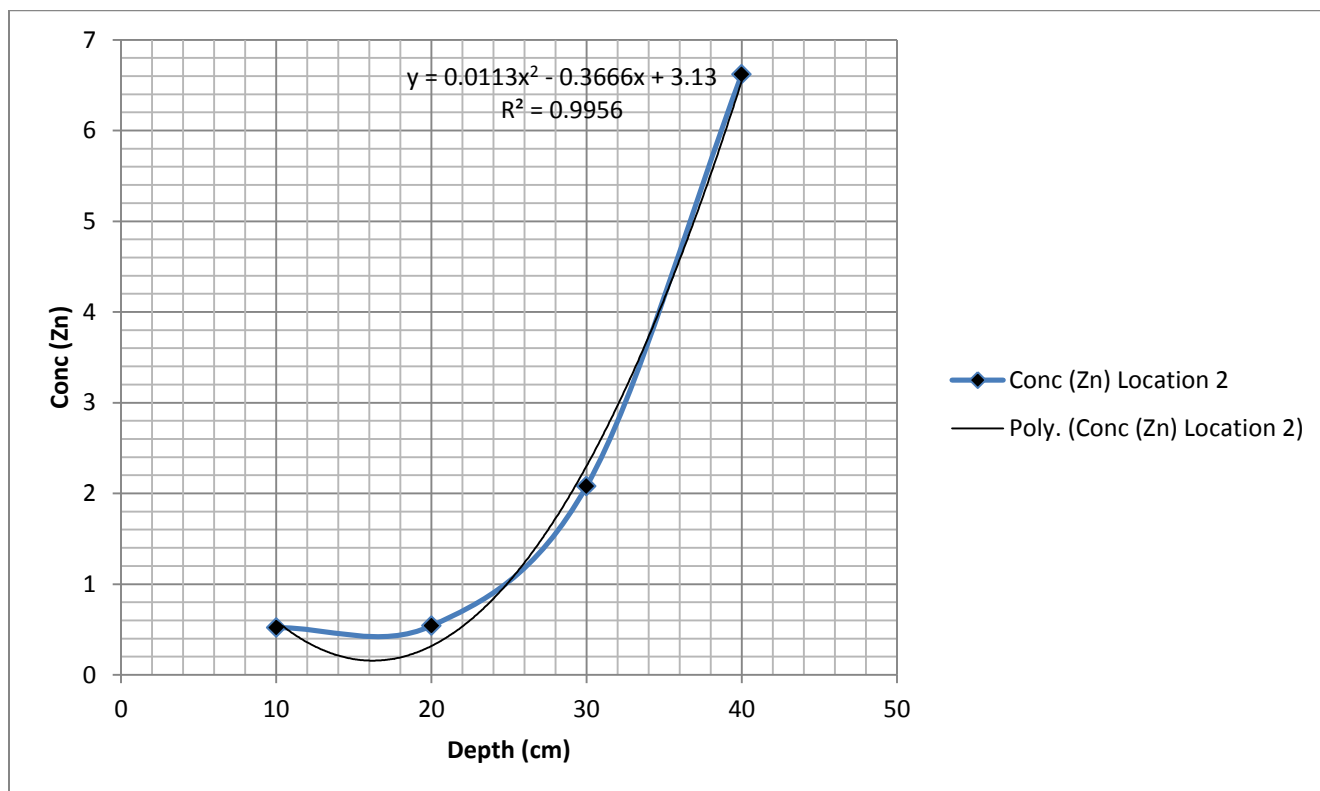


Figure 5: heavy metal depositions at different depth

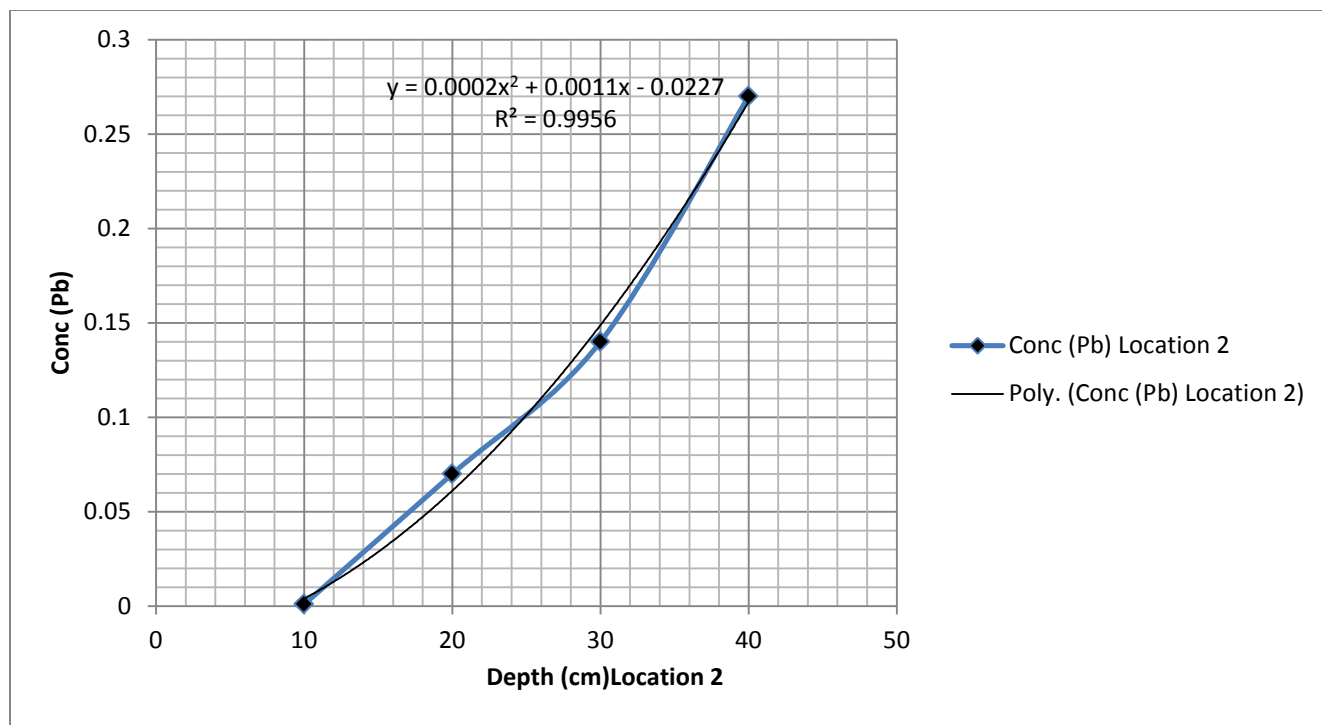


Figure 6: heavy metal depositions at different depth

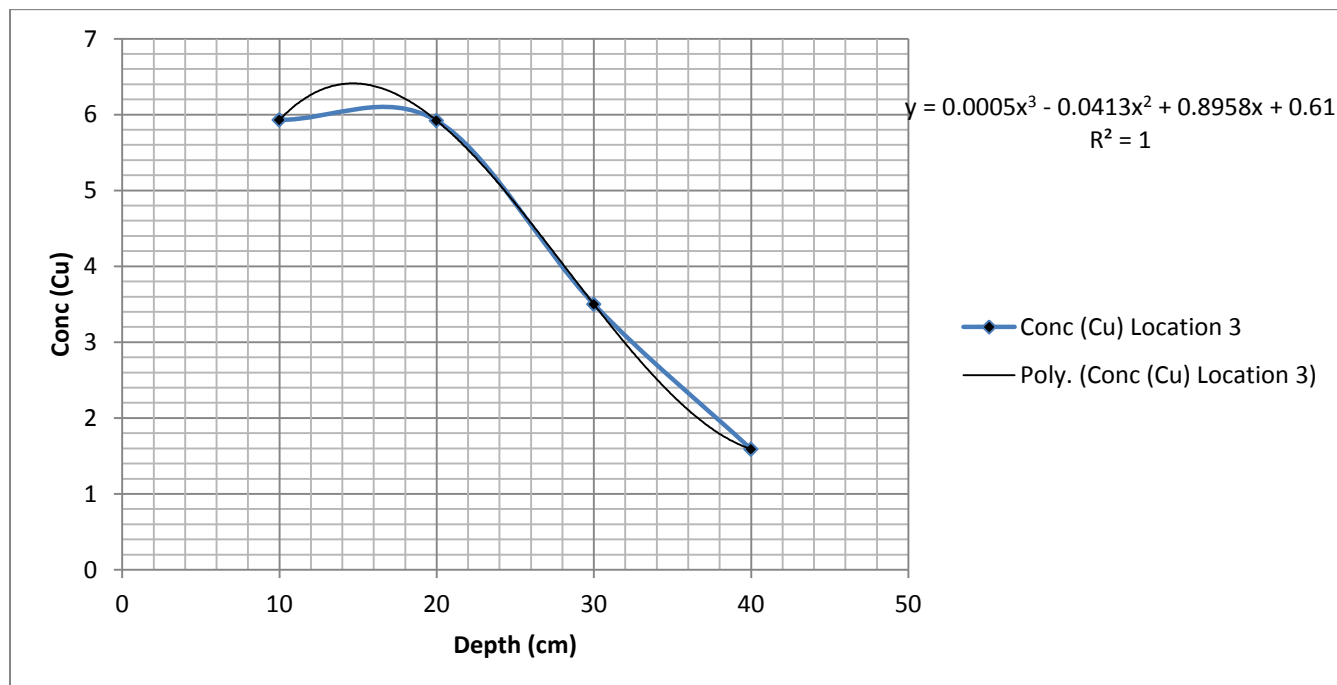


Figure 7: heavy metal depositions at different depth

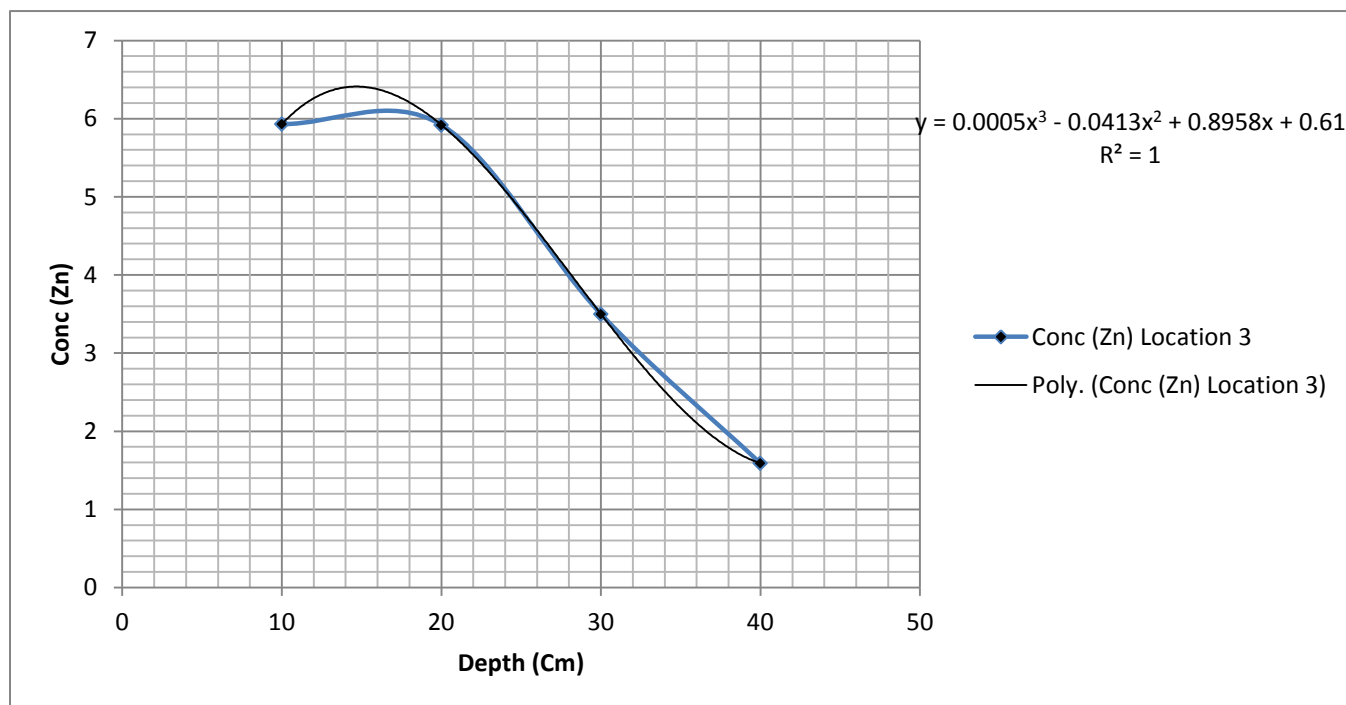


Figure 8: heavy metal depositions at different depth

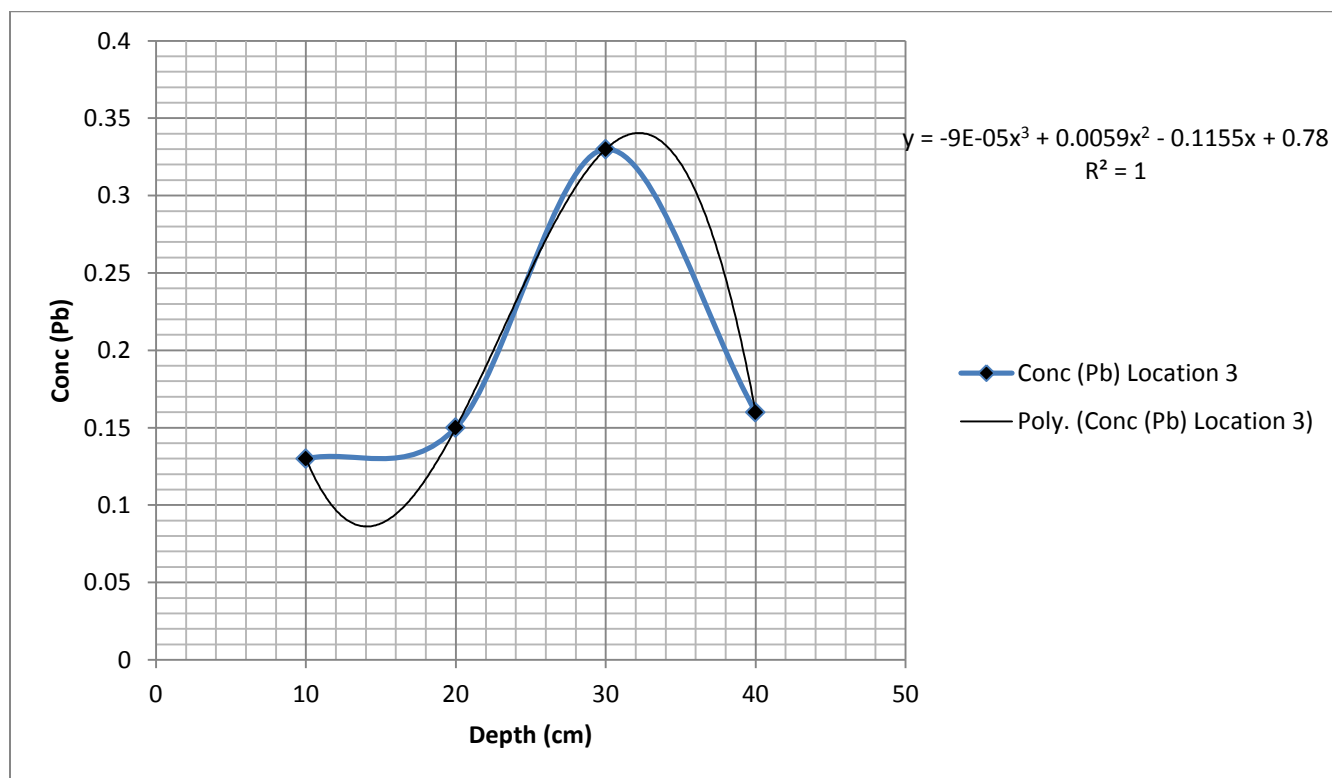


Figure 9: heavy metal depositions at different depth

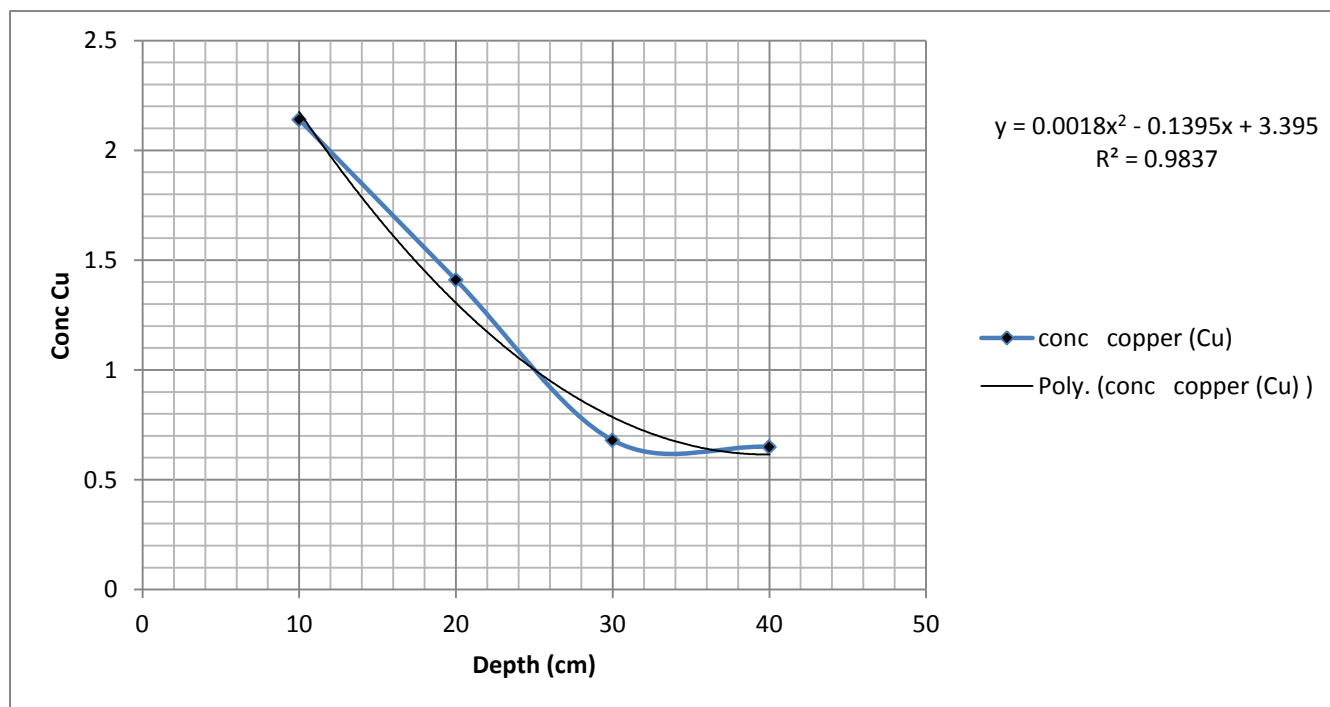


Figure 10: heavy metal depositions at different depth

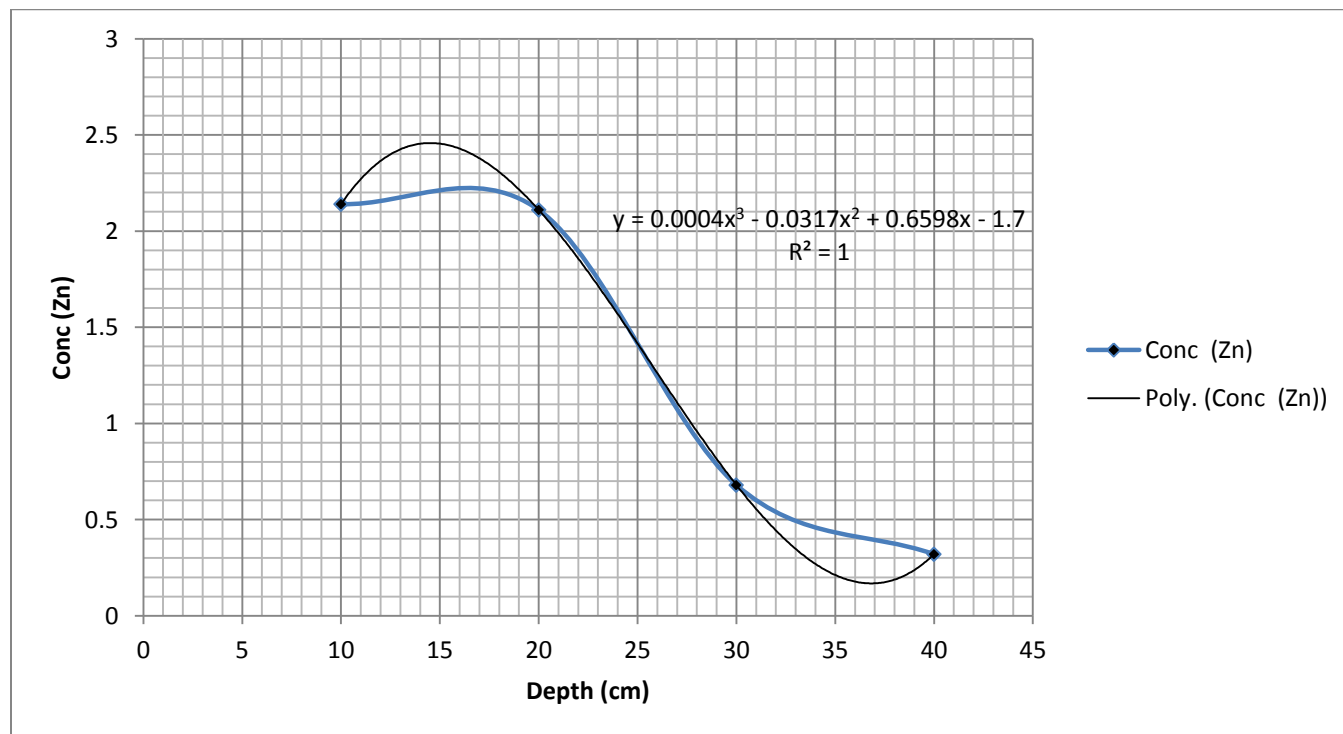


Figure 11: heavy metal depositions at different depth

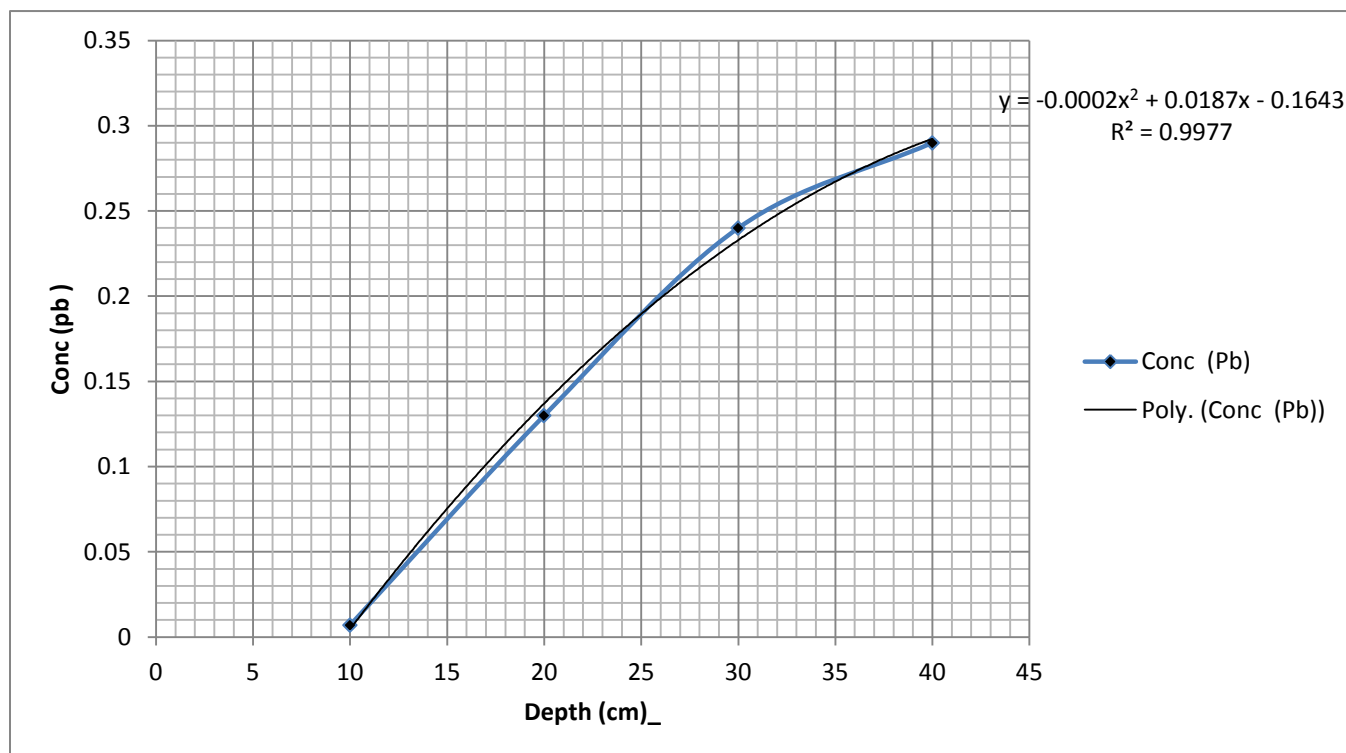


Figure 12: heavy metal depositions at different depth

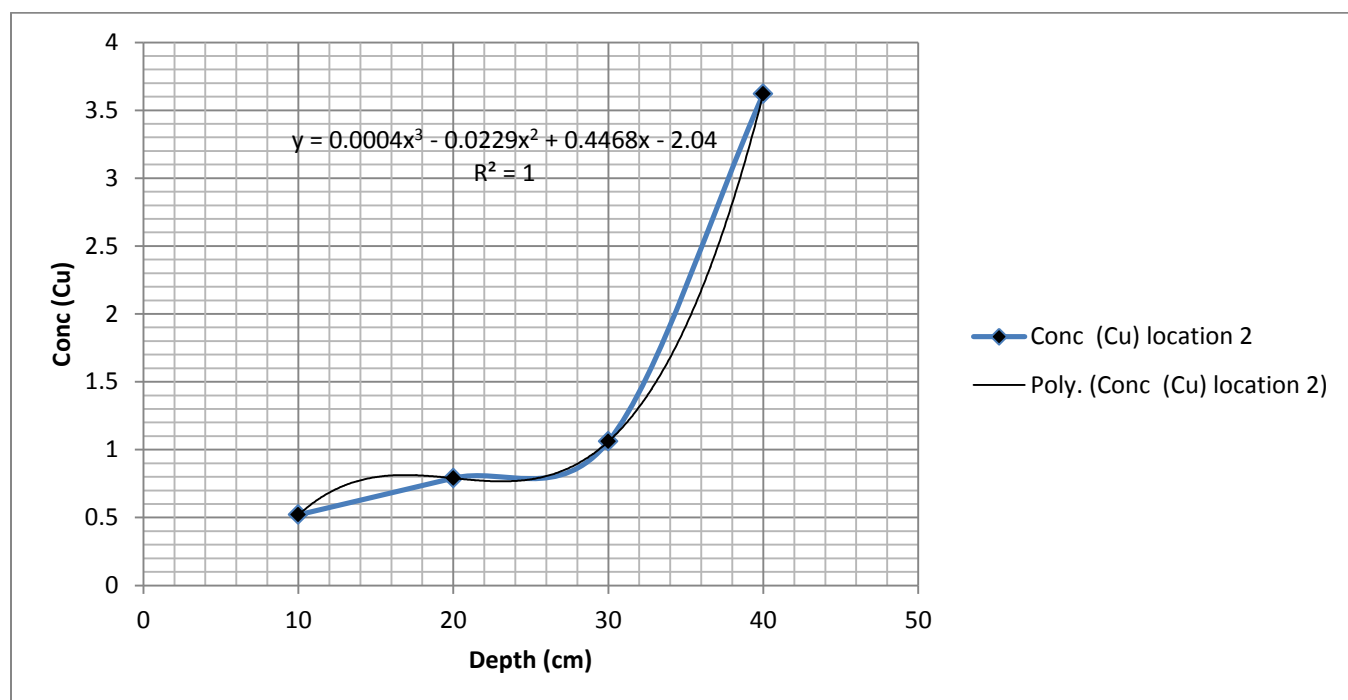


Figure 13: heavy metal depositions at different depth

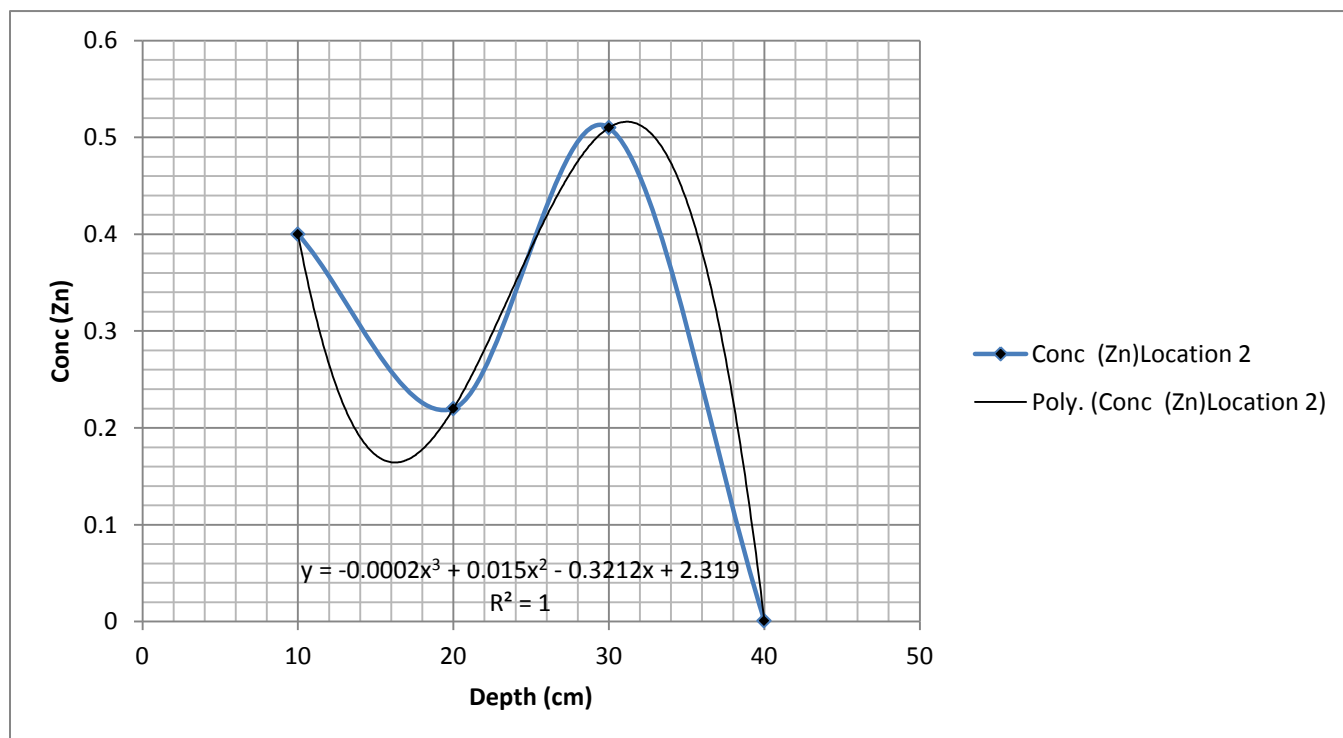


Figure 14: heavy metal depositions at different depth

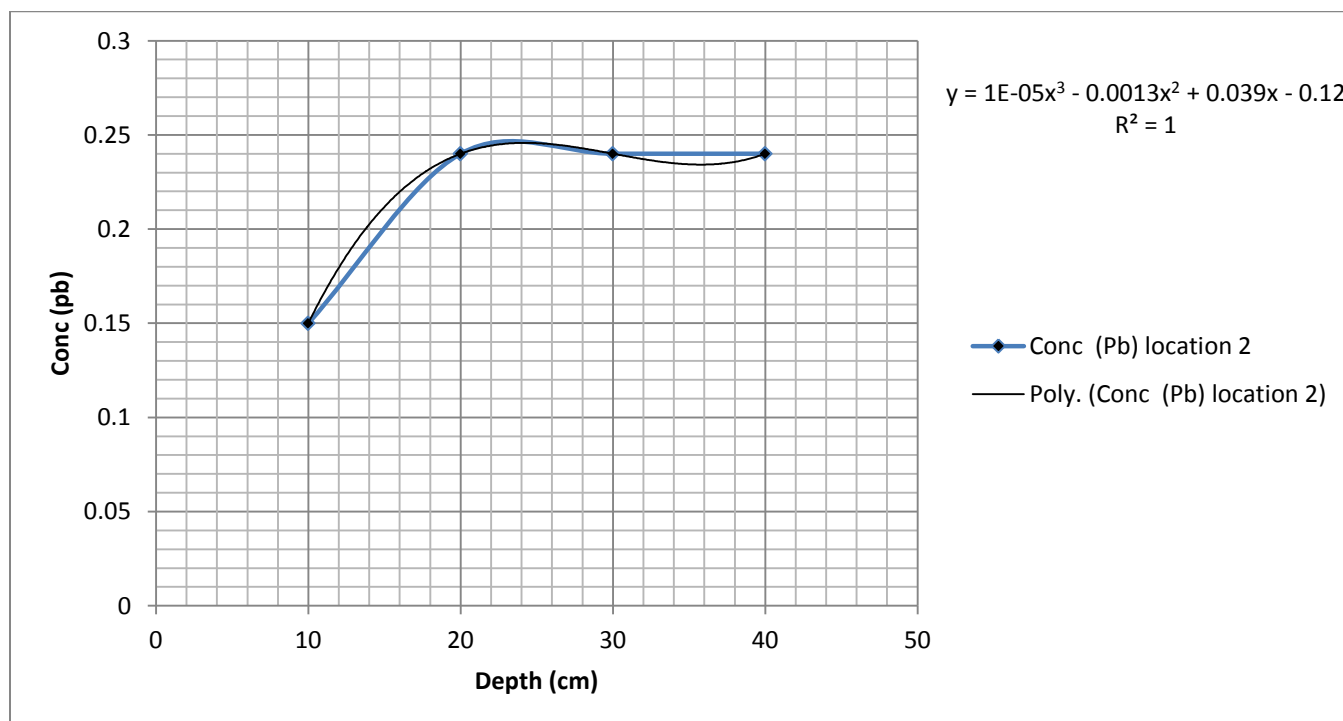


Figure 15: heavy metal depositions at different depth

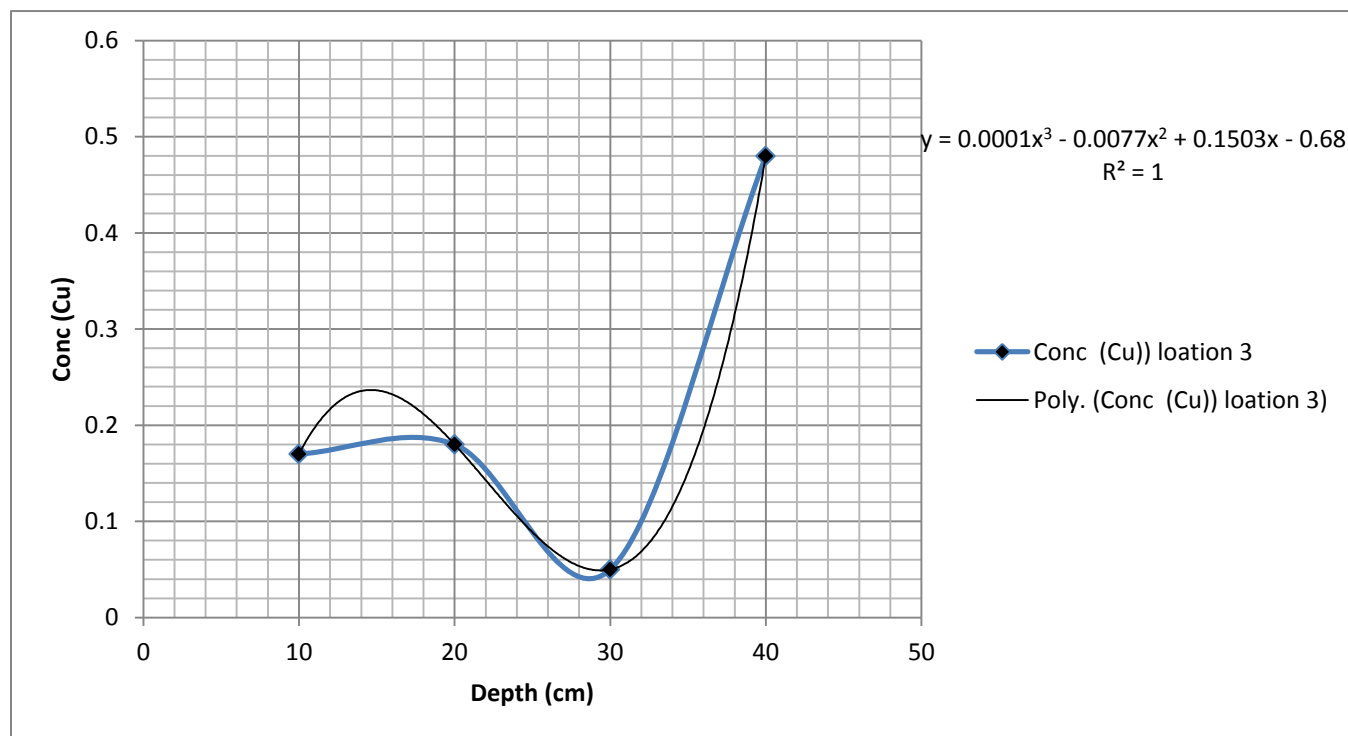


Figure 16: heavy metal depositions at different depth

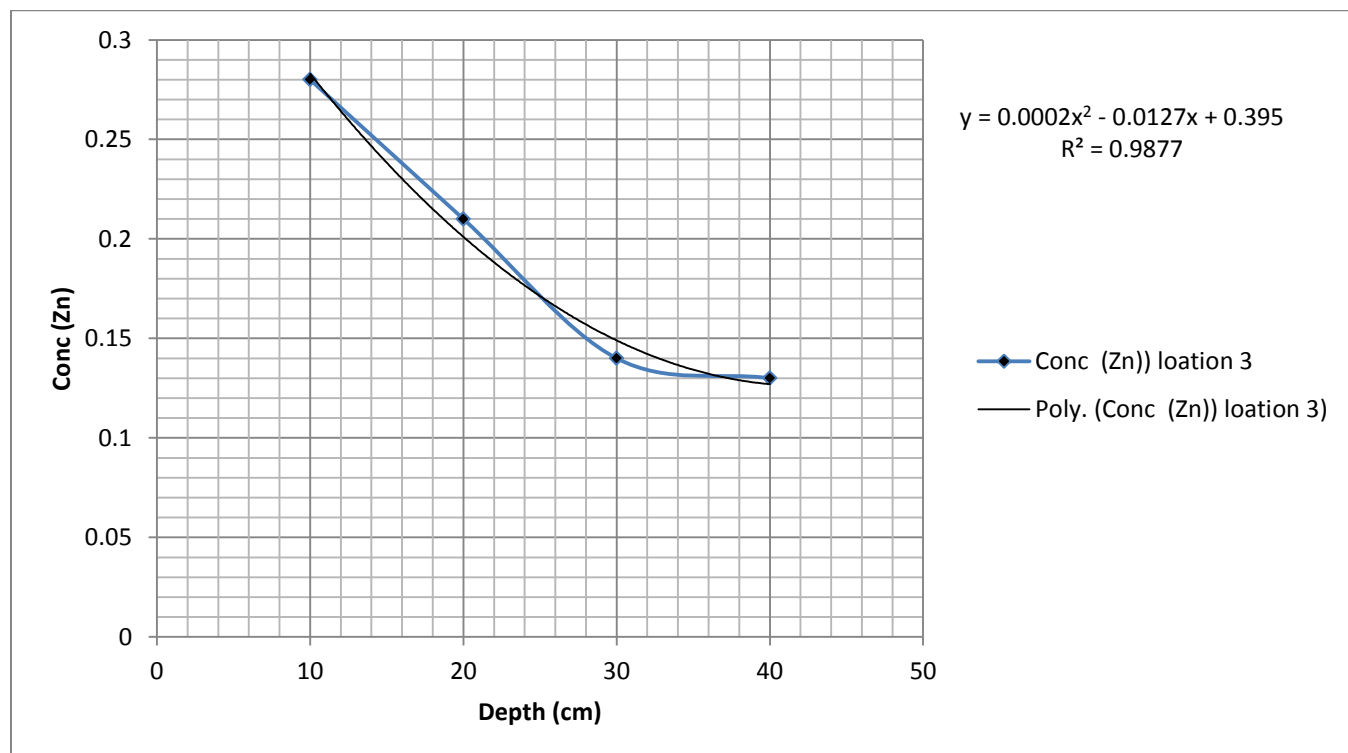


Figure 17: heavy metal depositions at different depth

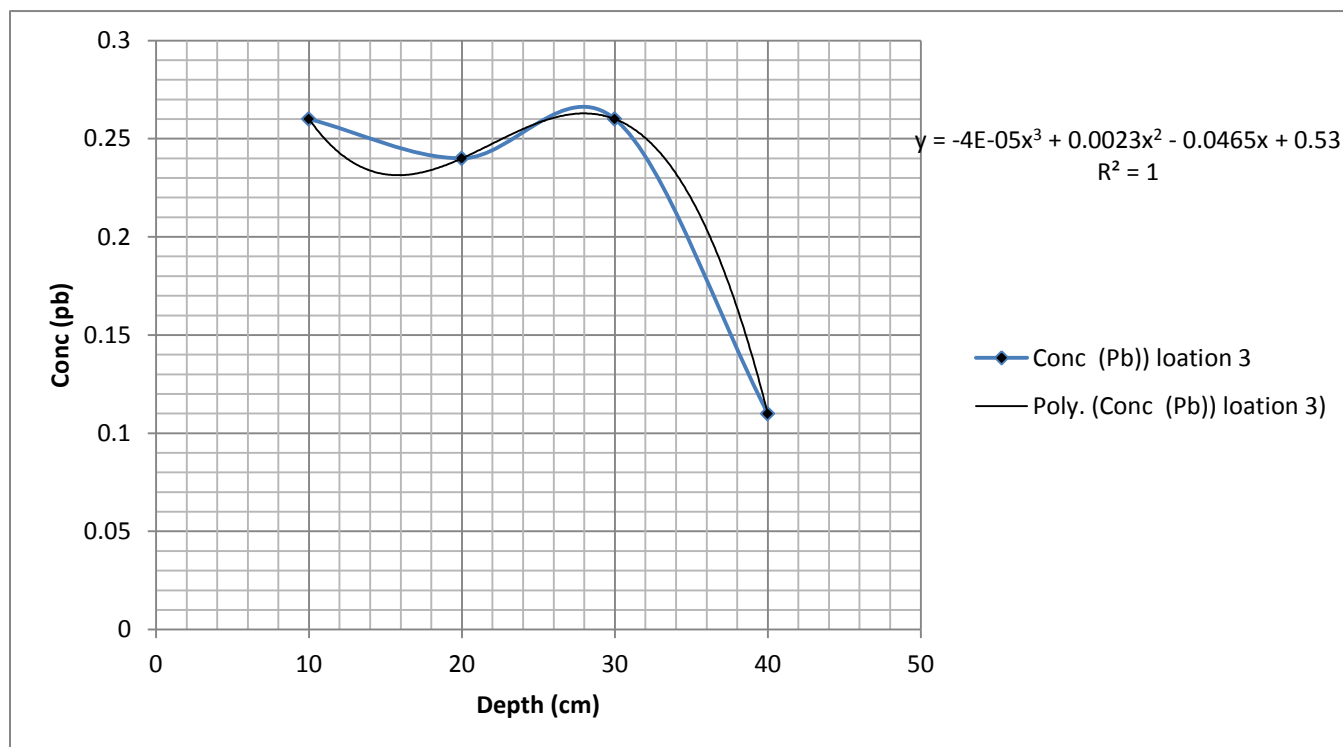


Figure 18: heavy metal depositions at different depth

Figure 1 shows that the concentration of the heavy metal deposited a gradual increase at 10cm deep and suddenly decrease to 20cm and finally increase with increase in depth at 2.8mg/l, 40cm deep where the optimum value were recorded. Figure 2 produced an oscillation deposition, the heavy metal in the soil were found to deposit in a fluctuation form, where an optimum value were recorded at 3.49mg/l, 30cm deep and finally decrease to 2.8mg/l at 40cm deep. Figure 3 where found to produced its highest concentration at 10cm of 0.9mg/L and suddenly decrease with increase in depth in an oscillation form to where the lowest were recorded at 0.44mg/l, 40cm deep. While figure 4 produced its lowest deposition of metal at 10cm, 0.5mg/L and it gradually increased to the optimum level at 3.5m/l of 40cm deep. Figures 5 and 6 developed the same form of deposition, the lowest of figure 5 at 0.03mg/l while figures 6 at 0.05 mg/l, the optimum level were found to deposit at 6.6 and 0.37 respectively. Figures 7 deposited its highest rate of heavy metal at 5.9mg/L of 10cm and gradually decrease with depth down to where the lowest were recorded at 14 mg/l of 40cm deep. Figure 8 were found in an oscillation form, the lowest, 0.113mg/l at 10cm it increased in a fluctuation form and recorded its optimum level at 0.333mg/L and finally decrease down to 0.16 mg/l at 40cm deep. Figure 9 is similar to figure 8, it also deposited its metals in soil in an oscillation form like figure 8 where the lowest were recorded at 0.113mg/l and the optimum level at 0.32mg/l and finally decrease down to 0.16mg/l at 40cm deep. Figure 10 produce its highest, 2.21mg/L at 10cm and gradually decrease to where the lowest were found to deposit at 0.51mg/l, 40cm deep. Figure 11 were found to contain 2.2mg/L at 10cm and it gradually decrease with depth down to the lowest at 0.03mg/L, 40cm. Figure 12 increase with depth, the lowest content of metal were found at 0.5mg/l and gradually increase with depth to the optimum level at 0.37mg/L, 40cm deep. figure 13 in a fluctuation form deposited the lowest 0.00, 40cm deep and to the optimum at 0.5mg/l. Figure 14 developed slight fluctuation the lowest content were found to deposit at 0.15mg/L, 10cm deep and its optimum 22cm, it slight decrease between 30mg/l and 40cm of 0.25mg/L figure 15 deposited its metal content in an oscillation form the lowest at 0.02mg/l and it increase to the maximum level at 0.5mg/l, 40cm deep. Figure 16 the

metal deposition developed its concentration in an oscillation where the lowest were recorded at 0.02mg/L and the optimum at 0.49mg/L at 40cm deep. Figure 17 developed its level of deposition in gradual process the optimum were recorded at 0.26mg/L, 10cm and gradually decreased to 0.013mg/l at 40cm, finally figure 18 produces a similar result like figure 17 but with slight fluctuation, the optimum value were recorded at 0.20mg/L and it decreased down to where the lowest were recorded at 0.12, 40cm deep. The deposition of the heavy metals in the study location generated a lot of variation; it produced a high percentage of heavy metal content in organic soils. The study location is in a waste dump site, with high deposition different type of heavy metals, a continuous process of waste dump will definitely leach to ground water aquifer; it implies that there is high risk of ground water pollution emanated from heavy metals. The causes of this fast contamination are based on the geological formation of the area. The high level of porosity, permeability and void ratio will no doubt increase the high percentage of heavy metal concentration, as a deltaic environment, the deltaic nature produce short fresh water aquifer and water table increase from high rain intensities, the contamination from this condition will definitely develop a lots of dispersion and diffusion, this condition implies that the contaminants will spread a large area and pollute ground water aquifer, this ugly serge is a serious issues, that why the study is imperative because most settlers are suffering from water related diseases including high rate of death. Finally there should be a risk assessment in the study area, and the results from the study should be integrated in the design and construction of groundwater and other environmental issues.

4. Conclusion

High content of heavy metals in organic soil has been observed, the results from organic soil from zero to forty centimeters has produced results showing high deposition of heavy metals in the study location. The results also show high level of risk from heavy metals pollution. This is not environmental friendly; the content of heavy metals shows high rate of pollution on soil and water environment, this metal will definitely leach to groundwater aquifer, this ugly serge is a serious issue, this study is imperative because the risk level should be assessed. Hence high content of heavy metals in soil dispersing and diffusing to ground water aquifer is a serious risk to human life in the study area. There should be thorough risk assessment on heavy metals, these results should be integrated in design and construction of water boreholes in other to avoid death trap for human.

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