World Journal of Science and Technology Research
Vol. 1, No. 6, August 2013, PP: 124-134, ISSN: 2329 - 3837 (Online)
Available online at www.wjst.org

Research article

MODELING THE TRANSPORT OF ARSENIC ON PORE FLUID AND SOLID SURFACE IN HETEROGENEOUS SOIL FORMATION, NIGER DELTA OF NIGERIA

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Abstract

Mathematical model that express the trace of Arsenic contaminant has been thoroughly evaluated, the model were established to trace the transport of arsenic in shallow aquifers, theoretical values generated from the model where compared with other experimental values for validation, both parameters establish a favorable fit as presented in the figures, the values express high concentration of Arsenic at three metres in ten days, why rapid increase were observed at the porous medium were increase of contaminant were recorded between nine metres and at the period of thirty days, but the optimum values was recorded at ten days at three metres, it deposited one hundred and seventy-nine milligram per liter. Arsenic as a contaminant could not experience any inhibition from any microbial deposition; this was observed on the lowest deposition of the metal at thirty meters at the period hundred days, it still at a very high degree of concentration, despite its degradation in the figure presented, it is recommended that ground water system with treatment plant should be designed in such contaminated zone in the study area to avoid high death rate from such pollution. **Copyright © WJST, all rights reserved.**

Key words: modeling Arsenic transport on pore fluid and heterogeneous formation

1. Introduction

The rate arsenic in pore fluid on soil water environment has been thoroughly assessed, different types of pollution such as carcinogenic, mutagenic and teratogenic [plant et al, 2003] arsenic (As) is a major component in more than 245 minerals and is ubiquous in the surroundings [karl]. It is responsible for bladder, kidney, liver, lung, and skin cancers and is listed as a Class A human carcinogen by the USEPA [Mandal and Haris, 2002]. Both acute and chronic poisoning to humans has raised great concerns, especially in heavily contaminated areas such as Bangladesh and West Bengal, India and Nigeria. The severe health tribulations were described as "the furthermost mass poisoning in human history" by World Health Organization [Chen and Haris, 2002]. The average concentration of arsenic in terrestrial environments is around 1.5 to 3 mg/kg. Arsenic in the environmental comes from natural and anthropogenic sources. Arsenic is present in dropping marine sediment, iron deposits, sedimentary iron ores and manganese nodules and is commonly associated with iron hydroxides and sulfides. Among the 245 minerals, approximately 60% are arsenates, 20% sulfides and sulfo-salts and the remaining 20% includes arsenides, arsenites, oxides, silicates and elemental arsenic [Vatamaan, et al,2000]. The levels of soil arsenic range from 0.1 to 40 mg/kg in various countries. Anthropogenic sources generally exceed natural sources by 3 to 1in the environment. Arsenic can substitute for Si, Al or Fe in silicates minerals; therefore, contaminated soils usually have arsenic-rich parent materials [Ritchie, 1980, Fittz and Wenzel 2002].The utilization of natural resources by human's releases arsenic into the air, water and soil. Arsenic may accumulate in soil through use of arsenical pesticides, application of fertilizers, dusts from burning of fossil fuels, and disposal of industrial and animal wastes. It has been estimated that there are 41% of the superfund sites in the USA are contaminated with arsenic [EPA, 1997], 1.4 million contaminated sites within the European Community impacted by arsenic [ETCS.1998], and more than 10,000 arsenic contaminated sites reported in Australia [9]. These anthropogenic sources will adversely affect plants, animals and microorganisms. The main arsenic producers were USA, Russia, France, Mexico, Germany, Peru, Namibia, Sweden, and China, and these countries accounted for about 90% of the world production [Smith and Alston, 2002]. In the past, about 80% of arsenic consumption was for agriculture uses such as insecticides and pesticides. The inorganic arsenicals, primarily, sodium arsenite, were widely used since 1890 as weed killers, particularly as non-selective soil sterilants [Mandal and Suzuki, 2002]. Two thousand and five hundred tons of H_3AsO_4 were used as desiccants on 1,222,000 acres (about 495,000 ha) of U.S. cotton in 1964 [6]. Fluor- chrome-arsenic-phenol (FCAP), chromated copper arsenate (CCA) and ammoniacal copper arsenate (ACA) were used in 99% of the arsenical wood preservatives [10]. Several arsenic compounds are currently used for feed additives, such as H_3AsO_4, 3-nitro-4-hydroxy phenylarsonic acid, 4-nitrophenylarsonic acid etc Mebarg and ,Hartler, 2002 Karl, 2003].

Changes in arsenic speciation occurs both abiotically and biotically, the latter was catalyzed by organisms. Arsenite oxidation can be catalyzed by iron oxides, manganese oxides and organic compounds when the oxidation potential is high enough and usually at low pH (< 3), though it is slow. Most arsenite is oxidized microbiologically as a detoxification mechanisms or as elector donor, which are known as heterotrophic arsenite oxidizers (HAOs) or chemolithoautotrophic arsenite oxidizers (CAOs) [Perter, 1981]. HAOs incorporate a periplasmic enzyme to catalyze the oxidation reaction, which converts arsenite encountered on the cell's outer membrane. This presumably makes it less likely to enter the cell. On the other hand, CAOs use As an analogue of the macronutrient phosphorus, arsenic is somewhat unusual comparing with transition metals and metalloids. Plants growing on arsenate contaminated soils will assimilate high levels of arsenate unless they have altered phosphate transport mechanisms [Chen and stolz,2003]. In spite of that, arsenate resistance has been identified in a number of plant species growing on arsenic contaminated soils including *Andropogon scoparius, Agrostis castellana, A. delicatula, A. capillaris, Deschampsia cespitosa,* and *Plantago lanceolata* [Sharpes et al, 2010]. In those plants, resistance is generally achieved via suppression of the high affinity phosphate uptake system. It is thought that this suppression reduces arsenate influx to a level at which the plant can detoxify by constitutive mechanisms [Mebarg and Macnair, 1994]. Thus, arsenate sensitivity is intimately linked to phosphate nutrition, with increased phosphate status leading to reduced arsenate uptake [Mebarg and Macnair, 1994]. Indeed, most arsenate resistant plants always suppress the high affinity uptake system and are insensitive to plant phosphorous status [Mebarg and Hertley, 2002, Anhini, 2009].

2. Materials and Method

Column experiments were also performed using soil samples from several borehole locations, the soil samples were collected at intervals of three metres each (3m). An Arsenic solute was introduced at the top of the column and effluents from the lower end of the column were collected and analyzed for Arsenic and the effluent at the down of the column were collected at different days, analysis, velocity of the transport were monitored at different days. Finally, the results were collected to be compared with the theoretical values.

3. Theoretical background

$$\frac{\phi\partial C}{\partial t} = \frac{\partial C}{\partial z_i}\left[\phi Dy\frac{\partial C}{\partial z_i}\right] - \frac{\partial C}{\partial z_i}\left[\phi CUi\right] - C^{*}\alpha^{*} + \nabla \qquad \ldots\ldots\ldots\ldots\ldots\ldots \qquad (1)$$

$$\frac{\partial C}{\partial t} = SC_{(t)} - C_{(o)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad (2)$$

$$\frac{\partial C}{\partial z} = SC_{(z)} - C_{(o)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad (3)$$

$$\frac{\partial C}{\partial z_i} = SC_{(z)} - C_{(o)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad (4)$$

$$\frac{\partial C}{\partial z_i} = SC_{(z)} - C_{(o)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad (5)$$

$$C = C_o \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad (6)$$

Substituting (2), (3), (4), (5) and (6) into (1) yield

$$\phi\left[SC_{(t)} - SC_{(z)} - C_{(o)}\right] - \phi Dy\left[SC_{(z)}\right] - SC_{(z)}\left[\phi Ui\right] - C^{*}\alpha^{*} + \nabla \qquad \ldots\ldots\ldots \qquad (7)$$

$$\phi SC_{(t)} - \phi SC^{1}{}_{(z)} - C_{(o)} - \phi Dy\, SC_{(z)} - SC_{(z)}\,\phi Ui - C\,\alpha + \nabla \qquad \ldots\ldots\ldots \qquad (8)$$

Considering the following boundary condition

at $t = 0,\ C^{1}{}_{(0)} = C_0 = 0$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad (9)$$

$$C_{(z)} \neq 0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad (10)$$

But considering the boundary condition

At $t > 0,\ \ C^{1}{}_{(0)} = C_{(0)} = C_{(0)}$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad (11)$$

$$\phi SC_{(t)} - \phi Dy\, SC_{(z)}\ C_{(z)} - \phi Ui - C\,\alpha + \nabla - \phi SC_{(o)} + \phi C_{(o)} + \phi DyCUi\,Ca + \nabla C_o \qquad (12)$$

$$\left[SC_{(t)} - SC_{(z)} - \phi Dy\,\phi CUi\ C\,\alpha + \nabla S\right]C_{(t)} - C_{(z)} - \left[\phi S + \phi + \phi Dy\,\phi CUi + C\alpha + \nabla\right]C_o \qquad (13)$$

$$C_{(z,t)} = \frac{\phi S + \phi + \phi Dy\,\phi CUi\ C\alpha + \nabla}{\phi S - \phi S - \phi Dy\,\phi CUi\ \ C\alpha + \nabla}C_o \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad (14)$$

Applying quadratic expression we have

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad (15)$$

Where $a = \phi$, $b = \phi Dy\phi CUi$, $c = C\alpha\nabla$

$$S = \frac{\phi Dy\phi CUi \pm \sqrt{\phi Dy\phi CUi^2 + 4\phi C\alpha\nabla}}{2\phi} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \qquad (16)$$

$$S_1 = \frac{\phi Dy\phi CUi - \sqrt{\phi Dy\phi CUi^2 + 4\phi C\alpha\nabla}}{2\phi} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \qquad (17)$$

$$S_2 = \frac{\phi Dy\phi CUi + \sqrt{\phi Dy\phi CUi^2 + 4\phi C\alpha\nabla}}{2\phi} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \qquad (18)$$

$$S_1 = \phi Dy\phi CUi + \frac{\left\lfloor\sqrt{\phi Dy\phi CUi^2 + 4\phi C\alpha\nabla}\right\rfloor}{2\phi} S_2 + \phi Dy\phi CUi - \frac{\sqrt{\phi Dy\phi CUi^2 + 4\phi C\alpha\nabla}}{2\phi} -$$

$$\ell^{\left[\phi Dy\phi CUi + \frac{\sqrt{\phi Dy\phi CUi^2 + 4\phi C\alpha\nabla}}{2\phi}\right]\frac{L}{V} + \phi Dy\phi CUi - \phi Dy\phi CUi \frac{\sqrt{\phi Dy\phi CUi^2 + 4\phi C\alpha\nabla}}{2\phi}} \qquad \ldots\ldots\ldots\ldots\ldots \qquad (19)$$

Applying Laplace inverse of the equation, we obtained

$$C_{(t)} = \left[\frac{\phi}{t} + \phi + \phi Dy\phi CUi + \phi C\alpha\nabla\right] C_o\, \ell^{\left[\phi Dy\phi CUi \frac{\sqrt{\phi Dy\phi CUi + 4\phi C\alpha\nabla}}{2\phi}\right]t} +$$

$$\ell^{\left[\phi Dy\phi CUi - \frac{\sqrt{\phi Dy\phi CUi + 4\phi C\alpha\nabla}}{2\phi}\right]t} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad (20)$$

But if $t = \frac{z}{v}$

$$\left[C\left[Z,V\right] = \frac{\phi}{\frac{t}{Z}} + \phi + \phi Dy\phi CUi + \phi C\alpha\nabla \right] C_o \left[\phi Dy\phi CUi \frac{\sqrt{\phi Dy\phi CUi + 4\phi C\alpha\nabla}}{2\phi} \right]^{\frac{Z}{V}} \qquad (21)$$

Considering the following boundary condition at

$$t = 0,\ C^1{}_0 = 0,\ C_0 = 0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad (22)$$

$$C_{(t)} = \left[\frac{\phi}{t} + \phi + \phi Dy\phi CUi + \phi C\alpha\nabla\right] C_o\, \ell^{\left[\phi Dy\phi CUi + \frac{\sqrt{\phi Dy\phi CUi + 4\phi C\alpha\nabla}}{2\phi}\right]\frac{Z}{V} + \phi Dy\phi CUi + \frac{\sqrt{\phi Dy\phi CUi + 4\phi C\alpha\nabla}}{2\phi}\frac{Z}{V}} \qquad (23)$$

At $C^{1}{}_{(o)} = t \neq 0$

Again $C_0 = C_0$ so that

$$C_O = \left[\phi + \phi Dy \phi CUi + \phi C\alpha\nabla\right] C_o \left[1+1\right] \; i.e. \; 0 = \left[\phi + \phi Dy \phi CUi + \phi C\alpha\nabla\right]^2 \tag{24}$$

$$\Rightarrow \qquad \phi Dy \phi CUi + \phi Dy \phi CUi = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \tag{25}$$

$$C_{(x)} \left[2\frac{\phi}{t}\right] C_o \, Cos \left[\frac{\phi Dy \phi CUi \sqrt{\phi Dy \phi CUi + 4\phi C\alpha\nabla}}{2\phi}\right] \frac{Z}{V} + \left[\phi Dy \phi CUi \frac{\sqrt{\phi Dy \phi CUi + 4\phi C\alpha\nabla}}{2\phi}\right] \frac{Z}{V} \tag{26}$$

$$C_{(x)} \left[2\frac{\phi}{t}\right] C_o \, Cos \left[\frac{\phi Dy \phi CUi \sqrt{\phi Dy \phi CUi + 4\phi C\alpha\nabla}}{2\phi}\right] \frac{Z}{V} \quad \ldots\ldots\ldots\ldots\ldots \tag{27}$$

4. Results and Discussion

Modeling the transport of arsenic on pore fluid and solid surface in heterogeneous soil formation
Are presented in table and figure bellow

Table1: comparison of theoretical and Experimental values of Arsenic at various depths

Depth	Theoretical values	Experimental values
3	179	178
6	89.98	87
9	59.97	58.99
12	44.96	45
15	35.95	35.45
18	29.95	31
21	24.75	24.67
24	22.43	22.55
27	19.92	21
30	17.91	18

Table2: comparison of theoretical and Experimental values of Arsenic at various depths

Time	Theoretical values	Experimental values
10	179	178
20	89.98	87
30	59.97	58.99

40	44.96	45
50	35.95	35.45
60	29.95	31
70	24.75	24.67
80	22.43	22.55
90	19.92	21
100	17.91	18

Table3: comparison of theoretical and Experimental values of Arsenic at various depths

Depth	Theoretical values	Experimental values
3	96.99	98.67
6	47.99	45.88
9	31.99	33.99
12	23.27	25.78
15	18.99	18.78
18	15.99	15.77
21	12.99	12.88
24	11.99	11.67
27	9.99	10.1
30	9.59	10.11

Table 4: comparison of theoretical and Experimental values of Arsenic at various depths

Time	Theoretical values	Experimental values
10	96.99	98.67
20	47.99	45.88
30	31.99	33.99
40	23.27	25.78
50	18.99	18.78
60	15.99	15.77
70	12.99	12.88
80	11.99	11.67
90	9.99	10.1
100	9.59	10.11

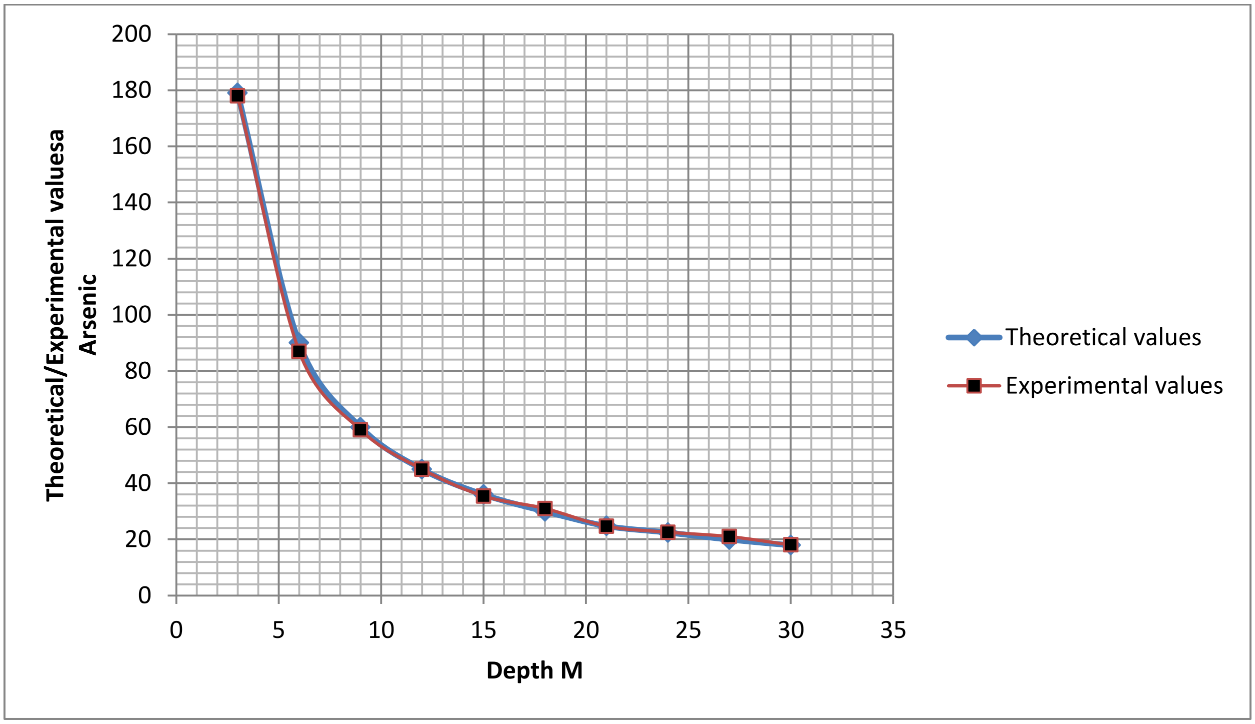

Figure1: comparison of theoretical and Experimental values of Arsenic at various depths

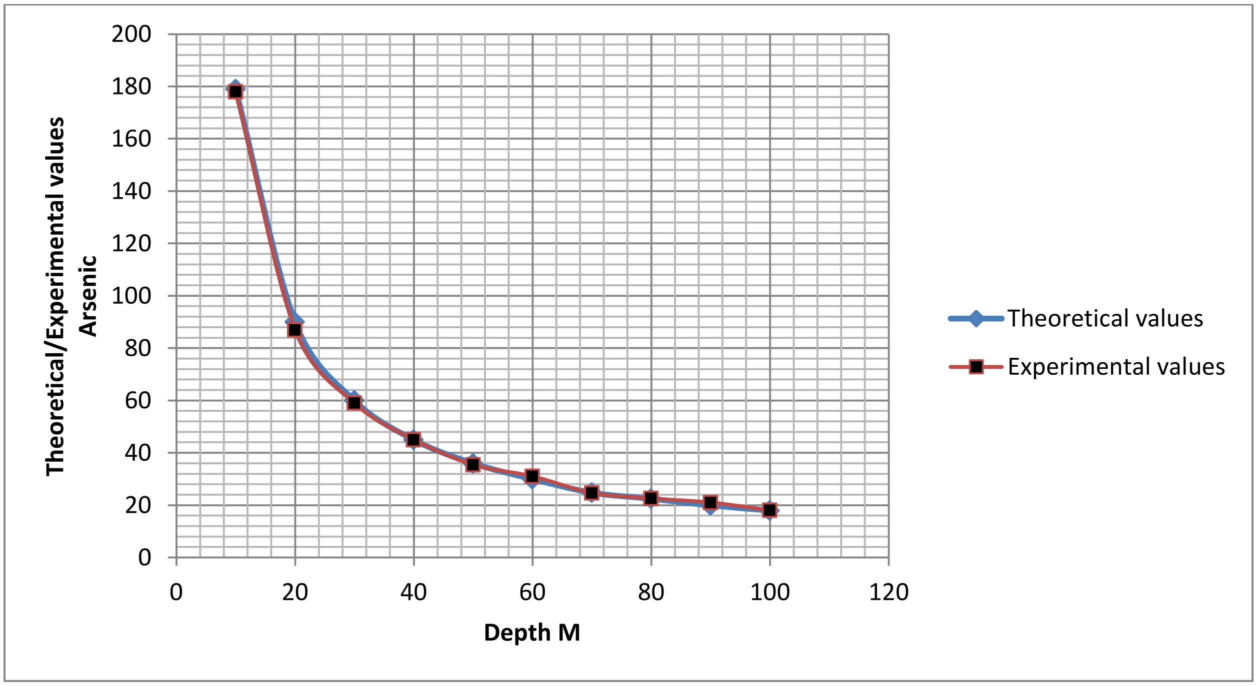

Figure 2: comparison of theoretical and Experimental values of Arsenic at various depths

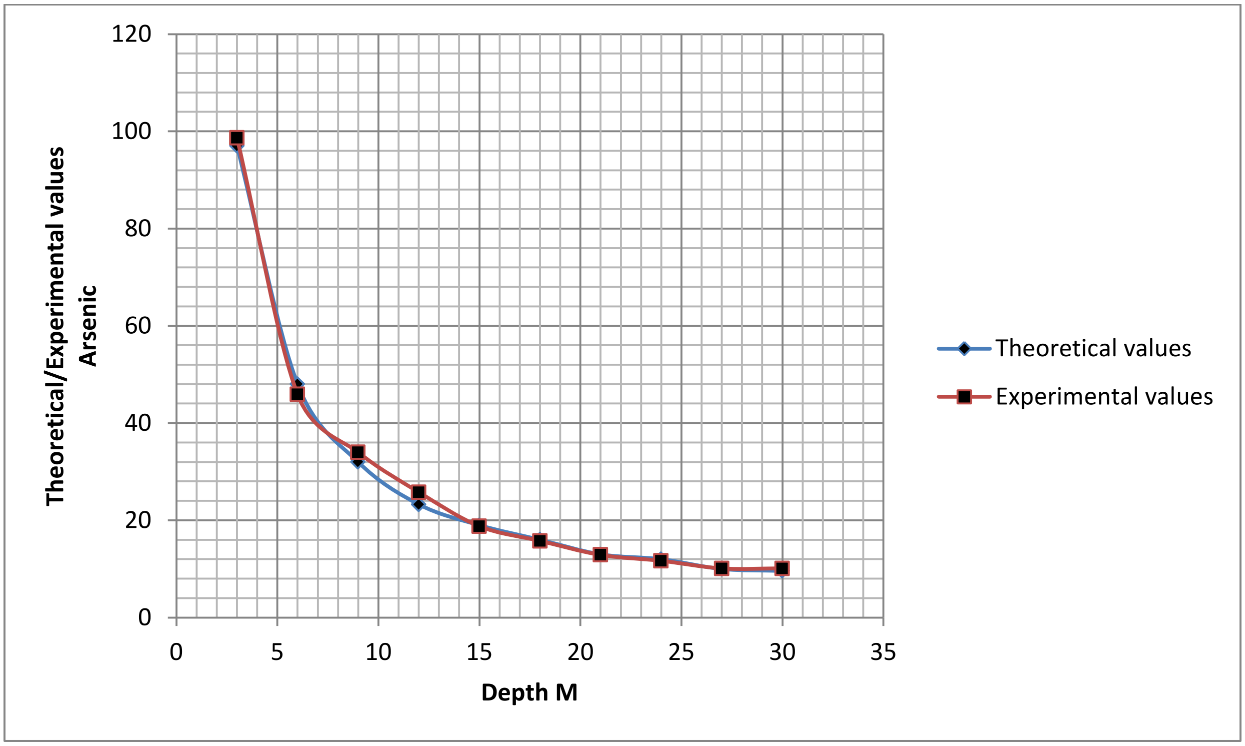

Figure 3: comparison of theoretical and Experimental values of Arsenic at various depths

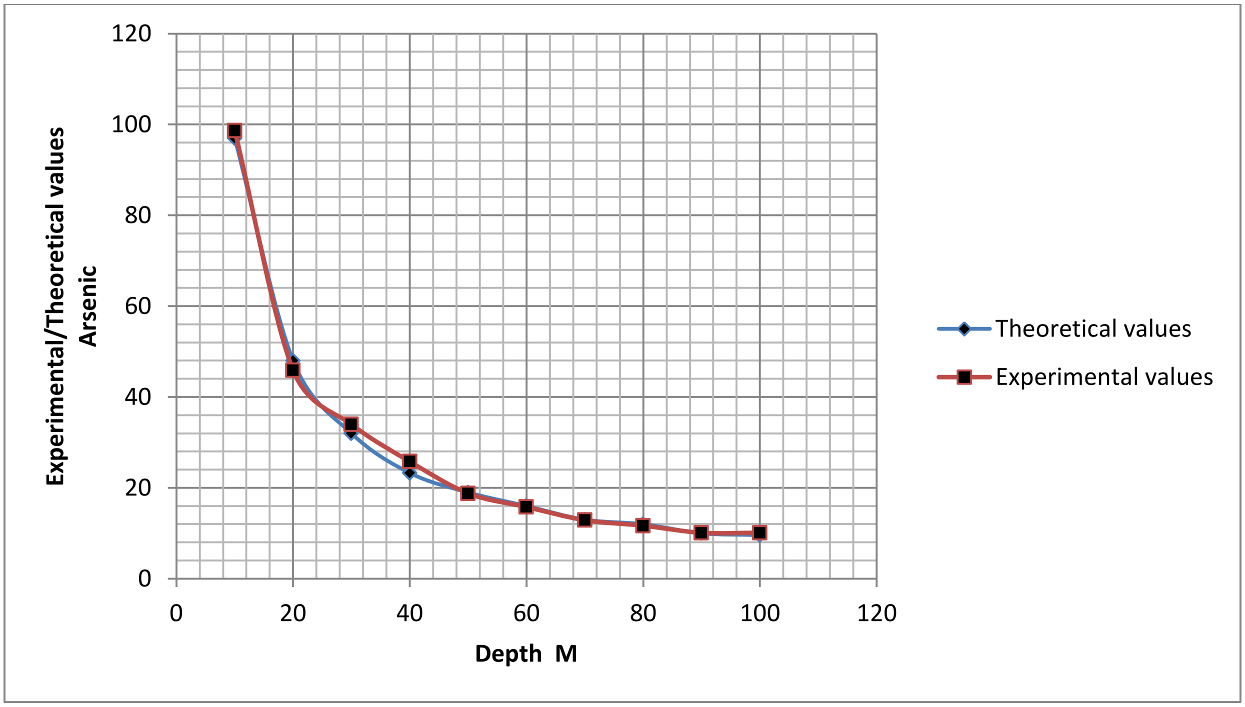

Figure 4: comparison of theoretical and Experimental values of Arsenic at various depths

Figure one: presented confirmed the deposition of heavy metals at three meters at ten days base on the rate of the generation and the deposition of metals in the study location. Sudden decrease where observed with in twenty and forty days, thus gradual decrease of the contaminant influenced by high rate of velocity of flow generating change in concentration from high to low concentration were expressed. Similar condition where observed in figure two as initial concentration were recorded at ten days, sudden decrease were experienced between forty to hundred days. This condition can be attributed to change in concentration with respect to depths thus the stratification of the formation. Figure three experienced rapid increase at ten days and observed sudden decrease from twenty days to hindered days, the rate of velocity of transport were confirm to have influence the concentration with respect to change in depths thus in general concept trace of heavy metals in the study location express the degradation even if it is still high base on the stipulated standard by word health organization the contaminant experienced this conditions due to man made activities, this condition have stream line the porosity influence at various strata including the homogenous nature of the soil. Permeability were confirmed to influence the condition of change in concentration of the contaminant, formations that develop high rate of deposition of heavy metal are known to be the organic and lateritic soil. High rain intensity played a major role on the accumulation of this contaminant between the formations, this were expressed on the establishment of high concentration of arsenic as presented in the figure. The study is imperative because it has established initial concentration zone in the formation finally it has also detailed the reason for high contaminant below the world health organization at the aquiferous zone.

5. Conclusion

Mathematical model to monitor the rate of arsenic in the study location has been expressed, various formation established different rate of high deposition of arsenic, the highest concentration were observed at ten days between the lateritic soil, while fast degradation of contaminants were experienced as silty and coarse fine sand base on the rate porous medium, . Homogenous nature of the soil in some certain region where found to influence the migration of the contaminant that experienced degradation compared to the optimum at ten meters, although the trace metals deposited between thirty and seventy days were compared with to world health organization, the trace metal at the aquiferous zone where confirmed to be much higher even if the figures express degradation, base on the stipulated standard, it is recommended that treatment plant should be designed for such location.

References

[1] Plant, J.A., D.G. Kinniburgh, P.L. Smedley, F.M. Fordyce, B.A. Klinck, D.H. Heinrich, and K.T. Karl. 2003. Arsenic and selenium. Treatise on Geochemistry:17–66.

[2] Mandal, B.K., and K.T. Suzuki. 2002. Arsenic round the world: a review. Talanta 58:201-235.

[3] Chen, M., L.Q. Ma, and W.G. Harris. 2002. Arsenic Concentrations in Florida Surface Soils: Influence of Soil Type and Properties. Soil. Sci. Soc. Am. J. 66:632-640.

[4] Vatamaniuk, O.K., S. Mari, Y.-P. Lu, and P.A. Rea. 2000. Mechanism of Heavy Metal Ion Activation of Phytochelatin (PC) Synthase. Blocked Thiols are Sufficient for Pc Synthase-Catalyzed Transpeptidation of Glutathione and Related Thiol Peptides. J. Biol. Chem. 275:31451-31459.

[5] Ritchie, A.R. 1980. Handbook of geochemistry. Earth-Science Reviews 16:59-60.

[6] Fitz, W.J., and W.W. Wenzel. 2002. Arsenic transformations in the soil-rhizosphere-plant system: fundamentals and potential application to phytoremediation. J. Biotechnol. 99:259-278.

[7] EPA, U.S. 1997. Recent Developments for In Situ Treatment of Metal Contaminated Soils. EPA-542-R-97-004 p. 8.

[8] ETCS. 1998. Topic report—Contaminated sites. European Topic Centre Soil. European Environment Agency.

[9] Smith, E., R. Naidu, and A.M. Alston. 2002. Chemistry of Inorganic Arsenic in Soils: II. Effect of Phosphorus, Sodium, and Calcium on Arsenic Sorption. J. Environ. Qual. 31:557-563.

[10] Mandal, B.K., and K.T. Suzuki. 2002. Arsenic round the world: a review. Talanta 58:201-235.

[11] Perker, C.L. 1981. USEPA Contract No. 68-01-5965. The Mitre Corporation:1.

[12] Oremland, R.S., and J.F. Stolz. 2003. The ecology of arsenic. Science 300:939-44. 2003. Sharples, J.M., A.A. Meharg, S.M. Chambers, and J.W.G. Cairney. 2000. Evolution: Symbiotic solution to arsenic contamination. Nature 404:951-952.

[13] Meharg, A.A., and J. Hartley-Whitaker. 2002. Tansley Review No. 133. Arsenic Uptake and Metabolism in Arsenic Resistant and Nonresistant Plant Species. New Phytol. 154:29-43.

[14] Meharg, A.A., J. Bailey, K. Breadmore, and M.R. Macnair. 1994. Biomass allocation, phosphorus nutrition and vesicular-arbuscular mycorrhizal infection in clones of Yorkshire Fog, *Holcus lanatus* L. (Poaceae) that differ in their phosphate uptake kinetics and tolerance to arsenate. Plant and Soil 160:11-20.

[15] Meharg, A.A., and J. Hartley-Whitaker. 2002. Tansley Review No. 133. Arsenic Uptake and Metabolism in Arsenic Resistant and Nonresistant Plant Species. New Phytol. 154:29-43.

[16] Anhui H 2009 characterization of arsenic resistant bacterial communities in the rhizosphere of an arsenic hyperaccumulator *pteris vittata* l. a thesis presented to the graduate school of the University of Florida in partial fulfillment of the requirements for the degree of master of science